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Chloride diffusion in ordinary, blended, and alkali-activated cement pastes and its relation to other properties

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Abstract

Chloride transport into cementitious materials is critical from the viewpoint of protection of reinforcement. This paper is part of a larger study of the characteristics and performance of alkali-activated cementitious materials (AAC) whose properties equal or exceed those of normal Portland cement-based materials. Steady state chloride diffusion studies have been made of pastes of Type I Portland cement, and its blends with different proportions of ground granulated blast-furnace slag. Very substantial reductions in diffusion rates have been found with increased proportion of slag. In addition, alkali activation has been shown to reduce the diffusion rate by at least a factor of two. Other properties determined include: density, porosity, pore size distribution (Hg), BET (N_2) surface area, shrinkage, compressive and flexural strength, leaching, alkali-aggregate reaction, and freezing and thawing resistance. Comparisons with results of previous studies and with other blending components are discussed.

Keywords: Diffusion; Chloride; Alkali-activated cement; Granulated blast-furnace slags; Pore size distribution

1. Introduction

The demand worldwide for high-performance cement-based materials has increased and predictions are that it will reach a major industrial dimension during the early 21st century. The key factor in bringing more new or enhanced high-performance cement-based products to fruition is understanding the fundamental microstructure–property–performance relationship. The work reported here is part of a larger study to examine the microstructure, properties, and the activation processes occurring during the synthesis and use of alkali-activated cementitious materials (AAC).

Building from a history starting in the 1940s, there have been many recent developments in alkali-activated cements [1–34]. Studies of the alkali activation of glassy blast-furnace slag have a long history in the former Soviet Union, Scandinavia, and Eastern Europe [1]. The Trief cements and F-cements from the Scandinavian countries [2,3] and alkali-activated blended cements (sold under the trade name Pyrament) or geopolymers [6] are more recent examples [4–6]. In recent years, particular emphasis has been placed on the utilization of industrial by-products in chemically bonded ceramics [4,7].

There is considerable interest in utilizing such by-product materials in the synthesis and processing of high-performance cementitious materials. Recent advances have led to the development of new families of high-performance cementitious materials, including very high strength (for cements) materials. Some of these materials cross the boundaries of what have been defined as traditional cementitious materials, and the term chemically bonded ceramics has been used to classify such new materials. Chemically bonded ceramics are defined as ceramic-like materials formed as the result of chemical reactions occurring at or near ambient temperatures [7]. Additionally, these cements may be more durable than hydrated Portland cement.

The last century has focused quite properly its technology on Portland cements, those cementitious materials based on compositions in the $MeO–Me_2O_3–SiO_2$ system, concentrating on the development of binding systems consisting of the high calcium content minerals, C_3S, C_2S, C_3A, and C_4AF.

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Table 1
Density, surface area, and particle size distribution data of starting materials

Material	Density (g/cm^3)	BET specific surface area (m^2/g)	Size distribution range (μm)
OPC (type I) (I33)	3.12	0.85	1.1–50
Class F fly ash (G-05)	2.45	0.70	2.0–40
Granulated blast-furnace slag (G42)	2.90	0.75	0.7–40
Silica fume (G-15)	2.05	18.02	0.1–5.0

For detailed characterization results, the reader is referred to [Ref. 34].

These systems have served well, but not without some drawbacks: synthesis of high CaO minerals involves large fuel and energy consumption. Because Portland cement and concrete derived from it constitute the largest volume manufactured material in the world, it is a significant source of carbon dioxide. This is the result of decarbonation of limestone in the kiln during manufacturing $5CaCO_3 + 2SiO_2 \rightarrow 3CaO \cdot SiSiO_2 + 2CaO \cdot SiO_2 + 5CO_2$ and the use of fossil fuel in the kiln. The production of 1 ton of Portland cement accounts for 1 ton of CO_2 [16]. Furthermore, there are certain limitations regarding the durability of the concrete products. Therefore, it is appropriate that now more attention should be given to more conservative systems that, yet, may have high performance.

