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CONCRETE MADE WITH SUPPLEMENTARY CEMENTING MATERIALS

E.E. BERRY

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ERRATUM FOR CANMET REPORT 79-32 - CONCRETE MADE WITH SUPPLEMENTARY CEMENTING MATERIALS by E.E. Berry

Page 1, paragraph 4, should read "...effects on concrete (2-13)." and not "...effects on concrete (2, 13)."

CONCRETE MADE WITH SUPPLEMENTARY CEMENTING MATERIALS

by

E.E. Berry*

SUMMARY

Supplementary cementing materials such as granulated blast furnace slag, fly ash or natural pozzolans may replace a portion of the portland cement used in concrete. Because they are produced by less energy intensive procedures than the portland cement that they replace, their use can reduce the energy consumed in making concrete and can thus lower construction costs.

High quality supplementary cementing materials, used with appropriate proportioning procedures make it possible to produce durable concrete of adequate early strength and good workability. It has been found that some supplementary cementing materials can improve the resistance of concrete to sulphate attack and to deterioration caused by alkali-aggregate interaction.

Although much is already known of the general application of supplementary cementing materials, research is urgently required to improve quality control, develop specification tests and assess their long-term performance in concrete structures.

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BETON FABRIQUE A PARTIR DE MATERIAUX
CIMENTAIRES SUPPLEANTS

par

E.E. Berry*

SOMMAIRE

Des matériaux cimentaires suppléants tels que les laitiers granulés provenant des hauts-fourneaux, les cendres volantes et les pouzzolanes naturelles peuvent remplacer une partie du ciment portland employé dans le béton. Comme la production de ces matériaux requiert moins d'énergie que celle du ciment portland qu'ils remplacent, leur emploi peut réduire la consommation d'énergie nécessaire à la fabrication du béton et peut donc contribuer à réduire les coûts de construction.

Les matériaux cimentaires suppléants de haute qualité employés en suivant les méthodes de dosage appropriées rendent possible la production de béton durable, de résistance initiale adéquate et de bonne ouvrabilité. On a trouvé que certains matériaux cimentaires suppléants peuvent améliorer la résistance des bétons aux attaques du sulfate et à la détérioration due aux réactions alcali-agrégat.

Quoique l'on connaisse déjà beaucoup les applications des matériaux cimentaires suppléants, il faudrait effectuer une recherche pour améliorer le contrôle de la qualité, mettre au point des essais de normalisation et évaluer leur rendement à long terme dans les structures de béton.

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INTRODUCTION

Recent concern for reducing energy consumption and conserving raw materials has led the North American cement and concrete industries to reconsider blended cements, slags and pozzolans to supplement normal portland cement (1). Although these materials have been used for many years elsewhere in the world, they have been accepted only slowly in North America. However, in recent years there has been a growing trend towards their increased use and a very considerable increase in research into their effects on the properties of concrete.

The properties of concrete depend on the characteristics and relative proportions of the materials used in its manufacture. In fresh concrete, the coarse and fine aggregates are suspended in cement paste. The consistency of the mass is controlled by the fluidity of the paste and by the quantity and grading of the aggregate. In hardened concrete, properties such as strength are functions of the density of the paste, which in turn is controlled by the ratio of water to cement in the original mixture. If the aggregates are of satisfactory quality, the performance of concrete in service is primarily influenced by the strength and impermeability to water of the hardened paste.

The inclusion of a supplementary cementing material in concrete, either as a separate component at the concrete mixer or as a blended cement, affects all of its properties. As a part of the composite that forms the concrete mass, it functions both as a fine aggregate and as a cementitious component. It influences the rheological properties of the plastic concrete - the strength, finish, porosity and durability of the hardened mass - and the cost and energy consumed in manufacturing the final product.

Over the past 40 years a number of authors have reviewed the properties of pozzolans, fly ashes and slags and their effects on concrete (2,13). This review draws together the major points relating to their use as reflected in the recently published literature.

ENERGY SAVINGS

Beijer has shown that portland cement accounts for 30 to 50% of the energy used in the manufacture of reinforced concrete, the exact proportions being dependent on the type of concrete and the degree of reinforcement (14). Clearly, any savings in the energy required to produce cement will contribute substantially to savings in the total energy consumed in concrete construction and would presumably be reflected in reduced costs.

The manufacture of portland cement involves three separate groups of operations: quarrying and preparing raw materials, pyroprocessing, and finish grinding. In North American practice 80 to 85% of the total energy consumed in these processes goes into pyroprocessing. Table 1 shows typical heat consumption in pyroprocessing for the three main kiln types used.

