Preparation and characterization of a new alkali-activated binder for superfine-tailings mine backfill

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Abstract

Recently, the increasing of ultrafine-tailings increases the amount of ordinary Portland cement (OPC) in cemented paste backfill (CPB), which leads to the rise of CPB cost and carbon emission. Alternative binders should be then developed. The present work focuses on the preparation of binder using slag activated by a mixture of calcined quarry dust (CQD, mainly consists of reactive CaO and MgO) and NaOH at a mass ratio of 1:1 with contents ranging from 6 % to 10 % up to 90 d. The results indicated that CQD/NaOH was more effective than using NaOH or CQD alone in activating slag and also showed better performance than OPC. The compressive strength of the CPB samples using 10 % CQD/NaOH was around 3.78 MPa after curing for 90d, around 42 % higher than the OPC-based CPB samples. The reaction products of CQD/NaOH activated slag consisted mainly of C-(A)-S-H, Ht phases, and M-S-H. The generation of Ht phases lowered the Al incorporation into the structure of C-S-H, resulting in lower average Al/Si ratio and mean chain length.

Introduction

Cemented paste backfill (CPB) is one of the effective ways for tailings disposal (Guo et al. 2021). In recent years, with the national regulation and control of sand and gravel aggregate policy, the production of sand and gravel aggregate is reduced. Thus, some mining enterprises classify tailings and sell coarse particles as aggregates, which results in the reduction of the grain size of the tailings used for CPB. In addition, with the increase of refractory ore year by year and the decrease of ore grade, the grinding fineness becomes finer and finer (super-fine tailings, particle size < 20 μm), which makes it difficult for the CPB to reach the ideal strength (Guo et al. 2021). Ordinary Portland cement (OPC) dosage has to be increased when using such super-fine tailings in CPB, resulting in the increase of CPB cost. On the other hand, carbon emission from the OPC production contributes to the greenhouse effect (Cao et al. 2018, Qiu et al. 2019). As a result, alternative binders need to be developed.

Alkali activated materials (AAMs) are one type eco-friendly cementitious composites and are widely investigated in the last decades (Provis and van Deventer 2014). In the production of AAMs, NaOH and Na_2SiO_3 are widely used alkali activators. Moreover, blast furnace slag (BFS) attracts more attention to be used as the raw precursors due to the abundant sources considering the rapid growth of demand for iron and steel with current rapid industrial development and high economic increase year-by-year. In comparison, the high-temperature treatment for the production of calcined clay can increase the cost of the manufacture of AAMs. The most extensively explored alkali activators in AAMs production are NaOH and sodium silicates. Being a strong alkali, NaOH is propitious to prepare alkali-activated slag (AAS) with competitive cost (Burciaga-Díaz and Betancourt-Castillo 2018). While it is difficult to manipulate the NaOH solution resulting from the highly corrosive nature (Kang et al. 2019). In particular, related safety training and personal protective equipment will be indispensable considering the serious threat to workers' health and safety from alkali solutions (Provis 2018). These features make the large-scale utilization of AAS less appealing for construction companies and markets. Besides, it is commonly that AAS prepared from NaOH presents relatively low compressive strength due to the quick setting and

coarse pore structure. Sodium silicate (Na_2SiO_3) has been commonly used with NaOH to provide AAS composites with superior properties including satisfactory compressive strength and durability. Although the superior properties, Na_2SiO_3 is the most energy-intensive component, which is the major concern of the environmental footprint in AAS composites.

AAS composites can also be produced by alternative alkali activator activators with lower environmental implication. Lime (CaO) was explored for the AAS production due to its lower cost compared with NaOH (Park et al. 2016). Calcium silicate hydrates is the primary hydration product in CaO -activated BFS. Magnesium oxide (MgO) has also been examined as an alternative alkali activator. Shen et al. (Shen et al. 2011) investigated the hydration of slag-fly ash binders activated by MgO , the results showed that C-S-H, $\text{Mg}(\text{OH})_2$, and MgCO_3 were the main reaction products. Jin et al. (Jin et al. 2015) investigated the activation effects of reactive MgO on the properties of AAS composites. The results showed that the slag activated by reactive MgO contributed to higher strength than that of hydrated lime activated slag composites. Similar phenomenon was also found by Yi et al. (Yi et al. 2014), who reported that slag-based binders activated by MgO gave higher strength than the hydrated lime-based composites. Gu et al. (Gu et al. 2014) studied the synergistic effect of CaO and MgO mixtures on the properties of AAS composites. The results indicated that MgO increased the strength at the later curing ages due to the formation of Ht phases, although CaO could promote the C-S-H generation.

