DEVELOPMENT OF STUDIES AND APPLICATIONS OF ACTIVATION TECHNIQUES OF FLY ASH

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Abstract

As green building material, fly ash is advantageous to solving the question of environmental protection and energy conservation. In this paper, combined with the author's research production, the latest development of studies and applications of activation techniques of fly ash is summed up, which is being looked forward to being useful to researchers and engineers. The latest researches show that when weight of fly ash reaches 20%-80% of cement, 32.5 grade cement or C40 concrete with high properties can be prepared through using activating techniques such as adding some high-efficiency fly ash activating admixture in cement or fly ash concrete.

1. Introduction

1.1 Source of pulverized fuel ash

Pulverized fuel ash, the solid dust collected from boiler flue in power plants, is also called fly ash. In recent years its discharge per year has been nearly upon 200 million tons. Because it can obviously improve the structure and properties of cement grout for the "morphological effect," "micro-particle effect," and "active effect" it has, it has become the most frequently used mineral admixture in the cement concrete engineering and one of the prime ingredients in preparation of High Performance Concrete in China. Pulverized fuel ash generally comprises monox 45%-60%, aluminum oxide 20%-30%, ferric oxide 5%-10% [1] as well as some minor calcium oxide, magnesium oxide, sulfur oxide, etc., and its major ingredients are influenced by combustion conditions and types of coal. Aluminum oxide and monox usually exist in the state of vitreous body, and the configurations are mostly silicon-oxygen tetrahedron, aluminum-oxygen tetrahedron or aluminum-oxygen trihedron that have large degree of polymerization, high bond energy along with low activity and slow hydration rate.

1.2 Utilization of pulverized fuel ash

Comprehensive utilization of pulverized fuel ash has great value. First, through substituting partial cement, it can be used as gel materials, and thus could reduce the pollution caused by cement production and the burden of environment. For example,

when producing one-ton cement, the amount of carbon dioxide discharged is about one ton, which pollutes air much. Second, mass utilization of pulverized fuel ash can save a large quantity of energy. Furthermore, it can also improve some engineering techniques such as the enhancement of the workability of fresh concrete, the improvement of the durability of concrete and the decrease of the hydration heat of cement in mass concrete construction, etc. In a word, taking advantage of pulverized fuel ash, which is a kind of green material or environment coordination material makes social benefit and economic benefit advance together, and conforms well to the strategy of continuable development. Hence, with further understanding and study in pulverized fuel ash, focus on how to enhance its activity so as to increase its amount in concrete has gradually been one of central problems.

1.3 Source of Activity in Pulverized fuel ash

If taking into account of the chemical component, the potential activity of pulverized fuel ash is determined by the content of activated aluminum oxide and activated monox. According to the prescript of ASTM C618 in the United States, total content of SiO_2, Al_2O_3, and Fe_2O_3 must be over 70%; The JISA 6201 in Japan requires that percentage of SiO_2 be greater than 45% which is 40% prescribed in IOCT 6269 put forth in the period of the Soviet Union [2]; In most power plants in China, content of SiO_2 plus Al_2O_3 is over 60%. While in consideration of phase structure, the potential activity is related to the content of vitreous body as well as that of amorphous aluminum oxide and monox. Moreover, as for the pulverized fuel ash with the same specifications or characteristics, the major factor is the degree of fineness. Usually, higher degree of fineness corresponds to larger specific area, higher surface energy and more acting faces, which illustrate higher activity. These factors mentioned above are important to improve activity of ash coal, and should be studied specifically.

2. Evaluation of Activity

Lime absorption value method and lime strength method are generally used to evaluate activity of pulverized fuel ash.

2.1 Activity index

According to "The Pulverized fuel ash Used in Concrete and Cement," the criterion in China, activity of pulverized fuel ash is assessed by the compression strength ratio. Two shares of cement are prepared**,** one contains 30% pulverized fuel ash, and the other is ash-free. Then make mortars of the two cements with the same fluidity. The ratio of the compression strength of them calculated after 28 days is the value. It is prescribed that the value of grade must be greater than 75% and that of grade be greater than 62% [3]. Activity is considered enough when the value is up to 0.85 [4].

2.2 Index Number K proposed by Г.Н.КииГиа of USSR

$$\mathbf{K} = \frac{Al_2O_3 + CaO}{SiO_2}$$

Pulverized fuel ash can be classified into four categories according to different values of **K** [5].

