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An investigation of the microstructure and durability of a fluidized bed fly ash–metakaolin geopolymer after heat and acid exposure

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This study aims to investigate durability and microstructure of fluidized bed fly ash and metakaolin based geopolymer exposed to elevated temperatures and acid attack. Geopolymer specimens were prepared by combination of fly ash and metakaolin activated by sodium silicate and sodium hydroxide solutions and were cured in microwave radiation environment plus a heat curing period. Compressive strength and several key durability parameters for geopolymer and ordinary Portland cement (OPC) were assessed and compared. Microstructure formation and development was characterized in terms of morphology and pore structure as well as simulation.

The experimental results reveal a dense microstructure of geopolymer compared to OPC. In terms of resistance to the acidic solution and elevated temperatures, geopolymer is superior to OPC as indicated by the relatively lower strength loss and lower mass change. Compressive strength shows a dramatic drop in OPC while geopolymer shows a strength increase after 400 °C. The mass loss curves of geopolymer are similar to OPC, but it shows relatively lower mass loss compared to OPC. The result of saturated water absorption after 28 days curing indicates less water absorption in geopolymer before and after thermal and acid exposure. Durability of geopolymer is demonstrated by monitoring the pore structure.

1. Introduction

Cement production is associated with the emission of considerable amount of greenhouse gas [1]. The amount of carbon dioxide released in the manufacture of cement is about one ton for one ton cement clinker. Therefore, it is considered vital to search for alternative low CO_2 emission binders for concrete in order to reduce its carbon footprint and the development of alternative binders utilizing industrial by-products is one of existing strategies.

Geopolymer is such an emerging alternative binder, which is prepared using by-product materials such as fly ash (by-product of coal combustion in thermal power plants with an average size of less than 20 μm and low bulk density (0.54–0.86 g/cm^3), high surface area (300–500 m^2/kg) and light texture with spherical in shape and consist of solid spheres, cenospheres, irregular-shaped debris and porous unburnt carbon), blast furnace slag (produced when iron ore is reduced by coke at about 1350–1550 °C in a blast furnace. It normally contains more than 95% of glass. Generally, they are ground to fine powder, called ground granulated blast furnace slag), metakaolin (produced by calcining kaolin at 650–800 °C. The main components are amorphous Al_2O_3 and SiO_2 with high pozzolanic activity. Besides the filling effect, metakaolin reacts with calcium hydroxide, which is one of the hydration products of Portland cement, to form calcium silicate hydrate gels) or a combination of them instead of cement and results in less CO_2 emission to reduce the environmental impact of the cement production.

During the last decade, increased research efforts [2–9] have been directed to this area due to the wide range of potential applications of these by-product materials, which has gained increasing attention due to the energy conservation, economic and environmental considerations.

By-products of industry are some of the most complex and abundant of anthropogenic materials. They cause water and soil pollution, disrupt ecological cycles and environmental hazards [10]. The current worldwide annual production of fly ash, one of such by-products, is estimated around 750 million tones [11]. At present, only a minor part of this material is utilized (20–30%) on

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worldwide basis, while the rest is still disposed of in landfills, thus contributing to the pollution of soil, water and air.

The environmental impact of coal fly ash is well known for its massive generation, large usage of land for disposal and short and long term impact on surrounding areas. The principal environmental concern stems from the possible leaching of heavy metals and organic compounds and their migration into ground water or nearby surface water. In addition, fly ash could also affect human health through direct inhalation or ingestion of airborne or settled ash. The unproductive use of land and its maintenance results in long-term financial burden [12].

Aggressive efforts have been undertaken recently to recycle fly ash [13–17] in concrete production as mineral admixture, soil amendment, zeolite synthesis, and as filler in polymers. However, these applications are not sufficient for complete utilization of fly ash, thereby it is imperative to develop new recycling techniques for fly ash.

The concept of sustainable solutions for fly ash is closely linked with technologies with aligned vision for environment, economy and societal goals. Fly ash was widely used as the source material to manufacture geopolymer products owing to its aluminosilicate composition, fine size, significant amount of glassy content and availability across the world [14,18–20]. This is one of the existing important strategies and it is believed to be the sustainable solution for utilization of fly ash. It will consume large part of fly ash and relieve the pollution of soil, water and air.

The term geopolymer was introduced in 1970 by Davidovits, who made a significant breakthrough in understanding and development of binders from metakaolin and alkaline metal solutions. Geopolymer was originally applied to three-dimensional aluminosilicate materials formed by condensation of a solid aluminosilicate source such as dehydroxylated kaolinite (metakaolin) with an alkali silicate solution under highly alkaline conditions [21].