In the current and related studies, the influence of activators on pore solution composition, heat of hydration, setting behavior, and the rheological, electrical, physical, and mechanical properties of blended cement have been determined. The potential to optimize the use of mineral admixtures in terms of activation and processing has been evaluated. The effect of alkali activation on the microstructure of these materials was analyzed at the micro- and nanometer scale; and numerous studies were performed to characterize the phases present in these systems. Slag, fly ash, and silica fume, as well as blended cements containing mixtures of these and other components were characterized. A set of ordinary Portland cement samples served as a control. This study confirmed that AAC materials have great potential because they generate very early high strength, and have greater durability and higher performance compared to conventional cements. Among the benefits derived from this research is a better understanding of the factors that control concrete properties when using AAC materials, and a method of controlling the chemistry and processing parameters necessary to produce desired microstructures and properties. Pastes, mortars, and concrete prepared with substantial amounts of AAC are increasingly known for their durability and, in particular, resistance to harmful species penetration and diffusion.

Table 2
Surface area change after hydration at W/S[a] = 0.4 and activation for 28 days

	Slag (G42), $m^2\ g^{-1}$	OPC (I33), $m^2\ g^{-1}$
Unreacted	0.7003	0.8074
Activated with 5 M NaOH	12.12	ND
Unactivated	ND	7.964

ND = not determined.

[a] W/S = water/cementitious solids.

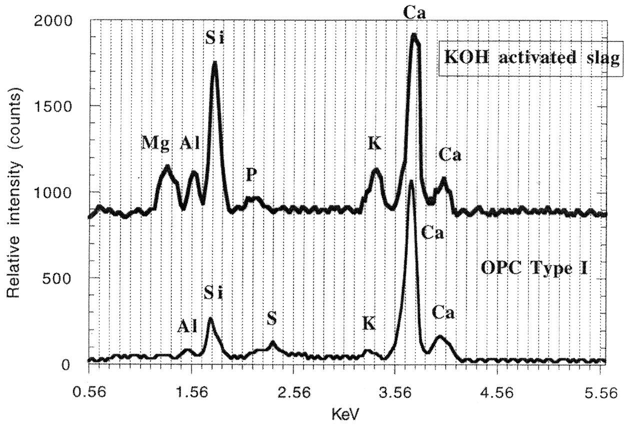

Fig. 1. Peaks in an energy-dispersive spectrum of slag (G42) with 5 M KOH contrasted with that of Type I Portland cement, both W/S = 0.4 and hydrated 28 days.

The overall objectives of the current research were: (a) to identify the different activation mechanisms operating in alkali-activated cements, (b) to characterize the hydration products of alkali-activated cements, and key properties such as transport and diffusion, and (c) to compare effectiveness of different alkalis on activation.

2. Experimental studies and results

2.1. Materials characteristics

The materials activated include: ground granulated blast-furnace slag, fly ash, silica fume, and other pozzolans whether alone or when combined with Portland cement. The activators used were NaOH, KOH, Na_2SO_4, Na_2CO_3,

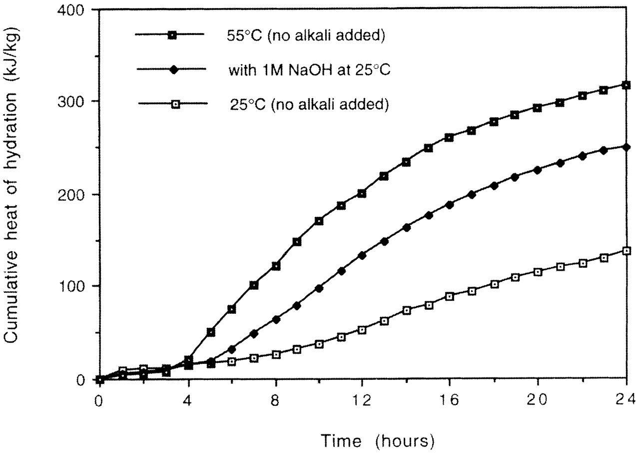

Fig. 2. Total heat evolved as a function of time for blended slag cement at two temperatures with and without alkali during the first 24 h of hydration. Slag (G42)/OPC Type I (I33) = 65:35 at W/S = 0.75.

Table 3
Total porosity, pore size distribution by mercury intrusion porosimetry, and density of AAC hydrated 28 days (W/S = 0.35) compared with control Portland cement without added alkali

Mixture	Porosity (%)	Median pore size (nm)	Density
OPC (Type I, I33)	17.22	14.8	2.10
Slag (G42) with 4 M NaOH	6.2	1.8	2.15
OPC/FA (G07) = 70:30 with 2 M NaOH	13.4	2.9	2.30
OPC/slag (G42) = 35:65 no alkali added	18.3	8.5	2.56
OPC/slag (G42) = 35:65 with 4 M NaOH	14.6	6.2	2.60

$CaSO_4$, and soluble silicates of sodium and potassium. The microstructural observations and properties test results presented in this work have been used to rationalize the factors that govern the course of alkali activation. The effects of different activators on the processing and reaction products have been compared. The materials used and their characterization methods have been described previously [34]. Except when designated otherwise, experiments were carried out at 25°C.

