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Hydration of Fly ash Blended Cement

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Abstract—*During the last few decades, there has been a drastic increase in the production of coal fly ashes in the world due to increased amount of energy being generated by coal-fired power plants. Coal fly ashes rapidly accumulate and cause enormous problems of disposal unless a way can be found to utilize these by-products through resource recovery programs. Although many applications have been developed for coal fly ashes, there are still many obstacles for practices. The use of coal fly ash as a cement replacement in concrete is the most attractive one because of its high volume utilization and widespread construction. The usage of blended cement is growing rapidly in construction industry due to the considerations of cost saving and environmental protection.*

1. INTRODUCTION

Concrete is the most widely used man made construction material in civil engineering world. As the demand for concrete as a construction material increased, the world production of cement has greatly increased since 1990. The global warming is caused by the emission of greenhouse gases such as CO_2 to the atmosphere by human activities. [1] Among the greenhouse gases, CO_2 contributes about 65% to global warming. The cement industry is responsible for about 6% of all CO_2 emissions, because the production of one tonne of Portland cement emits approximately one tonne of CO_2 into the atmosphere. Although the use of Portland cement is still unavoidable until the anticipated future, many efforts are being made in order to reduce the use of Portland cement in concrete. These efforts include the utilisation of supplementary cementitious materials such as fly ash, silica fume, granulated blast furnace slag, rice-husk ash and Metakaolin, and finding alternative binders to Portland cement. [2]

2. PORTLAND CEMENT

Cementitious materials and concrete are used since thousands of years by mankind. The oldest archaeological finds of concrete in the broadest sense (mix of sand, rock fragments and cementitious binder) in human history date back to about 5,600 B.C., used in the floors of huts in Serbia [1]. The romans used mortar and concrete based on lime and pozzolana, which was the basis of the strength and durability of Roman architecture of which some buildings, such as the Panthenon, still stand today [2]. Portland cement was first patented by Joseph Aspdin in 1824 [3] and a modern version of this cement is nowadays used in numerous applications ranging from various kinds of mortar and concrete over plaster and screed to special products like tile adhesives. Today, Portland cement based concrete is the most used, solid material on earth. In the year 2011 estimated 3.4 Gt of cement were produced world-wide [4] and the demand for cement is predicted to grow in the medium-term future [5]. Obviously, an industry branch of this size is also involved in the present discussions about global warming caused by anthropogenic greenhouse gas emissions. Scientific studies show that the global warming since 1900 is at least partially due to anthropogenic components like the emission of greenhouse gases [6]. As a consequence, the reduction of the greenhouse gas emissions was decided by the United Nations Framework Convention on Climate Change (UNFCCC) conference of the parties in Cancun in 2010 in order to restrict the increase of the global average temperature below 2 °C above pre-industrial levels [7]. Scenarios that meet this 2 °C limit have global emissions in 2050 of a level, which is roughly 40% below the emissions in 1990 and roughly 60% below the emissions in 2010 [8].

3. BLENDED CEMENT

Blended cements are produced by intimately and uniformly intergrinding or blending ordinary portland cement (OPC) with one or more supplementary cementitious materials (SCMs). Most SCMs, such as ground granulated blast-furnace slag (GGBFS) or fly ash (FA), are industrial by-products. These materials are generally not used as cements by them selves, but when blended with OPC, they make a significant cementing contribution to the properties of hardened concrete through hydraulic or pozzolanic activity [9].SCMs are increasingly used in concrete because of following benefits [10]:

- Reduction of economic and environmental concerns by utilizing industrial wastes, reducing carbon dioxide emissions, and lowering energy requirements for OPC clinker production; and
- Improvements in concrete properties, such as workability, impermeability, ultimate strength, and durability, including enhanced resistance to alkali-silica reactions,

corrosion of steel, salt scaling, delayed ettringite formation, and sulfate attack.

