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Advances in Fly Ash Based Geopolymer

Li Yang[1], Fu Yong[1,2]
[1]School of Resources and Environment, Henan Polytechnic University, Jiaozuo 454003, China
[2]Henan Jianbo New Material Science and Technology Limited Coporation, Zhengzhou 450000, China

ABSTRACT: The current research on the resource utilization of fly ash is summarized, the physical and chemical properties of fly ash and some of the research results of fly ash based geopolymers in resource utilization are introduced, the current situation of the application of fly ash geopolymers is discussed, and the main problems and development trends in high-value utilization are analyzed.

KEYWORDS: fly ash, geopolymer, resource utilization, research advance

0. QUOTES

Today, the main source of electrical energy in China is still coal-fired thermal power generation. Fly ash is an industrial solid waste resulting from the combustion of various inorganic and organic components at high temperatures during the coal-fired thermal power generation process [1]. Despite China's increasing use of environmentally friendly energy sources for electricity and heat production, such as tidal, wind and solar energy, the demand for coal burning remains high, with raw coal production reaching 3.75 billion t in 2019 alone [2]. However, while the amount of fly ash generated increases year by year, the amount of comprehensive utilization does not change much, with the amount of fly ash generated by key published survey industrial enterprises in 2015, 2016, 2017, 2018 and 2019 being 440, 450, 490, 530 and 540 million t, respectively, and the amount of comprehensive utilization being 380, 380, 380, 380, 400 and 410 million ton [3-7]. The amount of fly ash stockpiles is increasing year by year, resulting in an increase in pressure on its disposal year by year. Reasonable resource utilization of the piled fly ash can create huge economic value and realize high value utilization of resources while effectively solving the environmental pollution problems.

1. PROPERTIES OF FLY ASH

1.1 Physical properties

Fly ash from thermal power plants in China is mainly spherical, with particle sizes ranging from 0.5 to 200 μm. It is mainly composed of silica, alumina, ferrous oxide, iron oxide, calcium oxide, titanium oxide and other components.

Fly ash is composed of solid or hollow amorphous spherical particles, irregular unburned carbon particles and mineral particles such as mullite, quartz and hematite. It is normally off-white or grey-black in colour, often with a particle size of 0.5 to 300.0ųm and a density of 1.0 to 1.8 g/cm3 and 2.1 to 2.6 g/cm3 depending on the density [8]. The fineness and particle size of fly ash are closely related to its properties. The pH value of fly ash ranges from 1.2 to 12.5, but most of it is alkaline [1].

1.2 Chemical properties

Different types of fly ash differ in their chemical composition content Table 1 compares the chemical composition of lignite fly ash, sub-bituminous coal fly ash and bituminous coal fly ash [1]. It is clear that sub-bituminous coal fly ash contains high levels of silica and aluminium trioxide, bituminous coal fly ash has high levels of iron trioxide and lignite fly ash has high levels of calcium oxide and magnesium oxide. In addition to this, the American Society for Testing and Materials (ASTM) classifies fly ash into two types, as shown in Table 2. The pH value of fly ash ranges from 1.2 to 12.5, but most of it is alkaline [1]

Table 1. Main chemical composition of different types of coal combustion fly ash (mass fraction/%) [1]

Type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
Bituminous coal	20 ~ 60	5 ~ 35	10 ~ 40	1 ~ 12	0 ~ 5	0 ~ 4	0 ~ 4	0 ~ 3	0 ~ 15
Sub-bituminous coal	40 ~ 60	20 ~ 30	4 ~ 10	5 ~ 30	1 ~ 6	0 ~ 2	0 ~ 2	0 ~ 4	0 ~ 3
Lignite	15 ~ 45	10 ~ 25	4 ~ 15	15 ~ 40	3 ~ 10	0 ~ 10	0 ~ 6	0 ~ 4	0 ~ 5

Table 2. Classification of fly ash

Type	Classification
High calcium Class C fly ash	$SiO_2 + Al_2O_3 + Fe_2O_3 \geq 50\%$
Low calcium Class F fly ash	$SiO_2 + Al_2O3 + Fe_2O_3 \geq 70\%$

1.3 Mineral composition of fly ash

Fly ash consists mainly of crystalline and amorphous phases, with the crystalline phase including quartz and mullite phases. The amorphous phases include vitreous, carbon and secondary limonite. The quartz phase is largely inactive and the vitreous body contains more active material, thus the activity of fly ash is mainly dependent on the vitreous body. Table 3 shows the approximate mineral composition of fly ash.