Physical properties of the main materials discussed here are given in Table 1.

2.2. Physical, chemical, and mechanical properties

A comparison of the effects of alkali activation on the specific surface area of cementitious materials is illustrated in Table 2, which contrasts slag, one of the most important source materials for AAC with ordinary Portland cement. The results show that the surface area of granulated blast-furnace slag hydration product is enhanced to a much greater extent by alkali activation than is a normal Portland cement hydration product. These data simply demonstrate the effectiveness of the alkaline activation mechanism.

Further contrast of the chemical characteristics of an activated slag (activated with 5 M KOH) and normal Portland cement hydration products as measured by SEM/EDX is shown in Fig. 1. This figure illustrates both the lower Ca/Si ratio in the slag, and the proportions of other components that play an important role in the formation of an AAC material from slag: Mg, Al, and K.

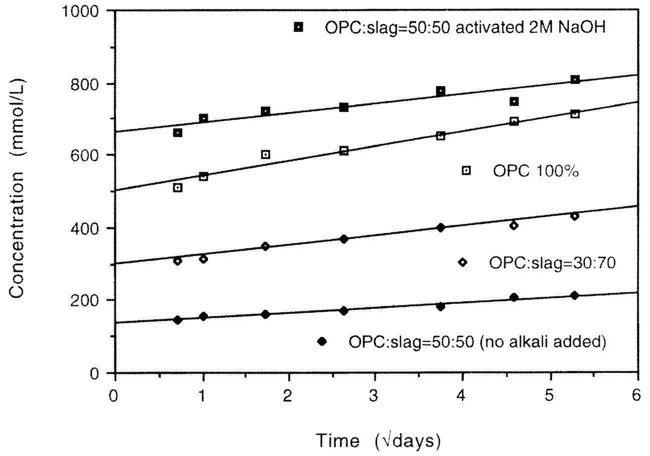

Fig. 3. Total alkali levels Na + K of pore solution of blended ground granulated blast-furnace slag (G42) cement mixtures at W/S = 0.5 compared to OPC Type I (I33) control.

The effect of alkaline activation upon the rate of hydration of cementitious materials is illustrated in the isothermal hydration calorimetry data of Fig. 2, which contrasts the effectiveness of thermal and alkali activation. A 65:35 (mass) ratio slag/Portland cement is shown in each case. One molar NaOH at 25°C doubles the amount of heat released in 24 h hydration, though the increase is not as great as with thermal activation at 55°C. Further contrasts in the characteristics of the hydration products of Portland cement are found in the results of thermogravimetric analyses. The slag products show characteristic peaks for C-S-H, AFm, and hydrotalcite, while normal Portland cement shows C-S-H and $Ca(OH)_2$ [34].

The effect of alkali activation on physical properties of hydration products of materials with OPC, slag, and fly ash is shown in Table 3. In all cases the activation results in both reduced total porosity and median pore size. Finally, the effects of activator (NaOH) on the composition of pore

Table 4
Analysis of pore solution from slag and fly ash samples[a] activated by 1 M NaOH at W/S = 0.5

Mix	Curing time (days)	Concentration (mmol/l)							
		Na^+	K^+	Ca^{2+}	Si^{4+}	Al^{3+}	Fe^{2+}	Cl^-	SO_4^{2-}
Slag (G42) and NaOH	1	750	14	1.5	2.1	4.8	0.050	0.57	2.3
	3	730	15	1.2	1.7	4.4	0.054	0.60	2.6
	7	670	14	0.95	1.4	4.7	0.050	0.45	2.3
	28	650	11	0.90	1.8	4.4	0.062	0.35	2.4
	90	630	10.5	1.2	2.0	4.1	0.056	0.31	2.7
FA (G05) Class F and NaOH	1	650	8	2.5	1.4	5.2	0.01	0.027	80
	3	560	8.4	2.1	1.5	5.3	0.01	0.025	90
	7	540	8.3	2.6	1.1	4.9	0.01	0.022	85
	28	520	11	2.3	1.3	5.1	0.01	0.020	95

[a] These are pure slag and fly ash (100%).