Table 1 - Heat input to kilns for pyroprocessing

	Heat input (MJ/kg)	
Kiln type	Canada*	U.S.A. 1973**
Dry (long)	4.15	6.33
Wet (long)	6.78	7.55
Preheater (dry)	3.39	5.26

*From reference (15)

**From reference (1)

Neither granulated blast furnace slag nor fly ash require pyroprocessing to prepare them as supplementary cementing materials. Slag may require drying and does require grinding. Fly ash is usually collected in a dry state if it is to be used as a cement supplement. In some instances grinding, classification and beneficiation have also been used to improve the quality of fly ash for use in concrete. Some natural pozzolans require only drying, grinding and classification; others also require calcination. All of these procedures consume energy. The energy savings offered through the use of these materials depend on the difference between the energy cost in preparing pozzolans or slags and the usually much higher energy cost of manufacturing portland cement.

Estimates of the energy consumed in preparing slags and pozzolans as supplementary cementing materials are shown in Table 2. These values may be compared with an average energy cost, as reported by Howe, of 6.57 MJ/kg required to make portland cement in Canada in 1975 (15).

HYDRAULIC ACTIVITY OF PORTLAND CEMENT AND SUPPLEMENTARY CEMENTING MATERIALS

To understand how portland cement and supplementary cementing materials used together, influence concrete, it is first necessary to consider their individual compositions and properties, and their interaction in the presence of water.

PORTLAND CEMENT

Portland cement may be defined as a product obtained by intimately mixing materials composed of calcium oxide, silica, alumina and iron oxide, heating them to a temperature at which partial fusion occurs and grinding the resultant clinker with a small amount of calcium sulphate. The cementing action of portland cement derives from the presence in the clinker of four principal chemical combinations of CaO, SiO_2, Al_2O_3 and Fe_2O_3: tricalcium silicate, β-dicalcium silicate, tricalcium aluminate and ferrite solid solutions of compositions approximating $4CaO.Al_2O_3.Fe_2O_3$. The hydration of these materials modified by the presence of calcium sulphate, minor clinker components and the influences of temperature determines the setting and hardening properties of portland cement. Taylor attributes the cementing action of portland cement, cured at ordinary temperatures, to the formation of colloidal hydration products described as tobermorite gel (19). He offers the following summary of the processes which cause hardening and setting:

> "The initial result of mixing the cement with water is to produce a dispersion; the water/cement (w/c) ratio needed to produce a paste (0.3-0.7 w/w) is such that the grains of cement are not close packed. Reaction with water quickly produces a surface layer of hydration products on each grain. These occupy space partly at the expense of the grains, and partly at that of the liquid. The particles of the hydration products at this stage are largely of colloidal dimensions (10-1000 Å), but some large crystals [$Ca(OH)_2$ and Al^{3+}, Fe^{3+} and SO_4^{2-} containing phases] may also be formed. The solution quickly becomes saturated with Ca^{2+}, OH^-, SO_4^{2-}, and alkali cations. With further reaction, the coatings of hydration products extend and begin to meet each other, so that a gel in the classical sense is formed in the spaces between the grains. This is the stage of setting. With still further reaction, the particles between the clinker grains become increasingly densely packed until the material can equally well be regarded as a mass of particles in contact with each other. Differentiation of the gel occurs in that it becomes more densely packed in some regions and less so in others, so that pores are formed."

BLAST FURNACE SLAG

Blast furnace slag is a byproduct of the manufacture of iron in the blast furnace. The composition of slag can vary over a wide range depending on the nature of the ore, the flux, the coke and the kind of iron being made. A typical range of chemical analyses for North American slags is given in Table 3.

In the blast furnace, molten slag rises to the surface and is tapped periodically. Its conversion from the molten state into useful products depends upon subsequent processing. Slag that is allowed to cool slowly solidifies into a largely crystalline, stony mass termed air cooled slag, which is used as road or concrete aggregate. More rapid cooling produces a porous, foamed slag frequently used as lightweight aggregate. Neither of these materials is of value as a cement. For this purpose, the slag must be rapidly quenched

Table 2 - Estimated energy requirements for preparing slags and fly ashes as supplementary cementing materials

Material	Estimated energy requirement (MJ/kg)*		
	ref (16)	ref (17)	ref (18)
Ground granulated b.f. slag	2.23	1.65	2.21
Fly ash	0.49 (including 0.37 MJ/kg for drying)	0.05	0.17

*Estimates do not include transportation.

Table 3 - Typical range of chemical composition of North American blast furnace slags (20)

Per cent by weight				
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
33-42	10-16	0.3-2.0	36-45	3-12

to a glassy state. The most commonly used procedure has been termed granulation and the product is widely known as granulated blast furnace slag (21).