Table 3. Range of mineral composition of fly ash [9]

Name of mineral	Moray Stone	Cryogenic Quartz	High iron content glass beads	Low iron content glass beads	Carbon content	SiO_2 in glassy state	Al_2O_3 in glassy state
Content range	11.3 ~ 29.2	1.1 ~ 15.9	0 ~ 21.1	42.2 ~ 70.1	1.0 ~ 23.5	26.3 ~ 45.7	4.8 ~ 21.5
Average	20.4	6.4	3.2	59.8	8.2	38.5	12.4

2. CURRENT STATUS OF FLY ASH BASED POLYMER RESEARCH

As a class of silica-aluminium inorganic polymers, geopolymer are receiving increasing attention for their excellent mechanical properties and low energy and carbon footprint. The synthesis of geopolymer begins with the excitation of silicon and aluminium-rich mineral raw materials by an alkaline solution (e.g. sodium hydroxide, potassium hydroxide, sodium silicate, potassium silicate solution, or a mixture of solutions), followed by the polymerisation of the silicon and aluminium oxides released by dissolution [10].

In order to solve the problem of massive fly ash accumulation and to achieve the environmental protection objective of treating waste with waste, the use of fly ash as the main raw material for the preparation of geopolymer has also become a current research hotspot. Fly ash-based geopolymer are produced by using fly ash as the basic raw material and using exciters such as acids, bases and salts to increase the activity of the fly ash, thereby polymerising to form a three-dimensional mesh of inorganic gelling materials with Si-Al-O cross-linking.

In the preparation of fly ash based polymers, parameters such as the conditioning regime, the type of exciter and the ratio of raw materials become the main factors affecting the final properties of the product [11]. In order to optimise the performance of fly ash-based polymers and to improve their deficiencies, researchers usually add additional slag, steel slag and kaolin to the raw materials to increase their compressive strength and improve their curing properties, and also add foaming agents and stabilisers to prepare new lightweight insulation materials or to produce corrosion-resistant materials.

3. COMPREHENSIVE UTILIZATION OF FLY ASH BASED GEOPOLYMER

3.1 Adsorption and solidification of heavy metals

Several studies in recent years have shown that soluble heavy metals such as Ba, Cd, Co, Cr, Cu, Nb, Ni, Pb, Sn and U in fly ash, slag or other industrial and residential waste can be immobilised in the three-dimensional structure of fly ash-based polymers, with the main mechanisms including physical encapsulation and chemical stabilisation.

Li Yang [12] investigated the optimum curing concentration of fly ash based polymer for Pb^{2+} and the effect of various factors on the physicochemical properties of the cured body, and compared the curing effect with that of cement cured body. The results showed that the optimum curing concentration of fly ash-based polymer for Pb^{2+} was 2.0%. Qiu Xiumei et al [13,14] from China University of Geosciences showed that fly ash based polymers were able to cure Cu^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+} to some extent.

Liu Sifeng et al [15] investigated the mechanism of Cr^{3+} sequestration in fly ash based polymers using Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS) analysis, and the results revealed that Cr^{3+} is involved in the polymerisation of silicic acid structures in fly ash based polymers, and that Cr^{3+} sequestration in fly ash based polymers is not only a physical wrapping effect, but is mainly the result of a chemical reaction.

Liu Ze, Zhang Yuan et al [16] demonstrated that the CFA-based matrix polymer and Zn^{2+} have good compatibility and dense microstructure, the strength of 90 d blank samples reached 85.2 MPa, and the strength remained about 50% at 1.5 wt% Zn^{2+} doping, the CFA-based matrix polymer can achieve good curing of large Zn^{2+} doping, and the curing rate is above 99%.

Mao Linqing, Wu Shuanglei et al [17] showed that the solidification of chromium in sludge by fly ash-based polymers can be attributed to the formation of hydrated sodium silicate aluminate gels and the solidification and adsorption of chromium ions by zeolites during their hardening process.

