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A new method to evaluate the hydraulic activity of Al-Si materials

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Slag, fly ash, gangue and 500℃ calcined gangue are analyzed by using identical coupled plasma optical emission spectroscopy (ICP), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR) and magnetic angle spinning nuclear magnetic resonance (MAS NMR). Research results show that there is a negative linear relationship between the Si 2p and Al 2p binding energies of Al-Si materials and the compressive strength of aluminosilicate based cementitious materials prepared with these Al-Si materials, i.e. the lower the binding energies, the higher the compressive strength. Indeed, the Si 2p and Al 2p binding energies of Al-Si materials can be used to indicate their hydraulic activity. The binding energies of the four examined materials increase in the order of slag, fly ash, 500℃ calcined gangue and untreated gangue. Moreover, the binding energies of Si 2p, Al 2p and O 1s of every Al-Si material have excellent correlation. By using the Al 2p binding energy and ^{27}Al MAS NMR spectra, the coordination number of aluminum in slag is determined to be four, while that in gangue, is six. Based on the aforementioned discoveries, this paper presents a new effective method to evaluate the hydraulic activity of Al-Si materials by using the surface binding energies of silicon and aluminum of Al-Si materials.

waste management, Al-Si materials, activity evaluation, binding energy, X-ray photoelectron spectroscopy (XPS)

1 Introduction

In order to effectively utilize potential resources (Al-Si wastes), save energy and protect the environment, much effort has been devoted to the conversion of large deposits of Al-Si wastes into value-added cementitious materials. There has been no uniform classification of solid wastes up to now. Currently, the solid wastes used in the cementitious material field are commonly classified based on their origins into three groups: industrial wastes (slag, fly ash, steel slag, red mud and so

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on), mining wastes (tailing and gangue) and construction wastes (waste bricks, tiles and concrete). Since the aforementioned solid wastes are composed largely of Si and Al, they can be referred to as Al-Si materials. In order to assess the hydraulic activity of Al-Si materials, numerous researchers have presented activity evaluation methods, which fall into three groups: chemical, physical and mechanical[1−4]. Unfortunately, results given by these methods have poor correlation[1,4]. Moreover, the existing methods only work for some Al-Si materials; there is no comprehensive test that works for several Al-Si materials at the same time. Considering the hydration reaction mechanism, i.e. hydration reaction happens on the surface of the particle, as well as the chemical composition and the mineral characteristics of Al-Si materials, a new test method based on surface binding energy is put forward. In order to experimentally verify this method, slag, fly ash, gangue and 500℃ calcined gangue are analyzed by using ICP, XPS, IR and MAS NMR. Moreover, the contrast tests between Si, Al binding energies of Al-Si materials and the compressive strengths of aluminosilicate based cementitious materials prepared with these Al-Si materials are carried out.

2 Experimental

2.1 Raw materials

The chemical compositions of gangue (from Ji'an, Jiangxi Province), slag (from Tangshan Iron and Steel Cooperation Group), and fly ash (from Shijingshan Power Plant, Beijing) are determined by means of X-ray fluorescence analysis (Table 1). By using X-ray diffraction, untreated gangue is found to contain kaolinite, quartz, siderite and illite, while calcined gangue is found to contain illite, quartz and magnetite. Slag is predominantly of noncrystalline phase; its crystalline phase is akermanite. Fly ash is partially noncrystalline; its two crystalline phases are mullite and quartz.

2.2 Experimental methods

The gangue, slag, fly ash, and 500℃ calcined gangue are mixed with minor compounds in a liquid to solid mass ratio of 0.5. The samples are cast into 40 cm×40 cm×160 cm cubes and cured at 20℃ and 95 RH (relative humidity). The specimens are demolded 24 h after the start of mixing and then are allowed to cure in the same condition until the compressive strength is tested. The compressive strength test is performed using a TY-50 press machine. The mass proportion of Al-Si material in aluminosilicate based cementitious materials is 70%. Identical coupled plasma optical emission spectroscopy (ICP) is tested by ICP PROFILE from Leeman Company. The ^{29}Si NMR spectra are recorded on a JOEL JNM-ECA600 spectrometer operating at 119.23 MHz in D_2O with TMS as internal reference. All the experiments are carried out using the standard single pulse sequence at room temperature. The infrared spectroscopy is determined using the Spectrum GX FTIR spectrophotometer (PE, USA). The ^{29}Si and ^{27}A1 MAS-NMR spectra are obtained at 59.62 MHz and 78.20 MHz on a solid state spectrometer (BRUKER-AM300) employing magnetic angle spinning at 4 kHz. XPS analysis is performed using a PHI-5300 ESCA fitted with Mg and Al X-ray source operating at 400 W. The typical residual pressure of this system is 10^{-8} Pa.

