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Research article

A novel process for preparing fireproofing materials from various industrial wastes

Yi Su[a,b], Lei Wang[a,b], Fu-Shen Zhang[a,b,*]

[a] Department of Solid Waste Treatment and Recycling, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
[b] University of Chinese Academy of Sciences, Beijing, 100049, China

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ABSTRACT

In the current study, the possibility of incorporating various industrial wastes into fireproofing materials was investigated. It was found that the newly developed materials showed excellent air sealing and fireproofing performance, with air permeability coefficients 3 to 4 orders of magnitude smaller than traditional fire prevention materials. The influence of different parameters on the air permeability was investigated, and the air sealing mechanisms were clarified through microstructure analysis. In addition, the workability and mechanical properties of the fireproofing materials for practical application in coal mine were studied. The new materials derived from industrial wastes had a compact and monolithic structure, and the excellent air tightness could be attributed to the pozzolanic activity of the industrial wastes and the film-forming property of organic polymers. Among the industrial wastes examined, a special coal fly ash with high pozzolanic activity and little free calcium oxide derived the best product with air permeability coefficient, tensile strength and breaking elongation of 4.17×10^{-8} m^2/s, 2.14 MPa and 48.90%, respectively. This study provides an economical, environmentally friendly and promising approach for industrial wastes recycling.

1. Introduction

Over 10 billion tons of industrial wastes are produced in China every year, occupying large area of farmland and causing serious environmental pollution (Xu et al., 2010). One traditional recycling approach is to incorporate the industrial wastes into construction materials, including cement (Jayaranjan et al., 2014), bricks (Siqueira and Holanda, 2013), concretes (Gonzalez-Corrochano et al., 2009), ceramics (El-Amir et al., 2016) and other cement composites. However, the reuse rate of industrial wastes in this field is still limited due to the concern of product quality. Besides, the development of novel functional materials from industrial wastes has aroused more and more interests, such as absorbent for water treatment (Likon et al., 2011), catalyst (Zhang et al., 2012), zeolite (Ansari et al., 2014), and fire prevention materials (Qin et al., 2015). Recently, incorporating industrial wastes into fire prevention materials has become a promising recycle approach (Kang et al., 2017) because of the fire resistance and low cost of industrial wastes.

As the largest coal producer in the world, China has always suffered from coal fire causing by the spontaneous combustion of coal. According to the State Administration of Work Safety of China, over 50% of the state owned coal mines have the tendency of coal spontaneous combustion, and the occurrence of spontaneous coal fire is up to 400 times every year, causing serious waste of coal resource, environmental pollution and economic loss. Preventing the contact between air and coal seam is the most effective way to prevent the spontaneous combustion of coal (Song and Kuenzer, 2014). Currently, top soil is considered as the major choice to cover the coal seam; however, it is observed from practical experience that the soil should be piled up to 3 m with full compression (Singh et al., 2008), which requires large amount of top soil and thus causes a waste of natural resource.

Recently, several types of fire prevention materials have been developed to prevent the contact between air and coal seam such as grouting materials (Colaizzi, 2004), composite gel (Deng et al., 2015), three-phase foam (Qin et al., 2014) and coating materials (Hussain et al., 2012). The inorganic fireproofing materials (Zhou et al., 2013) are cheap, stable and non-toxic; however, they are easy to crack and have weak tenacity. While the organic fireproofing materials are more effective in air sealing (Li et al., 2016), their prices are high up to $4000–6000 per ton. These disadvantages make both inorganic and organic fireproofing materials less applicable in practice. The incorporation of industrial waste could reduce the cost of fireproofing materials as well as improve the air tightness. As reported in literature

* Corresponding author. Department of Solid Waste Treatment and Recycling, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China.
E-mail address: fszhang@rcees.ac.cn (F.-S. Zhang).

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(Twardowska and Stefaniak, 2006), fly ash in the form of a dense mixture with water showed penetration resistance to air 1–2 orders of magnitude higher than that of the natural sealing materials. Song et al. (2016a) reported a sealing coating for the wall of underground coal mine with 60% ultra-fine fly ash addition and its air permeability coefficient was 3.841×10^{-10} cm^3 $cm/m^2s{\cdot}cmHg$.

The effects of several industrial wastes on the fireproofing materials are expected as the same as coal fly ash (CFA), such as construction and demolition (C&D) waste, ferronickel slag (FNS), steel slag (SS) and red mud slag (RS). The chemical compositions of these materials are very similar to CFA with high content of SiO_2, Al_2O_3 and Fe_2O_3, which could be characterized as pozzolanic materials. In our previous studies, various functional materials, such as porous creamiste (Wang et al., 2013) and CTAB-modified sorbent (Li and Zhang, 2014) have been developed from C&D waste. However, to the best of our knowledge, there is no literature about using C&D waste and other industrial wastes in fireproofing materials. Moreover, there is a lack of overall investigation into the parameters which influence the air sealing performance of the fireproofing materials, and the air sealing mechanism. The aims of this study were to evaluate the feasibility of incorporating various industrial wastes into polymer-modified cement fireproofing materials and clarify the air sealing mechanisms, which could be guidance to utilize the industrial wastes for fire prevention practice.

