



Investigation of Anti-Deliquesce Properties of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ Crystal Particles in Double-Layer Coated Materials with Epoxy Resins and Portland Cement

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In order to improve anti-deliquesce properties and other unsatisfactory performance of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals in applications, a double-layer coating technology with epoxy resins and Portland cement was used. Double-layer coated samples were characterized through FTIR, DTA and multiple optical microscopy spectrometers analysis and natural moisture absorption performance test in the atmosphere. The results showed that compared to epoxy coated materials the moisture absorption growth rate of these double-layer coated samples increased slowly and reduced about 85-90 %, which means that it effectively avoided $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals deliquescent at room temperature. It is considerable significance for double-layer coated $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals in the deep-rooted using fields of building functional materials, other industries and agriculture.

Keywords: Deliquesce, Surface coating, Calcium nitrate tetrahydrate, Moisture absorption growth rate, Cement.

INTRODUCTION

In recent years, thermal energy storage with phase change materials has attracted widespread attention in the engineering applications and scientific research activity¹. Due to the development of building functional materials, thermal energy storage with phase change building materials can offer a high thermal storage density with a moderate temperature variation and play an important role in maintaining desirable thermal comfort². However, calcium nitrate tetrahydrate and its mixtures with some other inorganic salts or organic compounds have been considered to be phase-change materials for thermal energy storage with a high latent heat of fusion and low melting point³. But there bring about serious problems in mixing $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals and other additives with cement mortars directly, one the hand, cement mortars cannot be easy harden. On the other hand, usage life of matrix composite is deduced significantly. Meanwhile, the melting and decomposing point of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal is lowering about 40 °C and has easily soluble in water with a low critical humidity absorption at room temperature⁴, which pose large limitation for their wide use. Therefore, it is essentially to treat surface of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals. The surface of it can be coated by microencapsulation technique, which can pack sensitive ingredients within a coating material to protect $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals from physico-

chemical effects of the surrounding matrix under room temperature and can be gained into stable forms⁵.

In our previous research, a series experiments have been carried out to solve easy deliquescence problem of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals at room temperature by a dry mechanical encapsulation process with epoxy resins. Finally, the treated composite can be deposited and does not liquefy within 3 months, which have achieved satisfactory results⁶. These composite are needed to dry by vacuum drying unit process for a long time after coated by epoxy resins and still exist a certain degree of natural moisture absorption about 3 months later. In order to solve completely the problems above, it is necessary to carry out secondary coating treatment of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ composite.

Due to the supplements of a high level of durability, little or vanishing degradation, an ideal corrosion resistant and physico-chemical stable environment for exposure to potable or waste water⁷, ordinary Portland cement materials with lower liquid and gas permeability can inhibit many active species migration through hardened matrix. Especially, cements are easy to be obtained and relatively inexpensive⁸. Therefore, cement materials can be used as coating materials in environmentally sensitive materials like $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal coated by epoxy resins^{9,10}.

In this work, a double-layer coating technology of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ particles coated by epoxy resin and cement

materials was proposed. Combined with multifunctional optical microscopy, the FTIR spectra, moisture absorption performance test in the atmosphere and DTA thermal analysis techniques, the moisture absorption growth rate, as well as macro and microphotograph of double-layer coated composites were fully determined and analyzed. The results show that the double-layer coating technology is significantly effective for the surface modification and anti-deliqescence of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals at room temperature. Meanwhile, there have been few studies of the surface double-layer coating processes of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals with epoxy resins and cement at room temperature in related literature so far.

EXPERIMENTAL

The materials used are listed in Table-1 and the basic chemical components and key performance of PO 42.5 Portland cement is shown in Table-2.

Preparation of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ double-layer coated composite under room temperature: Based on the previous work⁶, firstly, the surface of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal was coated by epoxy resins optimum formation with epoxy, alcohol and diethylenetriamine of mass ratio of 7:1:1.05, which is numbered EC 5 %. And then, the monolayer coated composite was stirred 5 min and capsulated with ordinary PO 42.5 Portland cement with 100, 110, 120, 130, 140 and 160 % mass weight of the above monolayer coated composite and numbered PC100, PC110, PC120, PC130, PC140, PC160 for testing.