Table 1 Chemical compositions of raw materials (wt%)

Name	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	Fe_2O_3	SO_3
Gangue	65.66	23.78	1.92	0.19	2.34	0.64	2.72	2.72
Slag	35.93	14.35	35.13	0.23	0.40	10.14	0.80	3.00
Fly ash	55.56	32.78	3.81	0.15	1.14	0.90	4.91	0.74

3 Results and discussion

3.1 Dissolution extent of Al-Si materials

Figure 1 shows the aluminum and silicon dissolution extent of different Al-Si materials in K-Na silicate solution (mass concentration: 45 wt%, the molecular ratio of SiO_2/R_2O: 1.5). The Si ions dissolution extent of calcined gangue is higher than that of other Al-Si materials. The extent of Al dissolution of slag is the highest. The trend of dissolution extent of Si of these four Al-Si materials is different from the trend of Al; thus dissolution extent of Si and Al do not appear to have synchro-dissolution behavior in K-Na silicate solution. Figure 2 is the plot for the compressive strengths of aluminosilicate based cementitious materials prepared with the four different Al-Si materials. The samples prepared with slag have the highest 3-day, 28-day and 90-day strengths, while the one prepared with untreated gangue has the lowest strength, which is only 18.6 MPa for the 90-day test. The compressive strength of the sample with fly ash is higher than that of the sample with gangue calcined at 500℃. From Figures 1 and 2, it is shown that the dissolution extent of Si and Al cannot be used to evaluate the hydraulic activity of different Al-Si materials.

3.2 Si 2p binding energy analysis

Figure 3 shows the Si 2p spectra for the four types of Al-Si materials under study (slag, fly ash, untreated gangue and 500℃ calcined gangue). From the figure, one can deduce the following

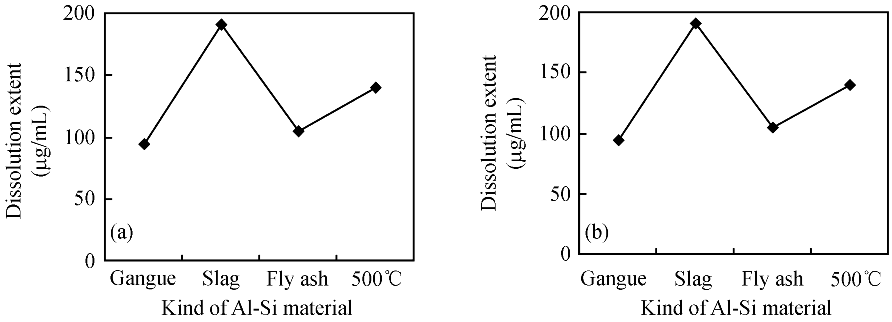

Figure 1 Dissolution extent of Si^{4+} and Al^{3+} of Al-Si materials in K/Na silicate solution. (a) Si; (b) Al.

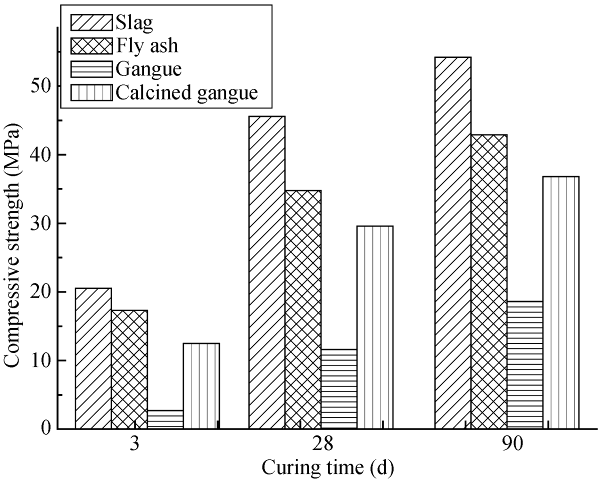

Figure 2 Compressive strengths of aluminosilicate based cementitious materials samples.

