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Waste Materials in Construction: Putting Theory into Practice

Response of Various Solidification Systems to Acid Addition

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Abstract

Experiments were conducted to examine the responses of five different solidification systems, with and without waste, to acid addition. The chosen cementing systems were: portland cement, portland cement with silica fume, alkali-activated blast furnace slag, lime and coal fly ash, and high alumina cement with lime and gypsum. The solidified products were tested at several ages using the Acid Neutralisation Capacity test, a series of batch extractions of ground wastes with varying amounts of nitric acid, which allows a titration curve to be plotted. Experimental results indicate that different cementitious systems vary in their response to acid addition; the location of the pH plateau of the titration curve depends on the nature of the hydration products formed by the binder system and is affected by waste components.

1. INTRODUCTION

Stabilisation/solidification is used to convert wastes into non-hazardous materials, which can potentially be used in construction applications. Conventional cement-based solidification processes provide a high pH environment in which heavy metal contaminants have a low solubility. Contaminants can also be captured within the physical structure of a monolithic cement-based matrix. Acid attack can result in contaminant release by 1) reducing the pH to a range where heavy metal contaminants become more soluble, and 2) corroding the physical structure of the cement-based matrix.

Evaluation of the efficacy of solidification processes usually emphasises the first mechanism. For example, the USEPA Toxicity Characteristic Leaching Procedure (U.S. Federal Register, 1986) examines the solubility of metals upon addition of a limited amount of acid, and the Acid Neutralisation Capacity test, recommended by the Wastewater Technology Centre (1991), focuses upon the amount of acid required to achieve a pH of 9, below which the solubility of many metals increases.

However, a non-monolithic, soil-like waste product will have a high permeability, so that even a high acid neutralisation capacity can readily be depleted by environmental influences such as carbonation, acidic rain or ground water. Thus, production of a dense, durable monolith is the key to successful containment of contaminants.

Acid resistance is an important aspect of the durability of a monolithic solidified waste product, and the pH at which dissolution of the solidified waste matrix occurs may not be the same as that at which precipitated metals dissolve. Resistance of a cement matrix to acid attack will depend on 1) the matrix morphology, including the density and porosity, and 2) the ability of the matrix components to neutralise acid. Passivation by deposition of reaction products on the surface of the monolith may also play a role.

The present work was undertaken in order to examine the response of different solidified waste matrix components to acid addition.

2. BACKGROUND

2.1. Solidification Systems

Although some wastes are alkaline and have their own acid neutralisation capacity, this is usually minimal. Thus, the acid resistance of a solidified product is normally associated with the binder system. The binder system may comprise from 20 to 60% of the solidified product. While portland cement is still one of the more frequently used binders, other cementing materials are being increasingly utilised in the solidification industry. These materials are often industrial by-products, which may be available at a lower cost than portland cement, and may even result in a superior solidified product if they are used appropriately. Some common binders for waste solidification include portland cement, cement kiln dust, Class C or Class F coal fly ash, and blast furnace slag. Additives such as silica fume may be used for matrix densification; high calcium lime may be added for pozzolanic activation; dolomitic lime, or even limestone may be added primarily to provide acid neutralising capacity.

All of these binder systems are principally composed of oxides of calcium and silicon, with lesser amounts of aluminum, iron and sulphate. Minor quantities of other elements, such as sodium, magnesium, potassium, carbonates, and chlorides, may also play a role in these systems.

The portland cement manufacturing process is controlled to result in a relatively consistent product, consisting of approximately 45% tricalcium silicate, 27% dicalcium silicate, 11% tricalcium aluminate, 8% tetracalcium aluminoferrite, and 3% gypsum[1]. Upon reaction with water, these crystalline compounds produce a matrix which is approximately 50% calcium silicate hydrate (CSH) and 20% calcium hydroxide; the remainder of the matrix is composed primarily of hydrated calcium sulphoaluminates, calcium sulphoaluminates, including ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$), which has been touted for its uptake of contaminants (McCarthy, Hassett and Bender, 1992 and Bambauer et al., 1988) and calcium aluminoferrites.

