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Research Article

Utilization of Iron Ore Tailings as Raw Material for Portland Cement Clinker Production

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The cement industry has for some time been seeking alternative raw material for the Portland cement clinker production. The aim of this research was to investigate the possibility of utilizing iron ore tailings (IOT) to replace clay as alumina-silicate raw material for the production of Portland cement clinker. For this purpose, two kinds of clinkers were prepared: one was prepared by IOT; the other was prepared by clay as a reference. The reactivity and burnability of raw meal, mineralogical composition and physical properties of clinker, and hydration characteristic of cement were studied by burnability analysis, differential thermal analysis, X-ray diffraction, and hydration analysis. The results showed that the raw meal containing IOT had higher reactivity and burnability than the raw meal containing clay, and the use of IOT did not affect the formation of characteristic mineralogical phases of Portland cement clinker. Furthermore, the physical and mechanical performance of two cement clinkers were similar. In addition, the use of IOT was found to improve the grindability of clinker and lower the hydration heat of Portland cement. These findings suggest that IOT can replace the clay as alumina-silicate raw material for the preparation of Portland cement clinker.

1. Introduction

IOT are the solid wastes generated during the beneficiation process of iron ore concentration and are one of the main pollution concerns in the mining industry. Continuous development of the iron and steel industry has led to the increasing amount of IOT; there are over 300 million tons of IOT discharged per year, but the comprehensive utilization rate of IOT is still less than 10%; stockpiling is still the most common and cost-effective way in the management of IOT [1, 2]. However, the huge amount of stockpiled IOT brings a series of environmental and social problems. In recent years, IOT as secondary resources have received considerable attention in many countries in the word. At present, the researches about comprehensive utilization of IOT mainly focused on the recycling of useful metal and producing of building materials, among which utilizing IOT to produce the building materials is a more effective solution for resource recovery and management of IOT [3, 4]. Utilization of IOT as raw material for building industry not only consumes large amount of IOT and realizes zero-emission of IOT wastes, but also is beneficial to protecting natural mineral resources.

Portland cement clinker production consumes large amounts of natural resources (limestone, clay, etc.), and clay has been widely used as traditional alumina-silicate raw material for good reasons [5]. Cement industry has undergone a tremendous development in the past decades, but it causes excessive exploitation of clay resource and considerable environmental damage. Now, the cement industry is facing the challenge of the insufficient supply of raw materials and environment protection, so it has for some time been seeking alternative raw materials for Portland cement clinker production. It is well known that various industrial solid wastes have been utilized as alternative raw materials in Portland cement clinker production such as steel slag, waste sludge ash, and ceramic wastes [6–9]. With the benefit of high content of silica and iron, IOT can be utilized as silicate or iron corrective material during the Portland cement clinker

Table 1: Chemical composition of the raw materials/wt%.

Materials	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
IOT	1.22	45.41	19.07	10.86	12.41	7.23	0.44
Clay	4.34	65.44	17.27	5.53	0.98	1.59	0.10
Limestone	42.97	0.49	0.16	0.05	55.78	0.35	0.12
Quartz sand	0.21	97.83	0.52	0.20	0.27	0.10	—
Iron ore	10.23	32.69	8.05	33.60	1.92	2.84	3.50

production, but the consumption of IOT is rather low. In addition, the effect of using IOT as raw material on the properties of raw meal and hydration characteristic of Portland cement has also been seldom discussed. Comparing with being used as corrective material, utilizing IOT as alumina-silicate raw material for Portland cement clinker production can consume more IOT and decrease the mining of clay; however, there is little information about IOT replacing clay as alumina-silicate raw material for the preparation of Portland cement clinker so far.

The possibility of utilizing IOT to completely replace clay as alumina-silicate raw material for Portland cement clinker production was investigated in this paper; the properties of raw meal, clinker, and cement were studied by burnability analysis, differential thermal analysis, X-ray diffraction technique, and hydration analysis. On one hand, it can solve the environment problems of IOT and improve the comprehensive utilization rate of IOT. On the other hand it can provide an alternative alumina-silicate raw material for cement industry.

2. Materials and Methods

2.1. Materials. In this study, IOT was obtained from iron ore dressing plant in Henan province. Clay was from a brick plant in Shiyan and iron ore was from Jiugang Group. Limestone and quartz sand were acquired from Huangshi XinHai Trade Co., Ltd., and Jingyou Sand Co., Ltd., respectively. IOT, clay, limestone, quartz sand, and iron ore were used as raw materials for Portland cement clinker production. Two different kinds of alumina-silicate material (clay and IOT) were used in the experiment. The calcareous material was limestone. Quartz sand and iron ore were used as corrective materials to adjust the contents of silicate and iron of raw meal, respectively.

