

Article

Hydraulic Activity and Microstructure Analysis of High-Titanium Slag

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Abstract: To explain the relationship between the hydration activity of high-titanium slag and its microstructure, the hydration activity of high-titanium slag was determined, then the mineral phase and microstructure characteristics of high-titanium slag glass phase and blast furnace slag were investigated using a series of analytical methods, which contain X-Ray Di raction (XRD), Scanning Electronic Microscope (SEM), Fourier Transform Infrared spectroscopy (FTIR), Raman spectroscopy, and Nuclear Magnetic Resonance spectroscopy (NMR). The results showed that in slow-cooled high-titanium slag, the hydration inert mineral content was about 98%, and the glass phase content was less than 2%, hence, the hydration activity of slow-cooled high titanium slag accounted for less than 25% of that of the blast furnace slag. The content of the glass phase in water-quenched high-titanium slag was 98%, but the microstructure of the glass phase was very di erent from that of the blast furnace slag. The glass phase of high-titanium slag has stable forms, which are TiO₄ monomers, chain or sheet units O-Ti-O, and a small amount of 6-coordination Ti⁴⁺. The Ti makes the SiO₄ tetrahedron in a glass phase network not only a monosilicate, but more stable forms of disilicates and chain middle groups also appeared. The relative bridge oxygen number increased to 0.2, hence, the hydration activity of water-quenched high-titanium slag took up less than 37% of that of the blast furnace slag.

Keywords: high-titanium slag; glass phase; mineral phase; microstructure; Raman spectroscopy

1. Introduction

High-titanium slag is a kind of granular or massive waste slag that is produced by the quenching or natural cooling of molten slag discharged from the pig iron obtained via smelting vanadium titanium magnetite [1]. Hydraulicity refers to the property that a material can be hardened in humid air and water to form a stable compound after being ground into a fine powder and mixed with water to form a slurry, also known as hydraulic activity, which is the most basic property of cementitious material. Because the content of TiO₂ in high-titanium slag is about 20%, and because the slag has low latent hydraulic activity (simply termed as hydraulic activity, also known as pozzolanic activity), it cannot be widely used as a building material. Therefore, it is stored in slag yards, thus occupying a lot of land and causing the waste of titanium resources [2]. At present, 80 million tons of high-titanium slag have accumulated in China, and it is still increasing at a rate of 3 million tons per year, and the utilization rate is less than 3% per year [3-7]. Chemical and mechanical activation have been used to improve the hydraulic activity of high-titanium slag, but these methods have not had a significant e ect. Su et al. compared the e ects of several alkali activators. When the mix proportion of the high-titanium slag was 70% in the cementitious materials, and the mix proportion of the activator was

4% in the cementitious materials, the best result increased the compressive strength of the cement mortar after 28 d from 6.5 MPa to 8.0 MPa, which is an increase of only 1.5 MPa [8]. Yang et al. studied the characteristics of grinding activated high-titanium slag. When the mix proportion of the high-titanium slag was 30% in the cementitious materials, and its specific surface area was in the range of 300–500 m²/kg, the compressive strength of cement after 28 d did not increase monotonically with the fineness, but there is a suitable fineness value of 400 m²/kg for the highest compressive strength. The compressive strength of the cement after 28 d was only 23 MPa, which still indicates a very low hydraulic activity [9].

The hydration characteristics of slag are closely related to its hydraulicity. Ao compared the hydration products of blast furnace slag and high-titanium slag, and found that there was no significant di erence in the types and morphology of the hydration products of the two kinds of slag cement, except that the amount of high-titanium slag hydration products was small and the C-S-H gel crystallinity was poor and had an irregular rolled shape, and the strength of the cement specimen was lower due to lower density [10]. Shi et al. studied the hydration behavior and hydration products of crystalline minerals in slow-cooled high-titanium slag. It was thought that the existence of elemental Ti promoted the formation of hydration inert minerals such as perovskite and titanopyroxene, which is the main reason for the low hydraulic activity of the slow-cooled hightitanium slag [11]. In fact, even after water quenching treatment, the hydraulic activity of hightitanium slag was still lower and the setting time longer than that of blast furnace slag. The content and microstructure of the glass phase were the key factors a ecting the hydraulic activity of slag [12–14]. What is the content of glass phase in high-titanium slag? Does the low content of glass phase restrict the hydraulic activity of high-titanium slag? What are the di erences between the glass phase microstructure of high-titanium slag and that of blast furnace slag, and how do these di erences a ect the hydraulic activity of the glass phase?

