Water Res. Vol. 16, pp. 699 to 705, 1982
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0043-1354/82/050699-07$03.00/0

A SIMPLIFIED BUFFER CAPACITY MODEL FOR SANITARY LANDFILL LEACHATE

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(*Received July* 1981)

Abstract—An initial simplified buffer capacity model for landfill leachate is postulated and compared to that of two different leachate samples from the same landfill. This equilibrium model is based on the products of anaerobic decomposition. The number of species is reduced by considering all organic acids as acetic acid. This simplification reduces the number and complexity of chemical analyses required to measure the species, and also, lessens the calculations involved.

The model predicts maximum buffer capacity pH within a ΔpH = 0.35, and underpredicts the magnitude by 16%.

INTRODUCTION

Sanitary landfill leachate is an important source of pollution to both surface and ground waters. Ninety percent of all municipal solid wastes generated in the United States are disposed of on land (Apgar & Langmuir, 1971). The leachate solution contains water soluble salts and redox sensitive substances plus the products of decomposition of organic matter. The composition of the leachate depends on the nature of the refuse deposited in the landfill, the cover material used, the earth surrounding the landfill and whether the decomposition is either aerobic or anaerobic. Secondary factors influencing composition are: amount of refuse, time of storage, degree of compaction, amount of water in contact with the refuse and temperature.

The chemical composition of municipal refuse varies considerably. However, the range of values in Tables 1 and 2 represent an approximation of the refuse being disposed (Bell, 1963; Kaiser, 1967).

Formation of leachate

Most water which enters landfill refuse cells will not appear as leachate until all the refuse layers have reached field capacity (all voids are filled with water) (Zanoni, 1973). This water is needed to sustain the microbial processes or organic decomposition. The microbial activity starts as soon as the refuse is discarded. Since oxygen is readily available initially, the initial decomposition is aerobic. A simplified chemical reaction for aerobic decomposition is (Apgar & Langmuir, 1971):

$$C_xH_yO_z + NH_3 + O_2 \xrightarrow[\text{Trace salts}]{\text{Aerobic microorganisms}} \text{new cells} + CO_2 + H_2O + \text{heat.} \quad (1)$$

However, when refuse is placed in the landfill and no oxygen is available, the microbial activity changes to anaerobic, whose simplified chemical reaction is:

$$C_xH_yO_z + NH_3 + H_2O \xrightarrow[\text{Trace salts}]{\text{Anaerobic microorganisms}} \text{new cells} + CH_4 + CO_2 + H_2O + NH_3 + N_2 + \text{heat.} \quad (2)$$

Anaerobic decomposition is the dominant reaction in the formation of leachate. Anaerobic organic reactions shown above occur in two distinct stages. The first is liquifaction or acid formation, where complex

Table 1. Chemical composition of municipal refuse*

Component	Percent weight as received
Moisture	21–28
Carbon	25–28
Total hydrogen	3–3.5
Oxygen	21.1–22.4
Nitrogen	0.33–0.5
Sulfur	0.1–0.16
Noncombustible	22.0–24.9

* Bell, (1963) and Kaiser (1967).

Table 2. Organic analysis of municipal refuse*

Component	Percent weight as received
Moisture	21.0
Cellulose, starch, sugar,	46.6
Lipids	4.5
Protein (6.24% N)	2.06
Other (plastic)	1.2
Ash, metal, glass	24.9

* Bell (1963).

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Table 3. Organic acids produced in a simulated landfill

Acid component	Average percentage* of all organic acids	pK_a (dilute sol)†
Acetic	24	4.76
n-Butyric	15	4.82
Carproic	23.3	4.80
iso-Butyric	11.2	4.82
iso-Valeric	8.5	4.78
n-Valeric	18.3	4.86

* Zison (1974).

† The Chemical Society (1964).

organic compounds are broken down principally to organic acids (Zanoni, 1973). The simplest acid is acetic acid. Table 3 is a summary of the typical acids produced, their average percent of total acid production for a similated landfill, (Zison, 1974) and their respective dissociation constants (The Chemical Society, 1964). In the second step, the organic acids are further broken down into gaseous end products.

