



SINTEF Building and Infrastructure

Address: NO-7465 Trondheim
NORWAY
Location: Richard Birkelands vei 3
Telephone: +47 73 59 52 24
Fax: +47 73 59 71 36

Enterprise No.: NO 948 007 029 MVA

SINTEF REPORT

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Ternary Blended Cements with Fly Ash and Limestone.
Part I: Activation of Fly Ash

State of the art

AUTHOR(S)

Klaartje De Weerdt

CLIENT(S)

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS, Veidekke ASA and The Research Council of Norway

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ABSTRACT

There is a rising interest in the production of composite cements due to mounting environmental awareness and the diminishing natural resources. In composite cements considerable parts of the clinker is replaced by supplementary cementitious materials. Within two STAR's we will focus on the fly ash and limestone as replacements for part of the clinker.

This first part will mainly focus on the reactivity, activation and reaction products of fly ash. Fly ash is a relatively slow reacting pozzolan. Its reactivity depends on the alkalinity of the cement, the curing temperature, the replacement level and the water-binder ratio.

The reactivity of fly ash can be improved by thermal, chemical or mechanical activation. Thermal activation is based on the fact that higher curing temperature leads a faster increase of the pH, and an increased solubility of the glassy silicate phase of fly ash. Although it might be of interest for prefabrication industry, it is not really an option for every day use on the construction side.

When discussing chemical activation, it is clear that alkalinity place a major role. At room temperature fly ash only starts to react noticeable at a pH higher than 13.3. This level of alkalinity is only reached after one or more days in ordinary Portland cement. By increasing the alkalinity of the cement, the early stage reactivity of fly ash could be boosted. Though care should be taken with regard to the alkali reactivity of the aggregates and the user-friendliness of such high alkaline cement.

The third activation technique, mechanical activation, appears to be one of the more promising technique. One possibility is the extraction of the finer, more reactive particles from the bulk fly ash by air classification. Another method is based on intensive grinding of the fly ash. Cements prepared with a clinker replacement levels up to 25% have shown an improved strength development compared to reference cement.

KEYWORDS	ENGLISH	NORWEGIAN
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GROUP 2	Concrete	Betong
SELECTED BY AUTHOR	Cement	Sement
	Blended	Blandet
	Fly ash	Flygeaske

Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

For more information, see www.sintef.no/coin

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1 Introduction

Due to the rising environmental awareness and diminishing natural resources, there is a growing interest in composite cements in which considerable parts of the clinker are replaced by for example slag, fly ash or limestone. Of particular interest are the ternary cements consisting of clinker and a combination of two of the above named replacement materials. Combining them makes it possible to compensate for their individual disadvantages. In this state of the art we will focus on the combination of fly ash and limestone. High replacement levels of clinker by fly ash result in a decrease the early strength development due to the slow activation of the pozzolanic reaction, whereas fine ground limestone accelerates the early hydration due to its filler effect. Different ways to optimise the reactivity of both fly ash and limestone and some research results on their combination will be discussed. Part I of this state of the art will focus on the reactivity and the reaction products of fly ash in combination with clinker. The same topics will be investigated for limestone in Part II. Subsequently a conclusion will be formed regarding the possible combination of fly ash and limestone in composing a ternary cement.

2 General

Fly ash is a by-product recovered from the exhaust gas produced during the combustion of pulverized coal in thermal power plants. Due to the high temperature reached in the furnace most of the mineral components contained in the coal, melt and form small fused drops. Subsequent fast cooling transforms them partly or entirely into spherical glassy particles. Hence the chemical composition of the resulting fly ash is dependent on the inorganic part of the coal used. Based on the chemical composition, fly ash can be divided into two different categories according to ASTM C 618: Class F fly ash produced by burning anthracite and bituminous coal normally containing less than 10% lime (CaO), and Class C fly ash originating from burning younger lignite or subbituminous coal generally containing more than 20% lime. Therefore Class C fly ash is often referred to as high-calcium fly ash and Class F fly ash as low-calcium fly ash. Class C fly ash exhibits self-cementitious properties, due to its high lime content whereas class F fly ash acts more as a pozzolan meaning that it needs an external source of lime in order to produce C-S-H-like reaction products. In this paper the focus will be on Class F fly ash. Fly ash will refer to Class F fly ash if not stated differently. The chemical composition of fly ash can vary as indicated in Table 1.

Table 1: Analyses of low-lime fly ash (per cent) [Hewlett, 1998].

Country	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	C	LOI ^a
France	51.68	27.01	6.25	1.72	1.88	0.54	4.49			4.70
France	48.10	24.68	6.50	1.41	1.82	0.56	4.06			11.70
Belgium	55.74	24.14	6.02	2.47	2.22			1.04		2.74
Taiwan	48.75	23.21	4.15	3.93	1.00	0.24	1.10			10.39
UK	50.09	28.1	11.7	1.62	1.54	0.28	0.62			1.27
Poland	50.8	23.9	8.6	3.6	2.8	0.8	2.9	0.8		2.9
Denmark	53.98	22.27	11.60	3.95	1.97	2.71	eq.	0.73		2.13
Netherlands	50.46	25.74	6.53	4.32	2.24	2.04	4.43			3.95
Canada	47.0	17.7	25.3	2.1	1.0	0.7	2.3	0.3		2.4
Japan	57.5	26.1	4.0	5.1	1.3	1.50	1.35	0.4		1.6
UK	48.0	38.2	4.5	3.3	1.5	0.3	1.7	0.37		2.3
Japan	53.53	23.55	6.23	5.85	1.60	2.20	1.75		2.14	3.44
USA	52.24	19.01	15.71	4.48	0.89	0.82	2.05	1.34		0.92
Canada	43.8	22.1	16.2	3.5	0.8	4.4	eq.	1.1		5.0
Germany	51.2	29.6	6.8	3.4	1.2	0.6	3.1	0.5		3.3

^aOften includes carbon content as well.

Table 2: Mineral analyses of fly ash (per cent) [Hewlett, 1998].

Fly ash source	Country	Quartz	Mullite	Hematite	Magnetite	Carbon	Glass	Anhydrite
Dunston	UK	4.5	11	2.7	1.4	3.1	77	
Ferrybridge	UK	2.8	6.5	1.6	1.9	1.5	86	
Hams Hall	UK	3.5	10	1.6	1.2	0.6	83	
Rye House	UK	8.5	14	2.1	2.5	2.4	71	
Skelton Grange	UK	4.1	10	2.4	2.6	2.1	79	
Northeast P26	UK	7	28	9	7	4.0	45.0	
Northeast P27	UK	2	9	7	7	3.0	70.0	
EFA	NL	1.8	2.1		0.7		95.4	
LM	NL	5.1	22.8		0.5		71.6	
Lubbenan	D	17.1			10.4	2.7	75.8	11.4
Eophenhain	D	1.4			1.9	3.8	74.3	12.9
Swarze Pumpe	D	2.0			5.7	1.0	74.3	16.9
Vackarode	D	2.0			6.2	2.2	80.2	9.4
Hagenwerder	D	0.3			5.1	6.1	85.1	3.3
Hirshfeld	D	1.8			3.8	5.1	93.6	0.7

In order to be used in concrete, fly ash has to comply with certain requirements. EN 450, describes the European regulations for siliceous fly ash. In order to be classified as a siliceous fly ash the main constituents have to be present in certain proportions: reactive calcium oxide content lower than 10%, reactive silicon content not lower than 25%, and the sum of silicon oxide, aluminium oxide and iron oxide not be less than 70%. The content of detrimental components has to be limited: the alkali content (Na_2O equivalent) lower than 5%, magnesium oxide not greater than 4,0%, LOI of category A (<5%), chloride content not greater than 0,10%, sulphuric anhydrite lower than 3,0%. Besides chemical requirements also physical and other demands can be found in the EN 450 norm.

Glass content of fly ash can vary between 50 and 90%. The remainder primarily consists of crystalline phases. In Class F fly ash only a few crystalline phases are observed: quartz, mullite, hematite and magnetite (Table 2).

The fly ash glass is an aluminosilicate glass containing glass modifying elements such as Ca, Na, K, Mg and Fe. The content of glass phase in fly ash depends on the chemical composition and the combustion procedure of the coal. Zones with different chemical composition are observed in the glass phase. The “interior glass” contains more crystalline phases (mullite, hematite, quartz) and fewer trace elements than the “exterior glass”. This can be explained either by migration of trace elements to the surface or by deposition on the surface during cooling [Pietersen, 1993]. Fly ash particles are typically spherical particles with smooth and glassy surfaces. The spherical particles can either be solid or hollow (cenospheres). Some of the hollow spheres are filled with smaller spheres, they are called plerospheres. Occasionally, incompletely melted particles with irregular shapes can be found [Bensted and Barnes, 2002].

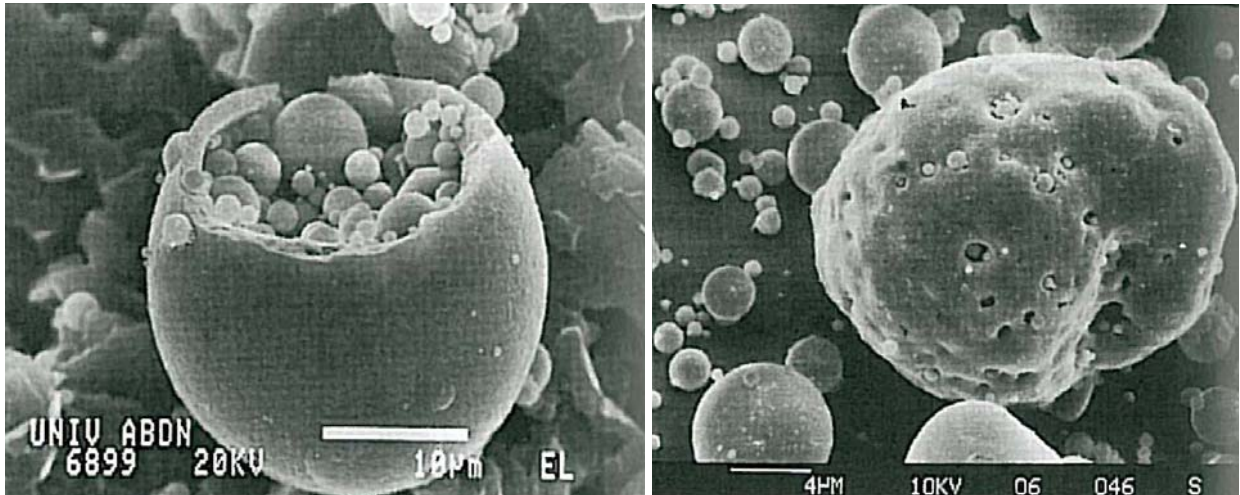


Fig. 1: left: plerosphere; right: incomplete melted particle

The particles size distribution of fly ash correlates strongly with the one of the pulverized coal particles size [Pietersen, 1993]. In practice the particle diameters of fly ash range from 1 to 150 micrometer. The surface area is extremely variable, ranging from 200m²/kg to 800m²/kg (Blaine) but sometimes higher and lower values occur [Hewlett, 1998].

3 Reactivity

In the very early stage of cement hydration, fly ash particles serve as precipitation and nucleation sites for Ca(OH)₂ and C-S-H gel which result from the cement hydration [Pietersen, 1993]. The fly ash, or in fact fly ash glass, itself will only react noticeably after a so-called “incubation period”, the length of which is believed to depend mainly on the alkalinity of the pore water [Fraay et al., 1989,1990]. The pH of the pore water should at least be 13.3 (at 20°C) to observe clear signs of activation. Calcium hydroxide saturation provides a pH of approximately 12.5. This means that supplementary alkalis are required to obtain a sufficiently high pore water pH. Fraay et al. (1989) measured the effect of replacing part of the Portland cement with sand flour or fly ash, on the pH development in the pore water (Fig. 2). The paste prepared with sand flour shows the dilution effect due to constant water/(cement+sand) ratio, which results in a lower OH⁻ concentration than the reference paste. The fly ash replacement resulted in a higher pH than the paste with sand. Initially it appears that the fly ash contributes to the pore water alkalinity, due to the potassium and sodium ions which dissolve from the surface of the fly ash particles. Later the difference between the fly ash and the quartz containing pastes diminishes as most of the alkalis are part of the glass phase of the fly ash, and they will only be released when the fly ash starts to dissolve.

