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Compressive Strength Enhancement in Early Age Acid Activated Mortars: Mechanical Properties and Analysis

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Abstract: To increase the hydration reaction rate and the amount of hydration products, different types and proportions of acids were mixed into mortars. The effects of the acid type and content on the early compressive strength of cement-based materials and the strengthening mechanism were assessed via X-ray diffraction and Fourier-transform infrared spectrum analyses. The addition of acetic acid or hydrochloric acid significantly increased the compressive strength of mortars at 1 d and 3 d, and slightly increased it at 28 d. With increasing acetic acid content, the strengthening effect increased first and then decreased with the best content at 4%. With increasing hydrochloric acid content, the strengthening effect decreased gradually with the best content at 2%.

Keywords: acid activated; mortars; compressive strength; hydration reaction; calcium silicate

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1. Introduction

Portland cement is widely used in various engineering constructions because of its wide range of available raw materials, low price, excellent mechanical properties, frost resistance, and good wear resistance [1]. After mixing cement and water, dicalcium silicate, tricalcium silicate, and tricalcium aluminate are continuously dissolved. Cement hydration reaction occurs in a strong alkali reaction environment (pH range between 12 and 13), forming hydrated calcium silicate gel, thereby, gradually establishing specific mechanical properties [2].

The strength development of cement-based materials is a slow and complex process, which requires the dissolution of active substances, hydration reaction, and the formation and gradual strengthening of hydrated calcium silicate [3]. Moreover, the hydration reaction rate is low, and the reaction duration is long, resulting in insufficient early strength, slow strength development, and a long curing time of cement-based materials [4]. Generally, under laboratory conditions, cement-based materials must be cured for 28 d to reach standard strength, while in actual projects, cement-based materials must be cured for at least 7 d before the mold can be removed and construction continued.

With the acceleration of urbanization, building structures are developing towards super high-rise and long-span properties, and building constructions are developing towards the goals of high quality and short construction periods. However, the development of early-age strength of cement-based materials is often insufficient, and the requirement of a long curing period runs counter to the modernization goals [5]. Therefore, it has become a hot issue in the field of cement-based materials to improve early-age mechanical properties, accelerate the hydration reaction rate, and shorten the curing cycle.

Although the use of an early-age strength agent can improve the early-age mechanical properties and shorten the curing cycle, it also increases the preparation cost of cement-based materials, delays the setting time, and causes a sudden drop in the mechanical properties [6]. The use of early strength agents containing chloride and sulfate will lead to a significant reduction in the durability of cement-based materials (because of resistance to chloride and sulfate corrosion) [7].

Therefore, although the addition of an early strength agent can improve the early-age mechanical properties of cement-based materials, the negative impact is severe. With the continuous development of technology, scholars remain committed to developing a low-cost, high-efficiency, and side-effect-free method to improve the early-age mechanical properties of cement-based materials and shorten the maintenance cycle [8]. These goals are of great importance for the further development of building structures and construction.

In this study, different kinds and proportions of acids were mixed in the preparation of cement-based materials. The goals were to stimulate the hydration reaction activity of cement particles, accelerate the dissolution of active substances, improve the hydration reaction rate, and increase the production of hydration products. Ultimately, these treatments were employed to improve the early-age mechanical properties of cement-based materials and shorten the required curing period. The influence of acid excitation on the time-varying law of the development of mechanical properties of cement mortar specimens at an early age was analyzed from a macro perspective. Furthermore, the enhancement mechanism of acid excitation was analyzed and expounded from the micro perspective by Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD).

2. Experimental Materials and Mix Proportions

2.1. Experimental Materials

2.1.1. Portland Cement

P·O 42.5 ordinary Portland cement produced by a cement plant in Huainan City was used in the experiment. Its performance meets the standard of general Portland cement (GB175-2007) [9]. The chemical composition of the cement was measured using X-ray fluorescence spectrometry (XRF) and is presented in Table 1.

Table 1. Chemical composition of the Portland cement (%).

Raw Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Others	Loss
Portland cement	21.42	5.31	2.68	61.37	2.26	0.32	0.18	2.21	1.82	2.34

2.1.2. Acetic Acid and Hydrochloric Acid

To ensure the same amount of H^+ in acetic acid solution and hydrochloric acid solution of the same quality, the acetic acid used in the experiment is of chemical grade and has a concentration of 30%. The hydrochloric acid used in the experiment is also of chemical grade and has a concentration of 18%.

2.1.3. Others

The fine aggregate used in the experiment is medium–coarse river sand with a fineness modulus of 2.7. The experimental water is tap water. The pH value of tap water is 8.1, and the turbidity is less than 1 NTU.

2.2. Experimental Mix Proportion

The experimental coordination of mortars is shown in Table 2. Test sample C-1 (i.e., the control group) was not mixed with any acid solution. Samples C-2 to C-6 were mixed with different proportions of acetic acid (2%, 4%, 6%, 8%, and 10%, respectively) to test the regulatory effect of acetic acid on the properties of cement-based materials. Samples C-7 to C-11 were mixed with different proportions of hydrochloric acid (2%, 4%, 6%, 8%, and 10%, respectively). The excitation effects of hydrochloric acid on cement-based materials were tested and compared with those of acetic acid.

Table 2. Mix proportions of cement mortars (g).

Samples Number	Portland Cement	Water	Acetic and Hydrochloric Acid	Sand	Liquid–Solid Ratio
C-1	450	225	0	1350	0.5
C-2	450	216	9 g (2%)	1350	0.5
C-3	450	207	18 g (4%)	1350	0.5
C-4	450	198	27 g (6%)	1350	0.5
C-5	450	189	36 g (8%)	1350	0.5
C-6	450	180	45 g (10%)	1350	0.5
C-7	450	216	9 g (2%)	1350	0.5
C-8	450	207	18 g (4%)	1350	0.5
C-9	450	198	27 g (6%)	1350	0.5
C-10	450	189	36 g (8%)	1350	0.5
C-11	450	180	45 g (10%)	1350	0.5

Note: H^+ content in 9 g acetic acid = 9 × 30%/60 = 0.045 mol; because cement is strongly alkaline, it can completely react with H^+ in acetic acid; H^+ content in 9 g hydrochloric acid = 9 × 18%/36.5 = 0.044 mol.