In 1967, for the first time I.A. Smith in England put forward **k** [6], the gelatinization coefficient of pulverized fuel ash, which represents the amount of cement substituted by 1 kg pulverized fuel ash added in concrete as the cementing material. Its practicability is limited because many factors need to consider and thus influence its application.

2.3 The specific strength proposed by Pu Xincheng

Professor Pu Xincheng defined the "specific strength" to evaluate the contribution ratio of pulverized fuel ash activity to cement [7]. It is defined that the "specific strength of cement" is the contribution of 1% unit clinker to the strength of cement mortar in fly ash cement of certain proportion at different age, it equals the result when the compressive strength or the bending strength is divided by the amount of clinker needed with the proportion at each age. The ratio of the specific strength of cement (or concrete) with active mineral filler and cement without active mineral filler is defined as the "specific strength coefficient," and ratio of the specific strength of cement (or concrete) without active mineral filler and cement with active mineral filler is defined as the "strength contribution coefficient." The plot of volcanic ash effect on the basis of these parameters can reflect the volcanic ash effect of pulverized fuel ash accurately.

2.4 Activity ratio proposed by Lian Huizhen

Professor Lian Huizhen in Tsinghua University defined the activity ratio of pozzolanic material [8] Ka. It is the percentage of total quantity of SiO_2 and Al_2O_3 reacted in saturated limewater in the total quantity of SiO_2 and Al_2O_3 of initial materials. The experiment shows that Ka not only reflects the chemical reactivity properties of pozzolanic material, but also relates to many physical properties of the material such as other components, degree of fineness and content of crystal, etc. By this method the activity ratio can quickly evaluate the quality of pozzolanic material in 8 hours. Quick determination and evaluation of activity of pozzolanic material is the major advantage of this method.

2.5 Gel coefficient method proposed by Wang Lijiu

Professor Wang Lijiu in Dalian University of Technology defined the gel coefficient of pulverized fuel ash βwhich has better practicability [9]. It means that when adding some pulverized fuel ash whose mass is F in 1 m^3 of concrete, and at certain age, the contribution of the pulverized fuel ash to the concrete strength is βF times as that of cement.βreflects the performance of pulverized fuel ash to the strength effect of concrete. To speak of the physical meanings, it is accordant with gel efficient coefficient **k** of pulverized fuel ash. The mathematical model is given by the following:

$$\beta = Af^{x}c^{y}w^{z}$$

where f is the degree of fineness (the 45 μm square mesh sieve residue, %); c the loss on ignition (namely content of carbon, %); w the ratio of water demand; A, x, y, z are undetermined coefficients.

In accordance with the current experimental standards and international conventions, the strength ratio of pulverized fuel ash-cement mortar test piece and cement mortar test piece is the basis to determine the gel coefficientβ. Experiment results are given as follows:

$$14d:\ \beta = 2.93f^{-0.37}c^{-0.68}w^{-2.05}$$

$$28d:\ \beta = 1.19f^{-0.045}c^{-0.5}w^{-6.31}$$

$$56d:\ \beta = 1.85f^{-0.07}c^{-0.25}w^{-4.8}$$

The influence of the ratio of water demand on pulverized fuel ash quality is reflected indirectly through the two factors: the degree of fineness and the loss on ignition [10]. The experiment results show that the ratio of water demand influences the gel coefficient less. Its simplified model is as follows:

$$\beta = m(f \times c)^{n}$$

According to the experiment data:

$$14d:\ \beta = 3.58(f \times c)^{-0.55}$$

$$28d:\ \beta = 3.68(f \times c)^{-0.53}$$

$$56d:\ \beta = 5.14(f \times c)^{-0.42}$$

Generally, the age of 28 days is adopted to calculate the value of β.

Analysis of experiment results shows that the gel coefficient increases with the augment of the degree of fineness, and decreases with augment of the content of carbon. The gel coefficient of pulverized fuel ash β also increases with the augment of age. This could be explained well in the aspect of the action mechanism of pulverized fuel ash in concrete. The classification of pulverized fuel ash is based on the gel coefficient β.

3. Major Activation Techniques of Pulverized Fuel Ash and Applications

3.1 Activation of chemical substances and its application

Chemical substances are widely used to excite the potential activity of pulverized fuel ash.

