Field Evidence for the Effect of Acetate on Leachate Alkalinity

by J. F. Devlin[a]

Abstract

Alkalinity measurements are routinely conducted as part of standard water-quality determinations. Often, very little interpretation of the values is attempted, and the entire alkalinity is attributed to carbonate or bicarbonate. When landfill leachates are involved, this assumption could be misleading in terms of plume mapping, determining the incrustation potential of the water, or assessing the likelihood of methane generation because substances other than carbonate, for example acetate, can contribute significantly to the sample's alkalinity.

A set of landfill leachate samples was collected and analyzed for alkalinity and volatile fatty acids. Acetate was the only organic acid identified. A very strong correlation was observed between acetate and alkalinity. Actual titration curves (volume of acid vs. pH) were compared with curves calculated assuming that acetate and bicarbonate were the two major species contributing the total alkalinity. Excellent agreement was observed between the experimental and theoretical data. Distinct differences in the shapes of the curves for carbonate-dominated and acetate-dominated alkalinities make it possible to distinguish these two classes of water solely on the basis of alkalinity measurements. Water containing acetate titrates with an equivalence point which is less distinct than water containing only carbonate.

Introduction

Alkalinity measurements are routinely conducted as part of standard water-quality determinations. Typically, these values are taken to be an indication of the concentration of bicarbonate (HCO_3^-) or carbonate (CO_3^{2-}) in the sample (Wiley et al., 1975; Nicholson et al., 1983; and Clark and Piskin, 1977). In leachates containing high concentrations of calcium (Ca^{2+}) at near neutral pH's, this assumption leads to the conclusion that the leachate is supersaturated in calcium carbonate ($CaCO_3$). This conclusion could influence the planning of such activities as the installation of leachate collection wells, since a supersaturated leachate could result in early incrustation of the well screens.

Another possible implication which follows from the assumption of carbonate alkalinity is that calcite dissolution is the source. This, in turn, implies that a large percentage of dissolved calcium in the leachate has originated from natural sources. However, the above conclusions may be incorrect if the alkalinity is partially due to substances other than carbonate.

Factors Contributing to Solution Alkalinity

The alkalinity of a solution is defined as the acid neutralizing capacity of the solution (Stumm and Morgan, 1980). Thus, any strong and many weak bases dissolved in the sample will contribute to the total alkalinity. An example of a strong base is OH^-; weak bases include CO_3^{2-}, HCO_3^-, NH_3, and fatty acid anions such as acetate.

Strong bases are seldom observed in significant concentrations in natural waters or leachates. The presence of a high concentration of a strong base will be immediately apparent as an abnormally high solution pH. However, weak bases can be present in high concentrations at near neutral pH's, and as a result, significantly increase the total alkalinity.

Wiley et al. (1975) examined oil field waters containing high concentrations of Ca^{2+} and HCO_3^- at near neutral pH values. The data suggested that the ground water was supersaturated in $CaCO_3$. Further investigation revealed that a significant portion of the solution alkalinity was the result of short chain aliphatic acid anions and not HCO_3^- as first assumed.

Short chain aliphatic acids are produced during the course of fermentation reactions in landfill wastes (Farquhar and Rovers, 1973). Initially, the waste passes through an aerobic stage in which available oxygen is quickly consumed. This is followed by an acidification stage in which the organic acids are produced along with carbon dioxide

---

[a] Water and Earth Science Associates Ltd., 182 Victoria St. S., Kitchener, Ontario, Canada N2G 2B9.

Received May 1989, revised February 1990, accepted February 1990.

Discussion open until May 1, 1991.

(CO_2) and hydrogen (H_2). Hoeks and Borst (1982) stated that the acidification stage may last several years at a landfill. Acetate has been identified as the dominant product in this stage (McCarty, 1963; Kotze et al., 1969; and Hoeks and Borst, 1982). Finally, the organic acids are consumed in the methane fermentation stage which yields methane (CH_4) and CO_2 as end products. Thus, the detection of acetate in a landfill leachate might be related to the potential for methane production.

