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High-performance concretes from calcium aluminate cements

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Abstract

Calcium aluminate cements have a radically different chemistry to Portland cements. Due principally to their higher cost, they do not compete directly with Portland cements. Nevertheless, concretes based on these cements have very high performance in specific applications. Two of these are discussed in this article: resistance to acid attack and particularly biogenic corrosion and abrasion resistance in hydraulic structures. Such applications extend the range of applications for cementitious materials.

Keywords: Calcium aluminate cement; High-performance concrete; Acid resistance; Abrasion resistance; Resistance to thermal shock

1. Introduction

The term “high performance” is frequently equated, implicitly or explicitly, with high strength, although there is more and more emphasis on durability. However, this view is firmly linked to the idea that concrete is only used for buildings and structures. A wider view of concrete or cementitious materials indicates that there are alternative domains in which concrete can compete with other materials, such as metals or plastics, or be combined with them to achieve high levels of performance.

Calcium aluminate cements are considerably more expensive than Portland cements (around four to five times as expensive) and so do not compete with the latter in any application where conventional or high-performance concrete made with Portland cement performs satisfactorily. However, there are applications in which the unique properties of calcium aluminate cements enable them to be used in severe environments where they are often in competition with noncementitious materials. Such high-performance concretes extend the range of applications for cementitious materials.

This paper presents the basic chemistry and microstructure of calcium aluminate cement concrete, which are responsible for the unique properties of these materials. Two high-performance applications are presented in detail: use in sewage networks, where sulfuric acid generation by bacteria is a problem, and use in hydraulic dams, where resistance to abrasion is critical. Both examples illustrate that in particular cases durability cannot be generalised from strength and that tests of performance must be specifically adapted to the conditions of use.

2. Chemistry and microstructure

The basic difference between Portland and calcium aluminate cements (CACs) lies in the nature of the active phase that leads to setting and hardening. Portland cements contain lime (CaO) and silica (SiO_2) as the principal oxides, in the form of tricalcium and dicalcium silicate (C_3S and C_2S). On reaction with water, amorphous calcium silicate hydrate (C-S-H) and crystalline calcium hydroxide (CH) are the principal hydrates formed. In contrast, CACs contain CaO and Al_2O_3 as the principal oxides, with little or no silica. These combine to give monocalciumaluminate (CA) as the principal active phase in the cement, which reacts with water to give calcium aluminate hydrates.

The two major fields of application of calcium aluminate cement (which will not be discussed in this paper) are in refractory concrete for industrial use in processes involving high temperatures (e.g., steel making) and in so-called “building chemistry” where it constitutes one part of an often complex mixture of mineral and organic ingredients for applications such as self-levelling screeds and tile cements. Outside these two major areas, there is a huge diversity of

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Table 1
Composition ranges for calcium aluminate cements

Grade	Colour	Al_2O_3	CaO	SiO_2	Fe_2O_3 + FeO	TiO_2	MgO	Na_2O	K_2O	Countries of manufacture
Standard low alumina	Grey or buff to black	36–42	36–42	3–8	12–20	<2	~1	~0.1	~0.15	France, Spain, Croatia, USA, India, eastern Europe
Low alumina, low iron	Light buff or grey to white	48–60	36–42	3–8	1–3	<2	~0.1	~0.1	~0.05	France, USA, India, Korea, Brasil
Medium alumina	White	65–75	25–35	<0.5	<0.5	<0.05	~0.1	<0.3	~0.05	France, UK, USA, Japan, China, India, Korea, Brazil
High alumina	White	⩾80	<20	<0.2	<0.2	<0.05	<0.1	<0.2	~0.05	USA, France, Japan, Brasil, Korea

applications, among which is use in conventional concrete to provide good durability in severe environments.

Despite the existence of several special Portland cements, such as sulfate resisting or white cement, the range of chemical compositions of calcium silicate-based cements is much smaller than for the family of CACs. The standard grades contain around 40–50% Al_2O_3 and are made from limestone and bauxite generally by complete melting in a reverbatory furnace (leading to the term “fondu,” French for melted). Grades containing up to 80% Al_2O_3 are made by sintering for refractory purposes. Table 1 gives approximate chemical compositions for the standard grades, which are those used in the concretes discussed here.

On reaction with water the nature of the hydrates formed is dependent on the temperature of hydration, as shown in Fig. 1. At lower temperatures CAH_{10} is the first hydrate formed, at intermediate temperatures C_2AH_8 and AH_3, and at higher temperatures C_3AH_6 and AH_3. The stable phases are C_3AH_6 and AH_3, and the other phases will inevitably convert to these at a rate dependent on temperature and moisture. C_3AH_6 has the highest density of the calcium aluminate hydrates, resulting in a higher porosity at a given degree of hydration. However, the conversion reaction also leads to the release of water, which is available for further reaction of remaining anhydrous material. For this reason the strength development curve of calcium aluminate ce-