3. Experimental Contents and Methods

3.1. Preparation and Curing of Test Pieces

The preparation and curing of samples were conducted according to the standard of mortar strength test method (ISO method) (GB/T 17671-2020) [10]. Taking sample C-2 as an example, first, acetic acid was added to the test water according to the mix proportion shown in Table 2. The sample was mixed evenly and placed in a mixer (JJ-5 planetary cement mortar mixer, Shanghai Meiyu Instrument Technology Co., Ltd. Shanghai China).

Then, cement was added into the mixer, the mixture was mixed slowly for 30 s, and then quickly for 30 s. Next, test sand was added and mixed quickly for 60 s, and finally, the prepared mortar was poured into 40 mm × 40 mm × 160 mm mold for formwork removal and curing. When the specimen was prepared, it was placed in the curing room immediately, cured for 24 h, and the formwork was removed. After formwork removal, the specimen remained in the curing room until the experimental age was reached. The temperature of the curing room was kept at 20 ± 1 °C, and the relative humidity was greater than 95%.

3.2. Compressive Strength Test

The compressive strength test was performed according to the standard of cthe ement mortar strength test method (ISO method) (GB/T 17671-2020) [10]. The test adopted the YAW-300D automatic cement mortar test machine produced by Instrument and Equipment Co., Ltd. in Jinan, China, and the compressive strengths of samples cured for 1, 3, and 28 d were tested. The experimental results are presented as the average value of six measurements.

3.3. Microscopic Inspection

(1) X-ray diffraction analysis

The mineral crystal composition of cement paste samples C-1, C-2, C-3, C-6, C-7, and C-11 was analyzed by using the D8 advance X-ray diffractometer produced by Bruker company, Germany, to test the promoting effects of acid excitation on mineral crystal formation and time-varying law. The anode target of the instrument adopted Cu Target and Ka radiation, and the measurement range was (2θ) between 5° and 70°.

(2) Fourier-transform infrared spectroscopy analysis

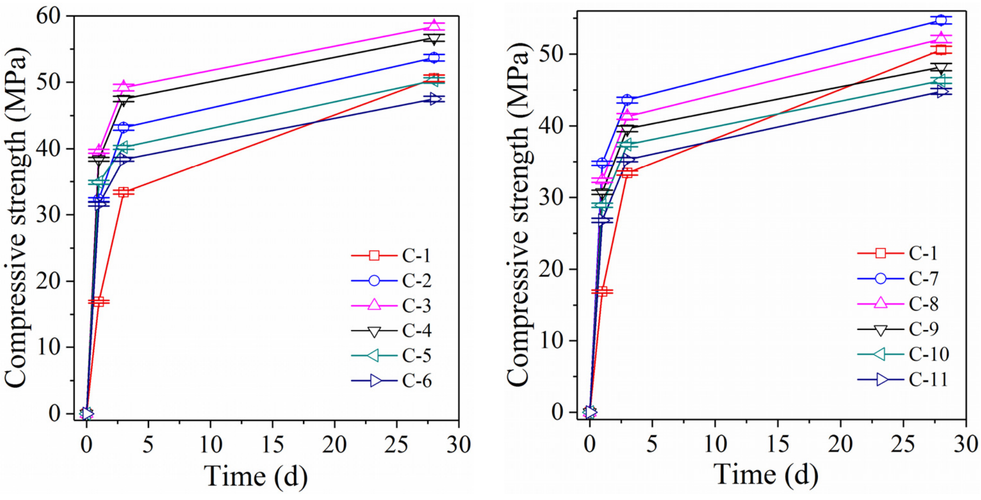
The molecular composition, structure, and chemical bond types of cement paste samples C-1, C-2, C-3, C-7, and C-11 were analyzed using a vertex 80V Fourier-transform infrared spectrometer and micro infrared system produced by the Bruker company, Germany. The promoting effect and time-varying law of acid excitation on the formation of silicate and aluminate were assessed. The spectral measurement range was between 4000 and 400 cm^{-1}.

4. Experimental Results and Analysis

4.1. Acid-Induced Compressive Strength

4.1.1. Compressive Strength of Mortars

Figure 1a shows the development law of the mechanical properties of mortars excited by acetic acid. Without acid excitation, the compressive strength of sample C-1 after curing for 1 d reached 16.9 MPa. After curing for 3 d, it increased to 33.4 MPa and further increased to 50.6 MPa after curing for 28 d. Sample C-1 had excellent mechanical properties. However, the compressive strengths of samples cured for 1 and 3 d were only 33.3% and 66%, respectively, of the strength of sample cured for 28 d. This shows that the early compressive strength was clearly insufficient, and the growth rate was low.



(**a**) (**b**)

Figure 1. Effects of acids on mechanical properties. (**a**) Effects of acetic acid; (**b**) Effects of hydrochloric acid.

4.1.2. Effects of Acetic Acid Contents on Mechanical Properties

(1) Excitation with 2% acetic acid

After the addition of acetic acid (2%), the development law of the mortar mechanical properties changed greatly. The compressive strengths of sample C-2 cured for 1 and 3 d increased to 32.3 and 43.2 MPa, respectively, which were 91.1% and 29.3% higher than the compressive strengths of sample C-1. The addition of acetic acid (2%) notably improved the early mechanical properties, and the range of the increase was the largest when curing lasted for 1 d. With an extended curing age, the compressive strength of sample C-2 (cured for 28 d) increased to 53.7 MPa, which was 6.1% higher than that of sample C-1. The enhancement effect of vinegar excitation decreased gradually with increasing curing age and only slightly improved the compressive strength at the later stage. The compressive strengths of sample C-2 cured for 1 and 3 d reached 60.1% and 80.4% than if cured for 28 d, which were considerably higher than the compressive strengths of sample C-1.

The addition of acetic acid significantly improved the early compressive strength and slightly improved the compressive strength in the later stage. Acid excitation improved the hydration reaction activity of cement particles, accelerated the dissolution of active substances, increased the hydration reaction rate, and improved the formation of hydration products [11]. The enhancement mechanism of acetic acid was further confirmed via microscopic analysis.

(2) Excitation with 4% acetic acid

With increasing acetic acid content, the compressive strengths of sample C-3 (mixed with 4% acetic acid) cured for 1 and 3 d further increased to 39.6 and 49.2 MPa, respectively, which were 22.6% and 13.9% higher than those of sample C-2. When the curing age reached 28 d, the compressive strength of sample C-3 increased to 58.4 MPa, which is 8.8% higher than that of sample C-2. The compressive strengths of sample C-3 cured for 1 and 3 d reached 67.8% and 84.2% more than when cured for 28 d. Compared with sample C-2, the early mechanical properties of sample C-3 developed faster, and the range of improvement was still significant. With increasing acetic acid content, the compressive strength at the early age continued to increase, and the range of this increase was apparent; however, the improvement effect on the later compressive strength was not clear. Therefore, with increasing acetic acid content, the improvement of acid excitation gradually increased.

