Producing vaterite by CO₂ sequestration in the waste solution of chemical treatment of recycled concrete aggregates

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Abstract

A recent study showed that the properties of recycled concrete aggregates (RCAs) can be significantly improved by acetic acid treatment. This study demonstrates that a useful product, vaterite, a metastable polymorph of calcium carbonate, can be produced from the waste solution of this treatment through an improved pH swing method. The salient feature of this improved method is that ethanol is added into the waste solution to not only prohibit the phase transformation of vaterite, but also to suppress the ionization of the regenerated acetic acid. This method allows not only more vaterite to be produced, but also more acetic acid to be regenerated from the waste solution through a CO₂ bubbling method. Meanwhile, CO₂ can be permanently stored in the produced vaterite to achieve sustainable CO₂ sequestration. Experimental results confirm that near-pure vaterite can be produced from the waste solution by adding 20% ethanol into the waste solution. 1 kg RCAs can be used to produce about 76.6g vaterite and permanently store 33.7g CO₂ by using this new method. The potential application of the produced vaterite as an internal curing agent for high performance concrete has also been demonstrated.

Keywords: vaterite; waste treatment solution; recycled concrete aggregates; CO₂ sequestration; internal curing.

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1. Introduction

Construction and demolition (C&D) waste is one of the largest waste flows in the world (Shi et al., 2015). Many technologies have been developed to recycle these C&D wastes. Among them, recycling waste/demolished concrete as aggregates for new concrete is one of the most promising. However, recycled concrete aggregates (RCAs) have inferior qualities compared with natural aggregates (NAs) because a layer of residual cement mortar is coated on the surface of the gravel in the RCAs. The porous nature of this residual mortar layer introduces many undesirable properties to the RCAs (Behera et al., 2014). The quality of the RCAs can be improved by removing this porous layer through soaking the RCAs in hydrochloric acid (Ismail and Ramli, 2013) or sulfuric acid solution (Tam et al., 2007) in which some hydration products of the cement can be dissolved. Some loose and cracked mortar can be removed from the RCAs by this method. However, strong acids are required, making this treatment unsafe. Moreover, these acids can introduce detrimental ions such as Cl^- and SO_4^{2-} to the RCAs, which can cause durability issues in concrete with RCAs. The waste solution generated by this process is also hazardous. Disposal of the waste treatment solution will create new environmental problems.

To address these drawbacks of the existing method, an environmentally friendly and cost-effective method was proposed to treat RCAs in our previous study (Wang et al., 2017). As shown in Fig.1, in this new method, RCAs are first soaked in diluted acetic acid, which reacts with cement hydration products in the cement mortar attached to the surface of the RCAs, as described by:

In the above equations, $\text{Ca}(\text{OH})_2$ and $\text{CaO}\cdot n\text{SiO}_2\cdot m\text{H}_2\text{O}$ (calcium silicate hydrate (C-S-H)) are major hydration products of cement in the RCAs, while CaCO_3 was introduced into the RCAs by carbonation of $\text{Ca}(\text{OH})_2$ in the RCAs after long-time exposure to air. This process removes unbound particles from the RCAs and weakens the attached mortar, making it possible to remove it from the RCAs through mechanical rubbing. This treatment can significantly improve the quality of the RCAs. Once used as aggregate in new concrete, these RCAs can enhance the compressive strength of the concrete at 28 days up to 25% (Wang et al., 2017).

Fig.1 Scheme for RCA treatment and value-added products produced from the waste solution

More importantly, a useful product, vaterite – a metastable polymorph of CaCO_3 as explained later – can be produced from the waste solution of this treatment through a simple CO_2 bubbling method. As shown in Eqs. (1-3) and the authors' previous study (Wang et al. 2017), the major chemical composition in the waste solution of this treatment is calcium acetate. By bubbling CO_2 to this waste solution, following reaction will occur:

This reaction produces precipitated calcium carbonate (PCC), which not only partially compensates the cost of the treatment, but also produces multiple environmental and economic benefits, including: 1) no waste material is produced, eliminating the environmental issues created by the disposal of waste chemical solutions as in the existing methods; 2) CO₂ is permanently stored in the produced PCC, contributing to the mitigation of global climate change due to greenhouse gas emissions; and 3) acetic acid can be regenerated, further reducing the cost of the treatment.