The production of organic acids is accompanied by the development of a high chemical oxygen demand (COD) and a coinciding increase in total alkalinity. Harmsen (1983) reported that up to 95% of the COD may be attributable to short chain fatty acids ranging from acetate to caproic acid. Baedecker and Back (1979) attributed between 11% and 52% of a leachate alkalinity to short chain aliphatic acid anions including acetate (Ac^-), propionate, isobutyrate, butyrate, isovalerate, valerate, isocaproate, and caproate.

The purpose of this paper is to show that acetate has a significant effect on leachate alkalinity, and to present methods of determining whether fatty acids are contributing significantly to a sample's alkalinity.

Measurement of Alkalinity

Alkalinity is frequently measured by titrating the water sample of interest with a standardized acid solution, either to a fixed end point (e.g., pH 4.5 is often used if it is assumed that carbonate species are the dominant contributor to the alkalinity) or until the equivalence point is achieved. The equivalence point exists when the acid added to the sample is chemically equivalent to the substances with which it is reacting. It may be seen as the point of maximum slope in a plot of "volume of acid added" vs. "solution pH" (Figure 1).

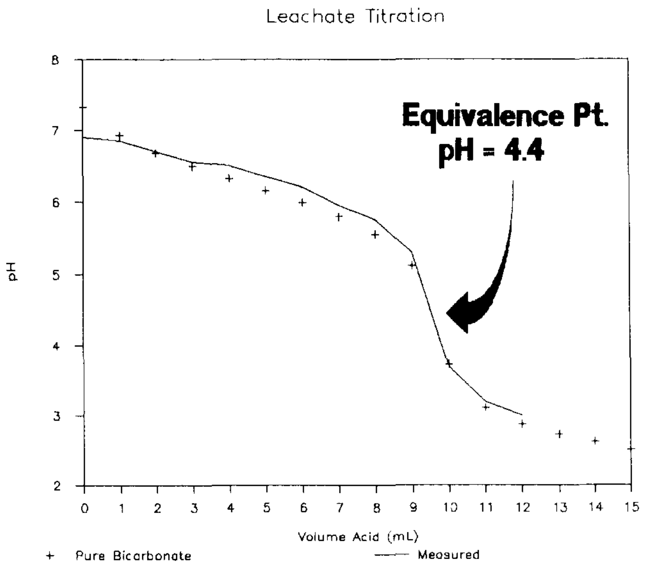

Fig. 1. Calculated and measured titration curves for a leachate sample. The calculated curve is based on 0 meq/l acetate and 9.8 meq/l bicarbonate. The sample actually contained <1.0 meq/l acetate and 9.5 meq/l bicarbonate based on chemical analysis.

In a solution containing a mixture of bases, several equivalence points will exist, one for each base with a unique association constant. However, if several species exist with similar association constants, the equivalence points may obscure one another.

In general, titrating to equivalence is the preferable method of determining a sample's alkalinity because it does not require a presumption of carbonate-controlled alkalinity. This is particularly true in the analysis of leachates. However, in the analysis of natural (unpolluted) waters, the assumption of carbonate alkalinity is often valid and titrating to a fixed end point may be the most practical and economical method of determining alkalinity.

Hydrogeologic Setting

Samples of a municipal waste leachate were obtained from the Gloucester Landfill located 5 km south of Ottawa, Canada. The leachate plume was migrating in a shallow (6 m total depth), surficial aquifer comprising fine to coarse sand. At the time of sampling, the leachate was estimated to be between 9 and 12 years old.

Experimental Methods

Samples were collected from multilevel sampling devices in polypropylene syringes, using a peristaltic pump. Alkalinity measurements were conducted in the laboratory on 20 ml aliquots of the samples on the same day that they were collected. Thus, the total storage time preceding analysis did not exceed 6 hours. Samples were titrated against a 0.02 N standardized solution of HCl using a Metrohm E536 potentiograph, and E535 Dosimat auto titrator. A continuous recorder provided a plot of pH vs. volume of acid added. End points were taken to be the points of maximum slope on the potentiographs.

