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Communication

Differential acid neutralisation analysis

G.K. Glass*, N.R. Buenfeld

Department of Civil and Environmental Engineering, Imperial College, London, SW7 2BU, UK

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Abstract

The acid neutralisation behaviour of cement may form the basis of a quantitative analytical technique. In this work a method of analysing acid neutralisation data, termed "differential acid neutralisation analysis," that transforms the data into a series of peaks at different pH values is presented. This analytical technique may be used to obtain information on the quantity, type, and condition of the phases in materials like concrete that resist acidification at particular pH levels and may also quantify the inhibitive properties arising from a resistance to a fall in pH. Closely spaced peaks may be readily identified allowing the quantity of acid corresponding to a particular component to be accurately determined. However, further work is needed to improve the collection of the data, identify the phases corresponding to particular peaks, and assess the application of the technique to materials other than concrete. This may be assisted by methods of accelerating the achievement of the solid-solution equilibrium and by the addition of standards to the material tested.

Keywords: Characterisation; Hydration products; Corrosion; Acid resistance; Concrete

1. Introduction

The acid neutralisation capacity of cement pastes was first investigated in the mid-1980s [1,2]. It involves plotting the steady state pH against the quantity of acid added to a series of ground samples to obtain a titration curve. Its main use has been to investigate the leaching resistance of cement-based solidified waste matrices [2,3]. However, the ability of cement to resist a fall in pH not only affects leaching [4], but is also one of the most important inhibitive properties affecting carbonation [5,6] and the quantity of chloride required to initiate corrosion of steel embedded in concrete [7].

The acid neutralisation capacity test has been recognised as a possible quantitative analytical technique and, in addition to quantifying one of the inhibitive properties of concrete, may provide information on its cement composition [1,8]. The basis for this is that different hydrated phases dissolve at different pH levels. In this brief work a new method of analysing acid neutralisation data is presented. This may advance the characterisation of both the composition and the inhibitive nature of the material examined.

2. Acid neutralisation data

A typical titration curve obtained on an ordinary Portland cement (OPC) concrete (400 kg/m^3 of OPC with an approximate Bogue composition of 62% C_3S, 13% C_2S, 7% C_3A, and 9% C_4AF) is presented in its standard form in Fig. 1. A batch of 16 tests were undertaken to obtain this curve; each point is the result of adding a predetermined quantity of acid (up to 5 mL of 2.5 M nitric acid) to 5 g of ground sample that had been mixed with distilled water (the total volume of liquid added was 11 mL) and measuring the pH until no further change occurred (typically 8 days). Similar curves obtained on cement pastes have previously been reported [1,8].

Three plateaus arising from a resistance to a fall in pH are clearly evident. It has been postulated that these result from the dissolution of the various hydration products of cement. For example, the plateau that occurs at a pH of approximately 12.5 in Fig. 1 may have arisen from calcium hydroxide. Different plateaus have arisen from the presence of other components resulting from the use of pulverised fuel ash (PFA) and ground granulated blast furnace slag (GGBS) replacement materials [1].

3. Data analysis

A method of analysing data that has not previously been applied involves transforming this titration curve into a spectrum of peaks at pH values where a resistance to acidi-

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* Corresponding author. Tel.: +44-171-594-5956; fax: +44-171-225-2716.

E-mail address: g.glass@ic.ac.uk (G.K. Glass)

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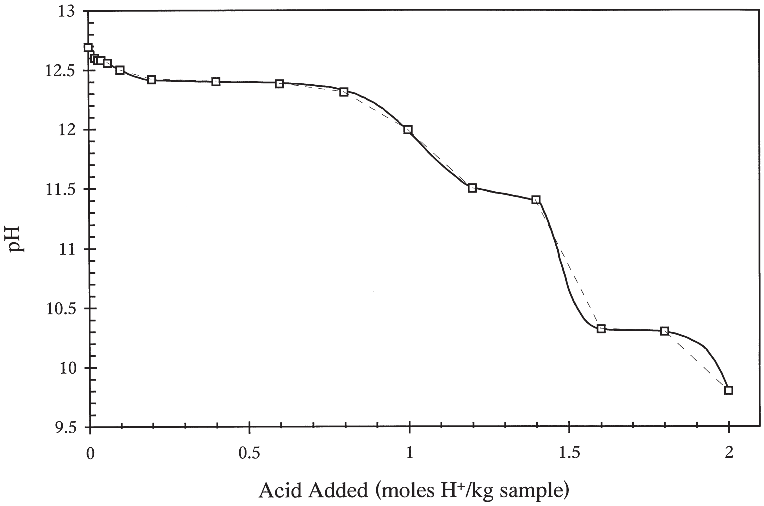