By contrast, industrial by-products may vary considerably in their characteristics, both within and between the facilities that produce them. The most hydraulically reactive materials of this type are composed of aluminosilicate glass, with significant concentrations of calcium, iron and other modifiers. Some reactive crystalline materials may also be present. Often, the reactivity of industrial by-products can be enhanced by the addition of chemical activators, such as sodium silicate, or potassium or sodium carbonate or hydroxide.

Because of the varying composition of industrial by-product binders, and the vitreous nature of some, the reactive species can not easily be expressed as stoichiometric compounds, as can those in portland cement. However, the hydration products of industrial by-product-based binders are also mainly CSH, with hydrated calcium aluminates, calcium sulphoaluminates, and calcium aluminoferrites. By contrast with portland cement, silica-rich industrial by-products react with calcium hydroxide to produce CSH; therefore, calcium hydroxide is not a reaction product, although excess calcium hydroxide may be present initially, and some may remain after hydration is complete.

2.2. Cement Hydration Products and pH

Although there are cement and concrete structures which are thousands of years old, conventional cement and concrete products are not generally designed to maintain their integrity over the very long time spans which would be desirable for durability of solidified products. Hence, acid resistance of cements is not of equal interest for construction purposes, and has not been extensively researched. Nevertheless, review of the literature yields information about the chemistry of cement hydration products which is relevant to the consideration of acid neutralisation capacity.

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[1]The difference from a total of 100% is accounted for by variations in these percentages, and the presence of other minor components.

Lime and Calcium Silicate Hydrate

In investigating the structure of CSH, several researchers have studied the pH of CSH formed in pure calcium oxide-silica-water systems at different Ca/Si mole ratios. Figure 1 plots data generated by Greenberg and Chang (1965), and data from a paper by Grutzeck, Benesi and Fanning (1989), which are also in agreement with data generated by earlier researchers. With a small shift in pH between the two studies, the data appear to indicate three pH regimes, controlled by different types of CSH, in combination with silica gel or lime. At a Ca/Si ratio of 2 to 3, such as is found in portland cement, calcium-rich CSH, with a Ca/Si ratio of approximately 1.7, coexists with lime. The lime is highly soluble, and controls the pH at 12.3.

Taylor (1993) found that the CSH in portland cement blended with industrial by-product binders has a lower Ca/Si ratio, and falls over time, due to the consumption of lime by silica. For example, the initial Ca/Si ratios of the CSH in systems containing fly ash and silica fume are 1.55 and 1.5, respectively, and fall to 1.45 and 1.0 over time. Aqueous solubility of calcium and silica from this CSH is relatively low (Atkinson, Goult and Hearne, 1985).

For Ca/Si ratios from 1.7 to 1.1, the pH falls from 12.3 to 11.9; at a Ca/Si ratio of 1.1/1.0, there are indications of pH control at 11.9 by co-existing calcium-rich and silica-rich CSH; then, for Ca/Si ratios from 1.0 to 0.65, the pH decreases from 11.9 to 9.9. At pH 9.9, silica-rich CSH with a Ca/Si ratio of 0.65 coexists with silica gel (Grutzeck, Benesi and Fanning, 1989). Due to the presence of increasing quantities of silica gel, which takes on water, and has a relatively high solubility, a structurally stable matrix can not exist in this low pH range.

Mathematical modelling of portland cement-based wasteform durability (Atkinson, Goult and Hearne, 1985) has shown that, under certain specified leaching conditions, it would take in the order of 10^5 years for the pH to drop from 12.5 to 12.0, corresponding to a decrease in the Ca/Si ratio from 3 to 1.7, due to leaching of lime, but, due to the low solubility of CSH, it would take another more than 10^6 years for the pH to drop from pH 12 to 10.5, corresponding to a decrease in Ca/Si ratio from 1.7 to 0.8.

The significance of solidified waste pH control by soluble alkaline components is further illustrated by earlier data for a heavy metal plating sludge solidified with four different binder systems, at the Wastewater Technology Centre (Côté, 1986). Table 1 summarises the decrease in leachate pH and specimen mass over a two-year modified ANS/ANSI 16.1 test.

The mass losses recorded for specimens containing fly ash were significantly lower than those for portland cement-based specimens not containing fly ash, even though the fly ash systems showed a greater decrease in pH. It is postulated that both the loss of mass, and decrease in pH in the portland cement specimens was due to leaching of alkali and lime. By contrast, the pH of the fly ash systems may have decreased partly due to reaction of lime to form less soluble calcium silicate hydrate.