The nitrogen system also undergoes a biochemical process reducing nitrate and nitrite to nitrogen gas (denitrification). Ammonia gas is formed from organic compounds that contain nitrogen. An oxidation reduction reaction also takes place for sulfur containing compounds. This reaction has hydrogen sulfide as an end product. Nitrite takes less energy to reduce than sulfate as shown in Fig. 1. (These two redox systems are based on equations from Stumm & Morgan (1970)). Thus, if the same amounts of nitrogen and sulfur are present, the hydrogen sulfide concentration should be much lower than ammonia.

The object of this paper is to create an initial analytical model of the buffer capacity of leachate. This solution property is important since leachate buffer capacity affects the pH of the ground and/or surface waters which mix with leachate. pH determines the solubility, predominant ionic species, and complex formation in aqueous solution. Toxicity is also affected by these parameters.

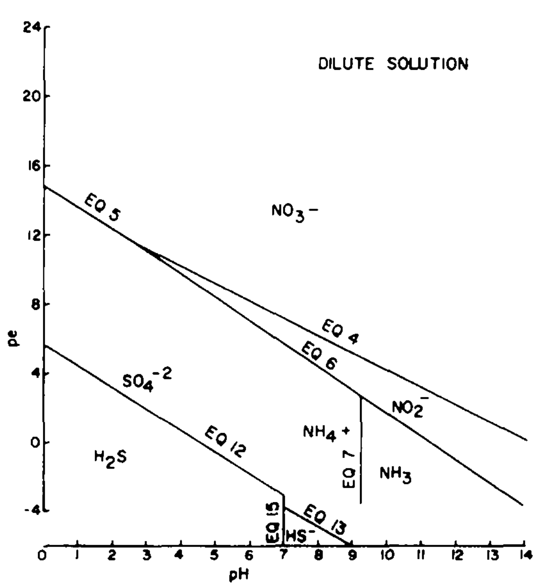

Fig. 1. Nitrogen and sulfur redox predominance diagrams in dilute solution. See Stumm & Morgan (1970, p. 318) for equations (4)–(7), (12), (13) and (15).

The modeling approach taken is to start from the simplest set of criteria or fewest number of terms in an additive equilibrium model and then exercise the model by comparison with the real data (Suffet, 1977). If there is unsatisfactory agreement additional parameters can be added in an interative process by which the phenomenon modeled becomes better understood and new phenomena or research paths may be revealed.

EXPERIMENTAL

The samples are from a landfill with an impervious underliner in Bucks County, Pennsylvania (Buchanan, 1977). The physical dimension of this landfill are:

1. Maximum depth ≤ 70ft.
2. Average depth ≃ 30 ft.
3. Area ≃ 30 acres
4. Sideslopes ≃ 45
5. Volume ≃ 48,300 cubic yards.

The leachate generation varies between 7000 and 50,000 gallons day^{-1} depending on the seasonal rainfall. The average leachate production is approx. 20,000 gallons day^{-1}. The impervious liner underlying the entire landfill catches the liquid passing through the refuse and directs it to a sump. The leachate is then pumped from the sump to a nearby treatment plant. Grab samples were taken from the treatment plant influent. These samples represent a composite of the products of chemical, physical and biological processes during the time the water passes through the landfill (Fig. 2). The sump composites leachate vertically and horizontally from all areas of the landfill. The processes occurring locally are average throughout the landfill.

Chemical analysis of leachate

The characteristics of leachate listed in Table 4 were determined using the analytical techniques in *Standard Methods* (APHA, 1976) except for ammonia and ionic strength. The chemical properties and their associated analytical methods are listed below:

1. Iron atomic absorption spectrophotometry on Perkin Elmer 4000.

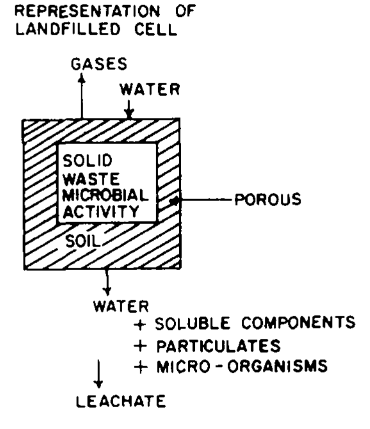

Fig. 2. Representation of idealized landfill cell.

