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Acid corrosion resistance of different cementing materials

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Abstract

This study has investigated the corrosion of different hardened cementing materials, such as Portland cement (PC), alkali-activated blast furnace slag cement (ASC), lime–fly ash (LFA) blend and high alumina cement with gypsum and lime (HAC), in pH 3 nitric acid, pH 3 acetic acid, and pH 5 acetic acid solutions. Experimental results indicated that PC pastes were corroded faster than ASC and LFA pastes, and pastes consisting of HAC were quickly dissolved in these acid solutions. PC pastes are more porous than ASC pastes but much less porous than LFA pastes. Thus, the corrosion of hardened cementing materials in acid solutions depends on the nature of the hydration products rather than the porosity of the hardened cementing materials: calcium silicate hydrate (C-S-H) with a low C/S ratio is the main hydration product in ASC and LFA pastes, while C-S-H with a high C/S ratio and $Ca(OH)_2$ are the main hydration products in hardened PC pastes. $Ca(OH)_2$ decomposes as the pH drops below 12, and C-S-H decalcifies as the pH decreases, and decomposes for pH values below 9. The mixture of high alumina cement, gypsum, and lime results in the formation of an ettringite-based matrix, which was dissolved very quickly in these acid solutions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Acid corrosion; Pastes; Portland cement; Lime–fly ash cement; Alkali-activated slag

1. Introduction

The acid corrosion of hardened cementing materials has drawn more and more attention recently due to the corrosion of concrete sewer pipes and concrete structures at municipal wastewater treatment plants [1–3], the impact of aggressive substances from animal feed and manure [4,5], and concerns regarding the acid corrosion resistance of cement-solidified wastes [6]. Some studies have been published about the acid corrosion of Portland cement (PC) paste and concrete with or without supplementary cementing materials such as silica fume, fly ash, and ground blast furnace slag [7]. However, very little work has been done on improving the acid corrosion resistance of cementing materials [8]. pH adjustment and corrosion resistant linings are often used for sewer pipes and concrete structures at municipal wastewater treatment plants at a substantial additional cost [3].

In the waste stabilization/solidification industry, acid neutralization capacity (ANC) of treated wastes is sometimes used to evaluate a formulation. For example, the USEPA toxicity characteristic leaching procedures [8] examines the solubility of metals upon addition of a limited amount of acid, and the ANC test, recommended by the Wastewater Technology Centre [9], focuses upon the amount of acid required to reach a pH of 9, below which the solubility of many metals increases.

Acid corrosion resistance is an important aspect of the durability of monolithic solidified waste products. Resistance of a cement matrix to acid corrosion will depend on (1) pore structure characteristics, (2) the ability of the matrix components to neutralize acid and (3) the products of acid corrosion. Passivation by deposition of reaction products will prevent the matrix from further corrosion. Some cementing materials may have low ANC, but high acid corrosion resistance due to the passivation effect.

This paper investigates the corrosion of four hardened cement pastes—conventional ASTM Type I PC, alkali-activated blast furnace slag (ASC), a lime–fly ash (LFA) blend and high alumina cement with gypsum and lime (HAC), in pH 3 nitric acid, pH 3 acetic acid, and pH 5 acetic acid solutions. The main purpose of the this work is to

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Table 1
Chemical composition of raw materials

	PC	Blast furnace slag	Fly ash	High alumina cement	Sodium metasilicate	High calcium hydrated lime	Gypsum
SiO_2	21.6	35.3	46.9	4.5	47.0	0.4	0.3
Al_2O_3	4.2	9.9	25.4	41.2	NA	0.1	<0.01
Fe_2O_3	3	0.6	8.2	11.3	NA	0.1	0.1
CaO	62.8	34.7	3.7	39.8	NA	73.6	33.5
MgO	3.1	14.6	1.0	0.6	NA	0.8	0.5
SO_3	2.5	4.0	0.9	Nil	NA	<0.1	45.2
Na_2O	0.41 (eq. As Na_2O)	0.3	0.3	0.1 (Na_2O + K_2O)	51.0	NA	<0.01
K_2O		0.4	1.7		NA	NA	<0.02
I.L.	2.1	0	9.5	0.3	NA	23.9	NA

NA = not analysed.

examine the effects of the nature of hydration products on corrosion resistance of hardened cement pastes.

