# Trace metals and anaerobic digestion of leachate

Robert D. Cameron, Frederic A. Koch
University of British Columbia, Vancouver

Recently, concerned awareness of the deleterious nature of leachates from municipal landfill operations has begun to focus attention on the need to treat these highly complex, often toxic discharges. These concerns are well-founded as shown by investigators who have documented serious environmental damage resulting from the uncontrolled release of leachates to receiving streams and ground waters.

The development and application of suitable leachate treatment methods is not, however, a simple task. The extreme complexity of leachates and their great variability in terms of both strength and composition poses challenging problems. Hydraulic loading is equally variable and thus is a further complication when it comes to treatment design. Depending on the age and nature of a particular landfill, leachates may also contain significant quantities of toxic materials that can upset biological treatment systems.

In various leachate treatability studies, researchers have investigated a wide range of different treatment options, including biological, chemical, and physical-chemical treatment methods. In an early study, Cook and Foree [1] considered aerobic biostabilization of a medium strength leachate. They concluded that aerobic treatment was a highly effective means of stabilizing leachates, provided detention times were greater than or equal to 10 days. Reduction of biochemical oxygen demand (BOD) by this method was reported to be in excess of 99%, indicating almost complete biological stabilization.

Boyle and Ham [2] conducted an investigation designed to evaluate the efficiency of a number of biological treatment processes. In their studies, anaerobic treatment showed the most promise by reducing BOD more than 90% when hydraulic retention times were greater than 10 days (at design temperatures of 23°

to 30°C). Temperature effects on the anaerobic treatment process were found to be significant, yielding a temperature coefficient of 1.111 between 11° and 23°C. Aerobic polishing of the anaerobic effluents produced a marked improvement in overall effluent quality. Additional testing by Boyle and Ham [2] using aerobic treatment methods, showed some promise although these studies were plagued with problems encountered as a result of foaming and poor solids-liquid separation, which hindered settling of the biological floc.

In these early studies, no attempt was made to investigate the effects or distribution of metals in the biological leachate treatment processes. More recently, Uloth and Mavinic [3] investigated the aerobic biological treatment of a high strength leachate waste and paid particular attention to the fate of metals in the process. Using high mixed liquor volatile suspended solids (MLVSS) of 8 000 to 16 000 mg/l, and a 10- to 60-day range of sludge ages, chemical oxygen demand (COD) in the effluent was reduced from 48 000 to 400 mg/l for a COD removal efficiency that exceeded 97%.

Data were provided characterizing the trace metals contained in this high strength leachate. Aerobic bio-stabilization proved to be an effective means of removing these metals. Better than 95% of the aluminum, cadmium, calcium, chromium, iron, manganese, and zinc; 85% of the lead; and 77% of the nickel were removed. Between 49 and 96% of the magnesium was also removed from the mixed liquor. The metals were found to be associated mainly with sludge solids, removed by the settling of the biological floc in the final clarifier. Potassium and sodium were found to pass through the treatment system and remained almost completely associated with the liquid fraction of the mixed liquor.

While other studies have shown success with various biological and physical-chemical treatment methods singularly or in combination, these have, for the most part, not been concerned with the effects or fate of metals in the treatment process.

Recognizing that anaerobic digestion of leachates could be effective, especially for a high strength waste, this research focused on this method of treatment. Emphasis was placed on producing preliminary data regarding the distribution of trace metals in the process.

## EXPERIMENTAL PROCEDURE

Three bench-scale anaerobic digesters, operating in the mesophilic range (29° to 38°C), were used in this investigation. Each had a capacity of 14 litres and was equipped with a mechanical mixer and a thermostatically controlled heater. The digester contents could thus be stirred continously to ensure complete mixing and held at a constant, controlled temperature (34°C ± 1°C).

Digester start-up was achieved by introducing 7 litres of anaerobically digested, domestic wastewater sludge to each digester, then sealing the units and operating them for 24 hours to make certain that anaerobic conditions prevailed as indicated by the onset of gas production. Leachate was then added at the rate of 0.5 l/d with no wasting of digester contents. This procedure was continued for a period of 2 weeks, then the digesters, completely filled, were allowed to become fully stabilized prior to commencement of the first phase of the study.

Digester stability during start-up and for the duration of this phase of the experiment was determined by monitoring pH, alkalinity, suspended solids, volatile suspended solids, volatile acids, gas production rate, and gas composition. Alkalinity and volatile acids determinations were made on filtered samples using the procedure outlined in "Standard Methods."[4] Gas production was measured using a volumetric gas flow meter (Wright); gas composition analyses were made using a gas partitioner (Fisher-Hamilton). In addition, comprehensive testing of the leachate was conducted to fully document feed characteristics (Table I). All leachate analyses were conducted using procedures outlined in "Standard Methods."[4] Metals determinations were made on feed and digested samples using an atomic adsorption spectrophotometer (Jarell-Ash Model 810).