In this study, the hydraulic activities of high-titanium slag and blast furnace slag are compared. Then, the mineral phase characteristics and the microstructure characteristics of the glass phase of high-titanium slag and blast furnace slag are investigated contrastively, using a series of analytical methods such as XRD, SEM, FTIR spectroscopy, Raman spectroscopy, and NMR spectroscopy. The inevitable connection between the glass phase microstructure and the hydraulic activity is also revealed, with a view to providing new theoretical guidance for improving the hydraulic activity of high-titanium slag.

2. Experiment

2.1. Raw Materials

Three kinds of slag were used in the experiment. The slow-cooled high-titanium slag was procured from Panzhihua Iron and Steel Corporation (Panzhihua, China) and was labeled TM. The water-quenched high-titanium slag was procured from Tranvic Group (Chengdu, China) and was labeled TS. In addition, the blast furnace slag was procured from Beijing Shougang Group(Beijing, China), and was labeled PS. The chemical composition (mass fraction) of the three types of slag was determined according to GB/T 176—2017, the measurement results were within the error range specified in this standard, listed in Table 1.

Table 1. Chemical composition of slag (wt%).

| Sample | CaO | SiO ₂ Al ₂ O ₃ | TiO ₂ | Mg(| Fe ₂ O ₃ | Na ₂ O | LOI | Sum |
|--------|-------|---|------------------|-------|--------------------------------|-------------------|------|-------|
| TM | 26.64 | 24.76 13.22 | 20.39 | 8.37 | 1.20 | 0.95 | 1.64 | 97.17 |
| TS | 28.36 | 26.36 13.33 | 17.18 | 8.39 | 1.31 | 0.16 | 1.30 | 96.39 |
| PS | 35.92 | 33.65 16.90 | 0.07 | 10.13 | 0.13 | 0.33 | 1.55 | 98.67 |

2.2. Instruments

An X-ray di ractometer (D/Max 2200, Japan, Cu K ray with = 0.15418 nm) was used for X-ray di raction. A field emission scanning electron microscope (Hitachi S4800, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (EDS) was used in this study. In addition, a microinfrared spectrometer (Bruker VERTEX70 from Cernet Co., Ltd. Germany), having a frequency band range of 400 to 4000 cm⁻¹ and a resolution of 2 cm⁻¹, was used for infrared spectroscopy. A laser Raman spectrometer (Horiba HR Evolution, Japan) was used for Raman spectroscopy. The experiment was conducted at room temperature with a laser wavelength of 532 nm and within a frequency band of 100–2000 cm⁻¹. Moreover, a fully digital NMR spectrometer (AVANCE 400 (SB) from Bruker Bio-spin, Switzerland) was used for NMR spectroscopy. The resonance frequencies of ²⁹Si and ²⁷Al were 79.49 Hz and 104.23 Hz, respectively.

2.3. Test Method

2.3.1. Hydraulic Activity Test

(1) According to Appendix A of GB/T 18046—2017, the compressive strength ratio of the prepared 50% slag powder sample and Portland cement reference samples was taken as the index of hydraulic activity A of their age. (2) The content of active SiO_2 and Al_2O_3 dissolved in saturated limewater was determined by the method of boiling circumfluence [15]. The percentage of the amount of SiO_2 and Al_2O_3 dissolved to the total amount of SiO_2 and Al_2O_3 is the pozzolanic activity rate K_a of the slag.

2.3.2. Content of Glass Phase

(1) According to Appendix C of GB/T 18046—2017, Jade software was used to fit the XRD patterns of the slag. The ratio of the crystal di raction peak area to the total di raction peak area is slag crystallinity, and 100% minus the crystallinity is the glass phase content. (2) The alkali–acid two-stage dissolution method [16] was used to dissolve the glass phase and f-CaO in the slag. The glass phase content was obtained by subtracting the f-CaO content from the mass reduction rate.