Accelerated carbonation of minerals containing alkaline earth oxides has been used to permanently store CO₂ in insoluble carbonates. Although natural minerals rich in calcium and magnesium are widely available for CO₂ sequestration, industrial solid residues rich in calcium and magnesium are also examined because they are cheaper; available in industrial areas; and require no mining activities, crushing, or grinding. As one of largest industrial solids rich in calcium, cement-based materials have already been studied extensively for CO₂ storage through accelerated carbonation (Galan et al., 2014). However, existing studies show that directly carbonating minerals is not efficient due to thermodynamics (Sun et al., 2011). Therefore, a two-step carbonation technique (Azdarpour et al., 2015) is adopted in this study. In this technique, calcium ions are first extracted from the RCAs using acetic acid, as shown in Fig. 1 and Eqs. (1-4) and then carbonated in solution through CO₂ bubbling. The efficiency of carbonation can be drastically improved since the carbonation of calcium in liquid is much faster than direct carbonation. However, a large amount of destabilized solid residue is generated in existing two-step carbonation techniques (Chiang et al., 2014). This is not an issue in the proposed method since the solid residue generated by this carbon sequestration method is the RCAs with improved quality.

CaCO_3 has several different schemes of atomic arrangements or polymorphs, which are vaterite, aragonite, and calcite. These are listed in order by thermodynamic stability of the individual form (Trushina et al., 2014). In the ambient environment, vaterite and aragonite are metastable and only calcite is thermodynamically stable; therefore, calcite is the predominantly polymorph in the produced PCC in existing studies. A previous study demonstrated that the polymorphs of CaCO_3 can be well manipulated in ethanol/water mixed solution by tuning the composition of this binary solution (Chen et al., 2006).

Compared with calcite, vaterite has many salient features such as high solubility, biocompatibility, colorlessness, low density, large surface area and porous structure (Udrea et al., 2012). It has found many highly useful applications in drug delivery, paper making, paints, reaction catalyzing, pollution adsorbing, plastics, and rubber manufacturing (Udrea et al., 2012). In particular, vaterite can transform into stable calcite through a dissolving-recrystallization process. In this process, vaterite first dissolves releasing calcium and carbonate into the solution, which then re-precipitates on the surface of the growing calcite crystals (Juan Diego et al., 2011). Due to this phase transformation process, vaterite exhibits some “reactivity” in water, and therefore can be used as a binder to cement aggregates together, as demonstrated in the field of biomaterials (Combes et al., 2006) and recent applications in concrete (Chen et al., 2013). This provides a way to close the cycle of calcium in RCAs as a binder. In RCAs, calcium mainly comes from the hydration products of cement. In existing methods, calcium can only be recycled as fillers through the carbonation if no extra energy input such as calcination is used.

Eq. (4) suggests that acetic acid is regenerated the proposed process, which can dissolve the produced PCC so that very limited PCC can be produced in Eq. (4). To overcome this problem, a pH swing process (Azdarpour et al., 2015) is commonly used, in which the pH value of the

solution is increased to favor the formation of PCC. In this study, this pH swing method is modified by an ionization suppressing technique (Liu et al., 2015) to maximize the yield of PCC. As a weak acid, acetic acid reacts with the water in a reversible fashion to form hydronium and acetate ions as shown in Eq. (5):

The equilibrium constant for this reaction is referred to as the acid dissociation constant, $K_a = [\text{H}^+][\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]$. Eq.(5) suggests that less H^+ should be produced in order to produce more PCC, which is equivalent to reducing the dissociation constant K_a . This can be done by adding an organic solvent such as ethanol to the waste solution, as the dissociation constant of acetic acid can be significantly reduced by the presence of an organic solvent (Grunwald et al., 1951). More importantly, ethanol is needed to prohibit the phase transformation of the produced calcium carbonate so that the majority of the polymorphs present in the PCC are vaterite.