Acclimatization of the digester microorganisms to the leachate feed proved to be difficult. This was mainly because of its low pH and phosphorus levels. After several months, however, during which time pH was adjusted by adding $Ca(OH)_2$ and nutrients were added in the form of di-ammonium phosphate to maintain an adequate BOD:nitrogen:phosphorus ratio (100:5:1), complete stabilization was achieved in all three digesters as indicated by the establishment of stable base-line parameters. Lime additions were not needed after 4 weeks of operation. The volume in each digester was then reduced to 10 litres and a routine feeding procedure implemented. This consisted of withdrawing 0.5, 1, and 2 litres of mixed digester contents daily from digesters 1, 2 and 3, respectively, and replacing these with equal aliquots of fresh leachate feed. The resultant solids detention times were thus 20, 10, and 5 days.

During the first of the experimental runs, which lasted a total of 64 days, digester effluent was analyzed for COD and metal concentrations. Metal determinations were also made on the centrate from digester effluent samples that were centrifuged for 20 minutes at 2 000 rev/min on a centrifuge (International Equipment Co. Model CS).

After completion of the first experimental run, Digesters 2 and 3 were connected in series to test their extended operation in a high rate, two-stage configuration. Sludge age was initially held at 10 days, then reduced to 5 days during the latter stages of the run. Few data were collected during this phase except for gas composition data, which were obtained weekly to provide an indirect measure of digester performance stability. After about 10 months of operation, the digesters were emptied and a comprehensive set of analyses made of their entire contents.

## EXPERIMENTAL RESULTS

**Phase I—digester performance study.** Once the initial difficulties encountered with acclimatization of digester microorganisms to the leachate feed were overcome, stable digester performance was easily maintained throughout the duration of the study. Leachate feed characteristics (summarized in Table I) are shown for each of the four different feed batches used. It will be noted that there was a definite reduction in leachate strength during the first phase of experimentation. This occurred because over a period of time the leachate was taken from solid waste test

lysimeters, which resulted in the loading rate variability as shown in Table II.

While BOD was chosen as the main performance parameter, COD and volatile solids (VS) data were also collected and are summarized in Table III. BOD removal usually improved slightly with decreased leachate strength. The results for BOD removal plotted as a function of detention time are shown in Figure 1, which demonstrates that effluent settling was responsible for removing only 2 to 3% of the BOD. The COD removal is plotted as a function of detention time in Figure 2. It should be noted that these data are based solely on results from the third leachate feed batch (Days 26 to 47). Results are comparable to those for BOD, with COD removals being slightly lower.

Figure 3 shows the percentage BOD removal for settled effluent as a function of organic loading. The expected trend is evident: continuously decreasing removal efficiencies with increases in organic loading. It is readily apparent that somewhat higher removal efficiencies would have been achieved had longer solids detention times of 25 or 30 days been used. Longer detention times were not investigated because of lack of time and because in a field situation longer detention times would require higher capital costs coupled with reduced cost-effectiveness as the leachate strength declined with time.

Digester gas composition data are tabulated in Table IV. These are typical of anaerobic digestion and do not indicate any inhibition as a result of toxic substances. In fact, as is shown in Table V, methane production based on COD removal was actually somewhat greater than the theoretical value for methane production, 0.35 m³/kg COD removed, as reported by

