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Research on the Compatibility of Concrete Thermal Storage Material and Nitrate

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To research the influence of molten nitrate erosion on concrete thermal storage material, it firstly selects several main components of thermal storage concrete, makes them mixing with and soaking in molten nitrate in high temperature respectively, and then analyzes the phase transformation, and determines whether the two substances involve in chemical reaction by combining with the thermodynamic calculation results in this paper. The experiment selects the two influencing factors of erosion temperature and time, and it gives analysis from such aspects as mass and apparent morphology of the sample before and after etching. The research results indicate that the concrete does not show greater destruction after suffering three times of erosion by circulation in different temperature. However, after suffering sixty times of erosion by circulation in 450℃, the surface shows obvious crack, few peeling and pits; along with rising of erosion temperature and extension of erosion time, serpentine corrosion and iron ion oxidization in concrete aggravate, concrete aperture enlarges, and porosity increases gradually. It follows that nitrate content in concrete reduces gradually from erosion interface to the outward, and the measured value obtained by quantitative analysis with electronic probe can better coincide with the fitted value obtained by establishing one-dimensional diffusion model.

1. Introduction

Energy is the important material basis for survival and development of the human being, and most of the energy consumed in the global currently comes from such non-renewable mineral fuels as coal (John et al., 2013), petroleum and natural gas. At present, energy shortage and the environmental problem caused by fossil fuel have become the major factors restraining global economic and social development (Skinner et al., 2014), and they shall affect future living state of the human being simultaneously (Strasser and Selvam, 2014). Along with rapid development of economy and acceleration of industrialization and urbanization (Salomoni et al., 2014), energy demand increases continuously, and it is faced with great challenge to build the stable, economic, clean and safe energy supply system (Motte et al., 2015). Solar energy is the best clean energy recognized in the world currently, and it is also a renewable energy simultaneously (Wu et al., 2014), so how to better use solar energy has a great significance to the development of new energy technology. Thermal storage system is an indispensable part of solar thermal power generation system (Martins et al., 2015), and the simple solar thermal power generation system possesses such problems as the mismatching of solar power generation cycle and power demand cycle and the discontinuity and instability of solar radiation energy (Wu et al., 2016). To promote power generation efficiency, reduce power generation cost and enhance stability and continuity of solar thermal power generation system, it needs to add thermal storage device to the power generation system (Htun et al., 2014), so that system can still satisfy power generation demand at the time of having no solar radiation energy (Pielichowska and Pielichowski, 2014). Currently, the conventional thermal storage system is mainly composed of the two parts of thermal storage module with thermal storage material and heat transfer medium (Tatsidjodoung et al., 2013).

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2. Experiment of the Influence of Molten Nitrate Erosion on Concrete Thermal Storage material

2.1 Experimental Design

To research on the compatibility of molten salt and thermal storage concrete, a formula with better overall performance is selected and used in preparing the specific concrete container, with dimensions: inner diameter×outer diameter×height×depth=50cm×100cm×100cm×70cm. After concrete moulding, it shall be maintained in room temperature for three days before de-moulding.
Experiment of the influence of erosion temperature on thermal storage concrete: select six groups of concrete container samples, give thermal insulation in 110°C oven for 24h, measure the quality, add in the prepared nitrate, take out after giving cyclic erosion in temperatures 250°C, 350°C, 450°C, 550°C and 650°C respectively, pour out the residual molten salt in container, and then measure mass change of concrete and mass loss of nitrate.
Experiment of the influence of erosion time on thermal storage concrete: select three better moulded concrete container samples, give thermal insulation in 110°C oven for 24h, measure the quality, add in the prepared nitrate, and then put them into 450°C muffle furnace for cyclic etching, take them out after erosion for 3, 7, 15, 30 and 60 times respectively, and then measure concrete mass and nitrate quality. During the etching, nitrate shall be added continuously according to the residual nitrate in concrete. The concrete mass growth rate and the relative mass loss rate of nitrate can be calculated by adopting the formula below:

$$\omega_t = \frac{m_a \quad m_b}{m_1} \times 100\% \tag{1}$$

Where, m_t refers to the relative mass loss rate of the nitrate after etching; m_a refers to mass of the nitrate added, with unit g; m_b refers to the residual nitrate mass after erosion, with unit g; m_1 refers to concrete sample quality, with unit g.
Select samples not suffering erosion and suffering cyclic erosion for three times in 350°C and for sixty times in 450°C respectively, make them crushing, and measure the porosity with mercury injection apparatus. Select samples not suffering erosion and suffering cyclic erosion for sixty times, take the cross sections, and observe sectional morphologies of the samples with scanning electron microscope; detect Na+ and K+ ion distribution on section of the samples after erosion with electronic probe and X-ray microscopic analysis technology (EPMA), and discuss the diffusion behaviour of nitrate in samples. Collect the residual molten salt on the bottom of concrete container, analyze the phase change in sample by using X-ray diffractometer, and detect the physical phase in molten salt after erosion with differential scanning calorimeter and by combining with thermogravimetric analysis.

2.2 Raw Materials of the Experiment

Main raw materials used in the experiment are as follow: CA-80 aluminate cement, produced by Zunyi Yaxi Shenghua Cement Co., Ltd, with concrete performance indexes as shown in table 1; slag powder, passing 200-mesh sieve, produced by one company in Guangxi, with concrete indexes as shown in table 2; silica powder, passing 200-mesh sieve, provided by one company in Shaanxi; water reducing agent, produced in laboratory; absolute ethyl alcohol, analytical pure grade, provided by Sinopharm Chemical Reagent Co., Ltd.

Table 1: Physical property indexes of cement

Al_2O_3	SiO_2	Fe_2O_3	Specific area (m^2/kg)	Initial setting time (mins)	Final setting time (h)
78-80	0.1-0.4	0.1-0.4	>500	60-240	2-10

Table 2: Physical property indexes of slag powder

Density($g \cdot cm^{-3}$)	Specific area (m^2/kg)	Moisture content/%	Ignition loss/%	28d activity index
3.0	≥400	≤0.5	≤0.1	≥98

2.3 Experimental Equipments

The main equipments used in experiment are as follows: mercury injection apparatus, provided by Micromeritics Instruments Co., Ltd, with model Autopore9500; electronic probe; precision electronic balance; box-type energy-saving resistance furnace; fan blown type electric drying oven; X-ray diffraction analyzer.

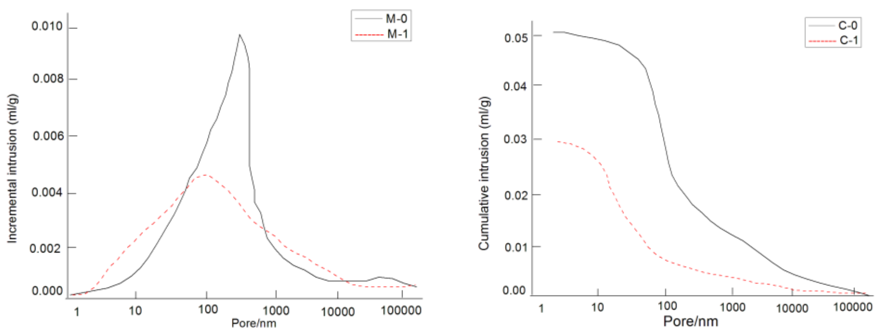
2.4 Characterization and Test Method

X-ray diffraction analysis: to determine phase composition of the residual nitrate in concrete container after molten nitrate etching, X-ray diffraction analyzer is used in giving chemical component analysis to the sample. Target material: Cu target; pipe pressure: 40KV.
Electronic probe microscopic analysis: to determine penetrating depth of the molten nitrate during etching, the experiment selects the concrete sample suffering sixty times of cyclic etching, takes the cross section, and gives microarea quantitative analysis to cross section of the sample with the backscattered electron image of electronic probe and by coordinating with the energy disperse spectroscopy.
Concrete MIP analysis: to determine influence of the molten nitrate erosion on the porosity of thermal storage concrete, the experiment adopts mercury injection apparatus in measuring the overall porosity of concrete sample before and after erosion and the distribution of pores with different sizes. Size of the concrete sample for measurement is 3-7mm.
TG-DSC analysis: to determine stability of the nitrate after suffering cyclic etching, the experiment measures thermal stability of the sample with differential scanning calorimeter and by combining with thermogravimetric analysis, calibrates the instrument with standard substance before use, and reduces instrument error to the level within ±2.0%. The measurement is conducted in air, temperature range is room temperature -500°C, temperature rising rate is 10°C /min, and sampling volume of the experiment is about 10mg.