Natural moisture absorption growth rate of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ composites: After all samples dried by vacuum under room temperature, each of samples (3 g) was added in precision electronic scales to test mass change until 4 h at intervals of 15 min.

Characterization: The surface morphological spectra were observed using a multifunction optical spectrometer (Japan, BX51-P, Olympus Corp.). The FTIR spectra were measured with a FTIR spectrometer (America, Nicolet5700) in the wavelength range from 4000 to 500 cm^{-1} under KBr pressured tablet of mass ratio of 1:100 with composites. The DTA thermal properties analysis was recorded on a thermal analysis spectrometer (Germany, Netzsch STA-449-C) at the heating rate of 10 $^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. The natural moisture absorption growth rates of particles were obtained using an electronic analytical balance (America, AR1140,

Ohaus corp. Pine Brook Co.) with range from 0.0001 to 110 g. The crystal structure of double-layer coated composites was investigated using D/max-IIA XRD machine (Japan, CuK_α , 40 kV, 150 mA).

RESULTS AND DISCUSSION

Morphology and optimum process analyses of the composites: In comparing treated effect of all double-layer coated calcium nitrate tetrahydrate samples, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal particles were mixed directly with cement mortar. The experimental results show that all samples of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal were added directly in varied mass contents of cement with water or not, which all liquid within 1 min to 1 h and fast with mixed water increasing and that means this kind of treatment process is unrealistic. According to the experimental process, the above problem will not generate by the method of double-layer coating treatment for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal particles with epoxy/cement raw materials under room temperature. According to the Figs. 1 and 2, the surface of particles in monolayer treated by epoxy resins has been coated by cementing materials and showed dark gray dispersed particles. That means double-layer coating technology for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal particles treated is effective.

It is extremely important step to measure the natural moisture absorption growth rate of all double-layer coated samples and the results showed in Fig. 3. According to experimental tested curves, in comparison with monolayer treated sample by epoxy resins (curve EC 5 %), the moisture absorption growth rate of all double-layer coated samples are decreasing significantly and reduced about 85-90 % than the former and the moisture absorption growth rate curves of all double-layer coated samples tends to be stable after 50 min. Especially, the deliquesce problem of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal in all double-layer treated samples has not been generated with deposited time lasting and the surface of all double-layer coated samples numbered for PC110-PC160 is more drying with the hydration processing of outer cement paste. The particles of PC110-PC160 samples are all dispersed separately and dried and can be bagged to be used in time. Moreover, coupled with economic considerations, the best coating mass content of cement is 100-110 % weigh of sample EC 5 %. The biggest advantage of the double-layer coating methods used here is to omit the vacuum dry process and bagging immediate problems.

TABLE-1
RAW MATERIALS USED IN EXPERIMENTS

Raw materials	Grade	Source
Epoxy resin E-44	Industrial grade	Wuxi resin processing plant, China
Ethyl alcohol	AR graded	Chengdu union chemical industry reagent research institute, China
Diethylenetriamine	AR graded	Chengdu Kelong chemical reagent factory, China
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ reagents	AR graded	Chengdu Kelong chemical reagent factory, China
PO 42.5 Portland cement	Industrial grade	Jiangyou double horse cement plant, China

TABLE-2
BASIC CHEMICAL COMPONENTS AND KEY PROPERTIES OF PO 42.5 PORTLAND CEMENT

28d compressive strength (MPa)	28d flexural strength (MPa)	Chemical components distribution (%)							Initial setting time (min)	Final setting time (min)
		Loss rate	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3		
49.55	9.78	2.85	23.43	7.20	2.95	55.1	2.23	2.85	122	225