However, experience also shows that concrete performance (such as workability, entrained air stability, and strength development) varies with the source and proportion of SCMs used. SCM concrete often displays slow hydration, accompanied by slow setting and low early-age strength. This effect is more pronounced as the proportion of SCMs in the blended cement is increased and when the concrete is cured at a low temperature. Therefore, more research is needed to have a better understanding of the effects of blended cement materials on concrete performance under different material, construction, and service conditions. Recently, the maturity concept has become widely used in Iowa for evaluating the in-situ concrete strength and for determining the appropriate time to open concrete pavement to traffic. In order to estimate concrete maturity, a datum temperature of the concrete, below which the concrete has no strength gain, is needed for calculation. The datum temperature of concrete is actually a function of concrete materials and mix proportions. However, due to lack of test data for SCM concrete, datum temperature of a typical OPC concrete, -10°C, is commonly used in the field regardless of concrete materials and mix proportions. Questions are raised on the accuracy of maturity estimation of SCM concrete based on the datum temperature of OPC concretes. In order to reduce the above problems, the present research was conducted to investigate the effects of clinker type, fly ash, and slag amount on set time, heat evolution, and strength development of SCM concrete.

4. FLY ASH

Fly ashes are heterogeneous fine powders consisting mostly of rounded or spherical glassy particles of variable SiO_2, $Al2O_3$, Fe_2O_3 and CaO. The composition of fly ash depends on the coal used, but also on the various substances injected into the coal or gas stream to reduce gaseous pollutants or to improve efficiency of particulate collectors. When limestone and dolomite are used for desulfurization of the exit gases, CaO and MgO content in fly ash will be increased. Conditioning agents such as sulfur trioxide, sodium carbonate and bicarbonate, sodium sulphate, phosphorus, magnesium oxide, water, ammonia and triethylamine are often used to improve the collection efficiency. There are also irregular or angular particles including both unburned coal remnants and mineral particles. According to ASTM C618 [11], fly ash belongs to Type F if the (SiO2+Al2O3+Fe2O3) > 70%, and belongs to Type C if 70%>(SiO2+Al2O3+Fe2O3)>50%. Both fly ashes consist mainly of spherical particles. No difference in their shape and size could be discerned. Type F fly ash particles have a clean surface while there are deposits of various condensates, such as alkalis and sulphates, on the surface of Type C fly ash particles. [12]

5. CLASSIFICATION OF FLY ASH

Fly ash is comprised of the non-combustible mineral portion of coal. When coal is consumed in the power plant, it is first ground to the fineness of powder. Blown into the power plants boiler, the carbon is consumed, leaving molten particles rich in silica alumina and calcium. These particles solidify as microscopic, glassy spheres that are collected from the power plants exhaust before they can fly away- hence the products name fly ash [13]. There are two basic types of fly ash: Class F and Class C. According to ASTM C618, fly ash belongs to Class F if (SiO_2+Al_2O_3+$Fe2O_3$) > 70% and belongs to Class C if 70% > (SiO_2+Al_2O_3+Fe_2O_3) > 50% [14]. Both these fly ashes undergo pozzolanic reaction with lime (Calcium hydroxide) created by hydration of cement and water to form calcium silicate hydrate like cement. In addition, some Class C fly ashes may possess enough lime to be self cementing in addition to the pozzolanic reaction with lime from cement hydration.[12]

Through pozzolanic activity, fly ash combines with free lime to produce the same cementitious compounds formed by the hydration of Portland cement [15].

$C_3S + H_2O \rightarrow$C-S-H + C-H (hydration of OPC).

$SiO_{2\,+}$ C-H $\rightarrow$ C-S-H (pozalonic reaction)

Due to this series of chemical reaction, rate of strength gain for fly ash concrete is relatively slower at early ages of curing. During the last few years, some cement companies have started using fly ash in manufacturing cement, which is known as "Pozzolana Portland Cement," but the overall percentage utilization remains very low and most of the fly ash is dumped at landfills [16].The benefits of using fly ash in concrete include the following [17]:

- Improved workability,
- Lower heat of hydration,
- Lower cost concrete,
- Improved resistance to sulfate attack,
- Improved resistance to alkali-silica reaction,
- Higher long-term strength,
- Opportunity for higher strength concrete,
- Equal or increased freeze thaw durability,
- Lower shrinkage characteristics, and
- Lower porosity and improved impermeability.