Although lime and MgO activated binders continue to attract the attention of researchers due to their uniqueness in some respects, the lower compressive strength and the slower setting compared with that of NaOH based binders and OPC seem to restrict the large-scale applications. Therefore, as one solution for these disadvantages, the use of auxiliary activators to lime or MgO has been proposed. In previous work (Zhao et al. 2020b), we explored the effects of Na_2SO_4 dosage on the properties of CaO activated BFS considering the slow strength development. The incorporation of only 1 % Na_2SO_4 increased the compressive strength of the AAS binders (Zhao et al. 2020b). The beneficial effects can be attributed to the accelerated reaction of slag due to the increased pH value of the reaction environment and the additional ettringite (AFt) formation (Zhao et al. 2020b). A more previous work by Park et al. (Park et al. 2016) investigated the influence of gypsum with contents from 0 to 15 wt.% on the CaO -activated slag composites. The results indicated that the 10 % of gypsum addition gave the best final compressive strength resulting from the pore-size refinement effect due to the formation of AFt. Oswaldo et al. (Burciaga-Díaz and Betancourt-Castillo 2018) reported the results of strength and hydration products of AAS binders prepared by a mixture of MgO and NaOH at a mass ratio of 1 added at 4-8 %. The results showed that the AAS composites activated using only 4% MgO -NaOH presented higher strength than that of composites with 6% NaOH. This is attractive considering the lower dosage of NaOH used in the activator mixture (Burciaga-Díaz and Betancourt-Castillo 2018).

Although the endeavors illustrated above, no reports were found about the AAS production using a mixture of CaO - MgO -NaOH. Reactive CaO and MgO was provided from the quarry dust (mainly consists of dolomite) after calcination. In our previous work (Zhao Yingliang et al. 2020), we explored the

properties of calcined quarry dust (CQD) activated slag composites, while relative early strength was obtained, only 3.8 MPa and 28.1 MPa at 1 d and 28 d. Strategies are necessary to further modify the properties of the AAS composites. Therefore, this paper studies the preparation of AAS binders activated using a mixture of CQD/NaOH, which was used for superfine-tailings CPB. The compressive strength of CPB samples was compared with OPC based samples. The reaction kinetics was explored by the isothermal calorimeter, BSE/IA, and quantification of the chemically bound water content (CBW). Besides, the hydrates were studied via XRD and TG analysis. Finally, MIP, SEM combined with EDS, and ^{27}Al and ^{29}Si MAS NMR spectroscopy were used to investigate the microstructure and the elemental composition of the reaction products.

Materials And Methods

2.1. Materials

Blast furnace slag (BFS) and quarry dust (QD) were collected from Shandong and Hebei, China, respectively, and their chemical composition was listed in **Table 1**. Sodium hydroxide (NaOH, 98% purity, powder) was bought from Kemeiou Chemical Reagent Co. LTD. Calcined quarry dust (CQD) was produced using the method in (Zhao Yingliang et al. 2020), and the XRD patterns of QD and CQD were shown in **Fig. 1**. Artificial silica tailings (AST) with SiO_2 content higher than 99.8% was used to replace the natural tailings as aggregate in this study, as reported in previous studies (Guo et al. 2021). About 85% of AST particles are smaller than 20 μm .

Table 1. Chemical composition of the raw materials (wt. %).

Materials	CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	SO ₃
slag	37.50	9.70	30.3	15.30	0.37	0.19	0.32	0.85
QD	63.56	31.35	4.46	0.29	0.59	0.02	0.01	0.003

2.2. Sample preparation

Three AAS composites were prepared using a mixture of CQD-NaOH at a mass ratio of 1/1 incorporated at concentrations of 6%, 8%, and 10% by the mass of slag content. Two reference AAS composites activated only by 8 % NaOH and 8 % CQD, respectively, were also elaborated as comparison. The details are given in **Table 2**. Solid NaOH particles were dissolved in water and cooled at 20 °C before mixed with slag. To prepare AAS paste samples, CQD and slag were dry mixed in a pan for 1 min. NaOH solution was then added into the mixture and stirred for 5 min. After that, the slurry was transferred into molds and cured at 20 °C and 95% R.H. until the designated aging.

For the CPB samples preparation, AST were dry blended with the binders. The binder/tailings ratio was 1/8 in the present work. The following methods was similar to the paste sample preparation, as illustrated above.

