

The pH of an aqueous solution is a measure of the concentration of hydrogen ions. The pH scale is logarithmic, ranging from 0 to 14. A pH of 7 is neutral, below 7 is acidic, and above 7 is basic. The pH of a solution can be measured using a pH meter or a pH indicator. The pH of a solution can also be estimated using various methods, such as titration, colorimetry, and potentiometry. The pH of a solution is an important property that affects many chemical and biological processes. The pH of a solution can be controlled by adding acids or bases. The pH of a solution can also be affected by temperature and ionic strength. The pH of a solution is a key parameter in many scientific and industrial applications.

The Importance of the pH Buffering Capacity – Comparison of Various Methods to Estimate the pH Properties of a Waste Material

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The pH buffering capacity of a waste material is a measure of its ability to resist changes in pH. This property is important for the safe handling and disposal of waste materials. The pH buffering capacity of a waste material can be estimated using various methods, such as titration, colorimetry, and potentiometry. The pH buffering capacity of a waste material is an important property that affects many chemical and biological processes. The pH buffering capacity of a waste material can be controlled by adding acids or bases. The pH buffering capacity of a waste material can also be affected by temperature and ionic strength. The pH buffering capacity of a waste material is a key parameter in many scientific and industrial applications.

ABSTRACT

The final pH of the leach water controls the leaching of many metals from MSWI ash in construction materials and landfills. The buffering properties of the ash determines the final pH of the leachate and is therefore one of the most important properties of a waste material. In this study three different methods to investigate the pH buffering capacity of ashes have been compared; two batch methods and one flow-through method. The results of this study showed that the MSWI bottom ash used here had a large buffering capacity in the pH region where the solubility of most pH-sensitive metals is lowest, around pH 8. The buffering reactions are slow. The duration of an experiment should therefore be about 50 days if all material should have time to react. A comparison of the results of the experiments showed that at least 50 % of the buffering capacity in a batch system comes from dissolved constituents, that would not buffer in a flow-through system.

INTRODUCTION AND BACKGROUND

Solid residues, like ashes and slags, often have physical properties that make them suitable for utilisation in civil engineering applications. This can save large quantities of geological material and also substantially decrease the amount of waste sent to landfills. Before utilising a residue, the environmental impact of the construction has to be studied. One of the main concerns in utilising an ash is the long-term mobility of heavy metals. The mobility of metals is controlled mainly by the pH of the leachate. The effects of pH on leachability have been studied in several investigations.^{1,2,3,4,5,6} The pH has a significant influence on the aqueous concentrations of Al, Ca, Cd, Cu, Fe, Mn, Ni, Pb and Zn. The pH range for minimum leaching is often pH 8-10. At a pH above 10, the potential leaching of Cu, Pb and Zn increases. At a pH value below 7, there is a sharp increase in the leachability of metals within one or two pH units. To avoid the mobilisation of trace elements, the amount of acidic degradation products must not be significant in comparison with the acid neutralisation capacity of the waste material.

Somewhat aged MSWI bottom ash has a pH slightly over neutral, the region where the leaching of many toxic elements is low. In time, the pH buffering capacity will be depleted by intruding acidic rain, oxidation of organic material or metals, and reactions with carbon dioxide. This will decrease the pH value of the leachate and thereby increase the solubility of pH sensitive metals, sometimes by several orders of magnitude. As the pH buffering capacity in the upper layer is depleted first, while the buffering capacity at lower levels remains, a pH front will be formed between these regions. At the pH front the pH in the leach water will change from acidic to more alkaline within a very short distance. At this front trace metals can accumulate because the solubility changes with pH. This phenomena has been observed in natural systems. When the acid neutralisation capacity is depleted in all the material, large amounts of metals can be released from the ash within a short time period. The leachate concentration may then exceed the levels that the local environment can tolerate. This phenomena can not be observed in short term laboratory column experiments, nor in field studies of landfill sites where the leachate concentrations for the initial processes are measured. We have, however, observed the accumulation in the serial batch pH titration experiment, described later.