**TABLE I. Composition of leachate feed used during study.**

| Component | Batch 1 Concentration (mg/l) Day 1 to 4 | Batch 2 Concentration (mg/l) Day 5 to 25 | Batch 3 Concentration (mg/l) Day 26 to 47 | Batch 4 Concentration (mg/l) Day 48 to 64 |
|---|---|---|---|---|
| BOD | 16 011 | 12 655 | 11 487 | 11 811 |
| COD | 32 562 | 27 870 | 23 571 | 21 146 |
| Total carbon | 11 140 | 9 500 | 8 500 | 7 300 |
| Organic carbon | 11 140 | 9 500 | 8 500 | 7 300 |
| Total solids | 15 880 | 14 015 | 11 245 | 10 303 |
| VS | 9 397 | 8 150 | 6 363 | 5 588 |
| Dissolved solids | 15 405 | 13 357 | 10 789 | 9 812 |
| Aluminum | 3.4 | 2.3 | 1.6 | 1.2 |
| Barium | 0.44 | 0.20 | 0.31 | 0.11 |
| Beryllium | <0.1 | <0.1 | <0.1 | <0.1 |
| Calcium | 1 680 | 1 415 | 1 170 | 1 065 |
| Cadmium | 0.025 | <0.005 | 0.20 | <0.005 |
| Chlorine | 1 060 | 1 014 | 851 | 620 |
| Chromium | 0.40 | 0.20 | 0.16 | 0.12 |
| Copper | 0.005 | 0.037 | 0.04 | 0.03 |
| Iron | 560 | 628 | 588 | 620 |
| Mercury | <0.001 | 0.01 | 0.006 | <0.001 |
| Potassium | 710 | 585 | 480 | 350 |
| Magnesium | 156 | 128 | 100 | 84 |
| Manganese | 20.6 | 24.6 | 13.5 | 12.8 |
| Nitrogen-total | 693 | 693 | 517 | 511 |
| $NH_3$ | 624 | 494 | 454 | 401 |
| Sodium | 690 | 575 | 450 | 400 |
| Nickel | 0.27 | 0.12 | 0.21 | 0.15 |
| Phosphorus-total | 12.3 | 13.1 | 10.1 | 10.9 |
| Lead | 1.41 | 0.37 | 0.88 | 0.37 |
| $SO_4$ | 473 | 410 | 350 | 192 |
| Zinc | 90 | 65 | 57 | 46 |
| Tannin-like compounds | 640 | 592 | 396 | 530 |
| pH[a] | 5.1 | 5.15 | 5.21 | 5.31 |

[a] Not in mg/l.

**TABLE II.  Digester loading rates for various feed batches.[a]**

| Unit | Detention Time (days) | Unit Loading Parameter | Batch 1 | Batch 2 | Batch 3 | Batch 4 | Batch Average |
|------|------|------|------|------|------|------|------|
| 1 | 5 | BOD | 660 | 522 | 474 | 487 | 533 |
|   |   | COD | 1 333 | 1 333 | 972 | 871 | 1081 |
|   |   | VS | 386 | 386 | 263 | 231 | 253 |
| 2 | 10 | BOD | 330 | 261 | 237 | 244 | 269 |
|   |   | COD | 666 | 575 | 487 | 436 | 541 |
|   |   | VS | 194 | 168 | 131 | 115 | 152 |
| 3 | 20 | BOD | 165 | 131 | 118 | 122 | 135 |
|   |   | COD | 333 | 288 | 224 | 218 | 260 |
|   |   | VS | 96 | 85 | 66 | 58 | 75 |

[a] All rates expressed as $g/m^3 \cdot d$.

McCarty.[5]  Coupled with relatively low $CO_2$ values, this supports the theory that some $CO_2$ is reduced to $CH_4$.[5]  Total gas production based on BOD removal varied from 0.71 to 0.94 $m^3/kg$ BOD removed, averaging 0.88, 0.91, and 0.84, respectively, for Digesters 1, 2, and 3 (Table III).

A decrease in the methane fraction was observed with increased solids retention time accompanied by a corresponding increase in nitrogen (Figure 4).  The $CO_2$ fraction was seen to be essentially independent of solids retention time.  To explain the observed trend,

a nitrogen balance was performed on the influent and effluent of each digester and this analysis showed that there was a decrease in total nitrogen levels in the effluent with increased detention time.  This decrease was most noticeable in Digester 3 (Table VI).  While ammonia nitrogen levels did not change during digestion, total nitrogen was reduced by 2.3, 6.2, and 13.1% at the 5-, 10- and 20-day detention times, respectively.  Thus it appeared that a small degree of denitrification was taking place during the digestion process, and that with increased detention times, the

**TABLE III.  Digester performance during study related to various feed strengths.**

| Unit | Detention Time (days) | Performance Parameter | Batch 1 | Batch 2 | Batch 3 | Batch 4 | Batch Average |
|------|------|------|------|------|------|------|------|
| 1 | 5 | BOD in effluent (mg/l) | 2 530 | 2 165 | 1 992 | 1 897 | 2 146 |
|   |   | BOD removal (%) | 84.2 | 82.9 | 82.3 | 83.9 | 83.3 |
|   |   | COD in effluent (mg/l) | — | — | 8 250 | — | 8 250 |
|   |   | COD removal (%) | — | — | 65.0 | — | 65.0 |
|   |   | Gas production (m³/kg BOD removed) | 0.74 | 0.91 | 0.94 | 0.94 | 0.88 |
| 2 | 10 | BOD in effluent (mg/l) | — | — | 1 005 | 865 | 935 |
|   |   | BOD removal (%) | — | — | 91.1 | 92.7 | 91.9 |
|   |   | COD in effluent (mg/l) | — | — | 7 324 | — | 7 324 |
|   |   | COD removal (%) | — | — | 68.9 | — | 68.9 |
|   |   | Gas production (m³/kg BOD removed) | — | — | 0.91 | 0.91 | 0.91 |
| 3 | 20 | BOD in effluent (mg/l) | 594 | 415 | 541 | 188 | 435 |
|   |   | BOD removal (%) | 96.3 | 96.7 | 96.9 | 98.4 | 97.1 |
|   |   | COD in effluent (mg/l) | — | — | 4 875 | — | 4 875 |
|   |   | COD removal (%) | — | — | 79.3 | — | 79.3 |
|   |   | Gas production (m³/kg BOD removed) | 0.71 | 0.87 | 0.89 | 0.89 | 0.84 |