Table 2. Mixture formulations.

NO.	Binder				Binder/AST (w/w)	solid concentration (wt.%)
	slag (wt. %)	CQD/NaOH (1/1 by mass)	NaOH (wt. %)	CQD (wt. %)		
6 %- CQD/Na	100	6	0	0	1/6	76
8 %- CQD/Na	100	8	0	0		
10 %- CQD/Na	100	10	0	0		
8%-Na	100	0	8	0		
8%-CQD	100	0	0	8		

2.2. Characterization methods

Unconfined compressive strength (UCS) of the CPB samples was tested after curing for 1, 3, 7, 28, 90 days according to the standard ASTM C39 (ASTM C191-19). The average value for triplicate samples was used as a final UCS. The pore structure of the samples was characterized via MIP using an Autopore IV 9500, which can analyze pores with diameters of 0.006-100 μm . Reaction kinetics were measured using a I-Cal 8000 HPC. About 8 g sample were placed in an ampoule and the test was conducted at 20 °C for 72 hours. The mineralogical composition of the hydrated sample was tested by XRD using a Shimadzu XRD-7000 in the range of 5° to 50°; TG analysis was conducted using a STA409PC from room temperature to 1000 °C. A small piece was cut from the hardened sample and rinsed using isopropanol (A.R., 99.7%) for 3 d. Next, they were dried for 3 d in a vacuum oven. Zeiss Gemini 300 equipped with an energy dispersive spectrometer (EDS) was used to investigate the microstructure of the hardened samples. Backscattered electron images were taken in a high vacuum environment. An acceleration voltage of 15kV and a working distance of 3-5 mm were used. The hydration degree of slag (DoH) was investigated using backscattered electron images analysis (BSE/IA) following the method reported in (Kocaba et al. 2012). A Bruker 400M NMR spectrometer was used to obtain ^{29}Si and ^{27}Al MAS-NMR spectra. Mean chain length (MCL) and average molar Al/Si ratio was calculated following the methods in (Myers et al. 2013).

Results And Discussion

3.1. Unconfined compressive strength (UCS) of the CPB samples

The effect of alkali activator on the UCS of the CPB samples up to 90 d is shown in **Fig. 2**. At 1 d, the UCS of CPB samples activated by 6 %-CQD/Na was around 0.43 MPa, while those with 8 % and 10 %-CQD/Na developed UCS of 0.59 MPa and 0.67 MPa, respectively. The UCS rapidly increased until 28 d, reaching 2.82 MPa, 3.15 MPa, and 3.56 MPa for 6 %-, 8 %- and 10%-CQD/Na, respectively. After that, the CPB samples witnessed marginal strength gain.

CPB samples activated by CQD/Na presented higher UCS after curing for 7 d, although 8%-Na enjoyed the highest UCS value at the initial curing period. At 28 d, the UCS for sample 8%-Na was only approximately 2.90 MPa. Previous reports also demonstrated that AAS composites with NaOH as an activator presented higher initial strength but lower strength development rate after curing for a long time. Besides, AAS with 8 % CQD presented the lowest strength at the early curing ages and reached about 2.95 MPa at 28 d, which is comparable with that of the composites 8%-Na. Lower early strength in CaO or MgO activated slag has also been reported elsewhere (Zhao et al. 2020b), mainly resulting from the lower pH value of the reaction environment.

CPB samples using OPC as a binder were also prepared to be used as references. The lowest UCS values were noticed in OPC-based samples after curing for 28 days. Thus, it can be concluded that OPC is not suitable to be used in CPB with ultra-fine tailings.

3.3. Characterization of the binders

3.3.1. Reaction kinetics

Fig. 3 shows the heat flow rate and total heat release of the binders hydration during the first three days. An exothermic peak was noticed in the very first hours of the composites reaction, as shown in **Fig. 3a**, resulting from the initial wetting and dissolution of the raw materials (Yang and Jang 2020). This peak was followed by a sudden slowdown to the induction period. After that, a second exothermic peak was noticed at around four hours, mainly caused by the massive precipitation of the reaction gels (Zhao et al. 2020a). Variation of the alkali activator did not seem to change the occurrence of the second peak but the intensity. Using NaOH as an activator presented the highest heat flow rate in the second peak, resulting from the higher pH value of the pore solution (**Fig. S1**). By comparison, a lower heat flow rate was noticed in binder 10 %-CQD/Na during this period. Binder 8 %-CQD showed the lowest heat flow rate due to the slow reaction between slag and CaO/MgO, agreeing with previous reports (Zhao et al. 2020b, Ruan and Unluer 2018). The slow hydration of CaO or MgO activated slag for AAS production is considered as one of the main factors restricting its wide application as illustrated in the introduction section.

