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Utilization of fly ash from coal-fired power plants in China

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Abstract: The rapidly increasing demand for energy in China leads to the construction of new power plants all over the country. Coal, as the main fuel resource of those power plants, results in increasing problems with the disposal of solid residues from combustion and off gas cleaning. This investigation describes chances for the utilization of fly ash from coal-fired power plants in China. After briefly comparing the situation in China and Germany, the status of aluminum recycling from fly ash and the advantages for using fly ash in concrete products are introduced. Chemical and physical analyses of Chinese fly ash samples, e.g., X-ray diffraction (XRD), ICP (Inductive Coupled Plasma) and particle size analysis, water requirement, etc. are presented. Reasonable amounts of aluminum were detected in the samples under investigation, but for recovery only sophisticated procedures are available up to now. Therefore, simpler techniques are suggested for the first steps in the utilization of Chinese fly ash.

Key words: Fly ash utilization, Aluminum recycling, Concrete, Chemical and physical analyses
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INTRODUCTION

Fly ash is the finely dispersed mineral residue resulting from the combustion of pulverised coal in power plants. It is the largest amount of industrial waste in the world. The main components of fly ash are α-quartz (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$), hematite (Fe_2O_3), magnetite (Fe_3O_4), lime (CaO), and gypsum ($CaSO_4 \cdot 2H_2O$) mainly in the form of spherical particles (White and Case, 1990; Giere *et al*., 2003).

Even though many attempts have been made to find new application fields for fly ash, for example, such as environmental and agronomic amendment (Zhang *et al*., 2004; Garg *et al*., 2005), the production of inorganic polymers (Steveson and Sagoe-Crentsil, 2005), the filler in fly ash polymer composites (Chand and Vashishtha, 2000), and the production of nanostructure materials (Paul *et al*., 2007), the utilization in concrete and cement is still the most effective one, both from economic and ecologic point of view.

The aim of this work is to investigate the qualities of Chinese fly ash for developing reutilization methods under the local conditions and demands. Four fly ash samples from a power plant in Northern China have been analyzed by chemical and physical analyses, with respect to composition and utilization in construction and building materials.

ALUMINUM RECYCLING FROM FLY ASH

The mass proportion of alumina (Al_2O_3) in fly ash ranges from 20% to 40%. Since long time ago, scientists have been focusing on aluminum recycling from fly ash due to the increasing costs of the primary metal caused by high energy consumption for its production. Many possible approaches were developed, for example, Sintering-Alkalization Method (Xie and Tang, 1996), NH_4F-Solubilization-Acidification Method with Lime (Liu and Li, 2006), Polyacrylamide Dispersant Method to produce $Al(OH)_3$ (Gui and Fang, 2004), and Solubilization by Microwave (Zhao and Tian, 2005).

India, dealing with similar problems as China with respect to increasingly high amounts of fly ash, is deeply researching on alumina recycling

(Balasubramanian *et al*., 2004; Bhattacharya *et al*., 2004). In contrast, Europe has lower interest in alumina recycling from fly ash, due to own bauxite sources and high energy consumption for the recovery processes. Energy consumption is also the reason that the above-mentioned methods on alumina recovery are only developed on lab scale. At the moment, the most promising method seems to be the substitution of aluminum by fly ash instead of its recycling, for example by "application in synthesizing low costs metal matrix composites for automotive and other applications", where aluminum is substituted by fly ash up to 10% (Rohatgi *et al*., 2006).

Nevertheless, such special application will not be the solution to reduce the increasingly high amounts of Chinese fly ash. For an effective solution, the most reasonable way to recycle fly ash will be applied in construction and building materials industry.

ADVANTAGES OF USING FLY ASH IN CEMENT AND CONCRETE

Fly ash has a successful history of use in concrete around the world for over 50 years. In the United States of America more than 6×10^6 t, and in Europe more than 9×10^6 t are used annually in cement and concrete (Ian and Lindon, 2004). Fly ash is used in all sectors of the concrete industry, covering ready-mixed, precast, and on-site applications due to many advantages summarized below (Lutze and vom Berg, 2004):

(1) Improvement of long-term strength performance and durability.

(2) Reduction of permeability, which reduces shrinkage, creep and gives greater resistance to chloride infiltration and sulphate attack.

(3) Risk minimization of alkali silica reaction.

(4) Reduction of temperature rise in thick sections of construction elements (bulk concrete).

(5) Increase of cohesion in concrete leading to reduced bleeding rate, easier compaction, better pumping properties, and improved surface finish.