3.2 Preparation of new building materials

3.2.1 Used for the manufacture of foamed fireproof insulation materials

Traditional inorganic wall insulation materials are mainly made of cement foam, which has the advantages of good insulation performance and durability, but the production process is complicated and the price is high; while organic synthetic insulation materials have good insulation performance, but there are safety hazards due to their poor fire resistance, which also limits its use. Therefore, there is an urgent need for a new wall insulation material that is safe, energy-saving, green and economically viable. The matrix of geopolymer material, formed by foaming technology to form geopolymer porous inorganic material, has low preparation cost, high temperature resistance and low thermal conductivity, which can be used as thermal insulation material.

Liu Ruiping [18] et al. prepared a fly ash-metakaolin base geopolymer by selecting three different foaming agents through alkali excitation reaction at low temperature using fly ash, metakaolin, sodium hydroxide and water glass as the main raw materials. The results showed that the foaming effect of hydrogen peroxide was better than that of aluminium powder and sodium perborate; the optimum conditions for the preparation of the geopolymer were 0.5% hydrogen peroxide content, 40°C curing temperature, 70% curing humidity and 7d curing time; the bulk density of the obtained geopolymer was 0.985g/cm3, the compressive strength was 8.9MPa, the thermal conductivity was 0.10W/(m-K) The geopolymer has a very good thermal insulation and heat preservation effect.

Wang Xia et al [19] prepared lightweight fly ash-based polymer foams with different grade densities by regulating the amount of blowing agent and the ratio of graded ash. Under the same conditions, the higher the amount of blowing agent, the lower the dry density of fly ash-based polymer foams; Micro CT pore size data showed that the larger the average pore size of fly ash-based foams, the higher the total porosity, open pore rate and closed pore rate, and the predominantly open pores, all with lower thermal conductivity, are very good insulation materials.

Kang Yixing [20] et al. prepared foamed geopolymers by blending lithium slag into circulating fluidized bed fly ash, using sodium hydroxide and water glass as the exciter and adding hydrogen peroxide. The test results showed that the lithium slag dosing had no significant effect on the apparent density of the foamed geopolymer; however, the lithium slag contained gypsum phase, whose swelling would destroy the structure of the foamed insulation material, causing the compressive strength of the geopolymer to decrease with the increase of lithium slag dosing and to increase with the extension of the curing time, and the highest compressive strength of 0.48 MPa was achieved after 28 d of curing at 10% lithium slag dosing.

Shao Ningning [21] used SDBS-based foam stabilizers and calcium stearate to optimize and adjust the bubble structure by comparing the use of HGB hollow glass beads doped with SDBS-based foam stabilizers for the adjustment of bulk weight and strength to achieve its high performance. It is concluded that calcium stearate is much more effective than SDBS-based stabilizers in adjusting the pore structure of alkali-excited foams; by using both HGB doping and hydrogen peroxide foaming in parallel, the alkali-excited gelling materials can be prepared with ultra-lightweight, high reinforcement, and ultra-low thermal conductivity, corresponding to the optimal material performance (the correlation between bulk weight class - compressive strength - thermal conductivity) of 200 kg/ m^3 vs. 1.4 to 1.6 MPa vs. 0.0522 W/(m·K).

In summary, traditional geopolymer can be prepared by adding foaming agents to create uniform pores within them, which can be supplemented by the use of light aggregates and other means to greatly reduce the mass and density of the material. At the same time, the good thermal and fire resistance properties of the material make it a good prospect for development in the construction sector.

3.2.2 Used for the manufacture of corrosion resistant materials

Ordinary silicate cement concrete contains calcium hydroxide, calcium sulphate and C-S-H gels which swell in volume and reduce strength in an acidic environment, making the surface prone to cracks and voids, thus accelerating the degradation of the building's protective coating. Geo-polymer concrete can be used in the construction industry to produce acid resistant materials due to the presence of a large amount of Si-O and Al-O structures, which do not react with acids at room temperature and have low production energy consumption and low CO_2 emissions compared to cementitious materials.

