ISSN : 0974 - 7435

Volume 10 Issue 24

2014

BioTechnology

An Indian Journal

FULL PAPER

BTAIJ, 10(24), 2014 [15572-15582]

Effect of rare earth Ce^{4+} content on the properties and form mechanism of foamed concrete

Zhang Jing[1,2], Liu Xiangdong[1]

[1] School of Materials Science and Engineering, Inner Mongolia University of Technology, Hohhot, Inner Mongolia 010051, (CHINA)

[2] Inner Mongolia Technical Collage of Construction, Hohhot, Inner Mongolia 010070, (CHINA)

ABSTRACT

Foamed concrete is prepared with sulphate aluminum cement, fly ash, H_2O_2, $FeCl_3$, calcium stearate and $Ce(SO_4)_2.4H_2O$ in this paper. In the component of foamed concrete, ash is used replacing cement partially (up to 20% by weight), H_2O_2 and $FeCl_3$ as a foaming agent, as a foam stabilizer and $Ce(SO_4)_2.4H_2O$ as additives. The impact of the content of fly ash, H_2O_2 and $Ce(SO_4)_2.4H_2O$ on the properties of density and compressive strength of foamed concrete was investigated respectively, as well as the additive of rare earth Ce^{4+} in the formation of foamed concrete was analyzed. Results of the study show that foamed concrete with the properties of density of 215-320kg/m^3 and compressive strength of 0.2-0.65Mpa can be prepared. Ce^{4+} can be used as foam stabilizer, make shorting the foaming time, improving the foaming ability, and reducing the dry density of the foamed concrete apparently.

KEYWORDS

Foamed concrete; Ce^{4+}; Fly ash; H_2O_2; $FeCl_3$.

INTRODUCTION

Foamed concrete is a kind of cellular concrete, which is composed of cementations mortar surrounding disconnected random air bubbles, with the air typically occupying more than 50% of the volume[1,8,9]. In recent years, reducing the weight of wall vastly becomes the focus of research as the development of high-rise buildings. As a result, light-weight concrete gradually becomes more important to meet the requirements of energy efficiency and environmentally friendly. Foamed concrete is a kind of light-weight concrete, has been widely used in many fields such as construction industry in virtue of its good properties: low density, high thermal insulation values, environmental protect compared to normal-weight concrete. So that it is one of the most attractive materials used in the basic constructions of countries that can't be substituted in the development of construction industry. However, it is also be severely restricted in other practical application fields due to some fatal deficiencies, for example, it performs low strength property when it has low density. Especially in the product of low density of 100 to 300 kg/m3 has the lowest strength that can't lend itself to expanded applications in the worldwide. Therefore it is urgent to enhancing its property of strength.

Chemical composition and microstructure of foamed concrete decides the density and strength of it. It is critical that obtain small, uniform and non-connected pore in foamed concrete is important to obtain it with the perfect property of low-density and high compressive strength. Literature[2] indicates that adhesion of asphalt and aggregate has been enhanced greatly through adding rare earth elements into asphalt concrete pavement so that the performance of asphalt pavement has been improved. Adding rare earth compounds changes the chemical composition and microstructure properties, subsequently improves density and strength of foamed concrete. The formation mechanism is investigated.

Foamed concrete can be processed with both chemical and mechanical foaming methods[3,10]. Mechanical foaming method is through mixing pre- prepared foam blowing agent and water with water slurry. However, foaming agent costs a lot as the source of prepared foam. While chemical foaming method is through natural chemical reaction of chemical materials with cement, fly ash and other substances. This method costs little and easy to be handled. However, it has not yet been widely investigated due to its complex process of foaming formation, hard controlling of foaming process, even disappointing foaming effect.

In this experiment, substances of FeCl3 and H2O2 is used as blowing agents, calcium stearate as a foam stabilizer to obtain foamed concrete through the method of chemistry in order to reduces cost of production of foamed concrete greatly compared to mechanical foaming method. With Ce(SO4)2.4H2O additive for its changes the performance, in this preliminary studied Ce4+ contribution to the formation process of the foamed concrete.

EXPERIMENT MATERIAL AND METHOD

Experiment material

42.5 Class rapid hardening sulphoaluminate cement, fly ash (grade two of dry ash), polynaphthalene sulphonate, $FeCl_3$, H_2O_2 (27.5% by concentration), calcium stearate, polypropylene fibers, water, $Ce(SO_4)_2.4H_2O$.

Test material preparation

1. Ce $(SO_4)^2.4H_2O$ and polynaphthalene sulphonate were dissolved and stirred in water.

2. Water temperature was controlled at 35 ℃.

3. First, cement, fly ash, calcium stearate and polypropylene fibers were mixed completely for 3-5mins with a high-speed mixer made by laboratory. Second, solutions of Ce $(SO_4)_2.4H_2O$ and polynaphthalene sulphonate obtained through step one were added into it and stirred for 2mins. Last, $FeCl_3$ and H_2O_2 were added also successively, stirred 30s and poured into mold.

4. Mold was disassembled after 24 hours.

5. Standard specimens were made as 100mm × 100mm × 100mm, then placed into standard curing room for 28 days.

Test method

1. Dry density test was performed according to GB / T 11970-1997<<Test methods of properties of density, moisture content and moisture absorption of foamed concrete>>

2. Compressive strength test was performed according to GB / T 11971-1997 <<T Test methods of mechanical properties of foamed concrete>>

3. Thermal conductivity test was preformed according to GB/T 10294-2008<<Thermal insulation-Determination of stesdy-state thermal resistance and related properties-Guarded hot plate apparatus>>.