Fig. 3b showed the total heat release through the first 72 hours of reaction. Binder 8 %-Na showed the highest cumulative heat release at the initial reaction periods, reaching around 162 J/g after three d. This corresponds to the highest UCS value in the early periods. A relative lower cumulative heat release was found in CQD/Na activated slag, about 127 J/g and 91 J/g for 10 %- and 6 %-CQD/Na, respectively. Using single CQD as an activator reported the lowest total heat release (only around 87 J/g) due to the slow reaction. All these data agreed well with the early strength evolution of the CPB samples.

An isothermal calorimeter is a semi-quantitative method to estimate the reaction kinetics of the slag hydration. Thus, BSEM/IA was subsequently conducted to quantize the hydration degree of slag (Kocaba et al. 2012). The results are shown in **Fig. 4a**. Slag hydration was greater in 8 %-Na before 28 d. By 1 d, the DoH of slag was around 25 % for 8 %-Na, while this number was about 19 % for 10%-CQD/Na. While after 90 d, binder 10 %-CQD/Na presented the highest DoH value, reaching approximately 56 %. This is correlated well with the UCS development as shown in **Fig. 2**. More reacted slag indicated higher content of hydration gels formation, favoring the UCS evolution. This could also be confirmed by the chemically bound water (CBW) content from thermal analysis, as shown in **Fig. 4b**. CBW content has also been used to examine the extent of hydration (Deboucha et al. 2017, Ukpata et al. 2019). Similar to the BSEM/IA method, binder 8%-Na presented the highest CBW content at early hydration periods, but no strong increase was noticed at later ages. The CBW content for binder 10% CQD-NaOH experienced a rapid increase after 3 d, reaching around 23 % at 90 d, which is higher than that of paste 8 %-Na (about 19 %).

Even though the methods used here to study slag reaction are characterized by the high measurement uncertainty, all of them indicate that a similar trend: slag activated by NaOH presents faster reaction at the early stages (evidenced by the isothermal calorimeter results in **Fig. 3**), which contributes to the early strength development as shown in **Fig. 2**. While although CQD/Na based binders presented slower reaction at the initial periods, the later reaction was intensive than that of NaOH based composites. This contributed to the increased slag reaction in later ages, favoring the strength increase.

Fig. 5 presents the relationship between UCS and DoH and CBW content. The linear relationship between the strength and DoH and CBW content can be described as $y = 8.84 + 11.84x$ ($R^2 = 0.9$) and $y = 7.36 + 3.52x$ ($R^2 = 0.8$), respectively. The increase in the DoH and CBW content is beneficial for the increase of the CPB strength due to additional hydration products formed in the matrix.

3.3.2. X-ray diffraction

Fig. 6 shows the X-ray diffraction (XRD) patterns of the binders at 1 d and 90 d and the raw slag is also included as a reference. As shown in **Fig. 6**, slag was mainly amorphous with a minor content of crystalline phases like akermanite and gehlenite.

In NaOH activated slag (8 %-Na), calcium silicate hydrate (C-S-H) was identified as the major reaction products. C-S-H has been reported to be the predominant contributor to the mechanical properties in AAS with various types of alkali activator and cement-based materials. Hydrotalcite like phase (Ht) was

distinguished at around 11.6° , 23.1° , 36.7° , and 39.5° 2θ . Ht is a common reaction gel in AAS samples when sufficient magnesium is present in the raw materials or alkali activators (Haha et al. 2011). In previous work, the formation of additional Ht was found to contribute to a denser matrix, contributing to the strength development (Jin et al. 2014, Burciaga-Díaz and Betancourt-Castillo 2018). Therefore, the generation of more Ht could be related to the higher compressive strength developed in CQD/Na activated binder. The peak of hemicarboaluminate (Hc, $C_4Ac_{0.5}H_{12}$) at around 10.7° 2θ as reported by (Baquerizo et al. 2015, Zajac et al. 2014) was noticed in the XRD pattern. Hc is a carbonated AFm phase similar to monocarboaluminate (Mc, C_4AcH_{11}) with half of the CO_3^{2-} replaced by OH^- (Baquerizo et al. 2015). Slight carbonation seemed to take place with the presence of peaks located at about 29.4° and 43.2° 2θ . These peaks were assigned to calcite (CC), forming due to the reaction between the dissolved CO_3^{2-} and Ca^{2+} released from the slag. Besides, the remaining akermanite and gehlenite were also present in the unreacted slag, in line with other works about AAS composites (Burciaga-Díaz and Betancourt-Castillo 2018).

