studies, made using radiocaesium /3/ confirm that this mechanism is one of sorption, at least during the initial stages of reaction. This alkali removal leads to a lowering of the pH of the solution, relative to the control.

Experiments designed to demonstrate the effect of less-reactive pozzolans at "normal" temperatures will clearly have to extend over periods longer than 90 d, and probably over several years, in order to determine what, if any chemical control these materials exert on the pore-fluid chemistry. Elevated temperatures may, within limits, be useful to accelerate reaction thereby compressing the time scale required to assess the effect of specific additives.

These preliminary experiments are, it is felt, instructive, because not only do they give some indication of how the more reactive materials behave, but they also give insight to the chemical nature of the alkaline pore fluid. Both Na and K evidently contribute equally to the alkalinity; thus a "fully ionized" model is appropriate to describe the chemical state of the major components at least up to ionic strengths of 0.2 M. Further work with a high alkali cement would be desirable to determine whether this simple description extends to pore fluids of still higher ionic strength in which, moreover, $A\ell$ may be increasingly soluble.

We also find these prelinary studies helpful to indicate how an internal 'alkali balance' can be constructed using experimentally - attainable data. The objective of the alkali balance model will be to explain the partition of alkali between unreacted constituents (clinker, pozzolan), aqueous phase, cement hydration products and a potentially reactive aggregate. Much of the oral presentation will centre about the development of this 'alkali balance' model, its data input and its assumptions.

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THE POZZOLANIC BEHAVIOUR OF FLY ASH IN BLENDED PORTLAND-FLY ASH CEMENTS

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SUMMARY

This discussion concerns some adventitiously occurring variations in the physical and chemical composition of fly ashes which are derived from different coals and which receive different preparative and combustion treatments.

In addition some difficulties encountered in producing and controlling the performance characteristics of blended cements are mentioned briefly along with some problems which may occur in concrete when blended cements are substituted for straight portland cements.

Although fly ash additions may improve some properties of concrete and reduce the magnitude of some problems, they should not be regarded as an assured universal cure-all for all the defects of portland cement concrete.

INTRODUCTION

The general upward trend in electricity demand and in mining and industrial activities throughout the world has accentuated the need for the effective disposal of increasingly large quantities of waste materials such as mine tailings, washery residues, furnace slags, fly ashes, alumina refinery red muds etc. All of these waste products have potential uses. Economic considerations will of course determine the extent of their utilization and such factors as an assured supply of suitable quality material, its processing cost, its proximity to processing plants and markets and the market acceptance of waste products must be evaluated against the costs of alternate methods of transport and disposal and the availability of dumping sites. The imposition of increasingly restrictive environmental protection limitations on waste disposal will inevitably promote the utilization of such materials.

The future trend towards the increased use of pulverized coal in place of oil for electricity generation will accentuate certain operational problems in the production, handling, combustion and safe storage of pulverized solid fuel simultaneously with the need to handle and dispose of increasingly large quantities of fly ash. At its power station source fly ash has a negative value since it must be handled and transported to a dumpsite. Consequently, the use of fly ash as a portland cement replacement, especially in pre-mixed concrete, is becoming increasingly prevalent. Fly ash may be dispensed directly into the mixer as a separate component of the concrete mix or it may be interground with portland clinker and gypsum to produce a blended portland-fly ash cement which is somewhat comparable to other types of blended cements such as portland-pozzolan and portland-granulated blast furnace slag cements.

The present paper therefore discusses the desirable properties and preferred quality of fly ash and the production and performance of blended portland-fly ash cements and blended cement concretes under normal working conditions. In addition the mechanism of fly ash reaction and the behaviour of fly ash reaction products are discussed together with some of their effects on the properties and performances of concrete.