4. The phase compositions of fly ash were analyzed by X-ray diffraction (XRD) APD-10 (CuK_{α}-radiation) at U=40kV, I=80MPa, and the scanning rate of 0.02deg/min.

5. The microstructures of foamed concrete were observed using scanning electron QUANTA-400 microscope (SEM).

RESULTS AND CONCLUSION

The combination of foamed concrete, polynaphthalene sulphonate, $FeCl_3$, calcium stearate, polypropylene fibre and water-cement ratio (w/c) to keep constant, use fly ash to replace partially 42.5 Rapid hardening sulphoaluminate cement to obtain group CI pieces. Groups C2 and C3 are obtained through changing the content of H_2O_2 and $Ce(SO_4)_2.4H_2O$ on the bases of group C1 pieces, as shown in TABLE 1 below.

TABLE 1: Variation of content in foamed concrete (mass%)

Serial of test piece	Component	Concent				
C1	Fly ash	0	5%	10%	15%	20%
C2	H_2O_2	4.5%	4.6%	4.7%	4.8%	4.9%
C3	$Ce(SO_4)_2.4H_2O$	0.1%	0.2%	0.3%	0.4%	0.5%

The impact of fly ash on the density and strength of the foamed concrete

Rapid hardening sulphoaluminate cement and fly ash are the key component to the foamed concrete, cement is formed by materials as CaO, SiO_2, Al_2O_3, Fe_2O_3, C_3S, C_2S and C_3A. The fly ash used in this test is the second level, the Figure 1 shows the phase composition of fly ash and its chemical composition presented in TABLE 2.

TABLE 2: Fly Ash Chemical Composition（mass%）

Al_2O_3	SiO_2	CaO	Fe_2O_3	Na_2O+K_2O	TiO_2	others
45.4%	47.2%	1.9%	2.8%	0.46%	1.4%	0.84%

As can see in TABLE 1 and Figure 1, the main component of fly ash as an active oxide is Al_2O_3 and SiO_2, phase composition are mainly Al, Si and O. The nature of the fly ash is not only depending on its chemical composition, but physical and structural characteristics are closely related. As can see in Figure 2, fly ash contains a large number of spherical or hemispherical aluminum silicate crystal, sphere's diameter is mostly between 10-100μm. The mullite and quartz (Silicate mineral and crystals) contained in the fly ash, after meets water, in the surface of fly ash form a hydrated oxide, showed a greater adsorption capacity, as the interaction of the dispersed particles in the water in the cement, after hardened will be more strength. Cement and fly ash under the action of water will get gelling reaction; the detail process is as below.

$$2\mathrm{Ca(OH)_2} + \mathrm{SiO_2} + 2\mathrm{H_2O} \rightarrow 2\mathrm{CaO} \cdot \mathrm{SiO_2} \cdot \mathrm{H_2} \quad \textbf{(1)}$$

$$3\mathrm{Ca(OH)_2} + \mathrm{AiO_2} + 6\mathrm{H_2O} \rightarrow 3\mathrm{CaO} \cdot \mathrm{Al_2O_3} \cdot 6\mathrm{H_2} \quad \textbf{(2)}$$

$$3\mathrm{CaO} \cdot \mathrm{Al_2O_3} \cdot 6\mathrm{H_2O} + 3\mathrm{CaSO_4} + 26\mathrm{H_2O} \rightarrow 3\mathrm{CaO} \cdot \mathrm{Al_2O_3} \cdot 3\mathrm{CaSO_4} \cdot 32\mathrm{H_2} \quad \textbf{(3)}$$