Besides the technical advantages, the reuse of fly ash in cement industry has also ecological benefits like an efficient reduction of greenhouse gases. The substitution of Portland cement by fly ash reduces not only the CO_2 emission being generated during the production of clinker but also the high energy consumption necessary for the process. The replacement of 1 t of Portland cement reduces the overall CO_2 emissions by approximately 1 t (Ehrenberg and Geisler, 1997). Additionally, natural resources such as gravel and sand are saved.

FLY ASH PRODUCTION AND UTILIZATION IN CHINA

In China, the reutilization rate of fly ash is increasing, but still lower than 70%. Besides the reuse in concrete, Chinese industry is interested in recycling the high alumina content from fly ash. This belongs to the fact that 60% of the industrial Al_2O_3 needs to be imported which is about 10×10^6 t annually (Yang and Zhang, 2006).

From early 1950s, China has pursued a policy of ash utilization technology, and supported research and development activities. The utilization rate of the ash remained on a low level at around 10% until the 1980s. However, during the 1990s, the utilization rate grew significantly and reached more than 53%, and according to the government statistics, the total ash production in China in 2002 was 150×10^6 t, of which about 100×10^6 t was utilized. The predicted amounts of coal-generated fly ash in 2010 and 2020 will be 320×10^6~380×10^6 t and 570×10^6~610×10^6 t, respectively (Ian and Lindon, 2004).

In some developed areas, the situation is already better. In Nanjing City of Jiangsu Province, the utilization rate of fly ash was 100% in the past five years. In Shanghai City since 1997 the produced fly ash was also 100% reused, mostly in earthwork of road construction and wallboard materials (Wu and Zhang, 2005). In developing areas, the problem is also going to be solved. In Henan Province, the accumulated piled fly ash was 130×10^6 t until 2005, of which 34×10^6 t were produced in 2005. The reused rate of 2005 was 80%, and the half was used in cement production (CUBN, 2006).

Due to new laws, clay solid bricks will be forbidden in most of Chinese cities from 2007 on, in all urban area from 2011, and all over the country gradually (SCNPC, 1996; 2003). In 2004, the total production of bricks was 850 billion pieces, of which 500 billion pieces were solid clay bricks (Wei, 2006). The big gap caused by banning the use of solid clay bricks will be a new chance for solving fly ash disposal problems. A sharp increase in demand for masonry materials and other construction units like pavement bricks containing fly ash is expected.

CURRENT UTILIZATION OF FLY ASH IN GERMANY

On average, Germany produces 4.3×10^6 t of fly ash a year with increasing tendency. Bundesverband Kraftwerksnebenprodukte e.V. (BVK) is the federal association for marketing the by-products from power plants in Germany. The recent data collection from BVK is presented in Fig.1, showing the total amount and different utilisations in construction and building materials of marketed fly ash within Germany during the period of 1997~2005 (BVK, 2006). The figure indicates that in the last 8 years almost 100% of fly ash has been recycled with only small changes in the application areas.

More than 50% of the reused fly ash is utilized for ready-mix concrete. The second largest application area with approximate 17% is mining and dry construction materials, followed by precast units with approximate 12%.

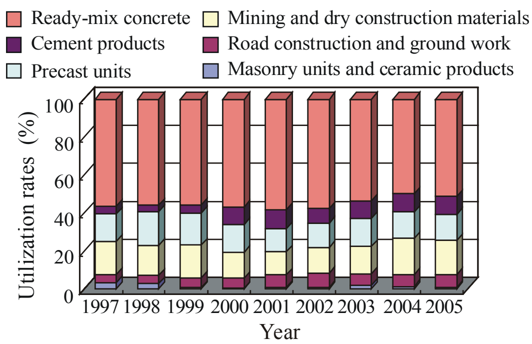

Fig.1 Utilization rates of fly ash in different application areas from 1997-2005

The driving force for the high recycling quote is the German "Act for Promoting Closed Substance Cycle Waste Management and Ensuring Environmentally Compatible Waste Disposal" (KrW-/AbfG, 1994). German fly ash fulfills strong quality criteria guaranteed by extensive technology. Cements with fly ashes are classified according to European standard EN 197-1 (2000), allowing fly ash contents up to 35%. Altogether the organized marketers and producers in the BVK counted that in future a further stabilization of their sales will be obtained by purposeful utilization of the various material properties of their products. Close cooperation between producers and marketers as well as the continuously operated extension of applications with strong focus on the changing demands of the market has been proved as substantial success factors for the utilization in high-quality construction and building materials guaranteeing high recycling rates for fly ash.

EXPERIMENTAL

To investigate the utilization possibilities of Chinese fly ash, four fly ash samples from a power plant in Northern China have been analysed.