2. Experimentation

2.1. Raw materials and cement pastes

The chemical composition of the raw materials is listed in Table 1. The PC used was a typical commercial ASTM Type I PC. The blast furnace slag was a ground pelletized slag. Anhydrous sodium metasilicate was used as an alkaline activator for the slag. The fly ash was an ASTM Type F fly ash. Commercial hydrated high calcium lime was used in LFA pastes, and with high alumina cement and commercial gypsum powder to produce an ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$)-based cement paste.

Four cementing materials were prepared to test their acid corrosion resistance: 100% typical commercial ASTM Type I PC, ASC, LFA and HAC. Cement pastes, rather than mortars or concrete, were used in order to avoid the interference of aggregates with the results. The composition of the cement pastes is shown in Table 2. Pastes were cast into 4.5-cm diameter and 7.5-cm high polystyrene cylinder vials. The PC, ASC, and HAC pastes were cured in a moisture chamber at 23°C and the LFA paste was cured in a moisture chamber at 46°C. Specimens were demolded after 1 day and were placed back into the curing chambers for continued curing until testing.

Table 2
Composition (by mass) of cement pastes

	Sample designation			
Component	PC	ASC	LFA	HAC
PC	100	–	–	–
Blast furnace slag	–	72.5	–	–
Sodium metasilicate	–	7.5	–	–
Hydrated calcium lime	–	–	80	10
Fly ash	–	–	20	–
High alumina cement	–	–	–	60
Gypsum	–	–	–	30
Water	40	40	40	40

2.2. Acid corrosion test

In order to evaluate the acid corrosion resistance of these cementing materials, the cement pastes were tested in three acid solutions: pH 5 nitric acid, pH 3 acetic acid, and pH 5 acetic acid. Nitric acid, HNO_3, was chosen because it is a strong mineral acid, which dissociates completely, whose salts are soluble. It has been used for the measurement of the ANC of ground samples. Acetic acid, CH_3COOH, is a weak organic acid (K_a at 25°C = 1.8×10^{-5}) which is often used in laboratory tests, such as the USEPA toxicity characteristic leaching procedure, to represent organic acids produced by decay of organic matter in landfills.

The test procedure was very similar to that described by Pavlik [11]. After 1 year of curing, each specimen was saturated and cemented into its polystyrene mold using epoxy glue such that only one end of the cylinder was exposed. Then, the specimens were suspended with the exposed surface facing downwards in one liter of nitric acid or acetic acid solutions. Concentrated acid was added manually from time to time, in order to maintain the target pH values. However, the target pH 3 for acetic acid solution was difficult to reach due to a buffer effect and the actual value ranged between 3.0 and 3.5. Target pHs of 5 for both the acetic acid and 3 for the nitric acid were maintained easily. Initially, the pH of the acid solutions was adjusted to the target values two or three times each day and rose high as 11.8 during the pH adjustment interval. As time progressed, the change in pH of the acid solutions decreased and the number of pH adjustment decreased correspondingly.

Corroded depth of cement paste could be visually distinguished and measured with a ruler. Four measurements were carried out across the section of each specimen and the reported results are the average of these four measurements.

3. Results and discussion

3.1. Corrosion in pH 3 nitric acid solution

Fig. 1 shows the corrosion depth of cement pastes in pH 3 nitric acid solution. After 580 days of immersion in the acid, the PC pastes were corroded approximately 2.5 mm. The ASC pastes were corroded less than the PC pastes. The LFA pastes exhibited less corrosion than either the PC or ASC pastes.

Although no permeability or pore structure test was done on these pastes, it could be visually estimated that LFA pastes were much more porous or permeable than PC or ASC pastes. Thus, the difference in acid corrosion resistance between these hardened cementing materials seems to be caused by the nature of their hydration products, rather than their porosities.