The pH buffering capacity of a material is more important for the final pH of the leachate, and thereby the solubility of trace elements, than the initial pH of the leaching media. The pH buffering capacity has been studied in several investigations.^{1,4,7} In this study three different experimental methods to investigate the pH buffering capacity of a weathered MWSI ash is compared. Two of the methods are batch titration methods: pH static titration, and pH batch titration. The third method is a flow-through pH titration; a serial batch pH titration. The former two are used by several other researchers and the latter is developed within this study.

MATERIALS AND METHODS

Material

The MSWI bottom ash used in this investigation was from Tekniska Verken in Linköping, Sweden. The ash was sorted with a magnet and should, therefore, be free from magnetic metal pieces, but there are still some caps, screws, and coins in the ash. The finest and largest particles of the ash were sorted and the fraction between 2 and 35 mm was used. The ash still contained a small fraction of fine dust. The bulk density of the MSWI ash was about 1.4 tonne per cubic metre. The composition of the ash is shown in table 1.

Preparation of samples

The sample was dried at 105°C to constant weight and stored in a closed plastic container. The ash was ground and sieved until all the material passed the 0.16 mm sieve and most of the material passed the 0.125 mm sieve. A few metal pieces were impossible to grind. These pieces, plus a small fraction of metal grains, were omitted. This fraction was less than one per cent of the total mass of ash.

pH-static experiments

In a pH-static experiment, the pH was kept constant by the addition of acid or base. In this case nitric acid was used. In the experiment, the pH-buffering capacity and the leaching at various pH levels was characterised.

40 g of ground material was put into a 500 ml Nalgene bottle; 200 g of water (Barnstedt quality) was added. The sample was titrated to the pH used in the experiment with nitric acid, using a Metrohm 719 S Titrino, and the pH was automatically kept constant for at least 1-2 weeks by the titration device. The samples were then put into a shaker, and the pH was manually adjusted for several months using a Metrohm 645 Multi-Dosimat and Metrohm 691 pH Meter. A 4 ml sample was taken out after 1 week for analysis.

pH-batch experiments

The aim of this experimental series was to determine the pH buffering capacity and the leaching at different pH levels. All the acid is added to the ash initially. This experiment does not require any equipment to be used constantly and therefore, many different experiments can be run simultaneously. This is a simpler procedure than the one used in the pH-static experiment.

2.5 gram of ground material was put into a 250 ml Nalgene bottle. Nitric acid and water (Barnstedt quality) were added to an L/S ratio of 100. The bottles were placed in the shaking device. The pH was measured after 5 minutes, 1, 7 and 50 days. 4 ml samples were taken for analysis after 7 and 50 days.

Serial batch pH-titration

This version of a serial batch experiment corresponds to a flow-through system where the contact time can be controlled. Sampling is also possible in several parts of the system. The principle of the experiment is shown in figure 1. The results can be used to simulate flow-through systems. The technique can also detect moving reaction fronts. We have previously used this method with pure water^{8,9}.

100 grams of the sample was weighed into each of 10 polypropylene bottles. 100 grams of 0.104 M nitric acid was added to bottle number 1 each time the water was shifted. The interval between water shifts was 2-3 days, sometimes more. The bottles were open to the atmosphere. The pH was measured and a 4 ml sample was taken from the last bottle at each water shift. The pH was measured and samples were taken from all 10 bottles occasionally. The first sampling occasion was when the water left the tenth bottle for the first time. The experiments were continued for 5 months.

Analyses

The samples were analysed by ion chromatography for bromide, calcium, carbonate, chloride, cobalt, chromium, copper, potassium, lithium, magnesium, manganese, sodium, nickel, lead, silica, sulphate, zinc. The ion chromatography system consists of a Dionex model DX-300, with both suppressed conductivity detection and a post-column reaction with UV-detection.

RESULTS

The most important factor controlling the leaching of many metals is the pH. Figures 2a-d show the leachate concentration of Mn, Fe, Cu, and Zn versus pH in the pH batch experiments. The concentrations in the pH static experiments are close to those from the pH batch experiment. The solubility of these metals is strongly pH-dependent. Fe, Cu and Zn have leaching minima at pH's of 6-8, 7-9 and about 9 respectively, whereas the leaching for Mn decreases with increasing pH and was not detected in the samples in which the pH was over 8.