Table 1: Summary of 2-years of pH and leaching data

System	pH decrease	Mass lost
Soluble silicate/portland cement	0.9	13%
Clay/portland cement	0.4	7%
Coal fly ash/portland cement	1.3	3%
Coal fly ash/lime	1.3	3%

Calcium Sulphoaluminates

Depending on the tricalcium aluminate and gypsum content of ordinary portland cement, the maximum ettringite content of the hydrated product at early ages is approximately 15%; cementing systems containing industrial by-products, such as fly ash, with lime and gypsum may have a higher ettringite content of, for instance, 20% (Solem and McCarthy, 1992); expansive cements based on calcium aluminates could have an ettringite content of up to approximately 50%. Because of the potential for uptake of contaminants by ettringite mentioned above, use of high ettringite systems for waste management has been advocated. However, such systems can be expected to have a different pH response to acid addition than cements based primarily on CSH.

Although the pH stability of ettringite has not been specifically addressed, some studies, both in the areas of cement and concrete, and waste management, have touched on this issue. Day (1992) cites existence of a crystalline ettringite in the pH range from 11.5 to 11.8, and a non-crystalline phase with a similar composition from pH 12.5 to 12.8. Ghorab and Kishar (1986) found the pH of an ettringite solution to be 11.2, whereas a group of workers based at the University of North Dakota have variously observed pH values from 9.8 to 12, although their most recent work states that ettringite is not stable below pH 11 (McCarthy, Hassett and Bender, 1992, Kumarathasan et al., 1990, and Hassett et al., 1989).

Literature values of the solubility product for ettringite range from 10^{-35} to 10^{-45} (Day, 1992, and Deng and Tang, 1994), from which the theoretical pH of a saturated solution may be calculated as ranging between 11.0 and 11.6.

3. METHODS AND MATERIALS

3.1. Preparation of Solidified Wastes

The present work examined the response of five different solidification systems, with and without waste, to acid addition. The chosen cementing systems were: portland cement, portland cement with silica fume, alkali-activated blast furnace slag, lime and coal fly ash, and high alumina cement with lime and gypsum. The formulations used to prepare laboratory batches are labelled 1 to 5 in the heading for Table 2. "W" indicates the batches containing waste.

The first four systems were selected for their differing compositions, particularly their Ca/Si mole ratios (shown in the last row of Table 2), and were used to solidify a plating sludge containing heavy metals; the latter is a high ettringite system, which was used to solidify a hazardous waste incinerator ash. This ash contained high levels of chloride and sulphate and was 69% soluble in water. Gypsum was omitted when the ash was solidified, to cause the sulphate and chloride in the ash to form part of the ettringite matrix.

The laboratory batches without waste were all prepared at a water to cement ratio of 0.4, whereas a water to solid ratio of 0.5 was required for thorough mixing of the samples containing waste. All specimens were cured for 7, 28 and 56 days at 22°C in a moisture chamber before testing, with the exception of the fly ash/lime samples, which were cured at 46°C to accelerate curing.

3.2. Measurement of Acid Neutralisation Capacity

After each of the three curing periods, the solidified products were subjected to the Acid Neutralisation Capacity (ANC) test (Wastewater Technology Centre, 1991). This test involves batch extraction of a series of 5.0 g subsamples of finely ground (<0.2 mm) solidified material with 30 mL of nitric acid for 48 hours, in sealed plastic bottles. The concentration of nitric acid in each subsample is adjusted so that plotting of the final extract pH values yields a titration curve.

Total dissolved solids contents were determined by drying aliquots of selected extracts at 105°C, to obtain an indication of the solubility of the solidified waste matrix at different pH's.