At room temperature, a fully hydrated PC paste consists of 50–60% C-S-H with a high C/S ratio of 1.5 to 1.8, 20–25% $Ca(OH)_2$, and 15–20% calcium sulphoaluminates (AFt and AFm) by volume, while ASC and LFA pastes consist mainly of C-S-H with a C/S ratio of around 1 [12]. $Ca(OH)_2$ decomposes at a pH below 12 and calcium sulphoaluminates decompose at a pH below 11. C-S-H releases Ca^{2+} as the pH drops. When the pH is below 9, C-S-H has released most of its lime and a layer of silica and aluminosilicate gels remains and prevents cement pastes from further corrosion. Further leaching of calcium and inward movement of acid to the corrosion front then becomes controlled by diffusion through this layer [10]. The dissolution of $Ca(OH)_2$ and calcium sulphoaluminates, and the decalcification of C-S-H with a high C/S ratio in hardened PC pastes leave a very porous corroded layer, while the low lime content in activated-blast furnace slag and LFA lime pastes results in a dense silica gel protective layer.

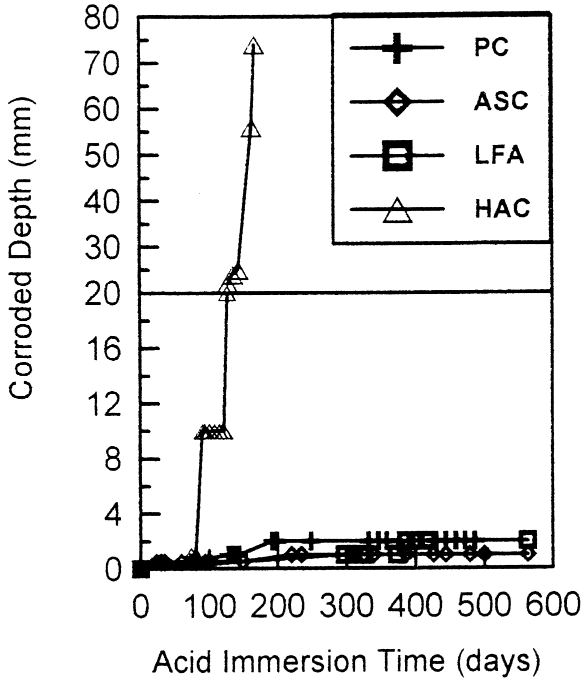

Fig. 1. Corrosion of different cement pastes in pH 3 nitric acid solution.

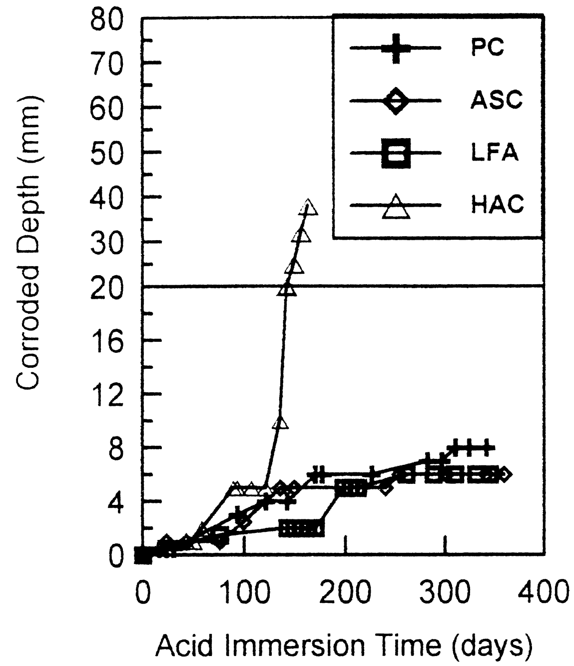

Fig. 2. Corrosion of different cement pastes in pH 5 acetic acid solution.