The focus of this paper is to demonstrate that vaterite can be produced from the waste solution of RCAs treatment using acetic acid through the improved pH swing method. As a preliminary study, commercially available pure CO_2 was used as the feeding gas to synthesize the vaterite. In the future, CO_2 containing industrial waste gas will be used. A series of characterization tests using Scanning Electron Microscopy (SEM), X-ray Powder Diffraction (XRD), and Field Emission Transmission Electron Microscopy (FETEM) were carried out to examine the morphology and phase of the produced vaterite, and the fusion growth of vaterite particles.

It should be pointed out that most chemicals used in this treatment – including acetic acid, ammonia, and ethanol – can be recycled in a way similar to that illustrated by Kakizawa et al. (2001). This will substantially reduce the cost of the proposed treatment.

As a value-added product, the produced vaterite can find many applications in concrete too. An existing study (Chen et al., 2013) shows that vaterite can be used as a binder for concrete. In this study, a new potential application of the produced vaterite as a water reservoir, or internal curing agent, for internally curing concrete was examined.

Autogenous shrinkage is an important phenomenon in early-age concrete, in which all the available water can be rapidly drawn into the hydration process and the demand for more water creates very fine capillaries. The surface tension within the capillaries causes autogenous shrinkage which can lead to premature cracks, making the concrete more vulnerable to the ingress of potentially aggressive species and thus severely reducing the durability of the concrete. Early age cracking due to autogeneous shrinkage is particularly serious for high-performance concrete (HPC) because of its low water to cement (w/c) ratio (Bentz and Weiss, 2011). To remedy this problem, the internal curing method has been developed in which water-filled internal curing agents are added to the concrete mixture. These internal curing agents are used as water reservoirs which can gradually release water to maintain a high relative humidity inside the concrete pores to prevent self-desiccation in concrete (Bentz and Weiss, 2011). As a result, the autogenous shrinkage of the concrete can be reduced or eliminated, ultimately minimizing cracking and significantly promoting the durability of the concrete.

2. Materials and methods

2.1 Materials and equipment

Reactants and equipment used in this experiment are listed in Table 1. Reactants were used as received without further purification. Chinese Grade 42.5 ordinary Portland cement was used to make concrete samples. Its chemical composition is shown in Table 2.

Table 1. Reactants and equipment

Reactants		Equipment
Name	Sources	
Ethanol	CH ₃ CH ₂ OH, >99.7%, YaSheng Chemical	Container
Ammonia water	NH ₃ •H ₂ O, 25~28%, YaSheng Chemical	Vibratory finishing machine
Hydrochloride	HCl, 36~38%, ZhongShi Chemical	pH meter
Acetic acid	CH ₃ COOH, >99.5%, YaSheng Chemical	Mechanical agitator
Ethylenediaminetetraacetic acid disodium salt	EDTA-2Na, 99.9%, ShangHai Chemical	Vacuum pump
Water	Doubly deionized water	Oven

Table 2. Chemical composition of Portland cement used to cast specimens

Compositions	CaO	SiO ₂	Al ₂ O ₃	SO ₃	MgO	Fe ₂ O ₃	K ₂ O	TiO ₂	Na ₂ O	CO ₂	P ₂ O ₅
Content (%)	49.7	29.6	7.7	4.7	3.6	2.4	0.9	0.4	0.4	0.2	0.1

2.2 Waste solution

To treat RCAs using the method proposed by Wang et al. (2017), RCAs were first immersed into solution containing 3% acetic acid by mass, which reacted with the hydration products in the RCAs as shown in Eqs. (1-3). Most of these reactions can be completed within 24 hours, as shown by Wang et al. (2017). After that, the RCAs were removed for further processing. The remaining solution was then filtered several times to remove other solid residuals in the solution. The resulting final waste solution exhibits a faint yellowish color (Fig. 2), and was used to produce vaterite and store CO₂. As shown in Eqs. (1-3), the major chemicals present in the waste solution are calcium and acetate ions, along with some residual acetic acid. The yellowish color of the solution suggests that some other ions were also present in the waste solution. An

Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Optima 7300 DV, Perkin-Elmer, USA) in a simultaneous mode was used to determine the content of these ions in the waste solution.