2. Materials and methods

2.1. Materials

Five kinds of industrial wastes, i.e. CFA, FNS, RS, SS, and C&D waste were employed as the aggregates and pozzolanic admixtures of the waste-derived fireproofing materials (WFMs). Two kinds of CFA were provided by Zibo Coal Fired Thermal Power Plant (Shandong Province, China) and Zhengzhou Coal Fired Thermal Power Plant (Henan Province, China), and were designated as ZB-CFA and ZZ-CFA, respectively. FNS, SS, and RS were supplied by an environmental technology company in Beijing. These three kinds of industrial wastes were processed to recycle iron in rotary hearth furnace by the company before using in this study. The C&D waste was supplied by a baking-free brick plant in Xianyang, Shaanxi province, China. The chemical, mineral composition and physical properties of the industrial wastes are listed in Table 1. It is obvious that the total amount of SiO_2, Al_2O_3 and Fe_2O_3 of all the industrial wastes was over 50%, which could be characterized as pozzolans according to ASTM C618-05. The particle size distributions of different industrial wastes are shown in Fig. S1. The particle sizes of ZB-CFA and C&D waste were smaller than those of other industrial wastes, and their distributions were more uneven.

The reference top soils for the coverage of coal seam were sampled from Qiyang city, (Henan Province, China) and Xianyang City (Shaanxi Province, China), respectively. The raw materials and top soils were dried and ground through 80 mesh sieves before using. Portland cement (42.5R) and tributyl phosphate (Analytical pure) were used as binder material and defoamer, respectively. Ethylene-vinyl acetate (EVA) copolymer emulsion BJ-707 was applied as modifier of the WFMs.

2.2. Preparation of the waste-derived fireproofing materials

The WFMs were prepared by mixing cement, industrial waste powder, EVA emulsion, water and defoamer homogeneously in glass beakers with magnetic stirrers. The EVA emulsion and water were firstly mixed and stirred with half amount of the defoamer. Then the cement and industrial waste powder were added gradually into the liquid. The slurries were slowly stirred for 60 s with the rest amount of defoamer in order to destroy the bubbles thoroughly. The slurries were either used for rheology tests or poured into the disk shaped molds of 80 mm diameter and 2 mm depth for the WFM samples. The samples were dried at room temperature for 24 h before stripped out from the molds. In order to eliminate the influence of water content on the air permeability tests, the WFM samples were dried in oven at 60 °C for 12 h before testing.

2.3. Air permeability test

The air permeability test was performed based on the pressure gradient method proposed by Figg (1973) with slight modification, and the calculation method was based on the equation proposed by Schonlin and Hilsorf (1988). The air permeability testing apparatus used in this study is shown in Fig. 1. The WFM sample was placed on the plastic perforated plate with a rubber washer on it, and their peripheries were sealed by silica gel in order to ensure a unidirectional air flow through the sample. The air tightness of this whole device was checked before testing. Valve 1 was closed and valve 2 was opened before starting the vacuum pump. Then valve 2 was closed when the vacuum degree of the vacuum chamber achieved 0.1 MPa. The air tightness of this apparatus was confirmed with no decrease of the vacuum degree after valve 2 was closed. Valve 1 was opened afterwards, and the time for the vacuum degree decreasing from 0.09 MPa to 0.08 MPa was measured. The air permeability coefficients of the WFM samples were determined according to Eq. (1),

$$K = \frac{V_S D}{At} \cdot \frac{P_2 - P_1}{P_0 - (P_1 + P_2)/2} \quad (1)$$

where K is the air permeability coefficient (m^2/s), V_S is the volume of vacuum chamber and all the tubes (m^3), D is the thickness of the sample (m), A is the actual area of the sample that the air flow goes through

Table 1
Chemical, mineral composition and physical properties of the industrial wastes.

Characteristics		ZB-CFA	ZZ-CFA	C&D waste	FNS	RS	SS
Chemical composition	SiO_2 (%)	29.33	45.83	57.43	42.21	23.56	37.73
	Al_2O_3 (%)	25.70	28.55	12.25	5.78	33.86	13.43
	Fe_2O_3 (%)	17.52	7.54	5.48	17.14	3.84	2.37
	CaO (%)	22.17	5.01	14.91	8.20	9.55	30.36
	MgO (%)	1.60	0.92	2.86	23.26	8.04	8.04
	Na_2O (%)	1.81	0.70	1.84	0.27	8.23	0.63
	TiO_2 (%)	–	1.42	0.56	–	7.74	–
	SO_3 (%)	4.15	0.47	0.59	–	–	1.62
	Loss-on-ignition (%)	0.27	7.49	0.96	2.91	5.03	0.96
	$SiO_2 + Al_2O_3 + Fe_2O_3$ (%)	72.55	81.92	75.16	65.31	61.21	53.53
	Total free calcium oxide (%)	5.59	–	0.42	0.22	0.15	–
Physical properties	Specific gravity (g/cm^3)	2.43	1.44	1.70	2.37	2.44	2.06
	Specific surface area (m^2/g)	2.42	0.44	7.03	0.22	0.23	0.18
Mineral composition		Calcium hydroxide, calcite, quartz, calcium sulfate	Quartz, mullite	Quartz, calcite, microcline, albite	Spinel, magnesium silicate	Nepheline, spinel	Akermanite, gehlenite, quartz