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Relationship between polymerization degree and cementitious activity of iron ore tailings

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Abstract: The aim of this study is to understand the relationship between the polymerization degree and cementitious activity of iron ore tailings. In light of the poor usage of iron ore tailings, stockpile samples from Tangshan were studied in terms of their ability to become cementitious materials. Compound thermal activation was used to improve the cementitious properties of the tailings, while analyzing methods, such as X-ray diffraction (XRD), infrared spectroscopy (IR), nuclear magnetic resonance (NMR), and X-ray photoelectron spectrometer (XPS), were employed to study the changes in phase and structure under different activation conditions. The results reveal clear relationships between the binding energies of Si2p and O1s, polymerization degree, and cementitious activity of iron ore tailings.

Keywords: iron ore tailing; polymerization degree; cementitious activity; thermal activation

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1. Introduction

Rapid industrialization has brought about a great deterioration in the quality of our environment. Being an essential component in many industrialized countries, the iron and steel industry is among the worst offenders in terms of environmental degradation and is the subject of concern for the public and governmental agencies [1-4]. In China, as the annual production of iron ore grew to exceed 800 million tons in recent years following the country's rapid economic developments, the amount of tailings discharged annually as a byproduct also grew to over 500 million tons. This massive output of iron ore tailings is one of the main contributors to China's growing stockpile of metal mining wastes. This stockpile is currently more than 10 billion tons in weight and covers an area in excess of 70 thousand hectares, making it to be the culprit of all kinds of environmental pollution and ecological damage [5-8].

Facing with the same problem in many countries, the research on using iron ore tailings as a secondary resource has become attached with great attention. This effort has brought about great achievements in the area and has led to comprehensive reclamation and re-extraction programs in many countries [9-14].

Despite this progress, the amount of wastes eliminated by these methods is still insufficient to offset the annual tailing output. Since the untreated iron ore tailing has very little cementitious activity, compound thermal activation was applied in the present study to improve the cementitious properties of tailing samples. The aim of the present investigation was to explore the relationships between the polymerization degree and the cementitious activity of iron ore tailings to develop it for making construction materials. The variation in phase and structure of the tailing samples after different treatment schemes was analyzed by using characterization methods such as X-ray diffraction (XRD), infrared spectroscopy (IR), nuclear magnetic resonance (NMR), and

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X-ray photoelectron spectrometer (XPS).

2. Experimental

2.1. Materials

The iron ore tailings used in this experiment were from Tangshan, Hebei Province, China. The chemical composition is shown in Table 1. Due to their high SiO_2 content (>60wt%), they are classified into the same type as the tailings from Anshan [15].

Table 1. Main chemical composition of iron ore tailings wt%

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
66.43	6.66	11.69	5.79	4.26

2.2. Experiment methods

2.2.1. Compound thermal activation

The test samples were prepared with 75wt% ground iron ore tailings and 25wt% lime. The samples were separated into two sets based on calcination temperatures. Set A was calcined at 900ºC and set B was calcined at 1100ºC. Moreover, a control set consisting of only the ground iron ore tailings without compound thermal activation was designated as O.

2.2.2. Testing methods

The XRD analysis was conducted on a Rigaku D/max 2550 spectrometer using Cu K_α radiation (40 kV, 200 mA) at a scanning rate of 8°/min from 5° to 70°. IR was performed using the Spectrum GX FTIR spectrophotometer (PE, USA). ^{29}Si magic angle spinning nuclear magnetic resonance spectra (MAS NMR) was obtained at 59.62 and 78.20 MHz on a solid-state spectrometer (BRUKER-AM300) employing magnetic angle spinning at 4 kHz. The XPS analysis was done using a PHI-5300 ESCA fitted with Al X-ray source operating at 400 W. The typical residual pressure of this system was 10^{-8} Pa.

Mechanical properties were tested in accordance with the Chinese National Standard GB/T17671−1999. Strength tests were conducted on 40 mm×40 mm×160 mm test blocks which were cured for corresponding days in the curing room as specified by the standard.

3. Results and discussion

3.1. XRD experiments

Fig. 1 presents the XRD patterns of the iron ore tailing samples examined in this study. From Fig. 1, it can be seen that the main mineral components of the iron ore tailings are quartz, anorthoclase, tremolite, calcite, mica, and magnetite. With reference to the untreated sample O, the peaks for quartz in sample A have lower heights, signifying a decrease in the crystallinity of the quartz content. At the same time, sample A calcined at 900ºC also shows peaks which are associated with wollastonite, akermanite, and Ca_2SiO_4. Since the peaks for Ca_2SiO_4 are broad, the crystallinity of Ca_2SiO_4 is low.