Table 2. Formulations used in acid neutralisation capacity experiments

Component	CaO	SiO_2	Percentage of dry mix									
	%	%	1	1W	2	2W	3	3W	4	4W	5	5W
Portland cement	63	21	100	40	80	32	-	-	-	-	-	-
Silica fume	0.3-0.6	93-96	-	-	20	8	-	-	-	-	-	-
Blast furnace slag	33-44	33-38	-	-	-	-	92.5	37	-	-	-	-
Sodium metasilicate	0	47	-	-	-	-	7.5	3	-	-	-	-
Class F coal fly ash	3.7	47	-	-	-	-	-	-	80	48	-	-
High calcium lime	74	0	-	-	-	-	-	-	20	12	10	10
High alumina cement	-	-	-	-	-	-	-	-	-	-	60	30
Gypsum	-	-	-	-	-	-	-	-	-	-	30	-
Metal plating sludge	-	-	-	60	-	60	-	60	-	40	-	-
Hazardous waste ash	-	-	-	-	-	-	-	-	-	-	-	60
Water	-	-	40	50	40	50	40	50	40	50	40	50
Ca/Si ratio	-	-	3	3	1.4	1.4	0.5	0.5	0.5	0.5	-	-

4. RESULTS AND DISCUSSION

For each of the above binder systems, titration curves of pH as a function of equivalents of nitric acid added per kg of dry cementing material were plotted. Selected data which illustrate particular features of these plots are shown in Figures 2 to 6. Total dissolved solids concentrations, corrected for the amount of nitric acid added, were used to estimate the fraction of the matrix which was dissolved by acid addition. The soluble fraction of the binder without waste addition has been plotted in Figures 2 to 5. Figure 6 shows the soluble fraction of the ettringite-based matrix, both with and without waste addition. For each system, the amount of acid necessary to achieve a pH of 9, and the fraction of the matrix dissolved at pH 9 were determined graphically and have been summarised in Table 3.

4.1. Portland Cement

Figure 2 shows the titration curves for the portland cement system with and without addition of the plating sludge after 56 days of curing. Because portland cement hydrates quickly, the titration curves for the samples cured for 7 and 28 days were not significantly different from those shown. From the pH data observed for pure systems summarised above in Section 2.2, the portland cement system, with a Ca/Si ratio of 3, would be expected to exhibit pH plateaus at 12.3, 11.9 and 9.9. In fact, while it is possible to distinguish plateaus at 12.3, and possibly 11.9, the titration curve also flattens at approximately 10.9, and 9. There is no evidence of a pH plateau at 9.9. Apparently, the presence of impurities in a real cement cause the formation of different CSH phases than are observed in a pure system.

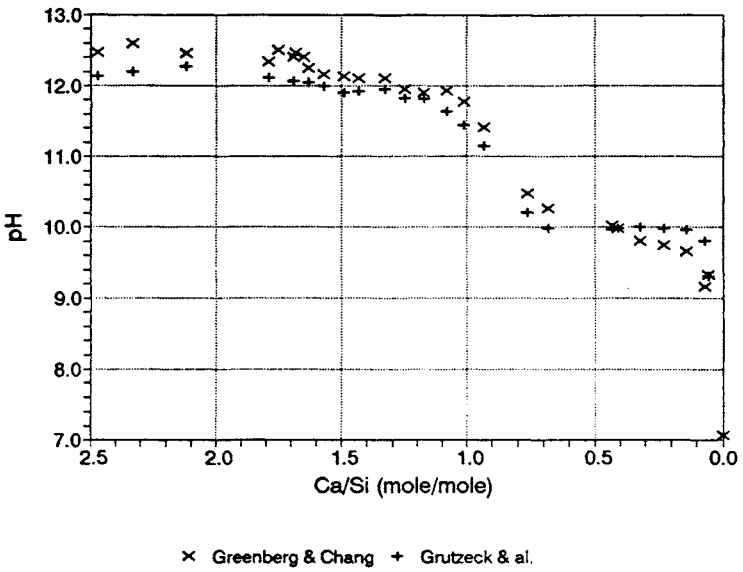

Figure 1. pH plotted as a function of Ca/Si mole ratio (adapted from Greenberg and Chang, 1965, and Grutzek, Benesi and Fanning, 1989).