The behavior of the HAC pastes was completely different from that of the other pastes. The HAC pastes were slowly dissolved during the first 90 days then dissolved completely over another 70 days. The initial slow dissolution may be attributed to the slow dissolution of the carbonated surface layer in the acid solution. The carbonation of the main hydration product AFt can be expressed as Eq. (1):

$$C_3A \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2 \rightarrow 3CaCO_3 + 3[CaSO_4 \cdot 2H_2O] + 2Al(OH)_3 + 23H_2O. \quad (1)$$

The carbonation product $CaSO_4{\cdot}2H_2O$ is stable, and the other products, $CaCO_3$ and $Al(OH)_3$ are dissolved very slowly in a pH 3 acidic solution. As $CaCO_3$ and $Al(OH)_3$ are depleted, AFt is exposed to the acid solution directly and decomposed quickly as Eq. (2):

$$C_3A \cdot 3CaSO_4 \cdot 32H_2O + 12H^+ \rightarrow 3Ca^{2+} + 2Al^{3+} + 3[CaSO_4 \cdot 2H_2O] + 32H_2O. \quad (2)$$

3.2. Corrosion in pH 5 acetic acid solution

All cement pastes in pH 5 acetic acid solution were corroded in according to a similar trend but faster than in pH 3 nitric acetic acid (Fig. 2). After 1 year of immersion, 9 mm of the PC pastes and 6 mm of the ASC and LAF pastes were corroded. Thus, it appears that acetic acid is much more

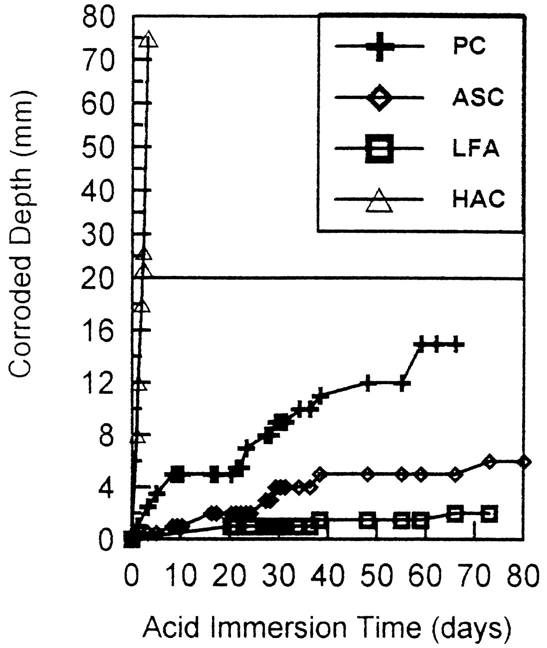

Fig. 3. Corrosion of different cement pastes in pH 3 acetic acid solution.

aggressive than nitric acid. However, it has been reported that, at the same concentration, mineral acids are more corrosive to hardened cement pastes than weak acids [10]. The contradiction can be attributed to the different testing conditions — constant pH was used in this study and a constant concentration was used by Pavlik [11].

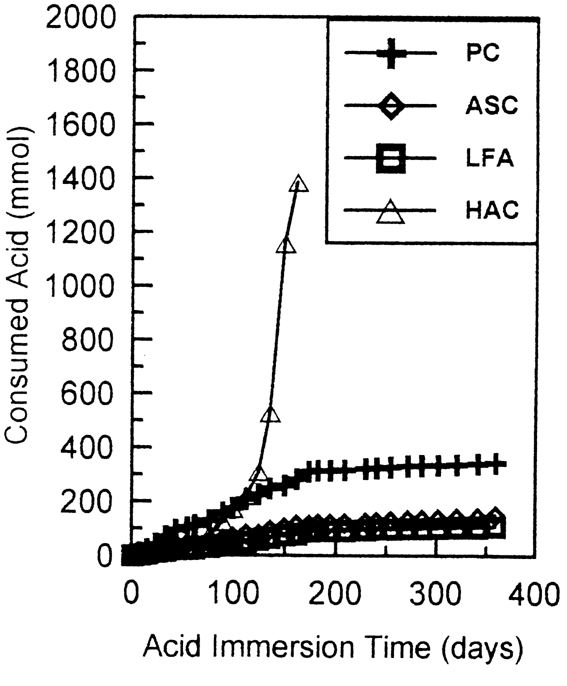

Fig. 4. Acid consumption of different cement pastes in pH 5 acetic acid solution.