PROPERTIES AND QUALITY OF FLY ASH

Fly ashes possess chemical and physical properties which are largely influenced by the characteristics of the raw coal ash. Inorganic residues which occur naturally as lenses or narrow bands in coal can have variable chemical and mineralogical compositions. The physical state of ash inclusions is first modified by the preparatory treatment of raw coal and secondly to a somewhat

smaller extent by the fracturing of ash particles and agglomerates when blended and interground with clinker and gypsum. The chemical and mineralogical compositions of fly ash may be modified during combustion and its physical condition affected by particle size segregation in different sections of the precipitator system. All these effects must be assessed and ash quality properly evaluated and controlled to ensure the production of a consistent quality blended cement. If defects in fly ash quality are not recognized and remain uncorrected erratic concrete performances and, in extreme cases, unexpected concrete problems may manifest themselves.

Although the chemical compositions of fly ashes may vary widely, they consist largely of silica, iron oxide and aluminium oxide with smaller amounts of calcium and magnesium oxides, alkalis (sodium and potassium oxides) and trace amounts of many other elements. The mineralogical composition of the raw ash affects its behaviour and compositional changes during combustion. A raw ash consisting largely of free silica (quartz) will undergo scant change with the possible formation of some cristobalite while a raw ash consisting largely of shale of clay-like hydrated alkali-iron-aluminium silicates would undergo extensive changes during combustion. These changes involve loss of combined water and the formation of siliceous glasses which, under moist conditions, can react with additional alkalis and calcium hydroxide to form alkali-lime silicate compounts.

The physical characteristics of fly ash should be assessed concomitantly with its chemical properties. Significant physical characteristics are particle shape and particle size distribution. Fly ashes derived from different coals may consist of widely differing particles. On the one hand fly ash may consist of relatively coarse, angular, quartz particles which will neither react with alkalis and calcium hydroxide nor improve concrete workability significantly, while on the other hand it may consist of fine, rounded, glassy silicate particles, which react readily with alkalis and calcium hydroxide and improve concrete workability significantly. The particle size distribution of fly ash depends basically on the mode of occurrence and especially the thickness of ash lenses in the raw coal, the particle size distribution of the pulverized coal and, after combustion, the efficiency of precipitating and handling ash. Since grinding processes do not produce fine, uniformly-sized particles, it can be assumed that ash has a variable particle size distribution which will be roughly comparable to that of the pulverized coal. Considerable significance thus attaches to the comminution process used for producing pulverized coal. During combustion rapid evolution of combined water in the incombustible compounds may cause shattering and consequent reduction in the size of ash particles.

The efficiency and control of post-combustion precipitation affects both the quality and uniformity in respect to the fineness of fly ash. Subsequent handling and intergrinding with portland clinker and gypsum breaks up weakly agglomerated fly ash particles but does not fracture significant amounts of fly ash unless the individual particles are very fragile. Various anamalous conditions may develop during combustion and lead to excessively strong ash particle agglomeration, deposition of ash together with condensing salts in cooler areas of precipitators, flues and ducts, particle bloating which produces very light hollow spheres and unduly large accummulations of unburnt carbon. All of these anomalies affect ash properties adversely and in turn may also affect the performance of blended cements adversely.

The causes of fly ash variability may therefore be summarized as,

(1) fly ashes produced from different coals may have different compositions,

(2) variations in the combustion of coal may modify ash mineralogical composition and physical condition,

(3) variations in coal grinding may produce variations in the particle size distribution of fly ash,

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(4) the zone of the precipitating system from which ash is extracted, and

(5) the presence of volatilized compounds which may condense in the precipitated ash.

During storage at atmospheric temperatures for relatively short periods of time fly ash is unlikely to undergo any significant deteriorating changes. Storage at elevated temperatures, however, and very slow rates of cooling may promote mineral inversion and devitrification of silicate glasses. Any changes observed in the performance of concrete containing an aged fly ash or blended cement must therefore be ascribed to some other cause rather than to fly ash deterioration. Some malfunctions of blended cement concretes and their causes will be mentioned briefly later in this paper.

TREATMENT AND UTILIZATION OF FLY ASH

Large amounts of fly ash are used as mineral admixtures in concrete. Fly ash may be added in desired amounts as a separate ingredient to the concrete mix at the mixer and consequently undergoes no physical change other than particle agglomerate breakdown during the mixing process. This procedure allows both the source of supply of fly ash and the admixture quantity used in concrete to be varied as required. Uniform blending of portland cement and fly ash, however, which must be achieved during the mixing time, will remain an unknown variable in this process.