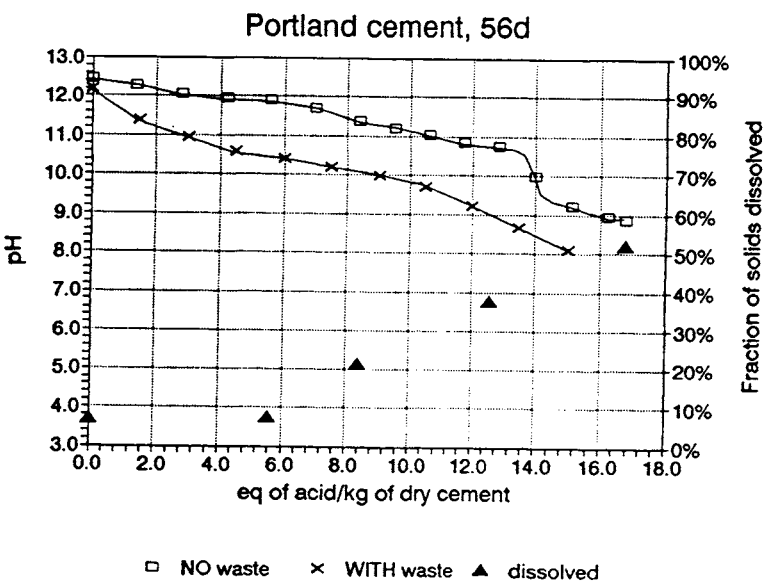

Figure 2. Titration curve for the portland cement binder system, with and without waste after 56 days curing, showing also dissolution of the portland cement matrix as a function of acid addition.

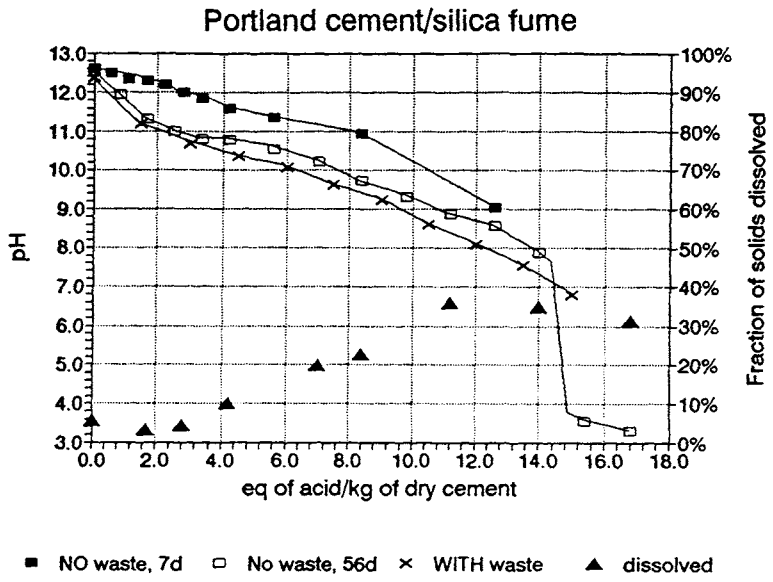

Figure 3. Titration curve for the portland cement and silica fume binder system, with waste after 56 days curing, and without waste after 7 and 56 days curing, showing also dissolution of the portland cement/silica fume matrix as a function of acid addition.

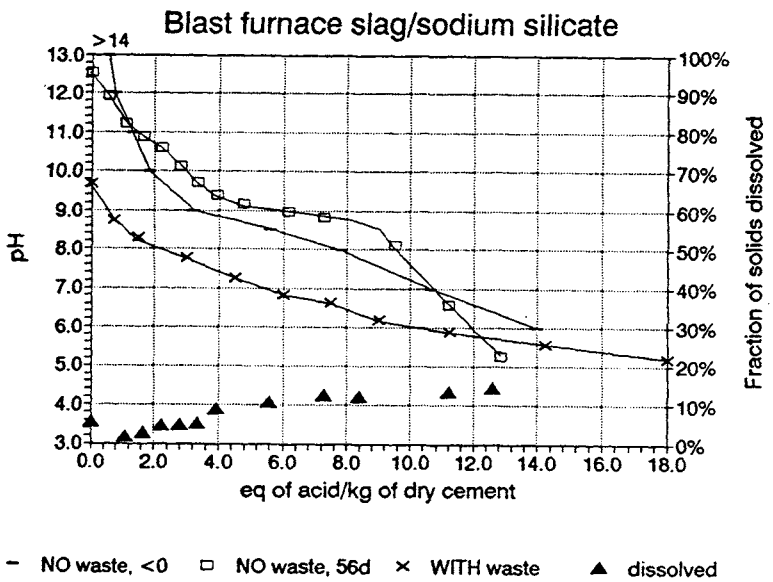

Figure 4. Titration curve for the blast furnace slag and sodium silicate binder system, with waste after 56 days curing, and without waste before mixing and after 56 days curing, showing also dissolution of the activated slag matrix as a function of acid addition.