The pH batch experiment series generated pH titration curves. The pH-buffering capacity close to the initial pH was low. The pH was measured at four different occasions during the experiment. The pH titration curves for the different occasions are shown in figure 3. This experimental series shows that the pH-buffering reaction kinetics differ in various regions. Another study of the pH buffering reaction kinetics has been performed (Yan et al., 1996). This study is based on the results of the pH static titration experiments, shown in figures 4 and 5.

The pH buffering reactions have shown to be rather slow. Figure 4 shows the consumption of acid necessary to maintain a constant pH of 8.5 for MSWI bottom ash versus time in the pH static experiment. These results show that the reaction time for solid wastes is rather long and that it is beneficial if the duration of an experiment with MSWI ash is at least 50 days. Only slightly more than 50% of the material has reacted after 24 hours, the normal time for a pH static experiment. This is also confirmed the pH batch experiment in figure 3.

Figure 6 shows the pH in the different bottles of the serial batch pH titration at various occasions. The leachate leaving the system had a constant pH (only slightly higher in the first leachate), whereas in the first five bottles the pH changed with added amount of acid. In this experiment we could observe that the solubility of iron was high in the acidic environment and lower in the neutral. When the experiment was interrupted, bottles number 4 and 5 were rust brown. This colour had followed the pH front developed between the acidic and the alkaline bottles. The dissolved oxidised iron re-precipitated in the first bottle with neutral solution and was later dissolved, when the solution became acidic.

A pH titration curve for a flow-through system was calculated from the data in figure 6. This curve was compared with the pH titration curve for the pH batch experiment and the pH static experiment, shown in figure 5. The pH buffering capacity of the ash is higher in a batch system than in a flow-through system.

DISCUSSION

The pH static method and the pH batch method both generate a pH titration curve for batch systems. The largest difference between those methods is that in the pH batch experiment all the acid is added at the start of the experiment. This leads to a very low pH in the beginning of the experiment. At this low pH, phases may buffer irreversibly, that would not buffer at the final pH. This can lead to errors in the titration curve. In the pH static experiments this problem is avoided as the pH is kept constant, by addition of acid.

In a batch system dissolved buffering species stay in the solution, and will therefore contribute to the buffering capacity. In a flow-through system these species will be flushed out and will not contribute to the buffering capacity. The results of this investigation show that 50% or more of the buffering capacity in the batch titration comes from dissolved species.

The pH batch titration is a simple experiment, but this method also has the most uncertainties of the three methods investigated in this study. The pH static experiment, that gives a more reliable titration curve is time-consuming, as only one pH value (one bottle) at a time can be made with the equipment. In our case every point on the pH titration curve occupied the equipment for at least one week. After that, the pH was adjusted manually. In the pH batch experiment all points on the curve can be run in parallel. This experiment only takes 50 days, with very little effort, and very little equipment. The serial batch pH titration also requires little equipment, but is rather time-consuming.

What method we choose depends on the purpose of the investigation. The batch titrations are more accurate than the flow-through titration, as the latter is sensitive to the concentration of the acid. Buffering agents can be dissolved and flushed out without contributing to the buffering capacity in the experiment. This can lead to an underestimation of the buffering capacity. In the batch titrations, on the other hand, the buffering agents stay in the solution, and buffer even though they should have been flushed out in a real situation (very few landfills and constructions are of a batch system type).

The choice between the pH batch experiment and the pH static experiment has to be a consideration between accuracy, time and cost. The results, shown in this report, indicate that there is no significant difference between the results of the two methods used, but the pH range is rather small. In the lower pH region there were a few points that deviated considerably from the pH batch titration curve, not shown here. We have, incidentally, not yet been able to reproduce these results because our pH static equipment broke down, and there has not been time to repeat them. Those experiments were the last made and may therefore be completely wrong.

The buffering capacity of the MSWI bottom ash is high at the level where the leaching of many metals is minimised. In a water saturated system the pH will remain at this level for a long time. In a partially water saturated system there are several reactions that can consume the pH buffering capacity. Carbon dioxide acts like an acid and will diffuse in from the atmosphere and react with the ash. Another source of acidity is oxidation of metals and uncombusted carbon. Carbonation and oxidation reactions are several orders of magnitude faster in a partially saturated system where air can diffuse into the ash than in a saturated system where the gases first have to dissolve in the water and then diffuse in the liquid phase. The buffering capacity will therefore last much longer in a saturated system than in the partially saturated system.