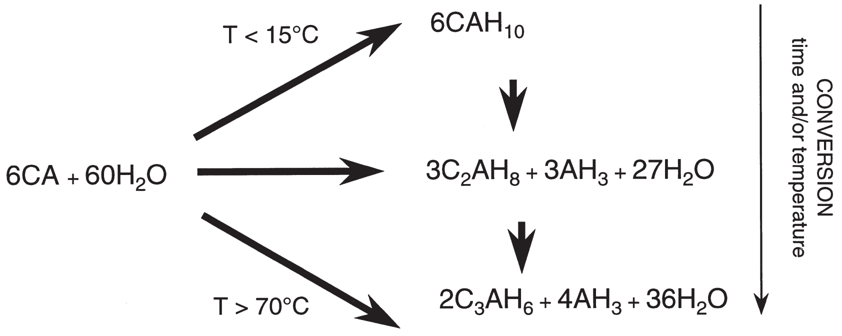

Fig. 1. Hydration reactions of monocalcium aluminate.

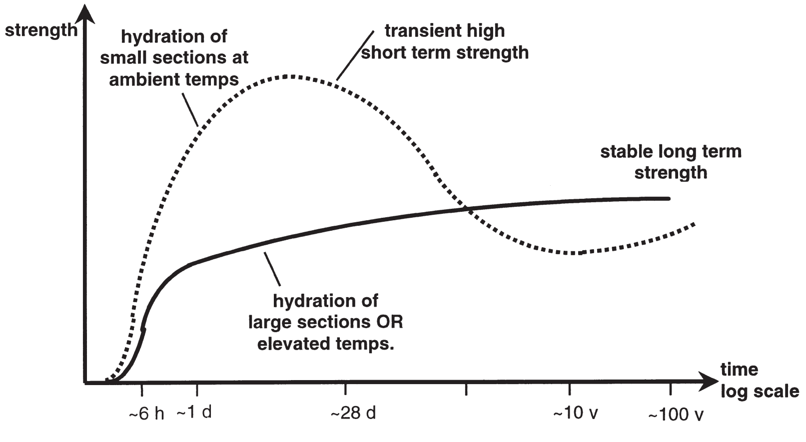

Fig. 2. Schematic strength development of calcium aluminate cements at a water cement ratio of about 0.4.

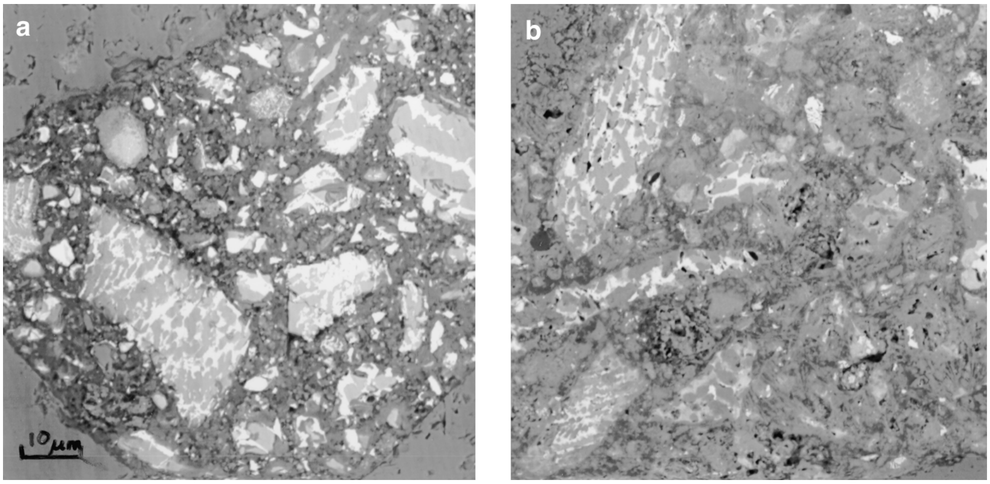

Fig. 3. Microstructures of concretes at w/c 0.4, cured for 7 days at (a) 20°C and (b) 70°C. At this low w/c the microstructure remains dense after conversion.

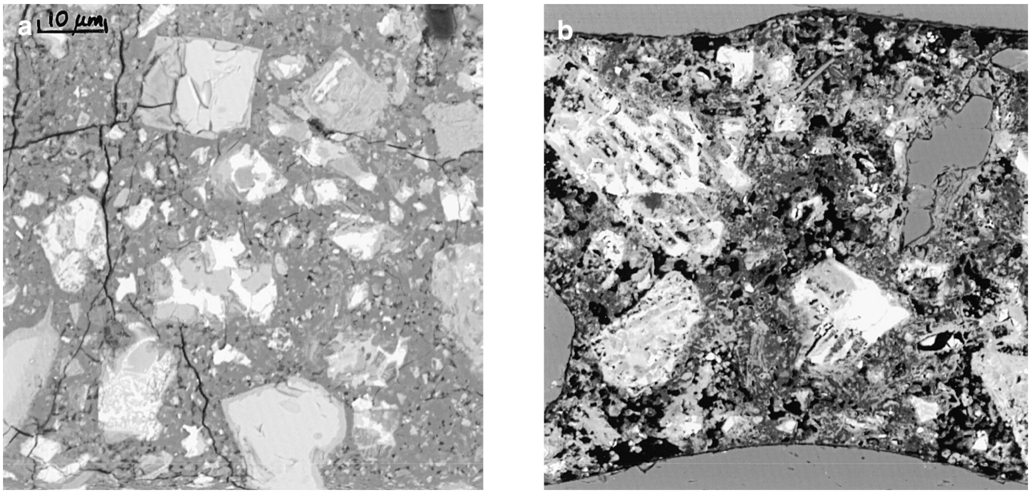

Fig. 4. Microstructures of concretes at w/c 0.7, cured at (a) 20°C and (b) 70°C. At this w/c conversion results in a very porous microstructure.