2. Total organic carbon— i.r. method on Beckman 915 analyzer.
3. Ammonia -specific ion electrode, Orion Corp. Model 95-10.
4. Total phosphate—ascorbic acid method.
5. Hydrogen sulfide—titrimetric method.
6. Total organic and volatile acids, as acetic—distillation and chromatographic separation method.
7. Ionic strength—calculated from total dissolved solids.

The ionic strength is estimated from the following equation from Stumm & Morgan (1970):

$$\text{Ionic strength} = \text{total dissolved solids} \times 2.5 \times 10^{-5}. \qquad (3)$$

Using the above equation, the winter and summer sample ionic strengths are approx. 0.40 and 0.28, respectively. These leachate samples cannot be considered dilute solutions and all dissociation constants, based on an infinite dilution scale, should be corrected for ionic strength. The correction is calculated by the Davies equation as presented in Stumm & Morgan (1970).

$$pK_1 = pK_a - \log_{10} F \qquad (4)$$

$$\log_{10} F = AZ^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.21\right) \qquad (5)$$

where:

$Z \equiv$ ionic charge;
$I \equiv$ ionic strength;
$A \equiv$ constant of proportionality $= 0.5$.

The above correction factor is applicable for ionic strengths < 0.5 and > 0.1. Each winter sample species at pK_1 and pK_2 are corrected by subtracting 0.15 and 0.62, respectively. The summer sample pK_1 and pK_2 corrections are 0.15 and 0.52, respectively.

The presence of ammonia and hydrogen sulfide may be determined qualitatively by their distinctive odors. Ammonia is detectable by its odor at a concentration of 50 ppm in air. The corresponding detection level for hydrogen sulfide is 5 ppm (American Conference of Government Industrial Hygienists, 1966). The gases are released from solution by adjusting the pH below the pK value for hydrogen sulfide and above the pK of ammonia. As nitrogen passes through the leachate, the gases in solution are forced out of solution and into the air.

DISCUSSION

Leachate model for buffer capacity

The initial model for leachate buffer capacity must include the anions of the products of microbial decomposition plus the anions of the weak acids and bases present in the earth bounding the refuse cells (Fig. 2). The components to be considered in this model are:

1. Organic acids (OA) as listed in Table 3;
2. Ammonia (Aq.): $pK = 9.25$;
3. Hydrogen sulfide (Aq.): $pK_1 = 7.0$, $pK_2 = 13$;
4. Carbonic acids: $pK_1 = 6.35$, $pK_2 = 10.25$.

$B_T = B_{OA} + B_{NH_3} + B_{H_2S} + B_C$, since total buffer capacity B_T is equal to the sum of its component parts. Each pK must be corrected for ionic strength by equations (4) and (5).

The proposed model of leachate buffer capacity may be simplified by assuming that the hydrogen sulfide concentration is small compared to that of organic acids ammonia and carbonate. This assumption is tested using the measured buffer capacity from the titration for the winter sample (Fig. 3). The total carbonate concentration is estimated by assuming the carbonate buffer capacity equals the difference between the total, and organic acids (measured as acetic) plus ammonia buffer capacities at pH = 7.0. The log concentration diagram of the species present in the winter sample (carbonate, ammonia and organic acids) are shown in Fig. 4. The species present in the summer