3. Results and Discussion

3.1. Hydraulic Activity Test

Table 2 shows the hydraulic activity test results of the three kinds of slags, in which A₇ and A₂₈ are the indexes of hydraulic activity for 7 d and 28 d, respectively. It can be seen from Table 2 that the 7 d indexes of hydraulic activity of the two kinds of high-titanium slag are less than 30% of that of blast furnace slag, and the 28 d indexes of hydraulic activity are less than 38% of that of blast furnace slag, so the hydraulic activity of high-titanium slag is far lower than that of blast furnace slag. Comparing the two kinds of high-titanium slag, the index of hydraulic activity for 7 d and 28 d of water-quenched high-titanium slag is 1.7 and 1.5 times that of slow-cooled high-titanium slag, respectively. The hydraulic activity of water-quenched high-titanium slag is obviously higher than that of slow-cooled high-titanium slag. K_a is the pozzolanic activity rate of slag. The order of the pozzolanic activity rate and the index of hydraulic activity of the three kinds of slag are the same: blast furnace slag > water-quenched high-titanium slag > slow-cooled high-titanium slag. The pozzolanic activity rate of water-quenched high-titanium slag is 57% of that of blast furnace slag, while the index of hydraulic activity of water-quenched high-titanium slag is less than 38% of that of blast furnace slag. Referring to Table 1, it can be seen that the active SiO₂ and Al₂O₃ in hightitanium slag not only have a low dissolution rate, but also have a lower content of SiO₂ and Al₂O₃ than blast furnace slag, due to the high content of TiO₂.

Table 2. Hydraulic activity test of slag (%).

| Sample | A ₇ | A28 K _a |
|--------|----------------|--------------------|
| PS | 125.6 | 95.6 99.3 |
| TS | 35.1 | 35.8 56.8 |
| TM | 21.2 | 23.5 35.7 |
| | | |

3.2. Mineral Phase Analysis

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Figure 1 shows the XRD patterns of three kinds of slag, all of which were thoroughly dried and 3.2.1. Mineral Phase Identification

ground to less than 5 m. There are broad scattering peaks of glass phase between 21 and 37 in Figure 1 shows the XRD patterns of three kinds of slag, all of which were thoroughly dried and

the PS and TS patterns that belong to water-quenched slag. The results show that whether it is blast ground to less than 5 µm. There are broad scattering peaks of glass phase between 21° and 37° in the furnace slag or high-titanium slag, if it is water-quenched, the main mineral composition is glass phase. PS and TS patterns that belong to water-quenched slag. The results show that whether it is blast

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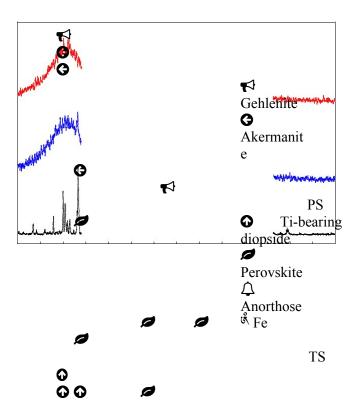
phase. A small amount of crystalline phases in blast furnace slag contain gehlenite akermanite (2CaO MgO 2SiO₂); there is no gehlenite or akermanite phase, and only a small amount (2CaO·Al2O3·SiO2) and akermanite (2CaO·MgO·2SiO2); there is no gehlenite or akermanite phase, and

of perovskite in water-quenched high-titanium slag. In slow-cooled high-titanium slag, there are only a small amount of perovskite in water-quenched high-titanium slag. In slow-cooled high-almost no broad scattering peaks of the glass phase, most of which are crystal minerals. In addition to titanium slag, there are almost no broad scattering peaks of the glass phase, most of which are crystal

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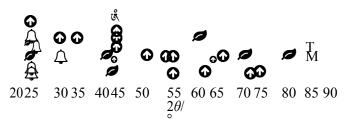


Figure 1. XRD patterns of three kinds of slag. **Figure 1.** XRD patterns of three kinds of slag.