(3) Excitation with 6% acetic acid

As the content of acetic acid was further increased to 6%, the compressive strengths of sample C-4 cured for 1 and 3 d reached 38.4 MPa and 47.5 MPa, respectively, which is 3.0% and 3.5% lower than the compressive strengths of sample C-3, respectively. As the curing age reaches 28 d, the compressive strength of sample C-4 increased to 56.7 MPa, which is 2.9% lower than that of sample C-3. Further increasing the acetic acid content does not continuously increase the compressive strength but eventually leads to a decrease, implying that there is an optimal dosage for the promotion of acid excitation. When the dosage of acetic acid was within 4%, the acid excitation increased with increasing acetic acid dosage.

When the dosage of acetic acid exceeded 4%, the acid excitation decreased with increasing acetic acid dosage. This decrease of excitation is because the excessive addition of acetic acid will severely affect the strong alkaline environment required for the cement hydration reaction, and the formation of hydration products must be completed under strong alkaline conditions. When the acetic acid content is low, the calcium hydroxide generated by cement hydration can compensate for the negative impact caused by acid excitation, fully reflecting the stimulating effect.

When acetic acid is added in excess, the calcium hydroxide produced by cement hydration is not sufficient to resist the reduction of the alkaline reaction environment caused by acetic acid [12], hindering the formation of hydration products and finally leading to a reduction of acid excitation. This reduction of acid excitation is the reason why compressive strength decreases with further increasing acetic acid content. The adverse effect of excessive acid excitation was further confirmed via microscopic analysis.

(4) Excitation with 8% and 10% acetic acid

As the content of acetic acid increased to 8%, the compressive strengths of sample C-5 cured for 1 and 3 d decreased to 34.9 and 40.2 MPa, respectively, which is 11.9% and 18.3% lower than those of sample C-3. The compressive strength of sample C-5 cured for 28 d also decreased to 50.3 MPa, which is 13.9% lower than that of sample C-3. Furthermore, as the content of acetic acid increased to 10%, the compressive strength of sample C-6 further decreased than that of sample C-3. With further increasing acetic acid content, the compressive strength showed a clear downward trend, with increasing range. However, compared with sample C-1 (without acid excitation), even if the content of acetic acid is excessively high (10%), the acid excitation still significantly increased the early compressive strength but adversely impacted the development of later strength.

Therefore, with gradually increasing acetic acid content, the mechanical properties increased first and then decreased gradually, and the best content was 4%.

4.1.3. Effect of Hydrochloric Acid on Mechanical Properties

(1) Excitation with 2% hydrochloric acid

Figure 1b shows the development law of the mechanical properties of mortar samples excited by hydrochloric acid. At a hydrochloric acid content of 2%, the compressive strengths of sample C-7 cured for 1 and 3 d increased to 34.8 and 43.6 MPa, which is 106%

and 30.5% higher than those of sample C-1, and even 7.7% and 0.9% higher than those of sample C-2 (mixed with 2% acetic acid), respectively. The compressive strength of sample C-7 cured for 28 d increased to 54.7 MPa, which is 8.1% higher than that of sample C-1 and 1.9% higher than that of sample C-2. The addition of hydrochloric acid also significantly improved the early mechanical properties and slightly improved the later mechanical properties. Moreover, at the same dosage (2%), the acid excitation effect of hydrochloric acid was better than that of acetic acid, because hydrochloric acid is a monobasic strong acid, which is completely ionized in water.

The rate and amount of hydrogen ions provided by hydrochloric acid are significantly higher compared to acetic acid, which can stimulate the reaction activity of cement particles quicker and more comprehensively, improve the contact rate and reaction degree between cement particles and hydrogen ions, and improve the dissolution rate and amount of active substances [13]. Through these effects, the early compressive strength can be increased, which is also the main reason why the excitation effect of hydrochloric acid (mixed with 2%) is better than that of acetic acid (mixed with 2%), and also why the compressive strength of sample C-7 is higher than that of sample C-2.

(2) Excitation with 4% hydrochloric acid

When the hydrochloric acid content increased to 4%, the compressive strengths of sample C-8 cured for 1 and 3 d increased to 32.4 and 41.3 MPa, which is 6.9% and 5.3% lower than those of sample C-7 and 18.2% and 16.1% lower than those of sample C-3 (mixed with 4% acetic acid), respectively. After curing for 28 d, the compressive strength of sample C-8 increased to 52.1 MPa, which is 5% lower than that of sample C-7 and 10.8% lower than that of sample C-3. Different from the enhancement law of acetic acid, the compressive strength decreases significantly with increasing hydrochloric acid, and the best effect is obtained at 2% hydrochloric acid. As hydrochloric acid is a strong acid, excessive addition strongly reduces the high alkaline environment of the cement particle hydration reaction and adversely affects the formation of hydration products, which is the main reason for the observed decrease in compressive strength.

Analysis of the maximum lifting effect of acid excitation showed that the compressive strength of sample C-3 (mixed with 4% acetic acid) was higher than that of sample C-7 (mixed with 2% hydrochloric acid). Thus, the maximum excitation effect of acetic acid is better than hydrochloric acid. The reason for this better excitation effect is that the H^+ in acetic acid can be slowly released into the hydration reaction environment, where it can react with the calcium hydroxide generated by the cement hydration reaction.

This reaction strongly reduced the amount of calcium hydroxide and increased the amount of calcium silicate hydrate. This shows that the compressive strength development of cement mortar mainly depends on the formation of hydrated calcium silicate, while calcium hydroxide formation is unfavorable. Therefore, acetic acid can not only stimulate the hydration reaction activity of cement particles but also reduce the formation of adverse substances, which is the best excitation effect of acetic acid.

(3) Excitation with 10% hydrochloric acid

With increasing amount of hydrochloric acid, the compressive strength continues to decrease, and the decreasing range increased. When the content of hydrochloric acid is increased to 10%, the compressive strengths of sample C-11 cured for 1 and 3 d increased to 26.8 and 35.5 MPa, increased by 58.6% and 5.7% compared with sample C-1 (without acid), respectively. After curing for 28 d, the compressive strength of sample C-11 increased to 44.8 MPa, which is 11.5% lower than that of sample C-1 (without acid). With increasing hydrochloric acid content, the compressive strength decreased significantly, and the best improvement effect was obtained by adding 2% hydrochloric acid.

