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Preparation of electrolytic manganese residue–ground granulated blastfurnace slag cement

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ABSTRACT

Electrolytic manganese residue (EMR) is added into ground granulated blastfurnace slag (GGBS) as an activator to prepare EMR–GGBS cement. The effects of chemical activation, mechanical activation, water-to-cement ratio and the curing process on the strength and setting properties of EMR–GGBS cement are investigated based on its slag activity index, setting time and compressive and flexural strength. The results show that EMR is an effective and efficient activator for GGBS. This composite activator excels in its purpose when mixed in an EMR/$Ca(OH)_2$/clinker at a weight ratio of 30:3:5. The cement strength exceeds that of Portland slag cement (P·S) 32.5 class, even reaching that of P·S 42.5 and 52.5 classes after adding 20–35% activator and over 5% clinker. It is necessary to ball-mill granulated blast furnace slag (GBFS) for 12 min or longer to achieve a high surface area, over 1.9688 m^2/g, and clinker for 24–30 min to achieve a surface area of over 2.2699 m^2/g, as well as to maintain the water-to-cement ratio between 0.45 and 0.64. The initial and final setting times of the cement are 180 min and 330 min, respectively, which is consistent with the desired times for applications of such cement. The cementitious material exhibits better performance after being cured at 30 °C for 24 h.

1. Introduction

Portland cement is a building material that is widely used around the world. A significant amount of clay and limestone is consumed, and at least 1 ton of CO_2, 0.74 kg of SO_2, 120 kg of dust and other pollutants are discharged into the atmosphere to produce 1 ton of cement clinker [1]. Therefore, it is necessary to develop some new cementitious materials to replace the clinker [2,3].

Electrolytic manganese residue (EMR) is a solid waste found in filters after sulphuric acid leaching of manganese carbonate ore, MnO_2 oxidative deferrisation and lime neutralisation. Approximately 6–7 tons of residue is discharged into the environment per ton of electrolytic manganese product [4]. The accumulated amount of EMR during the past years is huge; EMR is a rarely recycled resource [5]. Use in the preparation of building materials for wall, subgrade and concrete [6–10] is one method of EMR reutilisation. EMR has the properties of both gypsum and hydraulic industrial solid wastes due to its main chemical components, $CaSO_4 \cdot 2H_2O$, SiO_2 and small amounts of Al_2O_3, Fe_2O_3, MnO_2, etc. [11,12]. Its high moisture content, 20% to 30% water, and low activity of calcium sulphate, present in EMR as $CaSO_4 \cdot 2H_2O$, makes it difficult to use in cementitious material production. Its other components, such as SiO_2 and Al_2O_3, have low hydration rates. Therefore, EMR cannot be used as a chemical activator in cementitious materials until it is modified to promote the activity of its components and mixed with other appropriate auxiliary-activators [13].

Cement-making with EMR has mainly focused on Portland fly-ash cement and sulpho-aluminate cement. Li et al. [7] added 25% admixture, prepared by mixing 15% EMR treated at 300–850 °C with 85% fly-ash, into 75% 42.5 ordinary Portland cement (OPC) to make blended hydraulic cement. Hou et al. [8] prepared quasi-sulphoaluminate cementitious material by calcining large quantities of EMR together with limestone and kaolin at approximately 1200 °C. Studies of non-clinker or less-clinker ground granulated blastfurnace slag (GGBS) cement made with EMR as an activator are scarcely reported. GGBS is composed of glassy-state minerals in a three-dimensional structure formed by active CaO, SiO_2 and Al_2O_3. Kumar et al. [14] found that fibrous calcium silicate hydrates (C–S–H) and ettringite (AFt) were the predominant components of hardened GGBS cement paste based on a scanning electronic microscope (SEM) analysis. AFt is formed from the reaction of the active Al_2O_3 component in GGBS and a sulphate activator [15]. EMR is over 40% $CaSO_4$; thus, combining EMR and GGBS should result in a successful cement.