CONCLUSIONS

From this study some conclusions can be made.

- The pH buffering capacity at the initial pH is very low. The out-flow pH in a flow through system will reach a pH value of 8 fast and remain at that pH for a very long time. In this pH region the leaching of most toxic metals is minimised.
- The pH buffering reaction kinetic is slow. The duration of an experiment with MSWI should be at least 50 days.
- In a batch titration at least 50 % of the buffering capacity comes from dissolved species.
- The pH batch experiment is much easier to perform than the others.

ACKNOWLEDGEMENTS

The author wishes to thank Tomas I Ulväng for his help with the pH batch experiments, and him and Cecilia Möller for their help with the serial batch pH titration. This project was financed by the Swedish Environmental Protection Agency.

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Table 1. Composition of the MSWI bottom ash used in this study.¹⁰ The ash was digested in lithium metaborate melt for main components and with nitric acid in Teflon bomb for certain trace elements (As, Cd, Co, Cu, Hg, Ni, Pb, Zn). All elements were analysed on ICP-AES. ICP-MS was used for low concentrations. Results are means for duplicates.

Element	Concentration	Element	Concentration
Al	5.69%	Cd	5.8 ppm
Ca	8.79%	Co	19.1 ppm
Fe	10.8%	Cr	274 ppm
K	1.43%	Cu	3400 ppm
Mg	1.13%	Mo	16.0 ppm
Mn	0.14%	Nb	13.1 ppm
Na	2.64%	Ni	138 ppm
P	0.45%	Pb	737 ppm
S	0.86%	Sn	130 ppm
Si	20.9%	Sr	285 ppm
Ti	0.62%	V	58.7 ppm
As	16.0 ppm	W	33.9 ppm
Ba	1660 ppm	Zn	3080 ppm
Be	1.78 ppm	Zr	200 ppm
Loss on ignition 550°C	4.3%		

Hg was below detection limit

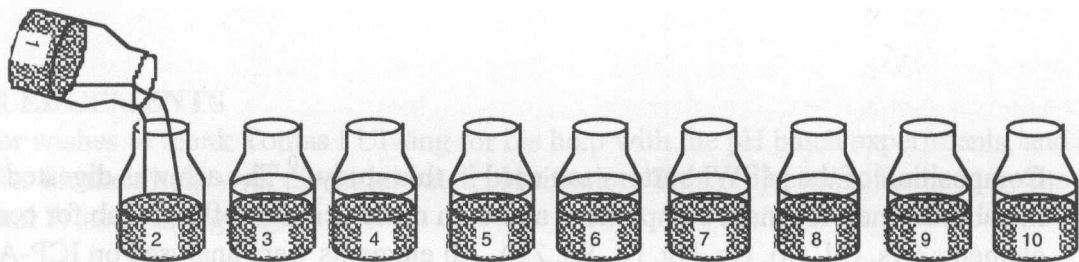
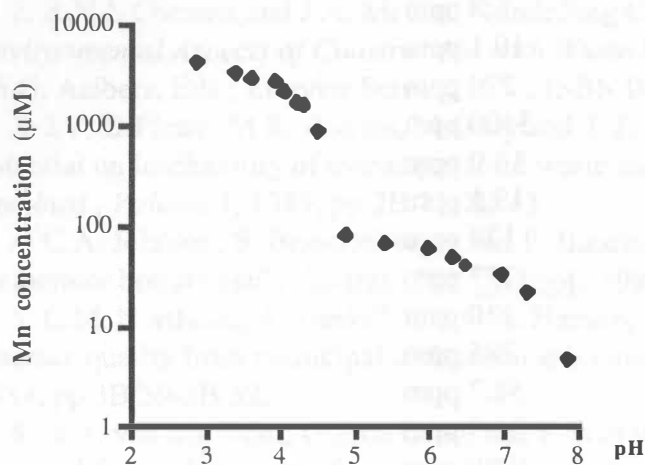
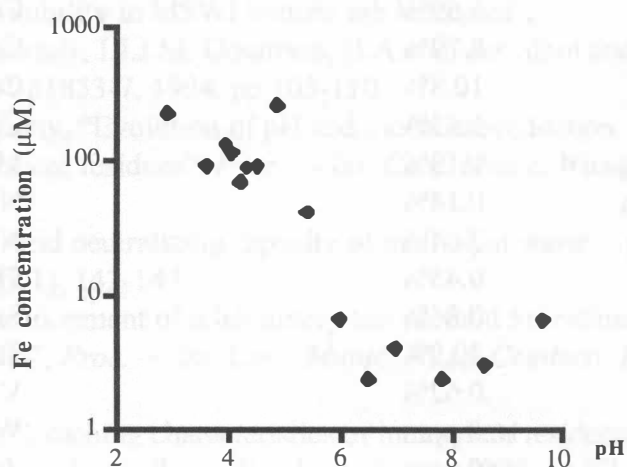