This new material was likely to have enormous potential to become an alternative to Portland cement and it is receiving increased attention due to the need of new binders with enhanced durability performance [22–28].

Although different source materials can be used to prepare geopolymer binders, fly ash, which provides the greatest opportunity for commercial utilization and has the potential to reduce the carbon footprint, has been extensively used and found to be the most practical source material suitable for concrete applications due to the plentiful worldwide raw material supply, which is derived from coal-fired electricity generation [29].

Excellent properties of fly ash-based geopolymer concrete have been reported in the last decades [30–38]. Fly ash-based geopolymer concrete has properties favourable for its potential use as a cementitious material due to excellent durability aspects. Some authors [39–43] have reported good engineering properties of geopolymer concrete that were favourable for its use as a construction material.

Geopolymer can be composed from metakaolin or wastes, such as fly ash, slag, and tailing [44–48]. Geopolymer can be used as building materials and fillers due to their flameproof characteristics [49–51]. In addition, geopolymer has several other advantages such as high strength, acid/alkaline resistance and heat resistance [44].

Having more outstanding mechanical properties and environmental friendliness, geopolymer, is considered to be a new cementing material with widely potential application value in construction. With the aim of reducing consumption of non-renewable raw materials whilst increasing the use of industrial by-products (residue), research has recently focused on the alkali activation of metakaolin and fly ash.

Some authors [52–57] explored some basic aspects of metakaolin or fly ash-based geopolymer activated using sodium alkali for high-temperature applications. They estimated that the structure was stable enough to resist to high temperatures.

On balance, ash-based geopolymer was prepared based on a precursor derived from fly ash, generally consisting of spherical particles, glassy or amorphous as well as crystalline phases.

Recently, increased utilization of fluidized bed technology led to the production of a great amount of fluidized bed fly ash including little glassy spherical particles, which forms by burning coal gangue in a low temperature. Circulation fluidized bed combustion is an advanced, clean and reliable coal firing technology for power generation. There are many unreacted CaO, desulphurized products $CaSO_4$ and a little $CaCO_3$ remaining in the fluidized bed fly ash.

Coal fly ash is typically found in the form of coarse bottom ash and fine fly ash, which represent 5–15 and 85–95 wt% of the total ash, respectively. Bottom ash refers to the ash that falls down through the airflow to the bottom of the boiler and is mechanically removed. The term coal fly ash is often used to refer to fine fly ash, particles of which are captured from flue gas and collected by electrostatic or mechanical precipitation.

Bottom ash is a coarse, granular, incombustible by-product that is collected from the bottom of furnaces that burn coal for the generation of steam, the production of electric power, or both. Bottom ash is coarser than fly ash, with grain sizes spanning from fine sand to fine gravel.

In general, fluidized bed fly ash differs from coal fly ash in terms of particle shape, chemical composition and amorphous phase content. Fluidized bed fly ash particles are approximately 1–300 μm in size, with irregular shape, while coal fly ash particles are normally slightly finer at approximately 1–200 μm in size and the content of amorphous phase is usually higher than that of fluidized bed fly ash. Coal fly ash is widely used as pozzolanic material for partial replacement of Portland cement due to its spherical shape and high reactivity. Comparing with coal fly ash, fluidized bed fly ash has higher contents of lime (CaO), gypsum ($CaSO_4$) and crystalline phase thus its usage as pozzolanic material is limited. The unique thermal history, featuring low combustion temperatures of 800–950 °C, makes fluidized bed fly ash differ greatly in physical and chemical characteristics from coal fly ash, whose typical firing temperatures are 1200–1400 °C.

It is well acknowledged that compositions and structure of precursors have significant effects on performance of geopolymer. Previous research efforts about the relevant topic mainly focused on cement paste [58–70], or preparation and properties of geopolymer but below 1000 °C, and acid attack was not mentioned [71–76]. Existing references on the utilization of fluidized bed fly ash to prepare geopolymer and the durability aspects investigation are scant, and the ash used belonged to high calcium fly ash, there have been very few published references on fluidized bed fly ash based geopolymer exposed to elevated temperature at 1000 °C from ambient temperature and acid attack.

In the present study, geopolymer specimens were prepared by combination of fluidized bed fly ash and metakaolin activated by alkaline activator and were cured in microwave radiation environment. Compressive strength was investigated and several key durability parameters for geopolymer and ordinary Portland cement (OPC) were assessed and compared. Microstructure formation and development was characterized in terms of morphology, pore structure and simulation.

2. Experimental

2.1. Materials

Fluidized bed fly ash was provided by Shenhua Junggar Energy Corporation in Junggar, Inner Mongolia, China. Metakaolin was obtained from Yunnan, China. The chemical analysis of those raw