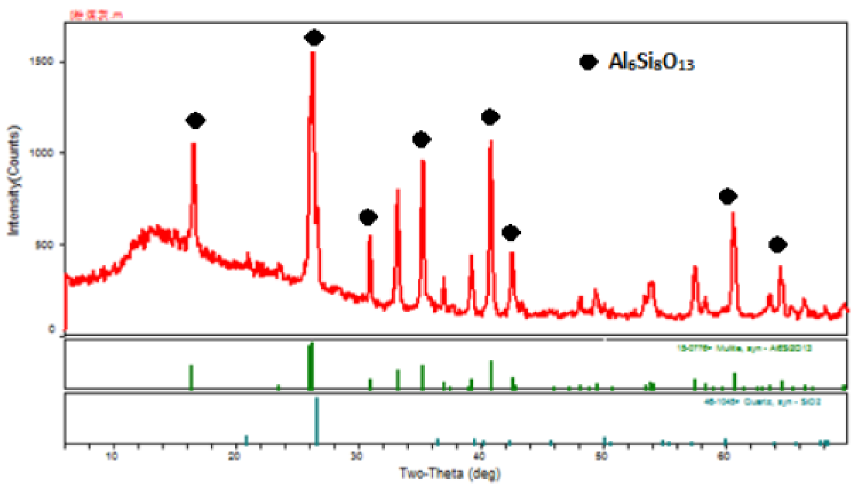

Figure 1: X-ray diffraction spectrum of Fly Ash

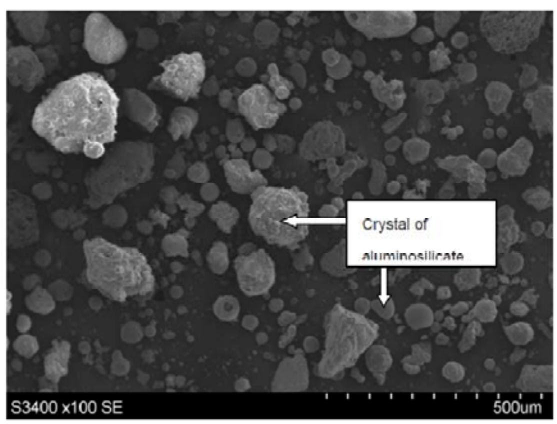

Figure 2: SEM Surface Morphology of Fly Ash

On the one hand, hydrated calcium silicate and hydrated calcium sulphoaluminate will be continually produced in the process of hydration, and then the slurry will continuously thickening. On the other hand, property of porous of fly ash make itself has an ability of absorption, hydrated oxide is formed in surface after meets the water, and the adsorption capacity improved rapidly. The water minerals will sculpt to have shape, and the cement paste will continuously change from flow substance to plasticity's, and then from plasticity's to elasticity's.

As we can see from Figure 3 and 4, when there isn't fly ash and only has cement, the foamed concrete density reaches the minimum level, can reach 215kg/m^3, and its strength is only 0.2MPa. With the proportion of fly ash increasing to 15%, density will be 240kg/m^3, strength become 0.4MPa. When is beyond 15%, its density will decrease, and its strength will not change. The test proved that when fly ash proportion is more than 20%, the capability to foam will decrease, partial will have collapse phenomenon.

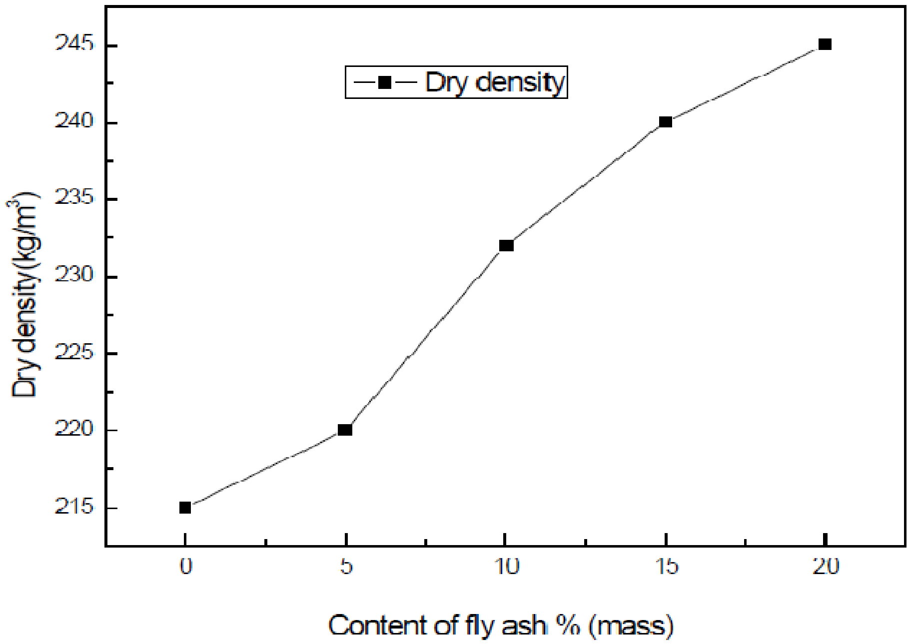

Figure: 3 Effect of content of fly ash on dry density of foamed concrete

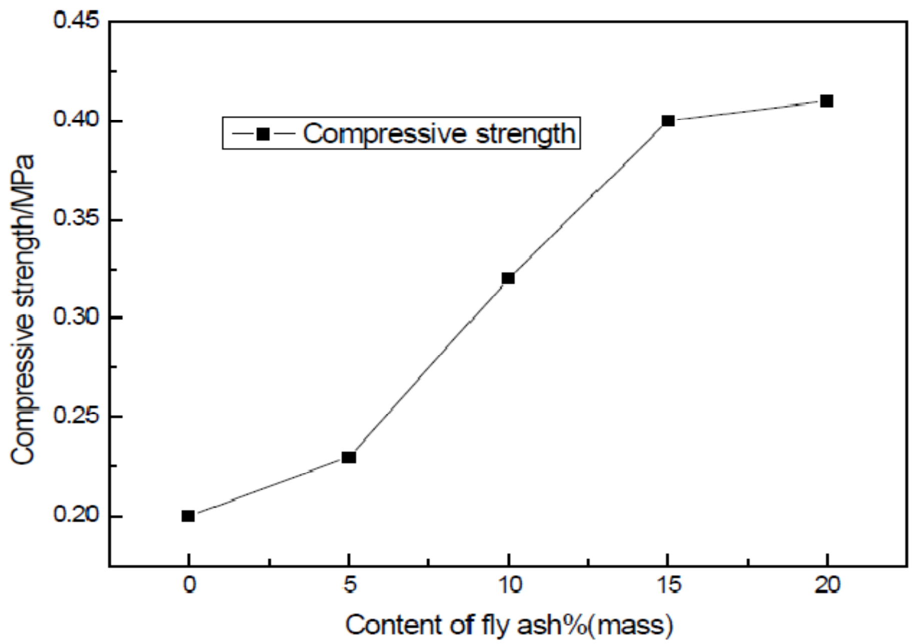

Figure 4: Effect of content of fly ash on compressive strength of foamed concrete