ment concretes, in small sections at ambient temperatures, has the form shown in Fig. 2, with an initial rapid increase to a high early strength (corresponding to CAH_{10} and C_2AH_8) followed by a slow decline to a minimum (during the transformation to C_3AH_6 and AH_3) before a further increase. Control of the initial water-to-cement (w/c) ratio is very important to ensure that the minimum strength is sufficient for the application and design must always be on the basis of this long-term strength. Over 60 years of practical and laboratory experience has shown that good long-term durability requires a w/c ratio at or below 0.4, and that in the absence of superplasticizers this necessitates a cement content of more than 400 kg/m^3.

Due to the rapid hydration reaction, there is a large release of heat during the early stages of hydration. The consequences of this release are that sections of more than a few tens of centimetres in thickness will attain temperature of up to 70°C or more during curing. Thus the conversion reaction will occur almost instantaneously, leading to a continuously increasing development of strength (Fig. 2).

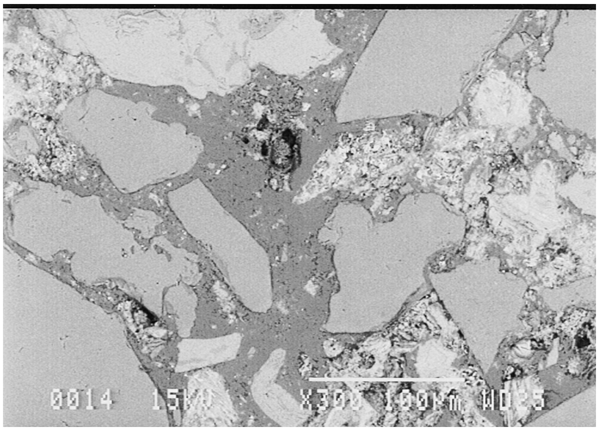

Fig. 5. Microstructure of concrete from a 30-year-old sewer lining. Extensive decalcification has occurred but the formation of alumina hydrate (homogeneous mid-grey product) results in a dense microstructure with low porosity.

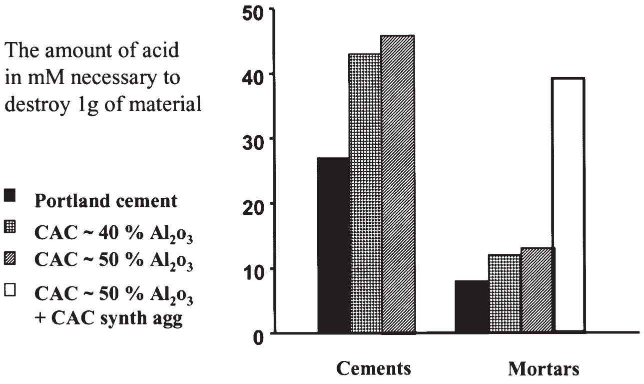

Fig. 6. Comparative neutralisation capacities for Portland and CAC pastes and mortars. For the pastes the higher neutralisation capacity for the CACs is as a result of the alumina content. For the mortars the extra benefits of having an aggregate of the same chemical composition as the paste are apparent.

The impact of w/c ratio in unconverted and converted concretes can be seen quite vividly in backscattered electron micrographs (Figs. 3, 4, and 5). Hydration at 20°C leads to a dense microstructure, with low porosity for all w/c ratios between 0.3 and 0.7. However, at 70°C the converted microstructure at 0.4 w/c remains dense, while at 0.7 a poor microstructure with large pores results. Further details of the hydration of calcium aluminate cement can be found in other works [1,2].

Of course, conversion may have an impact on other properties, although the chemical effects of hydrate type and physical effects of porosity are frequently confused. For example, the pH change during conversion is minimal and does not lead to depassivation of the reinforcement (the invariant points of the unconverted and converted phase assemblages at 25°C are $CAH_{10} + C_2AH_8 + aq$, $pH = 12.13$, and $C_3AH_6 + AH_3 + aq$, $pH = 11.97$) in practice the pH values will be higher due to the presence of minor amounts of alkalis. However, depassivation may occur due to carbonation (as for Portland cement), which may be more rapid in a more porous concrete.

3. Resistance to chemical corrosion

3.1. Acid attack

Acidic environments provide the most chemically aggressive conditions for hydraulic cements, which are all basic in nature. All concretes, both CAC and Portland, will be attacked in these conditions and their ability to provide an acceptable service life depends on several factors, primarily the rate of supply of the acid and the capacity of the concrete to neutralise the acid. The impact of porosity depends on the conditions of service and in some situations may be a parameter of secondary importance.