Finely ground granulated blast furnace slag possesses the property of latent hydraulicity. With some exceptions, most granulated slags do not set or do so only slowly when mixed with water alone, but will behave as hydraulic cements in the presence of activators. The activators used in modern practice are portland cement or mixtures of portland cement and calcium sulphate. Other activators include calcium, sodium and potassium hydroxides or other compounds which yield highly alkaline aqueous solutions. In the context of the present discussion, activation of granulated slag by the portland cement component of concrete will be the major concern.

The hydration of mixtures of portland cement and granulated blast furnace slag is complex, the hydration of the slag constituent being superimposed on that of the portland cement clinker. On its own, ground granulated blast furnace slag shows little hydraulic activity. On contact with water, calcium ions are released into solution, but the concentration of $Ca(OH)_2$ is very low when compared with that obtained from portland cement. Even after several months there is little or no evidence of the formation of hydration compounds (11,12,20). However, Nurse has shown that hydration of the slag occurs when it is placed in a saturated calcium hydroxide solution (12). Under these conditions, hydration continues at a gradually reducing rate as the concentration of $Ca(OH)_2$ in the solution falls. Unless the concentration of $Ca(OH)_2$ is maintained by replenishment above a certain level, reaction in the solution ceases.

These observations have led a number of authors to suggest that when slag is initially placed in contact with water, hydration is inhibited by the formation of impermeable acidic gels on the surfaces of the slag grains (11,12,13,20). In the presence of calcium hydroxide these surface coatings break down, permitting hydration to continue. Similar effects have been noted when other activators such as NaOH or $CaSO_4 \cdot 2H_2O$ have been used in place of $Ca(OH)_2$. In consequence, it has been concluded that effective activators are agents which can either react with the gel coating or, by reaction with water, can release sufficient $Ca(OH)_2$ to do so (12).

According to Nurse (12) and also Schröder (11), the hydration products distinctly identified in hydrated blast furnace slag cements are:

1. a calcium silicate hydrate phase similar to tobermorite,
2. a calcium sulphoaluminate phase of the ettringite type,
3. hexagonal calcium aluminate hydrate or a solid solution or intergrowth with tetracalcium aluminate monosulphate hydrate (12),
4. calcium hydroxide.

The tobermorite phase is considered to be the component mainly responsible for the development of strength.

Fulton states that effective granulation is fundamental to the development of potential hydraulicity of blast furnace slag (13). Rapid chilling inhibits the formation of crystalline structures and the resulting granulated slag is largely in the form of a glass which has good hydraulic properties when suitably activated.

Although it is generally accepted that the glass content of granulated slag is important in determining hydraulicity, it is still far from clear which factors are primary in determining the hydraulic potential of a particular vitrified slag (13).

Many investigators have attempted to use chemical moduli to define and predict the latent hydraulicity of slags. An example is the requirement of the Canadian Preliminary Standard CSA-A363 - M1977 (22) that:

$$(CaO + MgO + Al_2O_3)/SiO_2 \geq 1$$

(Each oxide being expressed as a percentage by weight.)

Other similar moduli have been examined and discussed by Stutterheim (23). However, as Lea has commented, whereas such empirical formulae are convenient for the rapid control of slag quality at a particular blast furnace, the only reliable guide to hydraulic quality is the strength developed in the presence of portland cement (20).

A recent U.S. patent indicates that there may be exceptions to the generally accepted view that only glassy slags are latently hydraulic (24). In this patent, Alderete et al. claim that a cement composition which in some respects is better than Type I portland cement can be produced by intergrinding from 1 to 25 parts by weight of air-cooled blast furnace slag with Type I portland clinker.

POZZOLANS

Pozzolans are siliceous or siliceous-aluminous materials which in themselves possess little or no cementing value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds possessing cementitious qualities (25). They may be conveniently divided into two classes according to their origin - natural and artificial. Natural pozzolans are usually materials of volcanic or diatomaceous origin. Artificial pozzolans are mostly products of the heat treatment of clays and shales or are finely divided ash residues from the combustion of pulverized coal or fly ash.

Table 4 shows the chemical compositions of a selection of natural and artificial pozzolans.

Among the natural pozzolans, those of volcanic origin consist of glassy or amorphous materials arising from the deposition and alteration of volcanic dust and ash. The natural volcanic pozzolans used in North America mostly have been tuffs containing 50 to 100% of rhyolitic glass with a silica content of 70 to 75% (20). Other high-silica minerals also show pozzolanic activity. The best known are the diatomaceous

Table 4 - Chemical composition of some natural and artificial pozzolans*

Pozzolan	Types**	Weight per cent composition							
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
USA ryolitic pumicite	N	72.3	13.3	1.4	0.7	0.4	1.6	5.4	4.2
Rhenish trass	N	54.6	16.4	3.8	3.8	1.9	5.1	3.9	10.1
Raw moler	N	66.7	11.4	7.8	2.2	2.1	-	-	5.6
Burnt moler	A	70.7	12.1	8.2	2.3	2.2	-	-	-
Bituminous fly ash	A	43.1	22.4	16.3	4.6	1.4	0.8	1.5	7.2
Sub-bituminous fly ash	A	50.4	24.3	5.15	12.1	1.9	3.6	0.6	0.3

*From references (20) and (26)

**N=Natural
A=Artificial

earths in which the main active component is opal, an amorphous form of hydrous silica.