Fig. 1. Steady state pH as a function of the quantity of acid added to samples of ground OPC concrete.

fication occurs (the pH plateaus in Fig. 1). This may be achieved by plotting the absolute value of the inverse slope of the dashed curve in Fig. 1 (a series of lines connecting adjacent points) against the pH. This is equivalent to transposing the axes and plotting the negative of the first derivative of the resulting curve against pH. The resulting spectrum is given in Fig. 2. The height of the plotted spectrum corresponds to the change in acid added per unit of induced pH change. The area under the spectrum between any two pH values is equal to the quantity of acid required to induce the corresponding change in pH. Four peaks at pH values of 10.3, 11.5, 12.4, and 12.6 were identified.

Because of the nature of the dashed curve, step changes occur at each measured pH value. For illustrative purposes, a more refined set of data might be represented by the solid curve in Fig. 1. This was produced by fitting a series of S-shaped shaped curves to each adjacent pair of pH plateaus. Fig. 3(a) gives a single S-shaped curve that is the expected titration curve resulting from the addition of a strong acid to a strong base solution [9], while Fig. 3(b) gives its transformation. (For comparison with Fig. 2, the y-axis units in Fig. 3(b) have been determined assuming 11 mL of solution contains 5 g of solid material.) Fitting series of S-shaped curves to the data in Fig. 1 ensures that an increase in the quantity of acid added will be accompanied by a decrease in pH. However, this amounts to smoothing of the data that results in the loss of information.

The transformation of the solid curve in Fig. 1 is given in Fig. 4. Again a series of peaks representing components in the system that resist acidification is produced with the area under the peaks giving the quantity of acid required to neutralise the associated component.

4. Discussion

The method of analysis explained above (plotting the difference in acid added per unit of induced pH change against pH) is analogous to differential thermogravimetric analysis and may be termed “differential acid neutralisation analysis.” The analogy may be clarified by transposing the axes

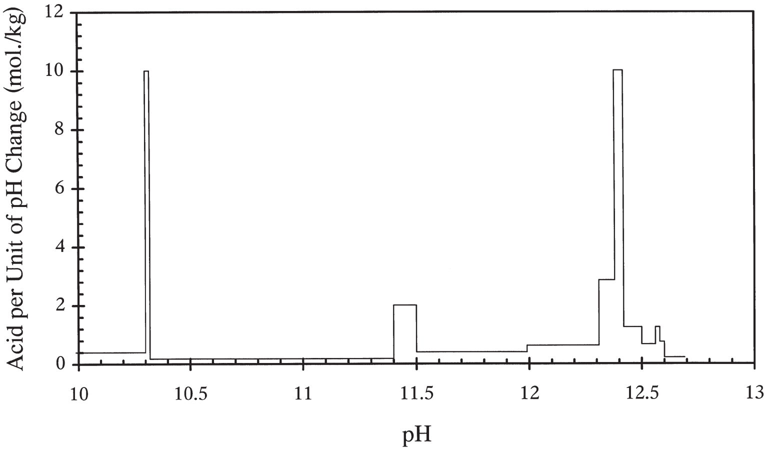

Fig. 2. Stepwise transformation of the measured data in Fig. 1.