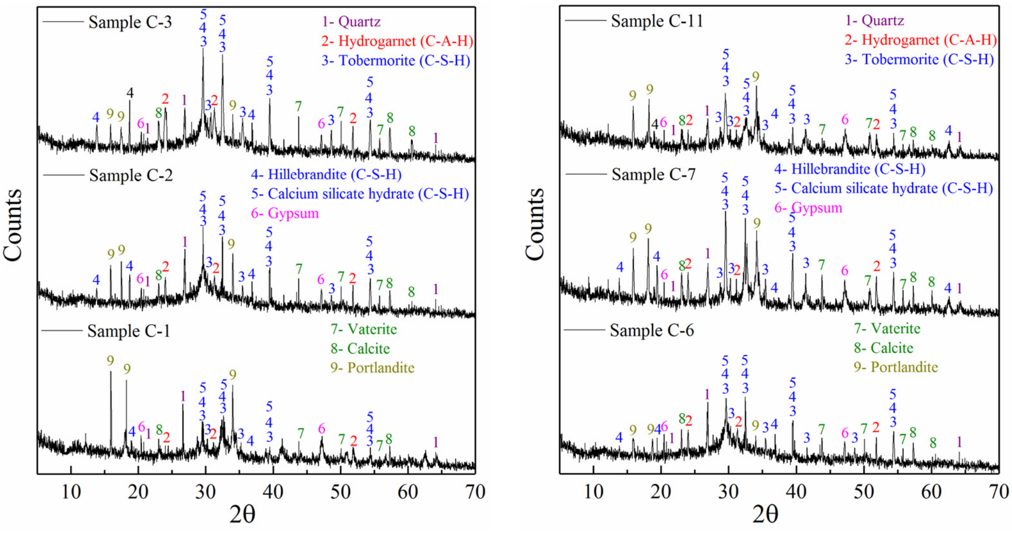
Although the excessive addition of hydrochloric acid can still significantly improve the early compressive strength, it exerts an adverse impact on the later mechanical properties. The reason for this adverse impact is that the excessive incorporation of hydrochloric acid will lead to a low pH of the cement hydration reaction. It consumes tricalcium silicate and other active substances in the cement particles and seriously affects the formation of

C-S-H gels [14], thus, leading to the insufficient strength development of sample C-11 in the later stage.

4.2. X-ray Diffraction Analysis of Acid Regulation

4.2.1. X-ray Diffraction Analysis of Paste Samples

The X-ray diffraction analysis of paste samples C-1, C-2, C-3, C-6, C-7, and C-11 cured for 3 d is shown in Figure 2. Figure 2a clearly shows characteristic peaks, such as quartz, gypsum, and portlandite in sample C-1, and weak mineral characteristic peaks, such as tobermorite, hillebrandite, hydrogarnet, calcite, and vaterite. As the raw materials (clay and limestone) for preparing Portland cement contain a large amount of quartz, which does not decompose under high temperature conditions, quartz is not generated by hydration reactions [15].



(**a**) (**b**)

Figure 2. X-ray diffraction (XRD) analysis of acid activated samples. (**a**) XRD analysis of samples regulated by acetic acid; (**b**) XRD analysis of samples regulated by hydrochloric acid.

Gypsum is added after the completion of cement firing, which is mainly used to adjust the setting time. The appearance of portlandite follows the hydration reaction of tricalcium silicate and dicalcium silicate in cement, which indicates that the hydration reaction is relatively sufficient. Tobermorite, hillebrandite, hydrogarnet, calcite, and vaterite are all silicate minerals that are commonly referred to as calcium silicate hydrate (C-S-H) gels [16], whose characteristic peak strength is very low.

4.2.2. X-ray Diffraction Analysis of Regulated by Acetic Acid

With addition of 2% acetic acid, the characteristic peak of sample C-2 changed to a certain extent. Compared with sample C-1, the characteristic peaks of quartz and gypsum minerals did not change significantly in sample C-2; however, the characteristic peaks of C-S-H gels in sample C-2 showed a distinct increase. This increase indicates that the hydration rate and reaction degree are significantly enhanced, and the amount of calcium silicate gel is also increased, which is the main reason for the increasing compressive strength.

The hydration reaction first requires the dissolution of active substances (i.e., tricalcium silicate and dicalcium silicate) from cement particles; however, the strong alkaline reaction environment is not conducive to the rapid dissolution of active substances [17]. Addition of acetic acid can reduce the strong alkaline environment around the cement particles, and more importantly, the acid-base neutralization reaction can significantly improve the hydration reaction activity of cement particles and promote the dissolution of active substances [18].

Moreover, addition of acetic acid will inevitably lead to a decrease in pH in the hydration reaction environment. The dissolution of active substances can improve the pH of the hydration reaction, form a highly alkaline environment conducive to the formation of hydrated calcium silicate, and eliminate the adverse effects caused by the addition of acetic acid [19]. Therefore, the addition of the appropriate amount of acetic acid can accelerate the dissolution of active substances without affecting the strong alkaline environment required for the formation of H-C-S gels. Finally, the characteristic peaks of C-S-H gel increased significantly in the sample C-2, and the mechanical properties clearly improved at the early stage.

With increasing acetic acid content, the characteristic peak of sample C-3 (mixed with 4% acetic acid) changes further. Compared with sample C-2, the characteristic peak of C-S-H gel in sample C-3 further enhanced, indicating that increasing the acetic acid content will further enhance the hydration rate and the crystallinity along with the yield of C-S-H gels. Due to the weak acidity and partial ionization of acetic acid, the excitation effect of adding 2% acetic acid cannot reach the best activation state of cement particles.

When the content of acetic acid increased to 4%, the acid excitation effect was further enhanced, and the active substances reached the best dissolution state. This best dissolution state enhanced the hydration reaction efficiency, promoted the formation of hydration products, and increased the characteristic peak of calcium silicate gel in sample C-3. All these beneficial effects are also the reason why the compressive strength at an early age increased further.

The intensity of the characteristic peak of portlandite in samples C-1, C-2, and C-3, decreased significantly with increasing acetic acid content. This observed decrease of peak intensity indicates that acetic acid can react with portlandite to produce an acid–base neutralization reaction, which can significantly reduce the portlandite amount. Portlandite is unfavorable for the development of compressive strength. Therefore, the addition of acetic acid can not only play the role of acid excitation but also reduce the formation of adverse substances in samples, thus, promoting the development of strength.