The impact of H_2O_2 on the density and strength of the foamed concrete

H2O2, known as hydrogen peroxide, it has the performance of better oxidizing property. O2 can be occurred because of the stabilized chemical reaction on H2O2 and diluted grout. The formula about detailed reaction is as below. The speed of foaming can be controlled under the use of FeCl3 and calcium stearate. C2 group is obtained through changing the content of H2O2 on the base of C1 group of the nature of foamed concrete on density of 240 kg/m3 and strength of 0.4MPa. Figure 5 and 6 demonstrate the impact of on the density and strength of the foamed concrete respectively. As can see from Figure 5 and 6, the density and compressive strength of foamed concrete are both decreased gradually with content of H2O2 increasing constantly. A kind of foamed concrete about density of 235kg/m3 and compressive strength of 0.35MPa can be prepared when the content of H2O2 is 4.9%.

When the content of H2O2 is continue increasing, the time of foaming is so short with the content of H2O2 increasing rapidly that generating collapse phenomenon. This is because of foamed concrete hasn't time to turn to pre-settled state, forming bubbles fall gradually under the action of its own weight. As proved in the test, time of forming shorter, collapse easier. The reason is due to foaming rate and slurry condensation rate are different[4]. Therefore, to control the foaming rate and condense time whether can reach the dynamic balance is the key to obtain the excellent foamed concrete.