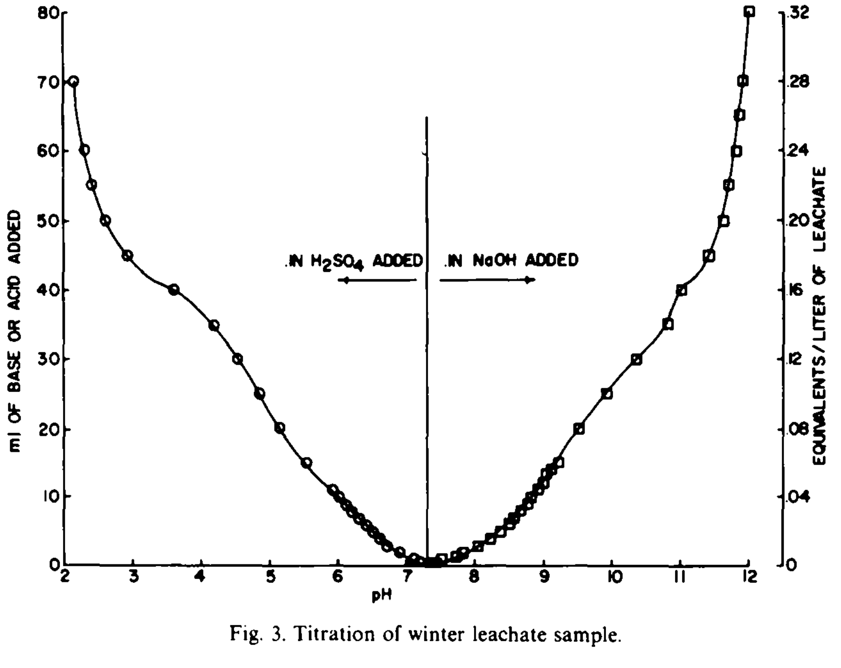

Fig. 3. Titration of winter leachate sample.

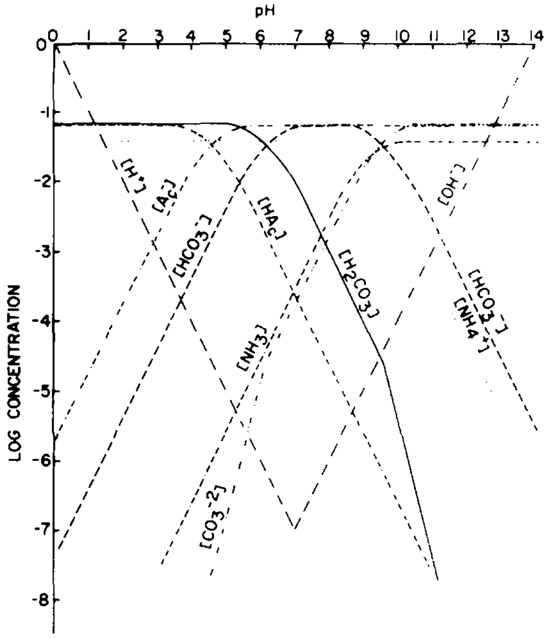

Fig. 4. Log concentration diagram of species in winter leachate sample.

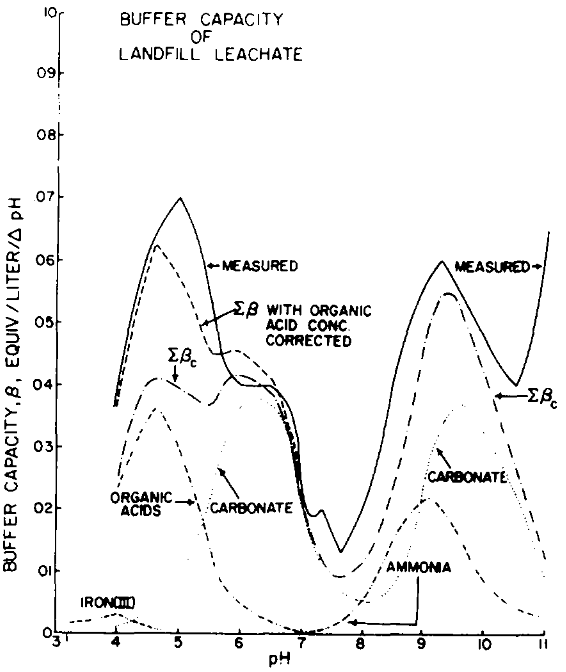

Fig. 6. Buffer capacity of winter leachate sample.

sample are shown on the log concentration diagram Fig. 5.

Figure 6 compares the leachate buffer capacity determined by the model with the measured buffer capacity. This graph shows that the simplified model (hydrogen sulfide not considered) matches the measured buffer capacity in shape and level over the pH range from 6 to 10. The grouping of all volatile organic acids into a characteristic acid does not create large errors because the principal acids produced by anaerobic fermentation have dissociation constants grouped within a ΔpK of 0.1, as shown in Table 3.