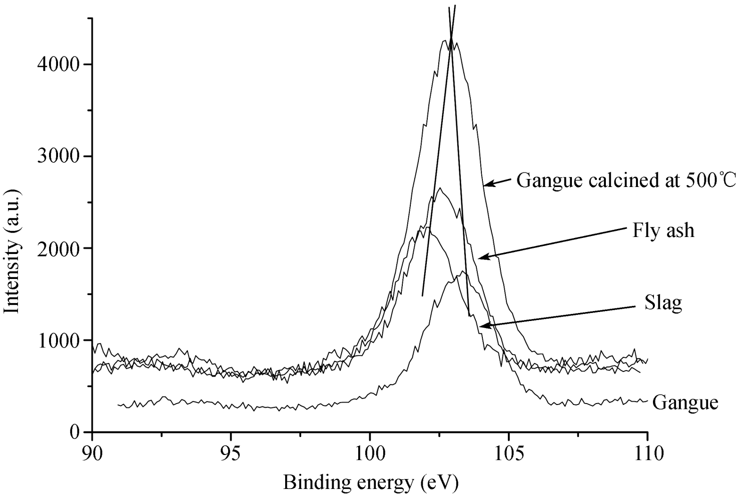

Figure 3 Si 2p binding energies of four Al-Si materials.

trends: Untreated gangue is experimentally determined to have the highest Si 2p surface binding energy (103.24 eV), which explains its low activity. The high Si 2p binding energy of untreated gangue is related to its mineral composition, which is mainly kaolinite, illite and a large fraction of quartz. Kaolinite has a layered silicate structure with a Si 2p binding energy of 102.59 eV, while quartz has a stable framework silicate structure with a high Si 2p binding energy of 130.4 eV. Slag has the lowest Si 2p surface binding energy (101.92 eV) because it is primarily noncrystalline, containing only a small amount of akermanite. Moreover, akermanite is pyrosilicate, which is less stable than framework and layered structures, and consequently it has a low binding energy of 101.85 eV. The Si 2p binding energy of fly ash is between those of slag and untreated gangue. In addition to the glass state contents, its main silicate mineral is mullite, whose stability is worse than that of framework silicates, but better than that of ring structured silicates. Finally, calcined gangue has a Si 2p binding energy (102.84 eV), much less than that of untreated gangue, and due to its large composition of quartz, its binding energy is also less than that of fly ash.

Okada et al.[5] studied the X-ray photoelectron spectra (XPS) chemical shifts of silicates with different polymerization structures. The results showed that the Si 2p binding energies varied from 101.3 eV in merwinite (monomeric structure) to 103.4 eV in quartz and cristobalite (three-dimensional framework structure). A clear chemical shift relation was observed, relating the polymerization structures of Si-O tetrahedron to the plots of their Si 2p XPS binding energy versus the kinetic energy of their Si(KLL) XAES spectra. Thus, the structure state of the surface silicates in various substances could be deduced from this chemical shift relationship. Judging from the Si 2p binding energy, the average silicate structure in slag is between monomeric and chain structure, while the average silicate structure in gangue has a degree of polymerization that is a little less than that of quartz-framework structure. These results are justified by that of IR test (Figure 4). In IR spectroscopy, the greater the wavenumber of Si-O-Si asymmetric stretching vibration band, the higher the degree of polymerization. For example, asymmetrical stretching of Si-O-Si in $(SiO_4)^{4-}$, $(Si_2O_7)^{6-}$, $(Si_3O_9)^{2-}$ and framework $[SiO_2]$ have corresponding wavenumbers between 830—890 cm^{-1}, 900—930 cm^{-1}, 950—970 cm^{-1} and 1060—1200 cm^{-1}, respectively[6]. Slag has the lowest degree of polymerization, which corresponds to a low wavenumber of 959 cm^{-1}, while untreated gangue has the highest degree of polymerization for silicon, which corresponds to a high wavenumber of 1033 and 1107 cm^{-1}. IR and XPS results for the four different sample materials show that the structure of silicates and their Si 2p binding energy are correlated. The surface binding energy of composites containing different silicate minerals has a weighted average characteristic. The surface binding energy is also affected by level of vitrification.