In the case of blended portland-fly ash cements, fly ash is interground with portland clinker and gypsum. In the mill agglomerated fly ash particles are readily broken down and a relatively uniform distribution of the different particles can be achieved. However, the fineness of fly ash will be increased by small but unknown amounts by additional particle fracture. Unless extensive concrol testing of materials is carried out, it is impossible to maintain effective control of fineness and performance characteristics of blended cements. Some problems concerned with cement malfunctions caused by lack of fineness control will be mentioned later in this paper.

PERFORMANCE IN CONCRETE

Incorporation of fly ash in concrete confers both advantages and disadvantages. The major advantage is an economic one since low cost fly ash replaces more costly portland cement. There are, however, very clear limits to the amount of portland cement which can be replaced by fly ash without inducing unacceptably deficient properties in concrete. Technically fine rounded fly ash particles increase concrete workability, decrease mixing water and concomitantly increase compaction and ultimate strength. Moreover, under appropriate conditions fly ash behaves similarly to granulated blast furnace slag by reducing heat evolution and early strength development.

Unwanted problems which may cause some variability in concrete properties involve (a) angular fly ash particle, (b) the presence of large amounts of alkalis or sulphate, (c) light, bloated (low density) particles which segregate readily and may be difficult to wet, (d) excessive amounts of unburnt carbon which may absorb large amounts of surface active admixtures and (e) coarse fly ash particles which continue reacting with alkalis for a long time and behave as reactive aggregate particles. In addition coarse and/or angular fly ash particles, especially when the portland cement replacemenet is large, can act in concert with a number of other factors to reduce the long term durability of some concretes when exposed to dry-wet cycling conditions. This is one of the possible causes, indicated earlier in this paper, of the seemingly apparent deterioration in the quality of fly ash as it ages. In this instance, however, concrete deterioration is caused by the continued hydration of coarse clinker particles and their contained uncombined lime which is present on occasions in most clinker, and fly ash merely acts passively by promoting clinker hydration.

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Some of the defective performances of portland fly ash cement concretes are induced by unsatisfactory cement or concrete production techniques. Adding fly ash at the mixer makes effective blending difficult and increases the probability that the distributions or fly ash and clinker particles will be non-uniform. Interground fly ash - portland clinker blends are more uniform but may exhibit other aberrations. Since cement mill control is generally maintained by monitoring the output fineness, variations in the fineness of the fly ash can induce wide variations in the particle size distribution of the clinker fraction. Variability in the particle size distributions of fly ash and portland clinker may cause low early concrete strengths and very slow setting times both of which can be greatly accentuated if the concrete also contains added water-reducing and set retarding admixture.

The opposite effect namely extremely rapid strength gain and excessively high heat evolution, has been observed in some blended cement concretes even though the opposite requirements, low rates of strength gain and heat evolution, were specified. In these latter instances the concern of cement producers, that the concrete would bevelop insufficient early strength, impeled them to grind the cement (mainly the portland clinker-gypsum fraction) to high early strength finenesses (approximately 4500 cm^2/g) and thus completely obviated the specified intentions with somewhat disastrous consequences for the concrete.

These brief comments should suffice to indicate the highly significant function of particle size distribution in modifying the properties of cements and the performance characteristics of concretes and further to emphasize the need to maintain effective control of the particle size distribution of cement during manufacture and at its end use in concrete.

MECHANISM OF REACTION OF FLY ASH IN CONRETE

The variable and random arrangement of fly ash and clinker particles, which evolves during the mixing process and becomes immutably fixed when the concrete is finally placed and compacted, is highly significant for understanding the various chemical reactions and physical changes that occur as well as the behaviour of fly ash in cement and concrete. Ideally in a blended portland-fly ash cement paste each fly ash particle should be completely surrounded and in contact with portland clinker particles. In a theoretical open-packed mass of equal sized shperes, each sphere will be in contact with six others, while in a similar close-packed mass, each sphere will be in contact with twelve other spheres. When such spheres are randomly close-packed with minimum boundary interference it is usually found that some 8-9 spheres are in contact with any specified sphere and that disconfirmities in packing produce a number of significantly larger voids than those present in an ideal close-packed mass of spheres. The size, frequency and functional effects of these voids on the reactions occurring in and on the properties of blended cement may be increased further by a variety of factors which are always operating in a portland cement-water system.