Portland cement is vulnerable to attack by acids because the calcium hydroxide is rapidly dissolved and opens up the porosity to further penetration of the acid, which then continues to attack the concrete over an increasing depth. The C-S-H gel is also decalcified to leave a structureless silica gel. Typically Portland cement concrete surfaces become very rough under acid attack and thickness loss occurs through attack of the cement paste and consequent aggregate pop-out.

The key to the good performance of CACs lies in the nature of the hydrates, particularly alumina hydrate (the usual crystalline form of alumina hydrate is gibbsite, AH_3, but this phase is often poorly crystalline in calcium aluminate cement pastes so the general term alumina hydrate is preferred). Alumina hydrate is stable down to a pH of about 3 or 4 and the dissolution of the calcium component of the other hydrates leads to the formation of additional quantities of this phase, which infills pores, protecting the concrete from further attack and generally giving a smoother attacked surface with less aggregate loss. See Eq. (1):

$$C_3AH_6 + 6H^+ \Rightarrow 3Ca^{2+} + 2Al(OH)_3\downarrow + 6H_2O \qquad (1)$$

Below a pH of around 3.5 the alumina hydrate dissolves, but in so doing neutralises more acid, as seen in Eq. (2):

$$AH_3 + 6H^+ \Rightarrow 2Al^{3+} + 6H_2O \qquad (2)$$

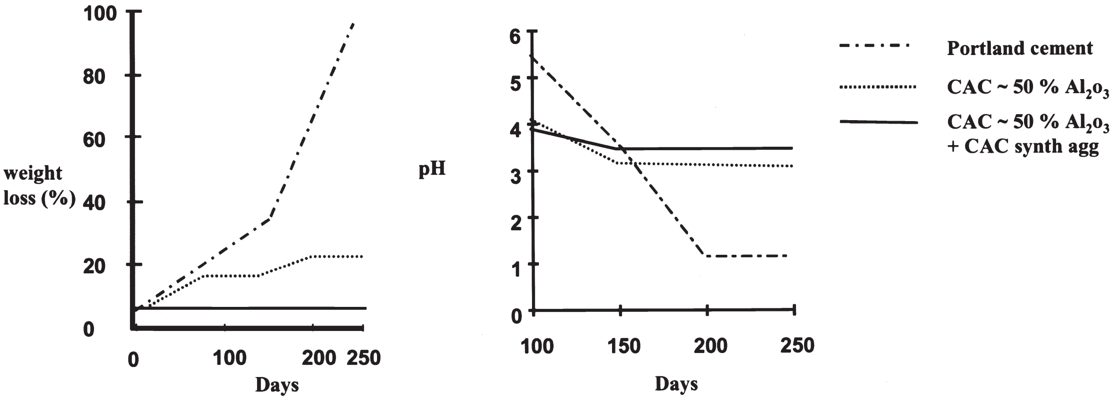

Fig. 7. Weight loss and pH evolution of Portland and CAC mortars tested in a chamber to simulate biogenic corrosion (left). Exposure for 250 days is equivalent to about 16 years of field exposure (right).

Table 2
Weight loss and neutralisation depth of concrete blocks suspended in sewer

	CAC + synthetic aggregate	CAC + siliceous sand	Slag cement + siliceous sand	Portland + siliceous sand (from separate test program)
w/c	0.38	0.32	0.32	n/a
Cement content	510	600	400	n/a
Porosity	11.4	13.4	15.9	n/a
Age at start of exposure	1 month	1 month	3 years	n/a
Weight loss (%)				
after 2 years	0	0.1	n/a	1.2
after 2 1/2 years	0	1.2	1.8	n/a
Neutralised depth				
after 2 years	0	0.2	n/a	1.0
after 2 1/2 years	0	0.6	1.2	1.7 (at 3 yrs)

Overall the neutralisation reaction is shown in Eq. (3):

$$C_3AH_6 + 2AH_3 + 24H^+ \Rightarrow 3Ca^{2+} + 6Al^{3+} + 24H_2O \quad (3)$$

At these lower pHs there will still exist a zone of intermediate pH between the pH at the surface and the unaffected core concrete, in which deposition of alumina hydrate provides a barrier to penetration of the acid. Fig. 5 shows a micrograph from a 30-year-old sewer pipe lining showing this dense microstructure containing predominantly alumina hydrate.

The comparative capacity of Portland and two aluminous cements to neutralise acids is shown in Fig. 6. Experimental determination of the neutralisation capacity is difficult because conventional titration procedures in which the pH is returned to near neutral do not measure the contribution from the alumina that reprecipitates during the titration. Fig. 6 also shows data for the neutralisation capacity of a calcium aluminate cement mortar containing a synthetic aggregate. This aggregate is made by a similar production process to the calcium aluminate cement and has a similar composition to it. This aggregate (tradename ALAG, Lafarge Aluminates, Paris, France) shows exceptionally good bonding with the cement paste. Consequently the attack of the surface is very even and the full neutralisation capacity of paste and aggregate can be realised.