2.3 Production of vaterite from the waste solution

Ammonia water was added to swing the initial pH value of the mixed solution to 10.3, which favors the formation of vaterite (Udrea et al., 2012). Some precipitants were produced after adding ammonia water. After filtering these precipitants, ethanol was added as the surfactant. Three concentrations of ethanol (0%, 10%, and 20% by volume) were used in the tests. Correspondingly, the produced blended solution with the waste solution, ammonia water, and ethanol are referred to as T0, T10, and T20, respectively. CO₂ was then continuously bubbled into 500 ml of the blended solution through an air stone at a rate of 2.5 L/min to produce vaterite according to Eq. (4). All tests were carried out at 28°C using a water bath and stirred at a speed of 700 rpm by a mechanical agitator. A pH meter was used to monitor the pH value of the solution. The pH value of the solution decreased quickly as CO₂ gas was bubbled into the solution. As soon as the pH value of the solution dropped to 8.5, tests were terminated. The precipitants produced in the solution were then immediately filtered and washed by deionized water and ethanol, respectively. After that, the precipitants were dried in an oven at 105°C for 24 hours.

2.4 Characterization of the produced precipitant

XRD (X'Pert PRO, Philips, Holland) analysis was performed to verify whether the produced precipitant was, in fact, vaterite. The morphology of the produced calcium carbonate was examined via SEM (Sirion200, FEI, USA) with an accelerating voltage of 10 kV. To gain a deeper understanding of the growth mechanism of the produced calcium carbonate, FETEM

(JEM-2100F, JEOL, Japan) analysis was conducted to examine the morphology of the particles in more detail.

2.5 Estimation of the potential of vaterite production and CO₂ sequestration

The potential of the waste solution in vaterite production and CO₂ sequestration mainly depends on the content of cement paste in the RCAs. The major treating parameters such as concentrations of the acetic acid and treating duration - along with the major parameters of producing vaterite from the solution such as the initial pH value and the concentration of ethanol – will also affect the yield and the polymorph form of the produced calcium carbonate. The optimal condition to produce the most vaterite and store the most CO₂ from the waste solution has not been obtained in this preliminary study. Therefore, an estimation of the potential of the proposed technique was carried out based on: 1) soaking the RCA sample in 3% by mass acetic acid solution, 2) producing vaterite with an initial pH of 10.3, and adding 20% ethanol (T20 case in Section 2.3). To this end, 0.5 kg RCA was immersed into a 2L 3% acetic solution for 48 hours. Then, the concentration of Ca²⁺ in the waste solution was measured by ethylene diamine tetraacetic acid (EDTA) titration using Eriochrome Black T as indicator. Then, the total amount of the produced vaterite and the absorbed CO₂ by the waste solution can be estimated by the yield of vaterite obtained in Section 2.3 for the case of T20.

2.6 Internal curing

To be used as an internal curing agent, the produced calcium carbonate (mainly vaterite) should have a high water absorption so that more water can be stored and delivered. To this end, the water absorption of the produced vaterite was first measured. Then four groups of mortar samples were cast with and without the produced calcium carbonate (mainly vaterite) as an

internal curing agent, as shown in Table 3. In this table, M0 is the control group in which no vaterite was added. The other three groups had 20g/Kg, 40g/Kg, and 60g/Kg vaterite added as internal curing agent, and therefore, are referred to as M20, M40, and M60, respectively, in Table 3. The cement shown in Table 2 was used as the binder and river sand with a fineness of 2.6 was used as the aggregate. Mix designs of the internally cured groups were obtained by replacing the sand of the control group with vaterite in volume.

Table 3. Mix designs of four mortar samples (g/kg)

Mix design	Cement	Sand	Vaterite	Water	superplasticizer	w/c	(w/c) _{ic}
M0	448	400	0	152	3.3	0.34	0
M20		390	20				0.02
M40		381	40				0.04
M60		371	60				0.06

The autogenous shrinkage of these specimens was measured using a corrugated tube method following ASTM C1698 (ASTM C1698, 2014). Three duplicate specimens were prepared and measured for each mixture in ambient temperature. In this method, fresh cement paste was encapsulated in a corrugated polyethylene tube with a length of 420 mm and a diameter of 30 mm. The length of the sample was measured on a dilatometer bench by a dilatometer with resolution of 1 μ m at a frequency of once per hour in the first day and then once per day during the first week after the final setting of the cement paste sample.