The major artificial pozzolans are calcined clays and shales, spent oil shales and fly ash. Of these, fly ash is by far the most important commercially at the present time.

Fly ash is a byproduct from the combustion of pulverized coal in thermal power plants. It is removed by mechanical collectors or electrostatic precipitators as a fine particulate residue from the combustion gases before they are discharged to the atmosphere.

The chemical composition of fly ash is determined by the types and relative amounts of mineral matter in the coal that is fired. Most fly ashes comprise chemical compounds and glasses formed from SiO, Al_2O_3, Fe_2O_3, CaO and MgO, along with some unburned carbon.

Fly ash particles are typically spherical, ranging in diameter from 1 to 150 µm. The range of particle sizes in any given fly ash is largely determined by the type of dust collection equipment used.

The hydration of portland cement/fly ash combinations has been studied by Kovacs (27). His investigations showed the products of hydration of fly ash cements to be identical with those of portland cement hydration, the only differences being restricted to the relative proportions of the hydrated products. Larger quantities of gel and carbonate phases and less $Ca(OH)_2$ were found in hydrated fly ash cements.

No single characteristic or simple combination of characteristics has been established as determining the usefulness of fly ash as a pozzolan. There is, however, agreement in the literature that pozzolanic activity is related in a general way to the chemical composition, fineness and phase composition of fly ash. In particular, there is a growing body of evidence that as with blast furnace slag, siliceous or aluminous materials in the glassy state are responsible for the major part of the hydraulic value of fly ash (7).

THE PRODUCTION OF CONCRETE CONTAINING SUPPLEMENTARY CEMENTING MATERIALS

Concrete, in which the binder is composed of portland cement together with some quantity of a supplementary cementing material, may be produced in one of three ways:

1. A prepared blended cement may be used to replace portland cement.

2. Portland cement and a supplementary cementing material may be added at the concrete mixer as separately dry-batched components.
3. A water slurry of the supplementary cementing material may be introduced at the concrete mixer.

Pozzolans or slags are used throughout the world, as integral components in the manufacture of blended cements. Although specifications differ in detail from one country to another, the definitions of some blended hydraulic cements specified by ASTM illustrate the typical nature of such materials (25).

Portland-blast furnace slag cement is defined by ASTM as an intimate and uniform blend of portland cement and fine granulated blast furnace slag produced either by intergrinding portland cement clinker and granulated blast furnace slag or by blending portland cement and finely ground granulated blast furnace slag, in which the slag constituent is between 25 and 65% by weight of portland blast furnace slag cement.

Portland-pozzolan cement is defined as an intimate and uniform blend of portland cement or portland blast furnace slag cement and fine pozzolan produced by intergrinding portland cement clinker and pozzolan, by blending portland cement or portland blast furnace slag cement and finely divided pozzolan or by combination of intergrinding and blending, in which the pozzolan constituent is between 15 and 40 wt% of the portland-pozzolan cement.

There has been considerable discussion in the literature over the relative virtues of intergrinding clinker with slag as opposed to separate grinding of the components and subsequent dry blending (13,28,29). Generally, portland cement clinker and granulated blast furnace slag differ markedly in hardness and hence in grindability. Usually slag is the more difficult to grind. As a result it has been found that under some circumstances intergrinding produces a blend in which the portland clinker is "overground" whereas the slag remains coarser than is optimal for its performance.

Whereas control over fineness has been the principal advantage claimed for separate grinding, an additional argument has been that it provides material from which a variety of blend proportions may be selected. When combined with job-site blending at the concrete mixer, this allows for cement composition to be chosen to suit a variety of types of concrete.

Two examples illustrate the use of slurry handling. According to Lawson and Nixon (29), a modification of the usual process for making blast-furnace slag cement was introduced into Belgium by M.V. Trief and was used during construction of the hydroelectric dam at Glenmoriston in Scotland, in 1953. In this process the slag is wet-ground and stored as a wet slurry until mixed with the portland cement and aggregate during batching of the concrete. The advantages claimed are a saving in fuel for drying the granulated slag and greater efficiency of grinding in the wet state.