X-ray diffraction (XRD) and Inductive Coupled Plasma (ICP) analyses were done for checking the possibility of Al-recycling. XRD has been done on one fly ash sample using spectrometer SPECTRO XEPOS. Aluminium content has been quantified by ICP spectrometry (ICP-OES Vista AX, "Varian Deutschland GmbH").

To prove the application possibilities in the concrete and cement domain, several parameters have been determined according to European standards as follows: Loss on Ignition (LOI) and free CaO have been determined according to EN 196-2 (2005) and EN 451-1 (2005), respectively; Particle size has been analysed by air jet sieving (HOSOKAWA ALPINE).

Water requirement property (EN 450), slump (EN 196-3), and particle density (EN 196-6) have been measured as well as compressive and bending strength after 28 d from mortar mixes of Chinese fly ash and cement. Bending and compressive strength have been tested with strength testing apparatus from "Toni Technik Baustoffprüfsysteme GmbH".

In addition, pavement bricks specimens made from Chinese fly ash have been prepared and their compressive strength has been measured.

RESULTS AND DISCUSSION

The XRD pattern in Fig.2 shows that the main crystalline phases of fly ash are mullite and quartz. Due to the rapid cooling at high temperature of fly ash,

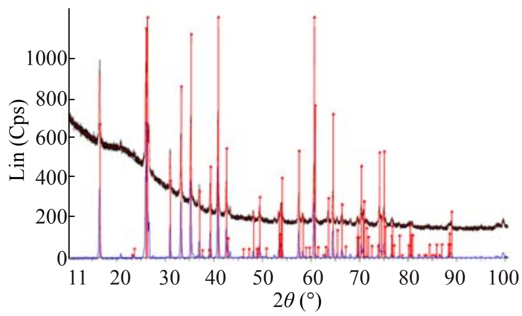

Fig.2 X-ray diffraction pattern of one Chinese fly ash sample

glass accounted for a large proportion. The broad hump in the region between 10° and 25° indicates the presence of glassy phases. The structure of Al-O-Si is very tight in glassy phases. Regarding the idea of Al-recycling, high amount of energy would be necessary for breaking the SiO_2-Al_2O_3 bond.

In Table 1 the average main composition of all fly ash samples determined by ICP analysis is presented. The high alumina content of 44% of the analyzed fly ash may give reasons for thinking of feasible recycling. Similar to aluminum recovery, alumina recycling out of an Al_2O_3-SiO_2-matrix like that in fly ash did not proceed beyond lab scale up to now for economic reasons. At present, Chinese government and industry should focus on using fly ash in the construction and building materials industry until new methods open more economic ways for recycling aluminum/alumina from fly ash in future.

Table 1 Average main composition of Chinese fly ash samples determined by ICP analysis

Oxide	Content (%)
Al_2O_3	44.0
CaO	0.9
Fe_2O_3	3.5
K_2O	0.9
MgO	0.4
Na_2O	0.3
SiO_2	43.7
TiO_2	1.5
SO_3	0.7

The high silicate content of the investigated samples of approximate 44% yields a good quality for puzzolanic reaction. The content of SO_3 in each sample is far lower than the upper limit value of 3% from both European Standards EN 450 (2005) and Chinese Standards GB 1596-79 (1979). Therefore, harmful Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) formulation (Richard, 1987) is minimized.

The results of the LOI and free CaO measurements as well as the particle size distribution determined by sieving are listed in Table 2.

Table 2 LOI, free CaO and particle size distribution of fly ash samples from China (unit: %)

Sample	LOI	Free CaO	Particle size		
			<20 μm	<40 μm	>200 μm
1	1.99	<0.010	31.2	50.5	2.5
2	12.4	<0.100	41.2	59.3	0.6
3	12.8	<0.100	39.4	62.1	0.3
4	12.8	<0.100	39.4	57.3	0.5

LOI is a parameter that when done with fly ash mainly describes the carbon content in the substance (Richard, 1987). Carbon has a low density and can absorb significant amounts of water. This means that the maximum dry density and optimum moisture content of fly ash are influenced by the LOI. Higher LOI ash is lower in density, but has higher optimum moisture contents. Generally, the lower the carbon content and the finer the ash particles, the better prospects for ash utilization, principally in cement-based formulations. When the ash is used in brick manufacturing, higher LOI is acceptable, or even welcomed, since the carbon in the ash could be burnt during the calcination process, thereby saving energy.

The LOI analysis of Sample 1 is about 2%; this result is very good for its utilization in cement referred to EN 450 (2005). But the other three samples show an LOI of about 12%, which is too high to be used in cement or concrete production. Only Chinese Standards (GB 1596-79, 1979) still allows utilization in the lowest Class III.

Free CaO is a recognized cause of unsoundness factor for concrete (Richard, 1987). The values of free CaO are all far less than 1%, which corresponds with EN 450 (2005).