When the acetic acid content increased to 10%, the characteristic peak of C-S-H gel in sample C-6 decreased significantly (compared with sample C-3), and the characteristic peak of portlandite also showed a downward trend. The formation of hydration products can only happen in a high alkaline environment (pH between 12 and 13), while a low alkaline environment will seriously affect the formation of hydrated calcium silicate [20]. The addition of 10% acetic acid can further promote the dissolution of active substances in cement particles but significantly reduces the alkalinity of the reaction environment. Even if a large amount of active substances is dissolved, they cannot return to the highly alkaline state, which seriously affects the formation of hydrated calcium silicate.

Excessive acetic acid reacts with dissolved tricalcium silicate, dicalcium silicate, and other active substances, resulting in a further decrease in the formation of hydrated calcium silicate [21]. Therefore, the incorporation of acetic acid can significantly increase the early compressive strength; however, the decreased reaction environment alkalinity, active substance content, and calcium silicate gel formation severely affect the development of compressive strength. This effect on compressive strength is the reason why the performance control effect gradually decreased with increasing acetic acid content.

4.2.3. X-ray Diffraction Analysis of Samples Regulated by Hydrochloric Acid

The XRD analysis of hydrochloric acid regulated samples C-7 and C-11 is shown in Figure 2b. When 2% hydrochloric acid is added, characteristic peaks of quartz, gypsum, portlandite, and hydrated calcium silicate minerals are clearly visible in sample C-7. Compared with sample C-1, in sample C-7, the characteristic peaks of quartz, gypsum, and portlandite did not change significantly; however, the intensity of the characteristic peak representing hydrated calcium silicate minerals increased significantly.

This increase indicates that addition of even a small amount of hydrochloric acid can promote the dissolution of active substances, accelerate the rate of hydration reaction, and increase the production of calcium silicate hydrate [22]. Comparison between sample C-2 (mixed with 2% acetic acid) and sample C-7 (mixed with 2% hydrochloric acid) showed that the characteristic peak intensity of hydrated calcium silicate mineral in sample C-7 was slightly higher than in sample C-2. This slightly higher peak intensity shows that, under the condition of a content of 2%, the regulation effect of hydrochloric acid is better than that of acetic acid. The early-age mechanical properties of sample C-7 are better than those of sample C-2, which further confirms this conclusion.

Hydrochloric acid is a strong acid and can be completely ionized. H^+ can be completely released into the reaction solution at one time. However, acetic acid is a weak acid, which can only be partially ionized, and its rate of releasing H^+ is significantly lower than that of hydrochloric acid. Therefore, the addition of hydrochloric acid cannot reduce the amount of portlandite-like acetic acid, which is confirmed because the characteristic peak of portlandite in sample C-7 is not reduced.

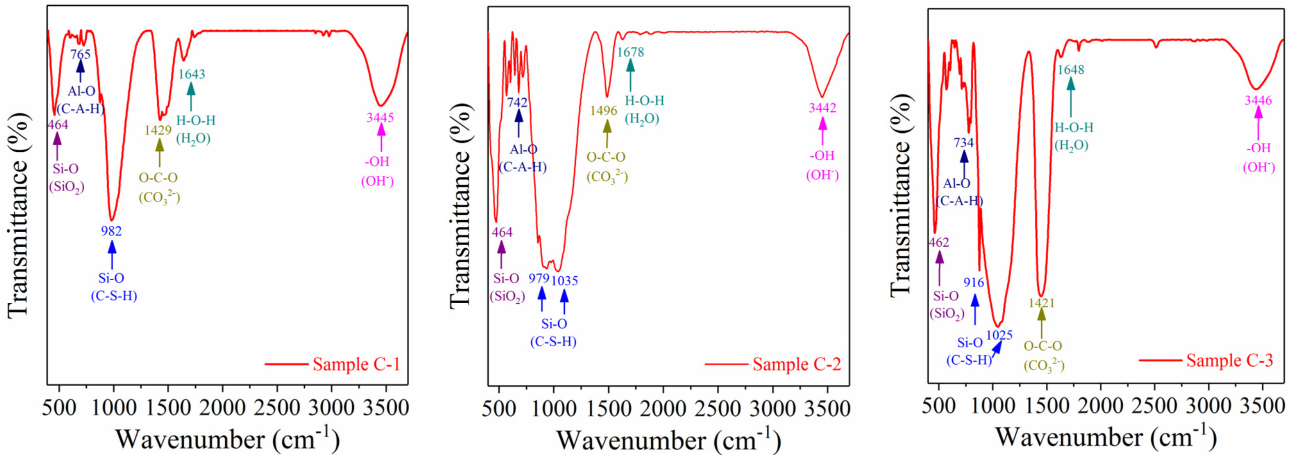
Compared with the regulation of acetic acid, hydrochloric acid can more efficiently enhance both the reaction rate and degree between cement particles and H^+, improve the dissolution rate and amount of active substances in cement particles, and promote the formation of silicate products [23]. These effects are the main reason why the early mechanical properties of sample C-7 (mixed with 2% hydrochloric acid) are better than sample C-2 (mixed with 2% acetic acid).

When the content of hydrochloric acid increased to 10%, the XRD diffraction pattern of sample C-11 changed dramatically. Compared with sample C-7, the intensity of the characteristic peak representing hydrated calcium silicate in sample C-11 is significantly lower. Excessive addition of hydrochloric acid can further promote the dissolution of active substances in cement particles but also leads to a significant decrease in the pH of the reaction environment, which is not conducive to the formation of silicate minerals [24]. This decrease in the pH is the reason for the observed decrease of the characteristic peak strength of hydrated calcium silicate minerals and also the main reason for the gradual decline of compressive strength.

4.3. Fourier-Transform Infrared Spectroscopy Analysis of Acid-Regulated Samples

4.3.1. Fourier-Transform Infrared Spectroscopy Analysis of Paste Samples

The results of FT-IR of paste samples C-1, C-2, and C-3 (cured for 3 d) are shown in Figure 3. Figure 3a shows the asymmetric stretching vibration of Si-O bond at 464 cm^{-1} in sample C-1 (without acid excitation), which indicates that there is a certain amount of silica [25], which is consistent with the characteristic peak of quartz in XRD.