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (4)$$

$$Ca(OH)_2 + H_2O_2 \rightarrow CaO_2 + 2H_2 \quad (5)$$

$$2CaO_2 + 2H_2O \rightarrow 2Ca(OH)_2 + O_2 \uparrow \quad (6)$$

$$2H_2O_2 \xrightarrow{Fe^{3+}} 2H_2O + O_2 \uparrow \quad (7)$$

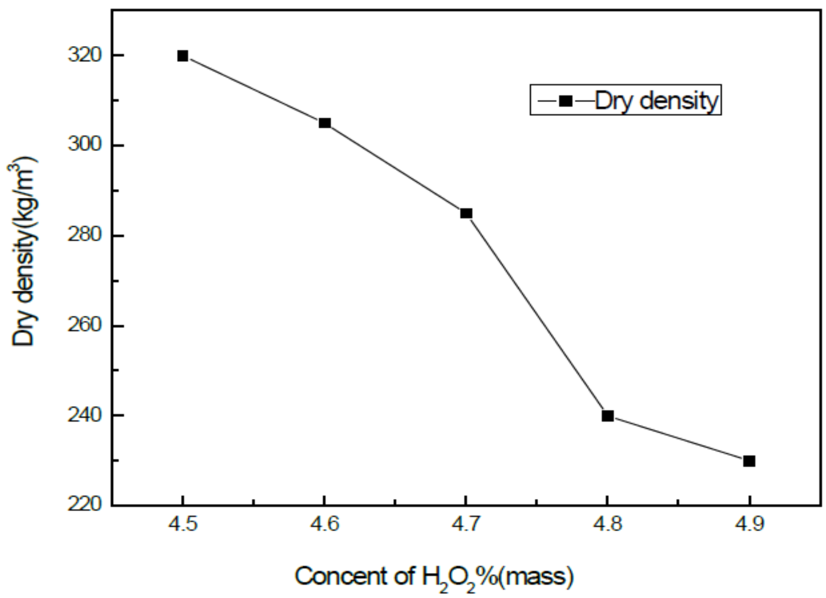

Figure 5: Effect of content of H_2O_2 on dry density of foamed concrete

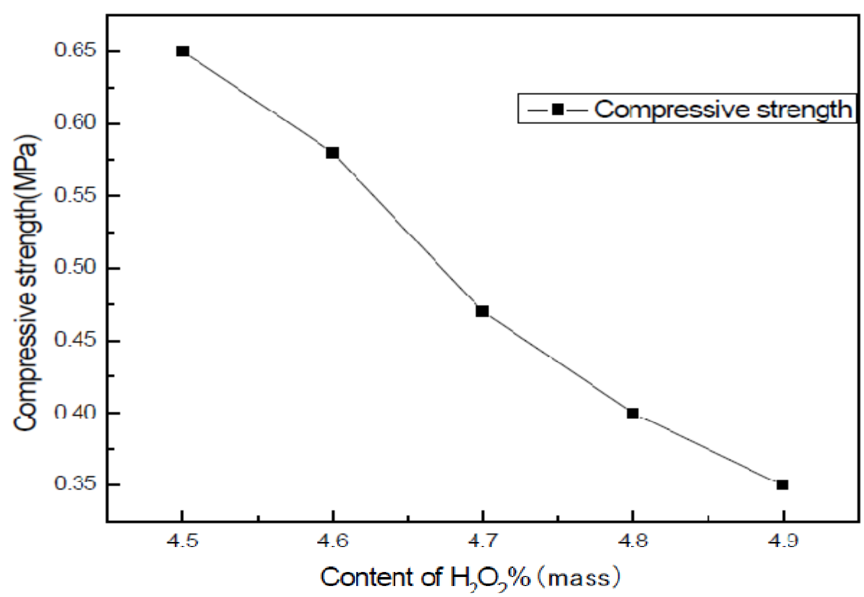

Figure 6: Effect of content of H_2O_2 on compressive strength of foamed concrete

Impact of Rare Earth Ce^{4+} on the Foam Process and Foam Stability

Chemical property of Rare Earth element is very active. $Ce(SO_4)_2.4H_2O$ is a kind of Rare Earth Oxide (REO), it can be dissolved easily in water, radius of Ce^{4+} is very small, only 0.172μm[5], apparently the specific surface area of it is bigger. Meanwhile, 47% of Rare Earth oxide contains RE-C key and 85% of it contains RE-O key in the compound. This reflects that Rare Earth ion is easily bond with oxygen to get RE-O key. Cement-fly ash slurry contains a big quantity of OH ion, O key separated can from it can bond with RE element's compound, and it is possible to turn the component of combined slurry. In the solution, Ce^{4+} is provided with a high oxidability $\varphi°(Ce^{4+}/Ce^{3+})=1.7$ V[6]. Moreover, Ce^{4+} directly returns to original phase by changing to Ce^{3+} in the process of oxidation-reduction reaction, it will not form intermediate products, the reaction rate turns to be faster. Therefore, it is have important influence on the property of foamed concrete through adding micro a little $Ce(SO_4)_2.4H_2O$.

The foamed concrete formation is actually that air continuously resisting the tension of solution surface and viscous forces, then the air volume continuously increase. When the solution system surface's tension is lower, solution can easily be homogeneous; foam distribution is also well distributed. According to Gibbs, theory about balance surface tension[7], every foam is an independent unity, as can be seen in Figure 10, foamed concrete has sealed pores respectively. Apparent tension of foam will continuously increase and make the solution around forming a gradient tension, solution moves to rare parts, the foam membrane elasticity can avoid it to break, obviously, when increase membrane elasticity is more helpful to the foaming process. The stability of the foam is one of the key issue to determinate obtain the small and well distributed foam. Adding Ce^{4+} changed the foam surface adsorption, and molecule's structure and their interaction.

C3 pieces are obtained on the basis of C2 through adding $Ce(SO_4)_2.4H_2O$ from 0.1% to 0.5%, of which the density is 240kg/m^3, strength is 0.4MPa. As shown in Figure 7 and 8, time of foaming become shorter, density decreasing and the foaming capability increasing also as the content of Ce^{4+} increasing. The addition of Ce^{4+} produces the effect to stabilize the foaming. As shown in Figure 8 and 9, when Ce^{4+} added from 0.1% to 0.5%, the density of foamed concrete decreases, but the compressive strength doesn't changed almost. The foamed concrete of that the density is 210kg/m^3 and its compressive strength is 0.35MPa can be prepared when the content of Ce^{4+} is 0.5%.