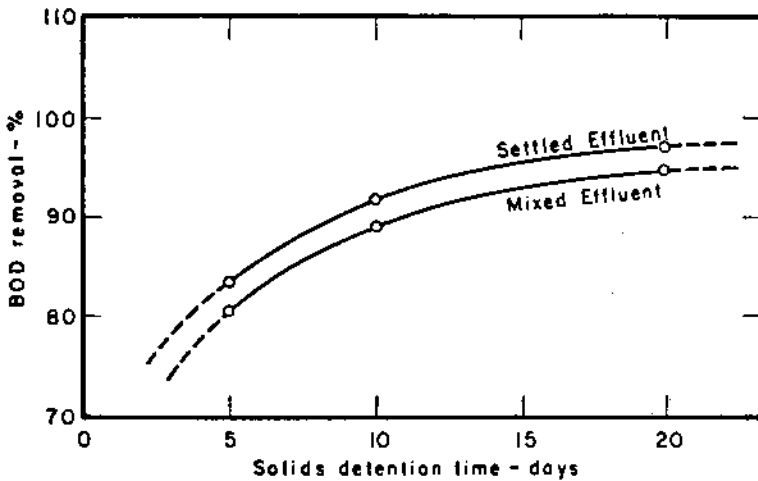NOTE: Dashes indicate no measurements taken.

FIGURE 1. Percentage BOD removal versus solids detention time.

conversion of nitrates and nitrites to free nitrogen was more significant. Also, the observed decrease in the methane fraction suggests that the methane formers and the denitrifying bacteria were competing for substrate. With longer mean cell residence times, conditions became more favorable for the denitrifiers. The effect of denitrifying bacteria on gas production as it relates to BOD removal is probably significant because of the potentially higher growth rates of the denitrifiers. For example, growth yield coefficients for denitrifying bacteria are in the range of 0.5 to 1.0,[6] whereas for the methane-forming bacteria growth yields are only 0.04 to 0.06.[7]

Coincidentally, methane production related to feed rate was not affected by the presence of the denitrifying bacteria. In fact, methane production showed slightly higher yields with increased detention time (6.77 litres of meth-

ane per litre of feed from Digester 3 compared with 6.50 and 6.41, respectively, produced by Digesters 1 and 2).

**Kinetic coefficients.** To obtain a better understanding of the biokinetics of anaerobic digestion as it is applied to leachate treatment and also to see how it compares with the anaerobic treatment of other wastes, the kinetic coefficients for growth rate and waste utilization were calculated (as outlined in References 7 and 8). The data are presented in Table VII along with the range of values normally used in anaerobic digester design.[8]

The high observed growth yield coefficient (Y) confirms the complete absence of biological inhibition in this study. It also suggests the presence of established bacterial populations other than the methane formers, providing support for the previously noted presence of denitrifying bacteria.
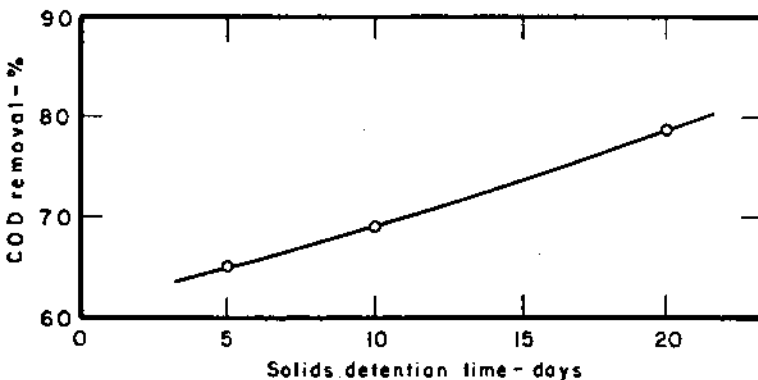