Kokubu reports that to overcome problems of uniformity and difficulties caused by pack-setting of dry stored fly ash, testing and research on the use of fly ash as a 50% slurry in water was carried out in association with the construction of the Okutadami Dam in Japan (5).

Clendenning and Loughborough report that a similar approach to storage and supply of fly ash from the Lakeview Generating Station is to be considered by Ontario Hydro (30).

With the exception of a few studies, the published research on supplementary cementing materials derives from experimental or field examination of concretes in which the cementing components were separately batched. It is assumed that the major properties of concretes will not be much influenced by the means chosen to introduce the components. Hence the general observations reviewed in this paper are assumed to be equally applicable to separately batched, blended cement or slurry batched concretes.

THE EFFECTS OF SUPPLEMENTARY CEMENTING MATERIALS ON THE PROPERTIES OF CONCRETE

For the purposes of the following discussion, consideration will be restricted to the effects of vitrified blast furnace slag or fly ash on the properties of concrete. This selection has been made on the grounds that these are the most important of the supplementary materials in current use in North America and that their use is increasing substantially. The selection of these materials for discussion in no way implies that others are necessarily inferior.

FRESH CONCRETE

Workability, Water Requirement and Bleeding

Fresh concrete should be relatively easy to mix, transport, place, compact and finish, and it should not segregate during these operations. These properties are expressed in a composite quality - workability - and must be achieved through appropriate choice of mix proportions which must be consistent with the requirements for strength and durability of the final product.

The small size and essentially spherical form of fly ash particles usually influence the rheological properties of cement pastes causing the amount of water required for a given degree of workability to be reduced from that required for an equivalent paste without fly ash. In this respect, as noted by Davis et al., fly ash differs from other pozzolans which usually increase the water requirement of concrete mixes (31).

The literature provides many examples of reports of improved plasticity and workability imparted by fly ash to concrete. Adbun-Nur considered improved workability to be "almost axiomatic" when fly ash is used in properly adjusted concrete mixes (3). However, some contrary data have been reported.

Brink and Halstead found that some fly ashes reduced the water requirement of test mortars, whereas others, generally of higher carbon content, increased water requirement above that of control mortars (32). Welsh and Burton reported loss of slump and flow for concretes made with some Australian fly ashes used to partially replace cement, when water content was maintained constant (33). Rehsi reported that experience with a number of Indian fly ashes showed that all those examined increased the water requirement of concrete (34).

Ground granulated slag has also been reported to reduce water requirement and hence aid workability. Stutterheim reports that it is common experience that concretes containing slag are appreciably more workable as a result of which it is possible to reduce water content compared with the case for portland cement (23).

Fulton has noted that fresh concrete containing blends of separately ground blast furnace slag with portland cement is more easily vibrated into place on the construction site than corresponding concretes made with portland cement alone (13).

Recent investigations performed at CANMET of concrete mixes incorporating a granulated slag in proportions varying from 25 to 65% by weight of cement, indicate that the water requirement was equal to or somewhat greater than that of the control mix (35).

Ryan reported that concrete mixes containing slag showed a tendency to bleed (36). Cesarini and Frigione investigated bleeding of fresh pastes made with mixtures of portland cement and milled granulated blast furnace slags (37). These authors reported that for all the slags tested, both the bleeding rate and the total amount of bleed water increased with increasing slag content.

TEMPERATURE RISE

The hydration of portland cement is accompanied by an evolution of heat which causes a temperature rise in the concrete. The resulting thermal gradients produced in mass concrete structures may lead to cracking. It is generally accepted that the use of supplementary cementing materials to partly replace portland cement is an effective means of avoiding this problem (11,38, 39,40).

HARDENED CONCRETE

Mix Proportioning and Strength Development

The development of strength in a concrete containing a supplementary cementing material is intimately related to the method used to select the mix proportions. Three basic mix proportioning approaches have developed with a view to obtaining either reduced heat of hydration or, to overcome difficulties encountered in obtaining acceptable strength at early ages.

The first method requires a direct replacement of a portion of the portland cement. Much research has shown that any percentage replacement of portland cement in concrete by fly ash, pozzolan or slag on a one-for-one basis, either by volume or by weight, results in lower compressive and flexural strengths at early ages, with the development of similar or greater strengths at and beyond 6 months. In mass-concrete, this reduced early strength is of less importance than the desired reduction in temperature rise.

Results of CANMET investigations associated with the strength development of concrete incorporating slag as a direct replacement of portland cement indicated (35):

(a) For low water/cement ratio mixes, the compressive strength of concrete containing slag, regardless of percentage, was generally lower than the corresponding strength of control concrete at all ages up to 1 year.

