Construction and Building Materials 129 (2016) 79–88

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of cattle manure ash on workability and mechanical properties of magnesium phosphate cement

Peng Feng [a], Shuguang Zhou [b,*], Juan Zhao [b]

[a] Postgraduate Brigade, Logistics University of Chinese People's Armed Police Force, Tianjin 300309, China
[b] Department of Architecture Engineering, Logistics University of Chinese People's Armed Police Force, Tianjin 300309, China

HIGHLIGHTS

- Workability and mechanical properties of 3 types of MPC-CMA mixture were studied.
- MPC mixed with CMA produced at 800 °C (MPC-CMA800) performed best.
- CMA promotes the formation of struvite in the hydration reaction of MPC.

ARTICLE INFO

Article history:
Received 8 July 2016
Received in revised form 31 October 2016
Accepted 1 November 2016
Available online 8 November 2016

Keywords:
Cattle manure ash
Magnesium phosphate cement
Sustainable cement
Mineral admixture

ABSTRACT

Cattle manure ash (CMA) is an industrial waste produced from the combustion of cattle manure. This research examined the effect of added CMA produced at combustion temperatures of 500 °C, 650 °C and 800 °C on the workability and mechanical properties of magnesium phosphate cement (MPC). The obtained data indicates that CMA decreases workability and mechanical properties of MPC to which it is added. However, relatively higher combustion temperature in CMA preparation can diminish the adverse effect that CMA exerted on mechanical properties and workability of MPC. CMA promotes the formation of struvite in the hydration reaction of MPC.

1. Introduction

With the continuous consumption and depletion of fossil fuels, various countries are seeking alternative energy sources. Biomass energy is of great interest and has developed rapidly around the world. In 2014, the world's biofuel production rose 7.4%, and the proportion of renewable energy in global energy consumption reached 3.0% [1]. In China, there are now more than 200 biomass power plants. Clear support for biomass power by the 13th Five-Year Plan of China is expected to result in 1000 plants by 2020 [2,3].

Cattle manure is a source of biomass energy that is available in large quantities. In 2014, there were 105.78 million cattle in China producing an estimated 500 million metric tons of dry cattle manure every year [4,5]. This amount of cattle manure would occupy vast frontiers of land and negatively influence environmental quality if not effectively managed. At present in China, the management of cattle manure follows three main methods of recycling: either as an energy source, as feed or as fertilizers [6,7]. Studies have found that there is abundant potential energy in cattle manure [8]. As a result, power generation through burning cattle manure as fuel has become a promising method by which to utilize cattle manure, as has been successfully practiced in many places such as the Imperial Valley in southern California and the Andalusia region in southern Spain [9,10].

The residual from combustion of cattle manure is cattle manure ash (CMA), which must be disposed or utilized. Research [9–13] has proved that CMA can replace part of ordinary Portland cement as a mineral admixture (similar to fly ash, FA). Appropriate utilization of CMA will not only protect the environment directly but also reduce the cost of treating cattle manure. Carlin et al. [14] established an economic model to describe the burning of coal in combination with cattle manure-based biomass, and showed that a

Abbreviations: CMA, cattle manure ash; CMA500, cattle manure ash produced at a combustion temperature of 500 °C; CMA650, cattle manure ash produced at a combustion temperature of 650 °C; CMA800, cattle manure ash produced at a combustion temperature of 800 °C; MPC, magnesium phosphate cement; FA, fly ash.

* Corresponding author.
E-mail address: zhouzsg_1019@sina.com (S. Zhou).

http://dx.doi.org/10.1016/j.conbuildmat.2016.11.001
0950-0618/

cattle biomass burn system retrofitted on an existing 500 MW_e coal plant would have a net present worth of 80.8 million USD.

Magnesium phosphate cement (MPC) is air-hardening gelled material composed of hard-burned magnesia, phosphate and a retarder. MPC has high early strength, good cohesiveness, wear resistance and many other advantageous properties. MPC can also solidify industrial waste, which makes MPC an appropriate material to mix with CMA [15,16].

Most researchers [16–18] believe that the hydration reaction of MPC is an exothermic reaction on the basis of a neutralization reaction, which releases much hydration heat with a fast reaction rate. In return, hydration heat accelerates the reaction rate. When MPC is mixed together with water, considerable amounts of NH_4^+, K^+, PO_4^{3-}, and H^+ are released. When MPC powder meets H^+ ions in the solution, Mg^{2+} ions are released at the surface of magnesia (MgO) particles; then, the Mg^{2+}, NH_4^+, K^+, and PO_4^{3-} ions form a complex amorphous magnesium phosphate hydration gel, crystallizing and precipitating gradually [19]. Although products of the hydration reaction are still controversial, the main hydration products are widely recognized to be struvite ($MgNH_4PO_4{\cdot}6H_2O$) and k-struvite ($MgKPO_4{\cdot}6H_2O$). The relevant equations for these chemical reactions are as follows [16]:

$$MgO + NH_4H_2PO_4 + 5H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \quad (1)$$