CQD/Na based samples (6 % and 10 %) presented similar phase assembles to that of 8 %-Na. While compared to 8 %-Na, the peak for C-S-H seemed to be sharper with a lower full width at half maximum (FWHM), 0.648 vs 0.749, as shown in **Fig. 6a**. This indicates that the C-S-H gels formed in CQD/Na based composites are slightly more ordered at the atomic level compared to that of 8 %-Na (Gong and White 2016). In NaOH activated slag, more Na can be incorporated into the structure of C-(A)-S-H with the formation of more C-(N, A)-S-H, which is predominately amorphous compared with C-(A)-S-H (White et al. 2015). Besides, less Ht was detected in the sample activated by 6 %-CQD/Na. Although reactive MgO was provided from the activator (CQD), the lower pH value of the pore solution (Fig. S1) did not favor the leaching of Al from slag, which limits the formation of Ht. In this case, the pH value of the pore solution determined the phase assembles and formation kinetics. Furthermore, no brucite magnesium silicate hydrate gels (M-S-H) was detected from the XRD patterns, mainly attributing to its amorphous nature and it is hard to detect by XRD (Jin and Al-Tabbaa 2013).

Lower peak intensity of C-S-H was noticed in CQD activated slag (8 %-CQD), mainly resulting from the lower pH value of the pore solution, as shown in Fig. S1. Lower pH value restricts the dissolution of slag, leading to fewer hydration gels formation. This is correlated well with the DoH of slag and CBW content (**Fig. 5**). This could explain the lower UCS value in CQD based AAS composites.

Long time curing (90 d) did not strongly modify the phase assembles but the intensity of the peaks was noticed to increase. This result is caused by the continual slag rection, which leads to the formation of more hydration gels. DoH of slag and CBW content increased with the hydration time confirmed this result.

3.3.3. Thermogravimetric analysis

Fig. 7 shows the TG/DTG results of the hydrated binders at 1 d and 90 d. The major humps and some tiny peaks were detected as illustrated below:

1. The dehydration of C-(A)-S-H gel occurred up to 200 °C according to (Kim et al. 2013, Ben Haha et al. 2011).
2. Hydrotalcite-like phases $[\text{Ht}, \text{Mg}_x\text{Al}_y\text{CO}_3(\text{OH})_{16} \cdot 4(\text{H}_2\text{O})]$ commonly showed two steps of decomposition, around 220 °C and 380 °C, respectively (Machner et al. 2018).
3. The peak located at around 530 °C was assigned to dehydroxylation of silanol (Si-OH) groups in M-S-H structure, as reported previously (Jin et al. 2015, Bernard et al. 2019). The decomposition of M-S-H also occurs between 30 °C and 250 °C due to the loss of the physically bound water (Bernard et al. 2019).
4. The decomposition of carbonate-containing phases was evidenced by the peak from 600 to 800 °C (Jin et al. 2015).

The weight loss was divided into two main stages (50 °C and 200 °C, 200 °C and 400 °C) and denoted as Δm_1 and Δm_2 , respectively. **Table 3** summarizes the weight loss of the main phases. All the two variables for the AAS composites increased with the curing time, resulting from the continual reaction and generating more reaction products. Composite 8 %-Na showed higher values for both Δm_1 and Δm_2 at 1 d due to the fast reaction of slag under the activation of NaOH with higher pH value (Fig. S1). This was followed by 10 %-CQD/Na and sample 8%-CQD gave the lowest values. After curing for 90 d, composite 10 %-CQD/Na witnessed the highest values for these two variables due to the continual hydration even after long time curing. This is confirmed by the DoH value of slag, showing that sample 10 %-CQD/Na presents the highest reaction degree after 7 d, as given in **Fig. 4**. All these data agrees well with the UCS test results and the hydration kinetics of the composites reaction.

One distinct hump detected on the DTG curve of CQD/Na based composites at 90 d was the presence of M-S-H especially in sample 10 %-CQD/Na. M-S-H is the main reaction product in Mg-Si binders, resulting from the reaction between the dissolved Mg and Si. Although more reactive MgO in sample 8 %-CQD, the lower pH value of the pore solution limited the dissolution of slag then the leaching of Si. The formation of M-S-H was then restricted. This was different from previous work (Burciaga-Díaz and Betancourt-Castillo 2018) about the AAS composites using a mixture of MgO and NaOH, which reported that no M-S-H was detected. The authors infer that this may be attributed to the variations on the characteristics of the slag and dosage of the alkali activators, which can make differences in the solids solution and then the phase assembles.