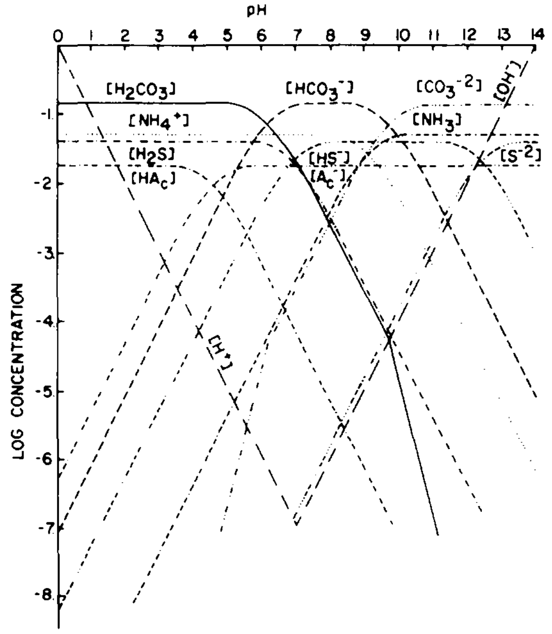

Fig. 5. Log concentration diagram of species in summer leachate sample.

The buffer capacity model under predicts the buffer capacity at pH <6. This suggests that iron is behaving as a weak acid during hydrolysis. This premise is calculated using iron(III) as the cation, and with the hydroxyl ion as the only ligand of iron. The use of iron(III) is valid because the acidimetric titration was performed in the presence of air and the solution stirred. Thus, very little, if any, iron(II) should be present in solution. The predicted iron(III) buffer capacity is also shown in Fig. 6 from pH 3.25 to 4.75. This capacity is less than 4% of the measured maximum buffer capacity and is far short of explaining the difference between the measured and the predicted buffer capacity. Another explanation for the low prediction is that the measured concentration of organic acids is incorrect in the winter sample.

A method of measuring total carbonate would eliminate the error that may exist in estimating carbonate as the difference in buffer capacity between the alkalinity measured and that of organic acids plus ammonia. One way is to assume that total inorganic carbon as measured by the i.r. method is solely the carbon in carbonate species. The summer sample is measured for total inorganic carbon and thus the model buffer capacity, shown in Fig. 7 is based on a direct estimate of total carbonate.

The gross under predicition at pH < 6 for the winter sample may possibly be due to the large error in the determination of the concentration of the organic acids. The analysis for volatile organic acids was by the chromatographic separation (APHA, 1975). It was found that the test recoveries of organic acids varied greatly. Therefore the summer sample

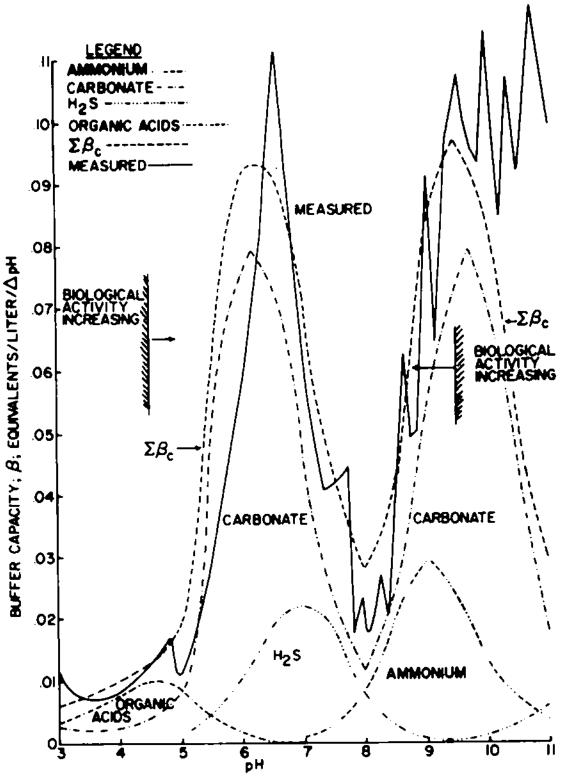

Fig. 7. Buffer capacity of summer leachate sample.