3.2. Biogenic corrosion

A particular case of acid attack can occur in sewers in which bacteria build up in the effluent. The anaerobic bacteria that live in the effluent reduce sulfates in the sewage and give off hydrogen sulfide, which in turn nourishes another

Table 3
Weight loss for converted and unconverted samples in chamber to simulale biogenic corrosion

Mortar curing conditions (time, days)	CAC + siliceous sand		CAC + fine synthetic aggregate	
	6 h, 50°C (converted) weight loss (%)	24 h, 20°C (unconverted) weight loss (%)	6 h, 50°C (converted) weight loss (%)	24 h, 20°C (unconverted) weight loss (%)
100	–	–	1	1
150	12	13	–	–
170	–	–	6	6
220	–	–	10	10
250	27	23	–	–
350	41	41	–	–

Table 4
Comparative test results for different abrasion tests

Test	Measure	CAC + synthetic aggregate (w/c 0.4)	Granite	Silica fume concrete (8% SF, w/c 0.38)	Conventional concretes (W/C ~ 0.5)
CNR abrasion test	vol. sample erroded/ vol. glass erroded	0.35–0.40	0.8	2	4–8
ASTM C-1138	% weight loss, 24 h	<0.5		0.5–1.2	1.5–2
	% weight loss, 72 h	<1	<2	3–4	5–7.5
CNR shock test	volume lost in cm^2	90–120	70–100	120–200	300–350

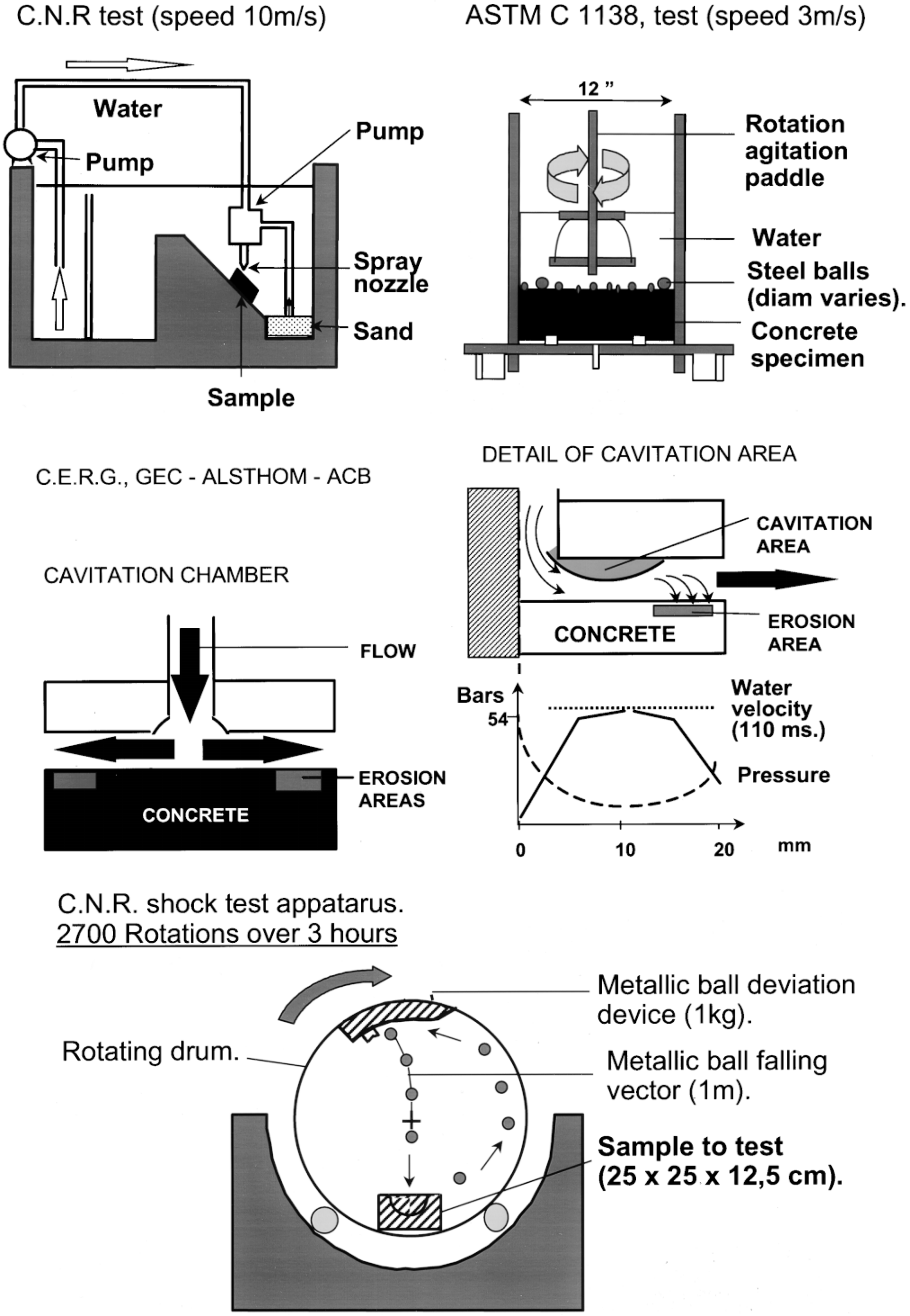

Fig. 8. Empirical test methods for (top) abrasion, (middle) cavitation, and (bottom) shock resistance of materials.