Table 3. Δm_1 and Δm_2 calculated from the TG analysis of AAS composites.

Weight loss (%)	6 %-CQD/Na		10 %-CQD/Na		8%-Na		8%-CQD	
	1 d	90 d	1 d	90 d	1 d	90 d	1 d	90 d
Δm_1	3.22	5.76	4.85	11.19	6.40	8.95	2.89	6.21
Δm_2	1.46	2.60	2.13	3.95	2.55	3.10	1.61	3.07

3.2.4. Pore structure

The pore structure of samples after curing for 1 d and 90 d characterized by MIP are shown in **Fig. 8**. **Fig. 8a** shows the porosity evolution over curing time. 8 %-Na presented the lowest porosity at the early curing ages, this is due to the fast reaction of slag activated by NaOH, leading to the more hydrates production. At 1 d, the porosity of 8 %-Na was around 41 %, then it decreased rapidly and reached about 34 % at 3 d. No significant changes were noticed after that and approximately 30% of porosity for 8 %-Na was noticed at 90 d.

By comparison, the porosity of CQD/Na activated CPB samples did not change significantly at the early stages. A decrease of only 3 % was noticed for 10 %-CQD/Na during the first 3 d, while this number was 15 % for that of 8 %-Na. This trend is consistent well with the results in section 3.2, which shows the less intensive reaction occurred at the initial stages for CQD/Na based AAS composites. The porosity for 10 %-CQD/Na then decreased rapidly after 3 d, reaching about 27 % after curing for 90 d. As reported in section 3.3, more Ht formed in sample 10 %-CQD/Na. The formation voluminous Ht has been reported to contribute to the matrix with lower porosity (Haha et al. 2011).

Using single CQD as an activator witnessed a slower evolution in the porosity with a marginal decrease during the first 3 d. This is in line with the isothermal calorimeter results, which indicated a slow reaction in CQD based AAS composites. After curing for 90 d, the porosity for 8 %-CQD was around 33 %. The higher porosity was caused by the lower pH value of the pore solution, leading to less hydration products. This agreed well with the DoH value in **Fig. 4**, which showed higher content of un-reacted slag remaining.

Fig. 8b and **c** show the pore size distribution of CPB samples after curing for 1 d and 90 d. All the samples presented the main peak at around 100 μm at 1 d, mainly as capillary pores, resulting from the low reaction extent of slag at the initial stages. 8 %-Na seemed to present more mesopores due to the relatively faster reaction. Most of the pores in the AAS composites were lower than 100 μm after curing for 90 d. The continual reaction of slag contributed to the formation of more gels, which could fill the voids between slag particles and lead to a more compact matrix. 8 %-Na contained a higher number of capillary pores, being one of the factors to the lower strength after a long time curing.

3.3.5. Backscatter scanning electron microscopy (BSEM)

Fig. 9 shows the BSEM of the AAS composites after curing for 90 d. Un-hydrated slag particles were identified to be dispersed in the matrix with a light gray tone in all AAS composites, while the grey regions between the un-reacted slag particles refer to the main binding phase. Among the three investigated composites, sample 10 %-CQD/Na presented the most compact matrix with less un-reacted slag particles remaining. This could be attributed to the higher content of hydration gels as reported in Fig. 6 and Fig. 7. A less homogenous matrix was noticed in composites 8 %-Na, although higher content of NaOH was incorporated, which may lead to lower compressive strength. Pore size distribution also confirmed larger pores and higher porosity in composites 8 %-Na, as shown in **Fig. 8**. More cracks and pores were found in sample 8 %-CQD, due to the lower reaction degree of slag. MIP test results also demonstrated that composites 8 %-CQD showed the highest porosity in all curing ages. The qualitative results from energy dispersive spectroscopy (EDS) indicated that the reaction products presented a high content of Si, Ca, Mg and Al. This suggests that the generation of C-(A)-S-H gel intermixed with Ht phases.