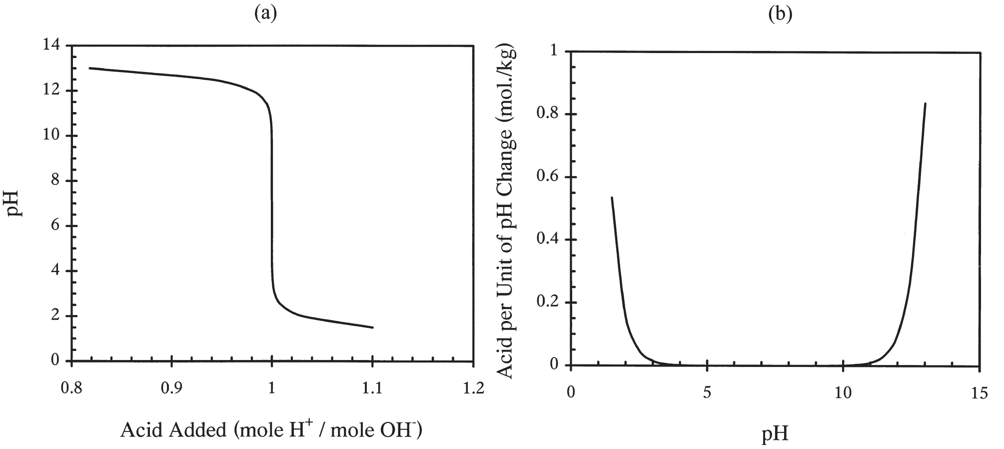

Fig. 3. A strong acid-base titration curve (a) and its transformation with y-axis units determined assuming that 5 g of sample corresponds to 11 mL of solution (b).

in Fig. 1 as indicated above. It may be noted that such analysis differs from that applied in differential titration chemistry, which is used to define the end point of a titration [9].

The identified peaks are well separated with two peaks occurring at pH values of 12.4 and 12.6. The resolution of such closely spaced acid neutralisation behaviour in this pH range has not previously been reported. Indeed, it would be easy to miss the small peak at pH 12.6 when examining the usual form in which titration data is presented (Fig. 1). This method of assessment therefore offers significant advantages over the current interpretation of acid neutralisation data, which tends to focus on the quantity of acid required to achieve a particular pH level [10].

The position and area of a peak are determined by the type, quantity, and condition of the associated component that is resisting acidification. For example, the peak associated with calcium hydroxide would be smaller and the peak associated with calcium carbonate would appear if the sample were carbonated. Attempts have been made to relate pH plateaus in the titration curve to the hydration products [8,11] on the basis of thermodynamic stability studies [12,13]. However, this is complicated by the interaction between the phases and the possibility that a particular phase in cement may give rise to more than one peak. For example, the dissolution of calcium hydroxide may be accompanied by the precipitation of other calcium-containing products that in turn will give rise to peaks at lower pH values. Thus further work is needed to identify these components.

The suggested transformation of the data into a spectrum allows one to subtract background effects to improve the accuracy of the measured acid neutralisation capacity of a particular component. The background resulting from the titration of an acid against a base is given in Fig. 3(b). It is evident that this may be significant at high and low pHs. An effective background may also arise from interfering reactions that do not affect all measured points equally. These include irreversible reactions that do not occur at the steady state pH, but may take place at the transient low or high pHs prior to achieving steady state and will alter the quantity of acid required to produce a particular pH.

Further work is also required to refine data collection. The identification of peaks requires the collection of closely

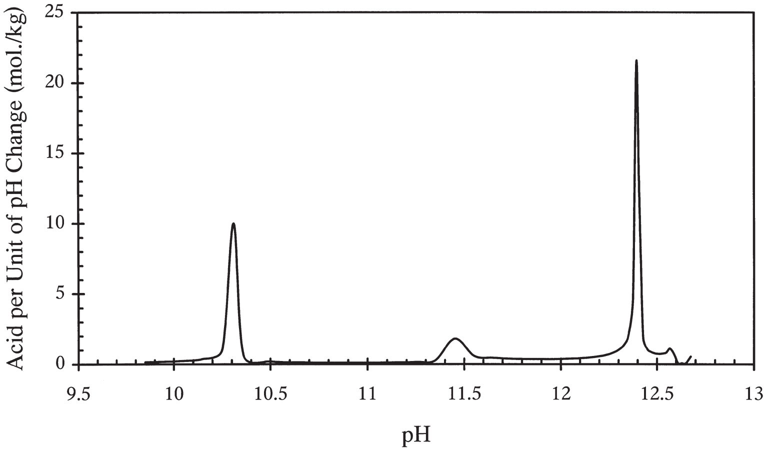

Fig. 4. Transformation of the solid curve in Fig. 1.

spaced points to define the titration curve. This may render the batch testing described above unsuitable because of the large number of samples required. However, the more general method of obtaining titration curves involving the successive addition of acid to a single sample may be affected by the kinetics of the pH-dependent dissolution behaviour of the solid, which would limit the rate at which acid may be added. This could impose a severe time penalty on the technique. Methods of accelerating the achievement of steady state conditions, such as the use of very fine grinding and ultrasonic agitation, may be needed to overcome this.