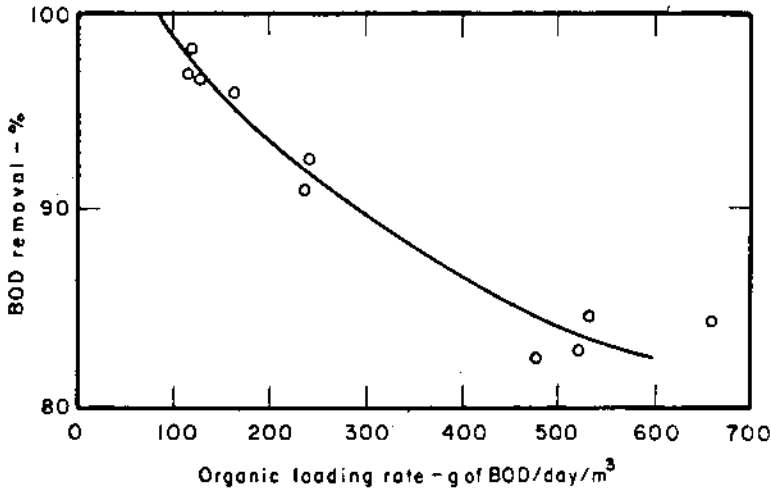FIGURE 2. Percentage COD removal versus solids detention time.

**FIGURE 3.** Percentage BOD removal versus organic loading rate.

The endogenous respiration coefficient ($b$) is very low, suggesting that the microorganisms were maintained well within their logarithmic growth phase. That is, food for the microorganisms was present in excess and thus there was no need for them to enter into endogenous respiration. This is confirmed by the near-zero endogenous respiration rates.

Waste utilization coefficients ($K$ and $K_s$) were found to be within the range of values normally found in anaerobic digestion. This again points to the healthiness of digester bacterial populations and their demonstrated suitability for stabilizing leachate wastes.

Based on these kinetic coefficient data, a minimum solids retention time, $\theta_c^m$, can be predicted below which washout of digester microorganisms will occur. The calculated value of $\theta_c^m$ is 1.7 days, which is slightly lower than the limiting solids retention time calculated or measured by other researchers that normally ranges from 2.6 to 8.0 days.[7] Thus, in terms of calculated biokinetics, anaerobic digestion of a complex waste such as landfill leachate is as good, if not better, than the application of this process to other less complex wastewaters.

**Heavy metal aspects of anaerobic treatment.** To determine the approximate distribution of trace metals in the anaerobic digestion pro-

**TABLE IV.** Composition of digester gas.[a]

| Unit | Detention Time (days) | Gas Components | Batch 1 | Batch 2 | Batch 3 | Batch 4 | Batch Average |
|------|------|------|------|------|------|------|------|
| 1 | 5 | $CH_4$ | 74.6 | 74.8 | 76.0 | 76.3 | 75.4 |
|   |   | $CO_2$ | 23.8 | 24.1 | 23.2 | 22.5 | 23.4 |
|   |   | $N_2$ | 1.3 | 1.1 | 0.6 | 1.1 | 1.03 |
|   |   | $O_2$ | 0.3 | 0.0 | 0.03 | 0.03 | 0.09 |
| 2 | 10 | $CH_4$ | — | — | 73.1 | 72.4 | 72.8 |
|   |   | $CO_2$ | — | — | 23.2 | 23.5 | 23.4 |
|   |   | $N_2$ | — | — | 2.7 | 3.2 | 3.0 |
|   |   | $O_2$ | — | — | 0.11 | 0.13 | 0.12 |
| 3 | 20 | $CH_4$ | 69.8 | 68.7 | 69.1 | 69.2 | 69.2 |
|   |   | $CO_2$ | 23.5 | 24.9 | 24.2 | 24.5 | 24.3 |
|   |   | $N_2$ | 6.0 | 5.8 | 6.5 | 6.1 | 6.1 |
|   |   | $O_2$ | 0.53 | 0.53 | 0.12 | 0.11 | 0.31 |

NOTE: Dashes indicate items not analyzed.
[a] Composition data shown as percentage.

cess, mass balances were performed for the metals in question. Metals in the leachate feed were analyzed in each of the four batches (see Table I) and, on two occasions, in the completely mixed digester effluent. At the end of the second phase of the investigation that consisted of operating two of the digesters for 10 months in a two-stage, high rate configuration, analyses were performed on the entire digester contents.