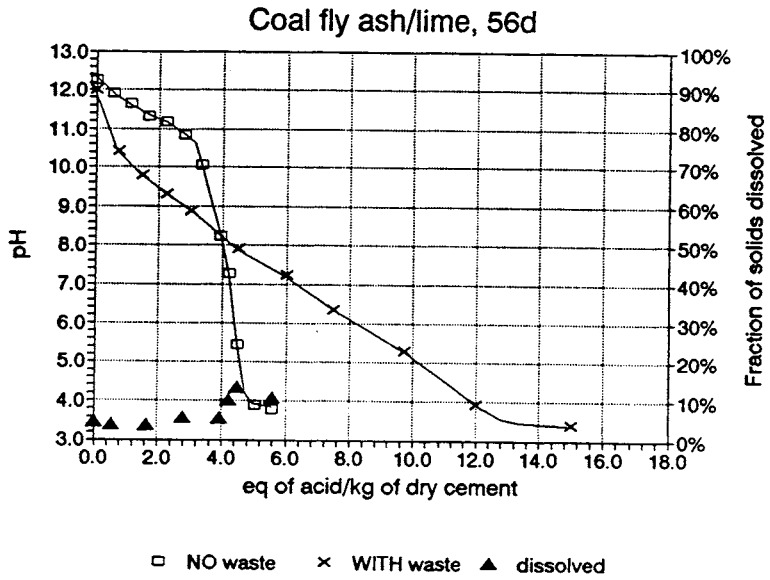

Figure 5. Titration curve for the coal fly ash and lime binder system, with and without waste after 56 days curing, showing also dissolution of the lime/fly ash cement matrix as a function of acid addition.

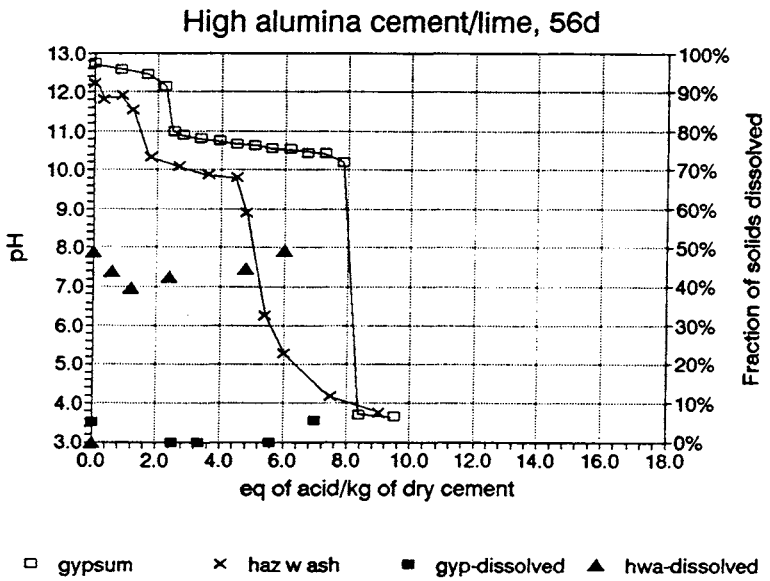

Figure 6. Titration curves and matrix dissolution as a function of acid addition for the high alumina cement and lime binder system, with gypsum, and with hazardous waste incinerator ash after 56 days curing.

Table 3. Dissolution of various binder systems at pH 9

Matrix components	Amount of acid to pH 9 (eq/kg of dry cement)	Percent dissolved
Portland cement	16.0	50%
Portland cement/waste	12.6	15%
Portland cement/silica fume	11.0	35%
Portland cement/silica fume/waste	9.5	15%
Blast furnace slag/sodium silicate	6.2	10%
Blast furnace slag/silicate/waste	0.5	5%
Coal fly ash/lime	3.6	7%
Coal fly ash/lime/waste	2.8	5%
High alumina cement/lime/gypsum	8.1	1%
High alumina cement/lime/haz. ash	4.8	45%

As expected, the first two pH plateaus, at 12.3 and 11.9, coincide with low solubility of the matrix, as indicated by total dissolved solids measurements. Matrix solubility appears to increase below pH 11.9. The portland cement system containing plating sludge does not exhibit a pH plateau at 12.3; it appears that the waste has consumed the lime, or altered hydration so that lime was not generated. The pH drops directly from 12.3 to 8, with a slight flattening at pH 10.5. Interestingly, the fractional solubility of this sample appeared to be much lower than that of the pure cement system. A detailed analysis of the plating sludge was not performed, but it may have contained a high proportion of insoluble components.