The main chemical composition of raw materials is shown in Table 1. The chemical composition of IOT is shown in the Supplementary Material available online at http://dx.doi.org/10.1155/2016/1596047. The main component of IOT and clay is similar and the aluminum content of IOT is rather high, which belongs to rich-aluminum type. The hazardous substances of IOT are SO_3 and Cl, but their contents are very low. The XRD pattern (Figure 1) shows that the major mineral phases of the IOT are ferrotschermakite and anorthite while augite and clinochlore occur as minor phases. However, quartz is not detected in the XRD pattern of IOT, which is a common constituent of IOT. The SiO_2 in the amphibole and feldspar is easier to combine with

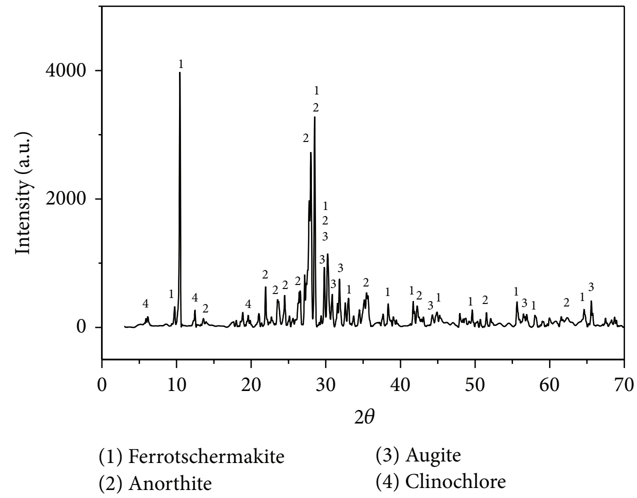

Figure 1: The XRD pattern of IOT.

CaO during the sintering process than in the quartz, which means that IOT has relatively high reactivity. Consequently, the IOT appears to be a suitable alternative alumina-silicate raw material for Portland cement clinker production.

2.2. Samples Preparation. Clinker modulus has always been used to control the production of Portland cement clinker. The compositional parameters of clinker modulus are listed as follows:

$$\begin{aligned}&\text{Lime saturation ratio (KH)}\\&\quad=\frac{\left(\mathrm{CaO}-1.65\mathrm{Al_2O_3}-0.35\mathrm{Fe_2O_3}\right)}{2.8\mathrm{SiO_2}},\\&\text{Silica modulus (SM)}=\frac{\mathrm{SiO_2}}{\left(\mathrm{Al_2O_3}+\mathrm{Fe_2O_3}\right)},\\&\text{Alumina modulus (IM)}=\frac{\mathrm{Al_2O_3}}{\mathrm{Fe_2O_3}}.\end{aligned}\tag{1}$$

Two kinds of samples were prepared; one was prepared by clay as a reference (RM-1) and the other was prepared by IOT (RM-2). The clinker moduli of two samples were both adjusted to the same values (KH = 0.90, SM = 2.50, and IM = 1.50). The blend ratios of raw materials of two samples are shown in Table 2.

The quartz sand passed through a 0.08 mm sieve by grinding, because coarse quartz sand has a negative effect on the burnability of raw meal. The raw meals were shaped in small spheres with a diameter of 15 mm and then dried in an oven at 105°C for 1 h. These small spheres were burned at 1450°C for 1 h. After the sintering process, the produced clinkers were cooled rapidly to room temperature. The produced clinkers were pulverized with 5% gypsum by weight for 2 minutes in a laboratory oscillating mill to produce the Portland cement.

The cement pastes were prepared to study the hydration products of Portland cement clinker. The pastes were prepared with water to solids ratio of 0.3 and cured in standard curing box. At 3 and 28 days, the hydration of pastes was

Table 2: Ratio of raw materials of two samples (%).

Sample	IOT	Clay	Limestone	Quartz sand	Iron ore
RM-1	—	17.65	77.08	1.38	3.89
RM-2	17.31	—	75.07	6.31	1.31

terminated by alcohol and dried at 80°C in a vacuum oven for 24 h for the further characterization.