In the case of sample B calcined at 1100ºC, the peaks for wollastonite and akermanite are more prominent, which mean that more substantial amounts of wollastonite and akermanite are generated. In contrast, the peaks for Ca_2SiO_4 disappear.

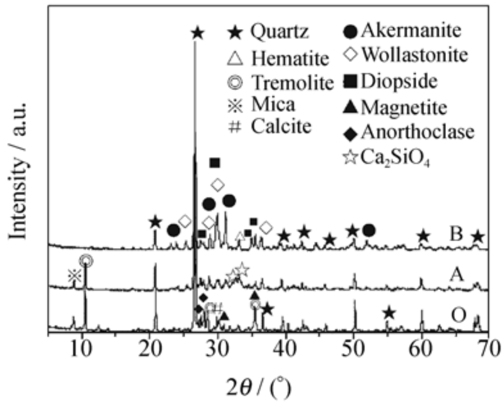

Fig. 1. XRD patterns of the iron ore tailing samples.

Based on the above observations, compound thermal activation can be chemically represented by the following equations:

$$2CaO+SiO_2 \rightarrow Ca_2SiO_4 \tag{1}$$

$$Ca_2SiO_4+SiO_2 \rightarrow 2CaSiO_3 \tag{2}$$

At an activation temperature of 1100ºC, Ca_2SiO_4 generated in Eq. (1) is consumed in Eq. (2), which can account for the disappearance of the peaks for Ca_2SiO_4 in the XRD pattern of sample B.

3.2. Infrared analysis

The infrared spectra of the iron ore tailing samples are shown in Fig. 2. As the background in IR spectroscopy, the greater the wavenumbers for the Si–O–Si asymmetric stretching vibration bands are, the higher the polymerization degree for the sample is. The wavenumbers at 1084, 797, 778, 694, and 459 cm^{-1} characterize the Si–O–Si vibration bands of quartz. After calcination at 900ºC, the 1084 cm^{-1} band for quartz shifts toward a lower wavenumber, signifying a decrease in the polymerization degree of quartz. The band at 1425 cm^{-1} indicates the existence of CO_3^{2-} in the form of $CaCO_3$. After calcination, this characteristic band disappears, which means that $CaCO_3$ fully decomposes. At the same time, new bands at 997, 903, and 518 cm^{-1} appear, they are the characterization bands of Ca_2SiO_4, a kind of nesosilicate. This means that quartz, which has a framework structure, depolymerizes to an island structure in sample A.

In the case of sample B, after calcination at 1100°C, the bands appear at wavenumbers of 937, 681, and 644 cm^{-1} which are attributed to wollastonite, a kind of chain silicate. Moreover, bands at 1018, 969, 857, and 476 cm^{-1} are also noted, which indicate the formation of akermanite, a kind of dimeric island structure silicate.

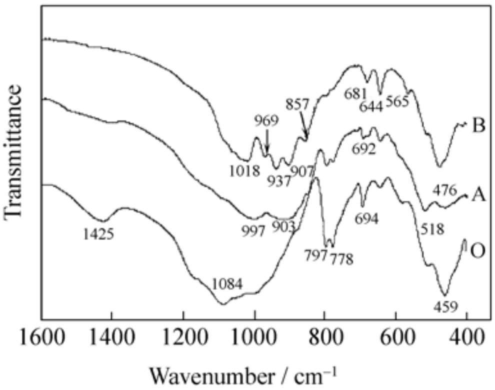

Fig. 2. IR spectra of the iron ore tailing samples.

3.3. ^{29}Si MAS NMR spectroscopy

Fig. 3 presents the ^{29}Si MAS NMR spectra of the three iron ore tailing samples. In the control sample shown in Fig. 3(a), the resonance peak at -108.42×10^{-6} represents $Q^4(0Al)$, the structural component of framework silicate (quartz); the resonance peak at -102.51×10^{-6} represents $Q^4(1Al)$, the structural component of framework aluminosilicate (anorthoclase); and the resonance peak at -97.25×10^{-6} represents $Q^3(0Al)$, the structural component of sheet silicate (mica). In sample A shown in Fig. 3(b), the ^{29}Si MAS NMR spectrum shows a sharp peak at -72.95×10^{-6}, which is attributed to Q^0. This means that monomeric island silicate (Ca_2SiO_4) is produced. At the same time, the new peak at -90.03×10^{-6} represents $Q^2(0Al)$, which means that the chain silicate wollastonite is also generated. Mica and quartz are still present in the sample, as displayed by the two peaks at -97.26×10^{-6} and -107.77×10^{-6}, respectively. Finally, in sample B shown in Fig. 3(c), a sharp peak at -89.37×10^{-6} occurs. This indicates the formation of large amounts of $Q^2(0Al)$, making chain silicate the major structure of the sample.