form of aerobic bacteria (*thiobacille*), which flourishes particularly in the crown of the sewer and convert the hydrogen sulfide to sulfuric acid. This is known as biogenic corrosion. The pH at the concrete surface may reach values below 2. This acid-generating cycle is exacerbated by certain conditions (long effluent retention times, elevated temperatures, sulfate-rich effluents, low ventilation, and turbulence). When these conditions are particularly severe or exist in combination, Portland cement linings deteriorate rapidly and do not give adequate performance.

Such complex field conditions are difficult to reproduce in the laboratory, but a simulation chamber has been developed at the University of Hamburg [3], which accelerates the degradation process more than 20 times by optimising the conditions for *thiobacille* to thrive. Fig. 7 shows the results of tests on Portland cement mortar, CAC mortar, and

Table 5
Comparative installed cost of various solutions*

Convention concrete (500 mm)	1
High-performance silica fume concrete	1.5
Epoxy-modified grouts (20 mm)	2.1
CAC + synthetic aggregate (50 mm)	2.5
Granite blocks	5
Steel plates	10
Cast iron plates	15

*These materials do not all give the same service life.

CAC mortar with synthetic aggregate. The influence of substrate can be seen, not only on the overall extent of degradation as measured by the weight loss, but also in the buffering effect on the pH levels.

These laboratory results are corroborated by data from field testing. Here blocks of mortars are suspended in a sewage manhole and the amount of degradation is measured in terms of the weight loss and the depth to which the concrete is neutralised. Table 2 shows comparative data for various CACs with siliceous and synthetic aggregate, and Portland and Portland slag mortars with siliceous sand.

When attacked by acids, both converted and unconverted hydrates give hydrated alumina gel that blocks the porosity, so the degree of conversion has no impact on the rate of attack, as shown in the results in Table 3 [4]. In cases where the CAC concrete lining is applied to iron pipes before installation, the pipes are subject to a steam-curing treatment before set to accelerate curing and assure the formation of the stable hydrate phases. In the field where CAC is applied to deteriorated manholes and sewers, the relatively high ambient temperatures associated with the occurrence of bacteriological corrosion will result in the conversion of the concrete in a matter of a few years or less.

There are many examples of long-term field performance. These include solid CAC concrete sewage pipes installed in Australia and in South Africa in the 1950s, centrifuged Portland pipes lined with CAC mortar and laid in Kuala Lumpur in the 1950s, and linings applied in Cairo in the 1980s and in the USA in the 1990s. All of these exhibit good performance to date. For such applications, the main competitor to CAC concretes and mortars is epoxy coatings. These can give good performance over small areas, but are much more expensive and can be prone to blistering and delamination.

4. Resistance to abrasion

The resistance to abrasion of a concrete, which is relevant under particular field conditions, is difficult to quantify, despite the existence of several test methods, because the practical conditions of solicitation may vary and degradation may occur by a combination of different mechanisms. Nevertheless the observed good performance of CAC concretes in environments subject to abrasion has led to it being used increasingly for repairs to hydraulic dams in