Ground portland cement particles are chips and plates rather than spheres and consequently when randomly packed produce large amounts of void space with many large individual spaces. Moreover, interparticle attraction forces ensure that the larger clinker particles are invariably completely coated with very fine clinker particles when dry and such coated clinker particles agglomerate rapidly to form large flocs which can envelop fly ash particles when cement is mixed with water. Fly ash particles, which do not possess the rapid flocculating characteristic of clinker particles, may never by ideally dispersed throughout the paste but will displace water in a blended cement paste and therefore increase its fluidity or workability. By reducing mixing water some increase in the density of paste and improvements in strength development can be achieved.

Although the overall density of cement paste is increased by a reduction in mixing water, large open spaces between flocculated clinker particles, at fly ash-clinker contacts and between adjoining fly ash particles will not be eliminated. The presence of these spaces permits the rapid movement of water into the paste which, is exposed to drying and wetting cycles, promotes massive hydration changes in the portland clinker phase. When clinker particles contain large amounts of free (uncombined) lime, and this condition occurs intermittently in most clinkers, but is not detected by usual free lime tests, unduly large, delayed concrete expansion and deterioration will occur. Such deterioration has been ascribed to various causes and, as noted earlier, may explain the strength losses which had been assumed to be due to various causes including loss of reactivity by ageing fly ash. The permeability to water penetration and movement should therefore be considered a most critical factor in determining the long term durability of hardened cement paste and concrete.

Although the measured heat evolved by blended portland-fly ash cement is reduced compared with that of a straight portland cement, at very early ages and for very short times, the rates of clinker hydration and heat evolution of the former may be significantly greater than those of the latter. The reason for this anomaly is clearly the delayed development of the hydration inhibiting process produced by gel coatings on the surfaces of clinker particles. In contact areas with very slow reacting fly ash particles, the gel coating build up on clinker particle surfaces proceeds slowly, but, as the hydration proceeds, the coatings increase in thickness and the rates of clinker hydration and heat evolution decrease.

Fly ash particles which consist of quartz, cristobalite and various siliceous glasses are essentially fine reactive aggregate particles. Components such as cristobalite and siliceous glasses react with solutions of alkalis and calcium hydroxide. Reaction with alkalis produce gels which continue to absorb water, swell and ultimately convert to fluid sols. These gels and sols may undergo further reactions with calcium hydroxide to produce lime-alkali-silica complexes which are associated with relatively small amounts of water and which possess limited swelling and shrinking characteristics. Calcium hudroxide also reacts directly with siliceous fly ash particles at a slower rate than that of alkalis to form limited swelling hydrated lime-silica compounds. These various reaction products may fill unoccupied spaces in the hydrated cement paste and thus contribute to its strength and impermeability. Since fly ash particles are generally fine and since large amounts of free space occur in the hydrated cement adjacent to their surfaces, they are unlikely to cause unduly large concrete expansions. Nevertheless, it is desirable to exclude large fly ash particles in order to maximize strength and impermeability improvements and to minimize the risk of disruptive expansions.

In should be noted that fly ash particles react and their reaction products behave rather differently in concrete from those produced from granulated blast furnace slag particles. The former react with solutions, slowly with calcium hydroxide and more rapidly with alkali solutions whereas the latter undergo autogenous hydration reactions in the presence of small amounts of alkalis or lime which act as catalysts, and their hydrated products may subsequently combine with additional amounts of lime and sulphate. While fly ash particles continue reacting, absorbing water and swelling provided the necessary reaction components, alkalis and water, are available, the products of granulated blast furnace slag particles behave in a way that is comparable to those derived from portland clinker compounds. Hydration ceases at an early age at contact areas between adjacent hydrating clinker particles and between hydrating particles and non-hydrating aggregate, reinforcement and formwork surfaces. The hydration products which may be both gelatinous and crystalline, in these contact areas do not exert expansion forces or cause cement paste and concreting disruption.