3.1.1 Alkaline reagents

These substances mainly include $Ca(OH)_2$, NaOH, etc. $Ca(OH)_2$, which is precipitated through the processing of hydration, reacts with activated SiO_2 and activated Al_2O_3, then produces hydrated calcium silicate and hydrated calcium

aluminate, etc. This kind of substances can break the Si-O, Al-O bands in the vitreous body of pulverized fuel ash, and accelerate the dissolution of Si^{4+} and Al^{3+}. When reacting with gypsum, they produce AFt.

$$SiO_2 \text{ (active)} + x\ Ca(OH)_2 + aq \rightarrow xCaO{\bullet}SiO_2.aq$$

$$Al_2O_3 \text{ (active)} + x\ Ca(OH)_2 + aq \rightarrow xCaO{\bullet}Al_2O_3.aq$$

These substances are usually combined with other kinds of substances in order to enhance the effect.

3.1.2 Alkali Salt

This kind of salt involves Na_2CO_3, $Na_2O{\bullet}nSiO_2$, etc.

$$Na_2SiO_3 + nH_2O \rightarrow 2NaOH + SiO_2{\bullet}(n\text{-}1)\ H_2O$$

The hydrate of Na_2SiO_3 could maintain the concentration of alkali in solution, and on the other side its product, silica gel, would change to gel with solid properties when the gel loses water gradually. In fact this gelatinization is the process of transformation from linear structure to reticular structure.

The active effect of Na_2CO_3 is not ideal; Liquid alkali (such as water glass) is a better active agent, while has several disadvantages: inconvenient; not easy to control setting time because of fast gelatinization, and must add retardant in it which will increase the price; about 1.5% of alkali would be carried into cement.

3.1.3 Sulfate

$CaSO_4$ and Na_2SO_4 belong to sulfate. In alkaline conditions, gypsum reacts with Al_2O_3 to produce hydrated aluminium calcium sulfate crystal (AFt):

$$Na_2SO_4 + CH + 2H_2O \rightarrow CaSO_4 \bullet 2H_2O + NaOH$$

$$Al_2O_3 \text{ (active)} + 3Ca(OH)_2 + 3(CaSO_4 \bullet 2H_2O) + 23H_2O \rightarrow 3CaO{\bullet}Al_2O_3 \bullet 3CaSO_4 \bullet 32H_2O$$

The above reactions continuously consume Al^{3+}, which accelerates the hydration of pulverized fuel ash, and makes the activity fully exploited.

It's rare to adopt individually the methods mentioned above. The active effect of Na_2SO_4 is not ideal either, and the amount of alkali carried into cement is about 1.0%–1.4% [11].

3.1.4 High molecular materials

By now reports in this field are few. According to the structural properties as well as the physical and chemical index, Liu Baozhu in Anhui University developed a new type of high molecular composite material—the so-called HB high-efficiency fly-ash activating admixture, which makes the activity fully exploited. The weight percentage of this material is only about 1.5%–2.0% of that of pulverized fuel ash. As a result of usage of this polymer activator, the overall economic effectiveness of China National Petroleum Corporation and Liaoning Jinxi Oil Refinery has increased about 40% [12]. The pulverized fuel ash content in concrete has been 30%-80%, and the concrete

strength C20-C35; the pulverized fuel ash content in cement produced has reached 30%-40%, and its strength index meets the ISO PF32.5R cement standards.

3.1.5 Special ion activator

Professor Wang Lijiu in Dalian University of Technology developed a high-efficiency fly-ash activating admixture, and its mechanism is ion activation. The composite activator, which is a kind of powder with gray color, has the effect of activation as well as that of water reduction. Some effective component in it could mend obviously the poor behavior of carbon resistance and seep resistance caused by increasing the pulverized fuel ash in cement, and thus take the mechanical performance and the endurance performance of cement into consideration at the same time. There are three kinds of this admixture, common water-reduced type, water-reduction and slow-coagulation type, and high efficient water-reduced type. When its weight accounts for 7.8% of the total weight of cement and fly ash, the early strength and the final strength could increase apparently, and the overall economic effectiveness can increase 20%-35%. It was approved by the urban authenticate, and has been used widely in the large-scale buildings in the region of Liaoning and Beijing. The transformation project of Dalian Luanjin Uptown, the first building that makes use of "Dipy formwork concrete" in China, adopted the admixture and pulverized fuel ash concrete entirely. The typical mix proportion and properties of concrete are showed in Table 1. (Cement: PO32.5 cement produced by Dalian Seven Star Cement Plant; sand: river sand; fineness modulus 2.7; stone: broken stone of 5-31.5 mm; pulverized fuel ash produced by Dalian Beihaitou Power Plant; water: tap water).