(**a**) (**b**) (**c**)

Figure 3. Fourier-transform infrared spectroscopy (FT-IR) analysis with acetic acid. (**a**) Not mixed with acetic acid; (**b**) Mixed with 2% acetic acid; (**c**) Mixed with 4% acetic acid.

There is asymmetric stretching vibration of Al-O bond at 765 cm^{-1}, which represents an alumina tetrahedron structure, indicating that a certain amount of aluminate has formed [26], which is consistent with hydrate garnet (calcium aluminate hydrate) mineral characteristic peak in XRD. Most importantly, there is a clear Si-O-Si bond at 982 cm^{-1} (v3 and v4), which implies out-of-plane bending vibration. This specific frequency (i.e., 982 cm^{-1}) is the tetrahedron characteristic of the hydrate chain structure of calcium silicate hydrate [27], which indicates that hydrated calcium silicate gel has formed in sample C-1.

Moreover, a symmetrical stretching vibration of O-C-O bond was found at 1429 cm^{-1}, which represents a carbonate ion ($CO_3{}^{2-}$) indicating that calcium carbonate type substances have formed [28], which is consistent with the calcite and aragonite minerals in XRD. At 1643 cm^{-1}, there is symmetric stretching vibration of the H-O-H bond, which represents a water molecule (H_2O), and indicates that there is a small amount of free water [29]. Asymmetric stretching vibration of -OH bond is found at 3445 cm^{-1}, which represents OH^- [30], and indicates that there are a large number of alkaline substances, such as NaOH or $Ca(OH)_2$ in sample C-1.

4.3.2. Fourier-Transform Infrared Spectroscopy Analysis of Samples Regulated by Acetic Acid

After the addition of 2% acetic acid, the FT-IR spectrum of sample C-2 changed greatly. Compared with sample C-1, the strength of the Si-O-Si bond characteristic peak at 979 cm^{-1} and the width of the Si-O-Si tetrahedron of sample C-2 increased clearly, indicating that the amount of C-S-H gel increased.

The characteristic peaks of an Al-O bond representing the aluminum oxygen tetrahedron structure at 742 cm^{-1} and O-C-O bond representing $CO_3{}^{2-}$ at 1496 cm^{-1} in sample C-2 were significantly stronger than in sample C-1, indicating that the formation of aluminosilicate minerals and carbonate had significantly increased. This increased formation of aluminosilicate minerals and carbonate further proves that the acid excitation of acetic acid can significantly improve the hydration reaction rate, promote the formation of high-strength hydration products, and improve the formation of hydration products, thus, significantly improving the early compressive strength.

However, the characteristic peak of -OH at 3442 cm^{-1} in sample C-2 is not lower than in sample C-1, which indicates that although the addition of acetic acid leads to a reduction of the alkalinity in the reaction environment, the OH^- released by the dissolution of cement particles completely offsets the negative impact of the addition of acetic acid after three d of curing. The hydration reaction environment returns to the highly alkaline state to avoid adverse effects on the formation of hydration products [31].

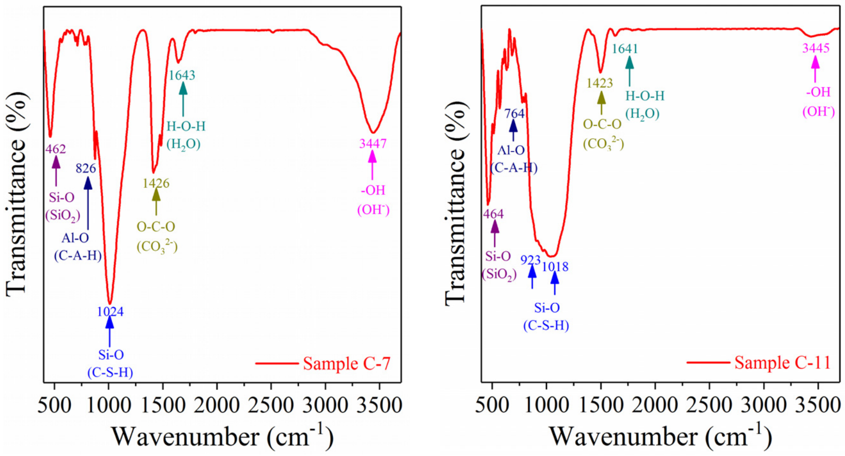
With increasing acetic acid content, the FT-IR spectrum of sample C-3 (mixed with 4% acetic acid) changed further. Compared with sample C-2, the Si-O-Si bond characteristic peaks representing silicon oxygen tetrahedron at 916 and 1025 cm^{-1} in sample C-3 are further enhanced. The characteristic peaks of Al-O bond representing the aluminum oxygen tetrahedron structure at 734 cm^{-1} and O-C-O bond representing $CO_3{}^{2-}$ at 1421 cm^{-1} in sample C-3 were significantly stronger than in sample C-2. With increasing acetic acid content, the formation of minerals, such as hydrated calcium silicate, hydrated calcium aluminate, and calcium carbonate, in sample C-3 increased significantly.

This increase of minerals shows that, with increasing acetic acid content, the acid excitation was strengthened further, the hydration reaction rate was further improved, and finally, the early compressive strength of sample C-3 was further increased.

However, compared with sample C-2, the intensity of the characteristic peak representing -OH at 3446 cm^{-1} in sample C-3 decreased slightly. This slight decrease shows that the addition of 4% acetic acid had an adverse impact on the highly alkaline hydration reaction environment, resulting in the beginning of the pH decline. The decline of the pH is because, with the increasing acetic acid content, the amount of H^- released to the reaction environment gradually increased, and the release duration increased strongly. The excess H^- not only reduced the alkalinity of the reaction environment but also affected the formation of hydration products, which explains why the excitation gradually decreased with the increasing acetic acid content [32].

4.3.3. Fourier-Transform Infrared Spectroscopy Analysis of Samples Regulated by Hydrochloric Acid

FT-IR spectra of samples C-7 and C-11 are shown in Figure 4. With the addition of 2% hydrochloric acid, the FT-IR spectrum of sample C-7 changed further. The characteristic peak of Si-O-Si bond representing the silicon oxygen tetrahedron at 1024 cm^{-1} in sample C-7 was significantly higher than in sample C-1 (without acid excitation). It was even significantly higher than in sample C-2 (mixed with 2% acetic acid) but slightly lower than in sample C-3 (mixed with 4% acetic acid).



(**a**) (**b**)

Figure 4. FT-IR analysis of samples excited by hydrochloric acid. (**a**) Mixed with 2% hydrochloric acid; (**b**) Mixed with 10% hydrochloric acid.