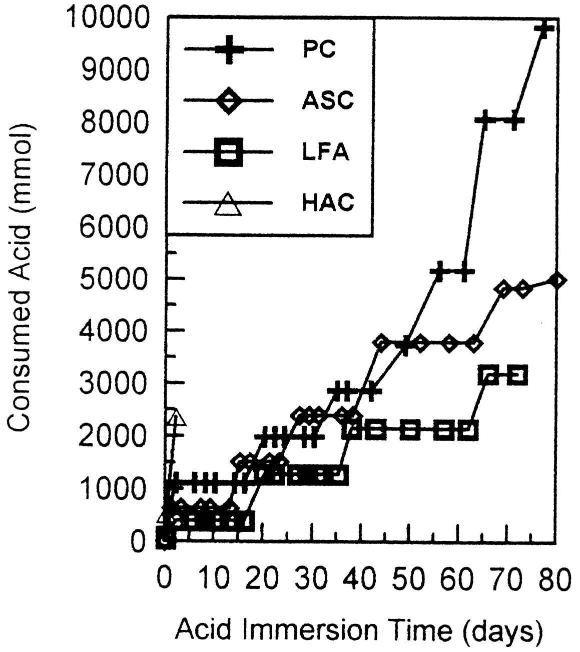

Fig. 5. Acid consumption of different pastes in pH 3 acetic acid solution.

3.3. Corrosion in pH 3 acetic acid solution

When the pH of the acetic acid solution was decreased to 3, all cement pastes were corroded much faster than by the pH 5 acetic acid solution and the difference in acid corrosion resistance became more obvious (Fig. 3). The HAC pastes were corroded most quickly and LFA pastes most slowly. After 60 days of immersion, 15 mm of PC, 5 mm of ASC, and 3 mm of LFA pastes were corroded. The HAC pastes were dissolved quickly even at the beginning due to the corrosion of a stronger acid solution, resulting in dissolution of the whole cylinder (75 mm high) within 2 days.

3.4. Acid consumption

The quantities of consumed acid in pH 5 and 3 acetic acid solutions during the testing period are plotted in Figs. 4 and 5. It can be seen that the consumed acid in pH 3 acid solution is much more than that in pH 5 acid

Table 3
Amount of acid required for complete matrix destruction

	Consumed acid (mmol of acid/g of dry hardened paste)			
Corrosion medium	PC	ASC	LFA	HAC
pH 3 HNO_3	19	25	17	7.0
pH 3 CH_3COOH	160	360	800	39
pH 5 CH_3COOH	21	12	12	21
ANC to pH 5*	>17	13	5.0	8.0

* From Ref. [6].

Table 4
Composition of non-corroded cement pastes and acid solutions

	Non-corroded (%)			pH 3 Nitric acid solution (mg/l)			pH 5 Acetic acid solution (mg/l)			pH 3 Acetic acid solution (mg/l)		
Component	CaO	SiO_2	Al_2O_3	Ca	Si	Al	Ca	Si	Al	Ca	Si	Al
PC	62.8	21.6	4.2	124	4.75	0.25	125	17.4	0.28	7570	46.3	67.5
ASC	32.1	36.2	9.2	60.8	23.8	3.87	41.4	15.7	0.26	1160	87.4	114
LFA	17.76	37.52	20.3	44.4	16.6	3.63	52.4	12.9	0.11	4480	101	200

Mol. ratio	Ca/Si	Ca/Al	Ca/Si	Ca/Al	Ca/Si	Ca/Al	Ca/Si	Ca/Al
PC	2.39	76.3	9.14	913	2.52	857	57.3	212
ASC	0.73	17.8	0.90	29.7	0.92	299	4.65	19.3
LFA	0.39	4.4	0.94	23.1	1.42	870	15.5	42.2

solution. The acid consumed during the testing is actually a measurement of the ANC of hardened cementing materials to a given pH. Table 3 summarizes the consumed acid (mmol) per gram of dry hardened cementing materials. Since no corrosion test was done in a pH 5 nitric acid solution, the ANC of each hardened cement paste from a previous study [6] is listed for the purpose of comparison.