Table 1: Mixture and properties of concrete

Strength scale	Mixture of concrete (kg/m^3)						Properties of concrete			
	C	F	S	G	W	DG-1	Slump (cm)	Compressive strength (Mpa)		
								7d	28d	56d
C15	103	336	634	1013	212	33.8	22	11.5	22.2	30.3
C20	171	239	664	1011	213	54.1	23	15.5	28.2	37.5
C35	292	175.5	625	1103	190.3	36.5	19	26.1	44.0	54.4

It is found in the table that if the designed age is 56 days, the grade of strength will rise 1-2 grades.

3.1.6 Composite activation

In most cases, the chemical substances mentioned above are optimizationally combined together through orthogonality experiments to complement each other. That the effect of composite admixture is much better than that of the individual

activators is just the meaning of the direction of exploitation of activating admixture. Actually the DG-1 activating admixture is also a kind of composite admixture. Professor Wang Zhenglan in Anhui Architecture and Industry Institute found that if compound component containing alkali (component of calcium pick-up), sulfate and water reduced component together, the pulverized fuel ash activating admixture produced could increase the early and the final strength apparently. The experiment results are showed in Table 2 [13]. (Cement: PO42.5 portland cement produced by Anhui Chaohu Cement Plant; sand: river sand; stone: broken stone of 5-16mm; pulverized fuel ash: ash of grade, produced by Huaibei Power Plant; water: tap water).

Table 2: Mixture and properties of concrete

No.	Mixture of concrete (kg/m^3)						Compressive strength (Mpa)			
	W	C	F	S	G	DG-1	3d	7d	28d	56d
1	0.92	1.00	1.00	3.49	6.48	0	11.4	21.9	29.5	37.2
2	0.92	1.00	1.00	3.49	6.48	0.075	16.1	23.0	33.2	49.9
3	1.92	1.00	1.50	4.36	8.10	0	8.6	13.0	20.6	30.1
4	1.92	1.00	1.50	4.36	8.10	0.075	10.9	17.9	23.1	33.4

Table 3: Mixture and properties of concrete

Strength scale	Mixture of concrete (kg/m^3)								Properties of concrete		
	W	C	F	S	G	Lime	Gyp-sum	MTN GE	Imperm-eability	Frost resist-ance	Carboniz-ation coefficient
C20	116	68	272	680	1360	17	10.9	4.1	0.8MPa	D100	1.01

By using pulverized fuel ash composite activating admixture and steam curing, Hu Mingyu in Nanchang University solved the problem that early strength of concrete with high volume pulverized fuel ash is very low. He thought that the concrete with high volume pulverized fuel ash might be widely used in the construction engineering [14]. Xi Guohua in Nanchang University prepared C20 concrete, whose mixture proportion and properties are shown in Table 3. The results show that the high volume fly ash concrete has excellent mechanical properties and durability [15].

Professor Yang Liyuan in Zhengzhou University developed the JC admixture, which is adulterated to produce the pulverized fuel ash and slag cement. It is found that when the content of pulverized fuel ash and slag adulterated is greater than 60%, the strength of cement could reach to 32.5 MPa. The cost is very low, and it is less than

that of other kinds of cement about $2 per ton. At the same time, the early strength is superior to common cement, and other properties are equal to common cement [16].

3.1.7 Other methods

The study of XieYoujun in Zhongnan University is based on the research of Red Mud, the solid waste discharged from aluminum oxide plant after the alkaline process of bauxite, to produce pulverized fuel ash activating admixture [17]. The results show that Red Mud can effectively excite the activity, and make the strength of cement mortar increase greatly. The optimum content of red mud adulterated is 3%-5%. Compared with reference test pieces, the compression strengths or bending strengths all increase 20%-40% at different ages. The strength of cement mortar with 40% pulverized fuel ash adulterated at 28 day is no less than that of pure cement mortar, and the strengths of cement mortar at 56 days and 90 days have exceeded that of pure cement mortar respectively. It is also found that the contribution of ending strength is greater than that of compression strength at 28 days.