3. Research on the Influence of Nitrate on Concrete Thermal Storage Material

3.1 Analysis on the Porosity Change of Concrete Sample

Pore size and porosity of concrete are the key factors affecting concrete strength and permeability. To determine change of the pore structure of sample before and after etching, the experiment adopts mercury intrusion method (MIP) in detecting porosity of the sample as follows: take concrete samples not suffering erosion and suffering three times of cyclic erosion in 650°C, break them to the specific size, put them in absolute ethyl alcohol, soak them for 72h, and then take them out, dry them in 110°C oven for 48h, and conduct MIP test after cooling of the samples. The measured results are as shown in figures 1(a) and (b): figure 1(a) shows pore size distribution, and figure 1(b) shows accumulated pore size distribution; M-0 and C-0 are curves of the sample not suffering etching, and M-1 and C-1 are curves of the sample after suffering etching.



(a) (b)

Figure 1: The pore size distribution of concrete samples

3.2 Influence of the Nitrate Erosion Temperature on Concrete Thermal Storage Material

To research on influence of the different temperature on molten salt permeation volume during the time when thermal storage concrete suffers cyclic erosion of the molten nitrate, the experiment determines mass change of the five groups of samples before and after etching, and the results are as shown in figure 2. It can be seen from the figure that: concrete mass shall increase by 9.99% after three times of cyclic erosion in 250°C, it shall increase gradually along with rising of erosion temperature, and it shall increase by 10.92% after three times of cyclic erosion in 650°C. Although the temperature rising makes for increment of concrete quality, the influence is not obvious, and concrete mass growth rate shall merely be promoted by 0.93% after promoting erosion temperature to 400°C. As there are more pores in concrete, and melting temperature of the mixed nitrate is about 220°C, the liquid molten salt shall permeate in the concrete gradually along with these pores when the temperature exceeds 250°C. Along with rising of temperature, the diffusion velocity in concrete shall increase, permeation volume of nitrate shall increase, and then concrete mass shall become large.

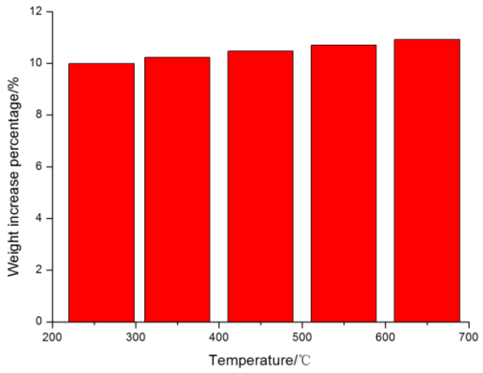


Figure 2: The weight change of concrete with erosion temperature

As molten salt can permeate in concrete during erosion, the molten nitrate serving as heat transfer medium shall reduce gradually, thus it needs to add nitrate for supplement during the experiment to ensure the smooth heat transfer. In different erosion temperature, the loss volume of molten nitrate is also different, so it needs to explore change law of the nitrate loss volume along with erosion temperature. In the experiment, it determines loss rates of five groups of nitrate, and the results are as shown in figure 3. It can be seen from the figure that: temperature has greater influence on the nitrate loss rate, and relative mass loss rate of the molten nitrate serving as heat transfer medium increases continuously along with rising of the cyclic erosion temperature, while the increasing range reduces gradually.