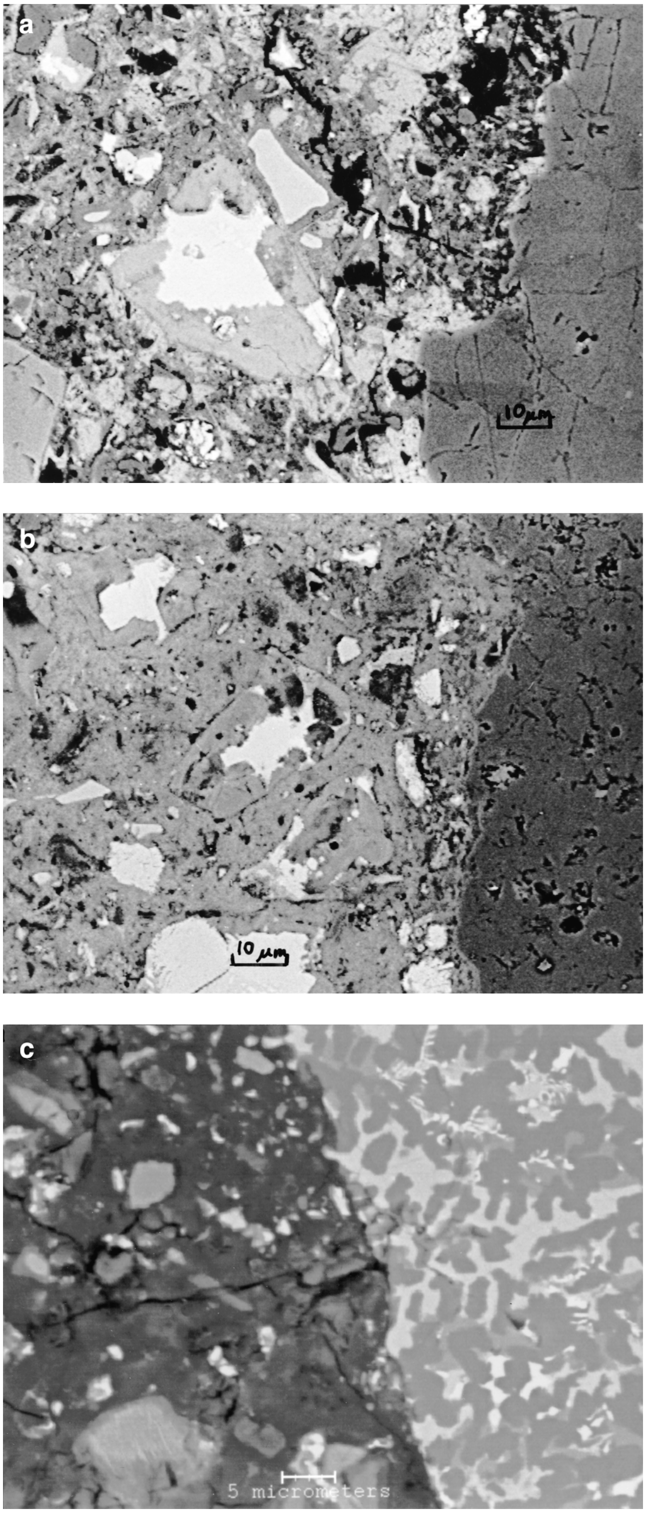

Fig. 9. Microstructure of ITZs in (a) plain cement concrete (w/c = 0.33) with a significant increase in porosity apparent close to the aggregate surface due to the initial packing of the cement grains; (b) Portland silica fume concrete (w/c = 0.33, 15% silica fume) with the presence of the fine silica fume particles filling in some of the porosity in the ITZ; and (c) CAC concrete with a synthetic aggregate (right) (w/c = 0.4) that show dense ITZ. Unreactive parts of the aggregate protrude into the paste.

areas susceptible to abrasion (spillways, sluice gates, and flushing tunnel linings). This in turn has lead to the adoption of various test methods to more quantitatively evaluate the performance of various materials. Fig. 8 shows several of these methods of testing abrasion, cavitation, and shock. These are basically empirical methods. Comparative results of some of these tests are shown in Table 4. These show that CAC concrete with synthetic aggregate perform significantly better than Portland cement concretes (even high-performance concretes with silica fume) and similar to or better than granite blocks, which have been widely used in such application. Field references for such applications date from 1984 (Switzerland) and include installations in Switzerland, France, Sweden, Peru, and the Philippines. Recent tests in India on the abrasion of concretes under practical conditions of rapid evacuation (fast flowing water, 50 m/s, charged by fine silt) showed a degradation of 30–50 mm of high-performance Portland/silica fume concrete with steel fibres, compared to 2–5 mm of CAC/synthetic aggregate concrete.

These results on performance have to be compared with the installed cost of various antiabrasion solutions that are shown in Table 5 on a comparative basis (relative to conventional concrete). It can be seen that the higher materials cost of calcium aluminate cements translates into an installed cost about two and a half times greater than conventional concretes, but only half that of the installed cost of granite blocks and considerably less than steel or cast iron plates, which are often used in areas that suffer from severe abrasion. Thus the calcium aluminate cement concrete provides a viable solution on a cost-performance basis. This illustrates the way in which CAC concretes extend the application range of cementitious materials, retaining the advantages of these materials (namely, that they can be cast in place, changing from a placeable fluid to a hard solid at ambient temperatures).

The microstructural features responsible for resistance to mechanical abrasion in concretes are not well known. In Portland-based concretes including high-performance concrete based on silica fume, there is a smooth increase in abrasion performance with strength. However, testing at Hong Kong University has shown that concretes from CAC with synthetic aggregates have twice the abrasion resistance of Portland-based concretes of the same strength. It is thought that the good performance of CAC with synthetic aggregate owes much to the formation of an excellent interfacial bond between the aggregate and paste. Fig. 9 shows backscattered electron micrographs taken in the region be-