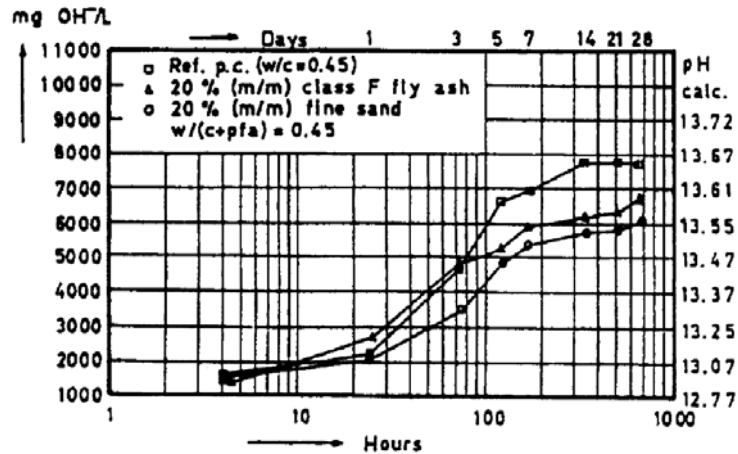


Fig. 2: Development of OH⁻ concentration in the pore water of Portland cement paste with fly ash and fine quartz sand. Temperature 20°C w/(c+FA/Q)=0,45 [Fraay,1989]

From these results it can be concluded that the pozzolanic reaction of the fly ash in the Portland cement paste investigated at 20°C can only start after one or more weeks, because only then the alkalinity of the pore water is high enough to dissolve the fly ash [Fraay et al., 1989].

Justnes et al. (1998) monitored the pozzolanic reaction of fly ash by measuring the chemical shrinkage. The total chemical shrinkage of fly ash was crudely estimated to 10.0 ml/100 g reacted fly ash, compared to 6.3 ml/100 g Portland cement. From Fig. 3 it can be seen that the rate of total chemical shrinkage increased with increasing pH for mixtures of fly ash with lime, indicating that the dissolution of the glassy aluminosilicate phase by alkalis are rate determining for the pozzolanic reaction.

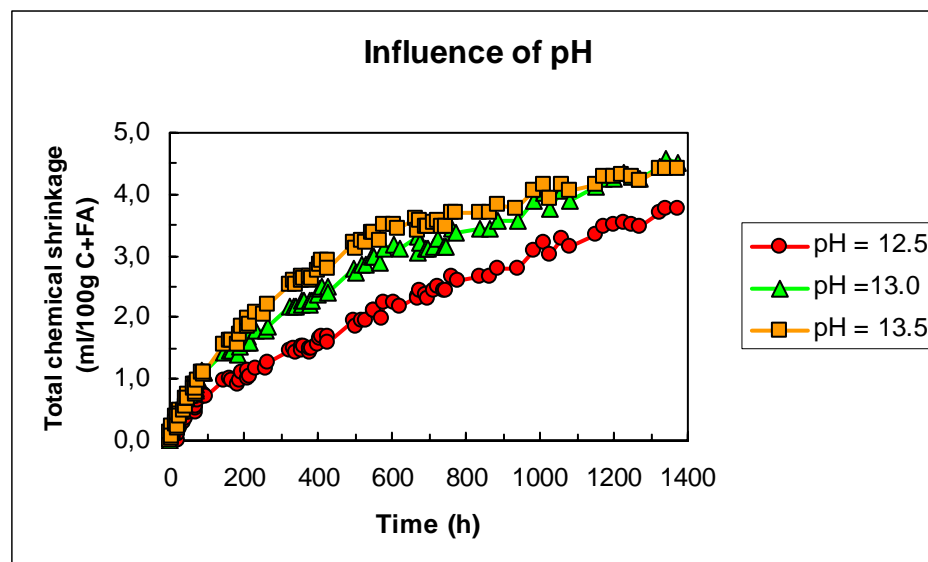


Fig. 3: Total chemical shrinkage of a fly ash-lime paste in function of the time of hydration for pH values varying from 12.5 to 13.5 [Justnes et al., 1998].

Therefore, the time required to activate the pozzolanic reaction of fly ash depends upon the cement type used. Cements with lower alkali content will have a delayed reactivity of fly ash [Pietersen, 1993].

The water/binder ratio also plays an important role as it greatly influences the pore solutions alkalinity [Pietersen, 1993 and Fraay et al., 1989]. Experiments conducted by Kobayakawa et al. (2003) on the other hand, show that the reaction ratio of the fly ash cured at 20°C increases at later age (>60days) with increasing water/powder ratio (Fig. 4).

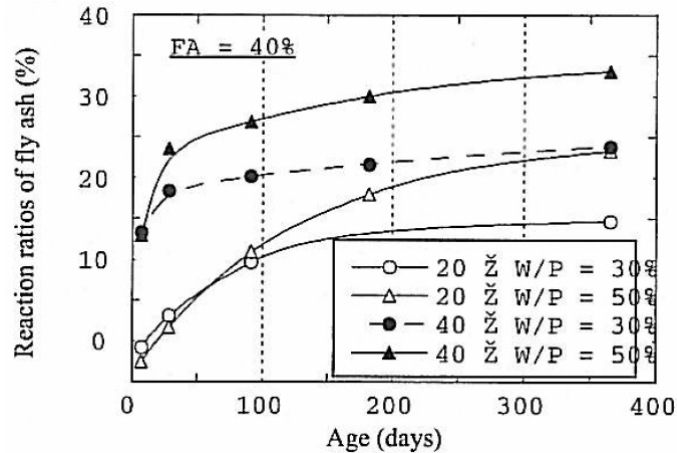


Fig. 4: Effect of curing temperature (\bar{Z} =°C) and water-powder ratio (W/P) on pozzolanic reaction ratio of fly ash in cement paste determined from the insoluble residue [Kobayakawa et al., 2003].

The reactivity of fly ash increases with increasing curing temperature. This can be mainly attributed to two facts: increased temperature increases the solubility of the glass phase and secondly it increases the rate of pH development [Fraay et al., 1989, 1990] (see Fig. 4 and Fig. 5).

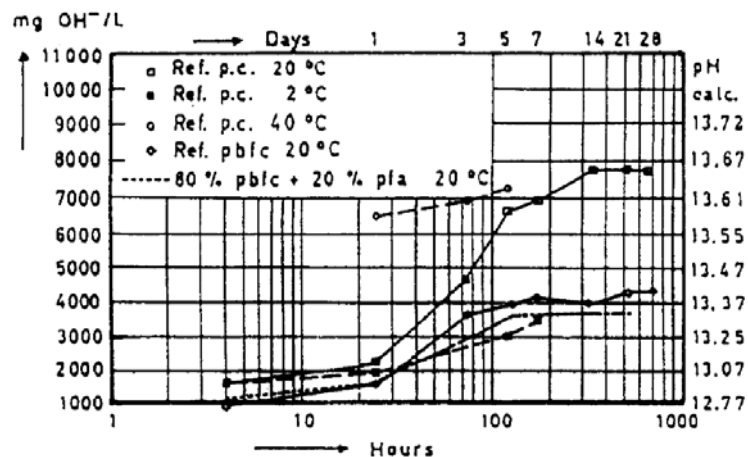


Fig. 5: The OH⁻ concentration as a function of the type of temperature (p.c. = Portland cement, pbfc = Portland blast furnace slag cement, pfa = class F fly ash, w/(pc+pfa)=0,45) [Fraay et al., 1989].

It is difficult to discuss the reactivity of fly ash since fly ash particles from the same batch are intrinsically heterogeneous and react differently. This demonstrated by a SEM micrograph (Fig. 6) showing particles in various stages of reaction in the same hydrated cement paste sample [Bensted and Barnes, 2002]. It should be noted that besides the fineness, the surface conditions also seem to play an important role in the reactivity of fly ash as smaller particles have been observed to stay unreacted whereas larger ones had start to react [Hewlett, 1998].

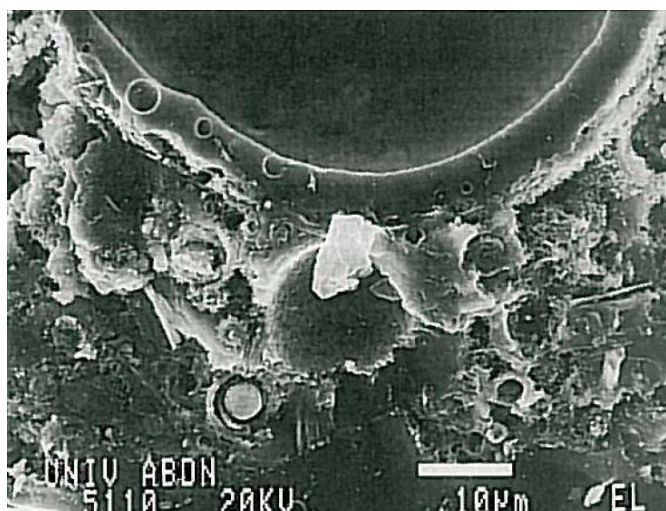


Fig. 6: SEM micrograph showing a large unreacted and smaller completely reacted sphere in a 6-year-old FA/OPC paste [Bensted and Barnes, 2002].

The pozzolanic reaction of fly ash in cement continues in the course of time and often less than half of the fly ash particles react within a year [Pietersen, 1993].

Canham et al. (1987) showed that when fly ash replaces part of the clinker the pH of the pore solution decreases after some months compared to the reference without fly ash (this besides the dilution effects due to constant water/(cement+fly ash) ratio). Taking into account the reduction in free water, this confirms that fly ash favours alkali incorporation into the hydration phases. The decrease in alkalinity of the pore water will result in a decreased reaction rate of the fly ash over time. This effect will even be amplified by the reduced permeability of the matrix.

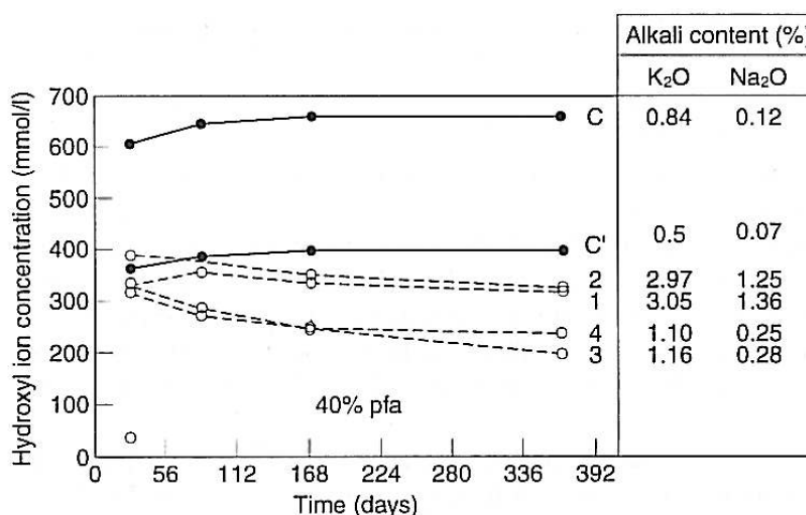


Fig. 7: OH⁻ ion concentration in pore solutions of Portland cement paste (C) and blended pastes containing 40% of various fly ashes (1,2,3,4) or 40% hypothetical cement of zero alkali content (C'). The alkali content of the Portland cement and the four fly ashes is indicated. [Canham et al., 1987]

Many models have been proposed to describe the pozzolanic reaction of the fly ash glass. According to Pietersen (1993), the pozzolanic reaction of the fly ash glass is initiated by a chemical attack of the SiO₂ or SiO₂+Al₂O₃ glass by OH⁻ ions. Subsequently silicon or other ions will be detached from the glass framework. They will either go into solution or remain in situ. The resulting negative surface charge of the glass has to be balanced either by H⁺ or by potassium or sodium cations from the pore solution. As a result an amorphous alkali rich phase is formed. This

phase is unstable in an environment with an abundant supply of Ca^{2+} ions and will transform into a C-S-H-like phase.

According to Takemoto (1980), it is the dissolution of the alkalis from the outer layer of the glass that triggers the pozzolanic reaction by transforming the glass phase into a Si and Al rich amorphous layer and increasing the pH locally. Ca^{2+} ions will then adsorb on the negatively charged surface layer and result in the formation of a C-S-H gel containing aluminium.