3. Results and discussions

3.1 Chemical ions in the waste solution

Inorganic chemical ions present in the waste solution determined by ICP-AES are shown in Table 4. As expected, calcium ions are the primary ions in the solution, accounting for 82% of the total inorganic ions detected in the solution. Secondary ions such as Al, Fe, and a number of

alkali metals are also present in the waste solution in very small amounts. These secondary ions are responsible for the yellowish color exhibited by the waste solution, as shown in Fig. 2. After adding ammonia water to the solution to bring the pH value of the solution to 10.3, precipitants were produced. After filtering these precipitants, the solution became colorless, suggesting that some of these secondary ions were removed by the ammonia water.

Table 4. Inorganic compositions of the waste solution

Element	Ca	Cu	K	Cs	Mg	Mn	Fe	Ru	Al	Si	S	Na	Sr	P
Content (%)	82.33	0.09	2.94	4.68	1.62	0.25	2.87	0.06	3.36	0.27	0.46	0.62	0.54	0.09

Fig. 2 Removal of impurities in the waste solution through pH swing

3.2 Effects of ethanol on the polymorph of the produced calcium carbonate

Fig.3 presents the typical XRD patterns of the calcium carbonate produced from T0, T10, and T20, respectively. The peaks at $2\theta=21.04^\circ$, 24.94° , 27.16° , 32.85° , 43.92° , 50.15°

and 55.85° represent (004), (110), (112), (114), (300), (118) and (224) planes of vaterite, respectively. The peaks at $2\theta=23.15^\circ$, 29.49° , 31.44° , 36.08° , 39.51° , 43.25° , 47.53° , 48.56° , 57.49° correspond to (012), (104), (006), (110), (113), (202), (108), (116) and (112) planes of calcite, respectively. Fig. 3 suggests that the major polymorphs of the produced calcium carbonate are vaterite and calcite. By using Rao's equation (Rao, 1973), the content of vaterite in the produced PCC can be determined by,

$$f_v = (I_{110V} + I_{112V} + I_{114V}) / (I_{110V} + I_{112V} + I_{114V} + I_{114V}), \quad (6)$$

where f_v is the percentage of vaterite in the total produced calcium carbonate, which is also referred to as the purity of vaterite in this study. I_V and I_C are the intensities of vaterite and calcite, respectively. Three suffixes in I_V and I_C are Miller indexes of each phase.

Fig.4 confirms that vaterite can be produced from the waste solution generated in chemically treating RCAs and more vaterite can be produced by adding more ethanol. Without ethanol, only 32.26% of the produced calcium carbonate is vaterite. With 10% ethanol, more than half of the produced calcium carbonate becomes vaterite, confirming that ethanol can prohibit the phase transformation of calcium carbonate from vaterite to calcite. This function of ethanol can be seen more clearly when 20% ethanol was added to the solution. In such a case, the phase transformation from vaterite to calcite was nearly completely inhibited, and 96.49% of the produced calcium carbonate is vaterite, as shown in Fig.4.

Fig.3 XRD patterns of calcium carbonate produced from the waste solution with different concentrations of ethanol

Fig.4 Content of vaterite at different concentrations of ethanol.

Fig.5 presents the typical SEM images of the produced calcium carbonate particles from the waste solution. The morphology of these particles without using ethanol is shown in Fig. 5(a). Two types of particles can be identified in this figure: the rhombic particles with a dense structure and the cauliflower-like particles with a porous structure. According to a previous study (Udrea et al., 2012), the first type of particles is calcite and the second type is vaterite. The high porosity and surface area of vaterite make it possible for many highly value-added applications, such as absorbent materials (Chong et al., 2014) or as carriers of drugs or other materials (Trushina et al., 2014).