Acetate concentrations were measured using a Dionex System 12 Analyzer. Calibration solutions were prepared fresh daily. Analyses were performed two ways to ensure that the identification of the acetate peaks was accurate. First, samples were analyzed by ion chromatography with an anion concentrator column, an anion separator column, and a suppressor column. Verification was conducted in the ion chromatography exclusion mode using a cation trap, separator column, and suppressor column. In this mode, chromatograms were examined for other fatty acids which might be present, but none were discernible.

Bicarbonate concentrations were estimated by subtracting acetate concentrations from the alkalinity value determined by titration.

Results

Titration Curves for Leachate Samples

Three curve types were distinguishable in the samples of leachate analyzed for alkalinity. In the first, a clear end point was visible at a pH of about 4.4, after the addition of between 5 to 10 ml of acid (Figure 1). In the second, the end point occurred at a slightly lower pH (4.3 in Figure 2), and was considerably less pronounced in terms of the curve's inflection. The third type of curve encountered was characterized by a long, steady slope with an end point at about pH

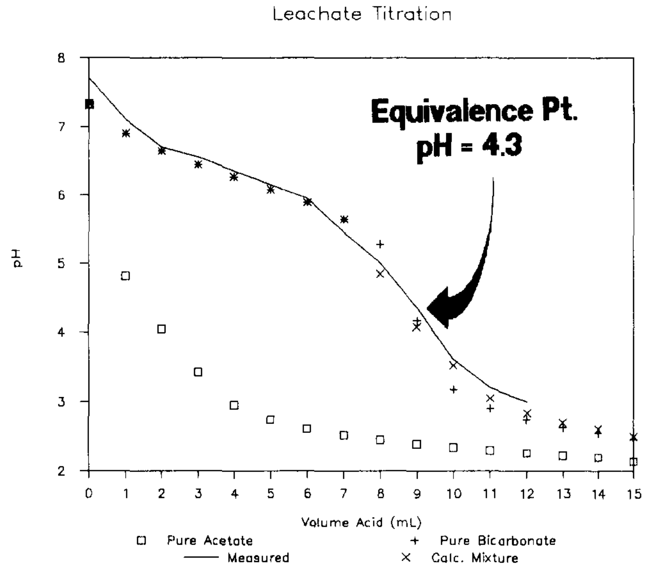

Fig. 2. Calculated and measured titration curves for a leachate sample. The calculated curve is based on 2.5 meq/l acetate and 9.0 meq/l bicarbonate. The sample actually contained 2.5 meq/l acetate and 6.5 meq/l bicarbonate based on chemical analysis.

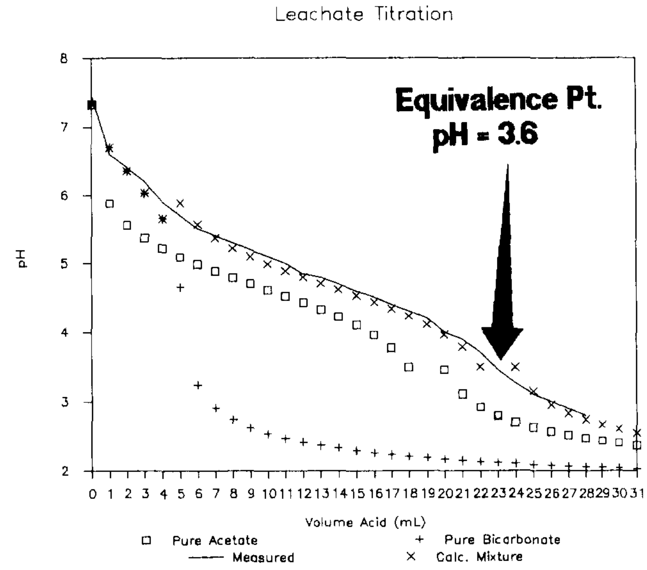

Fig. 3. Calculated and measured titration curves for a leachate sample. The calculated curve is based on 19.5 meq/l acetate and 5.2 meq/l bicarbonate. The sample actually contained 18.6 meq/l acetate and 3.8 meq/l bicarbonate based on chemical analysis.