Trace metal separation of mixed effluent samples was accomplished by centrifuging at a relative centrifugal force (RCF) of 950 grams. This high RCF coupled with a relatively long centrifuging time (20 minutes) gave good separation of mixed effluent metals into their dissolved and suspended fractions. From data provided by Chen et al.,[a] it can be estimated that this procedure removed well over 90% of the suspended particulate material contained in the digested effluent samples. Any suspended material remaining in the centrate would be only of colloidal size ($1\mu$), and would not be associated with any except perhaps the very smallest of particulate trace metal fractions.

Trace metal concentrations for both the centrate and dry sludge fractions, as obtained by the above separation method, are summarized in Table VIII along with mixed effluent concentrations for operation during the second and third feed batches. Because no relationship was found to exist between the distribution of trace metals and the associated solids retention time, data from all three digesters have been combined.

It will be noted that for a number of metals, mixed effluent concentrations exceed influent concentrations, particularly for the second feed batch. Practically, the two should be equal because effluent samples used for analysis were not collected until after at least 20 days of feeding, which should have been long enough to allow for a complete turnover of digester contents even at the longest detention time. In a number of instances, specifically zinc and
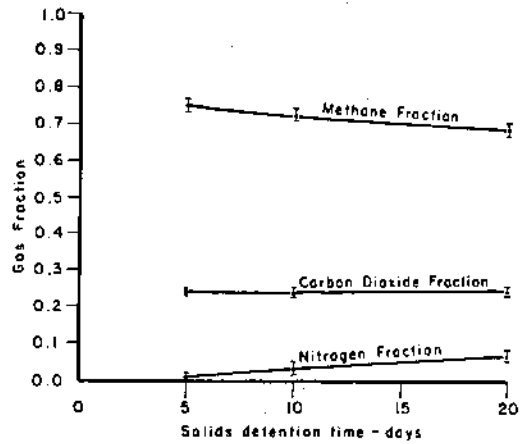


FIGURE 4. Gas composition versus solids detention time.

copper which were, respectively, 12 and 85% higher in the mixed effluent, this is likely attributable to metal contamination linked to corrosion of interior digester parts and apparatus such as the brass and copper fittings, metal stirring rods, and bearing surfaces. On the other hand, concentrations of calcium, iron, and manganese in the mixed effluent were as much as 50% lower than in the influent. This was likely a result of the formation of insoluble hydroxide and sulfide precipitates that accumulated underneath the paddle stirrers in each digester because of poor mixing in this zone.

Most of the metals in the effluent were found to be associated with the dry sludge fraction. This was particularly true for certain of the so-called heavy metals, specifically aluminum, cadmium, iron, mercury, nickel, and zinc, which were contained 80% or greater in the sludge solids (Table IX). Other heavy metals such as chromium, copper, lead, and manganese were found to have 45 to 70% of their fraction associated with the solids. For the alkali and alkali-earth metals, with the

TABLE V. Methane production related to COD removal.

| Unit | Detention Time (days) | Methane Production (m³/kg COD removed) | Methane Production (m³/l of feed) |
|---|---|---|---|
| 1 | 5 | 0.42 | 0.006 5 |
| 2 | 10 | 0.39 | 0.006 4 |
| 3 | 20 | 0 36 | 0.006 8 |

TABLE VI. Nitrogen balance in digester liquid.

| Unit | Detention Time (days) | Total Nitrogen in Feed— Including N Added (mg/l) | Total Nitrogen in Effluent (mg/l) |
|---|---|---|---|
| 1 | 5 | 478.9 | 467.8 |
| 2 | 10 | 478.9 | 449.0 |
| 3 | 20 | 478.9 | 416.4 |

## TABLE VII. Kinetic coefficients.

| Kinetic Coefficient | Values Normally Employed in Anaerobic Digestion Design | Values Determined in This Investigation |
|---|---|---|
| $Y$ | 0.04–0.6 mg VSS/mg BOD$_5$ | 0.10 mg VSS/mg BOD$_5$ |
| $b$ | 0.01–0.04/d | 0.006/d |
| $K$ | 3.0–8.0 mg BOD$_5$/mg VSS/d | 5.88 mg BOD$_5$/mg VSS/d |
| $K_s$ | 150–6 000 mg/l BOD$_5$ | 4 020 mg/l BOD$_5$ |

single exception of barium, the sludge solids were found to contain only 4 to 30% of the metal.

The metal percentages contained in the dry sludge show that anaerobic digestion can serve as an efficient metal removal process. Needless to say, the effectiveness of sedimentation will play a significant role in total metal removal. In spite of the fact that analyses were performed on centrifuged effluent samples, complete settling of anaerobic leachate effluent should result in metal removal efficiencies that approach those shown in Table IX.