6. HEAT OF HYDRATION

In large concrete block, 3.05 x 3.05 x 3.05 m, the maximum temperature reached in the middle of the block was 54°C (a rise of 35°C when the start temperature was 19°C) [22.] The control concrete incorporating ASTM type I Portland cement has a temperature rise of 65°C. A slower reaction rate of fly ash, when compared to hydraulic cement, limits the amount of early heat generation and the detrimental early temperature rise in massive structures [23.]The high-volume fly ash concrete used in the Liu Centre show a rather low autogenous temperature rise [18-21.] Several investigations have shown that the autogenous temperature rise of high-volume fly ash concrete was about 15-25°C less than that of a reference concrete without fly ash. This is an advantage where thermal gradient and stress are an issue. Concretes have been made using high-volume fly ash blended cements (55 % Class F fly ash), one coarse and one finer fly ash and concrete in which the same fly ash had been added as a separate material at the mixer [23.] Blaine of the fly ashes were respectively 196 and 306 m^2/ kg. Reference concretes (ASTM type III cement and laboratory made normal Portland cement) without fly ash were also made. The autogenous temperature rise was significantly lower and slower for the concrete incorporating fly ash (both fly ash blended cement and fly ash to the concrete mixer) than for the control concretes without fly ash.

7. MECHANICAL PROPERTIES OF FLY ASH BLENDED CEMENTS

With a mineralogy consisting of $CaCO_3$, MK, CaO and C_2S activated paper sludge ash can be water-hydrated and, like blast furnace slag, exhibits hydraulic properties. Gluth et al. [24] showed that standard mortar samples (4 x 4 x 16 cm), prepared with 100% APS ash (from a co-generation power station), yielded 28-day compressive strength of 12 MPa. Bai et al. [25], analysing the hydraulic properties of standard 50-mm cubic paste specimens made from 100% activated paper sludge ash (from flue gas generated by a paper sludge combustor), observed that their compressive strength was 8% lower than in OPC. With this hydraulicity, APS ash can serve as an activator in mixes with other pozzolans (such as ground granulated blast furnace slag) [26]. Vegas et al. [27], studied the mechanical strength of (up to) 90-day 10–20% blended cement mortars prepared with activated paper sludge (700 ^{0}C/2 h). They reported that blended mortars exhibited compressive strengths comparable to and in most cases higher than the control mortar (fig 2). As noted earlier, the activation conditions of this industrial waste play a prominent role in the subsequent behaviour of blended cement matrices, especially as regards mechanical performance. Research in this regard has focused on the effect of the ash obtained at temperatures of 600–750 ^{o}C and activations times of 2–5 h on mechanical strength [28]. Up to 720-day compressive strength of 10–20% blended cement mortars (fig. 1) shows that asa rule high activation temperatures (P700 ^{0C} and 5 h) have an adverse effect on strength development over time. This effect is more accentuated with 20% additions, which would be related, among others, to the impact of dilution, free lime hydration and a higher water demand for normal consistency, as noted above. That notwithstanding, these blended cements consistently meet the 28-day mechanical requirements specified in the existing legislation on ordinary cement [29]. Other studies by Vegas et al. [30] addressed the mechanical strength of ternary cements made with OPC and a 50:50 (wt) mix of activated paper sludge ash + fly ash at replacement rates of up to 50%. They reported that the ternary cements exhibited

8. REACTION KINETICS

Pozzolan/$Ca(OH)_2$ system

The earliest research on this cementitious system [24], using DTA and XRD, identified CSH gels, mono-carbo-aluminate (C4AcH11) and calcium hydroxide as the main reaction phases in laboratory scale activated paper sludge/Ca(OH)2 pastes (50:50, wt), activated at 700–800 ^{0}C. Bai et al. [25], however, reported that paper sludge ash from a fluidised bed boiler heated to temperatures of 850–1200 ^{0}C yielded C-S-H gel, C4AH13 and carbo-aluminate as the hydration products. That finding illustrates the significant impact of activation conditions on pozzolanic reaction kinetics. Given the importance of activating temperature in the subsequent performance of these binders, a group of Spanish researchers [31-38] conducted a series of exhaustive studies on paper sludge waste generated by one and the same paper plant that uses 100% recycled paper as a raw material. According to their findings, when the sludge was activated at 500–800 ^{0}C, pozzolanic reaction kinetics differed greatly from the kinetics observed in preliminary studies. The reaction products, CSH (and CASH) gels with different morphologies and metastable hexagonal phases such as C4AH13 and C2ASH8 (stratlingite, ST) (Fig. 1), were similar to the phases identified in a pure MK/lime system. Rodriguez et al. [37] identified hydrotalcite-like (HT) structures in activated paper sludge. These hydrates exhibited carbonate/metakaolinite-like structures with CaO, SiO_2, Al_2O_3 and MgO in their composition (Table 1). CSH gels prevailed act low temperatures and short reaction times, while the content of the other hydrated phases grew with rising temperature and hydration time.