3.6. This latter curve type required on the order of 20 ml of acid added before the end point was reached (Figure 3). The curves with the least pronounced inflections corresponded to samples containing acetate. A plot of alkalinity vs. acetate indicated that a strong statistical correlation does exist between the two parameters for acetate concentrations exceeding about 2 meq/l (Figure 4).

Simulating Leachate Titration Curves

In order to further test the hypothesis that acetate was the species responsible for the alkalinities, an attempt was made to simulate the observed curves using thermodynamic data (equations 1 and 2 for 25°C, Skoog and West, 1976).

$$H_2CO_3 \longleftrightarrow HCO_3^- + H^+ \qquad pKa = 6.35 \qquad (1)$$

$$HAc \longleftrightarrow Ac^- + H^+ \qquad pKa = 4.76 \qquad (2)$$

For each milliliter of acid added to the sample, the following equations were solved:

$$(Ac^-)_i = (Ac^-)_j - (H^+)_i \qquad (3)$$

$$(HAc^-)_i = (HAc^-)_j + (H^+)_i \qquad (4)$$

$$[Ac^-]_i = (Ac)_i / V \qquad (5)$$

$$[HAc]_i = (HAc)_i / V \qquad (6)$$

$$\{Ac^-\}_i = [Ac^-]_i \cdot F_{Ac^-} \qquad (7)$$

$$\{HAc\}_i = [HAc]_i \cdot F_{HAc} \qquad (8)$$

if $(Ac^-)_j > (H^+)_i$,

$$pH_{Ac} = -\log\left[\frac{(1.75 \times 10^{-5} \cdot \{HAc\}_i)}{\{Ac^-\}_i}\right] \qquad (9)$$

otherwise,

$$pH_{Ac} = -\log[(-[Ac^-]_i \cdot F_{H^+})] \qquad (10)$$

where (Ac^-) = mass of acetate in moles; $[Ac^-]$ = concentration of acetate (moles/l); $\{Ac^-\}$ = activity of acetate; F_{Ac^-} = activity coefficient for acetate; F_{H^+} = activity coefficient for hydronium ion; F_{HAC} = activity coefficient for acetic acid; pH_{Ac} = pH calculated on basis of acetate alone; V = solution volume (increasing with each addition of acid); i = subscript referring to condition after most recent addition of acid; and j = subscript referring to condition after previous addition of acid.

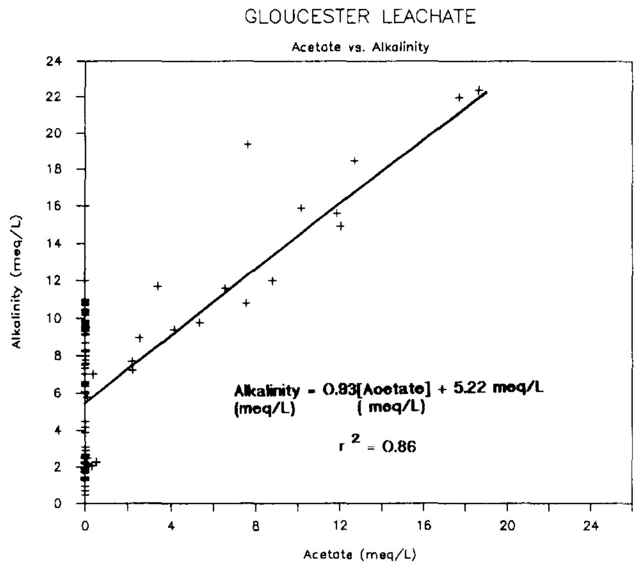

Fig. 4. Correlation between alkalinity and acetate concentration expressed in meq/l.

An analogous series of equations were solved for the carbonate condition, and the pH of a solution containing both carbonate and acetate was calculated as follows, if $(HCO_3^-)_j > (H^+)_i$,

$$(Ac^-)_i = (Ac^-)_j \tag{11}$$

$$pH_f = pH_{HCO_3^-} \tag{12}$$

Otherwise, acetate will begin reacting, equations (1) to (10) are evoked and,

$$pH_f = pH_{Ac^-} \tag{13}$$

where (HCO_3^-) = molar amount of bicarbonate; pH_f = pH of mixed solution; and $pH_{HCO_3^-}$ = pH of solution on the basis of bicarbonate alone.