was analyzed by the steam distillation method. To test this, a new estimate is made by assuming the ratio of total organic carbon to volatile organic acids is relatively constant between the two samples. The ratio for the winter sample TOC/organic acid = 1.178 while the summer sample is equal to 0.752. Using the summer sample ratio, the winter organic acid concentration should be 0.1 M instead of 0.07 M. With this 0.1 M adjusted value for organic acid, a new model buffer capacity is calculated that matches the measured buffer capacity much better at $\text{pH} < 6$, as shown as a dashed line on Fig. 6.

The assumption of negligible hydrogen sulfide was tested in the summer sample and found to be in error. The reintroduction of this new species is a simple matter of adding another term to the total buffer capacity model. This addition improves the prediction by decreasing the difference in the peak buffer capacity @ pH 6.2, from 0.03, to 0.018 equiv. $l^{-1}\ \Delta \text{pH}^{-1}$, although the model still predicts low values. The difference in pH at which the peak buffer capacity occurred between prediction and measured changed from 0.6 to 0.3. Thus, the addition of sulfide can be a significant contribution to leachate buffer capacity.

The lack of agreement between the model and the actual buffer capacity at $\text{pH} > 10$ for both samples is a matter that cannot be explained by the inclusion of hydrogen sulfide into the anaerobic decomposition buffer capacity model, as can be seen in Fig. 7. Other possible explanations not related to anaerobic decomposition are: (1) the presence of phosphate species; (2) the precipitation of metal hydroxides, carbonates and sulfides; (3) the hydrolysis of organic compounds; (4) the presence of humic and fulvic acids; and (5) the presence of other organic acids, i.e. phenols with $\text{p}K_a > 10$. The concentration of phosphate was measured for the summer sample and found to be negligible (4 mg l^{-1}) compared to the 0.37 M concentration of carbonate.

Humic acids can be considered dibasic with carboxylic and phenolic groups with dissociation constants of approximately $\text{p}K_1 \approx 4.8$ and $\text{p}K_2 \approx 10.5$ (Perdue, 1978). If there were a significant contribution to buffer capacity to account for the underprediction above pH = 10 then a similar contribution would be expected below pH 5. This would cause an overprediction of the buffer capacity at low pH. Therefore, the humic acids were not included in the buffer capacity model as it is not a likely cause of the underprediction. The remaining possible explanations are the precipitation of metal hydroxides, carbonates and sulfides, the hydrolysis of organic compounds and the presence of other organic acids as phenolics. These are areas of future investigation.

The origin of carbonate's large contribution (over 67% of the peak values) to the buffer capacity of landfill leachate requires more explanation. Carbon dioxide is a principle end product of either aerobic or

Table 4. Analysis of landfill leachate

	Winter 12/6/76	Summer 7/15/76
Total dissolved solids (mg l^{-1})	16000	11000
Total organic carbon (mg l^{-1})	4500	895
Total inorganic carbon (mg l^{-1})	·	1640
Total iron (mg l^{-1})	220	16
Total organic and volatile acids as acetic acid (mg l^{-1})	3820	1190
Total ammonia (mg l^{-1})	650	850
pH	7.3	7.7
Ionic strength	0.40	0.28
Total hydrogen sulfide (mg l^{-1})		1360
Total phosphate (mg l^{-1})	—	4

—No measurement recorded.

anaerobic decomposition. It has a considerable effect on geologic materials because it dissolves in water percolating through the landfill to form carbonic acid. In soils containing alkaline earth carbonates, this acid will react with the soil to form alkaline earth bicarbonates and iron bicarbonates if iron is present. This causes an increase in alkalinity, total hardness, total dissolved solids and ionic strength. If the surrounding soil cover is deficient in calcium and magnesium carbonates, a decrease in pH and increase in acidity will result (Zanoni, 1973). A concentration of CO_2 gas greater than 20 ppm is purported to cause these reactions (Hagerty & Pavoni, 1973). Thus, not only is the refuse a factor in the buffer capacity, but the chemical constituents of the soil surrounding the idealized refuse cell (Fig. 2) are as well.