Fineness has long been recognized as one of the most important characteristics of fly ash. The measured particle size distribution of the Chinese fly ash samples shows too high amounts of particles >45 μm according to EN 450 (2005), but corresponds to the requirements of Chinese Standards GB 1596-79 (1979).

Table 3 shows the results of measurements in water requirement, particle density, slump and compressive and bending strength after 28 d of cement-fly ash mortar mixtures with a ratio of 75%:25%, and of 100% cement as reference. The amount of water necessary for complete moistening of the cement, and a workable mixture with definite slump is reflected by the water requirement. Low water requirement is preferred yielding solid concrete due to low water/cement ratios.

Plasticity of fresh batches of concrete is described by slump test. High slump increases the workability and is desired if the water/cement ratio remains low. Normally, the admixing of fly ash with applicable properties leads to reduced water requirement and increased slump, due to a fluidizing effect caused by the spherical form of the fly ash particles (ball-bearing effect).

The water requirement of approximately 70% of the Chinese fly ash mortar mixtures is much higher than the typical required value of 20%~40% in Germany. A reason for this is the absorption of water by porous carbon particles as is indicated by high LOI values (Table 2). As a result, the slump testing value, in average 121 mm, is rather low compared to the reference cement sample whose value is 173 mm. In addition, the particle density of Chinese fly ash mortar mixtures being 2453 kg/m^3 on average is higher than the typical value of 2250 kg/m^3. Fly ash with lower particle density is preferred for usage in concrete.

The results indicate that the investigated Chinese fly ash cannot reach enough quality level to provide advantages in concrete fabrication according to European standards, even though the compressive and bending strengths are slightly better than the reference.

The compressive strengths for the prepared pavement brick specimen using Chinese fly ash are presented in Table 4.

Referring to the Chinese Standards JC446-91 (1991) the pavement bricks specimens have a good quality in pressure strength and fulfill the requirements of Class I for sidewalk and Class II for driveway. However, the low frost resistance caused by high LOI of the investigated fly ash must be taken into account.

CONCLUSION

Besides an already high reutilization rate of fly ash in general, China is actually interested in recycling the aluminum content in fly ash from coal-fired power plants. ICP analysis of fly ash samples from power plants in Northern China, showing an alumina content of more than 40% supports this idea. However, actual aluminium recycling from fly ash is limited to lab scale due to uneconomic energy consumption and technical restrictions. Thus, the suggestion is to focus on using fly ash in construction and building material industry until there is a promising and more economic way for recycling of the aluminum content in future.

Investigations on recycling potential of Chinese

Table 3 Construction and building material properties of mortar mixes from Chinese fly ash and cement

Sample	Water requirement (%)	Slump (mm)	Particle density (kg/m^3)	Compressive strength for mortar testing by 28 d (N/mm^2)	Bending strength for mortar testing by 28 d (N/mm^2)
Cement 100%	31.1	173	–	55.1 (100.0%)	8.3 (100.0%)
Cement:fly ash	65.6	123	2440	56.7 (102.9%)	9.3 (112.0%)
Cement:fly ash	72.0	129	2450	60.0 (108.9%)	9.5 (114.5%)
Cement:fly ash	71.8	110	2470	54.7 (99.3%)	9.4 (113.3%)

Table 4 Compressive strength of pavement bricks prepared from Chinese fly ash

Specimen	Pressure area (mm^2)	Height (mm)	Mass (kg)	Density (kg/m^3)	Breaking load (kN)	Compressive strength (N/mm^2)
1	7850	76.5	1.402	2335	405	51.6
2	7850	70.5	1.295	2339	441	56.2
3	7850	76.4	1.400	2334	398	50.7

fly ash in cement show a promising high silicate content of more than 40% yielding good puzzolanic reactions. Unfortunately, high LOI values of three from four samples, which all exceed 12%, restrict the chances of application. Moreover, the fineness was found to be quite coarse and just in the range of the acceptable limit. Most European standards for using fly ash in cement and concrete industry are not fulfilled.

Chinese standards still support the utilization of fly ash in cement, concrete in Class III, and in wall bricks in Class II or III. However, with respect to the environment and regarding the fast increasing Chinese economy and globalisation, Chinese legislations and standards are proposed to be, and should be, more stringent in order to correspond with the standards in developed countries.

Besides legislation, the operation of power plants in China should improve to actual state-of-the-art. Careful input control, efficient burn out, and an additional feed of suitable components to improve a high quality of fly ash with low LOI will ensure higher standards in the utilization of Chinese fly ash. For the time being, the best chance is to replace solid clay bricks which become banned from 2007 on.

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