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Figure 2. Figure 2a shows the micro-morphology of the mineral phase of water-quenched highFigure 2. Figure 2a shows the micro-morphology of the mineral phase of water-quenched hightitanium titanium slag. The uniform gray region 1 accounts for more than 95% of the whole field of view. The slag. The uniform gray region 1 accounts for more than 95% of the whole field of view. The chemical chemical composition of the micro-region as determined by EDS is Ca0.97SiMg0.49Al0.61Ti0.42O4.9, which composition is the composition is the composition of the micro-region as determined by EDS is Ca0.97SiMg0.49Al0.61Ti0.42O4.9, which composition is the composition is the composition of the micro-region as determined by EDS is Ca0.97SiMg0.49Al0.61Ti0.42O4.9, which composition is the composition of the whole field of view. The chemical composition of the micro-region as determined by EDS is Ca0.97SiMg0.49Al0.61Ti0.42O4.9, which composition is the composition of the micro-region as determined by EDS is Ca0.97SiMg0.49Al0.61Ti0.42O4.9, which composition is the composition of the micro-region as determined by EDS is Ca0.97SiMg0.49Al0.61Ti0.42O4.9, which composition is the composition of the micro-region as determined by EDS is Ca0.97SiMg0.49Al0.61Ti0.42O4.9, which composition is the composition of the micro-region as determined by EDS is composition in the composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the micro-region as determined by EDS is composition of the phase phase in the inthigh eabove - titanium XRD patterns, slag. $^{the} Corresponding ^{glassphase is the} to ^{main} the \\$

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titanium slag. In the gray-white area 2 in Figure 2a, the chemical composition of the micro-region is above XRD patterns, the glass phase is the main mineral phase in water-quenched high-titanium slag. CaTiO3, which belongs to perovskite in high-titanium slag. The maximum grain length is about 100

In the gray-white area 2 in Figure 2a, the chemical composition of the micro-region is CaTiO3, which µm. The large grains are mostly irregular in shape, otherwise, there are a large number of grains of

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in which there is more perovskite content than Figure 2a, and the degree of enrichment of mineral a dispersed distribution.

particles increases. There are many 20–50 µm perovskite grains, but no 10 µm perovskite grains. In Figure 2b shows the micro-morphology of the mineral phase of slow-cooled high-titanium slag the visual field, the matrix is the light gray area 3, and the chemical composition of the

in which there is more perovskite content than Figure 2a, and the degree of enrichment of mineral region is CaMg 0.62Si1.6Ti0.31O5.21, which belongs to Ti-bearing diopside in high-titanium slag

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CaMg_{0.62}Si_{1.6}Ti_{0.31}O_{5.21}, which belongs to Ti-bearing diopside in high-titanium slag as another major mineral of slow-cooled high-titanium slag. In the few dark gray areas marked as 4 in Figure 2b, the chemical composition of the micro-region is Na_{0.45}K_{0.31}AlSi_{1.19}O_{4.26}. The mineral belongs to anorthose in high-titanium slag, the grain size is about 20-50 m, and a pile of the grains is embedded Materials 2020, 13, x FOR PEER REVIEW in Ti-bearing diopside. In a few bright areas 5, the chemical composition of the micro-region is Fe. It residualembeddedetallic ironinTi-phbearingseindiopsidehigh-titanium.Infew slabright, with areas a 5, grain the chemical size of approximately of the 5 microto 15 - m and Materials 2020, 13, x FOR PEER REVIEW
a round or region_{long} is_{shape}Fe.It is a residual metallic iron phase in high-titanium slag, with a grain size of approximately 5 to 15 μm and a round or long shape. **\$**2 of embedded in Ti-bearing diopside. In a few bright areas 5, the chemical composition of the micro-region is Fe. It is a residual metallic iron phase in high-titanium slag, with a grain size of approximately 5 to 15 µm and a round or long shape. Figure SEM images of nds of images (15) two kinds of high transum Siage) (TMTS; Figure wo kinds of ${}_{3.2.2.\ Distribution} 3.2.2. Distribution {}_{Characteristics} \textbf{Figur} a cristics \textbf{2.} SEM_{of Elemental} of images elemental of two_{Ti} Tiknds~of$ Figure 3 is a surface image of the Ti distribution in high-titanium slag, where (a1) and (a2)

Figure 3 is 2 a surface Distribution image Characteristics of the Tidistribution of Characteristics high-titanium slag. (a) TS; (b) TM. ure 3^3 is 2^2 surface de surface de la s water-quenchedFigurehigh3is-titaniumsurface imageslag, the)andTidistribution(b)correspondinhigh-titaniumtoslowslag,-cooledwherehigh(a)to (bof andtitanium(a) slag. titanium slag. In water-quenched high-1titanium slag, 2 Ti is uniformly dispersed throughout 1 the glass 2 In water-quenched correspond high to water titanium quenched slag, high Tiis titanium uniformly slag, (bdispersed 1) and (b2) throughout correspond to the slow glass cooled phase high matrix, phase matrix, and he content of Ti in perovskite is higher than that of glass phase. In slow-cooled titanium slag. In water-quenched high-titanium slag, Ti is uniformly dispersed throughout the glass
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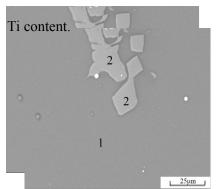
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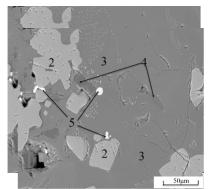
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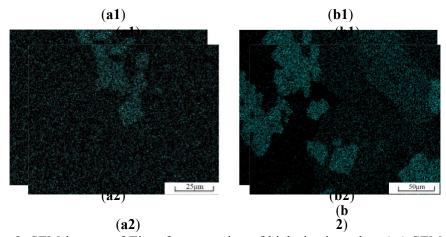
Ti content.