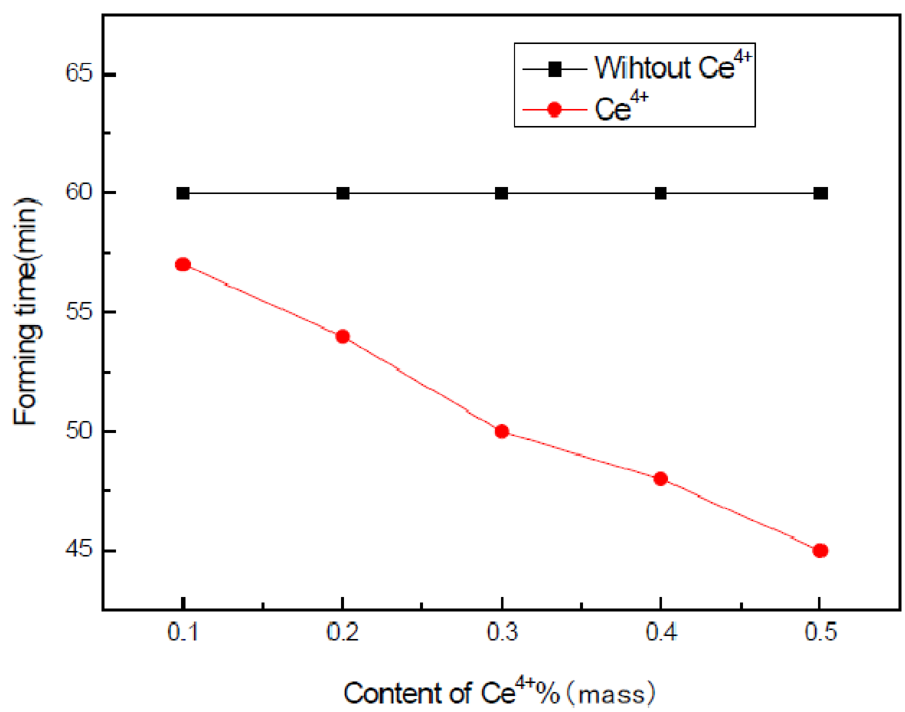

Figure 7: Impact of Ce^{4+} on the foaming time

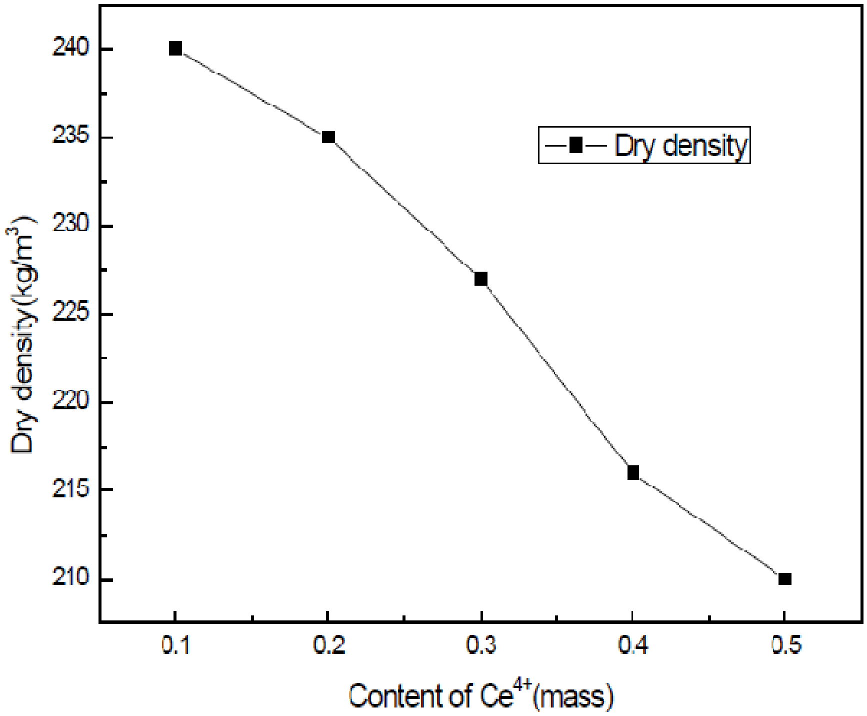

Figure 8: Impact of Ce^{4+} on dry density

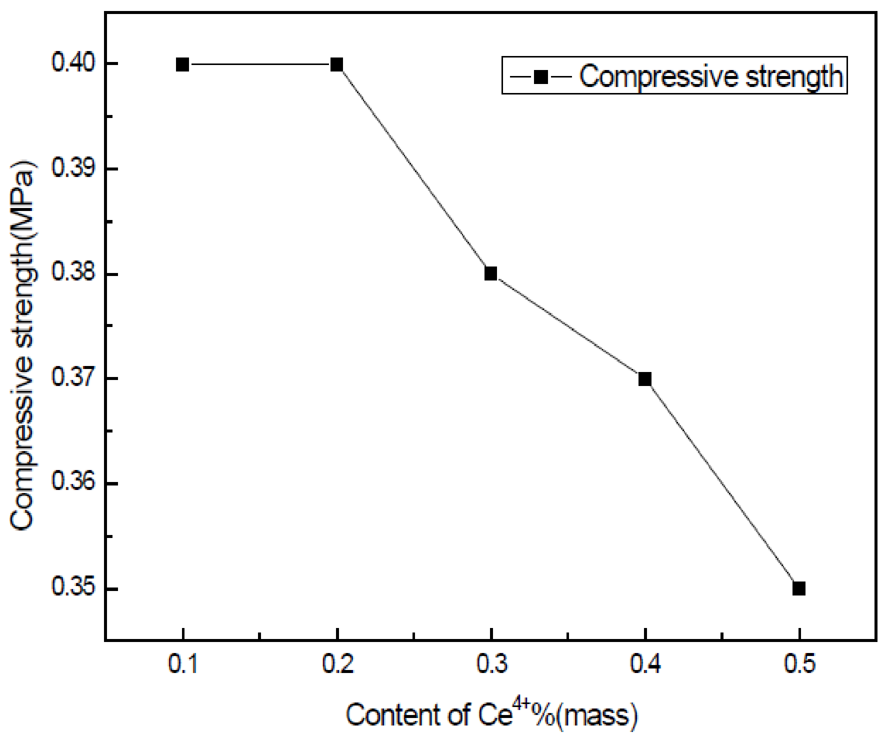

Figure 9: Impact of Ce^{4+} on compressive Strength

TABLE 3: Thermal conductivity of foamed concrete [W/(m.K)]

Rare earth	0	0.1%	0.2%	0.3%	0.4%	0.5%
thermal conductivity	0.067	0.058	0.049	0.052	0.047	0.045

