1. Introduction

Advanced materials that have properties of high water–solid ratio (W/S), low cost, good strength and durability, are required in the fields of mining engineering, tunnel engineering and oil–gas development. High water materials consisting of sulphoaluminate cement (or its clinker), gypsum and lime have been applied to these engineering fields as filling media. The compressive strength of the high water materials is very low at a high value of W/S, and the strength decreases over time due to water-loss. To improve the mechanical property of the high water materials, calcium aluminate cement (CAC) was added to sulphoaluminate cement to obtain a novel high water material composed of sulphoaluminate cement, CAC, gypsum, lime and other additives. However, when stirring water, sulphoaluminate cement, gypsum and lime together by a single-liquid grouting method, the setting time of the high water material pastes is excessively short, which cannot meet the requirements of field-scale applications. To avoid the rapid setting, the high water materials should be divided into two parts for stirring, and then the pastes after stirring are grouted via a common pipe by the double-liquid grouting method. This needs complex operations particularly in a small underground space. Therefore, it is meaningful to develop an advanced material that consumes much water and whose slurry can be grouted by a single-liquid grouting method.

Portland cement (PC) has been produced widely in the world, with low cost and rich resources. However, straight PC is not an ideal material to prepare the grouting slurry due to its long setting time, low early strength and obvious shrinkage at a high value of W/S. For CAC, high early strength is one of the major advantages. Besides, the CAC has other advantages of short setting time, chemical aggression resistance and high temperature resistance. However, because of the crystalline conversion from the metastable hexagonal CaO·Al2O3·3H2O (CAC10) or 2CaO·Al2O3·8H2O (C2AH8) to cubic 3CaO·Al2O3·6H2O (C3AH6), the porosity of CAC paste increases and the long-term strength decreases markedly as a consequence. Meanwhile CAC10 or C2AH8 can react with calcium silicate hydrate (C–S–H) gel to produce 2CaO·Al2O3·SiO2·3·H2O (C2ASH6), which is dependent on the availability of C–S–H gel during this reaction process. To obtain advanced materials with short setting time, good strength and low cost, PC and CAC are usually mixed to form PC–CAC binary system. At W/S < 0.6 : 1, when the mass proportion of PC is 5%, the early strength of PC–CAC binary system is improved, and no long-term strength reduction is detected; and when the proportion of PC is 20%, the long-
term strength decreases significantly. And, when the mass ratio of CAC is 20%, the early strength of PC–CAC binary composite material is higher than that of pure PC, and the strength rises over time. In addition, it was reported that there is an enhancement on the strength of materials consisting of PC or CAC after the addition of sodium silicate (SS).

The studies mentioned above provide some important guidance to the novel PC–CAC binary composite materials at low values of W/S. However, there were few studies conducted under rich-water conditions (W/S > 1 : 1). Our prior experimental results have shown that the long-term strength of the rich-water (RW) material composited of PC, CAC and gypsum at relatively high W/S values decreases over time. In the present study, SS was mixed to improve the mechanical properties of the RW material at the W/S value of 1.2 : 1, and the effects of SS on the RW material were investigated. We tested the compressive strength of RW materials containing different amounts of SS. Whilst, the mercury intrusion porosity (MIP), scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) were employed to characterize the microstructures of RW materials. Finally, the strength evolutionary mechanism of the RW material was discussed, which could contribute to the future study on this sort of material.

2. Experimental procedures

2.1. Materials and sample preparation

Starting materials used in this investigation include PC, CAC, gypsum and SS. PC is produced in Qian-ye Co. Ltd, China, and CAC is supplied by Hua-yan Co. Ltd, Jiaozuo, China. Gypsum with purity of 95% and SS (Na2SiO3·9H2O) with Na2O content of 28.0–30.0% are analytical reagents from Kermel chemical agent Co. Ltd, Tianjin, China. Chemical compositions of PC, CAC and gypsum are listed in Table 1. And, Fig. 1 shows the XRD patterns of the starting materials.

The experimental program is based on the study of four designs of the hardened RW paste. Mass proportions of PC, CAC and gypsum in RW are fixed at 65.5%, 14.5% and 10%, respectively. SS, as an additive blended in the RW material, accounts for 0, 1%, 2%, 3% and 4% of the total mass of the RW material, respectively.