Sakai et al. (2005) compared the reactivity of two fly ashes with different glass contents, respectively 38.2% and 76.6%. The glass content was calculated from the determined crystal amount (mullite, hematite, magnetite, CaSO_4 and loss on ignition). At first the fly ash with the highest glass content exhibited a higher hydration ratio. But after one year, the difference in hydration ratio became negligible. The glass content seems to play an important role up to approximately one year after that the hydration rate of both the fly ash batches was roughly the same.

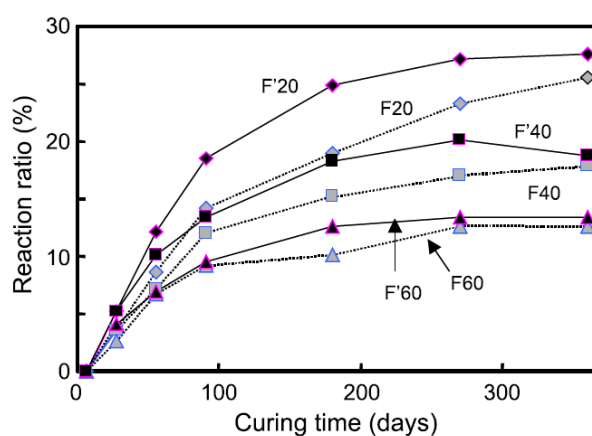


Fig. 8: Reaction ratio of fly ash; (◊) indicates the variant with the high glass content; 20, 40 or 60 indicates the amount of OPC which is replaced by the fly ash [Sakai et al., 2005].

4 Activation

4.1 Mechanical activation and classification

Fly ash can be pre-processed by mechanical activation and classification.

Mechanical activation or intensive grinding improves the reactivity of the fly ash through size reduction and alternation in the physico-chemical characteristics of fly ash. During the intensive grinding process, bulk changes, e.g. creation of structural defects, structural rearrangements and phase transformation, and creation of new surface and surface modification significantly alter the reactivity of the fly ash. Classification on the other hand results in separation of more reactive finer fraction of fly ash and increase in glass content. In this chapter some research results on grinding and classification will be presented.

Bouzoubaâ et al. (1997,1998) and Payá et al. (1995a,1996,1997) studied the influence of the time of grinding on the properties fly ash. The former ground the blended cement for 2, 4, 6, 8 and 10 hours with a laboratory ceramic grinding mill and the later ground for 10, 20, 30, 40 and 60 min with a laboratory ball mill. The results of fineness in function of grinding time are shown in Fig. 9. It can be seen that the decrease in particle size, increase in Blaine and increase in specific gravity was most significant at the beginning of the grinding and that further grinding was less effective. This is due to the presence of cenospheres, plerospheres and irregular particles in the original fly ash which were crushed during the first stage of the grinding. Grinding strongly affected the morphology and shape of the fly ash particles.

Both Bouzoubaâ et al. (1998) and Payá et al. (1997) observed an increase in the reactivity of fly ash as it was ground (i.e. crushing of hollow spheres increases available glassy wall surface to alkaline water). Fig. 10 shows an example of the difference in compressive strength between raw and ground fly ash at a 55% replacement level. Furthermore it seems to be beneficial to grind the clinker, gypsum and fly ash together instead of separately.

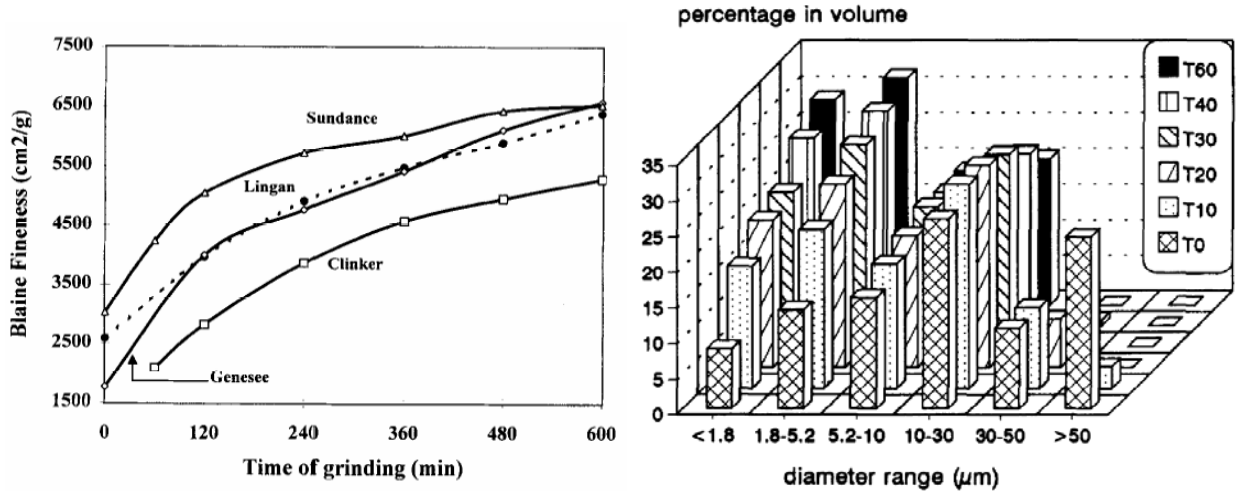


Fig. 9: Left: Comparison of the Blaine fineness as a function of grinding time for two different kinds of fly ash and clinker [Bouzoubaâ et al., 1997]. Right: Evolution of granulometric distribution of fly ash with grinding time (0-60min) [Payá et al., 1995]

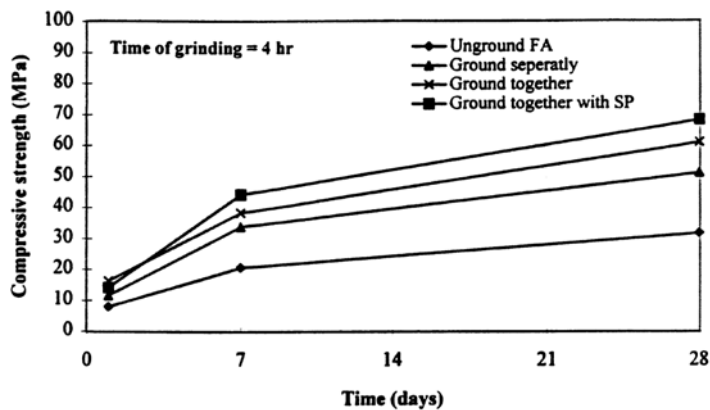


Fig. 10: Comparison of different modes of grinding (4hours) on the compressive strength of mortars with 55% fly ash replacement [Bouzoubaâ et al., 1998].

Kumar et al. (2006, 2007) pre-processed the fly ash by grinding it in a vibratory or an attrition mill and by classification. Fig. 11 shows micrographs of various types of fly ash tested, namely raw (RFA), vibratory milled (VMFA), attrition milled (AMFA) and jet mille classified (CFA). Typical median particle size of RFA, VMFA, AMFA and CFA obtained were 36, 5, 4.3 and 2.8 µm respectively.

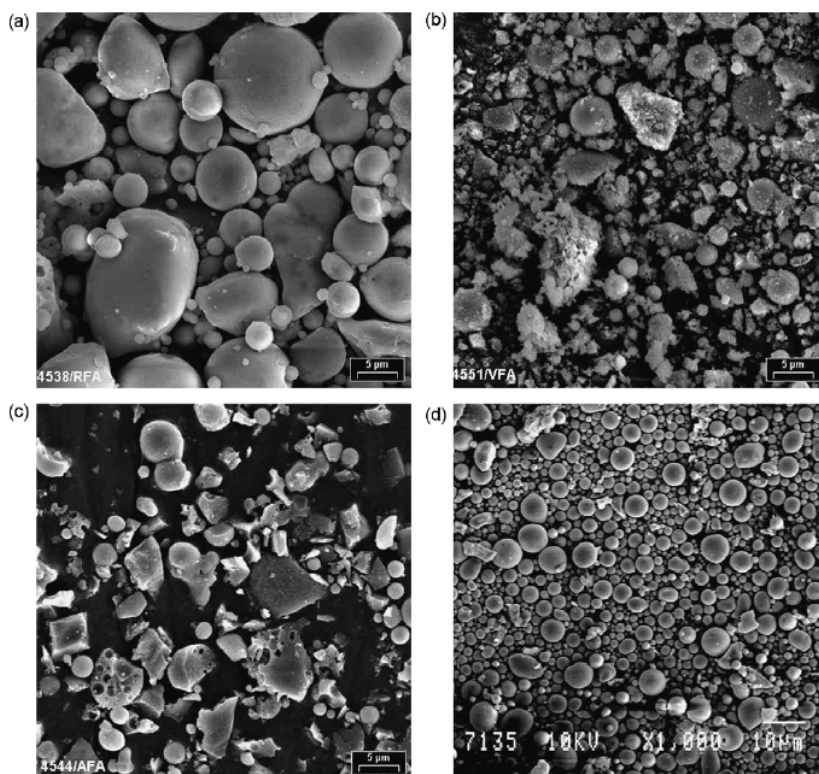


Fig. 11: SEM micrograph showing morphology of fly ash : (a) raw fly ash (RFA), (b) mechanically activated fly ash using vibratory mill (VMFA), (c) mechanically activated fly ash using attrition mill (AMFA), and (d) classified fly ash (CFA) [Kumar et al. 2007].

The exact mechanism of the strength development in Portland cement containing mechanically activated fly ash is not completely understood. X-ray powder diffraction studies did not indicate any susceptible change in fly ash due to mechanical activation. However, FTIR studies clearly showed changes in the intensity of IR peaks corresponding to Si-O-Si bending (460cm^{-1}), Si-O-Si symmetric stretching (798cm^{-1}) and T-O-Si (T=Si,Al) asymmetric stretching (913 , 1090 and 1160 cm^{-1}) indicating structural rearrangement during grinding (Fig. 12).

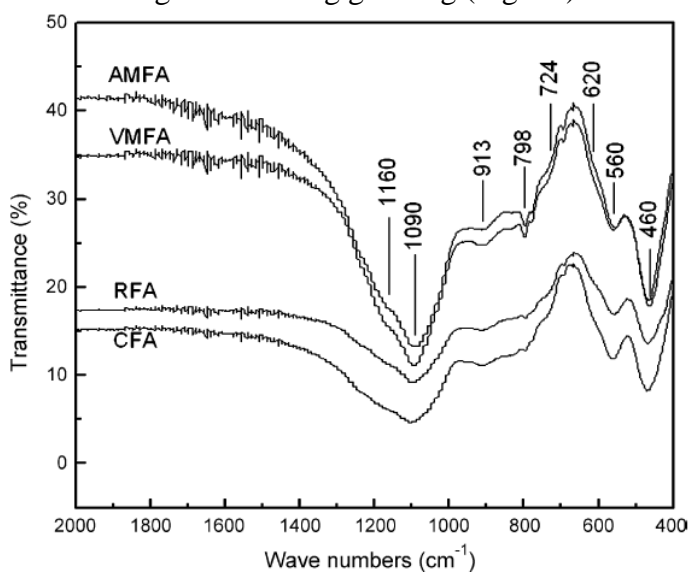


Fig. 12: FTIR spectra of raw fly ash (RFA), mechanically activated fly ash using vibratory mill (VMFA), or using attrition mill (AMFA), and classified fly ash (CFA) [Kumar et al. 2007].

In Fig. 13 typical isothermal conduction calorimetry curves are shown for cements containing 50% clinker and 50% fly ash. As activated fly replaced the untreated fly ash the curves clearly shift to the left, resulting in a shorter induction period. This confirms the ability activating fly ash by grinding.

Worth mentioning is the third heat-peak forming right after the main hydration peak. A similar peak was observed by Baert et al. (2007).

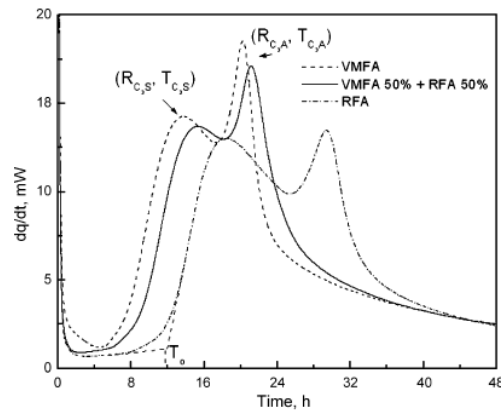


Fig. 13: Isothermal conduction calorimetry results showing effect of mechanical activation on heat evolved (dq/dt) during hydration of cements containing 50% clinker and fly ash as raw fly ash (RFA), vibratory milled fly ash (VMFA) and 50:50 mixture of RFA and VMFA ($w/c=0,5$, 27°C) [Kumar et al., 2007].