The close-up of these vaterite particles is shown in the inserted image at the up-right corner of Fig. 5(a). It can be seen that these porous vaterite particles are formed by the aggregation of smaller particles. This is because larger particles have lower free energy than smaller ones (Trushina et al., 2014), and therefore, are more stable. Compared with those vaterite particles produced by other researchers using chemically pure systems (Udrea et al., 2012; Watanabe et al., 2009; Zhao et al., 2013), vaterite particles produced from the waste solution exhibit a larger size and less orderly packing of small particles, as shown in Fig. 5(a). Clearly, this unique morphology of the vaterite produced in this study is induced by the presence of other ions in the waste solution, as shown in Table 4. It is possible that these ions may co-precipitate with the vaterite or be adhered to the surface of vaterite, influencing the nucleation or growth of the vaterite particles.

Fig.5 SEM images PCC synthesized at different concentrations of ethanol:(a) 0%,T0, (b) 10%, T10, (c)20%, T₂₀, and (d) 20%, T20, a typical broken particle.

When 10% ethanol was added into the waste solution, more vaterite particles were produced as shown in Fig. 5(b). These flower-like particles were formed by the aggregation of small olive-like particles. After 20% ethanol was added, almost all produced calcium carbonate particles are vaterite with a spherical shape and sizes ranging from 1 μm to 15 μm in diameter, as shown in Fig. 5(c). This is also in agreement with the XRD spectra shown in Fig. 3. The inner structure of the produced spherical vaterite particles can be revealed by a broken particle shown in Fig. 5(d), which shows that the larger vaterite particle consists of numerous nanosize smaller particles. According to a previous study (Yoshida et al., 2014),

these nanosize particles assemble together to a larger spherical vaterite particle through a layer-by-layer growing process, in which the newly produced small vaterite nanoparticles are deposited on the previously formed vaterite particle to form a new layer. This can be confirmed by Fig. 5(d), which shows that a denser outer layer with thickness of 0.5 μm is deposited on the core with 2.2 μm in diameter.

Figs. 4 and 5 suggest that addition of ethanol not only increases the purity, but also affects the morphology of the produced vaterite. This can be attributed to two possible reasons. First, ethanol can slow down the dissolving-recrystallization process of the produced vaterite, and therefore inhibit the formation of calcite. Second, the increased concentration of the ethanol reduces or shields the complicated effects induced by other ions existing in the waste solution, leading to more spherical vaterite particles produced.

3.3 Fusion growth of vaterite particles

The produced large spherical vaterite particles tend to grow into each other to form even larger ones as shown in the inserted image of Fig. 5(c). This fusion growth process may change the porosity and surface area of the produced vaterite, and hence, affect the function of vaterite as an absorbent or carrier for admixture/water. For this reason, the fusion growth process was further examined, as shown in Fig. 6. Fig. 6(a) shows two typical vaterite particles (A and B). Particle A does not have a typical spherical shape because it was formed by three individual vaterite particles merging together. The clear boundary between smaller particles in Particle A suggests that this particle is still in the early stage of fusion growth. While Particle B has a shape close to a perfect sphere. By carefully examining the image shown in Fig. 6(a), it still can be found that this particle was formed by the fusion growth of several smaller particles. The close-to-spherical morphology of particle B

indicates that this particle is in a later stage of fusion growth in which the fusion of smaller particles is almost completed. The different morphologies exhibited by particles A and B suggest that the fusion growth of vaterite is a time-dependent process. With the increase of vaterite particles produced in the waste solutions, some particles can be in contact with each other. In the contact zone, a dissolution-recrystallization process of vaterite may occur, leading to the merging of neighboring particles, as shown in Fig. 6(b). At the end of this continuous fusion growth, a larger particle can be produced by the fusion of a few smaller particles, as shown in Fig. 6(c). The produced large particle has a higher density as revealed by its FETEM image shown in Fig. 6(c), which has a darker color than that shown in Fig. 6(b). This suggests that the fusion growth can reduce the porosity and surface area of vaterite, and therefore, adversely affect the function of vaterite as an absorbent/carrier for admixtures/water. Inadequate space in the solution, slow stirring, and a low flow rate of CO₂ are major reasons responsible for the fusion of vaterite particles. A few methods can be adopted to avoid or minimize the fusion of vaterite particles, including: 1) diluting the waste solution to avoid or minimize the contact between different vaterite particles, 2) using a high stirring speed to break the possible fusion zone between different particles, and 3) using a high CO₂ flow rate so that vaterite can be produced in shorter amounts of time to minimize the time available for the fusion of individual particles.