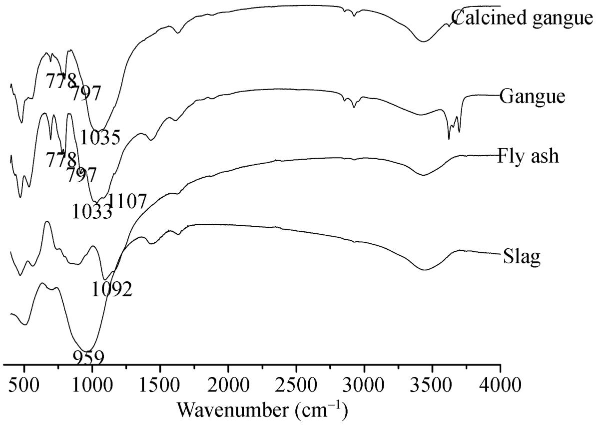

Figure 4 IR spectra of four Al-Si materials.

From the plot between compressive strength and Si 2p binding energy (Figure 5), there is a negative linear relationship between the Si 2p binding energies of these four Al-Si materials and the compressive strength of the aluminosilicate based cementitious materials prepared with them: the lower the binding energies, the higher the compressive strength.

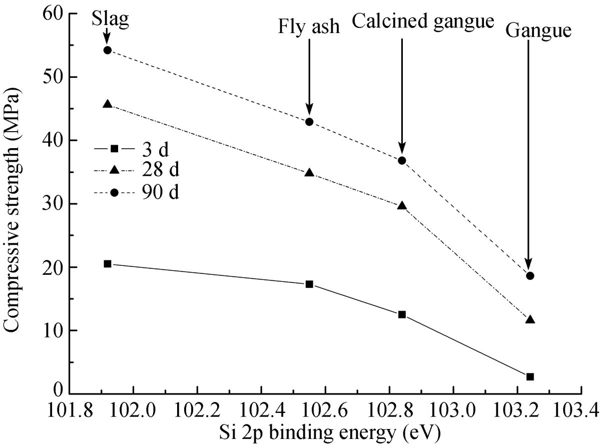

Figure 5 The correlation between Si 2p binding energy and compressive strength.

3.3 Al 2p binding energy analysis

The data for the Al 2p binding energies of the four Al-Si materials are shown in Figure 6. The Al 2p binding energy of slag is the lowest (74.23 eV), while the Al 2p binding energy of untreated gangue is the highest (75.06 eV). Wagner et al.[7] studied the relationships between the Auger electron kinetic and photoelectron binding energies in aluminum-oxygen and silicon-oxygen compounds (minerals and other compounds). Si 2p and Al 2p binding energies and $KL_{23}L_{23}$ Auger kinetic energies of silicate minerals vary systematically according to the structure of the minerals. The electronic environment with the octahedral-coordinated Al ion is more polarizable than that with tetrahedral-coordinated Al ion. The Al 2p binding energy of the octahedral-coordinated Al ion is in the range from 74.1 to 75.0 eV, while the binding energy of the tetrahedral-coordinated Al ion varies from 73.4 to 74.55 eV[8]. According to the Al 2p binding energies, most Al in slag is 4-coordianted while most Al in gangue is 6-coordinated. This is justified by the ^{27}Al MAS NMR spectra shown in Figure 7. The sharp ^{27}Al peak centered at 2.14 ppm for gangue indicates 6-coordinated aluminum while the small peak at 67.70 ppm indicates 4-coordinated aluminum. The main ^{27}Al peak for slag centered at 65.91 ppm denotes 6-coordinated aluminum while the minor peak at 12.20 ppm indicates 4-coordinate aluminum[6]. In contrast to the ^{27}Al MAS NMR spectra of gangue, ^{27}Al MAS NMR spectra of slag are broad which shows there is much glassy phase in slag. Regourd et al.[9] performed surface analysis on the hydration products of blast furnace slag. Their research showed that there is an excellent linear correlation between Ca 2p/Si 2p and Ca/Si and likewise between Al 2p/Si 2p and Al/Si. This means that the surface binding energy for different Al containing minerals in the complex system of slag has a weighted average effect on the overall Al surface binding energy, i.e. the contribution of the binding energy for a particular type of mineral to the overall binding energy of the system is equivalent to its binding energy multiplied by its fraction within the system. The same case is for Si. Moreover, for complex systems, there is also a strong relationship between the Al and Si surface binding energies. The trends for Si 2p and Al 2p binding energies of the four Al-Si materials are shown in Figure 8. Since the change in Al 2p binding energy is consistent with that of Si 2p, the Al 2p binding energies also have