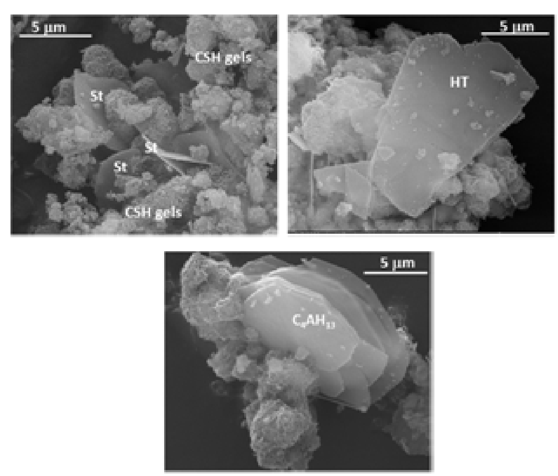

Fig. 1: Morphology of some of the hydrated phases obtained during the pozzolanic reaction in APS/Ca(OH)2 system.

At the highest temperature (800 ^{0}C), stratlingite and LDH were the most stable phases. Nonetheless, Frias et al. [41] found that industrially activated paper sludge (740–800 ^{0}C)

[39] contained high proportions (20%) of quicklime (CaO), favouring the formation of carbo-aluminate over LDH structures through the seventh day of reaction, after which the content of the former remained constant. Inasmuch as the generation of this LDH phase in activated paper sludge waste is a fairly recent discovery, further research is underway to define its structure. Garcia et al. [40] also identified traces of chabazite- and thomsonite-like zeolites with SiO_2/Al_2O_3 ratios of 2.60 after activation at 700 ^{0}C and 2 h of firing, although during the first 24 h only.

Table 1
EDX chemical analysis of 28-day hydrated phases in the pozzolanic reaction in by activated paper sludge (Rodríguez et al. 45

Oxide (%)	CSH gel	C_4AH_{13}	Hydrotalcite	Stratlingi
Al_2O_3	21.69 ± 0.52	35.09 ± 1.19	20.71 ± 0.79	31.51 ± 0
SiO_2	31.13 ± 0.79	11.63 ± 0.38	31.41 ± 0.95	29.72 ± 0
CaO	45.78 ± 0.93	53.28 ± 0.46	42.98 ± 1.18	38.77 ± 1
MgO	1.40 ± 0.17	–	4.90 ± 0.51	–
CaO/Al_2O_3	2.11	1.51	2.07	1.23
CaO/SiO_2	1.47	4.58	1.36	1.30
SiO_2/Al_2O_3	1.43	0.33	1.51	0.94

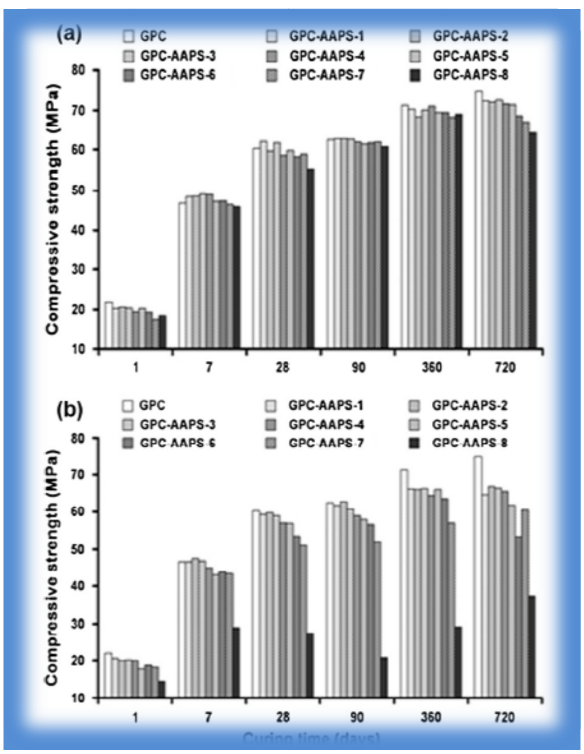

Fig. 1: Relative compressive strength vs. curing time in blended cement pastes: (a) 10% of replacement; (b) 20% of replacement (see note in

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10. CONCLUSION

Fly ash blended cement when used for making concrete will give green concrete. This will reduce the greenhouse gas emission, energy consumption and cost reduction. Although early strength development is poor but late strength is comparative to that of ordinary Portland cement concrete. Still there is need to activate the fly ash

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