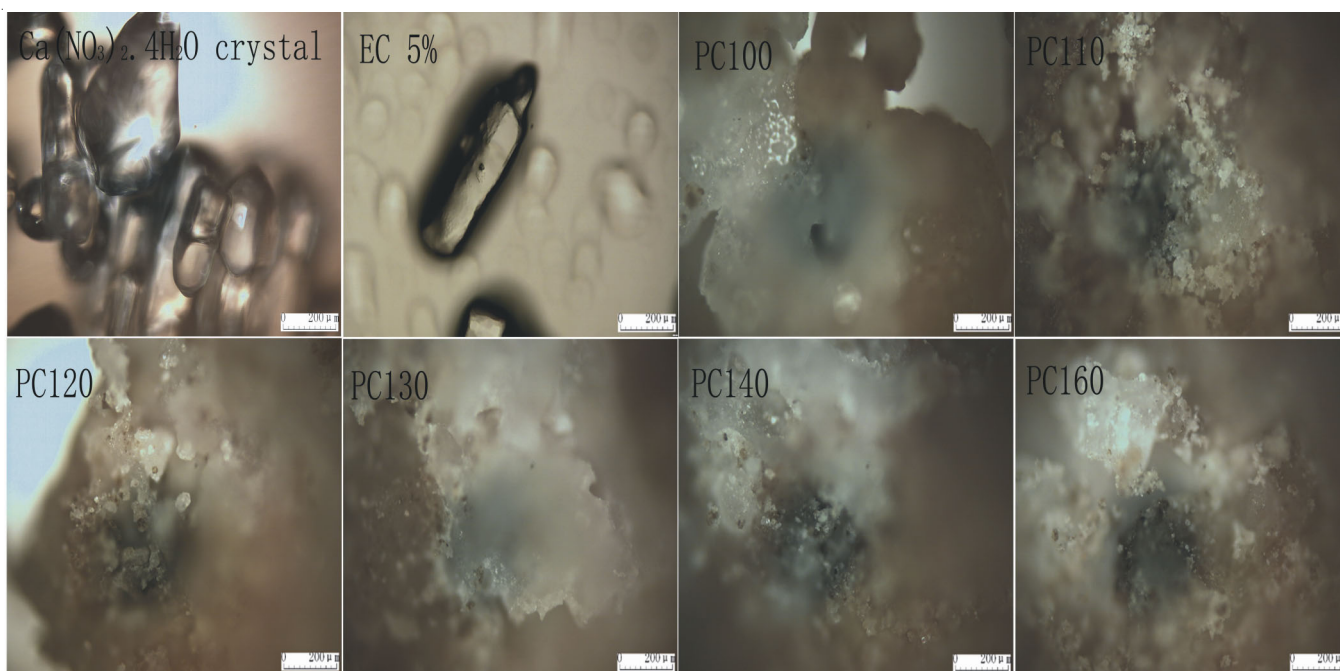


Fig. 1. Optical microscopy images of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals double-layer coated with different cement contents