The increase in early strength development can be seen (Fig. 14). Replacing 65% of the clinker by activated fly ash resulted in strength comparable to commercial cement containing 20-25% fly ash.

One of the important features of attrition and vibratory milled fly ash is that the coarser particles were reduced in size and small sized cenospheres ($<1\mu\text{m}$) retain their original shape (Fig. 11). This is in sharp contrast to fine milled fly ash in a ball mill where most of the cenospheres are destroyed [Payá et al., 1996]. The presence of cenospheres in the milled fly ash improves the flowability without any increase in water demand. The beneficial effect of mechanically activated fly ash is due to the increased reactivity and control over water demand attributed to the unique morphology of the ground fly ash.

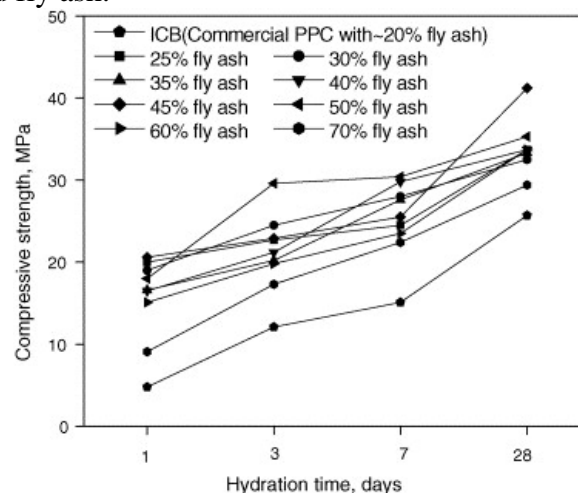


Fig. 14: Variations in compressive strength of Portland cement after 1, 3, 7 and 28 days of hydration using different proportions of vibratory milled fly ash [Kumar et al., 2006].

Kiattikomol et al. (2001) evaluated the properties of ground coarse fly ash. Class F fly ashes from five different sources with strongly differing shape, size and chemical composition were tested.

The ashes were processed as schematically depicted in Fig. 15. Compressive strength tests were performed on 5cm mortar cubes with a binder to sand ratio varying for 1 to 2.75. The fly ashes replaced 20wt.% Portland type I cement and the water to binder ratios were adjusted in order to obtain a standard flow of 110 ± 5 (specified by ASTM C 109). From Fig. 16 it can be concluded that for the Class F fly ashes used, the fineness and not the chemical composition is the principal characteristic affecting the compressive strength of the mortar. The mortars with finer fly ashes showed significantly higher strengths. The effect is noticeable as early as 3 days. Strength activity indices (ASTM C 311) as high as 121% could be obtained at 90 days when coarse fly ash was ground to a median particle size of $1.9 \mu\text{m}$ (Fig. 17). No significant difference in compressive strength was found between mortars containing classified and ground coarse fly ash of similar median size. This is contradictory with the findings of Kumar et al. (2007) and Eymael and Cornelissen (1996). They stated that grinding gave rise to slightly superior reactivity than classification and therefore yielded to improved strength development. Moreover grinding facilitates the utilization of the entire fly ash whereas with classification only part is used.

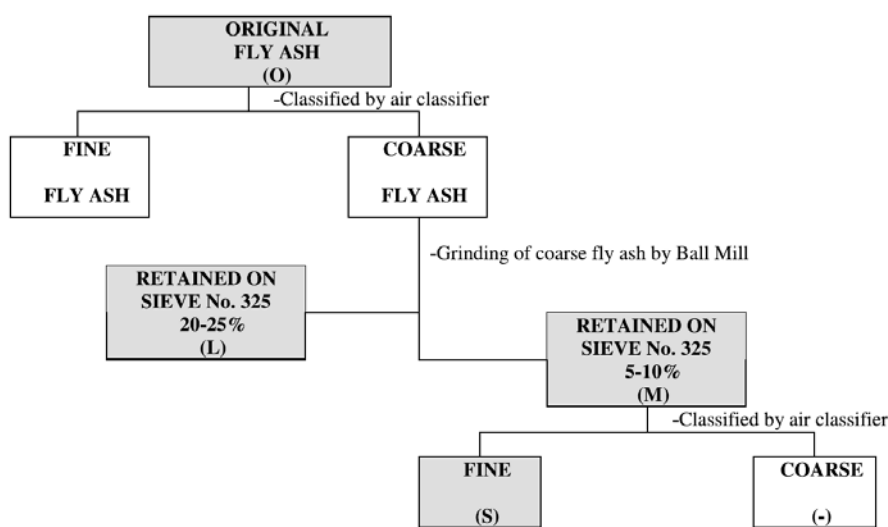


Fig. 15: Overview of the processing of the different types of fly ash used (gray=used in the experiments) [Kiattikomol et al., 2001].

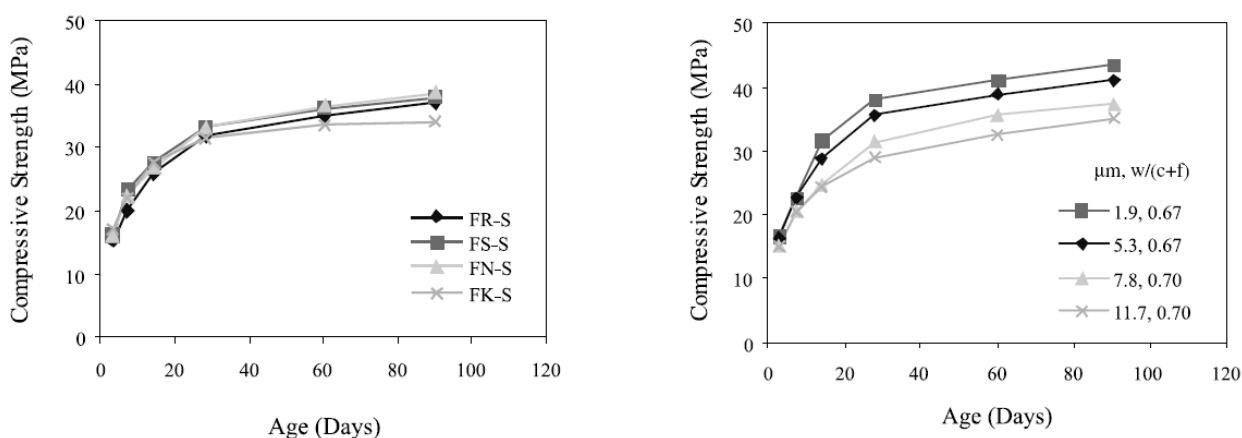


Fig. 16: Left: Compressive strength of mortars with the same fineness (S) of the fly ashes (FR,FS,FN,FK); Right: Compressive strength of mortars with the same W/(C+F) [Kiattikomol et al., 2001].

Payá et al. (1995b) and Schießl et al. (1989) observed a similar relation between strength and mean particle diameter as Kiattikomol et al. (2001), though the former for replacement levels of 60% and the later for replacement levels of 40%. The enhancement of compressive strength appeared to be mainly related to the content of fly ash particles smaller than $10 \mu\text{m}$, but for

flexural strength on the other hand, it was the granulometric distribution which seemed to be important [Payá et al., 1995b].

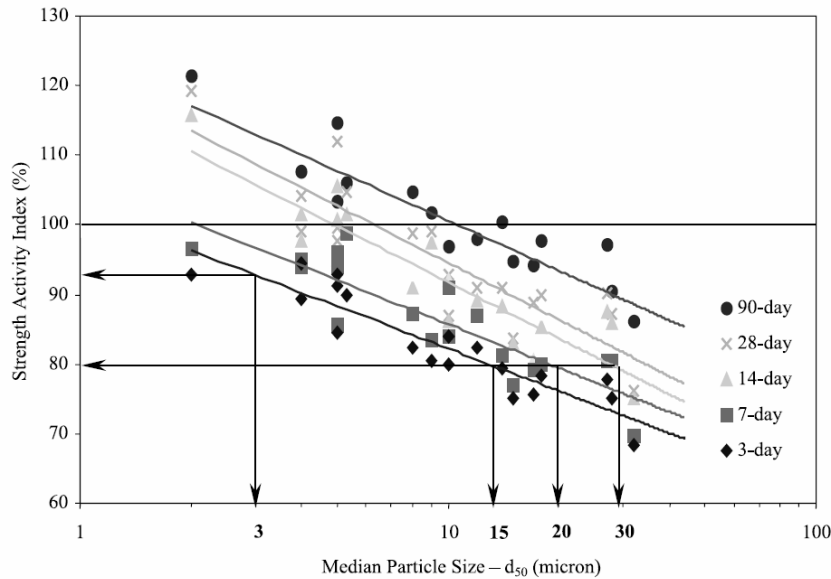


Fig. 17: Relationship between median particle size and strength activity index (ASTM C 311) [Kiattikomol et al., 2001].

Sekulic et al. (2004) mechanically activated the fly ash by grinding it in a vibromill. Cement blends with 75% clinker, 5% gypsum and 20% fly ash (FA) were studied. The fly ash and the Portland cement had an initial Blaine fineness of 300m²/kg and they were ground as well separately as together to a fineness of 500 m²/kg. The combination of fly ash and clinker required the shortest time to reach a fineness of 500 m²/kg, namely 3 minutes compared to 7 and 12 minutes for separate grinding of fly ash and OPC respectively. This is in agreement with the results obtained by Bouzoubaâ et al. (1998). He also observed a reduction in grindability as fly ash and clinker were ground together. The effect on the strength development is significant (Fig. 18). The setting time was reduced from 4h 40min for the untreated clinker fly ash blend to 3h 50min when fly ash and clinker were activated together, and to 4h 30min when only the fly ash was activated. Based on the results obtained by XRD analysis, it was found that during mechanical activation, the content of hydraulic phases increased in the finer fraction (<11µm). These results are in agreement with the strength results and might thereby explain the increased reactivity.

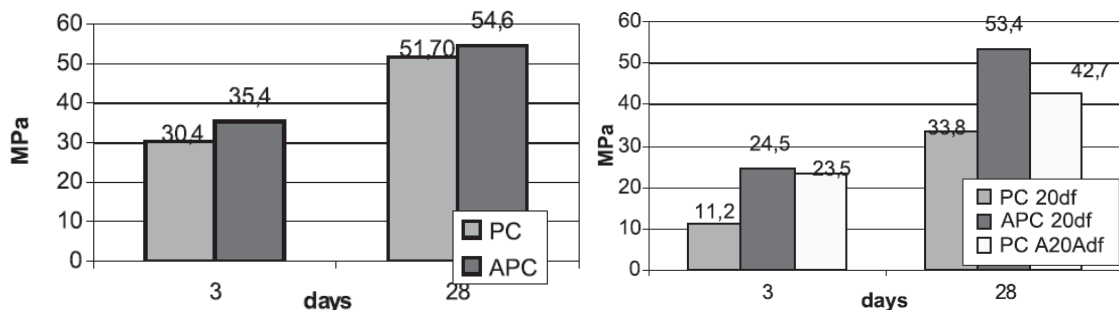


Fig. 18: Compressive strength after 3 and 28 days (PC = OPC, APC = activated OPC, PC 20df = OPC with 20% FA replacement, APC 20df = activated PC 20df, PC 20Adf = blend of 80% OPC and activate FA) [Sekulic et al., 2004].

Eymael and Cornelissen (1996) investigated the use of classified or ground fly ash in high performance concrete. The particle size distributions of the raw, classified and ground fly ash, and silica fume are shown in Fig. 19. Concrete samples were prepared with a water/cement ratio of

0.32. Fly ash and silica fume were added in dosages of 5, 10 and 15% (m/m cement). The results of the strength measurements performed are shown in Fig. 20. Air classification appeared to be an appropriate technique to separation of fly ash into various size fractions. By removing the coarse size fraction from the fly ash, a significant improvement of concrete properties could be achieved. The micronized (ground) fly ashes resulted however in an even higher strength in comparison with an air-classified fly ash in concrete with similar workability.