According to GB/T 1346-2011, at W/S of 1.2 : 1, the paste was stirred twice in a slurry agitator. The paste was casted into hollow cylinder moulds (radius of 50 mm and height of 100 mm), and demoulded after 24 hours to prepare cylindrical samples. All the cylindrical samples were cured at (20 ± 2) °C and humidity of (60 ± 5)% until they reached the test ages (3 day, 7 day, 14 day and 28 day).

Table 1 Chemical compositions of PC, CAC and gypsum

<table>
<thead>
<tr>
<th>Oxides (wt%)</th>
<th>PC</th>
<th>CAC</th>
<th>Gypsum</th>
</tr>
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<tr>
<td>CaO</td>
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<tr>
<td>SiO2</td>
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<td>0.25</td>
<td>18.56</td>
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<td>Al2O3</td>
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<td>2.36</td>
<td>0.06</td>
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<td>K2O</td>
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</tr>
<tr>
<td>MgO</td>
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<td>—</td>
<td>1.42</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.43</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

2.2. Measurements

2.2.1. Compressive strength. Adopting RMT-150 mechanical experimental test system (U.S.), the cylindrical samples cured for 3 days, 7 days, 14 days and 28 days were tested, respectively. Loading was set on the sample axially, and there was no confine radially. At a rate of 0.1 kN s⁻¹, compressive strength test was conducted until the sample cracked. The compressive strength value was taken to be the means found for three same samples.

2.2.2. MIP measurement. MIP is used to measure the volume of mercury driven into pores of materials at applied pressure. Surface tension of mercury is high and contact angle between mercury and solid is larger than 90°, thus the mercury is a non-wetting substance that only enters pores at the applied pressure. For materials with low elastic modulus, its volumes of pores can be measured accurately by MIP. In this study, MIP was employed to study the pores in the RW materials. The relation between the applied pressure p (MPa) and the pore diameter d (m) can be expressed via Washburn equation (eqn (1)).

$$pd = -4\sigma \cos \theta$$ (1)

where σ is the surface tension of mercury (N m⁻¹) and θ is the contact angle between mercury and solid. Generally, the value of term 4σ cos θ in eqn (1) is assumed as 1500 MPa nm. By eqn (1), we can obtain the pore distribution of the RW materials.

MIP tests were conducted in an AutoPore IV 9505 porosimetry (U.S.), whose applied pressure ranges from 0 to 228 MPa and measurable diameter of pore is 5 nm to 1000 μm. Cubic specimens (2.5 × 2.5 × 2.5 cm) sliced from the undamaged cylindrical samples that cured for 3 days, 14 days and 28 days, were prepared. Then, the cubic specimens were dried in
a vacuum-oven at a low temperature of 30 °C. This temperature selected was to avoid damaging the microstructure of the samples.

2.2.3. SEM. Unharmed cubic bulks (0.5 × 0.5 × 0.5 cm) were cut from the cylindrical samples that cured for 3 days and 28 days, respectively. Then, the cubic bulks were soaked in absolute ethyl alcohol for 48 hours to terminate hydration. Finally, the cubic bulks were dried in a vacuum-oven at 30 °C until there is no change in weight. To improve the surface conductivity, the cubic bulks were treated with spray-gold in the ion sputtering instrument (GVC-1000). Then, SEM (JSM-6390/LV, Japan) was used to study the micromorphy of the RW material under a high vacuum condition. Due to the well-conductivity of the surface after the treatment of spray-gold, we chose 15 kV as the acceleration voltage. The secondary electron imaging (SEI) mode was adopted to obtain the micromorphy of the RW material. And, at a magnification of 4000, clear SEM images could be obtained.

2.2.4. XRD and FT-IR measurements. The cylindrical samples cured for 3 days, 14 days, and 28 days were broken into bulks. These bulks soaked in absolute ethyl alcohol for 48 hours to stop the material from hydration. After that, the bulks were dried in a vacuum oven until there was no change in weight to ensure the elimination of ethyl alcohol. Then, the bulks dried were grounded to a very fine powder in a ball grinding mill.

Adopting X-ray diffractometer (D8 Advance, Bruker, Germany) with a 35 kV, 50 mA copper anode X-ray tube and a Cu Kα radiation, the fine powder was examined to determine the hydration products in different ages. Scanning was conducted between 5° and 55° with a 2θ increment of 0.02° s⁻¹.