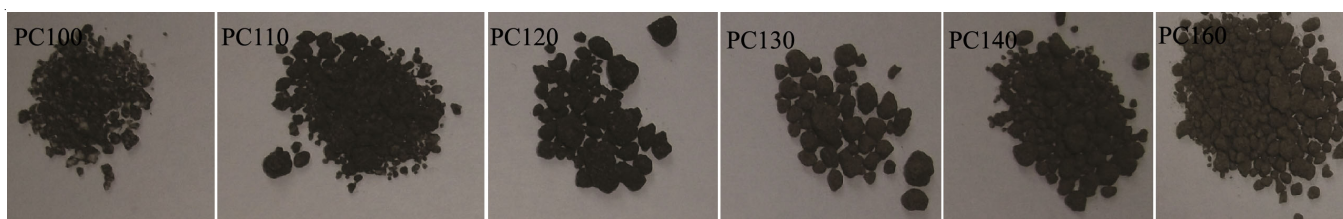


Fig. 2. Digital macrographs of samples by double layer coated method

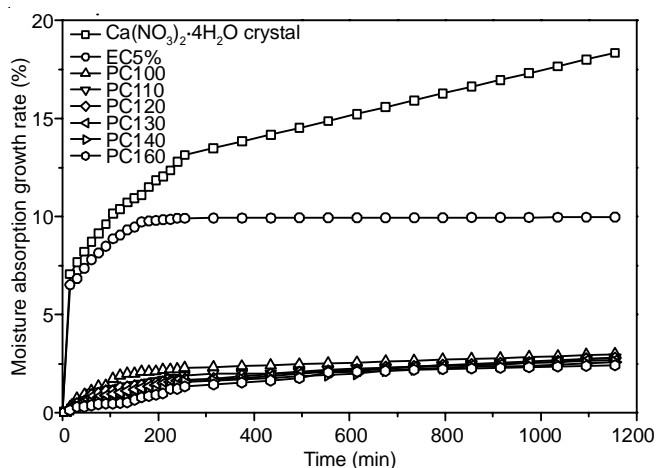


Fig. 3. Natural moisture absorption growth rates versus time of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ double-layer coated composites

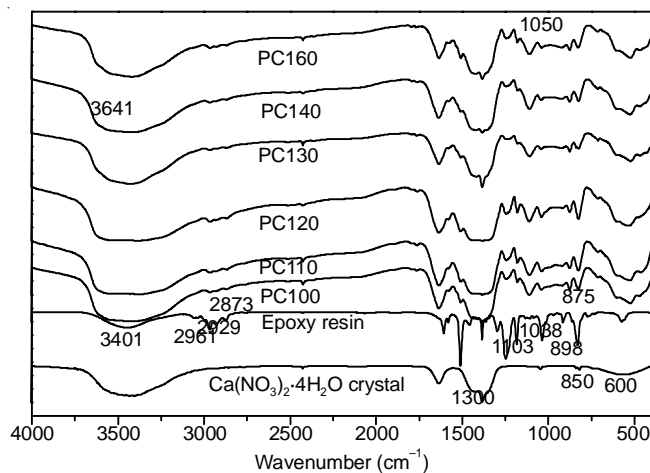


Fig. 4. FTIR spectra of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ double-layer coated samples

Effects of treatment on the structure of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ double-layer coated samples: Fig. 4 showed the FTIR spectra for the calcium nitrate tetra hydrate particles samples coated by epoxy resin and cement by the method of double-layer capsulation technology. As shown in Fig. 4, all samples numbered from PC100 to PC160 appear the characteristic peak of cement hydration products except the characteristic of epoxy resin, like as 3401 cm^{-1} -OH stretching peak and about 898 cm^{-1} characteristic peak for epoxy group and 850 cm^{-1} as C-N

stretching peak belonging to calcium nitrate tetra hydrate. For the reason, the main component of Portland cement is tricalcium silicate (C_3S), which hydration products are mainly calcium silicate hydrate (C-S-H) gel and hydration of calcium hydroxide (CH)¹¹. Therefore, about 3641 cm^{-1} peak attributes to hydration of calcium hydroxide¹², the most intense spectral features of C-S-H appear as a complex group bands in the range¹³ of $1100\text{-}900 \text{ cm}^{-1}$, which belongs to asymmetrical stretching vibrations of Si-O¹⁴. One can also note a band at

875 cm^{-1} due to C_3S spectral peak¹⁵. It indicates samples of PC100 to PC160 are all cladding with epoxy resins and cement, which are consistent with Figs. 3 and 4 images. It demonstrates the double-layer coating method for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal particles treated is expected to be very effective.

The microstructure changing of all double-layer coated samples can be measured by X-ray diffraction method and the results are shown in Fig. 5. According to the XRD spectra curves of all samples, there emerge characteristic peaks in the 2θ diffraction angle range of $29\text{--}32^\circ$ of C_3S and the new peaks of CH at 19° and 34° except for the spectral peaks of calcium nitrate tetrahydrate in the range of $10\text{--}20^\circ$ and $20\text{--}30^\circ$. That shows the monolayer coated samples are encapsulated by cement and the analysis results are consistent with FTIR and optical images analyses.