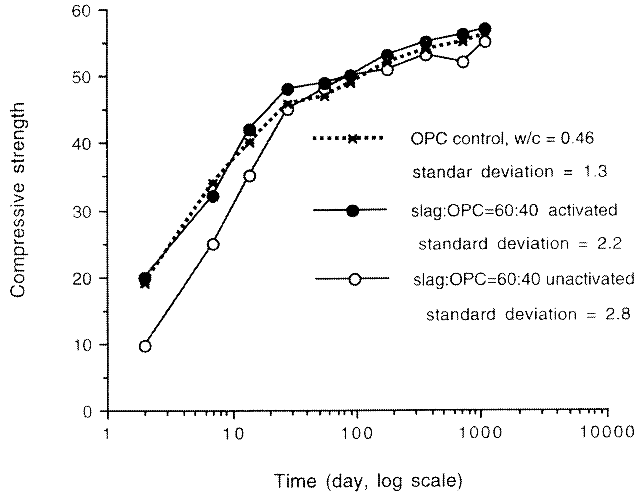

Fig. 4. Strength development mortar OPC Type I (I33)/slag (G42)/sand (C109) = 40:60:275 with 2 M NaOH at W/S = 0.46 as compared with OPC and unactivated mixture.

solutions of slag and fly ash individually at different stages of curing are illustrated in Table 4. Both show decreased Na ion concentrations with time, but residual sulfate is present in the class F ash pore solution. The total alkali (Na^+K^+) levels in pure Portland cement after different curing times are compared with different blends with and without alkali activation in Fig. 3. It is noted that the concentrations in the pore solution of the activated mixture, although higher than in 100% Portland cement up to 28 days, appear to be converging with the Portland cement values, which are increasing at a faster rate.

The development of strength with curing time of pure Portland cement and blends with slag, with and without activation, is illustrated in Fig. 4. The use of 2 M NaOH was sufficient to achieve strength equal at 2-days to that of pure Portland cement, while little difference was found beyond 28 days.

Steady state chloride diffusion through hardened paste was determined using a test originally developed by Hansson and Berke [35]. Slices of the hardened paste, approximately 3 mm thick were cut from cylindrical specimens after curing for 56 days in saturated $Ca(OH)_2$. These were glued to the neck of a plastic bottle in the bottom of which a hole was cut. The bottle was then inverted, set on a rack in a tank containing 1 M NaCl solution saturated with $Ca(OH)_2$ and filled to the level of the tank solution with a half saturated $Ca(OH)_2$ solution, as illustrated schematically in Fig. 5 [36,37]. Four to six samples of each mixture were tested. The concentration of chloride of the solution in the bottles was measured using a chloride ion-selective electrode. The electrode was an ionAnalyzer ORION EA 920 interfaced to a computer.

The effect of alkali activation was demonstrated in measurements of the effective diffusion coefficient. The effective coefficient for steady state diffusion of chlorides through these pastes was determined from Fick's first law:

$$J = -D\frac{\mathrm{d}c}{\mathrm{d}x}.$$

where J is the flux of ions, D is the effective diffusion coefficient and $\mathrm{d}c/\mathrm{d}x$ is the concentration gradient in the bottles. Here the prefix of D (effective diffusion coefficient)