The intensity of the characteristic Al-O bond peak at 826 cm^{-1}, which represents the aluminum oxygen tetrahedron structure in sample C-7, was also significantly higher than in sample C-1 and sample C-2 but slightly lower than in sample C-3. The addition of a small amount of hydrochloric acid can also play the role of acid excitation and significantly improve the production of hydration products, such as silicate and aluminate, which improves the early compressive strength.

However, the maximum increase range of the mechanical properties doped with hydrochloric acid (2%) is lower than that doped with acetic acid (4%). The acidity of hydrochloric acid is too strong, which not only accelerates the dissolution of active substances but also results in an acid-base neutralization reaction with alkaline substances dissolved in cement particles, which adversely impacts the formation of silicate and aluminosilicate. More importantly, hydrochloric acid is a strong acid and completely ionized.

Therefore, it cannot release H$^+$ slowly as with acetic acid, which reduces the formation of portlandite and finally reduces its impact on the development of compressive strength. Therefore, the regulatory effect of acetic acid is better than that of hydrochloric acid. When the content of hydrochloric acid is increased to 10%, the Si-O-Si bond characteristic peaks (representing silicon oxygen tetrahedron at 923 and 1018 cm^{-1} in sample C-11) are still significantly higher than those in sample C-1 (no acid excitation).

However, they are strongly lower than those in sample C-7 (mixed with 2% hydrochloric acid). The intensity of the Al-O bond characteristic peak (representing an aluminum oxygen tetrahedron structure at 764 cm^{-1} in sample C-11) is also significantly lower than that in sample C-7. Most importantly, the characteristic peak representing -OH at 3445 cm^{-1} in sample C-11 is significantly lower than that in sample C-7, and also lower than that in sample C-1.

This lower peak shows that, although the addition of 10% hydrochloric acid can lead to acid excitation, the pH of the hydration reaction environment is significantly reduced, and the generation of hydration products is also significantly reduced, thereby, resulting in a clearly insufficient development of compressive strength. Therefore, with increasing acetic acid (more than 4%) or hydrochloric acid (more than 2%) contents, the regulation effect on the mechanical properties begins to decrease. Therefore, too much acetic acid or hydrochloric acid adversely affects the development of the compressive strength.

5. Conclusions

(1) The addition of acetic acid and hydrochloric acid can lead to acid excitation, improve the hydration reaction activity of cement particles, and promote the dissolution of active substances. Moreover, it can accelerate the hydration reaction rate, improve the formation of hydration products, significantly improve the early compressive strengt and slightly improve the later mechanical properties.

(2) With increasing acetic acid content, the compressive strength increased significantly at first and then decreased gradually, and a content of 4% was found to be the best. The compressive strength of samples cured for 1 and 3 d increased by 134.3% and 47.3% compared with the sample without acid excitation. XRD and FT-IR analysis showed that the hydrogen ions released slowly by acetic acid reduced the negative effect of calcium hydroxide produced by hydration reaction, which was the main reason for the significant improvement of compressive strength. The best excitation effect of acetic acid was better than that of hydrochloric acid.

(3) With increasing hydrochloric acid content, the compressive strength showed a clear decreasing trend, and the content at 2% was the best. The compressive strength cured for 1 and 3 d increased by 106% and 30.5%, respectively, compared with the sample without acid excitation. XRD and FT-IR analysis showed that, when hydrochloric acid is added in excess, this not only affects the pH of the hydration reaction environment but also neutralizes many active alkaline substances in cement particles, which ultimately seriously hinders the formation of hydration products. The resulting diminished formation of hydration products is the reason why the compressive strength is significantly reduced when acids are added in excess.

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References

1. Bullard, J.W.; Jennings, H.M.; Livingston, R.; Nonat, A.; Scherer, G.; Schweitzer, J.S.; Scrivener, K.; Thomas, J. Mechanisms of cement hydration. *Cem. Concr. Res.* **2011**, *12*, 1208–1223. [CrossRef]
2. Zeng, Q.; Li, K.; Fen-Chong, T.; Dangla, P. Determination of cement hydration and pozzolanic reaction extents for fly-ash cement pastes. *Constr. Build. Mater.* **2012**, *27*, 560–569. [CrossRef]
3. Jeong, Y.; Kang, S.-H.; Kim, M.O.; Moon, J. Acceleration of cement hydration from supplementary cementitious materials: Performance comparison between silica fume and hydrophobic silica. *Cem. Concr. Compos.* **2020**, *27*, 103688. [CrossRef]
4. Ma, X.; He, T.; Xu, Y.; Yang, R.; Sun, Y. Hydration reaction and compressive strength of small amount of silica fume on Cement-Fly Ash matrix. *Case Stud. Constr. Mater.* **2022**, *16*, e00989. [CrossRef]
5. Hashmi, F.; Shariq, M.; Baqi, A. An investigation into age-dependent strength, elastic modulus and deflection of low calcium fly ash concrete for sustainable construction. *Constr. Build. Mater.* **2021**, *283*, 122772. [CrossRef]