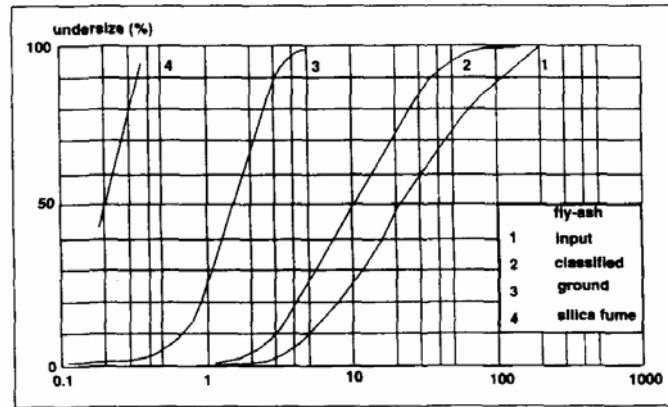


Fig. 19: Particle size distribution of tested raw, classified and ground fly ashes and silica fume [Eymael et al., 1996].

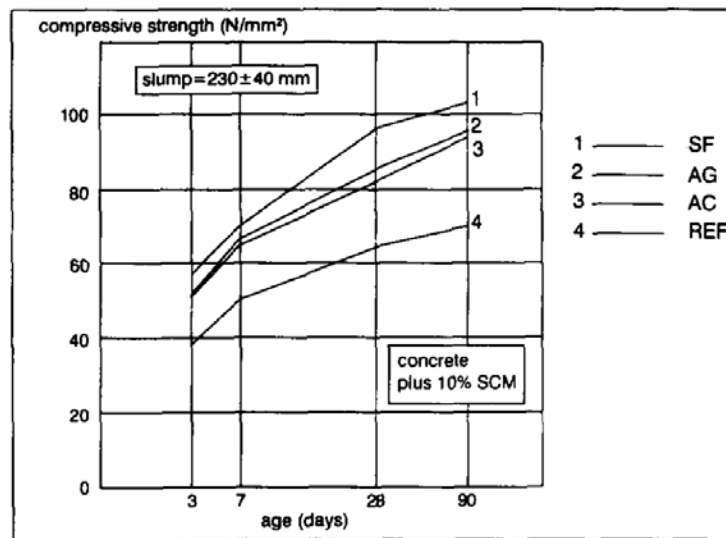


Fig. 20: Compressive strength for concretes with 10% added silica fume (SF), ground fly ash (AG) or classified fly ash (AC), and reference without SCM. All with approximately the same workability. [Eymael et al., 1996]

That mechanical activation is a feasible way of improving the characteristics of fly ash is confirmed by the fact that such products are all ready available. Duracem® F, for example, is a product produced at the Ash Grove Cement plant in Louisville, NE. It consists of fine ground fly ash, processed in a ball mill. Suchorski D. (2007) presented some characteristics of the product and its effect on the compressive strength and alkali reactivity when used in a 25/75 activated fly ash/OPC blend compared to 100% OPC. Approximately 20 to 25% of the mass of the raw fly ash is retained on the 45µm sieve. The end product, Duracem® F, only leaves 2% of its weight on the 45µm sieve. The grinding fractures the agglomerates and large-sized fly ash spheres as can be seen from Fig. 21. Still lots of round particles can be observed in the fine ground fly ash. This is contradiction to what was stated by Kumar et al. (2007). He claimed that unlike vibratory mills and attrition mills, ball mills crush most of the round particles.

The remarkable effect of pre-processing the fly ash in the ball mill on the compressive strength development is shown in Fig. 22.

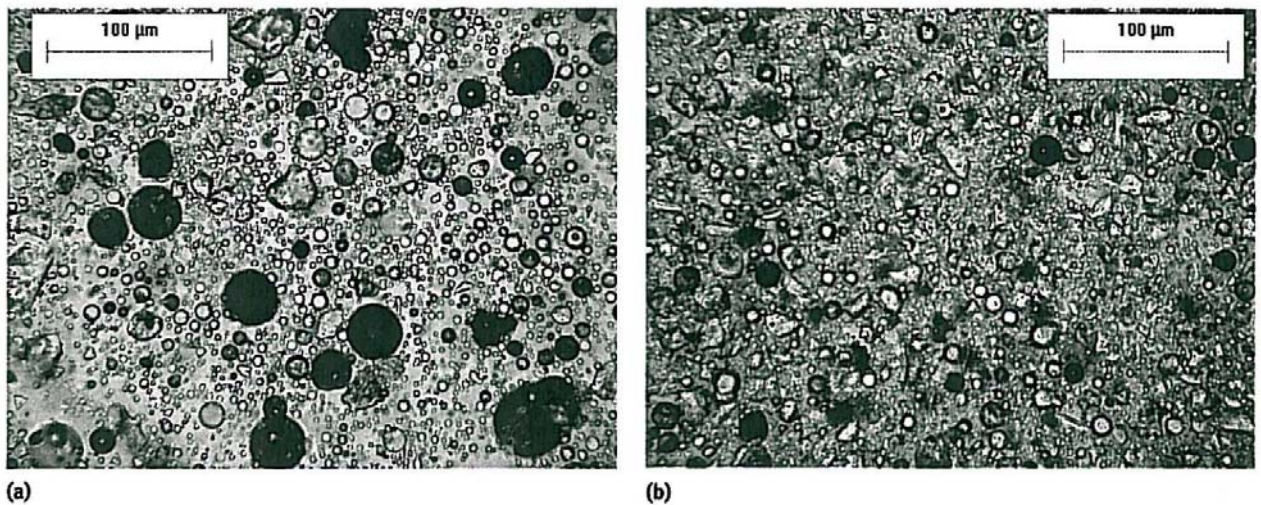


Fig. 21: Class F fly ash used to produce Durapoz® F: (a) as delivered from the power plant, the ash contains large, spherical particles, (b) after processing in a ball mill, the ash particles are significantly smaller and more angular [Suchorski D., 2007].

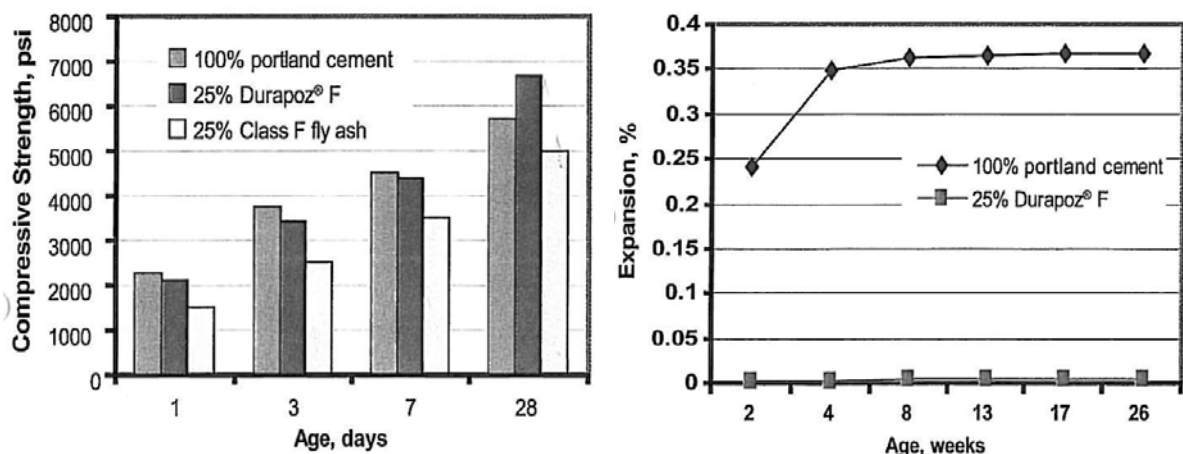


Fig. 22: Left: Compressive strength evaluated per ASTM C 109, 1 psi = 0,0069MPa; Right: Alkali reactivity evaluated per ASTM C 227 using Pyrex® glass as (highly reactive) aggregate [Suchorski D., 2007].

Energetically Modified Cements (EMC) is a type of mechanically activated cements. Those are intensively ground blended cements containing ordinary Portland cement (OPC) and pozzolanic material. The technology was developed at Luleå University of Technology in Luleå, Sweden, by Dr. Vladimir Ronin et al. in the early 1990's. The blended cements are activated by multiple high intensity grinding, which renders the surface of the particles more active.

Justnes et al. (2005, 2007) applied this technology on blended cements containing 50% fly ash. The resulting EMC had about 40% higher strength after 24 hours than the reference Portland cement. Compressive strength developments for the EMC are in line with that of the pure ASTM Type I Portland cement. EMC cements based on 30% of fly ash and 70% of Portland cement showed strength development in line with rapid hardening cement. EMC cement prepared with 50% fly ash had a lower water demand, improved sulphate and alkali-silica resistance, and finer pore system. This is a very interesting technique for the production of HVFA high performance cements and concretes.

4.2 Chemical activation

Katz (1997), Palomo et al.(1999), Puertas et al.(2003), Fernández-Jiménez et al.(2005), Criado et al.(2007) and Bijen et al.(1989) investigated the use of alkali-activated fly ash as a binders. Although that is not the main interest in this review, their research contains valuable information on the activation of fly ash. They activated fly ash with high alkali solutions such as NaOH, KOH, sodium silicate, potassium silicate and anhydrous sodium carbonate solutions and the curing temperatures were varied in the range of 20°C to 90°C.

It is clear that, the higher the alkalinity of the solution, the more it activates the hydration reaction of fly ash (Fig. 23) however the curing temperature seems to play a major role as well.

At ambient temperature, highly concentrated alkaline solutions were required to activate the fly ash to a reasonable extend. A 10M NaOH solution succeeded in activating a 50/50 slag/fly ash blend significantly and a 60MPa compressive strength was obtained after 28 days [Puertas et al., 2003]. At elevated curing temperatures the activation effect was amplified (Fig. 23). Compressive strengths up to 60MPa were obtained after curing for 24 hours at 65°C and 85°C [Palomo et al., 1999].

The effect of lowering the water/fly ash ratio is shown in Fig. 23. At 20°C and 50°C the hydration rate is low and the measured strength results mainly from inter-particle forces. Hence the system with the densest packing will give rise to the highest strength. At 90°C however reaction products have been forming. In this case an initially higher porosity leads to a higher compressive strength. Katz (1997) suggests that a solution with a high pH is important for the initiation of the process, the NaOH/FA ratio on the other hand seems to be a significant parameter in determining the type of hydration product formed in the process.

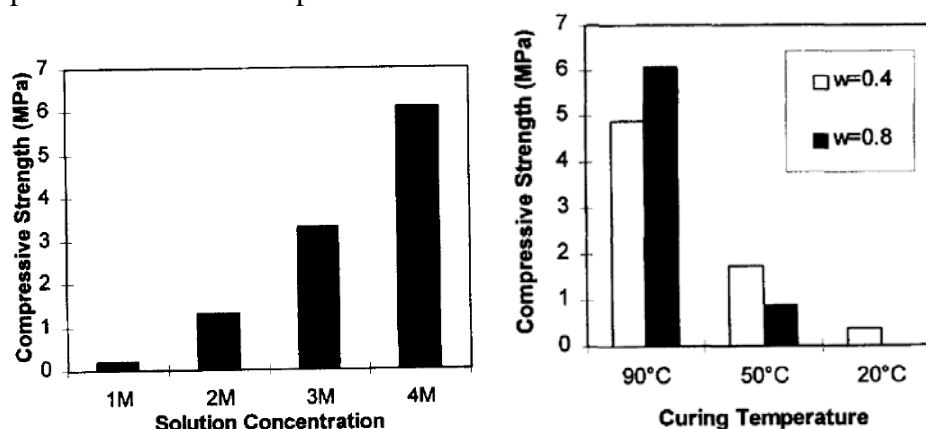


Fig. 23: Left: The effect of solution concentration on the compressive strength at 7 days; Right: The effect of curing temperature and water/FA ratio on the compressive strength (4M NaOH solution) [Katz, 1997].

