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Preparation of autoclaved aerated concrete using copper tailings and blast furnace slag

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ABSTRACT

Based on the background that large amount of copper tailings are stockpiled in China, the utilization of skarn-type copper tailings to prepare autoclaved aerated concrete (AAC) was studied. The AAC samples were prepared on a laboratory scale with a dry density of 610.2 kg m^{-3} and compressive strength of 4.0 MPa. Compared with the traditional AAC, lime was totally substituted by skarn-type copper tailings and blast furnace slag in order to develop a potential technique of reducing CO_2 emission during the AAC production process. The samples of different curing stage were examined by XRD, FESEM as well as ^{29}Si and ^{27}Al NMR analyses. Results show that the main minerals in the AAC product are tobermorite-11 Å, anhydrite, augite, quartz, calcite and dolomite, with small amount of other minerals brought in by the copper tailings. It was also suggested that most minerals in the copper tailings participated in the hydration reaction during the procuring process, and the chemical elements in them got into the structure of platy tobermorite in the subsequent autoclaving process.

1. Introduction

Copper tailings in China have been nearly totally piled up through the history of copper production. Now more than 2.4 billion tons of copper tailings are estimated to exist in China [1], posing a severe threat to the environmental condition. Skarn-type copper tailing (SCT) is one type of copper tailings to be most difficultly reused in the traditional building materials, due to its nature of very fine grain size and high CaO and MgO content. It has been reported that skarn-type copper tailings can be used to prepare autoclaved brick with good quality [2–4]. But the high transportation costs and low commodity prices restrict the broad commercialization of such brick.

Autoclaved aerated concrete (AAC) is a lightweight and highly porous wall material with excellent insulation ability [5,6]. According to Chinese national standard, AAC is the only one type of wall materials owning the ability to meet 50% of the building energy saving request without adding other affiliated thermal insulation materials [7]. The background that Chinese government is promoting building energy saving and carbon emission reduction gives autoclaved aerated concrete a broad application prospect. The commercial AAC is usually produced with cement and lime as calcareous materials, and with quartz sand or fly ash as the siliceous materials. To extend the range of raw materials and lower the production costs, several researchers have investigated the possibility of replacing the traditional raw materials of AAC by industrial waste, such as air-cooled slag [8], coal bottom ash [9], efflorescence sand and phosphorus slag [10], lead–zinc tailings [11] and iron ore tailings [12]. These studies mainly focused on exploring suitable alternative siliceous materials, and few researches involved the investigation into calcareous materials.

In this study, skarn-type copper tailings and water-quenched blast furnace slag (BFS) were used as mainly raw materials to prepare AAC. Because the high CaO and MgO content in both SCT and BFS, SCT and BFS was used to replace lime as calcareous material. Besides, SiO_2 in the BFS was considered as partly alternative siliceous resource to reduce the consumption of quartz sand. The object of the present work is to investigate the microstructural properties and phase compositions of the AAC prepared by SCT and BFS, and to make primary understanding of reaction mechanism during the process of precuring and autoclaving, especially the behavior of SCT in the hydrothermal reaction.

2. Experiments

2.1. Raw materials

The AAC samples were prepared by the following raw materials: SCT, BFS, quartz sand (QS), cement clinker (CC) and natural gypsum. They were all ground in a SMΦ500 × 500 type ball mill. The results of chemical analyses and specific surface area tests of the raw materials are listed in Table 1. The specific surface area of natural gypsum is 402.6 m^2 kg^{-1}. XRD of the SCT sample shows that the main minerals are augite, dolomite, phologipite, amphibole and calcite, accompanied

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Table 1
Chemical compositions and specific surface area of raw materials.

Oxide composition (wt%)	SCT	BFS	QS	CC
SiO_2	44.52	32.7	82.83	21.98
Fe_2O_3	1.94	0.4	0.53	5.13
CaO	13.56	38.79	1.83	60.38
Al_2O_3	5.36	15.4	7.13	5.54
MgO	19.92	8.97	1.14	3.03
K_2O	1.20	0.36	2.69	2.17
Na_2O	1.00	0.23	1.55	0.25
IOT	9.26	0.76	0.18	–
Specific surface area ($m^2\ kg^{-1}$)	656.8	562.6	792.7	380.6

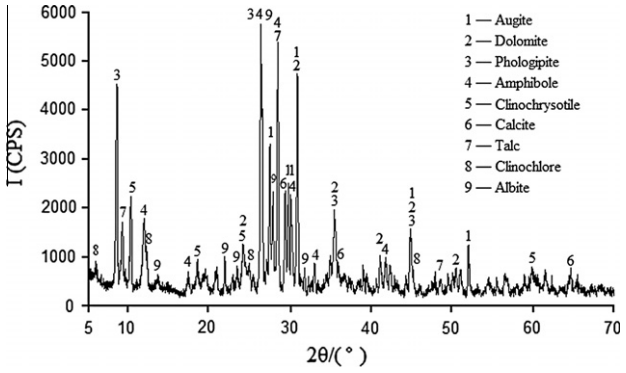

Fig. 1. XRD pattern of skarn-type copper tailings.

by minor phases including clinochrysotile, albite, talc and clinochlore (Fig. 1), in accordance with the chemical analysis result that most of the minerals included are rich in CaO and MgO. The XRD analysis of natural gypsum sample shows that the main mineral in it is $CaSO_4{\cdot}2H_2O$ and no other crystalline phases were identified. Aluminum powder was used as a gas producing agent for the slurry foaming, and naphthalene was used as superplasticizer.