Wet curing of blended cement concrete is considered to be necessary to achieve optimum cement behaviour because the hydration reactions of both fly ash and granulated blast furnace slag are relatively slow compared with those of portland clinker compounds. Provided the amount of fly ash admixture is not excessively high, it is most unlikely that the drying shrinkage of blended cement concretes will be significantly greater than those of comparable straight portland cement concretes.

CONCLUDING REMARKS

Fly ash has been and will continue to be used successfully and advantageously as a partial cement replacement in concrete provided certain precautions are taken such as, (a) selection of suitably reactive fly ash, (b) control of fly ash uniformity and quality, (c) control of the fineness of blended cement during its production, (d) effective use of chemical admixtures and, (e) adaptation of constructional practices to the requirements and performances of blended cement in concrete.

The quantity of portland cement that can be replaced by fly ash should be carefully considered. For economic reasons large replacements (approximately 20%) would be considered desirable while for technical reasons it would appear that the replacement quantity should be kept within a 12-15% range. The actual replacement quantity will depend on a wide variety of factors. Increments in fly ash replacement above this suggested level may increase the number of defects in the cement paste. These defects increase the tendency for strength to decline and more importantly could reduce the long term durability of concrete exposed to natural weathering conditions.

Fly ash admixtures can also be used as pozzolanic inhibitors of reactive aggregate expansion. For this purpose fly ash must be readily reacted by alkalis, contain negligible amounts of alkalis, and have a fine particle size (preferably all particles should be 40 microns). Inhibition of aggregate expansion requires a high level (approximately 40%) of portland cement replacement by fly ash. Lesser cement replacements are likely to reduce but not completely inhibit reactive aggregate expansion.

Damage of concrete cylinders with
REACTIVE SAND AND NON-REACTIVE, COARSE AGGREGATES
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The purpose of the present investigation has been to provide an introductory evaluation of a model for estimation of the expansion of concrete when knowing the expansion of the mortar and the amount of non-reactive, coarse aggregates used in the concrete.

The tests were carried out in co-operation with the Danish Engineering Academy, Section of Structural Mechanics, and the Technological Institute, department of Building Technique.

1. BACKGROUND

In 1956 the present Committe on Alkali Reactions in Concrete commenced a series of laboratory experiments with 48 nos. of ordinary concrete bars, size 100 x 100 x 600 mm. These pilot tests did not show convincing relations between the expansion of mortar bars, size 25 x 25 x 125 mm, and the expansion of concrete bars even when the same source of reactive sand was used. As in the case of the mortar bars, the elongation (expansion) measured was used to express the advance of the alkali silica reactions. In the concrete bars commercial crused granite as well as pit aggregates and maritime aggregates were used as coarse aggregates. A three per cent solution of NaCl was added to two of the mixes for the concrete bar tests in order to simulate a maritime environment. This was not the case in the mortar bar tests.

Many hypotheses have been advanced in order to explain the lack of deteriorating expansion and cracking of the concrete bars used for these tests. However, non of the hypotheses have been accepted so far on a basis of new laboratory tests.

2. MIX PROPORTIONS

In the present investigation tests have been carried out involving 10 different concrete mixes using reactive sand and non-reactive coarse aggregates. Furthermore, tests were carried out with two blind mixes, i.e. using non-reactive aggregates, fine as well as coarse. In order to check the accuracy of the measurements two of the mixes were repeated.

The basis of the mix design was a concrete with the following recipe:

Cement	300 kg/m^3
Water	150 "
Fine aggregates	805 "
Coarse aggregates	1150 "

This corresponds to a mortar with the following recipe:

Cement	521 kg/m^3
Water	261 "
Fine aggregates	1399 "
Coarse aggregates	0 "