According to Fernández-Jiménez et al. (2005) the reaction mechanism proceeds as follows: the high concentration of OH⁻ ions breaks down the Si-O-Si, Si-O-Al and Al-O-Al bonds of the vitreous phase of the ash and thereby forms Si-OH and Al-OH groups; these condense and form a zeolitic precursor. This gel possesses 3-dimensional structure build up, consisting out of Si and Al tetrahedral randomly distributed along cross-linked polymeric chains. The monovalent alkali metals are incorporated in the system and compensate the electrical load of the microstructure when Al³⁺ replace Si⁴⁺. OH⁻ ions can thereby be assumed as the catalysts during the activation and the alkali metals as the structure forming elements.

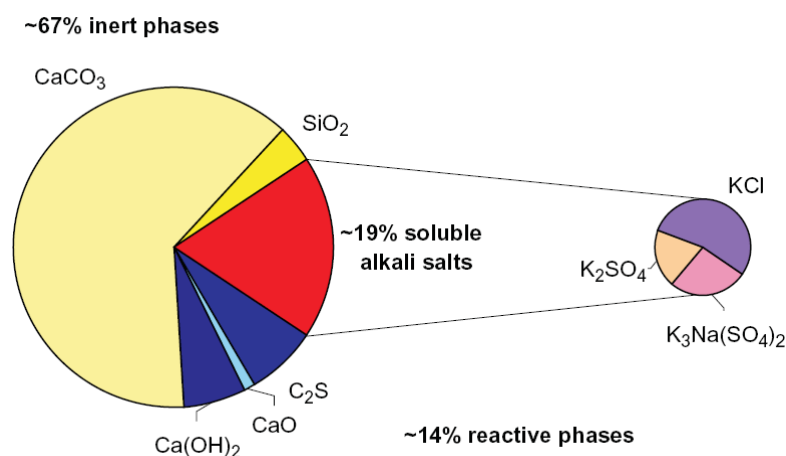
Palomo et al. (1999) and Criado et al. (2007) observed similar reaction products: gel-like amorphous alkali silicoaluminates, containing small proportions of quartz and mullite from the original fly ash.

The use of a sodium carbonate (Na_2CO_3) and NaOH blend as activator gave rise to a more porous microstructure and lower mechanical strength. However compared to only NaOH as an activator it appeared that carbonate ions promote the polymerization of the aluminosilicate gel since higher Si/Al ratios were observed. The sodium silicate is even a better activator as it provides soluble silicates. As a result high degrees of condensation (polymerization) were obtained by adding sodium silicate [Fernández-Jiménez et al., 2005].

Bijen (1989) points out some disadvantages on using alkali activated fly ash-slag cements, such as intensive salt efflorescence, reduced carbonation resistance, possible increased alkali silica reactivity and danger for persons handling the material because of the high alkalinity.

Wang et al. (2004) and Buchwald et al. (2005) investigated the use of cement kiln dust (CKD) as an alkali activator for fly ash. Both researchers prepared 50/50 CDK/fly ash blends. Wang (2004) tried to activate the fly ash in several ways: (1) natural activation, by simply blending CKD and fly ash, expecting that the alkalis from the CKD will activate the fly ash hydration; (2) chemical (alkali) activation, by adding 2 or 5% NaOH in the binder system to activate fly ash hydration; (3) physical (thermal) activation, by curing the pastes at elevated temperatures 38°C or 50°C instead of 24°C . He prepared pastes with a water-to-solid ratio of 0.52 and evaluated them after 7, 28 and 126 days of curing. The major crystalline hydration product appeared to be ettringite. The optimum hydration conditions were obtained by adding 2% NaOH and curing at 38°C . With these conditions a 27MPa strength was measured after 56 days of curing. The addition of 2% NaOH and the increase of the curing temperature from 24°C to 38°C significantly activated the hydration, but by raising the temperature from 38°C to 50°C or increasing the NaOH addition from 2% to 5%, the ettringite formation was reduced and the crystallisation was impaired which resulted in a lower strength development.

Buchwald (2005) made 50/50 blends with fly ash and CKD. Water was added to the paste so they obtained approximately the same workability. The samples were cured for one day at 35°C followed by 27 days at room temperature at 60% relative humidity. The two CKD's were chosen from a large collection of kiln dusts because of their strongly differing chemical composition. The results of the XRD and Rietveld analysis are shown in Fig. 24.



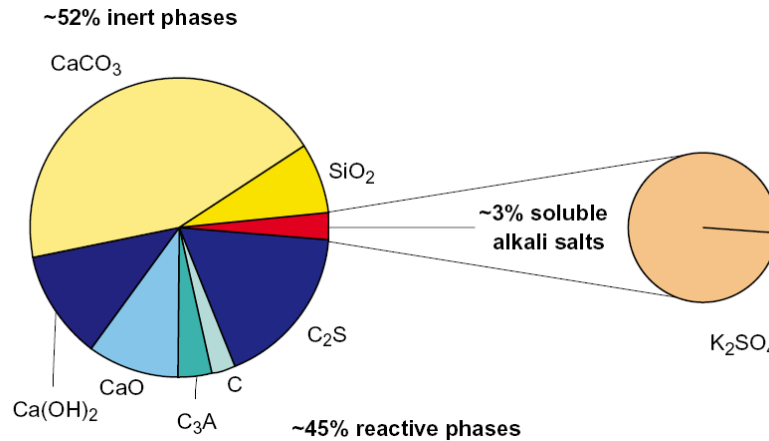


Fig. 24: Phase composition of two different cement kiln dusts (CKD) [Buchwald et al., 2005].

The phases can be divided into three main groups: (1) soluble alkali salts, (2) reactive cement and lime phases, meaning calcium silicate, -aluminate and free lime, and (3) inert phases, such as calcite and quartz. The two tested CKDs differ strongly in amount of reactive phase and amount of soluble alkalis. The compressive strength was determined after 28 days of curing. The combination of the high alkali CKD and fly ash gave rise low strength values ($\pm 2.5\text{MPa}$). This was attributed to the fact that the high alkali CKD could not produce a high pH to activate the fly ash since the alkalis were mainly chlorides. Hence the CKD with the high reactive phase content was more effective in activating the fly ash and a compressive strength of 12MPa was measured. The main hydration product of CKD determined by XRD is the crystalline calcium aluminate phase containing carbonate and chloride. CSH can not be spotted due to its low crystallinity but ettringite and portlandite were found. Through the addition of fly ash portlandite formed by CKD was consumed and the amount of crystalline calcium aluminate hydrate was increased.

Fraay et al. (1990) tested FA based courses consisting of 100 parts FA and 10-6 parts cement. The mixes exhibited bad mechanical and durability properties as the pH never reached high enough to activate the fly ash. Significant improvements were obtained by increasing the pH (>13) through the addition of NaOH or sodium silicate. An addition of 2% NaOH in the mixing water (water/solid = 0.22) appeared to be the optimum. Higher concentrations gave rise to strength decrease. The effect of the pH adjustment was especially large at low hardening temperatures (5°C). Fig. 25 shows the solubility of Si from Class F fly ash in KOH solutions compared to NaOH solutions after 1 week at 40°C without a lime buffer. The solutions with KOH appear to be somewhat less aggressive than the NaOH solutions. This may be due to the lower activity coefficient for K^+ compared to Na^+ .

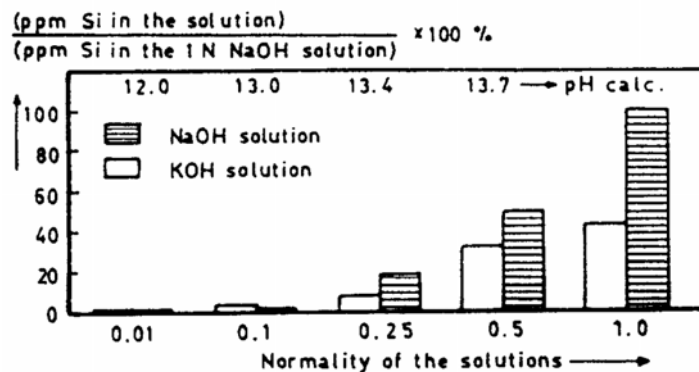


Fig. 25: Comparison of the solubility of Si from class F fly ash in a NaOH and a KOH solution [Fraay et al., 1989].

Antiohos et al. (2004, 2006, 2007) tried to activate class F fly ash with quicklime. They replaced 0, 5, 10 and 15% of the fly ash with lime and composed a cement with 20% of the fly ash-lime blend and 80% CEM I OPC. Mortars with a binder-to-sand ratio of 1:3 and pastes, both with a water-binder ratio of 0.5, were prepared. Strength measurements, and determination of the amount of $\text{Ca}(\text{OH})_2$ and non-evaporable water by thermal analysis were performed after 2, 7, 28 and 90 days of curing. The degree of reaction decreased with addition of quicklime after and initial increase (2 days). This is probably due to the fact that the concentration of reactive silica present in the pore solution decreased, as fly ash was replaced with quicklime, resulting in insufficient soluble silica available to react with the surplus of hydrated lime. The hydration products formed were monosulphoaluminates and ettringite. The pore volume was determined by mercury intrusion porosimetry (MIP). After a temporary decrease in the total volume after the first week, a consecutive increase was observed at 90 days of hydration. This confirms the absence of any activation of the fly ash by quicklime. SEM micrographs showed intact fly ash particles after 28 days of curing. The particles were extensively surrounded by calcium hydroxide (see Fig. 26), resulting in substantial limitation of the reactivity of the particles. In this case, the added quicklime acts more like an inhibitor than an activator.

Similar findings, on the used of quicklime as activator, were obtained by Jha B. (2007). He prepared mortars based on a lime-fly ash binder. The tested fly ash/lime weight-ratio ranged from 90/10 to 50/50. The compressive strengths barely reached a level of 2.5-3.5 MPa after 28 days of moist-curing at ambient temperature. A 30% lime level gave the optimal strength. Lowering or increasing the lime dosage resulted in a decrease of compressive strength.

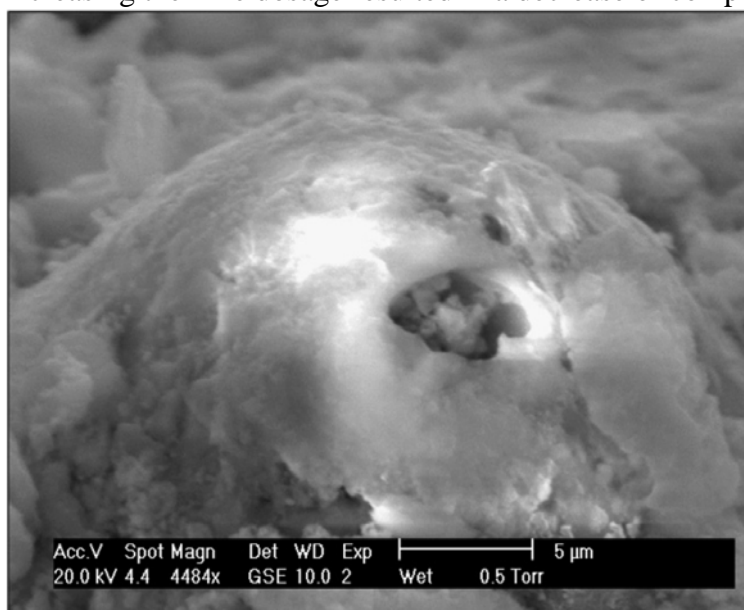


Fig. 26: Fly ash particle surrounded by massive CH production after 90 days of curing [Antiohos et al., 2006]

Ma (1995, 1997) investigated the hydrothermal activation of class F fly ash with 10% $\text{Ca}(\text{OH})_2$ and 10% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The fly ash-activator blend was cured for 24 hours at temperatures ranging from 25°C to 180°C under saturated steam pressure. Although Ma (1995) had found signs of activation after 24 hours of curing by measuring the development of the BET surface area of the hydrating paste, it seemed [Ma, 1997] that $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were not able to activate the pozzolanic reaction of the fly ash significantly since no strength could be measured after 24h of curing.

Blanco (2005, 2006) used two types of class F fly ash. They were mechanically activated by wet grinding for 1, 4, 8, 12 and 24 hours, and/or chemically activated by acid leaching with sulphuric

acid at ambient temperature, 50°C and 107°C for 1 or 9 hours. By grinding, the specific surface (BET and Blaine) and the average diameter decreased, and the pozzolanic reactivity (amount of fixed lime) increased. Leaching increased the silica content and decreased the aluminium and iron content. The results pointed out that chemical activation by leaching at elevated temperatures was more effective than mechanical activation. When both fly ashes were ground for 24h and subsequently leached for 9h at 107°C in sulphuric acid, they exhibit superior properties concerning strength and porosity when combined with clinker (20% replacement level) compared to silica fume.