2.2. Procedure

Firstly, the prepared powder of the raw materials and the superplasticizer were thoroughly dry mixed. Then warm water (48 ± 1 °C) was added and mixed for 2 min. Finally, aluminum powder was added and mixed with the slurry for another 30 s. The obtained slurry was casted into preheated steel molds of 100 × 100 × 100 mm to allow it to expand and harden at the temperature of 48 ± 1 °C for 12 h under a steam saturated condition. After their swollen up surface being cut to flat, the samples were demolded and put into an industrial autoclave for hydrothermal reaction for 8 h at 13.5 bars.

2.3. Analysis

The bulk density and compressive strength tests were conducted according to GB 11968-2008, "Autoclaved aerated concrete blocks" which specifies that bulk density should be determined by oven dry of 24 h at 60 ± 5 °C, and then another 24 h at 80 ± 5 °C, following by oven dry at 105 ± 5 °C until samples tested reached constant weight, and compressive strength tests were performed at loading rate of 2.0 ± 0.5 kN/s and on samples with moisture content of 8–12%.

The X-ray diffraction (XRD) spectra of different samples were obtained with a D/Max-RC diffractometer (Japan) with copper Kα radiation at 30 mA and 50 kV. A step size of 0.02° was selected over a 2θ range of 5–70°. The microstructure of the samples under different curing stage was observed with a SUPRA™55field emission scanning electron microscope (FESEM). The fractured surfaces of the samples were coated with carbon prior to examination. MAS NMR tests were conducted in a Bruker Avance III400 spectrometer operating at 59.62 MHz (^{29}Si) and 104.0 MHz (^{27}Al). The rotation frequency was 5 kHz for ^{29}Si and 10 kHz for ^{27}Al, and the delay time was 3 s for ^{29}Si and 1 s for ^{27}Al.

3. Results and discussion

3.1. Mechanical properties

The result of compressive strength test of the AAC sample and its related raw materials proportions are given in Table 2. Superplasticizer dosage was 0.8% of the total solid mixture and aluminum powder dosage was 0.10%. The water/solid ratio was 0.38. At the designed proportions, the compressive strength of AAC samples could get 4.0 MPa and the dry density of AAC was 610.2 kg m^{-3}. Additionally, the compressive strength of sample in the absolute dry condition (DCS) can reach up to 5.9 MPa, and its corresponding specific strength reaches as high as 9.7.

3.2. XRD analyses

XRD analyses were performed to investigate the phase changes in the AAC samples during the process of precuring and autoclaving. The XRD patterns of the dry mixture (DM) of raw materials, hardened aerated concrete (HAC) sample precured under the saturated steam curing for 12 h after being mixed with warm water and the final AAC sample are shown in Fig. 2. As indicated in DM's spectrum, most minerals in SCT are identified, except talc and clinochlore. The non-detection of these two minerals is likely due to the fact that the overall amount of those minerals originally comprising small amount in SCT are in more minor quantities after addition into the dry mixture with only 30% in weight, so that the XRD is not sensitive enough to allow detection at such low level. Quartz, gypsum and alite from the raw materials of quartz sand, natural gypsum and cement clinker, respectively, were detected as expected. A diffused band existing between 22° and 38° of 2θ was caused by the incorporation of BFS with glassy nature.

It can be seen from HAC's spectrum, after being precured around 48 °C for 12 h, the diffraction peaks of alite and gypsum disappeared. The AFt, a new phase, was formed. The broad band at around 17–38° of 2θ indicated the existence of C-S-H gels. The appearance of AFt and C-S-H gels and the disappearing of alite

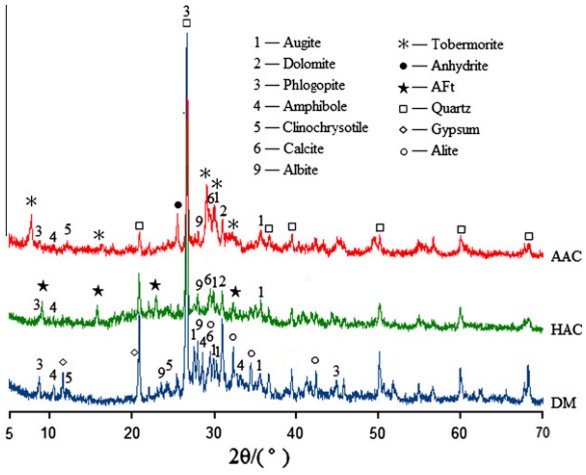

Fig. 2. XRD patterns of DM, HAC and AAC samples.

Table 2
Material proportions and mechanical properties of AAC sample.

Mixture composition of AAC (wt%)					Dry density (kg m^{-3})	Compressive strength (MPa)	DCS (MPa)	Specific strength
SCT	BFS	QS	CC	Gypsum				
30	35	20	10	5	610.2	4.0	5.9	9.7