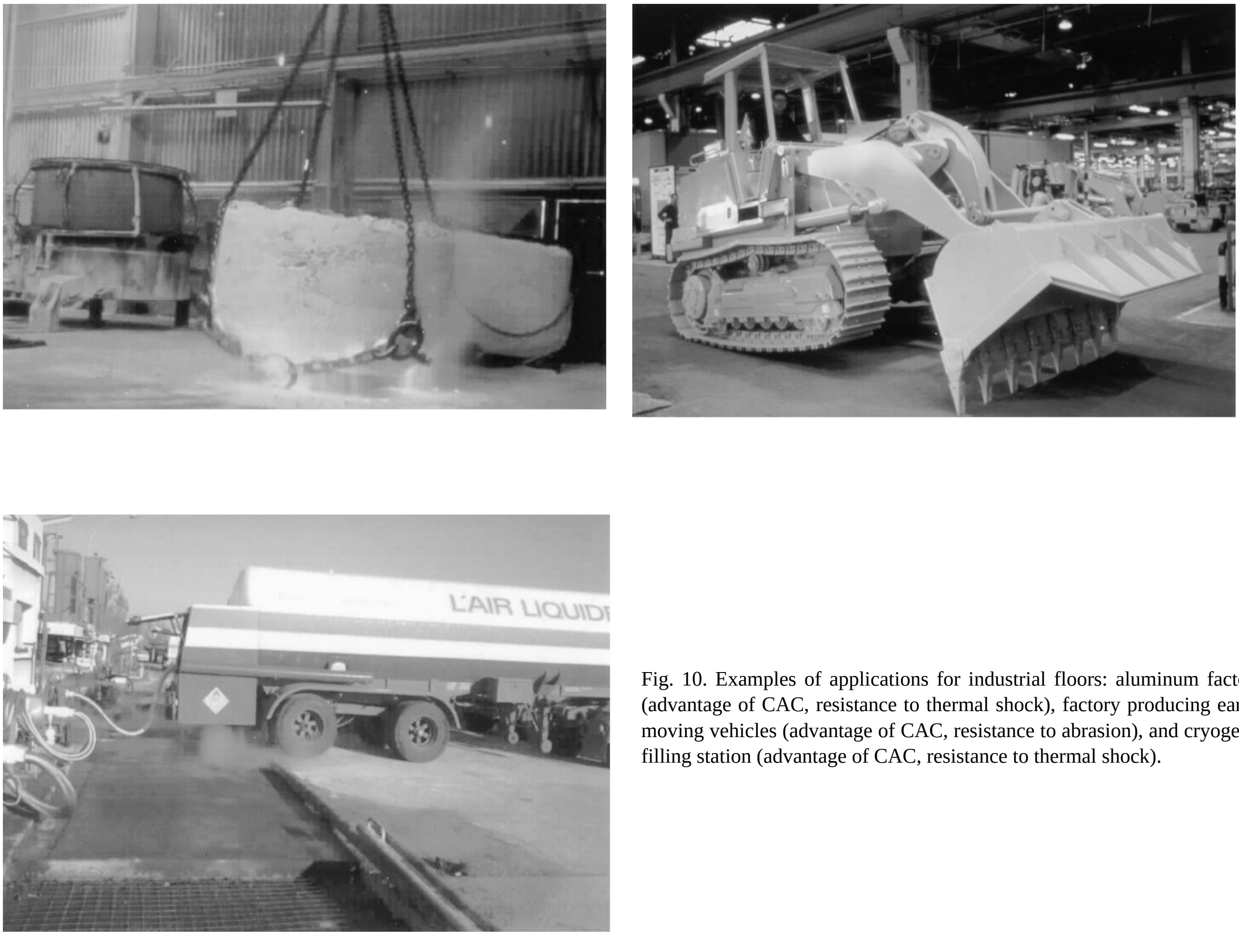

Fig. 10. Examples of applications for industrial floors: aluminum factory (advantage of CAC, resistance to thermal shock), factory producing earth-moving vehicles (advantage of CAC, resistance to abrasion), and cryogenic filling station (advantage of CAC, resistance to thermal shock).

tween paste and aggregate for CAC/synthetic aggregate and for normal Portland and Portland silica fume cements (adapted from Scrivener et al. [5]). Unlike the interfacial transition zone (ITZ) in Portland cement concrete, there is no indication of increasing porosity as the aggregate is approached. The wall effect observed in Portland cement concrete, where anhydrous grains cannot pack efficiently against the larger aggregate surface, must also be present in CAC concretes. However, it appears that the higher mobility of the aluminate ions (compared with silica) leads to more widespread deposition of hydrates throughout the ITZ. This, coupled with the fact that the aggregate itself can react to some extent at its surface, are sufficient to mitigate this wall effect in mature concretes. In addition, the partial reaction of the aggregate at its surface leads to the less reactive (iron-containing) phases being left protruding into the paste. This may improve the mechanical interlocking between paste and aggregate. The similarity between paste and aggregate and the good interfacial bond lead to even wear of the surface, avoiding the formation of cavities and spalling.

5. Industrial floors

The application of CAC concretes in industrial floors (Fig. 10) usually combines the aspects of resistance to chemical and mechanical corrosion. This leads to use in situations where there is heavy wear from industrial vehicles and/or spillage of mild acids, such as in breweries or dairies. On many occasions resistance to thermal shock is also important, such as in foundries or around cryogenic installations. Due to the combination of several criteria, specific laboratory tests are only indicative and the relative value of CAC concretes is best evaluated by in situ performance.

6. Summary

The few examples given here illustrate how specific environmental conditions can justify the use of a higher cost raw material to gain better life cycle cost and fulfill niches in which Portland cement does not perform satisfactorily. In this sense CAC concretes show high performance and extend the range of applications for cementitious materials.

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