The fine powder (2 mg) for FT-IR analysis was mixed with dry KBr powder (200 mg), and driven into disks. The infrared spectra of the disked powder were recorded by VERTEX 70 Fourier transform infrared spectrometer (Bruker, Germany) in the region from 4000 cm⁻¹ to 400 cm⁻¹ at a resolution of 4 cm⁻¹. And the powder was scanned 32 times. To eliminate the impact of vaporous water and carbon dioxide in the spectrometer, we collected the spectrum before putting the sample in the sample cell, which is background spectrum indicating the infrared absorption of the vaporous water and carbon dioxide in the spectrometer. By subtracting the background spectrum, the real spectra of the samples could be obtained. Further, the variations of bonds can be analyzed by peak areas of FT-IR. In this paper, the peak areas were calculated by peak-differentiating-fitting method combined with Gauss equation. The peak-differentiating-fitting method includes a process of baseline finding-creating, baseline subtracting, peak fitting, and peak area calculating. What’s more, it is required that the correlation coefficients of fitting and experimental curves should be above 0.90.

3. Results

3.1. Evolution of strength

Fig. 2 shows the compressive strength of the RW materials containing different amounts of SS. When the addition of SS is 0, the compression of the RW material on 3 day is 4.71 MPa. The RW materials containing SS exhibit a relatively high compressive strength on 3 day, and for SS contents of 1%, 2%, 3% and 4%, the corresponding strengths are 5.08 MPa, 5.11 MPa, 5.19 MPa and 5.26 MPa, respectively. For all the samples, the compressive strength increases until 14 day, and the strength of the RW materials containing SS is likewise higher than that of the RW without SS. It indicates that the early strength of the RW materials is improved by blending SS.

For the RW materials with SS contents of 0, 1% and 2%, their compressive strength decreases during 14 day to 28 day. However, this kind of strength retrogression reduces with the increase in the content of SS. Until the content of SS increases to 3% at least, compressive strength retrogression does not appear during 14 day to 28 day, indicating that the long-term strength retrogression of the RW material can be inhibited effectively by raising the mixing amount of SS.

3.2. Pore structure and micromorphy

The differential pore size distributions of the RW materials with different mixing amounts of SS are shown in Fig. 3. The pore diameters of the RW materials range from 100 nm to 10 μm. And, all the samples have differential peaks at pore diameters in the range of 400–630 nm. The pore sizes corresponding to the peaks reduce over time, the number of large pores (d > 1000 nm) gradually decreases, and the number of small pores (d < 300 nm) increases instead. These illustrate that the structure of the RW material became more compact from 3 day to 28 day, which is not consistent with the pure CAC paste porosity variation over time reported before.

On 3 day of hydration and for the hardened RW paste containing no SS, the most probable pore diameter that corresponding to the peak is about 619 nm. And, for the RW materials containing SS of 1% and 4%, the most probable pore diameters are about 552 nm and 516 nm, respectively. It indicates that the pore structure of the RW materials can be improved significantly by mixing SS at early hydration stage.
3.3. Mineral compositions and distribution

The XRD patterns of the RW materials containing different amounts of SS are shown in Fig. 5. By phase determinations and by reference to the XRD patterns showing the un-hydrated materials and a verification of the MIP results, the micromor-phology of the RW materials cured for 3 days and 28 days is shown in Fig. 4. An overview-SEM image at a magnification of 200 is plotted in Fig. 4a, indicating that the chosen areas are representative. And, Fig. 4b shows the SEM images at a magnification of 4000. On 3 day, the number of needle-shaped crystals of the RW paste without SS is more than that of the RW material with SS content of 4%; and for the RW pastes containing SS of 1% and 4%, the pores are filled by amorphous C–S–H gel, leading to a lower porosity. On 28 day, the numbers of the needle-shaped crystals both decrease for the RW materials with and without SS, and the pores are filled by the C–S–H further. Besides, the pore size of the RW material without SS is larger than that of the RW material containing SS of 4%, which is in agreement with the experimental results of MIP.

After 14 day’s hydration, the most probable pore diameters are 530 nm, 425 nm and 414 nm corresponding to the RW materials containing SS of 0, 1% and 4%, respectively. When curing period of 28 days, the most probable pore diameters of the RW materials are 486 nm, 408 nm and 401 nm corresponding to SS content of 0, 1% and 4%, respectively. Therefore, the difference in the most probable pore sizes of the RW materials between blending with SS and mixing no SS is notable. However, the most probable pore sizes are close for the RW materials containing SS of 1% and 4%. What’s more, the difference in the most probable pore size of the RW materials between blending 1% SS and 4% SS reduces over time.