4.2. Portland Cement with Silica Fume

Replacement of 20% of the portland cement with silica fume decreased the Ca/Si ratio from 3 to 1.4. Accordingly, it was expected that the pH plateau at 12.3 would disappear when the lime produced by hydration of the portland cement reacted with the silica fume. Indeed, the pH 12.3 plateau was apparent in the sample without waste at 7 days of curing, as shown in Figure 3, but had disappeared by 28 and 56 days of curing.

From 28 days of curing, the titration curves for the portland cement and silica fume samples were very similar, with and without addition of the plating sludge. These curves were also similar in shape to the portland cement and plating sludge sample (Figure 2), exhibiting a plateau between pH 10 and 11.

The matrix solubility indicated by the total dissolved solid measurements was lower than for the pure portland cement samples, increasing beyond the pH plateau. Again, the solubility of the sample containing waste was lower than that of the sample without waste.

4.3. Activated Blast Furnace Slag

The binder system produced by activation of blast furnace slag with sodium metasilicate has a low overall Ca/Si ratio of 0.5. Based on the earlier discussion of pH data for a pure system, this would predict the coexistence of low Ca/Si CSH and silica gel, but only a relatively small proportion of the slag hydrates, so the Ca/Si ratio of the CSH is higher, and silica gel is not formed.

The pH vs. acid addition data for the blast furnace slag samples for 7 and 28 days resembled the titration curves plotted at 56 days in Figure 4. The curve for the slag system without addition of waste shows an initial pH of 12.5, dropping to a pH plateau at approximately 9.

A titration curve for the unreacted mixture, calculated based on the acid neutralisation capacities of the individual components, has also been plotted in Figure 4. Comparison of the unreacted and reacted systems clearly demonstrates that a reaction takes place, with the products having a lower initial pH, and a higher and more distinct pH plateau, than the reactants. The total dissolved solids measurements indicate that the solubility of this system is low, even under acidic conditions. However, it does appear that the solubility increases at the start of the pH 9 plateau. The pH 9 plateau may represent CSH

coexisting with silica gel, its theoretical position having been altered by the presence of other components in the slag, such as Mg.

The plating sludge inhibited the set of the slag. These samples did not develop physical strength, and pH plateaus for reaction products associated with strength development are absent from the titration curve. It seems likely that the plating sludge reacted with the sodium silicate, and prevented activation of the slag. In spite of the lack of hydraulic reactions, the solubility of the slag/waste system was still low.

4.4. Coal Fly Ash and Lime

As coal fly ash alone has very little acid neutralisation capacity, and lime would control the pH at 12.3, the pH plateau between 11 and 12 for the fly ash and lime without waste in Figure 5 again confirms that pozzolanic reactions, creating CSH, have occurred. The data shown is for the sample cured for 56 days; the pH plateau in the sample cured for only 7 days was closer to 12, while the titration curve at 28 days was the same as that shown.

Again, the Ca/Si ratio was approximately 0.5, but, as was the case for the slag system, a significant proportion of the fly ash has remained unreacted, so that the Ca/Si ratio of the CSH formed is higher.

In this case, the development of strength by the samples containing plating sludge indicates that the presence of waste in the system did not inhibit the set. However, the titration curve for the sample containing waste is considerably different, exhibiting a rapid drop from pH 12 to 10.5, and then a linear slope to pH 4, with no discernible plateaus.

Examination of total dissolved solids data shows low solubility for this system, with and without waste, although it does appear that the solubility of the pure system jumps when the pH drops below 9, while that of the system containing waste increases steadily as the pH drops.