6. Nedunuri, S.S.S.A.; Sertse, S.G.; Muhammad, S. Microstructural study of Portland cement partially replaced with fly ash, ground granulated blast furnace slag and silica fume as determined by pozzolanic activity. *Constr. Build. Mater.* **2020**, *238*, 117561. [CrossRef]
7. Trauchessec, R.; Mechling, J.M.; Lecomte, A.; Roux, A.; Rolland, B.L. Hydration of ordinary portland cement and calcium sulfoaluminate cement blends. *Cem. Concr. Compos.* **2015**, *56*, 106–114. [CrossRef]
8. *GB175-2007*; Common Portland Cement. The State Bureau of Quality and Technical Supervision: Beijing, China, 2007.
9. *GB/T17671-2020*; Method of testing cements-Determination of strength-ISO China. The State Bureau of Quality and Technical Supervision: Beijing China, 2020.
10. Puertas, F.; González-Fonteboa, B.; González-Taboada, I.; Alonso, M.M.; Torres-Carrasco, M.; Rojo, G.; Martínez-Abella, F. Alkali-activated slag concrete: Fresh and hardened behavior. *Cem. Concr. Compos.* **2018**, *85*, 22–31. [CrossRef]
11. Telesca, A.; Marroccoli, M.; Pace, M.L.; Tomasulo, M.; Valenti, G.L.; Monteiro, P.J.M. A hydration study of various calcium sulfoaluminate cements. *Cem. Concr. Compos.* **2014**, *53*, 224–232. [CrossRef]
12. Liao, Y.; Wei, X.; Li, G. Early hydration of calcium sulfoaluminate cement through electrical resistivity measurement and microstructure investigations. *Constr. Build. Mater.* **2011**, *25*, 1572–1579. [CrossRef]
13. Hanjitsuwan, S.; Hunpratub, S.; Thongbai, P.; Maensiri, S.; Sata, V.; Chindaprasirt, P. Effects of NaOH concentrations on physical and electrical properties of high calcium fly ash geopolymer paste. *Cem. Concr. Compos.* **2014**, *45*, 9–14. [CrossRef]
14. Huang, G.; Ji, Y.; Zhang, L.; Li, J.; Hou, Z. The influence of curing methods on the strength of MSWI bottom ash-based alkali-activated mortars: The role of leaching of OH− and free alkali. *Constr. Build. Mater.* **2018**, *186*, 978–985. [CrossRef]
15. Huang, G.; Ji, Y.; Li, J.; Zhang, L.; Liu, X.; Liu, B. Effect of activated silica on polymerization mechanism and strength development of MSWI bottom ash alkali-activated mortars. *Constr. Build. Mater.* **2019**, *201*, 90–99. [CrossRef]
16. Huang, G.; Yuan, L.; Ji, Y.; Liu, B.; Xu, Z. Cooperative action and compatibility between Portland cement and MSWI bottom ash alkali-activated double gel system materials. *Constr. Build. Mater.* **2019**, *209*, 445–453. [CrossRef]
17. Ryu, G.S.; Lee, Y.B.; Koh, K.T.; Chung, Y.S. The mechanical properties of fly ash-based geopolymer concrete with alkaline activators. *Constr. Build. Mater.* **2013**, *47*, 409–418. [CrossRef]
18. Meller, N.; Kyritsis, K.; Hall, C. The mineralogy of the CaO-Al_2O_3-SiO_2-H_2O (CASH) hydroceramic system from 200 to 350 °C. *Cem. Concr. Res.* **2009**, *39*, 45–53. [CrossRef]
19. Li, C.; Sun, H.; Li, L. A review: The comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements. *Cem. Concr. Res.* **2010**, *40*, 1341–1349. [CrossRef]
20. Huang, G.; Yang, K.; Sun, Y.; Lu, Z.; Zhang, X.; Zuo, L.; Feng, Y.; Qian, R.; Qi, Y.; Ji, Y.; et al. Influence of NaOH content on the alkali conversion mechanism in MSWI bottom ash alkali-activated mortars. *Constr. Build. Mater.* **2020**, *248*, 118582. [CrossRef]
21. Walkley, B.; Nicolas, R.S.; Sani, M.-A.; Bernal, S.A.; Van Deventer, J.S.J.; Provise, J.L. Structural evolution of synthetic alkaliactivated CaO-MgO-Na_2O-Al_2O_3-SiO_2 materials is influenced by Mg content. *Cem. Concr. Res.* **2017**, *99*, 155–171. [CrossRef]
22. Huang, G.; Li, Y.; Zhang, Y.; Zhu, J.; Li, D.; Wang, B. Effect of Sodium Hydroxide, Liquid Sodium Silicate, Calcium Hydroxide, and Slag on the Mechanical Properties and Mineral Crystal Structure Evolution of Polymer Materials. *Crystals* **2021**, *11*, 1586. [CrossRef]
23. Bernal, S.A.; De Gutierrez, R.M.; John, L.P.; Rose, V. Effect of silicate modulus and metakaolin incorporation on the carbonation of alkali silicate-activated slags. *Cem. Concr. Res.* **2010**, *40*, 898–907. [CrossRef]
24. He, R.; Fu, C.; Ma, H.; Ye, H.; Jin, X. Prediction of Effective Chloride Diffusivity of Cement Paste and Mortar from Microstructural Features. *J. Mater. Civ. Eng.* **2020**, *32*, 04020211. [CrossRef]
25. Puertas, F.; Palacios, M.; Manzano, H.; Dolado, J.S.; Rico, A.; Rodríguez, J. A model for the C-A-S-H gel formed in alkali-activated slag cements. *J. Eur. Ceram. Soc.* **2011**, *31*, 2043–2056. [CrossRef]
26. Bernal, S.A.; Provis, J.L.; Walkley, B.; Nicolas, R.S.; Gehman, J.D.; Brice, D.G.; Kilcullen, A.R.; Duxson, P.; van Deventer, J.S.J. Gel nanostructure in alkali-activated binders based on slag and fly ash, and effects of accelerated carbonation. *Cem. Concr. Res.* **2013**, *53*, 127–144. [CrossRef]
27. Huang, G.; Zhu, J.; Zhang, Y.; Li, D.; Wang, B.; Li, M.; Jin, L.; Gong, J. The Effect of Slag on the Mechanical Properties of Coralline-Activated Materials and the Formation and Transformation of Mineral Crystals. *Crystals* **2022**, *12*, 470. [CrossRef]
28. Bernal, S.A.; de Gutiérrez, R.M.; Pedraza, A.L.; Provis, J.L.; Rodriguez, E.D.; Delvasto, S. Effect of binder content on the performance of alkali-activated slag concretes. *Cem. Concr. Res.* **2011**, *41*, 1–8. [CrossRef]
29. Sun, Z.; Vollpracht, A. Isothermal calorimetry and in-situ XRD study of the NaOH activated fly ash, metakaolin and slag. *Cem. Concr. Res.* **2018**, *103*, 110–122. [CrossRef]
30. Maraghechi, H.; Rajabipour, F.; Pantano, C.G.; Burgos, W.D. Effect of calciumon dissolution and precipitation reactions of amorphous silica at high alkalinity. *Cem. Concr. Res.* **2016**, *87*, 1–13. [CrossRef]
31. Huang, G.; Ji, Y.; Li, J.; Hou, Z.; Dong, Z. Improving strength of calcinated coal gangue geopolymer mortars via increasing calcium content. *Constr. Build. Mater.* **2018**, *166*, 760–768. [CrossRef]
32. Plusquellec, G.; Geiker, M.; Lindgård, J.; Duchesne, J.; Fournier, B.; De Weerdt, K. Determination of the pH and the free alkali metal content in the pore solution of concrete: Review and experimental comparison. *Cem. Concr. Res.* **2017**, *96*, 13–26. [CrossRef]