(b) For higher water/cement ratio mixes, the compressive strength of concrete containing slag, regardless of percentage, was always lower than the corresponding strength of the control concrete at ages up to 28 days. At later ages, the strength of slag concrete approached but rarely exceeded the strength of control mixes.

A general appreciation of the effects of the cement replacement approach may be obtained by referring to the work of Washa and Withey for the case of fly ash replacement and to the work of Fulton for replacement by slag (41,13).

The second method requires an addition of fly ash, pozzolan or slag to cement. The total cementitious content of the mix is thereby increased and mix adjustments are usually made through changes in aggregate content.

The third method requires a part of the cement to be replaced with an excess by weight of the supplementary material, with adjustments being made in fine aggregate content. The method probably originated in 1958 with the work of Lovewell and Washa who showed, by modification of mix proportions, that fly ash concretes could be made which had strengths at early ages comparable with those of control mixes (42). The main point of their conclusions was:

> "In order to obtain approximately equal compressive strengths at early ages, between 3 and 28 days, mixes made with fly ash must have a total weight of portland cement and fly ash greater than the weight of the cement used in the comparable strength portland cement mixes."

In 1968, Cannon reported research carried out by the Tennessee Valley Authority on methods of proportioning fly ash concretes to obtain strengths at 28 and 90 days equal to those of conventional control mixes (43). Cannon employed Abrams' relationship between strength and water/cement ratio and introduced a factor which took account of the relative costs of fly ash and portland cement. This approach combined with extensive laboratory investigations and field experience allowed Cannon to develop tables and graphs to facilitate proportioning procedures.

Just as Lovewell and Washa had advocated, Cannon's approach results in the use of a combined weight of portland cement and fly ash greater than the weight of the cement used in a comparable control mix. Cost savings using this method rest upon a significantly lower cost per tonne for fly ash than for portland cement.

In 1975, Ghosh further extended the approaches developed by Lovewell and Washa, and by Cannon (44). He published a series of empirical relationships derived from Abrams' principle which considerably simplified the mix proportioning of fly ash concrete.

Other relevant examples of the application of proportioning principles to the manufacture of concretes containing fly ash can be found in publications by Smith (45), Rosner (46) and Ryan and Ashby (47). Whereas the above discussion has referred to work related to the use of fly ash, it is obvious that the same principles may be applied to mix proportioning with slag as was shown by an investigation reported by Ryan (36).

The inherently slower rate of hydrate formation at early ages which is characteristic of blends of supplementary cementing materials with portland cement causes concretes made with these materials to be more susceptible to poor curing conditions than concretes made with portland cement alone. In particular, low temperatures and insufficient moisture significantly reduce the rate of strength development. The importance of adequate curing conditions for blast furnace slag cements has been recognized in South Africa, where considerable quantities are used, to the point where extended curing times for these cements are specified relative to ambient atmospheric temperatures (13).

USE OF SUPPLEMENTARY CEMENTING MATERIALS WITH WATER-REDUCING ADMIXTURES

Chemical admixtures that disperse and deflocculate cement particles have been used as water-reducing agents in concrete for some years.

In 1971, Lovewell and Hyland concluded from research and literature surveys that (48):

> "...combinations of pozzolans (including fly ash) with water-reducing agents, or with water-reducing-retarder agents, with and without air-entrainment can be used in concrete without creating abnormalities. All such ingredients should be checked for compliance of such mixes with specified quality parameters".

Fulton has concluded from experience in South Africa that water-reducing admixtures influence the behaviour of cements containing slag in the same manner and to the same degree as they influence the behaviour of ordinary portland cements (13).

In recent years there has been considerable interest in the production and use of very high strength concrete >48 MPa at 28 days. This type of concrete, which is a practical example of the combined use of fly ash and water-reducing admixtures, has found application in the columns of high-rise buildings, especially in the Chicago area. In high strength concrete, fly ash functions by providing increased strength at late ages of curing that cannot be achieved through the use of additional portland cement (49).

DIMENSIONAL STABILITY

Data on the dimensional stability of concretes made with supplementary cements are limited. Lohtia et al. have reported the results of studies on shrinkage, creep, and creep recovery of fly ash concretes made by replacing cement with equal weights of fly ash in the range of 0 to 25% (50). From this work they concluded that:

(a) Replacement of 15% cement by fly ash was found to be the optimum value with respect to strength, elasticity, shrinkage, and creep for the fly ash concrete studies.
(b) Creep-time curves for plain and fly ash concretes were similar with creep linearly related to the logarithm of time.
(c) Increase in creep with fly ash content up to 15% was negligible. However, slightly higher creep took place at fly ash contents higher than 15%.

Similarly, it seems that the use of fly ash in practical proportions does not significantly influence the drying shrinkage of concrete (31,48).