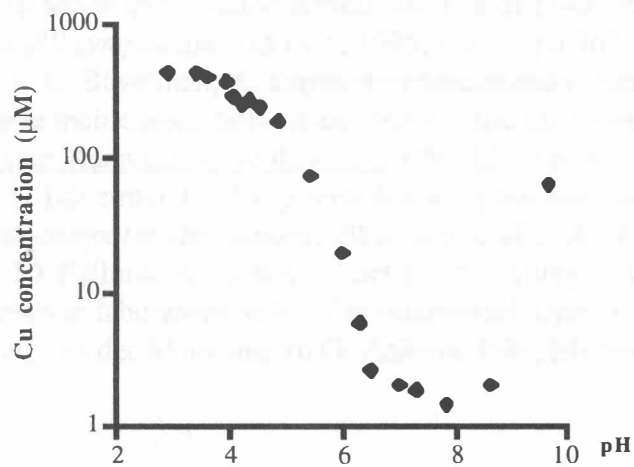
Figure 1. In the serial batch pH titration experiment, the water was poured from the first to the second, from the second to the third etc. at intervals of 2-3 days.



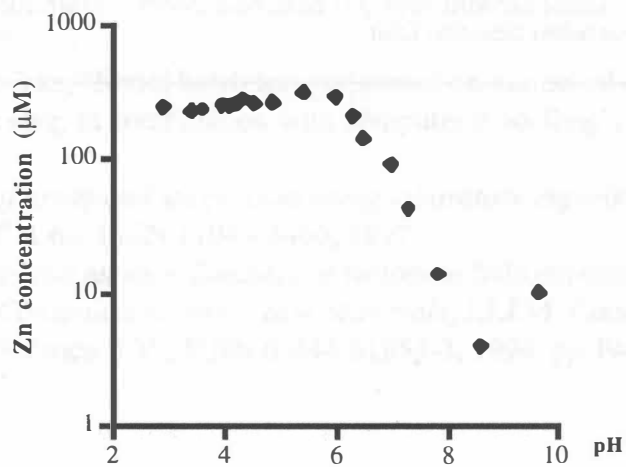
(a)



(b)



(c)



(d)

Figures 2a-d. The leach water concentration of Mn, Fe, Co and Zn in the pH batch experiments after one week of leaching.