The accurate measurement of hydroxyl activity using a pH electrode may also present problems associated with the electrode stability. To overcome this and to aid the identification of the peaks, it is postulated that standards with a known behaviour could be added to some samples prior to testing for the purposes of comparison. This could also be used to minimise the effect of errors in the concentration of acid used. Furthermore, it is possible that only the spacing between the peaks and not the absolute pH values may be necessary to “fingerprint” a specimen.

In this work the technique is applied to data obtained on concrete. However, differential acid neutralisation analysis has a potential use in assessing any material (both crystalline and amorphous) that has pH-dependent dissolution characteristics.

5. Conclusions

Differential acid neutralisation analysis is an analytical technique that may be used to characterise materials like concrete that contain phases that resist acidification at particular pH levels. It gives rise to a series of peaks at different pH values with areas that correspond to the quantity of acid required to neutralise the associated components. Closely spaced peaks can be identified and the effects of any background may be minimised. Such a spectrum contains information on the quantity, type, and condition of a material and may be used to quantify inhibitive properties arising from a resistance to a fall in pH.

Further work is needed to improve the collection of the data, to identify the components corresponding to particular peaks, and to assess the application of the technique to materials other than concrete. Differential acid neutralisation analysis could be enhanced by methods of accelerating the achievement of the solid-solution equilibrium and the addition of standards to the material under test. Interactions between components may complicate the interpretation of the spectrum.

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References

[1] G. Sergi, Corrosion of steel in concrete: Cement matrix variables, PhD Thesis, Aston University, 1986.

[2] J.A. Stegemann, P. Hannak, P.L. Coté, A. Liem, Method 7. Acid neutralization capacity, test methods for solidified waste characterisation, Wastewater Technology Centre and Alberta Environmental Centre, Canada, 1986.

[3] J.A. Stegemann, P. Coté, A proposed protocol for evaluation of solidified wastes, Science of the Total Environment 178 (1–3) (1996) 103–110.

[4] M.T. Webster, R.C. Loehr, Long-term leaching of metals from concrete products, J Env Engn 122 (8) (1996) 714–721.

[5] N.R. Buenfeld, N.M. Hassanein, A.J. Jones, An artificial neural network for predicting carbonation depth in concrete structures, in: 2d ASCE Monograph on Artificial Neural Networks in Civil Engineering, American Society of Civil Engineers, Reston, VA, 1997, pp. 77–117.

[6] G.K. Glass, C.L. Page, N.R. Short, Factors affecting steel corrosion in carbonated mortars, Corros Sci 32 (12) (1991) 1283–1294.

[7] G.K. Glass, N.R. Buenfeld, The presentation of the chloride threshold level for corrosion of steel in concrete, Corros Sci 39 (5) (1997) 1001–1013.

[8] J.A. Stegemann, R.J. Caldwell, C. Shi, Response of various solidification systems to acid addition, in: J.J.J.M. Goumans, G.J. Senden, H.A. van der Sloot (Eds.), Waste Materials in Construction: Putting Theory in Practice: Studies in Environmental Science 71, Elsevier Science, Amsterdam, 1997, pp. 803–814.

[9] P.W. Atkins, Physical Chemistry, 5th ed., Oxford University Press, Oxford, 1994, pp. 291–305.

[10] J. Isenburg, M. Moore, Generalized acid neutralization capacity test, in: Stabilization and Solidification of Hazardous, Radioactive and Mixed Wastes, T.M. Gilliam, C.C. Wiles (Eds.), ASTM STP 1123, American Society for Testing and Materials, Philadelphia, 1992, pp. 361–377.

[11] J.A. Stegemann, C. Shi, Waste acid resistance of different monolithic binders and solidified wastes, in: J.J.J.M. Goumans, G.J. Senden, H.A. van der Sloot (Eds.), Materials in Construction: Putting Theory in Practice, Studies in Environmental Science 71, Elsevier Science, Amsterdam, 1997, pp. 551–562.

[12] S.A. Greenberg, T.N. Chang, Colloidal hydrated calcium silicates. II. Solubility relationships in the calcium oxide-silica-water system, J Phys Chem 69 (1965) 182–188.

[13] D. Damidot, F.P. Glasser, Thermodynamic investigation of the CaO-Al_2O_3-$CaSO_4$-$CaCl_2$-H_2O system at 25°C and the influence of Na_2O, Adv Cem Res 7 (1995) 129–134.