Ti-bearing diopside, Ti. Thematrix has a mineral, low Ti Ti content; -bearing diopside, the perovskite has a low contains Ti content; the the highest perovskite Ti contains content the.

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(a2) (b) 2) Figure 3. SEM images of Ti surface scanning of high-titanium slag. (a₁) SEM image of TS; (a₂) Ti surface scanning of TS; (b₁) SEM image of TM; (b₂) Ti surface scanning of TM.

3.2.3. Glass Phase Content

In order to ensure the accuracy of the test results, the XRD method and the alkali-acid twostage dissolution method were used to measure the glass phase of three kinds of slag. The test results are shown in Table 3.

Table 3. Comparison of glass phase content in slag (%).

| Method | PS | TS | TM |
|-----------------------------------|-------|-------|------|
| XRD | 98.03 | 97.34 | 1.82 |
| alkali-acid two stage dissolution | 99.49 | 98.35 | 1.91 |

As can be seen from Table 3, the glass phase content of the slow-cooled high-titanium slag is quite low. The glass phase content of the two kinds of water-quenched slag is about 98%, and the results are similar. The presence of more visible perovskites in Figure 2; Figure 3 is shown intentionally to show the morphology of the perovskites, although this does not mean the perovskite content in water-quenched high-titanium slag is high. From this point of view, the hydraulic activity of the two kinds of water-quenched slag is quite di erent, and it is not caused by the di erence in the glass phase content. The microstructure of the two kinds of glass phase should be analyzed.

3.3. Analysis of Glass Phase Microstructure

3.3.1. FTIR Spectroscopy Analysis

Figure 4 shows the comparative FTIR spectroscopy of the two kinds of water-quenched slag. It can be seen from the Figure 4 that the e ective spectral range of 400–1200 cm⁻¹ is composed of three regions: 800–1000 cm⁻¹ with strong intensity, 400–600 cm⁻¹ with medium intensity, and 600–700 cm⁻¹ with weak intensity. The 800–1000 cm⁻¹ band is produced by the antisymmetric stretching vibration of the Si–O bond in the SiO₄ tetrahedron in slag [17]. Compared with blast furnace slag, the peak position of water-quenched high-titanium slag here is shifted toward a higher wave number. The 400–600 cm⁻¹ band is produced by the symmetric bending vibration of the Si–O–Si bond. Compared with blast furnace slag, the peak position of water-quenched high-titanium slag here is shifted toward a lower wavenumber. The 600–700 cm⁻¹ band is produced by the symmetric stretching vibration of the Si–O bond [18]. There was no significant change in the peak position of this band in the two kinds of slag. Sun et al. thought that the 800–1000 cm⁻¹ band shifted in the high wave number direction, and the 400–600 cm⁻¹ band shifted toward the low wave number direction, indicating that the degree of polymerization of the glass phase had increased [17]. Therefore, compared with blast furnace slag, the glass phase polymerization degree of water-quenched high-titanium slag increased and the hydraulic activity decreased.

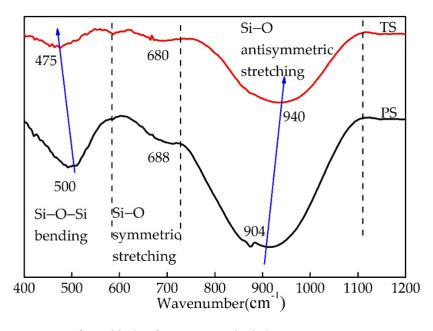


Figure 4. FTIR spectroscopy of two kinds of water-quenched slag. Figure 4. FTIR spectroscopy of two kinds of water-quenched slag. Figure 4. FTIR spectroscopy of two kinds of water-quenched slag.