2.3. Testing Methods. The chemical composition of raw materials was determined by X-ray fluorescence (AXIOS).

The mineral composition of IOT, clinkers, and paste was analyzed by X-ray diffraction (D/MX-IIIA).

The burnability tests of cement raw meal were performed according to Chinese National Standard GB/T 26566-2011. The cement raw meals were fired at 1350°C, 1400°C, and 1450°C for 30 min, respectively. The free lime content of clinkers was analyzed by the glycerol-ethanol method.

The reactivity analysis of raw meal was carried out by the differential thermal analysis (STA 449F3).

The mechanical tests of cement were carried out according to Chinese National Standard GB/T 17671-1999.

The physical properties of cement were examined according to the Chinese National Standard GB/T 1346-2001.

The hydration heat of cement was measured by microcalorimeter (C80, SETARAM). The water-cement ratio was 0.5 and the hydration time was 3 days.

3. Result and Discussion

3.1. Characterization of the Raw Meal

3.1.1. The Reactivity of Raw Meal. The reactivity of raw meal is defined by the reaction rate of the raw materials and is related to its mineral characteristic. The reactivity of raw meal was studied by DSC analysis. The DSC heating curves of two samples are presented in Figure 2. During the sintering process, the formation of clinker minerals is companied with endothermic and exothermic reactions. Endothermic peak at about 830°C is attributed to thermal decomposition of the limestone. Exothermic peak between 1230°C and 1260°C is attributed to solid state reactions, which means the progressive formation of C_3A, C_4AF, and C_2S [9]. Endothermic peaks at about 1330°C are attributed to the sintering of liquid phase and the formation of C_3S. It can be seen from Figure 2 that the solid state reactions temperature of RM-2 can be up to 30°C lower than RM-1, but the decomposition temperature of limestone and the sintering temperature of liquid phase in two samples are almost the same. The results of DSC analysis indicate that using IOT as alumina-silicate material promotes the solid state reactions and improves the reactivity of raw meal while it has little effect on the processes of limestone decomposition and reducing the formation temperature of C_3S. The chemical composition of IOT that is in the Supplementary Material shows that IOT contains trace elements (CuO, TiO_2, MnO, etc.), which can promote the solid state reaction [10].

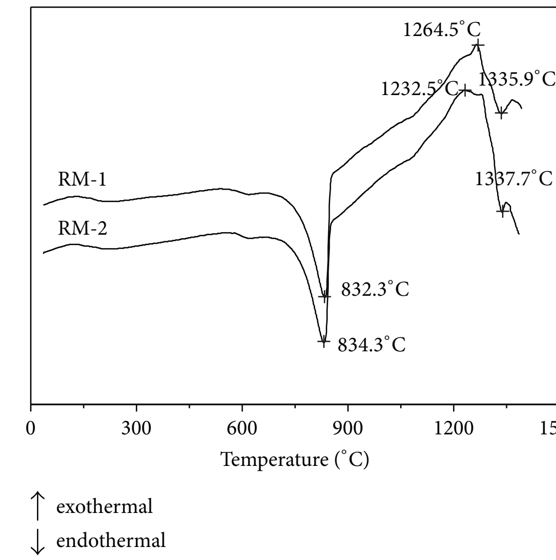

Figure 2: The DSC heating curves of raw meals.

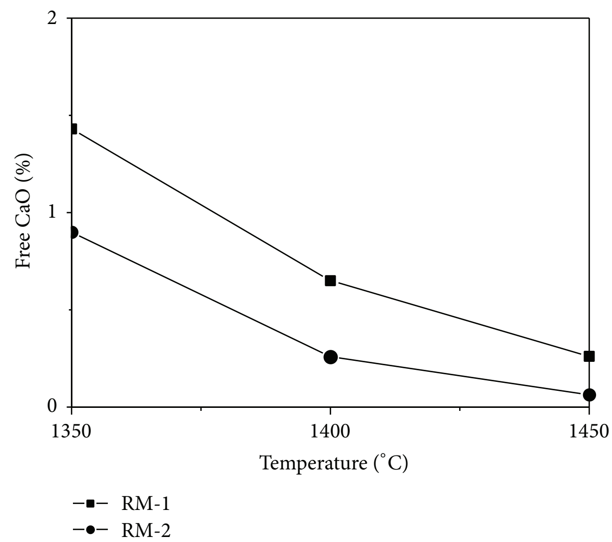

Figure 3: The burnability tests of raw meals.