Li (2000) used 2% NaOH, and 6% gypsum and 4% Na₂SO₄ (to the weight of fly ash) to activate fly ash (100%) at 60°C with a water/binder ratio of 0.45. The amount of chemically bound water, determined by thermal analysis, was used to compare the degree of hydration. It was found that NaOH increased the early hydration (7day) significantly whereas gypsum and Na₂SO₄ increased the strength at later age (14-90 day) when cured at 60°C.

Shi and Day (1994, 2000a, 2000b, 2001) studied the effect of Na₂SO₄ and CaCl₂ as chemical activators on the strength of lime-fly ash pastes. Two different fly ashes were used (LFA=low lime content and HFA=high lime content). The lime-fly ash cements consisted of 20% hydrated lime and 80% fly ash. The chemical activators were added in dosages ranging up to 5% of the lime-fly ash cement. The pastes were prepared with a water/solid ratio of 0.35 (LFA) or 0.375 (HFA), and moist-cured at 50°C. Na₂SO₄ and CaCl₂ clearly increased the pozzolanic reactivity, which resulted in a significant improvement of strength (see Fig. 27).

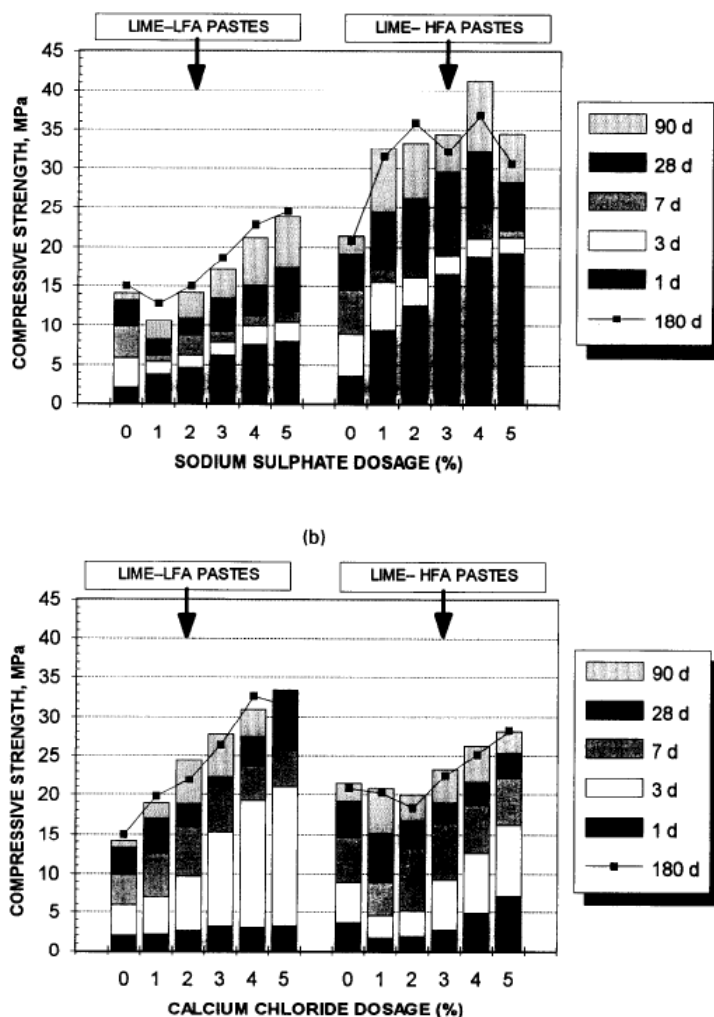


Fig. 27: Effect of sodium sulphate and calcium chloride activators on the strength development of lime-fly ash cements moist-cured at 50°C. [Shi and Day, 1995]

X-ray diffractometry (XRD) and scanning electron microscopy (SEM) were used to examine pastes with and without activators. The low lime fly ash (LFA) without any activator had a C-S-H-like phase as principal hydration product, and the second major hydration product was found to be C_4AH_{13} . The minor products detected were ettringite (AFt) at early age and C_2ASH_8 at later age. The addition of sodium sulphate resulted in an increase of the AFt phase and a decrease in the C_4AH_{13} phase. After 1 day the amount of AFt seemed to increase proportional with the amount of activator added and the C_4AH_{13} phase disappeared as Na_2SO_4 -dosages surpassed the 3% limit. After 7 days, the AFt phase rather than AFm phase was found and at a Na_2SO_4 -dosage of 2-5% only AFt was detected. The calcium chloride activator gave rise to the formation of the solid solution $C_4AH_{13}-C_3A \cdot CaCl_2 \cdot 10H_2O$.

The influence of the particular activators on the strength of the lime-fly ash pastes appears to be due to their influence on the quantity and types of hydration products.

Jueshi (1993) compared the effect of grinding for 30 minutes in a ball mill (no further information given) and chemical activation through the addition of 3-4% Na_2SO_4 . He found that chemical activation was more efficient than grinding. The chemical activation increased the 3 and 7 day-strength of a fly ash cement with a 30% replacement level, of approximately 5-10 MPa.

Day et al. (2007) published some results of the use of sodium sulphate (Na_2SO_4) as an activator for high volume fly ash concrete in practice. An EcoA concrete and a traditional concrete were compared. The mix proportions and the strength development are given in Table 3 and Fig. 28.

The results show that a fairly similar strength development was obtained with the EcoA concrete compared to the traditional concrete. Additional tests for alkali-aggregate reactivity (ASTM C1012) and shrinkage were performed. The addition of the activator appeared to produce a slight increase in expansion, but the expansion was still much smaller than for the traditional blend and well below the allowable limits. The EcoA concrete exhibited also lower shrinkage than the traditional concrete. This might be due to the lower cement content and lower water/binder ratio of the EcoA concrete. The laboratory and field results showed satisfactory performance of the EcoA concrete in the building industry.

Table 3: Mix proportions/m³ of EcoA and traditional (TRAD) SCC mix [Day et al., 2007].

	EcoA	TRAD
Cement (kg)	111	168
Fly Ash	259	42
Coarse Aggregate	813	1099
Fine Aggregate	809	747
Water	207	168
Activator	Yes	No

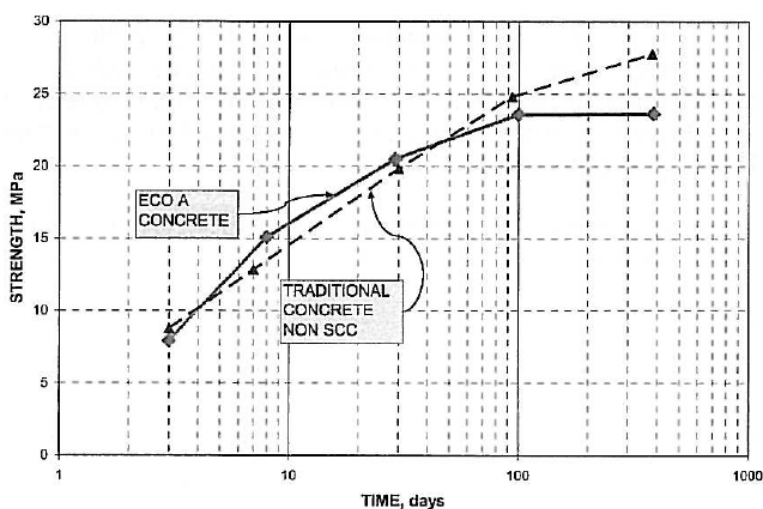


Fig. 28: Comparison of compressive strength between traditional concrete and ECOA concrete [Day et al., 2007].

Aimin and Sarkar (1991) performed a microstructural study of gypsum activated fly ash hydration in cement paste. They added 3 to 6% gypsum to a cement consisting of a low alkali, low C₃A (1.0%) clinker and low (30%) or high (60%) volume of Class F fly ash (FA). By using a low alkali cement, the effect of alkalis incorporated in the fly ash could be investigated. The low C₃A content of the clinker makes it possible to study the C₃A phase of the fly ash. The activation of fly ash by gypsum is namely based on the ability of sulphate ions to react with the alumina phase. This results in a denser structure as the pores will fill with ettringite and monosulphate. The gypsum accelerated the dissociation of the fly ash glass phase only after 7 days of hydration when the calcium hydroxide precipitation had start to slow down. This can be attributed to the fact that gypsum does not reach the dissolved state before the calcium hydroxide formation had slowed down. The addition of NaOH suppresses the solubility of the calcium hydroxide due to the common ion effect and thereby reduces the Ca²⁺ concentration in the solution. Alkalis incorporated in the glass phase of the fly ash did not seem to go into solution before the glass structure dissolves. Alkalis on the surface on the other hand can increase the OH⁻ concentration and as a consequence suppress the calcium hydroxide locally causing early precipitation of calcium hydroxide on the fly ash surface. Higher amounts of calcium hydroxide were produced in the pastes containing gypsum than in the ones without and more of it seemed to be consumed at

later age (see Fig. 29). This might be due to ettringite formation which consumes calcium hydroxide.

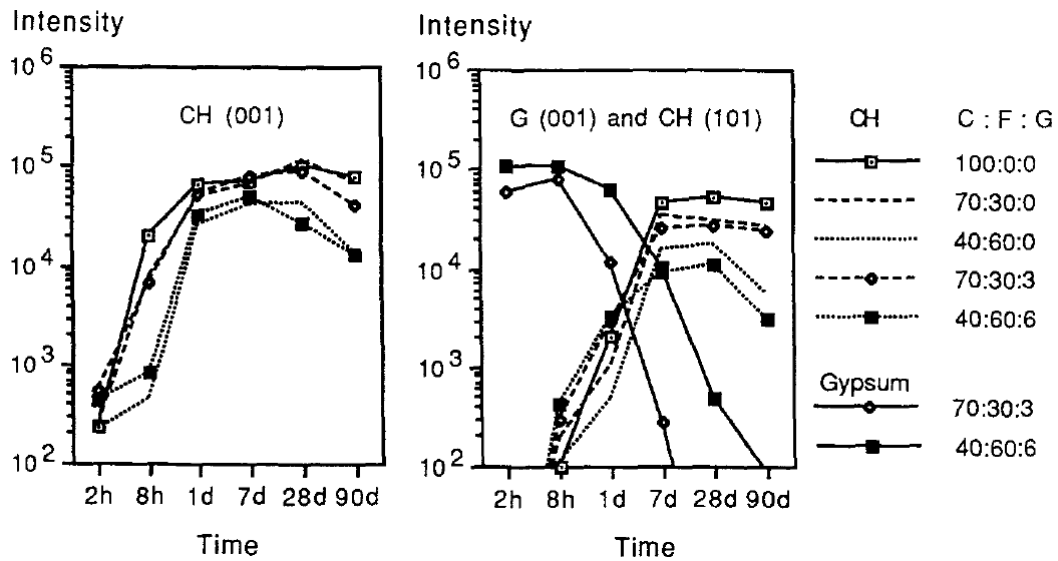


Fig. 29: Calcium hydroxide (CH) and gypsum (G) content in the pastes at different ages as determined by XRD [Aimin and Sarkar, 1991].

Between 3 and 28 days the amount of gypsum decreases significantly but only very little Aft formation was observed with XRD. SEM on the other hand revealed fly ash particles filled with Aft-like phases, presumably formed by ionic diffusion through the weak points of the FA surface. This was first detected in the 28day samples as the bonding between some fly ash particles and the surrounding paste had increased and fractures occurred through the particles (not only between the surface and its coating) so that the inner part of the fly ash particles could be observed.