For a further illustration of microstructures of the RW materials and a verification of the MIP results, the micromorphology of the RW materials cured for 3 days and 28 days is shown in Fig. 4. An overview-SEM image at a magnification of 200 is plotted in Fig. 4a, indicating that the chosen areas are representative. And, Fig. 4b shows the SEM images at a magnification of 4000. On 3 day, the number of needle-shaped crystals of the RW paste without SS is more than that of the RW material with SS content of 4%; and for the RW pastes containing SS of 1% and 4%, the pores are filled by amorphous C–S–H gel, leading to a lower porosity. On 28 day, the numbers of the needle-shaped crystals both decrease for the RW materials with and without SS, and the pores are filled by the C–S–H further. Besides, the pore size of the RW material without SS is larger than that of the RW material containing SS of 4%, which is in agreement with the experimental results of MIP.

3.3. Mineral compositions and distribution

The XRD patterns of the RW materials containing different amounts of SS are shown in Fig. 5. By phase determinations and by reference to the XRD patterns showing the un-hydrated phases in the starting materials (Fig. 1), we can find that when SS content is 0, in the XRD patterns of the RW materials hydrated for 3 day, there are significant diffraction signals of gypsum (CaSO₄·H₂O), tricalcium silicate (C₃S), dicalcium silicate (C₂S), monocalcium aluminate (CA) and calcium disilicate (CS₂), reflecting the incomplete hydration of the minerals of PC–CAC–gypsum ternary system. However, the tricalcium aluminate (C₃A) can’t be detected, indicating a complete hydration of C₃A before 3 day. Besides, on 3 day, significant diffraction signals of ettringite (AFt) crystals can be detected at d = 9.63 Å, 5.57 Å, 3.97 Å, 3.02 Å, and the calcium hydroxide (CH) can be found at d = 5.57 Å. We don’t find any clear diffraction signals of C–S–H gel, due to its amorphous property. However, amorphous C–S–H gel can be found in Fig. 4b. After hydration for 14 days, the height of AFt diffraction peak reduces, and calcium monosulphoaluminate (AFm) can be detected at d = 8.83 Å, 2.87 Å, this is because of the inadequate sulfate ions in the ternary paste. At d = 7.92 Å, there appears a diffraction signal of CAH₁₀; however, no diffraction signal of C₂AH₈ can be detected, which could be caused by the weak diffraction peak of C₂AH₈ or the overlapping diffraction peaks of C₄AH₁₀ and AFt. According to C. Eyju (2001), when there are adequate sulfate ions, the calcium aluminate-type minerals (CAₙ) will react with sulfate ions; and the reaction between CAₙ and water will not begin until the amount of sulfate ions reduces to a low level. Therefore, the formation of AFt is much earlier than CAH₁₀ and C₂AH₈. Besides, on 14 day, the diffraction peak of CH is much higher than that on 3 day, indicating the continuous hydration of calcium silicate-type minerals (CS₂), then it can be inferred that there will produce new C–S–H (gel) between 3 day to 14 day. The diffraction peak of CAH₁₀ disappears on 28 day, instead the diffraction signals of C₄AH₁₀ and gibbsite (AH₃) appear at d = 5.16, 3.18 Å and d = 5.55 Å, 4.36 Å, respectively.

When SS content is 4%, compared with the RW materials containing SS of 0 and 1%, the diffraction signal of AFt is the lowest at the same hydrated stages. On 14 day and 28 day, there is no obvious diffraction peak of C₄AH₁₀. When hydrated for 28 days, the diffraction intensity of C₆ASH₄ in the RW material with SS content of 4% is much higher than that of the RW material with SS mixing amount of 1%, revealing much more formation of C₆ASH₄ in the RW with SS content of 4%.