The studies of EMR utilisation in making cementitious materials have mostly centred on thermal modification of EMR and replacing gypsum with EMR as a retarder. Ke [9] treated EMR at 520–850 °C for Portland cement and noted that the strength of cement with less than 15% calcined EMR was the same as that of 52.5 OPC. Feng et al. [10] studied the feasibility of substituting EMR for gypsum in Portland cement with a maximum EMR content of 5%. These studies, however, ignore the effect of chemical and mechanical activation on the properties of cement. The successful activation of EMR sulphates on GGBS

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requires an alkalescent environment. On the one hand, the alkaline solution promotes dispersion and dissolution of GGBS [16]. On the other hand, the sulphates in EMR can react with the active Al_2O_3 in GGBS to make calcium sulphoaluminate hydrates in a $Ca(OH)_2$ solution [17]. Mechanical milling not only can reduce particle size and increase its surface area but also can cause lattice defects to appear and induce crystalline transformations and non-crystallisation on the surface of particles [18,19]. In addition, during milling, chemical bonds such as Si–O, Al–O, O–H and Al–O–Si are broken, producing unsaturated bonds, free electrons and ions [20,21]. All of these factors increase the surface free energy of particles and promote material reactivity.

In this work, the components and ratio of an EMR composite activator and the resultant effects on EMR–GGBS cement properties are studied. The composite activator studied is a mixture of EMR and auxiliary-activators ($Ca(OH)_2$ and clinker). The EMR–GGBS cement used is composed of the EMR composite activator, GGBS and clinker as a strength regulator. The effect of chemical activation on the cement properties depends on the proportions of composite activator and GGBS. Then, the effects of milling method and time on the strength and setting properties are revealed. Separate grinding and intergrinding are two different milling methods for cement making. In separate grinding, the materials are milled separately and then mixed together. Its advantage is allowing for independent control over the degree to which raw material is ground, making it possible to fully activate every component's reactivity to obtain better cement properties [22]. The management for this process, however, is complicated. Thus, the intergrinding process, in which materials are first mixed and then milled together, is also studied as a comparison. Finally, the optimum water-to-cement ratio and curing process are determined, completing the EMR–GGBS cement preparation. Water has two functions during cement hydration [23]; one is to provide a liquid environment for hydration reactions, and the other is to guarantee fluidity of the cement paste. With adequate water in the mix, the degree and rate of cement hydration allows a sufficient amount of C–S–H gel to be created in the cement interior, thus increasing the cement strength [24]. With too much water in the mix, the volume of the reticular floccule, which is composed of hydration products, becomes far larger than that of the original water–cement system, causing superfluous water to separate out, and evaporate off the cement surface. This, in turn, makes the surface structure loose and produces voids among the cement particles, weakening the bonding capabilities of the slurry and reducing the strength of the material [25]. Curing time, temperature and humidity are 3 curing process parameters that greatly affect the properties of cement [26]. Thus, the effect of both the water-to-cement ratio and the curing conditions on strength is studied.

2. Materials and methods

2.1. Raw materials

The EMR, granulated blast furnace slag (GBFS) and cement clinker were obtained from Xiangtan Electrolytic Manganese Dioxide Group Co. Ltd. (Hunan, China), Hunan Valin Xiangtan Steel Co. Ltd. (Hunan, China) and Hunan Pingtang Cement Plant (Hunan, China), respectively. The chemical compositions of the raw materials used in this experiment are given in Table 1. All grinding was performed using a planetary ball mill (Model: QM-3SP2, Nanjing NanDa Instrument Plant, China).

Wet EMR was dried to a consistent weight of 80 °C in a vacuum drying oven and artificially broken until it passed through a 16 square mesh sieve. Broken EMR was ground for 18 min at 580 rpm using 2-mm-diameter steel balls with a ball-to-EMR weight ratio of 3.8. The pretreated EMR was measured to have a median size (D_{50}) of 0.568 μm and a BET surface area of 13.14 m^2/g. Finally, the pretreated EMR was calcined at 350 °C in a muffle furnace for 1 h and cooled down naturally, creating modified EMR.