Ni Chenglin [22] showed that the mixing of microglauber and fly ash into geopolymers reduced their mass loss in acidic solutions, and the effect was more obvious as the acid leaching cycle was extended. The mass loss when double blending 10% microsilica fume and 12% fly ash was less than when blending alone.

Zhang Dengfeng [23] et al. used Class I fly ash from Shangdu Power Plant in Zhenglanqi to optimize the design parameters of cement-concrete mix ratio. The results showed that the range of fly ash admixture between 20% and 30% could reasonably control the water-cement ratio of concrete without being too large, and also ensure excellent frost resistance, chloride ion penetration resistance and sulfate erosion resistance of concrete.

Song Jinbo [24] et al. prepared a new type of geopolymer sand filter pipe by using partial kaolin, fly ash, clay, water glass, slag, quartz sand and porous agent as raw materials to address the problems of poor toughness, easy aging and environmental pollution in the manufacturing process of epoxy resin sand filter pipe. The results showed that the new geopolymer sand filter pipe was prepared under the condition that the mass ratio of water glass to slag was 0.30, the sand content was 70% and the addition of porous agent zinc powder (200 mesh) was 1.6%, which overcame the shortcomings of the original sand filter pipe manufacturing process and the compressive strength could reach 10 MPa, The sand filter pipe has a good resistance to the effects of water heat treatment. The sand filter pipe has good resistance to alkali, oil and salt water erosion, which can effectively extend the validity of sand control, but it is not resistant to hydrochloric acid corrosion and should be treated before application.

Zhao Jialin [25] et al. investigated the properties and composition of geopolymers prepared from kaolin and fly ash. The specimens were tested for compressive strength and compared with dried specimens by immersing them in acidic solutions, alkaline solutions and water for 7, 28 and 40 days after three years of curing at room temperature. The experiments showed that the strength of the geopolymer did not change much after three years of soaking in weak acids and bases, indicating that it is relatively resistant to weak acids and bases.

3.2.3 Used for the manufacture of environmentally protection materials

Compared to normal concrete, fly ash based polymer concrete on the one hand reduces greenhouse gas emissions by reducing the amount of cement used, while on the other hand the preparation of the alkali exciter and the energy consumed during high temperature curing increases greenhouse gas emissions.

Pu Yunhui [26] compared the greenhouse gas emissions of producing 1 m3 of fly ash-based geopolymer concrete with that of ordinary concrete. The study showed that the carbon dioxide equivalent of geopolymer concrete was 15% lower than that of ordinary concrete, and that the greenhouse gas emissions from geopolymer concrete were mainly concentrated in the preparation of alkali activator and post-high temperature curing, which accounted for about 90% of the total emissions.

4. PROBLEMS AND PROSPECTS

The preparation of geopolymer from fly ash is a promising pathway for the resourceful use of solid waste. However, due to various limitations in technology and cost, there are still many problems that need to be solved for large-scale resource utilization. For example, the price of single-component excipients with high mechanical properties for the preparation of alkali-excited geopolymer is now commonly used. In addition, the preparation of fly ash base polymers requires several hours of maintenance at high temperatures if early strength is to be improved, resulting in high overall costs, which is not conducive to the large-scale industrial utilization of fly ash.

Alkali-initiated geopolymer have characteristics that make them difficult to control in terms of setting time, for example, slag-based polymers usually take too long to set, while the setting time of fly ash-based polymers is significantly reduced by increasing the amount of initiator, both of which are difficult to meet the requirements of building construction standards and require further research. In addition, alkali-excited geopolymer are prone to shrinkage during curing, and the shrinkage resistant admixtures now commonly used in cement-based concrete are difficult to improve on this situation, making it difficult to achieve large-scale industrial applications.

The use of fly ash to prepare geopolymer can achieve the social value of recycling resources and economic environmental protection. While making full use of industrial solid waste to open up a new avenue of utilization and research and development, it can also reduce the environmental pollution and large amount of land occupation caused by the accumulation of these industrial wastes. As the raw material of this inorganic polymer is based on industrial waste, reducing the cost and energy consumption of the material, this material can be used as a new green energy-saving building material. Moreover, geopolymer materials have excellent tensile and flexural strengths, and higher modulus of elasticity and work of fracture compared to cement materials can meet the construction requirements of some special application infrastructures, which have great development potential and application prospects.

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