Further, FT-IR was employed to measure the adsorption bands at characteristic wavelength of chemical bonds that vibrate independently, to determine the chemical compositions of materials and to supplement the XRD results. In Fig. 6, the IR spectra for the RW materials containing different amounts of SS can be divided into a high wave number region (4000–1200 cm⁻¹) and a low wave number region (1200–400 cm⁻¹). In high wave number region, it is detected an O–H stretching vibration at around 3659 cm⁻¹ (W₁), indicating the formation of C₆AH₁₀ at 3642–3644 cm⁻¹ (W₂), there appear the O–H
vibration bands induced by CH. An adsorptive-water adsorption region can be found at 3441 cm\(^{-1}\) \((W_3)\), due to the existence of AFT\(^{38,39}\) and bending vibration bands that induced by the H\(_2\)O or OH of CAH\(_{10}\) appear at 1637–1639 cm\(^{-1}\) \((W_4)\). In low wave number region, the adsorption bands at 1102–1116 cm\(^{-1}\) \((W_5)\) is caused by the asymmetric vibration of SO\(_4^{2-}\) existing in AFT,
Fig. 5  XRD patterns of RW materials hydrated for 3 day, 14 day and 28 day. (a) SS addition of 0. (b) SS addition of 1%. (c) SS addition of 4%. (a: AFT, b: CAH10, c: CH, d: CaSO4·2H2O, e: C2AH8, f: CA2, g: CS, h: CaS, i: AFm, j: CA, k: AH3, l: C2ASH8) When SS content is 1%, the categories of the hydration products on 3 day are the same with those of the RW materials containing no SS. However, the diffraction signal of AFT is much lower, illustrating that the hydration process of CAH10 is delayed by mixing SS, and this finding agrees with Ding (1995, 1996) [32,34]. When hydrated for 14 day, the diffraction intensity of CH is lower than the material without SS; and there appear diffraction peaks at \(d = 11.75 \, \text{Å}, 6.24 \, \text{Å}\), reflecting the formation of C2ASH8. According to the studies carried out by Y. Jeong (2018), L. Xu (2017), M. Okoronkwo (2016) and T. Matschei (2007), C2ASH8 can be also detected at the similar peak positions in the calcium sulfoaluminate–belite cement–gypsum, calcium aluminate cement–Portland cement–anhydrite, Portland–CASH or CASH systems [35–37]. On 28 day, there appears the diffraction signal of C2AH8, but its diffraction intensity is weaker than that in the RW material without SS.
and the bending vibrations at around 605–616 cm\(^{-1}\) (W8) are also induced by the bands in SO\(_4^{2-}\);\(^{31}\) at wave number ranging from 965 cm\(^{-1}\) to 969 cm\(^{-1}\) (W6), there appear stretching vibrations induced by silicate/aluminate-oxide structures;\(^{31}\) and the adsorption bonds around 792–798 cm\(^{-1}\) (W7) are attributed to the symmetric stretching vibration of Si–O–Si.\(^{42}\)

Table 2 lists the area percentages of fitted peaks calculated using Origin 8.0, which can reflect the content of minerals to some extent. For the RW materials without SS, the peak area percentages at W2, W3, W5, W6, W8 are 2.92%, 45.26%, 17.99%, 9.44%, and 24.39% on 3 day, respectively. From 3 day to 14 day, there shows an increase trend in the area percentages at W2, W6.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Curing time</th>
<th>Area percentage/%</th>
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<tbody>
<tr>
<td></td>
<td>W1</td>
<td>W2</td>
</tr>
<tr>
<td>RW</td>
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<td>0</td>
</tr>
<tr>
<td>RW</td>
<td>14 day</td>
<td>0</td>
</tr>
<tr>
<td>RW</td>
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<td>3 day</td>
<td>0</td>
</tr>
<tr>
<td>RW + 1% SS</td>
<td>14 day</td>
<td>0</td>
</tr>
<tr>
<td>RW + 1% SS</td>
<td>28 day</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Fig. 6 Peak fitting of FT-IR spectra of RW materials containing SS amounts of 0, 1% and 4%. The curing time of the materials is 3 day, 14 day and 28 day.
and $W_8$, but it decreases in the area percentages at $W_3$ and $W_5$. It indicates the increase of the amount of the $O$–$H$ bonds in CH and Si/Al–$O$ bonds in C–$S$–$H$ and the decrease of the amount of AFt, which confirmed the XRD findings. The peak area percentages on 3 day and 14 day are both 0 at $W_1$, indicating no formation of $C_3A_H_6$; the peak area percentages at $W_2$ are 0 and 12.49% on 3 day and 14 day. However, on 28 day, the peak area percentage at $W_1$ raises to 2.87% and the peak area percentage becomes 0 on 3 day and 14 day. However, on 28 day, the peak area percentage at $W_1$ raises to 2.87% and the peak area percentage becomes 0 on 3 day and 14 day. This illustrates the formation of $C_3A_H_6$ and the decrease of CAH10.