Zanoni (1973) in his literature review states that the soluble end products of decomposition in landfills are attenuated in an underground aquifer by simple dilution. The buffer capacity model may be used to find the idealized dilution with complete mixing needed to change the pH in ground water to some specified level. A measurement of the effect of dilution with distilled water of pH 6.7 on the summer leachate sample pH is shown in Fig. 8. This figure represents a titration of leachate with a $[H^+]$ of $2 \times 10^{-}$ [illegible] molar. Thus, an ideal dilution volume ratio of 4500:1 is necessary for leachate to reach a pH of 7.0.

The buffer capacity of leachate in its environment at the bottom of a landfill will differ from that shown in Figs 6 and 7. This difference is caused by: (1) gases at higher than atmospheric pressure due to restrictions to gas flow by the refuse in the landfill; (2) constant *in-situ* temperatures partly from anaerobic decomposition but mostly because refuse acts as an insulator; and (3) the reducing environment from anaerobic decomposition. The leachate sample titrations are conducted in the presence of air at 22°C and 1 atm pressure, but the landfill leachate samples when taken effervesced and had a temperature of approx. 28°C. The differences in temperature and pressure will affect the solubilities of the three components of the model that are gases in solution, (ammonia, carbon dioxide and hydrogen sulfide). The reducing environment will cause an ion which can be reduced to be in their reduced state (e.g. iron II). Thus, the leachate buffer capacity and the species in solution in the landfill and/or ground water as measured in the laboratory should be corrected for the actual environment of the leachate. This would apply particularly to the concept of dilution, as measured in Fig. 8.

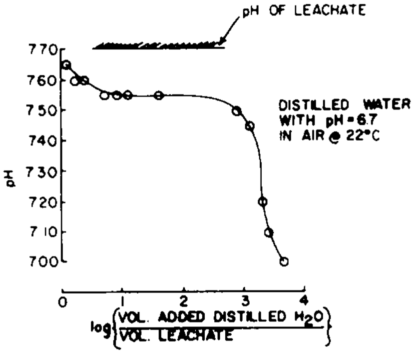

Fig. 8. Dilution and pH effects.

CONCLUSIONS

1. The model is an adequate predictor of the winter sample over a pH ranging from 6 to 10. For the summer sample, the accuracy of the buffer capacity is good over a pH ranging from 3 to 10. The difference in the pH range for accuracy between the two samples may be attributed to an apparent inaccurate measurement of the winter sample organic acids.

2. If the ratio of total organic carbon (mg l^{-1}) to organic acids (ng l^{-1}) does not vary between samples, the pH accuracy range of the model for the winter sample can be extended from $6 < pH < 10$ to $4 < pH < 10$.

3. The model predicts the magnitude of the maximum buffer capacity of landfill leachate from −16% to −8% of the measured value. The predicted pH of the peak buffer capacity falls within a ΔpH of 0.35 of the actual value.

4. The anaerobic model may be extended to include iron(II) and iron(III) hydrolysis, phosphoric acid and silicic acid depending on the relative concentrations of the species in the particular landfill leachate being analyzed.

5. The species with the largest contribution to the buffer capacity is carbonate with a minimum contribution of 67% of the predicted maximum buffer capacity.

6. Dilution of leachate can be treated as a titration. Thus, the model can be used to predict the effect of dilution on pH.

Recommendations

The effects of temperature, pressure and oxidation on the buffer capacity model need to be examined. The inclusion of the above parameters in the model will enable a prediction of leachate buffer capacity in the environment of the bottom of the landfill and/or ground water acquifer. Also the effect of metallic precipitates, the hydrolysis of organic compounds and the presence of weak acids with a $pK_a > 10$ are areas of future investigation.

Acknowledgements—We wish to thank the following for their assistance in the work upon which this paper is based: M. Lazanoff, City of Philadelphia Water Department and Dr R. J. Buchanan, Gilbert Inc., Reading, PA. We thank Ms Eloise Smith of the Environmental Studies Institute for typing the manuscript.

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