**Phase II—extended digester operation.** Gas composition data collected weekly during this phase of the study showed that digester performance remained essentially unimpaired for nearly a year of continuous operation. Performance stability, particularly of the first stage digester, was affected somewhat during several periods when high oxygen and nitrogen levels

were found in the digester gas stream. This had a marked effect on methane percentage and likely resulted from excessive air entrainment during feeding. Slight air entrainment was in evidence throughout most of this phase of experimentation. While this affected the degree of anaerobiasis, the gases from both digesters contained in excess of 50% methane (Table X).

In terms of the metal content of the digester contents, analyses showed that the settleable portion, which included the bottom layers resulting from precipitation deposits, were extremely rich in iron and calcium and, to a lesser extent, manganese. Concentrations expressed as milligram per kilogram dry weight were as high as 293 300, 38 700, and 3 550, respectively, for these three metals. Overall metal content was comparable to mixed effluent values obtained earlier. Hence, there were

## TABLE VIII. Trace metals in digester effluent.[a]

| Parameter | Second Feed Batch | | | Third Feed Batch | | |
|---|---|---|---|---|---|---|
| | Mixed Effluent Concentration | Centrifuged Effluent Concentration | Dry Sludge Concentration | Mixed Effluent Concentration | Centrifuged Effluent Concentration | Dry Sludge Concentration |
| Aluminum | 2.8 | 0.4 | 76.7 | 1.2 | N.D. | 38.8 |
| Barium | 0.25 | N.D. | 6.2 | 0.14 | N.D. | 4.5 |
| Cadmium | 0.02 | N.D. | 0.66 | 0.01 | N.D. | <0.7 |
| Calcium | 679 | 447 | 7 600 | 489 | 375 | 4 100 |
| Chromium | 0.24 | 0.10 | 4.6 | 0.10 | 0.06 | 1.1 |
| Copper | 0.24 | 0.12 | 4.0 | 0.18 | 0.07 | 1.8 |
| Iron | 417 | 26.0 | 69.7 | 223 | 61.7 | 5 230 |
| Lead | 0.73 | 0.14 | 19.1 | 0.29 | 0.19 | 3.6 |
| Magnesium | 129 | 121 | 390 | 96.7 | 91.3 | 317 |
| Manganese | 12.9 | 2.8 | 321 | 5.2 | 1.8 | 113.5 |
| Mercury | N.D. | N.D. | N.D. | 0.002 | N.D. | 0.07 |
| Nickel | 0.30 | 0.08 | 7.2 | 0.13 | 0.01 | 4.05 |
| Potassium | 669 | 677 | 625 | 481 | 307 | 1 290 |
| Sodium | 635 | 637 | 750 | 501 | 501 | 588 |
| Zinc | 73.5 | 0.64 | 2 330 | 34.7 | 0.42 | 1 100 |

NOTE: N.D. = not detected.

[a] Concentrations expressed as mg/l, except for dry sludge concentration, which is expressed as ppm.

no buildups in either the primary or secondary digester over the long-term experimentation.

## DISCUSSION

In general terms, the experimental scale anaerobic digestion process performed efficiently in its application to leachate treatment. Process stability was excellent throughout the entire investigation, including the long-term, high-rate study that pushed the process near its limits with high organic loadings and short solids retention times. The process did not fail either because of overloading or of the buildup of toxicants.

The advantages inherent in anaerobic digestion as a means of biostabilization are well known. These, coupled with the amenability of this process in its application to leachate stabilization suggests that it is worthy of consideration as a basis for full-scale leachate treatment facilities. Anaerobic digestion is a process well-suited to handling the large organic loads that often characterize leachates, in particular those that are discharged from "young" landfill sites. High treatment efficiencies can be achieved, particularly with high strength wastes, without the high operating costs that are associated with other treatment schemes that make use of aerobic, chemical, or physical/chemical treatment methods.

The cost of heat addition required for digester operation under mesophilic temperature conditions would not be excessive if the methane produced were used for heating purposes. Methane production is almost certain to be well in excess of the necessary requirements for heating purposes and might, in fact, provide some basis for incorporating additional energy recovery schemes in the design of a treatment facility. These could add significantly to the capital cost requirements of treatment, which in themselves are not excessive. This would, of course, require further investigation to determine feasibility.