4.5. High Ettringite System

The titration curves for the two calcium sulphoaluminate-based systems at 56 days have been plotted in Figure 6. The curves for 7 and 28 days had similar features.

Two distinct pH plateaus are visible in Figure 6. The pH plot for the system containing gypsum rather than hazardous waste incinerator ash levels off at pH 12.4 and 10.8. That for the system containing ash levels off at pH 12 and 10. The overall acid neutralisation capacity for the sample containing incinerator ash is lower because the ash contains components which do not participate in the reaction, whereas the gypsum reacted fully.

The pH 12/12.4 plateau is attributed to tetracalcium aluminate hydrate ($4CaO.Al_2O_3.13H_2O$) which would be expected to be the other main hydration product in this system, in addition to ettringite, which results in the plateau at pH 10/10.8. Unreacted lime may also contribute to this plateau.

The presence of impurities in the hazardous waste incinerator ash clearly affects the position of the pH plateaus, as compared with the gypsum system. Chloride may be incorporated in the ettringite, or form calcium chloroaluminate ($3CaO.Al_2O_3.CaCl_2.10H_2O$). Other researchers have found this product to be stable between pH 11 and 12.5 (Ben Yair, 1971).

Total dissolved solids measurements show the solubility of the ettringite system containing gypsum rather than incinerator ash to be extremely low. The solubility data plotted in Figure 6 show that the use of ash rather than gypsum in the matrix increases its solubility drastically. If it is assumed that the solidification process does not affect the solubility of the ash (69%), a matrix solubility due to ash dissolution of 41% may be calculated, based on 60% of ash in the matrix. In fact, a slightly higher matrix solubility is observed.

5. CONCLUSIONS

Except for the pH plateau at 12.3 caused by excess lime, the pH plateaus observed in response to acid addition for real binder systems do not exactly correspond to those observed for the pure CaO-SiO2-H2O system. Different hydraulic cements exhibit different pH plateaus, which probably reflect differences in the structure and composition of the CSH formed. In general, plateaus seem to occur at pH levels lower than those anticipated. The addition of waste to a cementing system also appears to lower the pH plateau. Solubility of all matrices was low above pH 11.5; depending on the binder system, matrix dissolution appeared to increase at pH values ranging from 9 to 11.5. The following conclusions are drawn for the specific systems studied:

- For portland cement, the amount of acid required to achieve a pH of 9 was 16 eq/kg cement, but greater than 10% matrix dissolution was observed at an acid addition of 6 eq/kg cement, and a pH of less than 11.5.
- Addition of silica fume to portland cement appeared to lower the pH at which significant matrix dissolution was observed to approximately 10.5, with an acid addition of 6 eq/kg cement.
- The activated blast furnace slag binder system showed increased matrix dissolution at pH 9, with an acid addition of 4 eq/kg cement, but overall low solubility over the pH range from 12.5 to 5.
- The solubility of the coal fly ash and lime system was also low over the pH range from 12.5 to 4. An increase in solubility was observed after addition of 4 eq/kg of acid/kg cement, below pH 9.
- The solubility of a high ettringite cement system, using gypsum to form calcium sulphoaluminates, is very low at pH values above 10, however, use of a high sulphate and chloride waste in place of gypsum results in a matrix with very high solubility.

6. RECOMMENDATIONS AND SUGGESTIONS FOR FURTHER WORK

- Rather than using a fixed pH as the criterion for performance in an acid neutralisation capacity test, it may be advisable to consider the pH at which a particular waste/binder system appears to undergo a significant increase in solubility.
- As waste materials are generally not alkaline, adjustment of binder formulations containing alkaline components such as lime or sodium silicate to compensate for their consumption by the waste material should be investigated.
- From tests on ground samples, the actual effect of acid addition on the structural integrity of a solidified matrix is not easily apparent, because disintegration of structural matrix components may occur without chemical dissolution. Also, the physical structure of the matrix, including density and porosity, as well as its chemical stability, will influence its acid resistance. Thus, the acid resistance of monolithic samples should be investigated.
- Chemical changes continue to occur in cements over long time periods, therefor, the acid neutralisation capacities of different binders at ages of several years should be investigated.
- While micromorphological studies may confirm inclusion of waste components in calcium sulphoaluminate phases, leaching studies should be conducted to evaluate the stability of these compounds in the environment.

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