3.2 Mechanical physical methods

Mechanical physical methods to improve the degree of fineness through method of pulverization and thus increase the surface area and surface energy greatly so as to enhance the volcanic ash reaction potency or activity. There are many reports about this subject. The action principle could be explained as follows:

- Pulverization breaks the vitreous body and increases their surface area, which makes activity higher. The pulverized fly ash not only has the effect of filling and micro-particle, but also changes from the guest to the host in hydration reaction and becomes important component. Calcium silicate and calcium aluminate generated can effectively block the capillary channels of cement mortar, which enhances the tightness of hardened cement paste.
- The pulverized fuel ash has larger surface energy as well as more effective "ball bearing" lubrication. Hence the performance of fresh cement concrete is improved, either with that of hardening concrete.
- Through pulverization, the substituting ratio is increased and the micro crack caused by the heat of hydration could be decreased also, which leads to the improvement of properties of cement and concrete.

Of course the degree of fineness cannot be increased indefinitely for the limited techniques as well as price.

3.3 Physicochemical methods

3.3.1 Low temperature calcinations

It is reported [18] that low temperature calcinations (800-1000^{o}C, 80-150 min.) of fly ash would change the chemical components and mineral structure when adding some limestone and mineralized agent. It was quenched after calcination, and then pulverized fuel ash of very high activity was obtained. When content amounts to 50%,

the 32.5 grade cement could be made. But the high cost of the calcination equipment limits the extensive use of this method.

3.3.2 Heat activation
This method is operated as follows [19]: First, blend the pulverized lime and pulverized fuel ash in a certain proportion, and then put in the autoclave. After heat activation with appropriate time and temperature, process with dehydration and cooling. The optimum conditions of pulverized fuel ash with different properties could be found out from experiments. The pulverized fuel ash obtained with this method has very high activity, and similar to the low temperature calcinations method, when the content amounts to 50%, the 32.5 grade cement could be made.

The major disadvantages of this method are its large investment and complicated techniques because the autoclave is needed.

3.3.3 Hydrothermal processing method
Yin Suhong in South China University of Technology researches on a new method of activating pulverized fuel ash, the hydrothermal processing of $NaSiO_3$ and $CaCl_2$ (or $CaCl_2$) on the mixture of pulverized fuel ash and CH. The product is called the activated ash. The mechanism is explained as follows: The PH value of solution determines the reaction rate of volcanic ash. The fact that the NaOH hydrolyzed from a little $NaSiO_3$ makes the PH value increscent, and that NaOH could be reproduced in the reaction would increase the reaction rate of volcanic ash. Meanwhile the introduced Cl^-, with strong transferring and penetrating power, could accelerate the erosion to pulverized fuel ash vitreous body. The introduction of Ca^{2+} could increase the quantity of soluble calcium, accelerate the generation of gel product in the reaction of volcanic ash, and improve the early and final strength of pulverized fuel ash concrete [20].

3.4 Mechanical activation combined with chemical activation
Utilization of mechanical activation and chemical activation at the same time makes the strength of fly ash concrete improved quite much [21].

4. Conclusions and Proposals

- All the three methods, chemical activation, mechanical activation and physico-chemical activation have good effect, and have its own advantages and disadvantages. While considered in all aspects, pulverization activation and combination of these activation methods are better than the others.
- Pulverized fuel ash should be used widely for the prominent economic benefit, environmental benefit, and social benefit it has. Utilization of it is not very balanced in China. Generally, the conditions in the south and the east are better than that in the north and the west. In the construction of

Shanghai construction engineering and Changjiang Sanxia irrigation works projects, the demand of pulverized fuel ash exceeded the supply of it. But in some other regions, the pulverized fuel ash is of no use at all.

- Now in China the utilization of pulverized fuel ash in the scientific circle is not very scientific and normative. The utilization of it is a systemic and complicated project that is related to many aspects. Although there are some achievements, the total situation in China is not very good, and more importance should be attached to it.
- The study in the durability of high volume fly ash concrete is still inadequate. The durability of concrete is a significant problem in the concrete project. There are many research developments and achievements in this subject, but profundity and normalization are not enough.

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