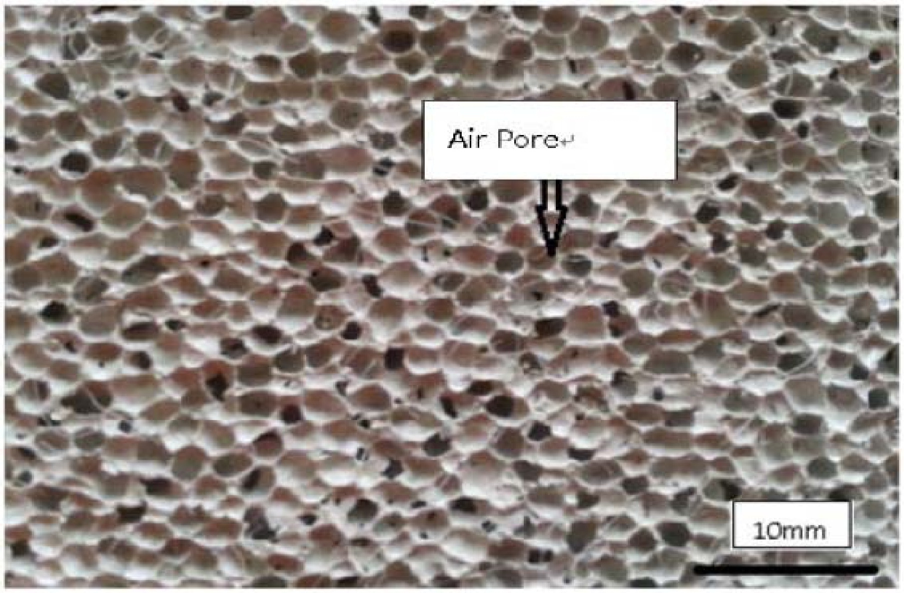

Figure 10: Section picture of foamed concrete through adding Ce^{4+}

Impact of Rare Earth Ce^{4+} on the micro-morphology of foamed concrete

Figure 11 and 12 show that, basically, the air hole of foamed concrete is an independent unit and the diameter of the hole is below 2mm. From Figure 11, we can see that it is easy to form a large connected channel between two holes of foamed concrete without Rare earth ions, and the longest length arrives about 4mm. In addition, we can observe small air holes in the bottom of many independent air holes, and therefore, it forms a connected channel between air holes on the surface and those out of surface. Figure 12 shows that these air holes are independent on average, but some of them have air channel at the bottom, the diameter of which is 0.2mm. Compared with Figure 11, the amount and the diameter of channel used to connect with air holes decrease. TABLE 3 shows that the coefficient of heat preservation of foamed concrete evidently reduces after adding rare earth. Rare earth is added into foam as additive, which makes the coefficient of thermal conductivity reduce. However, the coefficient of thermal conductivity of foamed concrete reduces because of obvious decrease of connected pores.

Figure 13(a) can be seen that, the thickness of the wall between air hole is about 250μm if there are without rare earth ions in the foamed concrete. After adding the rare earth, it is 100μm or so[Figure 14(a)]. With a greater density, rare earth compounds are added into cement paste as an additive, which makes the thickness of the wall between air holes become thinning, makes the air hole become sleek and complete, and the connecting channel is decreased obviously, thus reduces the density of foamed concrete.

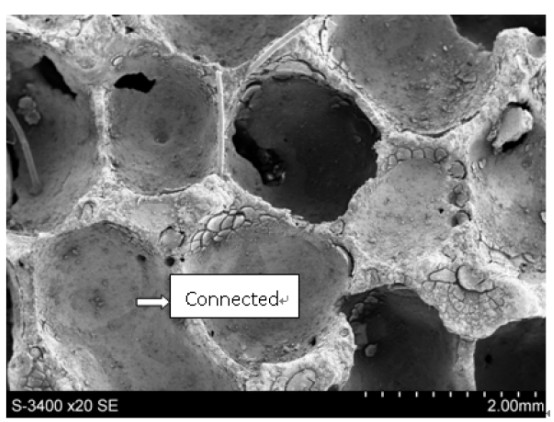

Figure 11: SEM of foamed concrete without Ce^{4+}

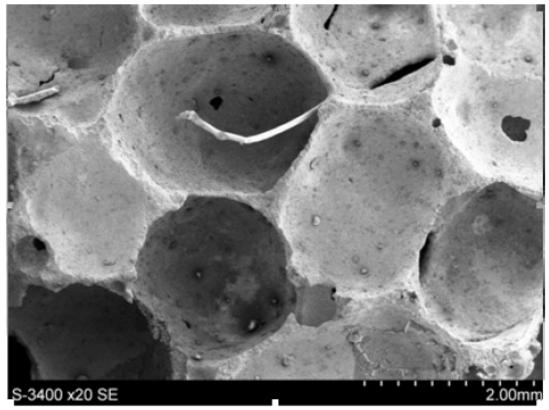

Figure 12: SEM of foamed concrete with Ce^{4+}

Compared Figure 13 (a) with 14 (b), we can see that the Figure 13 (a) need to be magnified 100 times, at the same time, the Figure 14 (b) need to be magnified 200 to clearly see the wall between air holes. Figure 13 (a) shows that the structure of pore wall is loose, appearing "crack" shape; Figure 13 (b) shows particles, the length of which is 50-200 microns, are attached to the substrate unevenly, and it is not dense with the substrate. In Figure 14 (a) and (b), we can easily see that, the wall of hole is smooth with well structure. It is made up with a multitude of $CaO{\cdot}SiO_2{\cdot}H_2O$、$CaO{\cdot}Al_2O_3{\cdot}6H_2O$ and other material with uniform distribution and dense structure. Foamed concrete with no Ce^{4+} is composed with a large number of striped and clubbed stringiest and a small number of clusters C-S-H gel compositions [Figure 13(b)]. Under the excitation of Ce^{4+} in foamed concrete, branches of C-H-S gel knot each other, and grow up in a knot point each other, thus forming a continuous three-dimensional space net, chain and reticular structure [Figure 14(b)].