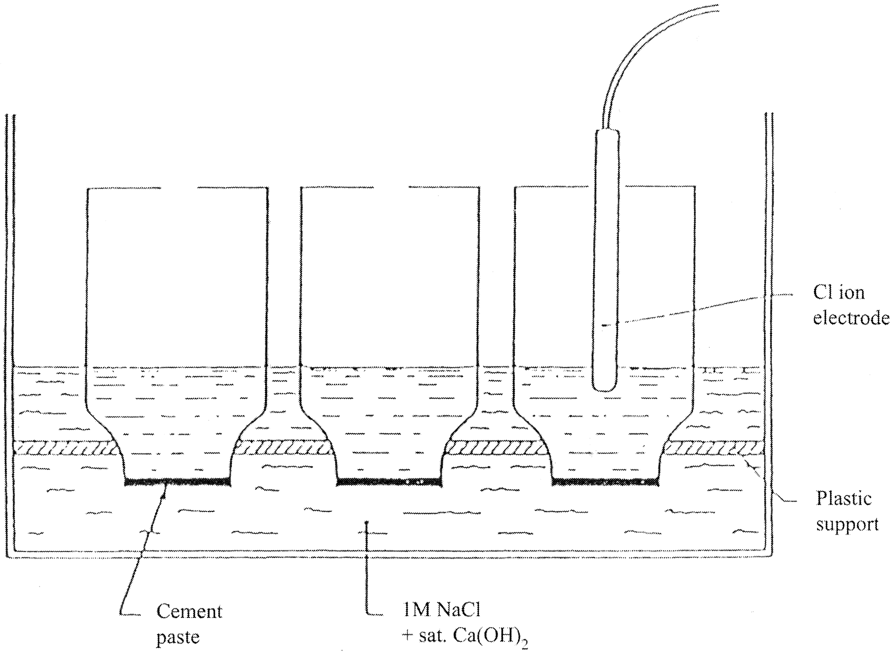

Fig. 5. Experimental set-up for measurement of chloride ion diffusion through cement paste.

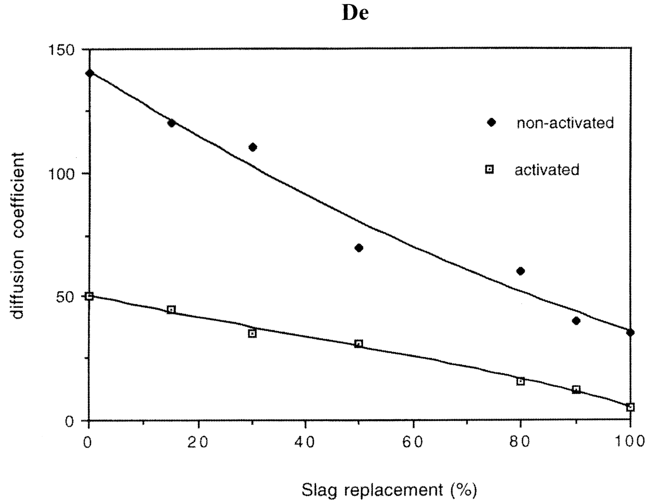

Fig. 6. The effective diffusion coefficient (De) (10–15 m^2 S^{-1}) of paste plotted as a function of the content of slag (G42) additive to OPC Type I (I33).

as used in Fig. 6, is 10^{-15} m^2/s. The values of *D* for the pastes with granulated slag additives are plotted versus the concentration of additive in Fig. 6 and show a clear trend of decreasing diffusion rate with increasing percentage slag. It is generally accepted that concrete durability is to a large extent governed by concrete's resistance to the penetration of aggressive media. The permeability of concrete for various agents has been considered to represent an important materials parameter, which could serve as a performance criterion for concrete durability.

3. Discussion/conclusions

It has been recognized for a long time that the use of mineral admixtures generally improves the durability of concrete. Many authors have concluded that pozzolanic cements or blends with slag, fly ash, or silica fume are best suited for applications where durability is a priority requirement. In such applications, a high resistance to chemical attack, freezing/thawing, and repressing alkali-aggregate-reaction are of concern. As a result, there is very convincing evidence to draw from in order to optimize the use of blended cements to produce concretes with properties equal to, or better than those using 100% ordinary Portland cement. For all types of chemical attack there is evidence that dispersed mineral additions may not only influence the perviousness of concrete but can also affect the chemical reactions during hydration and during corrosion [22,37–39]. Several pieces of evidence in this work may support this theory. The exploration of durability of AAC in this paper has been limited to slag-based mixtures. In the five related topics: chemical attack, leaching, resistance to steel corrosion, resistance to freezing and thawing, and alkali aggregate reaction, the results look optimistic if total alkali additions were kept at ~5% by mass of the slag content [34,37]. Washing of hardened alkali-activated cement samples with water shows that some sodium remained "bound" by the hydration products. Sodium in some zeolites is reported to have a very low solubility in water. Sodium in a typical zeolite is not normally removed by simple washing unless other cations are present in the water to replace the sodium. The need for relatively vigorous washing to remove the "bound" sodium suggests that some sodium is not totally "free" and thus may be bound to the negatively charged surface of C-S-H, or else is present in zeolitic materials or zeolite precursors.

This study and related work have confirmed that the advantageous properties of AAC are their high early strength, rapid hardening and high ultimate strength, low permeability, low heat of hydration, low corrosion rate of steel reinforcement in AAC concrete, and resistance to effects resulting from high chloride diffusion rates or from chemical attack. Finally, quite important properties are the low production cost, energy efficiency, and environmentally friendly characteristics of AAC.

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