3.3.2. Raman Spectrum Analysis 3.3.2. Raman Spectrum Analysis 3.3.2. Raman Spectrum Analysis

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the higher the molecular polarizability the molecular polarizability themoleculars. Generally, the higher the molecular polarizability, the stronger the Raman spectrum intensity.

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two kinds of slag glass phase is in the

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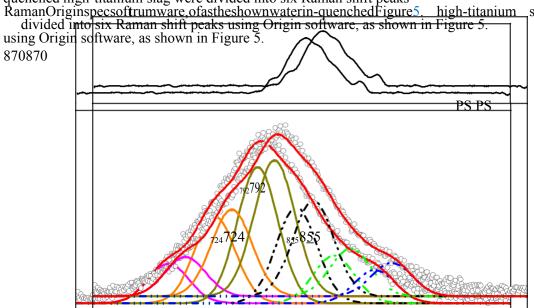
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700 750 800 850 900 9501000 1050 11000 750 800 65 900 65 - 000 105 010 1150 50 500 550 600 0 0, 550, 600, 650, 700, 750, 800,

In the silicate glass phase system, the structural units of the SiO₄ tetrahedron can be divided into Q^0 , Q^1 , Q^2 , Q^3 , and Q^4 according to the coordination number of the bridge oxygen around Si. Here, n in Q^n represents the coordination number of the bridge oxygen around Si. The lower the bridge oxygen coordination number, the higher the hydraulic activity. The Raman shift for blast furnace slag at 870 cm 1 was produced by the stretching vibration of the Si–O bond in Q^0 [19,20]. The integrated envelopes for water-quenched high-titanium slag were divided into six Raman shift peaks. Of these Raman shift peaks, the Raman shift at 792 cm 1 is generated by the Ti–O 2 stretching vibration in TiO₄ 4 monomers, the Raman shift at 724 cm 1 is generated by the deformation of O–Ti–O in chain or sheet units [21,22]. The Raman shift at 649 cm 1 is generated by Ti–O stretching vibrations in 6-coordinated Ti⁴⁺ [23]. The above three Raman shifts indicate that the Ti in the water-quenched high-titanium slag mainly exists as TiO₄ 4 monomers, the secondary form is O–Ti–O in chain or sheet units, and a small amount of Ti exists in the 6-coordinated form. The Raman shifts at 855 cm 1 , 915 cm 1 , and 981 cm 1 are generated by the stretching vibration of the Si–O bond in Q^0 , Q^1 , and Q^2 [24–26], respectively. The results show Q^0 , Q^1 , and Q^2 structural units of the SiO₄ tetrahedron in water-quenched high-titanium slag.

It can be seen from the above test results that the SiO_4 tetrahedron in blast furnace slag is mainly monosilicate represented by Q^0 , so its hydraulic activity is high. $TiO_4^{4^+}$ monomers in water-quenched high-titanium slag are more stable than the SiO_4 tetrahedron [23]. At the same time, there is O–Ti–O in chain or sheet units, which transform the original non-bridged oxygen to bridged oxygen, so that the number of bridged oxygen per SiO_4 tetrahedron increases, and the degree of network polymerization is enhanced. The Ti in water-quenched high-titanium slag enters the silicate glass system in the form of a network formers, which not only reduces the content of the SiO_4 tetrahedron, but also transforms some of the SiO_4 tetrahedron to the more stable form of Q^1 disilicates and Q^2 chain middle groups. Therefore, the glass phase structure of water-quenched high-titanium slag is more stable than that of blast furnace slag, and its hydraulic activity is lower than that.

3.3.3. NMR Analysis

(1) ²⁹Si spectrum and ²⁷Al chemical environment

The relationship between chemical shift and structure in ²⁹Si NMR is shown in Table 4. Al mainly exists in the form of four-coordination or six-coordination in the glass phase network in aluminosilicate. The chemical shift between +50 and +80 ppm belongs to the [AlO₄] tetrahedral structure, and the chemical shift between -10 and +20 ppm belongs to the [AlO₆] hexahedral structure [27].