At pH 3, each hardened paste consumed much more acetic acid than nitric acid, or acetic acid at pH 5. It seems that acetic acid and some other substance(s) form a buffer solution between pH 3 and 4.

The amount of acetic acid consumed at pH 5 was similar to or more than the ANC using nitric acid at pH 5. The difference between the two tests can be explained by (1) different acids and (2) possible incomplete corrosion of cement paste particles during the ANC testing.

The concentrations of dissolved Ca, Si, and Al from the PC, LFA, and ASC specimens, and the Ca/Si and Ca/Al ratios in the three acid solutions are shown in Table 4. HAC is not included, as these specimens were completely dissolved in all three acid solutions. The main features of the results are summarized as follows:

- The Ca/Si or Ca/Al ratios of all acidic solutions are higher than those in the uncorroded samples.
- The concentration of dissolved Ca, Si, and Al in acetic acid solution is much higher than that in nitric acid solution at pH 3.
- As the pH of the acetic solution is decreased from 5 to 3, much more Ca and Al entered into the acetic acid solution, the Ca/Si ratio of the solution increased, while the Ca/Al ratio of the solution decreased.

When cement pastes contact acid solutions, most Ca in the cement paste is rapidly dissolved and most Si is left in the form of $SiO_2 \cdot nH_2O$ as a protective layer of gel. In the studied pH range, the amount of Ca dissolved from the cement pastes is always much higher than that of Si or Al. Thus, the Ca/Si or Ca/Al ratio in these acidic solutions is higher than those in the uncorroded cement pastes. The concentrations of dissolved Ca, Si, and Al also confirm that acetic acid is more corrosive to hardened cement pastes than nitric acid solutions at pH 3.

As expected, the decrease in pH increases the corrosiveness of an acid solution and cement pastes are corroded faster. The drop of pH from 5 to 3 significantly decreases the remaining Ca, Si, and Al in the protective layer. However, the Ca/Si ratio in the acid solution increases. This means that the dissolution of Ca is more sensitive to the pH drop than Si. The Ca/Al ratio in the solution also increased as the pH of the solution decreased. According to the $Al_2O_3-H_2O$ phase diagram [13], Al exists in the form of different hydrated species in a solution depending on the pH of the solution. The solubility of the species at pH 3 is much higher than that of the species at pH 5. Thus, the concentration of Al in the solution increases significantly and the Ca/Al ratio decreases significantly.

4. Conclusions

This study investigated the corrosion resistance of hardened PC, ASC, LFA and ettringite-based (a mixture of high alumna cement, gypsum, and lime) pastes in pH 3 nitric acid, and pH 3 and 5 acetic acid solutions. The corroded depth, consumed acid, and dissolved main species in these acid solutions were measured. The following conclusions can be drawn based on the testing results and discussions based on publications.

After corrosion, hardened PC, ASC, and LFA pastes formed a protective layer consisting mainly of $SiO_2 \cdot nH_2O$ gel, which provided a barrier for the further corrosion of uncorroded pastes. Since ettringite decomposes completely in acidic solutions, hardened ettringite-based pastes were dissolved quickly in these acid solutions.

The resistance of cement pastes to acidic corrosion depended on the protective layer or the nature of the hydration products rather than on the permeability porosity of hardened cement pastes. At a given pH value, acetic acid is more corrosive than nitric acid. As expected, the lower the pH of an acid solution was, the faster the acid solution corroded cement pastes.

As the pH value of the acid solution decreased from 5 to 3, more Ca, Si, and Al entered into the acid solution. Ca was more sensitive to the pH drop than Si and less sensitive to the pH drop than Al. Ca/Si ratios in the acid solution increased and the Ca/Al ratio decreased as the pH of the solution dropped.

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