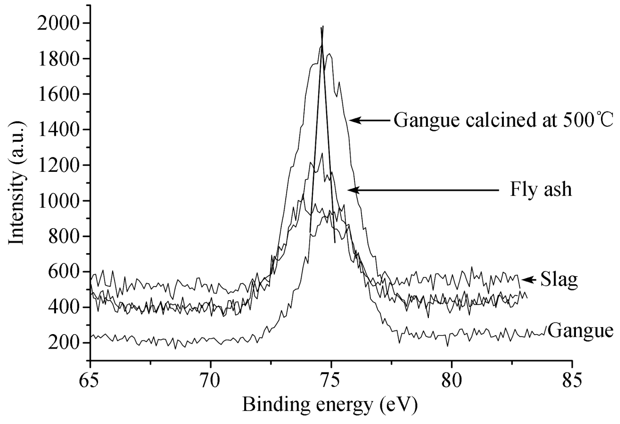

Figure 6 Al 2p binding energies of four Al-Si materials.

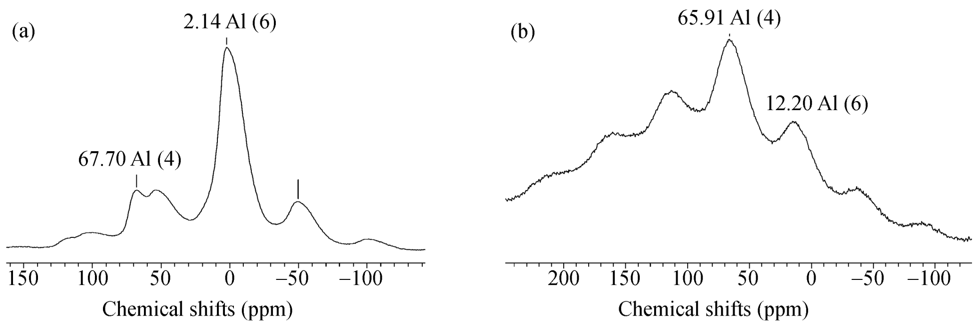

Figure 7 ^{27}Al MAS NMR spectra of Al-Si materials. (a) Gangue; (b) slag.

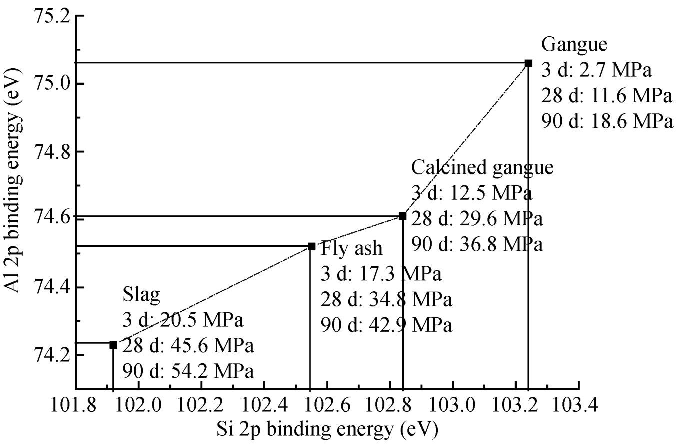

Figure 8 Change trend between Si 2p and Al 2p of binding energies of four Al-Si materials.

a negative linear relationship with the compressive strength of aluminosilicate based cementitious materials. As a result, both Si and Al binding energies can be used to evaluate activity of Al-Si materials.