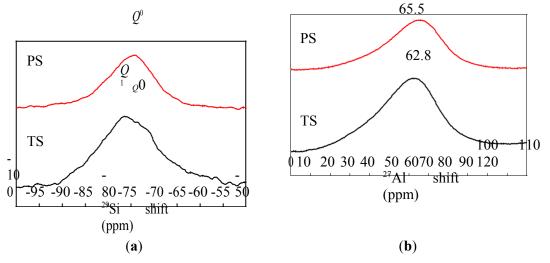
| Table 4 29 | 9Si NMR chemical | shifts of the structur | e unit of O | in solid silicates | 781 |
|------------|-------------------|------------------------------|-------------|---------------------|-----|
| I abic 7. | of twitt chemical | i siiiitis oi tiic sii uctui | c unit of Q | III solia silicates | 40. |

| Types of Si-O-X group | Symbol | Chemical Shift/ppm |
|----------------------------------|------------------|--------------------|
| | | 68 |
| Monosilicate | $_{\mathrm{Q}}0$ | - 76 |
| | | 76 |
| Disilicates and chain end groups | Q^1 | - 82 |
| | | 82 |
| Chain middle groups | Q^2 | - 88 |
| | | 88 |
| Layers and chain branching sites | Q^3 | - 98 |
| Three-dimensional networks | Q^4 | 98-129 |

Figure 6 shows the 29 Si and 27 Al NMR spectroscopy for two kinds of water-quenched slag, and Figure 6a shows the NMR spectrum of 29 Si. It can be seen from Figure 6a that there is only Q^0 peak in blast furnace slag, indicating that the SiO_4 tetrahedron in blast furnace slag only exists in the form of monosilicate. Relative to blast furnace slag, the chemical shift of water-quenched high-titanium slag moves to the high field, and the peak is not a Q^0 single peak, but the superposition peak of Q^0 and Q^1 . This shows that the SiO_4 tetrahedron in water-quenched high-titanium slag exists in the form of monosilicate and disilicates, which is consistent with the analysis of FTIR spectroscopy and Raman spectroscopy. Figure 6b shows the NMR spectrum of 27 Al. The 27 Al peaks of blast furnace slag and water-quenched high-titanium slag are 65.5 ppm and 62.8 ppm, respectively, so the chemical

environment of Al element in the two kinds of slag is [AlO₄] tetrahedral, and the presence of Ti has no obvious Materials 2020 influence, 13, xFOR on PE 9 of 12

ERthe structureREVIEW of Al.



Figurere 66.. ²⁹Si and ²⁷Al NMR spectroscopy ffor two kinds of of water-quenched-slag.. (a(a)) ²⁹²⁹Si NMR spectroscopy; ectroscopy; ((bb)) ²⁷All NMR spectroscopy. (²²Characterization of polymerization degree

The polymerization degree is an index reflecting the comprehensive influence of the chemical is an reflecting the influence

composition and glass phase structure on the hydraulic activity. The higher the polymerization degree, and glass phase structure on the hydraulic activity. The higher the polymerization

the lower the hydraulic activity. The change in the oxygen number can used to reflect degree, the lower the hydraulic activity. The changebridgingthebridging oxygen number can be used

the polymerization degree of the system. The bridging oxygen number increases with Si–O bond reflect the polymerization degree of he system. The bridging oxygen number increases with Si–O polymerization and decreases with Si–O–Si bond depolymerization. Therefore, the bridging bond polymerization and decreases with Si–O–Si bond depolymerization. Therefore, the higher the

oxygen number, the higher the degree of polymerization and the lower the hydraulic activity. bridging oxygen number, the higher the degree of polymerization and the lower the hydraulic In this study, the deconvolution of the ²⁹Si NMR spectroscopy of TS was performed using

activity.

Origin software, and the relative areas of the resonance peaks were calculated. The magnitude of In this study, the deconvolution of the 29Si NMR spectroscopy of TS was performed usi Origin the software, corresponding and the relative relative bridging areas of oxygen thereson an cnumber (RBO) peaks was were calculated according. The magnitude to the following of the

formula 1707 formu

n RBO= 1/1 × +2× n× 4 × n (1)
where Q corresponding ΣΣ
As shown in Figure 7, the ²⁹Si NMR spectroscopy of water-quenched high-titanium slag is where Qn is the relative area of the corresponding resonance peak.