When SS contents of 1% and 4%, compared with the RW materials without SS, the peak area percentage at $W_2$ decreases and that at $W_6$ increases on 3 day, respectively, showing much more formation of C–$S$–$H$, due to the reaction (eqn (2)). It can verify the porosity lowering induced by the filling effect of C–$S$–$H$.

CH + SiO$_2$\(^{2-}\) → C–$S$–$H$  \(\text{(2)}\)

For the RW material with SS content of 1%, the area percentage at $W_1$ is 2.06% on 28 day, which is lower than that in the RW material without SS. However, when the SS content in the RW material increases to 4%, the area percentages at $W_1$ are all 0 on 3 day, 14 day and 28 day, indicating no formation of $C_3A_H_6$. Besides, for the RW materials with SS additions of 0, 1% and 4%, the area percentage at $W_4$ decreased from 14 day to 28 day, indicating the consumption of CAH10. These are all consistent well with the XRD results (Fig. 5).

### 4. Discussion

#### 4.1. Impact of porosity on strength

Fig. 7 shows the variations of the strength with the diameter of the most probable pores for the RW materials with SS additions of 0, 1% and 4%. From 3 day to 14 day, the less the most probable pore diameter, the higher the strength of the RW materials with or without SS, indicating the strength enhancements may be caused by the decrease in the pore size in the materials, which agrees well with Matusinović (2003). However, the continuous decrease in the pore size cannot explain the strength retrogression of the RW materials containing SS of 0 and 1%. Therefore, it needs a further discussion on the strength evolution mechanism by analyzing hydration products.

#### 4.2. Impact of phase transformations on strength

Generally, formations of CAH10 and $C_2A_H_8$ are critical factors influencing the long-term strength of hardened CAC paste. However, due to the continuous hydration of $C_A$, minerals or the increase in temperature, the hydration products (CAH10 and $C_2A_H_8$) of CAC would transform to $C_3A_H_6$ (eqn (3)); furthermore, under the conditions of high alkalinity, $CA_x$ can directly combine with water to form $C_3A_H_6$ (eqn (4)).

\[
CA_x \xrightarrow{\text{High alkali environment}} C_3A_H_6 + AH_3  \text{(4)}
\]

CAH10 and $C_2A_H_8$ are meta-stable hexagonal hydrates, and $C_3A_H_6$ is a stable cubic hydrate. And, the intercrystal bonding force of the hexagonal hydrate is larger than that of the cubic one. Therefore, based on the results of XRD and FT-IR, the conversions of CAH10 and $C_2A_H_8$ to $C_3A_H_6$ can explain the strength decline of the RW materials with SS content from 0 to 2%. Besides, at initial hydration phase, when there exists SO4\(^{2-}\), $CA_x$ will hydrate and produce AFt crystals first (eqn (5)). However, excessive formations of AFt at early hydration stage will inhibit the hydration process of calcium silicate type minerals (CS$_x$); then, the formation of C–$S$–$H$ (gel) decreases to induce a lower early strength of the RW materials.

\[
CA_x + H_2O + SO_4^{2-} \rightarrow C_3A_S_H_3 (\text{AFt}) + AH_3  \text{(5)}
\]

For the RW material without SS hydrated for 14 day, the diffraction intensity of CH is larger than that on 3 day; besides, the peak area become larger at around 967 cm\(^{-1}\). Thus, it indicated the continuous reaction between CS and water (eqn (6)) during 3 day to 14 day.

\[
C_S + H_2O \rightarrow C–S–H (\text{gel}) + CH  \text{(6)}
\]