The equations were solved using a personal computer and a spreadsheet program. The simulated curves are plotted on Figures 1, 2, and 3, and are superimposed on the actual titration data. In general, the simulated curves match the experimental curves quite well. It should be noted that where a low concentration of acetate is present (Figure 2) the solution equivalence point is dominated by the carbonate contribution. The ensuing calculations could produce a total alkalinity value less than the true one.

Discussion

Assumptions

Equations (9) and (10) are valid only when $\{H^+\}$ and $\{OH^-\}$ are negligible compared to $\{Ac^-\}$, $\{HAc\}$, $\{HCO_3^-\}$, and $\{H_2CO_3\}$ (Butler, 1973). The breakdown of this assumption is evident in Figure 3 near the acetate equivalence point. The equation relating activities of the acetate species to Ka and hydronium ion activity in this region of the potentiograph is of third degree in $\{H^+\}$ and beyond the scope of this paper.

The simplistic way in which equations (11), (12), and (13) handle the transition between the carbonate-controlled portion of the potentiograph and the acetate-controlled portion initially assumes that $\{HCO_3^-\}$ and $\{H_2CO_3\}$ are much greater than $\{Ac^-\}$ and $\{HAc\}$. Later, an assumption of the same inequality in reverse is made. As soon as these assumptions break down and the activities approach equality, some error in the predicted curve results. For example, in Figure 3, at volume acid = 4 ml, pH = 6, but the predicted pH is only about 5.75.

In order to calculate the activities of the various anionic species, activity coefficients must be calculated. For the details of these calculations, the reader is referred elsewhere (Skoog and West, 1976; and Truesdell and Jones, 1974). The activity coefficients of acetate, H^+, and bicarbonate were estimated using a PC adaptation of the chemical equilibrium model PHREEQE (Parkhurst et al., 1980). The calculations were based on data collected during the alkalinity/acetate sampling program and previously published water-quality data for the same site (Jackson et al., 1985).

Despite the assumptions above, the errors in the predicted curves occur over relatively small portions of the potentiographs and are easily identifiable. The closeness of the agreement between the experimental and predicted curves strongly supports the hypothesis that acetate and bicarbonate are the two dominant factors contributing to the alkalinity of the Gloucester samples. Furthermore, it is possible to distinguish the samples containing high acetate concentrations simply on the basis of the potentiographs.

Distinguishing Carbonate Alkalinity from Acetate Alkalinity

The work above demonstrates that the shape of an acid titration curve can be used to distinguish carbonate-controlled alkalinity samples from others. Carbonate equivalence points are characterized by well-defined inflections in the potentiograph. The presence of other weak bases may dampen this inflection. Titrations to fixed end points will not provide the necessary data to make this distinction, leading to erroneous values of total alkalinity and erroneous assignments of this acid-neutralizing capacity to bicarbonate.

Wiley et al. (1975) suggested other methods of recognizing fatty acid-controlled alkalinities. They found that solutions containing primarily carbonate exhibited pH's which increased with increasing temperature. Solutions containing primarily organic acids exhibited decreasing pH's with increasing temperatures. In the field, the distinction could be made by acidifying samples and watching for effervescence. Samples with high alkalinities but which do not effervesce should be analyzed for fatty acids.

Conclusions

It may be concluded from the work presented above that the short chain fatty acids, particularly acetate, produced during the acidification stage of refuse decomposition at landfills, may contribute substantially to a leachate sample's total alkalinity. The correct assignment of the alkalinity to the organic acid anion depends upon the investigator's ability to interpret the analytical data. An incorrect assignment of alkalinity to carbonate species could result in inaccurate plume mapping or an incorrect assessment of the incrustation potential of a well. Titrating to a fixed end point does not provide the data necessary to identify the dominant control on alkalinity.

In the field, it may be possible to identify carbonate-controlled alkalinity on the basis of effervescence upon acidification. This would only be possible in samples with high alkalinities. This test might be misleading in cases where both high carbonate and organic acid alkalinity are present.