Fig.6 Fusion growth of vaterite particles observed in T20. (a) SEM image, (b) and (c) FETEM images.

3.4 Potential of vaterite production and CO₂ sequestration

EDTA titration, using Eriochrome Black T as an indicator, suggests that the concentration of Ca²⁺ in the waste solution is 1.24 mol/kg. According to the results of producing calcium carbonate using T20 mixture, 0.1 mol Ca²⁺ in the waste solution can produce 0.064 mol calcium carbonate. Since the purity of vaterite in the produced calcium carbonate is 96.49% (Fig.4), 0.5 kg RCAs can be used to produce 38.3 g (0.383 mol) vaterite using the production conditions of T20. Therefore, it is estimated that 1 kg RCAs can be used to produce 76.6 g vaterite, and sequester 33.7 g CO₂.

3.5 Internal curing agent to mitigate autogenous shrinkage

The absorption of the produced vaterite under vacuum saturation was measured as 80% of the oven-dry weight. This value surpasses that of traditional lightweight aggregates (5% to 40%) (Castro et al., 2011), suggesting that vaterite can be used as a water reservoir in internal curing, and a smaller amount of vaterite is needed to load the same amount of internal curing water than traditional agents. This can minimize the potentially negative effects induced by internal curing agents on both the mechanical properties and the durability of the concrete.

The autogenous shrinkage of four mixtures were measured and are shown in Fig.7. It shows that the autogenous shrinkage of all internally cured specimens is lower than that of the control specimen at any time, indicating that autogenous shrinkage of the specimens can be reduced by internal curing using vaterite. The autogenous shrinkage of all specimens reaches its peak about 12 hours after final setting, as shown in Fig. 7. This peak is positive for all internally cured specimens, suggesting that internally cured samples are expansive at this peak. That is not surprising since the internal curing water carried by the saturated vaterite replaces the water lost during the hydration of the cement paste. This can reduce the capillary tension and therefore, reduce the autogenous shrinkage (Bentz and Weiss, 2011) of the samples. However, completely eliminating autogenous shrinkage using the produced vaterite has not been achieved in this preliminary study. Further study is needed to optimize this new method to achieve better results via internal curing. Nevertheless, the use of vaterite as the internal curing agent enjoys a unique advantage: vaterite can also function as a binder in the concrete. Traditionally, internal curing agents such as lightweight aggregate can only be used as fillers after releasing water, while vaterite will transform into calcite

after releasing water through the dissolving-recrystallization process. In this way, vaterite that functions as a binder and as a novel CSH-CaCO₃ hybrid binder may be produced, which may contribute to higher mechanical strength and many other superior properties that have not been explored yet. Further study is needed to explore these functions of vaterite.

Fig.7 Results of autogenous shrinkage of four mixtures

4 Conclusions

This study proposes a new low-cost method to integrate value-added vaterite production and CO₂ sequestration into chemical processing of RCAs for better performance in concrete. The focus of this study is to verify that simultaneously producing vaterite and storing CO₂ can be achieved using the waste solution generated in RCA treatment. To this end, the commonly used pH swing method was improved through adding ethanol, which not only prohibits the phase transformation of vaterite, but also suppresses the ionization of acetic acid, leading to a higher yield of vaterite. Experimental studies confirmed that near-pure

vaterite can be produced from the waste solution by adding only 20% ethanol into it through the CO₂ bubbling method. This new method offers many environmental and economic benefits. It not only turns the hazardous waste solution into value-added vaterite and regenerates acid for RCAs treatment, but also permanently stores CO₂ in the produced minerals. It has been estimated that 1 kg RCAs used in this study can produce 76.6 g vaterite and store 33.7 g CO₂. One potential value-added application of the produced vaterite has also been demonstrated, which suggests that the vaterite produced from the waste solution can be used as an internal curing agent for high performance concrete.

Acknowledgments

The authors thank the Public Experimentation Center of the University of Science and Technology of China for their enthusiastic support in characterization analysis. This work was supported by the National Fund of Nature Science of China (NO. 51374189) and National Science Foundation of United States (CMMI #1000580).

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