During 0 to 14 day, the hydrates, CAH10, $C_2A_H_8$ and C–S–H (gel) are of benefit to the strength, which can explain the increase in strength of the RW material without SS. However, on 28 day, it can be detected the conversion of CAH10 and $C_2A_H_8$ to $C_3A_H_6$, inducing a lower long-term strength of the RW material without SS for the lower intercrystal bonding force of $C_3A_H_6$. The phase variations in the RW material without SS is plotted in Fig. 8a.
The variation of hydrates in the RW materials containing SS is plotted in Fig. 8b. Combining with XRD and FTIR results, for the RW materials with SS, the hydration rate of CAx is inhibited to cause a decrease in the formation of AFt,\textsuperscript{12,14} then, the hydration reaction of CS and the reaction between SS and CH are both accelerated to produce much more C–S–H (gel) to improve the early strength of the material.\textsuperscript{15} Due to sulfate ions reducing with further hydration, the CAx minerals reacts with water to form CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8}, this process is similar with that of the RW material without SS. After that, due to the existence of SS, CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8} could react with silicate ions to form the stable phase of C\textsubscript{2}ASH\textsubscript{8} before the conversion from the hexagonal crystal to the cubic one (eqn (7)),\textsuperscript{12} which was also reported by M. Heikal (2017) and J. M. Mercury (2007).\textsuperscript{6,17} Then, the conversion from the hexagonal crystal to the cubic one could be inhibited. C\textsubscript{2}ASH\textsubscript{8} is a stable hexagonal crystal, which cannot induce the strength retrogression of the RW material. On 28 day, C\textsubscript{2}AH\textsubscript{6} can be also detected in the RW material with SS mixing amount of 1%, it is because SS is consumed completely, which cannot react with all the hydrates of CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8}, and the remaining CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8} are converted to C\textsubscript{2}AH\textsubscript{6}. What’s more, based on Fig. 5 and 6, the formation amount of C\textsubscript{2}AH\textsubscript{6} in the RW material with SS of 1% is less than that in the RW material without SS, thus, the decrement of strength is less.

\[
\text{CAH}_{10}/\text{C}_2\text{AH}_8 + \text{SS} \rightarrow \text{C}_2\text{ASH}_8
\] (7)

According to the results of XRD and FT-IR, from 3 day to 14 day, the amounts of C–S–H (gel) and C\textsubscript{2}ASH\textsubscript{8} in the RW materials containing SS of 4% are more than those in the RW material containing SS of 1%, which can explain the higher strength. Besides, there is no evidence of the formation of C\textsubscript{3}AH\textsubscript{6} from 3 day to 28 day, indicating the silicate ions is so adequate that can consume CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8} fully. Therefore, the decrease in the long-term strength of the RW material can be inhibited effectively.

5. Conclusions

By way of summary, according to the findings of the strength and micro-structural characterizations of the RW materials containing different amounts of SS, the main relevant conclusions of this study are listed below:

(1) The strength of the RW material could be enhanced by mixing with SS. And the more the SS content, the higher the strength. However, when the addition of SS less than 3%, the long-strength retrogression is existed in the RW material hydrated for 28 days. When SS mixing amount is above 3%, the strength retrogression of the RW material can be inhibited effectively.

(2) The compactness of the RW material is improved by the addition of SS. Compared with the RW material without SS, the RW material containing SS have a lower most probable pore diameter, due to the filling effect of C–S–H (gel) that is produced by the reaction between silicate ions and CH. And, whatever the amount of SS mixed, the compactness of the RW material increases over time, it can probably explain the strength enhancement during 3–14 day, but cannot explain the strength retrogression of the RW materials detected on 28 day.

(3) For the RW materials containing SS and hydrated for 0 to 14 day, there are more hexagonal hydrates and C–S–H (gel) and less AFt crystals, it is of benefit to the strength. However, the phase conversion of the hexagonal hydrates (CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8}) to the cubic one (C\textsubscript{2}AH\textsubscript{6}) causes the strength retrogression of the RW materials with SS additions of 0 and 1%. Due to the reaction between silicate ions and CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8} to form C\textsubscript{2}ASH\textsubscript{8}, the content of C\textsubscript{2}AH\textsubscript{6} in the RW material containing SS of 1% is less than that in the RW material without SS, that is the reason why the long-term strength decrement of the RW material containing SS of 1% is less than that of the RW material without SS. In addition, for the RW material with SS addition of 4%, the formation of C\textsubscript{2}AH\textsubscript{6} is inhibited completely, thus, there is no long-term strength retrogression of the RW material.

Conflicts of interest

There is no conflict to declare.

Acknowledgements

This work was supported by the National Natural Science Funds of China (41872188), the Henan Province Science and Technology Innovation Talent Program, China (164200510002), and the Key Scientific Research Project of Henan Province Higher Education Institutions, China (15A440002) is also gratefully acknowledged.

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