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Study of cement-based thermal storage materials with fly ash

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ABSTRACT

In this paper, we investigate mechanical and thermal properties of aluminate cementitious thermal energy storage material with fly ash. According to the specific requirement of application of thermal storage materials in solar thermal power generation, we selected 350 °C and 900 °C as the heat treatment temperatures. It can be seen that after heat treatment, the compressive strength and porosity of the cementitious materials are both optimized with the optimal fly ash amount of 15 wt%. Moreover, thermal conductivity and volume heat capacity of the composite pastes incorporated with fly ash are enhanced as well, which is more suitable for the application in solar energy storage. The microstructure, the evaluation of hydration products, and the pore distribution were obtained by SEM, XRD and MIP, respectively.

1. Introduction

Nowadays, human productive activities and the consumption of energy not only have brought a series of environmental problems, but also will result in the growing crisis in energy. Solar energy, as a clean and renewable energy, has broad application prospect. In particular, solar thermal power is becoming more and more popular and reliable, and its cost has been reduced by the progress of technology and the demand of the market. Solar thermal power is a promising way to reduce energy consumption and carbon dioxide emission. Power generation system will not operate properly when solar radiation is intermittent and erratic. In solar thermal generation, thermal energy storage is the most important mode [1]. And a lot of effort has been carried out to optimize thermal energy storage material performances and improve thermal storage efficiency [2–6].

In current solar power plant projects, molten salt has been used most commonly for thermal energy storage. However, it has the disadvantage of high freezing points and high investment costs. Compared with molten salt, aluminate cement is much cheaper. The incorporation of functional materials into cementitious materials can effectively improve the thermal storage efficiency and mechanical behavior at high temperature [7–10]. What's more, cementitious/concrete material is an abundant and cheap resource, exhibiting non-toxicity and non-corrosiveness.

Researches on functional materials such as steel fibers [11], nanomaterials [12,13], and phase change materials [14] in cementitious materials have been carried out extensively since the early 2000s. In the preparation of cementitious materials, there will be a portion of cement cannot be hydrated. Superfine mineral powder material with active properties is much smaller than the average cement particle diameter, which can set off a chemical reaction in cementitious materials. Fly ash react with concrete to form hydration calcium silicate gel, which is hardly soluble in water. It not only reduces the chance of dissolution, but also fills the internal pore of the concrete [15–18]. Consequently, the strength and impermeability of concrete are enhanced effect. The pore structure was compacted by mineral powder reaction product. The strength, durability and performance of cement composite material are significantly enhanced. At the same time, using powder technology can effectively reduce the water–cement ratio of cement paste [19], which is great significance for solar power stations built in remote desert regions.

In this paper, we introduce fly ash, a kind of superfine powder, into aluminate cementitious materials to prepare thermal storage composite materials and study the performances and properties. As yet, few subjects about fly ash introduced into aluminate cementitious materials have been reported on thermal and mechanical performances in assessment of aluminate cementitious thermal energy storage materials.

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2. Experimental

2.1. Materials

The hydration products of aluminate cement will dehydrated at high temperatures, and the dehydration products reacts as follows.

$300\,^{\circ}C \sim 500\,^{\circ}C$ $7C_3AH_6(3CaO{\cdot}Al_2O_3{\cdot}6H_2O) \rightarrow 9CaO + C_{12}A_7(12CaO{\cdot}7Al_2O_3) + 6H_2O$ $AH_3(Al(OH)_3) \rightarrow Al_2O_3 + 3H_2O$

$500\,^{\circ}C \sim 1200\,^{\circ}C$ $Al_2O_3 + CaO \rightarrow CA(CaO{\cdot}Al_2O_3)$ $5Al_2O_3 + C_{12}A_7 \rightarrow$ CA (or $CA_2(CaO{\cdot}2Al_2O_3)$)

$Al_2O_3 + CA \rightarrow CA_2$ (When the volume of Al_2O_3 is ample)

Through the above reactions, we know that the solid cement stone consists of the hydration products of aluminate cement before 500 °C. Between 500 °C and 900 °C, it is comprised of secondary reaction products during hydration products and dehydration products. Solid-phase sintering begin to happen from 1000 °C. And the ceramics bond in refractories is produced above 1200 °C.

In the experiment, aluminate cement was used as cementing agent because of its higher usage temperature than Portland cement. The chemical compositions of aluminate cement are illustrated in Table 1 (R_2O represents equivalent oxidation sodium content and LOI means loss on ignition.).