Fig. 10 shows the Mg/Si vs. Al/Si ratios of the AAS composites after curing for 90 d. The presence of Ht phases could be confirmed by the linear slope (Haha et al. 2011). The Mg/Al ratio was noticed to decrease with the content of MgO in the raw precursors. Sample 8 %-CQD presented the highest Mg/Al ratio due to the highest MgO content in the alkali activator. This was followed by composites 10 %-CQD/Na, with a Mg/Al ratio of 1.94. The lowest Mg/Al ratio was noticed in sample 8 %-Na, reaching 1.77. The positive abscissa indicated the presence of Al in the C-S-H gels. The Al incorporation in C-S-H decreased with increasing MgO content from Al/Si = 0.17 for 8 %-Na to 0.11 for 10 %-CQD/Na and 0.07 for 8 %-CQD.

3.3.6. Solid state ^{27}Al and ^{29}Si MAS NMR spectroscopy

Fig. 11a shows the ^{27}Al NMR spectra of the samples. The spectrum of the anhydrous slag was observed as a hump located at around 60 ppm related to Al in AlO_4 in the slag structure (Shimoda et al. 2008). The broad character of the peak indicated the disorder and heterogeneity of the local structure of slag (Pedro Perez-Cortes and J. Ivan Escalante-Garcia). This result agrees with the amorphous character in XRD pattern (Fig. 7). In the activated binders, the peak related to AlO_4 shifted to a higher chemical shift value and new signals appeared corresponding to AlO_6 centered at around 9 ppm.

The spectrum deconvolution of ^{27}Al NMR indicated that Al was inserted into the structure of C-S-H with a sharp peak located at around 70 ppm (Myers et al. 2015a). This peak was more obvious in composite 10 %-CQD/Na, agreeing with the results in TG/DTG analysis in **Fig. 7**, indicating that more hydration gels formation in sample 10 %-CQD/Na. The resonance at chemical shift value around 9 ppm corresponded to AlO_6 in LDH structures including Mg-Al and AFm (Ke et al. 2016, Jones et al. 2003). Composite 8 %-CQD presented a higher proportion of AlO_6 resulting from the abundant MgO content. Thus, more Al was incorporated into LDH structure, resulting in lower Al content in C-(A)-S-H gels. This led to a lower Al/Si ratio in composite 8 %-CQD as evidenced in EDX results in Fig. 9.

The ^{29}Si MAS NMR spectra of anhydrous slag and AAS composites after curing for 90 d are reported in **Fig. 11b**. The slag showed a broad hump from -60 and -100 ppm, including Q^0 (-74 ppm), Q^1 (-78 ppm), and $\text{Q}^2(1\text{Al})$ (-82 ppm) sites, respectively. The small shoulder at -85 ppm indicated that the presence of Q^2 site. After alkali-activated, the spectra of all the investigated composites presented significant changes with the main peak shift toward more negative values. This implies the formation of reaction products with different chemical nature (Burciaga-Díaz and Betancourt-Castillo 2018).

The deconvolution results of ^{29}Si MAS NMR spectra indicated that the anhydrous slag still exists. While the decrease in the intensity of Q^0 suggested the consumption of slag to form C-S-H type hydration gels mainly containing four Q^n signals. The peaks located at -78 ppm and -80 ppm are corresponded to Q^1 sites, which are mainly related to the chain-end tetrahedral Si units in the C-(A)-S-H structure (Myers et al. 2013). The signal at -83 ppm is related to $\text{Q}^2(1\text{Al})$, which is caused by the isomorphous replacement of Si by Al in the C-(A)-S-H chain (da Silva Andrade et al. 2019). The peak at -86 ppm is assigned to Q^2 sites, in which tetrahedral Si units are located at the middle groups in the C-(A)-S-H structure. A single peak at around -90 ppm is related to $\text{Q}^3(1\text{Al})$ (Myers et al. 2013).

Table 4 shows the quantitative deconvolution results. From **Table 4**, it demonstrated a higher extent of slag in composite 10 %-CQD/Na, as evidenced by the lower residual slag fraction and higher C-S-H type reaction product content. By comparison, higher content of un-reacted slag was noticed in sample 8 %-Na and 8 %-CQD, agreeing well with the BSEM-IA results, as shown in **Fig. 4**. Compared to sample 8 %-Na, the content of $\text{Q}^2(1\text{Al})$ was noticed to decrease in sample 10 %-CQD/Na, indicating that less Al is incorporated into the C-S-H structure. This result is in line with the EDS results. This phenomenon is attributed to that more Al tends to form Ht phases in the presence of higher MgO content, confirmed by the lower Al/Si ratio. As has been reported that no cross-linked Q^3 and $\text{Q}^3(1\text{Al})$ signals existed in pure C-S-H and only very weak signals of Q^3 have been detected in C-S-H with low Ca/Si ratio (Bernard et al. 2017, Myers et al. 2015b). A significant quantity of $\text{Q}^3(1\text{Al})$ was noticed in the present work, indicating the formation of M-S-H. Similar results have been reported elsewhere (Bernard et al. 2017). This phenomenon is in line well with the TG/DTG results. The mean chain length (MCL) value of 13 was calculated for composites 10 %-CQD/Na compared with 15 for that of composite 8 %-Na. The substitution of Si by Al in the C-S-H structure occurs especially in the bonding tetrahedral position of “dreierkette” chains, leading to increase in the polymerization degree and MCL value (L'Hôpital et al. 2015). The competition of Al between LDH type gels and C-S-H contributed to the relative lower MCL of composite 10 %-CQD/Na.