A comparison of metal removal efficiencies obtained during this investigation with the exceptionally high values reported by Uloth and Mavinic[3] in their aerobic biostabilization of a similar, although stronger, leachate reveals that anaerobic treatment is not quite as efficient a means for removing metals. This finding is not unexpected when one considers the stronger affinity of aerobic sludges for metals, particularly from the heavy metal group. This has been documented by a number of investigators. For example, Neufeld and Hermann[10] showed that completely mixed

**TABLE IX. Summary of metal percentage contained in dry sludge.**

| Parameter | Percentage |
|-----------|-----------|
| Aluminum | 94.2 |
| Barium | 92.5 |
| Cadmium | 100 |
| Calcium | 30.6 |
| Chromium | 44.6 |
| Copper | 40.4 |
| Iron | 79.7 |
| Lead | 50.3 |
| Magnesium | 9.9 |
| Manganese | 68.5 |
| Mercury | 100 |
| Nickel | 86.2 |
| Potassium | 5.6 |
| Sodium | 3.7 |
| Zinc | 95.0 |

aerobic biological processes have a capability for long-term removal of heavy metal ions that is far superior to anaerobic processes.

In aerobically produced sludge, the metals that are usually completely associated with the sludge mass are most often organically bound through the formation of metal-organic complexes. High molecular weight exocellular polymers of the biofloc, which include polysaccharide, protein, ribonucleic acid, and deoxyribonucleic acid, provides many functional groupings that act as binding sites for the metals.[11] With anaerobic sludges the metals are usually considered to be distributed mainly between the precipitated (insoluble) and organically bound fractions, although other mechanisms such as ion exchange and chelation come into play.[12] Recent evidence presented by Hayes and Theis[13] in their quantitative investigation of metal distribution in anaerobic digestion suggests that as much as 30 to 60% of the metal accumulation in digested sludges are organically bound, contained in the intracellular portions of the biomass. Their conclusions were that microbial

**TABLE X. Average gas composition during Phase II—extended, high rate digestion.[a]**

| Parameter | Digester 1 (stirred) | Digester 2 (not stirred) |
|-----------|----------------------|--------------------------|
| Methane | 51.1 | 51.5 |
| Nitrogen | 27.7 | 26.4 |
| Carbon dioxide | 14.9 | 18.6 |
| Oxygen | 6.3 | 3.5 |

[a] Digestion expressed as percentage.

uptake activity competes with precipitation in the removal of heavy metals from digester supernatant.

The foregoing discussion raises some points that are of particular importance when considering the availability of the accumulated heavy metals in the sludge solids if they are reintroduced after treatment to the landfill. For example, if the metals are in the form of precipitates, mild acidification, which is common in the landfill environment, would result in immediate leaching of the heavy metals. On the other hand, if the major portion of metals are organically bound they will be released much more slowly even in acid environments at a rate dependent on the rate of degradation of the organic phase. The form of the metals will be equally important in determining, for example, whether or not land disposal or incineration can be utilized. More investigatory work is required to establish the exact form of metal present in the sludge solids after anaerobic digestion of leachate so that suitable sludge disposal techniques can be developed.

## SUMMARY AND CONCLUSIONS

Aerobic digestion of leachate at mesophilic temperatures is an effective means of biostabilization, removing between 81 and 96% of the BOD contained in a medium strength leachate. Settled effluent BOD removal efficiencies of 83, 91, and 97%, respectively, were obtained for solids detention times of 5, 10, and 20 days. Removal of COD was found to range from 65 to 80%.

Throughout this investigation the anaerobic digestion process was totally unaffected by the presence of heavy metals and other toxicants contained in the leachate feed. Methane production exceeded 0.37 m³/kg of COD removed, which is greater than that predicted for anaerobic treatment of wastewater sludge. Operation of the digesters over an extended period revealed that treatment process remained essentially unimpaired, attesting to the inherent, long-term stability of anaerobic digestion as a means of stabilizing leachates.

Calculated kinetic coefficients based on data collected during this investigation revealed that the biokinetics of anaerobic digestion of leachate are comparable to those for digestion of municipal wastewater sludge. In fact, measured yield coefficients were slightly higher, whereas endogenous respiration coefficients were slightly lower.

Heavy metal removal by anaerobic digestion was good although not quite as high as has been demonstrated using aerobic biostabilization of leachates. Metal removal efficiencies were greater than 85% for aluminum, barium, cadmium, mercury, nickel, and zinc; 80% for iron; 40 to 70% for chromium, copper, lead, and manganese; 30% for calcium; and less than 10% for magnesium, potassium, and sodium.

In terms of the distribution of trace metals in anaerobic digestion, most are associated with the sludge solids. Although the specific forms of the metals were not established explicitly in this investigation, they are likely to be either as insoluble precipitates or organically bound complexes. Determination of the metal forms is seen as a very important factor before assessment of a safe means of sludge disposal can be identified.

## ACKNOWLEDGMENTS

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