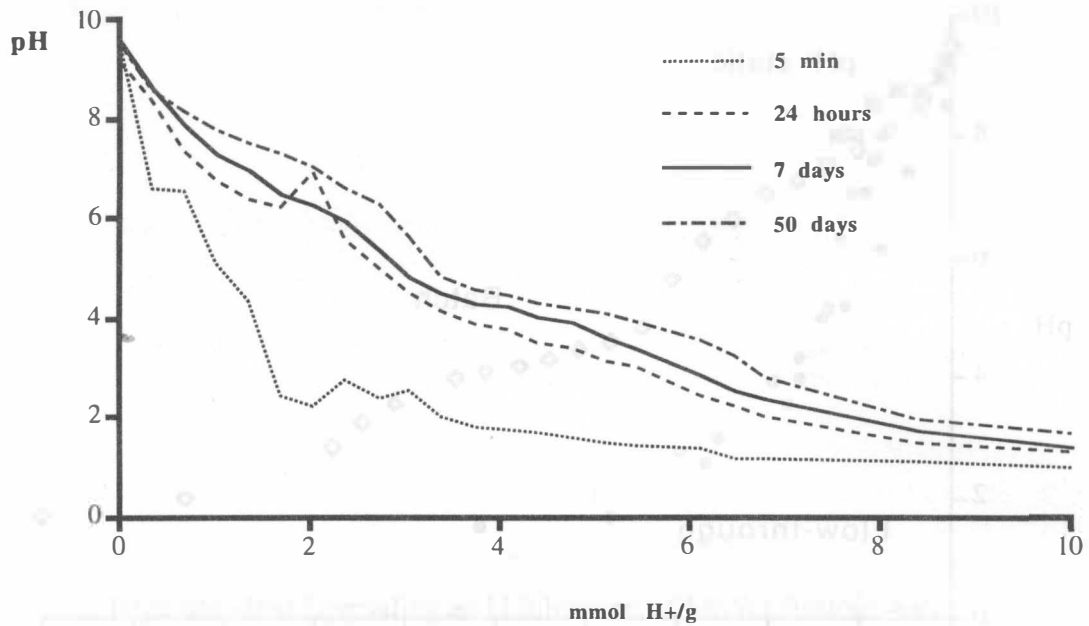


Figure 3. four The pH titration curve obtained from the pH batch experiments. The pH is measured on different occasions.

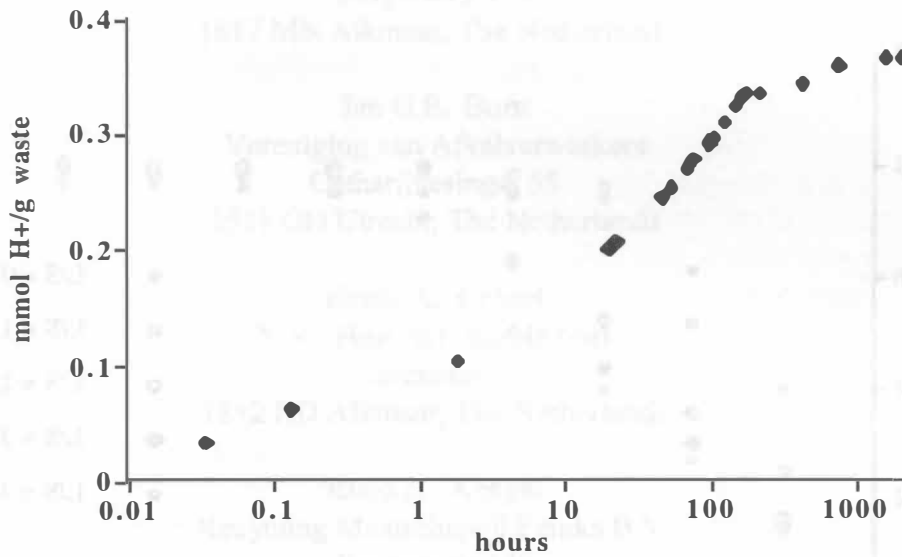


Figure 4. The amount of acid added to maintain the pH in the MSWI bottom ash at 8.5 versus time in the pH-static experiment.