Studies on blast furnace slag concretes suggest that these show slightly more creep and drying shrinkage than comparable portland cement concretes. However, as Fulton notes, the measured increased in creep may not be due to real differences in cement type but could be attributed to the characteristically slower rate of strength development in cements containing slags (13).

THE EFFECTS OF SUPPLEMENTARY CEMENTING MATERIALS ON THE DURABILITY OF CONCRETE

FREEZE-THAW DURABILITY

Cycles of freezing and thawing are extremely destructive to concrete that is not specifically proportioned and carefully enough placed to withstand such conditions.

The resistance of concretes containing supplementary cementing materials to freeze-thaw and salt-scaling action has been a highly controversial subject. Claims of improved resistance have been balanced by claims of poorer resistance. It is now generally accepted that air-entrainment renders concrete frost-resistant. It is probable that many of the generalized statements made with respect to the effects of freeze-thaw action on blended cement concretes have not taken sufficient account of the state of air-entrainment of the concrete studied.

Larson (51), presenting work on the use of fly ash in air-entrained concrete and reviewing the work of other investigators (52-57), concluded that the primary effect of fly ash was upon air-entraining agent demand and that it has no apparent ill effects on the air voids in hardened concrete.

In a study of six Type IP blended cements, Perenchio and Klieger found that air-entraining agent requirements were higher in every case for the Type IP cements than for comparable Type I cements (58). Increases ranged from 15 to 210%.

In a similar study of Type IS cements made by Klieger and Isberner, it is apparent from their data that concretes made with these cements also required increased dosages of air-entraining agents when compared with control mixes (59). This point was not emphasized by the authors. As free carbon cannot be held responsible in the case of Type IS cements, it would seem justifiable to examine further whether there is some other factor influencing the activity of air-entraining agents in concretes containing supplementary or blended cements.

Klieger and Isberner reported that the Type IS concretes were found to be as resistant to freezing and thawing but not as resistant to laboratory deicer scaling tests as the comparable air-entrained concretes made with Type I cement (59). The scaling effects, however, were not noted in specimens subjected to outdoor exposure. As with fly-ash concretes, it was found that the air-void systems of the hardened Type IS concretes were similar to those of Type I concretes.

CHEMICAL RESISTANCE OF CONCRETE

All the cementititous hydrates and some of the aggregates from which concretes are made are subject to chemical attack by solutions of sulphates, chlorides, acids, organic agents and even by pure water alone.

The mechanism of deterioration of hydrated portland cement in natural waters is generally one of two types:

(i) leaching processes in which constituents of the hardened cement paste are dissolved and removed by water; such leaching may be observed in concretes exposed to soft water or dilute acids;

(ii) expansion resulting from the formation of insoluble compounds by reaction between the hardened cement paste and ions in the natural water; sulphate attack is the most familiar example of this type of deterioration.

Although in both cases some surface deterioration takes place, serious attack is more often caused by penetration of aggressive water into concrete. The rate of deterioration is therefore determined in part by the chemical processes, and in part by the permeability of the concrete.

Use of a supplementary cementing material as a partial replacement for portland cement, has an indirect influence on both the chemical composition and the physical state of the binder phase. At early ages it serves only as an inert component and is therefore similar in effect to a reduction in cement content. At later ages it contributes to the formation of cementitious components but, as Kovacs (27) has shown for fly ash and as Nurse

(12) has pointed out for slag, it does so in a manner which changes the relative proportions of the usual hydrate materials. In particular, supplementary cementing materials influence the amounts of $Ca(OH)_2$ formed on hydration. For example, in the case of pozzolans, some of the calcium hydroxide is converted to less reactive calcium silicates and aluminates through the pozzolanic reaction. It is generally considered that in concrete this process leads to long-term gains in watertightness, strength and resistance to aggressive environments.

Except for general recognition of this final point, there seems to have been little consideration given in the research literature to the role played by supplementary cementing materials in changing the chemical balance of the cementitious components of concrete, either as a factor in concrete durability or in respect to the development of test methods.

A number of investigations have been made of the influence of fly ash on the relative permeability of concretes. Davis has considered the permeability of concrete pipes containing fly ash substituted for cement in amounts of 30 and 50% (60). Permeability tests were made at ages of 28 days and 6 months. The results of these tests are shown in Table 5.

It is clear from these data that the permeability of the concrete was directly related to the quantity of hydrated cementitious material at any given time. After curing for 28 days, at which time little pozzolanic activity would have occurred, the fly ash concretes were more permeable than the control concretes. At 6 months this was reversed. Considerable imperviousness had developed, presumably due to the pozzolanic influence of fly ash.