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O \quad (2)$$

In China, the application of MPC currently is very limited. An important research direction is to improve the performance and reduce the cost of MPC. Moreover, many studies have aimed to promote the properties of MPC by adding a mineral admixture or processing the raw materials. At present, the common solution for this issue is to use a retarder, FA and hard-burned MgO powder [15,19]. According to some research [19–21], calcination at temperatures exceeding 1300 °C can reduce the activity of MgO particles and increase the compressive strength of MPC. As a result, the setting time of MPC will increase. Previous research [22–24] has shown that borax can effectively prolong setting time of MPC, but can obviously decrease its early strength.

This research studied the effect of CMA produced at three combustion temperatures on the workability and mechanical properties of MPC.

2. Materials and methods

2.1. Materials

In the experiments, hard-burned MgO, ammonium dihydrogen phosphate ($NH_4H_2PO_4$ or ADP), potassium dihydrogen phosphate (KH_2PO_4 or KDP), and borax ($Na_2B_4O_7{\cdot}10H_2O$) were mixed together as the MPC.

Hard-burned MgO powder used in this work was produced by a company in Yingkou, Liaoning province, China. It was calcinated at 1600 °C for 4 h before being ground to four grades of powder having different specific surface areas. The chemical compositions are given in Table 1.

Industrial grade $NH_4H_2PO_4$, KH_2PO_4 and borax were provided by a company in Tianjin, China. FA was produced by a water purification plant in Gongyi, Henan province, China. Chemical compositions of these materials are shown in Table 1.

Dry cattle manure was collected from a dairy farm in Shaanxi province. The CMA used in experiments was produced by burning the manure in a muffle furnace at combustion temperatures of 500 °C (designated "CMA500"), 650 °C (designated "CMA650") and 800 °C (designated "CMA800") for 2 h. The CMA was then processed through a vibration sieve to remove particles larger than 0.63 mm. Photographs of the resulting CMA samples are shown in Figs. 1–4. The basic material property indexes for the CMA are shown in Table 2.

Chinese ISO Standard sand used in experiments was produced by a company in Xiamen, Fujian Province, China.

2.2. Methods

2.2.1. Preparation of a control sample

A control sample was prepared for which the compositions of MPC and water-to-binder ratio were determined. An orthogonal design and L16 (4^5) orthogonal table [25] were used in experiments. The compressive strength of MPC at 1 h age was taken as the main index, and the specific surface area of MgO, retarder, $NH_4H_2PO_4$ and KH_2PO_4 were chosen as influencing factors. Four levels for each influencing factor were chosen, and the best ratio of MPC was used as the standard ratio for later experiments. The orthogonal factors table and four levels for each influencing factor are displayed as Table 3. The mechanical properties of MPC resulting from air curing are higher than standard curing. All MPC specimens were demolded in 0.5 h and then cured in the laboratory at a temperature of 20 ± 3 °C and a relative humidity of 50 ± 5%. The water-cement ratio was 0.1.

2.2.2. Workability

An experiment was conducted to determine the suitable water-cement ratio for examining the workability of MPC referring to Standard *GB/T 17671-1999 (IDT ISO 679:1989)* [26]. The binder-sand ratio was 1:1.

To examine the effects of CMA500, CMA650, CMA 800 and FA on the workability of MPC, setting times of MPC were tested using a vicat apparatus referring to Standard *GB/T 1346-2011(NEQ ISO 9597:2008)* [27]. Because the initial setting time of MPC was near to its final setting time, only the initial setting time was determined in this experiment, referring to Standard *GB/T 1346-2011 (NEQ ISO 9597:2008)* [27]. The difference between this experimental procedure and that recommended in Standard *GB/T 1346-2011* was that the former used a fixed quantity of water, instead of the quantity of water needed to achieve a standard consistency. The water-binder ratio in the setting time experiment was 0.16.

Fluidity of MPC mortar was determined according to Standard *GB/T 2419-2005* [28]. A volume of MPC mortar was put on the fluidity test apparatus and vibrated 25 times. Fluidity was determined as the diameter of MPC mortar after vibration.

CMA and FA admixture proportions used in MPC are shown in Table 4.

Table 1
Chemical compositions of magnesium oxide and fly ash used to produce magnesium phosphate cement.

	Density (kg/m^3)	Specific surface area (m^2/kg)	MgO (%)	CaO (%)	Fe_2O_3 (%)	SiO_2 (%)	Al_2O_3 (%)
MgO	3420	133	96.76	1.34	0.76	0.72	0.26
		172					
		251					
		283					
Fly ash	2100	340	2.8	1.5	4.3	58	30