According to the XRD patterns shown in Fig. 1(a), the main mineral phase of aluminate cement is CA, as well as the minor phase includes $C_{12}A_7$, $2CaO{\cdot}Al_2O_3{\cdot}SiO_2(C_2AS)$ and CA_2. Fig. 1(b) illustrated the main mineral phase of fly ash is mullite $(3Al_2O_3{\cdot}2SiO_2)$ and quartz(SiO_2). Mullite is a high-quality refractory material, which has the features of uniform expansions, good thermal shock stability, high load softening point, and so on. In addition to the above raw materials, 1 wt% polycarboxylic water reducer was being employed for decreasing the dosage of water. Moreover, it contributed to improving the fluidity of the cement pastes. In order to reduce the porosity, we also introduced polyether modified polysiloxane defoamer into the composites. It had shown that this defoamer provides good defoaming effect. And the material preparation method and performance test refer to [20].

2.2. Sample preparation and curing

Water plays an important role in cement hydration process, therefore, controlling the volume of water is particularly important. Each mixture with a water-to-cementitious compound (include cement and fly ash) ratio of 0.2, 0.3% defoamer and 1% water reducer by weight fraction, respectively. The aluminate cement and fly ash were dry mixed for 6 h. The polycarboxylic water reducer and polyether modified polysiloxane defoamer were dissolved in deionized water and stirred for 1 min. And then the water solution was added to the cement and fly ash mixture for hydration reaction. Mixtures were prepared using aluminate cement and numbered as 0FA, 5FA, 15FA, 30FA, 50FA, each separately represent fly ash contents by mass of 0%, 5%, 15%, 30% and 50%. The pastes were shaped in 3 different specification moulds of 20 mm × 20 mm × 20 mm, 80 mm × 48 mm × 20 mm, and 5 mm × 5 mm × 50 mm to test mechanical properties, thermal conductivity and volume heat capacity, and thermal expansion coefficient, respectively. And then covered with a layer of plastic film and wet towels topside to moisturized 24 h. Afterwards the specimens were demoulded and cured in water for 7 days at room temperature. After that in order to eliminate the influence of free water in the sample, the specimens were dried in oven for 24 h at 105 °C prior to testing. The chosen heat treatment temperature is based on the environment that thermal storage material work. And the heating time of the samples of 6 h is consistent in applying the actual thermal storage, which is the minimum time that needs to execute a typical operating cycle. And, the work of longer heating time of the samples will be carried out to prove our matrix paste as a good substrate material can combine with other good thermal properties and volume heat capacity materials, which will be a significant candidate for thermal storage materials in the applications of solar thermal parabolic trough power plant in the future. Therefore, in this paper, the samples were heat treated at 105 °C, 350 °C and 900 °C for 6 h, respectively.

Table 1
The chemical compositions (by mass) of aluminate cement (%).

Materials	CaO	SiO_2	Al_2O_3	Fe_2O_3	R_2O	LOI
Aluminate cement	38.79	7.17	51.68	2.07	0.29	0.30

2.3. Test procedures

The samples were tested at 7 days and after heat treatment to determine the compressive strength, thermal conductivity and volume heat capacity et al. Automatic pressure test machine (Huanglong WHY-200, Huanglong Ltd., China) was used as the compressive strength measurement, which pressed at the rate of $500\,Ns^{-1}$. Thermal conductivity constant tester (TPS2500, Hot Disk Ltd., Sweden) was used for testing thermal conductivity and volume heat capacity. And thermal expansion coefficient apparatus (PCY-II, Xiangtan Xiangyu Instrument Ltd., China) was used to test thermal expansion coefficient. The micro-morphological structure was obtained by Scanning Electron Microscope (SU8010, Hitachi Ltd., Japan). Results obtained from the analysis by XRD (Rigaku D/Max-2500, Rigaku Ltd., Japan) show the phase change before and after heat treatment. Mercury intrusion porosimetry (PM-60-GT, Quantachrome Ltd., America) was served as porosity measurement of hardened pastes with additional of different content of fly ash.

3. Result and discussion

3.1. Mechanical properties

The aluminate cement decomposition products is more stable than Portland cement. Between 100 °C and 400 °C, the AH_3 and C_3AH_6 gradually decomposed into amorphous anhydrous compound and release water vapor. When the temperature ranges from 400 °C to 900 °C, dehydration reaction of hydration products continues, more and more C_3AH_6 dehydrate to form $C_{12}A_7H$. At the same time, AH_3 gradually dehydrate to form anhydrous compounds. At this stage, there is no obvious change in the system of the mineral phase composition. So the compressive strength of aluminate cement will not decline after long term cycling at high temperatures. Compressive strength of hardened cement paste with different contents of fly ash after heat treatment at different temperature is shown in Fig. 2.

When fly ash was not introduced into the aluminate cement, with rising of heat treatment temperature, the strength of the sample decreased significantly. And the content of fly ash is not the more the better. When low fly ash content (5% and 15%), the strength of the samples corresponding to different processing temperature from large to small sequencing is followed by 350 °C, 900 °C, 105 °C. It proves fly ash can improve the high temperature mechanical properties of cement-based materials to a certain