Resistance to sulphate attack is one of the most important aspects of the behaviour of concretes made with supplementary cementing materials or blended cements. In 1967, Dikeou reported the results of studies on a total of 30 concretes made from 8 portland cements, 3 portland-fly ash cements and 12 fly ashes (61). From this work it was concluded that all of the fly ashes tested showed greatly improved sulphate resistance.

Kalousek, Porter and Benton reported studies on the requirements of concrete for long-term service when exposed to sulphate (62). From this work they too concluded that fly ash improved sulphate resistance.

The fly ash samples examined by Dikeou and those examined by Kalousek et al. all originated from bituminous coals. In 1976, Dunstan reported the results of experiments on a total of 13 concrete mixes made using fly ashes from lignite or sub-bituminous coal sources (63). On the basis of this work he concluded that the lignite and sub-bituminous fly ash concrete general exhibited reduced resistance to sulphate attack.

Table 5 - Relative permeability of concretes with and without fly ash*

Fly ash			Relative permeability	
Type	Per cent by weight	W/(C+F)** by wt	28 days	6 months
No fly ash	-	0.75	100	26
Chicago fly ash	30	0.70	220	5
	50	0.65	1410	2
Cleveland fly ash	30	0.70	320	5
	50	0.69	1880	7

*From reference (60).

$$**W/(C+F) = \frac{\text{water}}{\text{cement + fly ash}}$$

Permeability data for slag concretes seem to be absent from the literature although there is ample evidence to indicate that slag concretes show good durability to aggressive solutions.

Schröder reviewed recent literature on the durability of slag concretes and concluded that the vast majority of laboratory studies and all the long-term studies confirmed that cements containing slag imparted better resistance to sulphate attack, chloride attack, acid-water leaching and sea-water attack than did ordinary portland cements (11). Schröder concluded, that for the best results, portland-blast furnace slag cements with more than 70% of slag component are required.

ALKALI-AGGREGATE INTERACTIONS

Control or suppression of reactions between cement alkalies and the soluble silica in some aggregates is an established property of many pozzolans and fly ashes and has also been shown to be a property of portland-blast furnace slag cements (31,64,65). The related, though dissimilar, alkali-carbonate reactions on the other hand have been shown to be relatively unaffected by pozzolans (66). Whether or not blast furnace slags might control alkali-carbonate reactions seems not to have been researched.

CORROSION OF REINFORCEMENT

In 1950 the question was raised as to whether there was a possibility of corrosion of reinforcing steel in fly ash concrete by the sulphur-containing components of fly ash (67). According to Nurse, similar statements have been made concerning blast furnace slag (12).

Gilliand noted that most sulphur in fly ash is present as sulphate and therefore would have an effect similar to the sulphate components in portland cement (68). Further, he pointed out that corrosion of steel is greatly affected by pH and that at the high pH prevailing in concrete, corrosion rates would be expected to be slow. Reported research has shown that fly ash concrete does not decrease the corrosion protection of steel reinforcing when compared with normal concrete (69,70). One recent study by Larsen et al. has found that corrosion protection is increased by the inclusion of fly ash in concrete (71,72). Fulton cites unpublished work by Zietsman in which it was concluded that portland-blast furnace cement used in concrete with not less than 38 mm (1.5 in.) cover offers better protection against corrosion than ordinary portland cement (13). Everett and Gutt reported on studies of steel in concrete with blast furnace slag aggregates that whereas theoretically the sulphide content of the slag may influence steel corrosion, in practice negligible corrosion was observed at low depths of cover (73). As the chemical processes of corrosion would be the same if slag were used as cement rather than as aggregate it seems reasonable to assume that these conclusions should apply to slag as a supplementary cementing material. An extensive discussion of the chemical processes relating to blast furnace slag and steel corrosion has been presented by Nurse (12).

CONCLUSIONS

The use of supplementary cementing materials in concrete has a number of advantages. In particular, costs and energy use are reduced. Concrete which develops low permeability and good durability can be produced if care if taken in the selection of materials and in proportioning, preparing and placing the concrete.

However, the use of supplementary cementing materials is not without some inconveniences. Either at the job site or at the cement plant extra materials will have to be stored, handled and their quality controlled. Unlike portland cement, quality control methods are as yet rather ill defined and in the case of industrial byproducts such as slags and fly ashes, are difficult to apply.

Unless rational proportioning methods are used, replacement of portland cement by a supplementary cementing material will cause the resulting concrete to develop strength at a slower than normal rate. This, combined with the sensitivity of supplementary cementing materials to curing at low temperatures, will lead to problems in placing concrete during cold weather.

The current lack of fundamental understanding of the hydraulicity of supplementary cementing materials means that the available performance standards are not completely adequate. More investigations of supplementary cementing materials and the development of more relevant standards are a most urgent need if they are going to contribute their full potential as concrete materials.

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