Hence, combing the NMR and IR analysis, it can be concluded that during the process of compound thermal activation, silica-oxy tetrahedrons of the sample first depolymerized from a framework structure to an island structure, and then repolymerized into a chain structure.

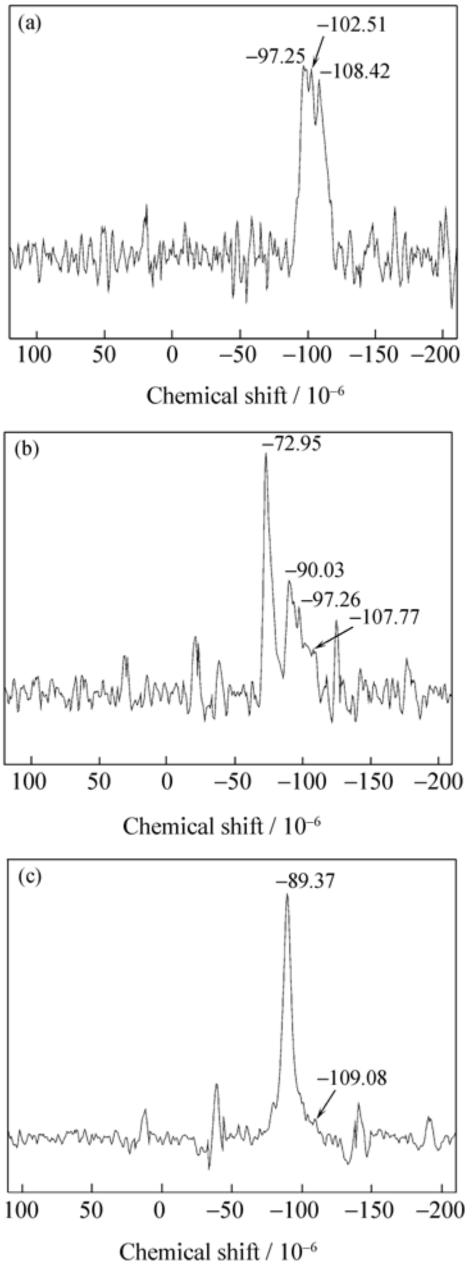

Fig. 3. ^{29}Si MAS NMR spectra of the iron ore tailing samples: (a) sample O; (b) sample A; (c) sample B.

3.4. XPS analysis

XPS is a very useful tool for obtaining a variety of information on the chemical and structural components of material surfaces, and it has been widely used for surface state analysis. Okada *et al.* studied the XPS chemical shifts of silicates with different polymerization structures [16], while Li used Si2p and Al2p binding energies to evaluate the hydraulic activity of Al-Si materials [17].

In this paper, the Si2p and O1s spectra for the iron ore tailing samples were studied. From Fig. 4, it can be seen that the untreated iron ore tailing has the highest Si2p and O1s surface binding energies. These high binding energies are related to the mineral composition of the tailing sample, which is predominantly quartz along with tremolite, anorthoclase, and mica. The sample treated at 900ºC by compound thermal activation has the lowest Si2p and O1s surface binding energies because monomeric silicate Ca_2SiO_4 is generated. The tailing treated at 1100ºC has energies that are between the untreated sample and the one calcined at 900ºC because consists of primarily chain structure silicate.

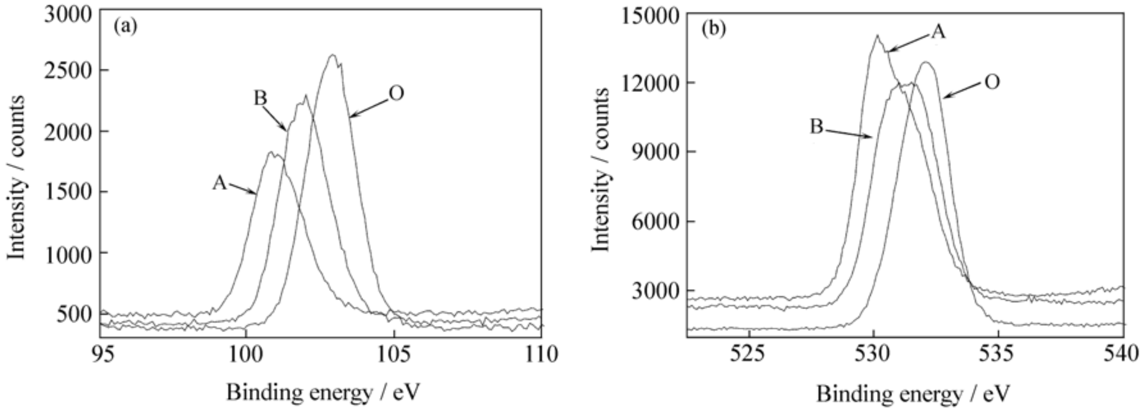

Fig. 4. X-ray photoelectron spectra of the iron ore tailing samples: (a) Si2p binding energies; (b) O1s binding energies.