Table 1
Chemical compositions of used raw materials (wt.%).

Material	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	MnO
EMR	5.45	30.60	6.83	7.19	17.10	0.94	24.50	5.45
Blast furnace slag	0.09	32.15	16.82	0.97	37.94	8.76	2.56	0.34
Cement clinker	0.38	22.13	5.41	3.62	66.33	0.68	0.5	–

The GBFS and clink were dried and broken following the same procedure used for EMR and then milled for 30 min with balls-to-GBFS and balls-to-clinker weight ratios of 3.8 and 3.4, respectively. The pretreated GBFS was measured to have a D_{50} of 5.67 μm and a surface area of 4.6677 m^2/g. The pretreated clinker was measured to have a D_{50} of 16.42 μm and a surface area of 2.2699 m^2/g.

2.2. Chemical activation

The modified EMR, CP $Ca(OH)_2$ and pretreated clinker were mixed according to an $L16(4^5)$ orthogonal table (see Table 2) to prepare the composite activator EMR mixture. The mixture was then added into pretreated GBFS in a 3:7 mixture to slag weight ratio, creating GGBS modified by EMR. Finally, the 7-day activity index (A7) and 28-day activity index (A28) of the modified GGBS were measured to evaluate the effectiveness of EMR mixture excitation on GGBS to determine the optimal composite activator ratio. The pretreated GBFS, EMR mixture in a 30:3:5 EMR/$Ca(OH)_2$/clinker weight ratio and pretreated clinker were mixed according to Table 3 to obtain EMR–GGBS cement. Then, the setting time and compressive and flexural strength of this cement were measured to evaluate the effect of chemical activation in the EMR mixture on GGBS cement to determine the optimal proportion for the composite activator. Different percentages of pretreated clinker, a 13% EMR mixture and pretreated GBFS were mixed to obtain EMR–GGBS cement. The compressive and flexural strength of these mixtures were measured to evaluate the impact of clinker on the strength of GGBS cement and to determine the optimal clinker content.

Table 2
Orthogonal experiment for the ratio of EMR mixture.

No.	Influence factors						Activity index	
	A	$Ca(OH)_2$	B	Clinker	C	EMR	A7	A28
1	1	3	1	2	1	15	83	64
2	1	3	2	4	2	20	98	89
3	1	3	3	6	3	25	89	82
4	1	3	4	8	4	30	96	81
5	2	4	1	2	2	20	68	74
6	2	4	2	4	1	15	74	73
7	2	4	3	6	4	30	91	97
8	2	4	4	8	3	25	71	65
9	3	5	1	2	3	25	71	76
10	3	5	2	4	4	30	91	85
11	3	5	3	6	1	15	72	72
12	3	5	4	8	2	20	80	83
13	4	6	1	2	4	30	103	75
14	4	6	2	4	3	25	79	70
15	4	6	3	6	2	20	76	77
16	4	6	4	8	1	15	77	78

Influence factors	A: $Ca(OH)_2$		B: Clinker		C: EMR	
Activity index	A7	A28	A7	A28	A7	A28
$\sum(1)$	366	326	325	289	306	287
$\sum(2)$	304	309	342	317	322	323
$\sum(3)$	314	316	328	328	310	293
$\sum(4)$	335	300	324	307	381	338
$\sum(1)/4$	91.5	81.5	81.25	72.25	76.5	71.75
$\sum(2)/4$	76	77.25	85.5	79.25	80.5	80.75
$\sum(3)/4$	78.5	79	82	82	77.5	73.25
$\sum(4)/4$	83.75	75	81	76.75	95.25	84.5
R	15.5	6.5	4.5	9.75	18.75	12.75