Table 4. Deconvolution results of ^{29}Si MAS NMR spectra.

Samples	Q ⁿ environments						C-(A)-S-H	
	Q ⁰	Q ¹	Q ² (1Al)	Q ²	Q ³ (1Al)	Q ³	Al/Si	MCL
10 %-CQD/Na	7.49	28.47	16.5	30.05	10.22	6.36	0.10	13
8 %-CQD	11.46	39.53	17.76	19.33	7.35	4.57	0.08	9
8 %-Na	12.76	27.52	18.31	26.72	16.11	0	0.15	15

Conclusion

Using OPC in ultrafine-tailings CPB commonly leads to lower compressive strength. A new slag based binder was prepared in the present work, the following conclusions are drawn as:

1. The CPB sample using CQD/Na as an activator gave a higher compressive strength after long time curing although slower reaction was noticed in the early stages. After curing for 90 d, the strength of sample 10 %-CQD/Na was around 3.78 MPa, which was higher than that of composite using 8 % NaOH as a single alkali activator and OPC-based sample.
2. The binder activated by CQD/Na presented a slower reaction rate compared NaOH activated sample in the early stages, confirming by the lower heat release rate and DoH values. However, the reaction rate of CQD/Na activated slag surpassed that of NaOH based samples after 7 d, reaching approximately 56 % after 90 d.
3. The sample 10%-CQD/Na showed a compact structure after long time curing, which contributes to its higher compressive strength. The hydration gels contain C-(A)-S-H, Ht phases and M-S-H.
4. CQD modified sample presented better environmental friendliness, considering its lower Eco₂ value, thereby, it was expected to be used as an alternative eco-friendly cementitious composite.
5. Although satisfactory strength was noticed for composites 10%-CQD/Na at later curing ages, the lower early compressive strength compared with NaOH-activated composites may limit the utilization in some cases where high early strength is necessary. Therefore, future studies should focus on the strategies for increasing the early strength.

Declarations

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Data availability

There are no repository data.

Authors Contributions

Yong Sun: Data curation, writing original draft. Yingliang Zhao: Supervision. Jingping Qiu, Xiaogang Sun and Shiyu Zhang: Conceptualization, Methodology. Xiaowei Gu: Visualization, Investigation

Ethics approval and consent to participate

Not applicable.

Consent to publish

Not applicable.

Competing interests

The authors declare competing interests.

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Supplemental Data

Figure S1 is not available with this version.

Figures

Figure 1

XRD patterns of QD and CQD (Zhao Yingliang et al. 2020): D-Dolomite, C-Calcite, L-Lime, M-MgO.

Figure 2

Compressive strength results of CPB samples.

(a)

(b)

Figure 3

Isothermal calorimeter results of binder hydration: (a) heat release rate, (b) cumulative heat release.

Figure 4

Degree of hydration for slag (a) and CBW content (b)

Figure 5

The relationship between CPB compressive strength and DoH or CBW.

Figure 6

XRD patterns of binders after curing for: (a) 1d and (b) 90 d.

Figure 7

Thermogravimetric analysis of AAS composites after curing for 1d (a) and 90 d (b).

(a)

(b)

(c)

Figure 8

The pore structure of the CPB samples: porosity evolution (a), pore size distribution at 1 d (b), and 90 d (c).

Figure 9

BSEM micrographs and EDS of the AAS composites at 90 d: (a) 10 %-CQD/Na, (b) 8 %-CQQ, (c) 8 %-Na.

Figure 10

Atomic ratios of Mg/Si vs. Al/Si in different AAS composites,

Figure 11

^{27}Al (a) and ^{29}Si (b) MAS NMR spectra of AAS composites cured for 90 d.