3.5. Strength

The iron ore tailing samples treated by compound thermal activation were combined with the blast-furnace slag, clinker, and gypsum to prepare mortar samples. The bending and compressive strengths of the mortar samples after curing for 3, 28, and 90 d are shown in Fig. 5. In Fig. 5, the notation “30wt%-3 d” means that the cementitious materials used to make the mortar contain 30wt% iron ore tailings, while its curing age is 3 d. As can be seen from Fig. 5, the bending and compressive strengths of the mortar with the iron ore tailings treated by compound thermal activation at 900ºC are significantly better. However, both the bending and compressive strengths of the mortar with the iron ore tailing treated at 1100ºC decrease in comparison to that of the mortar treated at 900ºC, although the values are still higher than the case of the untreated one. Mortars made of cementitious materials that contain 30wt% iron ore tailings treated at 900ºC meet the compressive strength requirement of 42.5# cement after 28 d.

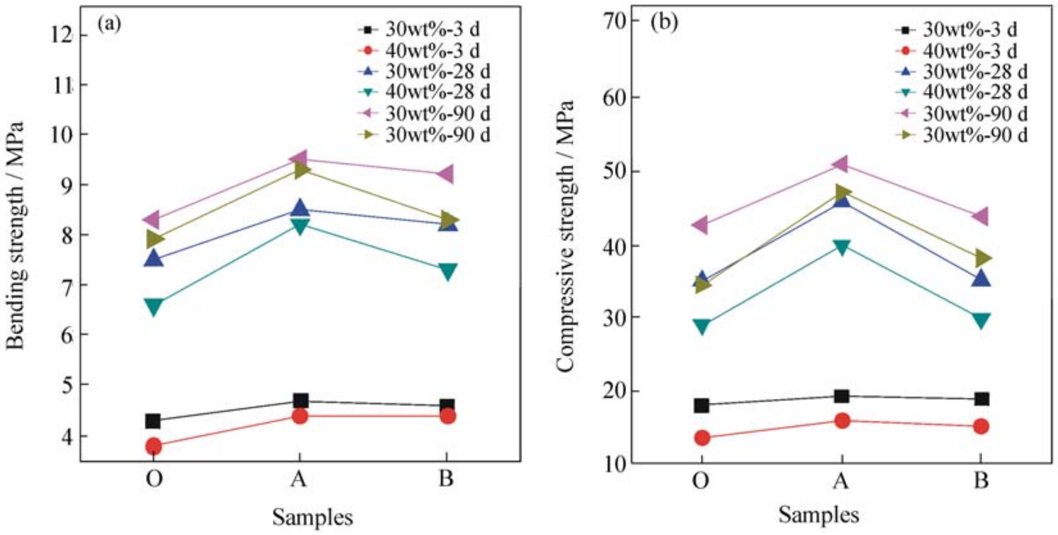

Fig. 5. Strength of mortars containing iron ore tailings: (a) bending strength; (b) compressive strength.

Based on the combined analysis of XRD, IR, NMR, and XPS, it can safely deduce that, the main product formed in the iron ore tailings after compound thermal activation at 900ºC is Ca_2SiO_4; while it is $CaSiO_3$ after the treatment at 1100ºC. Since Ca_2SiO_4 is a kind of nesosilicate, while $CaSiO_3$ has a chain silicate structure, the polymerization degree is higher in the latter case. Combining this result with the strength analysis, it can be concluded that silicate with a lower polymerization degree has a higher cementitious activity.

4. Conclusions

(1) Compound thermal activation is an effective way to improve the cementitious properties of iron ore tailings.

(2) In the process of compound thermal activation, silica-oxy tetrahedron depolymerizes from a framework structure into an island structure at 900ºC, and then repolymerizes into a chain structure at 1100ºC.

(3) Si2p and O1s binding energies of iron ore tailings are related to the polymerization structure of silica-oxy tetrahedrons. The lower the polymerization degree, the lower the Si2p and O1s binding energies.

(4) The polymerization degree is related to the cementitious activity of iron ore tailings. The lower the polymerization degree, the better the cementitious activity.

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