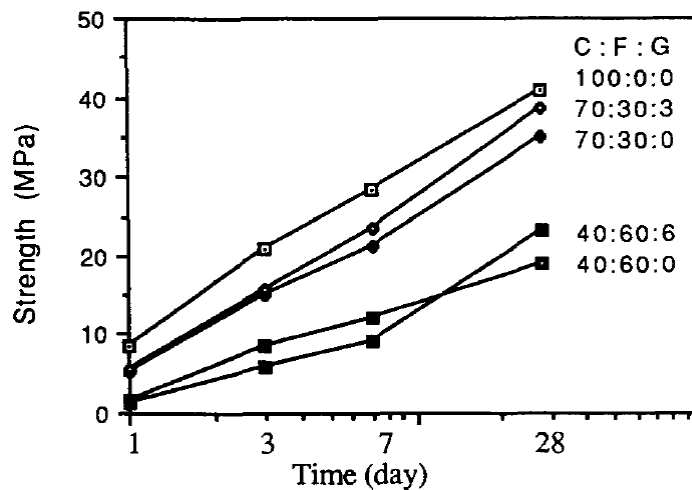


Fig. 30: Compressive strength development of mortar samples (C=cement, F=FA and G=gypsum) [Aimin and Sarkar, 1991].

The reaction at later age (when significant amounts of gypsum are dissolved) is diffusion controlled, involving the dissolution of SO_4^{2-} from the dissolved gypsum and Ca^{2+} from CH into FA and the subsequent dissociation of alumina and silicate from the FA glass into solution. This reaction occurs both inside and far away from FA particles. FA paste without additional gypsum develops more C_4AH_{13} . A more thorough FA hydration occurs in the pastes with additional gypsum giving rise to a denser microstructure, as indicated by their higher strength (Fig. 30). Outer diffusion, precipitation of hydration products originating from the reaction of fly ash, was

confirmed by the observation of needle-like AFt inside relicts of gypsum. Since the clinker had a very low C_3A content the aluminate had to be provided by the fly ash.

5 Reaction products

The reaction products resulting from hydration of Portland fly ash cements are generally similar to those formed in pure Portland cement [Pietersen, 1993, Shi and Day, 1995, Hewlett, 1998]. The main hydrates in the hardened paste are:

- C-S-H (calcium silicate hydrate)
- $Ca(OH)_2$ (CH, calcium hydroxide)
- AFt (ettringite)
- AFm (monsulphate)
- C_2ASH_8 (strätlingite)
- C_3AH_6 (hydrogarnet)

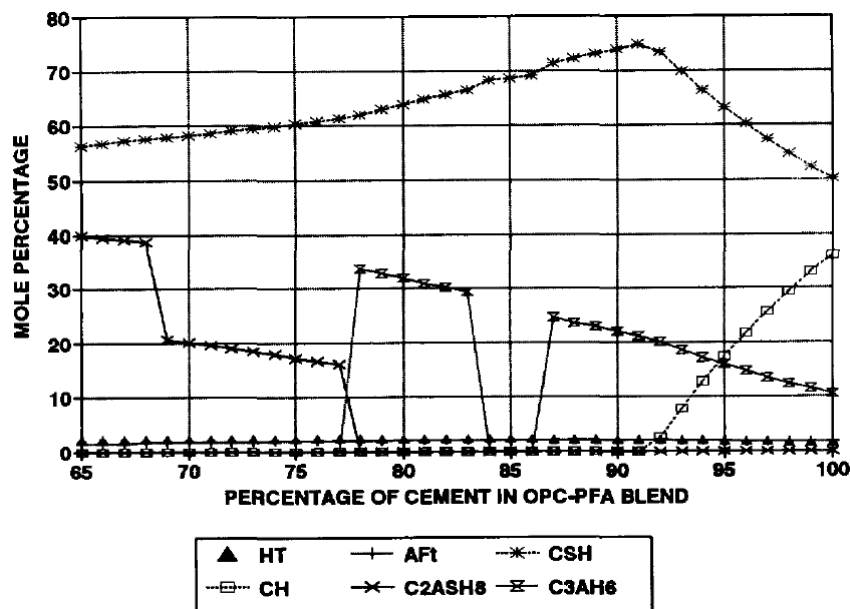


Fig. 31: Predicted phase proportions for Portland cement with fly ash. Since the Portland fly ash cement used in the calculation did not contain significant MgO or SO_3 , the ettringite (Aft) and hydrotoalcite (HT) are only formed in minor amounts [Pietersen, 1993].

Fly ash cements differ notably from Portland cements in the hydration rate of the clinker phases, the evolution of the $Ca(OH)_2$ content in the pore solution and composition of the hydration products [Uchikawa, 1986]. The influence of fly ash addition on the Portland cement hydration is strongly dependent on the chemical and morphological characteristics of the fly ash and cement used.

The addition of fly ash retards the hydration of C_3S until the dormant period and accelerates the hydration thereafter. The delaying effect might be explained by the adsorption of Ca^{2+} on the negative surface of the fly ash particles and the thereby delayed supersaturation and precipitation of $Ca(OH)_2$ [Uchikawa, 1986, Bensted and Barnes, 2002].

The replacement of 25% of clinker by fly ash increased the amount of reacted C_3S with 3-9% after 28 days of hydration [Hewlett, 1998]. The accelerating effect increases with increasing replacement levels.

Sakai et al. (2005) investigated the influence of fly ash on the hydration of the different phases of OPC by XRD quantitative analysis. It was confirmed that fly ash accelerated the long term hydration of alite. The belite and the C_4AF phase on the other hand were retarded.

This might be explained by increasing water availability and space for the hydrating cement grains and the provision of additional nucleation sites on the fly ash particles for C-S-H and $Ca(OH)_2$. On the other hand, it has been observed that fly ashes with a high aluminate content retard the silicates and accelerated the aluminates of the clinker [Halse, 1984].

The effect of fly ash addition on the hydration of the C_3A phase of the clinker depends strongly on the chemical composition of the fly ash, especially the aluminate content [Uchikawa, 1986].

Plowman (1981) found that fly ash delayed the onset of C_3A hydration and slowed down the reaction due to the formation of a protective layer of calcium aluminate hydrate layer stabilized by the incorporation of sulphate. Uchikawa (1980) observed the same combination of C_3A and fly ash but as gypsum was incorporated in the system, fly ash seemed to accelerate the hydration of C_3A . At later age it was found that the alkalis provided by the fly ash accelerated the conversion of ettringite to calcium aluminate hydrate by decreasing the stability of the ettringite.

The presence of fly ash tends to change the composition of the C-S-H phase. The Ca/Si ratio decreases with age and percentage of FA used [Bensted and Barnes, 2002, Hewlett, 1998, Sakai, 2005, Pietersen, 1993]. In Table 4 the differences in the C-S-H phase in cement paste by a 40% fly ash replacement are given. Increased Al, Fe and K contents in the matrix are also characteristic for fly ash cement.

Table 4: Composition of C-S-H in cement pastes with and with out 40% fly ash (w/c=0.40 , 20°C , age 4 years) by EMPA [Uchikawa, 1986].

	C/S	A/C	C/(S+A)	Na ₂ O (%)	K ₂ O (%)
OPC	2.03	0.06	1.81	0.03	0.11
fly ash cement	1.01	0.21	0.84	0.24	0.33

Fraay (1989) found C-S-H-like reaction products, in a 100 g OPC, 30 g fly ash and 60 g water blends, originating from the glass network of fly ash which had gone into solution. These hydration products were able to precipitate relatively far away from the fly ash particles and are thereby able to fill small spaces. This effect is confirmed with MIP (mercury intrusion porosimetry). A finer pore structure was observed for the fly ash cement (30% mass replacement) compared to the reference after a couple of months of curing.

The $Ca(OH)_2$ content initially increases due to the acceleration of the alite hydration but decreases at a later age due to the pozzolanic reaction [Pietersen, 1993, Baert et al., 2007]. Some results of Baert et al. (2007) obtained by thermogravimetry are depicted in Fig. 32.

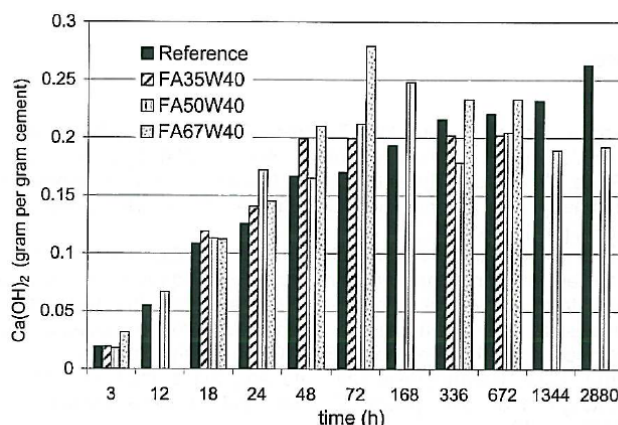


Figure 5 : Total calcium hydroxide content

Fig. 32: Mass of calcium hydroxide per mass of ignited cement in function of time, for fly ash replacement levels of 35, 50 and 67% and a water/solid ratio of 0.40 [Baert et al., 2007].

The use of sulphates, such as gypsum [Ohsawa, 1985, Aimin et al., 1991], sodium sulphate [Shi and Day, 1994, 2000a, 2000b, 2001, Day et al. 2007] or sulphates included in CKD [Buchwald et al., 2005], to activate the hydration reaction of fly ash, results in ettringite or monosulphate as the main reaction product observed by XRD.

6 Future research

When developing an all-round blended cement certain constraints are given. The cement has to have a satisfactory strength development between the temperature limits of 5 °C and 30°C and for a certain water-binder ratio.

This still leaves us with several ways of activating fly ash which are worthwhile looking into:

- Mechanical activation by grinding or classification of the fly ash. Finding optimum fineness (EURO/MPa)?
- The use of a high alkali clinker or addition of alkalis (e.g. NaSO₄ or NaOH) will boost the reactivity of the fly ash but how far can we go, taking into account the alkali aggregate reactivity.
- Finding the optimum amount of gypsum for the fly ash/clinker blend or alternatively limestone for carboaluminates (see STAR on limestone additions).

7 Conclusion

- A literature review showed that the **reactivity of fly ash** in combination with clinker strongly depends on the replacement level, water/binder ratio, alkalinity of the cement and curing temperature.
- The reactivity of fly ash can be significantly improved by **mechanical activation and classification**. The reactivity seems to be exponentially related to the fineness of the fly ash particles.

It was found that in the initial stage of grinding the fly ash increased significantly in fineness, but as grinding progressed, the increase in fineness declined.

Grinding together with the clinker appeared to be beneficial as both grindability and strength development improved.

When comparing fine ground fly ashes it appeared that the fineness of fly ash plays a far

more important role than the chemical composition in the strength development.

Air classification seems to be an efficient way of pre-processing the fly ash. Although some authors claim that it is not as efficient as mechanical activation by intensive grinding.

The activation mechanism behind the mechanical activation is not fully understood however FTIR spectrometry indicates some kind of structural rearrangement during grinding.

Mechanically activated fly ash performs superbly as a pozzolan. At replacement levels up to 25%, activated fly ash can improve strength development compared to the reference cement.

- When discussing **chemical activation**, it is clear that alkalinity plays a principal role. If the pH of the pore water stays below the 13.3 level, fly ash will hardly react at room temperature. Attempts to activate fly ash with quicklime at ambient temperature showed negligible activation of the fly ash since calcium hydroxide saturation only results in a pH of approximately 12.5. Concentrated NaOH and KOH solutions on the other hand were clearly able to boost the hydration of fly ash. Though care should be taken as some authors reported a decrease in strength as the amount of added alkalis surpassed a certain level. Cement kiln dust (CKD) was tested as an activator/cementitious material. Although it looked promising because of the high alkali content in CKD, rather low strengths were obtained. The results differed quite a lot as the composition of CKD is also highly variable.

Sulphates, such as gypsum and sodium sulphate seem to activate fly ash hydration by forming ettringite or monosulphate as the reaction products. Calcium chloride was able to accelerate the strength development of a fly ash cement by forming a solid solution $C_4AH_{13}-C_3A \cdot CaCl_2 \cdot 10H_2O$.

The effect of activators depends of course on the type of fly ash it is combined with as fly ashes can vary widely in chemical composition.

- The reactivity of fly ash is highly temperature dependent as it influences the pH development and the solubility of the silicates. **Thermal activation** is a very interesting topic but it is only applicable in for example prefabrication industri. For use on an every day construction site it is hardly an option.
- The **hydration products** formed in a fly ash Portland cement are generally similar to those formed in pure Portland cement. Fly ash though changes the composition of the pore solution and the composition of the hydration product. Calcium hydroxide is consumed and the alkalinity of the pores solution decreases over time. C/S ratio of the C-S-H-phase decreases and increasing amounts calciumaluminat hydrates, monosulphate or ettringite are formed, depending on the sulphate content.

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