3.1.2. The Burnability of Raw Meal. The burnability of raw meal describes the degree of difficulty of clinker formation during sintering process and is evaluated by the content of free lime in clinker. The lower the content of free lime in clinker is, the higher the raw meal burnability is. The results of burnability tests are given in Figure 3. The content of free lime in RM-2 is lower at all sintering temperatures, and the reaction of sintering process after 1350°C is mainly the formation of C_3S. The results of burnability analysis suggest that the use of IOT has improved the burnability of raw meal and promoted the formation of C_3S during the sintering process. The improvement of burnability can be attributed to the existence of trace elements and particular mineral composition of IOT.

The results of reactivity and burnability analyses show that RM-2 has higher reactivity and burnability. Comparing

Table 3: The physical properties of produced Portland cements.

Sample	Specific surface (m^2/kg)	Consistency/%	Setting time/min		Bending strength/MPa		Compressive strength/MPa	
			Initial time	Final time	3 d	28 d	3 d	28 d
RM-1	326.4	23.0	165	225	4.9	8.5	20.7	46.2
RM-2	355.5	23.8	160	235	4.9	8.7	20.8	48.6

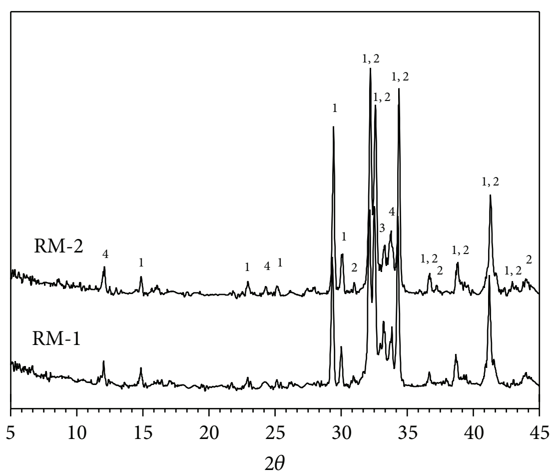

Figure 4: The X-ray diffraction of two produced Portland cement clinkers.

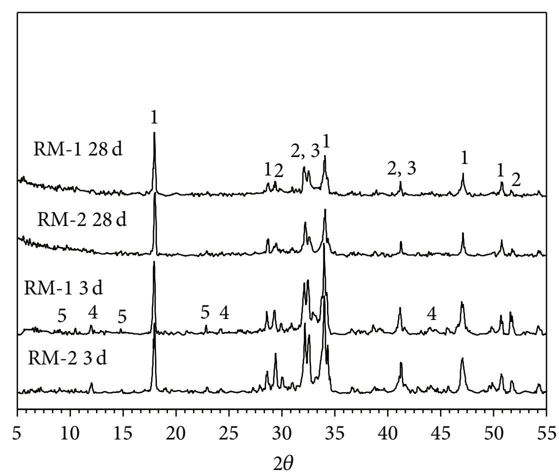

Figure 5: The X-ray diffraction patterns of pastes for 3 and 28 days.

with clay, utilizing IOT as alumina-silicate raw material for Portland cement clinker production can lower the sintering temperature or reduce sintering time during sintering process, which can lower the production costs of cement industry.

3.2. Characterization of the Clinker

3.2.1. XRD Pattern of Clinker. The XRD analysis of two produced Portland cement clinkers is given in Figure 4. In both clinkers, the main mineral phases of two produced clinkers were C_3S, C_2S, C_3A, and C_4AF, which were in accord with the characteristic minerals of a typical Portland cement clinker [11]. However, there is a small difference between the two clinkers that RM-2 contains less amount of C_2S, which is related to the promotion of sintering process. Free lime content is very low in both clinkers, so it cannot be detected in the XRD pattern. The results of XRD analyses indicate that the use of IOT does not affect the formation of characteristic mineralogical phases of Portland cement clinker.

3.2.2. Physical and Mechanical Testing. Table 3 presents the physical and mechanical properties of two produced Portland cement clinkers. The results of physical tests show that the use of IOT only slightly affected the setting times of produced Portland cement. However, RM-2 cement presents greater specific surface and water demand. The greater specific surface represents better grindability and leads to the greater water demand. The differences in mineralogical composition of clinkers significantly impact the grindability of clinkers; C_2S is known to be the most prominent strength giving components in all clinker minerals [12]. The grindability of RM-2 clinker increases as the amount of C_2S decreases.