deconvoluted into five peaks. Based on classification according to the chemical shift, there are two As shown in Figure 7, the 29Si NMR spectroscopy of water-quenched high-titanium slag is Q¹ peaks, two Q⁰ peaks, and one Q² peak. Therefore, the Q¹, Q⁰, Q² forms of the SiO4 tetrahedron deconvoluted into five peaks. Based on classification according to the chemical shift, there are two Q¹

exist in the water-quenched high-titanium slag. Because Q^1 has the largest area, it can be said that peaks, two Q0 peaks, and one Q2 peak. Therefore, the Q1, Q0, Q2 forms of the SiO 4 tetrahedron exist disilicate is the main form in water-quenched high-titanium slag. After calculating the integral area of in the water-quenched high-titanium slag. Because Q1 has the largest area, it can be said that disilicate

each peak, the relative areas of Q^1 , Q^0 , and Q^2 were found to be 100, 81.06, and 21.82, respectively, is the main form in water-quenched high-titanium slag. After calculating the integral area of each and the calculated RBO value was 0.2. Blast furnace slag has only one Q^0 single peak, consequently, its peak, the relative areas of Q1, Q0, and Q2 were found to be 100, 81.06, and 21.82, respectively, and the

RBO was 0. Therefore, the high degree of polymerization and more stable structure of the glass phase calculated RBO value was 0.2. Blast furnace slag has only one *Q*0 single peak, consequently, its RBO in water-quenched high-titanium slag are the main reasons for its low hydraulic activity. was 0. Therefore, the high degree of polymerization and more stable structure of the glass phase in water-quenched high-titanium slag are the main reasons for its low hydraulic activity.

4. Conclusions

4. Conclusion

The main mineral phase composition of the slow-cooled high-titanium slag included perovskite, The main mineral phase composition of the slow-cooled high-titanium slag included perovskite, Ti-bearing diopside, and anorthose. Because these mineral phases pertain to inert mineral crystals,

Ti-bearing diopside, and anorthose. Because these mineral phases pertain to inert mineral crystals, and the content of glass phase was less than 2%, the hydration activity was low. Although the content

and the content of glass phase was less than 2%, the hydration activity was low. Although the content

of glass phase in water-quenched high-titanium slag was 98%, Ti mainly existed in the glass phase of glass phase in water-quenched4- high-titanium slag was 98%, Ti mainly existed in the glass phase structure in the form of TiO4 monomers, chain or sheet units, and a small amount of 6coordination,

structure in the form of TiO44- monomers, chain or sheet units, and a small amount of 6coordination, which were relatively stable. The titanium oxygen structure in the glass phase not only

which were relatively stable. The titanium oxygen structure in the glass phase not only reduced the relative content of SiO₄ tetrahedron, but also made the SiO₄ tetrahedron in the glass phase network a relative content of SiO tetrahedron, but also made the SiO tetrahedron in the glass phase network a monosilicate, and more4 stable forms of disilicates and chain4 middle groups appeared. The relative monosilicate, and more stable forms of disilicates and chain middle groups appeared. The relative bridge oxygen number increased to 0.2, so the hydraulic activity of the water-quenched high-

bridge oxygen number increased to 0.2, so the hydraulic activity of the water- quenched high-titanium slag was also low. Based on the results of this study, the removal of Ti from high-titanium slag not slag was also low. Based on the results of this study, the removal of Ti from high-titanium slag not only increased the relative content of active SiO₂ and Al₂O₃ in the glass phase, but also improved the only increased the relative content of active SiO2 and Al₂O₃ in the glass phase, but also improved the hydraulic activity of the glass phase.

hydraulic activity of the glass phase.

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XRDNomenclatureX-rayDi

```
raction
SEM
              Scanning Electron Microscope
              X-ray Diffraction
Energy Dispersive Spectrometer
EDS
              Back Scattering Electron Image
Fourier Transform Infrared spectroscopy
Nuclear Magnetic Resonance spectroscopy
Back Scattering Electron Image
Water-quenched high-litanium slag
Fourier Transform Infrared spectroscopy
 FTIR
PS Blast furnace slag Slow-coolingNuclear fligh Magnetic titanium Resonance slag spectroscopy A Index of hydraulic activity for 7 d slag
Α
                         Water-quenched high-titanium
 Τ
 S7
 PS
                        Blast furnace slag
                        Slow-cooling high-titanium slag
 TM
```

- ${^{^{\Lambda}}28}\atop{K_a}$ Index of hydraulic activity for 28 d
- Oⁿ The pozzolanic activity rate
- Types of Si–O–X group, n is the bridge oxygen
- RB number of coordination around Si
 - Relative bridge oxygen number

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