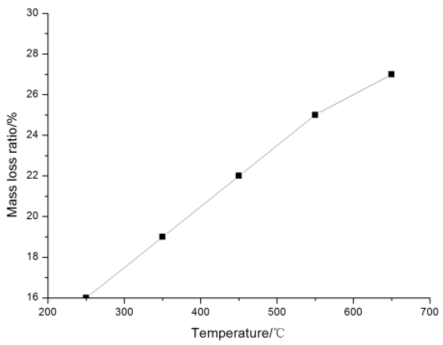


Figure 3: The mass loss ratio of nitrate with different temperature

3.3 Influence of the Nitrate Erosion Time on Concrete Thermal Storage Material

To research on influence of the different cyclic erosion times on permeation volume of molten salt during erosion of the thermal storage concrete by molten nitrate, the experiment determines mass change of the concrete sample after suffering five, ten, fifteen, thirty and sixty times of cyclic erosion by nitrate, and the results are as shown in figure 4. It can be seen from the figure that: concrete mass increases by 10.41% after three times of cyclic erosion in 450°C, and concrete mass increases gradually along with increment of the times of cyclic erosion, while the growth rate reduces gradually; after sixty times of cyclic erosion, concrete mass increases by 12.13%. Along with increment of the times of cyclic erosion, permeation volume of molten salt increases, and permeation depth increases, while permeation speed reduces, and concrete mass growth rate shows smaller change.

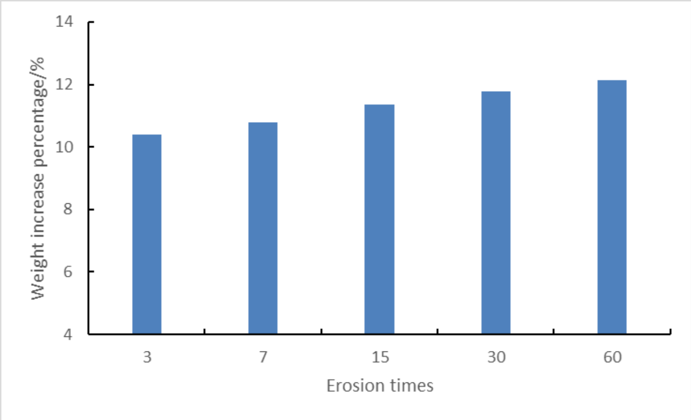


Figure 4: The weight change of concrete with erosion times

Figure 5 shows change curve of the nitrate mass loss in thermal storage concrete container along with the times of cyclic erosion. It can be seen from the figure that: different cyclic erosion times have greater influence on nitrate loss rate, and molten nitrate mass loss rate increases continuously along with increment of circulation times, while increasing range of the loss rate reduces gradually.

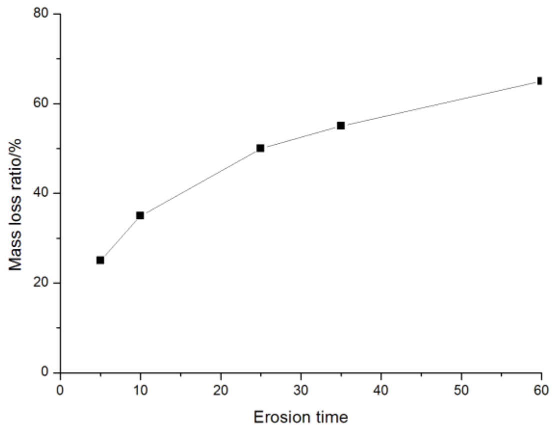


Figure 5: The mass loss ratio of nitrate with erosion times

4. Conclusions

In this paper, it mainly gives research on the compatibility of thermal storage concrete and molten nitrate, by analyzing the main components of concrete and the phase composition change of molten nitrate after soaking in high temperature and by combining with thermodynamic calculation. It selects the two aggregates of basalt and copper slag, and analyzes erosion of molten nitrate to the two aggregates by using several micro measurement means after cyclic erosion of molten nitrate. Finally, it gives research on influence of the molten nitrate erosion on concrete thermal storage material from the two aspects of erosion temperature and erosion time, and analyzes physical property change of the material before and after erosion. The experiment indicates that there is crack, peeling and falling shown on concrete surface during molten nitrate erosion process. As the compatibility of thermal storage material and molten nitrate is worse, it cannot satisfy the practical application requirements. To build the thermal storage system with concrete-molten salt compound thermal storage and molten salt transferring heat, it needs to improve the porosity and anti-permeability.

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