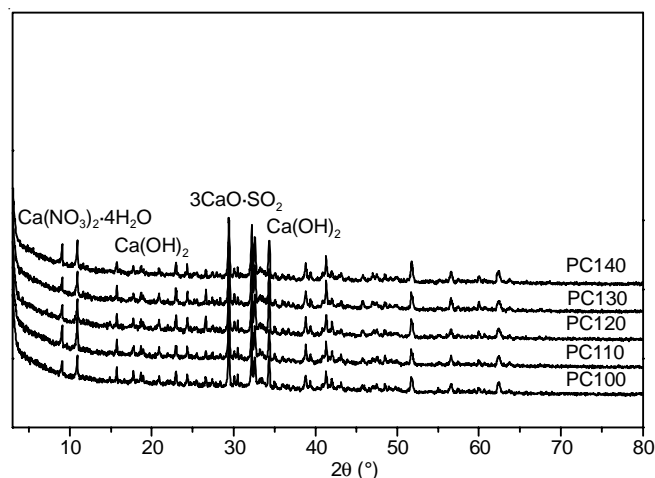


Fig. 5. XRD spectra of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ double-layer coated samples

DTA analyses: Fig. 6 displays the DTA thermal properties of pure cement, representative double-layer coated sample numbered PC100, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal and sample CE 5% within 400°C . For comparison in Fig. 6, the weight loss peak around 137.12°C is induced by C-S-H and ettringite dehydration and physically absorbed water in internal sample¹⁶. For comparison with samples of Ca and EC5%, the first endothermic peak of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal in sample PC100 is not appeared because of the double-layer coating effect, which leads to the heat resistance of the composite improved. The first endothermic peak of sample PC100 is emerged at 95.74°C and the first crystal water dehydrated for $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ into $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ molecular raises from 119.72°C to 127.08°C and the third and forth exothermic peaks have not emerged, but the decomposition peak at 312.09°C of epoxy resins is aroused to generate stable substance¹⁷. The result demonstrates that the heat resistance of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystal particles treated by epoxy resin and cement are enhanced effectively, which is advantageous for the further application of calcium nitrate.

Conclusion

At room temperature, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals are modified with epoxy resins (epoxy resin, ethanol and diethylenetriamine to the mass ratio of 7:1:1.05) and PO 42.5 Portland cement by double-layer coating technology. All of the double-layer coated

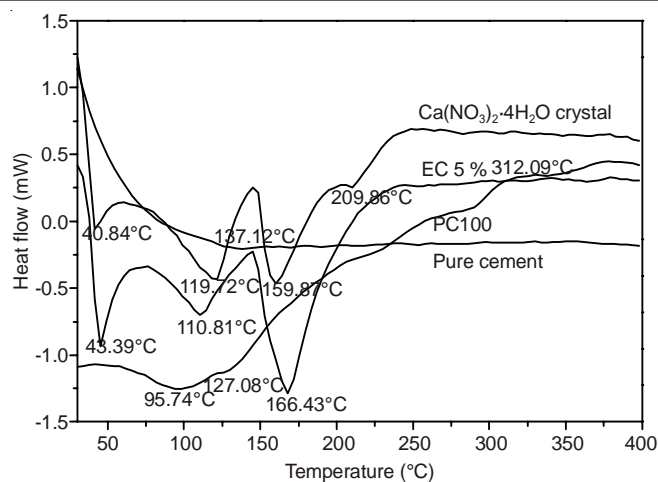


Fig. 6. DTA curves of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ double-layer coated samples with cement

samples are dispersed and dried gray particles. When the amount of cement used in the second treatment layer is greater than the 100% mass of monolayer coated sample EC5%, all double-layer coated composites can be deposited steadily at room temperature in the natural atmosphere and not be deliquesced. Finally, it effectively avoids the absorbing moisture losses of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals at room temperature in natural air gas. Deliquescence problems of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals are approvingly solved by double-layer coated technology, which is considerable current interest in further applications of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ crystals.

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