In the laboratory, it may be possible to identify organic acid-controlled alkalinity on the basis of the solution's pH response to increasing temperature, or, more simply, by the shape of the titration curve or potentiograph, if the sample is titrated beyond its equivalence point. Carbonate-controlled alkalinity is characterized by an equivalence point at a pH of about 4.0 to 4.5, and a clear inflection in the potentiograph. Acetate-controlled alkalinity is characterized by a weak inflection point. Since many other organic acids have acid dissociation constants below that of carbonate, the same influence on the shape of the titration curve might be expected from them.

References

Baedecker, M. J. and W. Back. 1979. Hydrogeological processes and chemical reactions at a landfill. Ground Water. v. 17, no. 5, pp. 429-437.

Butler, J. N. 1973. Solubility and pH Calculations. Addison-Wesley Publishing Co. Inc., Don Mills, Ontario. 104 pp.

Clark, T. P. and R. Piskin. 1977. Chemical quality and indicator parameters for monitoring landfill leachate in Illinois. Environmental Geology. v. 1, pp. 329-339.

Farquhar, G. J. and F. A. Rovers. 1973. Gas production during refuse decomposition. Water, Air and Soil Pollution. v. 2, pp. 483-495.

Harmsen, J. 1983. Identification of organic compounds in leachate from a waste tip. Water Research. v. 17, no. 6, pp. 699-705.

Hoeks, J. and R. J. Borst. 1982. Anaerobic digestion of free volatile fatty acids in soils below waste tips. Water, Air and Soil Pollution. v. 17, pp. 165-173.

Jackson, R. E., R. J. Patterson, B. W. Graham, J. Bahr, D. Belanger, J. Lockwood, and M. Priddle. 1985. Contaminant hydrogeology of toxic organic chemicals at a disposal site, Gloucester, Ontario, 1. Chemical concepts and site assessment. Environment Canada, Ottawa. National Hydrology Research Institute paper no. 23. 113 pp.

Kotze, J. P., P. G. Theil, and W.H.J. Hattingh. 1969. Anaerobic digestion II. The characterization and control of anaerobic digestion. Water Research. v. 3, p. 459.

McCarty, P. L. 1963. Principles and application in aquatic microbiology. Rudolfs Research Conference Proceedings, H. Heikelekian and N. C. Donero, eds., Rutgers, the State University. J. Wiley and Sons Inc., New York.

Nicholson, R. V., J. A. Cherry, and E. J. Reardon. 1983. Migration of contaminants in groundwater at a landfill: A case study. Journal of Hydrology. v. 63, pp. 131-176.

Parkhurst, D. L., D. C. Thorstenson, and L. N. Plummer. 1980. PHREEQE—A computer program for geochemical calculations. U.S. Geological Survey, Water-Resources Investigations 80-96. 210 pp.

Skoog, D. A. and D. M. West. 1976. Fundamentals of Analytical Chemistry. Holt, Saunders College, Philadelphia, PA. 804 pp.

Stumm, W. and J. J. Morgan. 1980. Aquatic Chemistry. Wiley Interscience, Toronto, Ontario. 780 pp.

Truesdell, A. H. and B. F. Jones. 1974. WATEQ, a computer program for calculating chemical equilibria of natural waters. Journal of Research, U.S. Geological Survey. v. 2, no. 2, pp. 233-248.

Wiley, L. M., Y. K. Kharaka, T. S. Presser, J. B. Rapp, and I. Barnes. 1975. Short chain aliphatic acid anions in oil field waters and their contribution to the measured alkalinity. Geochimica et Cosmochimica Acta. v. 39, pp. 1707-1711.

* * * * *

J. F. Devlin graduated from Queen's University with a B.Sc. (Hons.) in Chemistry in 1980, and with an M.Sc. in Geological Sciences in 1986. Between 1985 and 1989, he worked as a consultant in the field of contaminant hydrogeology with Water and Earth Science Associates Ltd. Devlin is currently enrolled in a doctoral program in the Department of Earth Sciences at the University of Waterloo, Waterloo, Ontario, Canada.