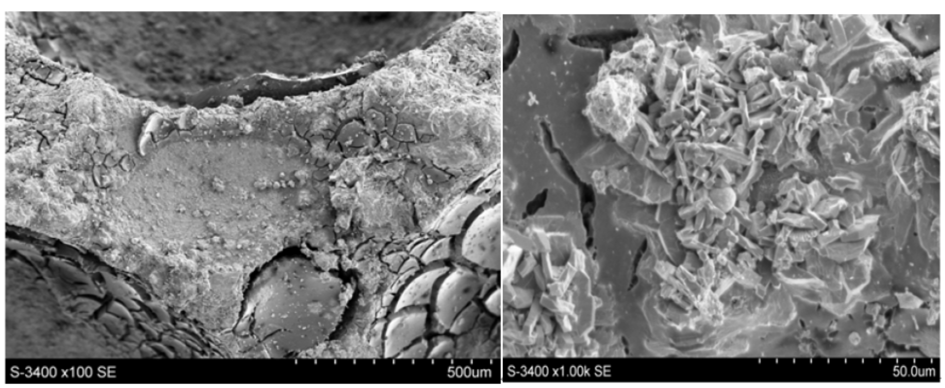

Figure 13: SEM of foamed concrete without Ce^{4+} (a) 100 magnification, (b) 1000 magnification

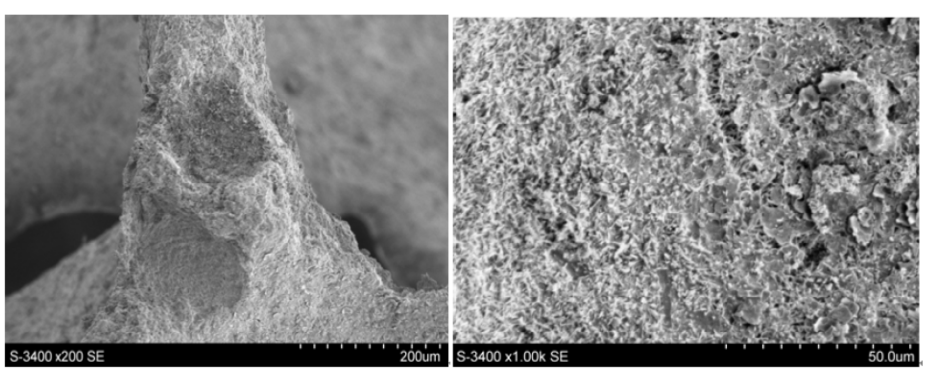

Figure 14: SEM of foamed concrete with Ce^{4+} (a) 200 magnification, (b) 1000 magnification

CONCLUSION

Foamed concrete of which density is 215-320kg/m^3 and compressive strength is 0.2-0.65Mp can be obtained though chemical foaming method.

To obtain strength of 0.35MPa to the concrete, the density can be decreased to 210 kg/m^3 through changing the proportion of it.

The active property and the structure of fly ash are important keys to increase the compressive strength of foamed concrete, using fly ash to replace partial cement may result increasing the strength of the concrete.

Air volume is provided with the cooperation of H_2O_2, cement and $FeCl_3$, which will form foams.

Ce^{4+} is very active, has an effect of foaming stability. Cement component and structure can be improved through adding Ce^{4+}, under the situation of not changing the strength, the density of foamed concrete can be decreased.

ACKNOWLEDGEMENT

The word was supported by Ash assistance by Inner Mongolia autonomous region education department "Effect of Rare earth additive on the performance of lightweight foamed concrete wall energy saving materials" (NJZC13344)

REFERENCES

[1] Paul J.Tikalsky, James Pospisil; A method for assessment of the freeze-thaw resistance of preformed foam cellular concrete, Cement and Concrete Research, **34**, 889-893 **(2003)**.

[2] M.R.Jones, A.McCarthy; Heat of hydration in foamed concrete: Effect of mix constituents and plastic density, Cement and Concrete Research, **36**, 1032–1041 **(2006)**.

[3] Ding Yi, Ren Qifang; Foamed concrete Research and Progress [J], Concrete., **264(10)**, 13-16 **(2011)**.

[4] Xulong, Qian Guanlong; Using chemical for foaming to foamed concrete preparation and research, Concrete and cement products, **12**, 1-3 **(2011)**.

[5] K.A.Cschneidner, Jr, F.W.Calderwood; Handbook on the Physics and Chemistry of Rare Earth[J], North-Holland Physics Publishing, **8(1) (1986)**.

[6] Du Ting, Han Qiyong; Rare Earth, Alkaline earth elements chemical and material use application [M], Technology Editors, 39-43 **(2011)**.

[7] Cai jianguo, Deng Xiu; CO_2 GAS Analysis HMX process of granulate appearance control [J], Manually crystallization research Diary, **13(1)**, 18-23 **(2004)**.

[8] E.K.Kunhanandan Nambiar, K.Ramamurthy; Sorption characteristics of foam concrete, Cement and Concrete Research, **37**, 1341–1347 **(2007)**.

[9] E.P.Kearsleya, P.J.Wainwright; The effect of high fly ash content on the compressive strength of foamed concrete, Cement and Concrete Research, **31**, 105-112 **(2001)**.

[10] E.P.Kearsleya, P.J.Wainwright; Porosity and permeability of foamed concrete, Cement and Concrete Research, **3**, 1805–812 **(2001)**.