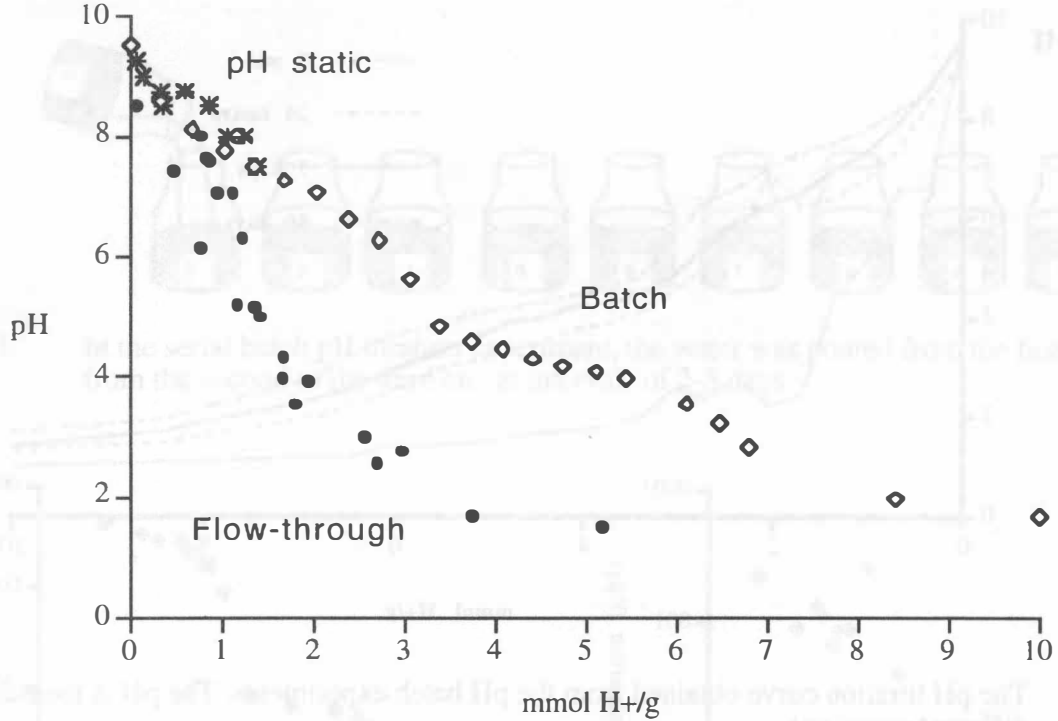


Figure 5. The pH titration curves obtained from the pH batch experiment and the serial batch pH titration.

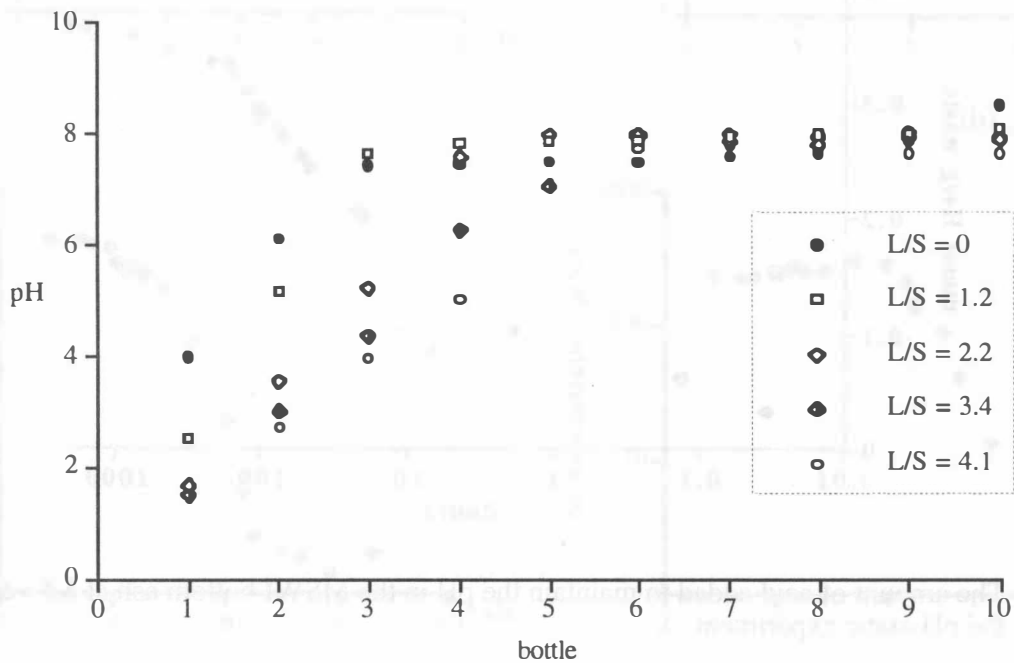


Figure 6. The pH in the different bottles in the serial batch pH titration. The pH is measured on five occasions. The L/S that has passed the bottles at the sampling occasions are indicated.