3.4 O 1s binding energy analysis

Al-Si minerals are made up of Si-O and Al-O tetrahedrons. In Si-O and Al-O tetrahedrons, the polarization of Si and Al ions by the O ion is the main reason for the change of Si 2p and Al 2p binding energies. Si-O tetrahedrons make up the framework of silicate minerals. The chemical environment of Si is dominated by O ions and the degree of polarity of O is obviously the cause for the changes in $\mathrm{Si}\alpha^*$ value of silicate minerals. The shield polarization ability of O in silicate minerals decreases with the rising of O/Si and $\mathrm{O}^{\mathrm{nb}}/\mathrm{O}^{\mathrm{b}}$ but increases with the increase of metallic characteristic of cations. The Auger parameter value of Si in silicate minerals decreases in the order of island-, ring-, chain-, layer- and framework types[10], while the Si 2p binding energy increases in this order. Carriere and Deville[11] studied more than fifty silicon-oxygen compounds (including monocrystal silicon, iron-silicon alloys, quartz, glass made up of different compositions, and natural silicates and aluminosilicates such as feldspars and micas) by using XPS. A statistical method was used to analyze the Si 2p binding energies in various silicon-oxygen compounds. The most oxidized state of silicon (quartz) shifted 5 eV with respect to pure silicon, the two intermediately oxidized states shifted 4.1 eV, and an incompletely oxidized state of silicon shifted 3 eV. Hence, the Si 2p binding energy and the oxygen environment of silicon are related to its oxidation state. The O 1s binding energies of the four Al-Si materials are shown in Figure 9. Every ion serves two actions: it polarizes the surrounding ions while being polarized by those ions. While Si and Al ions are being polarized by O ions, O ions are also being polarized by Si and Al ions. This can be observed from the variation in the O 1s binding energy. Consequently, from Figures 8 and 9, it can be seen that the variations in binding energies of O 1s, Si 2p and Al 2p are consistent.

4 Conclusions

(1) There is a negative linear relationship between the binding energies of the four types of Al-Si materials and the compressive strength of aluminosilicate based cementitious materials prepared with them. Hence, the Si 2p and Al 2p binding energies can be used to effectively evaluate the

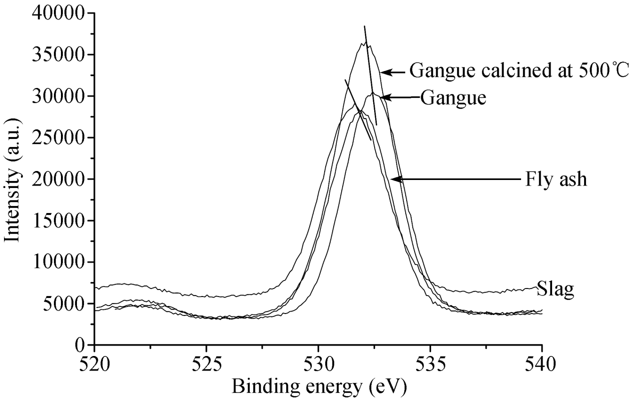

Figure 9 O 1s binding energies of four Al-Si materials.

hydraulic activity of slag, fly ash, gangue and calcined gangue. Moreover, this method can be used as a reference for evaluating the hydraulic activity of other Al-Si materials.

(2) The Si 2p, Al 2p and O 1s binding energies for the four types of Al-Si material have the same varying trend, indicating that they are closely related with each other.

(3) The surface binding energy of composites containing different silicate minerals has a weighted average characteristic. Moreover, the fraction of the compound in glass phase is also a factor affecting the surface binding energy.

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