Portland cement sample was made by grinding the 95 wt% of clinker with 5 wt% of gypsum, and the mechanical properties of produced Portland cement sample were tested for strengths after curing for 3 and 28 days. Both mortars gave quite similar bending and compressive strengths in the same days, and the mechanical performances of two Portland cement clinkers were in agreement with those of Portland cement of 42.5 MPa strength grade, which confirmed the probability of utilizing IOT as alternative raw materials for Portland cement clinker production.

3.3. Characterization of Hydration

3.3.1. XRD Pattern of Paste. The XRD patterns of two pastes, hydrated for 3 and 28 days, are given in Figure 5. In both pastes, the hydration products of two cement clinkers are $Ca(OH)_2$ and ettringite. No calcium silicate hydrate (C-S-H) was detected during the whole hydration process, presumably due to the amorphous characteristic of the calcium silicate hydrate itself [13]. The diffraction peaks of C_3S and C_2S are higher in RM-2 paste at 3 days, which indicates that the hydration velocity of calcium silicate of RM-2 cement is slower. With increasing hydration time, the peaks of C_3S, C_2S, and C_4AF decrease at 28 days.

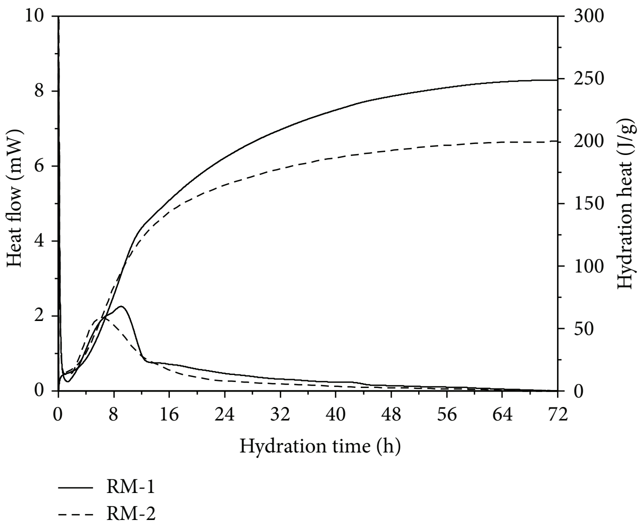

Figure 6: The hydration heat of two produced Portland cement clinkers.

3.3.2. Hydration Heat of Cement. The rate of heat liberation and hydration heat of two cement clinkers for 3 days is shown in Figure 6. In both cases, the heat liberation is quite intense in the first few minutes of the preinduction period. Soon thereafter, the hydration process is delayed and the rate of heat liberation decreases rapidly in the induction period. Then, a second main exothermic peak appears as a result of the formation of ettringite and hydration of C_3S [14]. And finally, the rate of heat liberation decreases gradually in the following period. It can be seen from Figure 6 that the end times of induction period of two cement clinkers are almost the same, the end times of induction period are related to the setting times of cement, and the analysis results of induction period are in good agreement with the results of physical tests. RM-2 has a weaker exothermic peak; however, the formation process of ettringite of two cement clinkers could be similar according to the results of setting time of two cement clinkers, so the weaker exothermic peak was due to the lower hydration rate of calcium silicate. The XRD analysis of two pastes also has the same results.

The hydration heat of RM-2 cement is lower in the early hydration period, which is due to the higher hydration liberation rate of RM-2 cement. The greater specific surface of RM-2 cement promotes the hydration process of cement in the initial hydration period and leads to higher hydration liberation rate of cement. As the heat liberation rate of RM-2 cement decreases faster in the following period, the hydration heat of RM-1 exceeds RM-2 after about 10 h and the gap of hydration heat of two cement clinkers gradually enlarges in the later period.

4. Conclusions

Chemical and mineralogical analysis of IOT has shown that it can be considered as a ready alumina-silicate raw material due to its high content of alumina and relatively high reactivity. Furthermore, the similar mineralogical, physical, and mechanical properties of two produced Portland cement clinkers have confirmed that IOT can completely replace clay as an alternative alumina-silicate raw material for the production of Portland cement clinker. However, the use of IOT is found to improve the reactivity and burnability of raw meal and promote the sintering process. In addition, the Portland cement clinker prepared by IOT presents better grindability and the hydration heat of Portland cement is lower. The availability and low cost of IOT make it attractive to replace clay as alumina-silicate raw material for the production of Portland cement clinker. This will be beneficial for the management of IOT, alleviating the raw materials supply problem of the cement industry and allowing the reduction in processing costs of raw materials.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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