

## Efficient Inorganic $^{14}\text{C}$ Removal using Ettringite from Waste Solution

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### 1. Introduction

Due to its long half-life (5730 years) and high mobility in environments, carbon-14 ( $^{14}\text{C}$ ) is a serious environmental concern [1]. The nuclear wastes containing  $^{14}\text{C}$  can be produced during the operation of nuclear reactors [2]. In addition,  $^{14}\text{C}$  generated from the nuclear power plant operation can be discharged from the nuclear facilities into surrounding aqueous media, increasing its concentration in the aqueous environment.  $^{14}\text{C}$  mainly exists as inorganic (dissolved) bicarbonate and carbonate species in alkaline waste solution [3]. Being one of the highly mobile radionuclides in the environment, it is necessary to impede the migration of  $^{14}\text{C}$  via sequestering it from alkaline waste solution as dissolved inorganic bicarbonate and carbonate species. In this research, we present the synthesis, characterization, and application of ettringite, a known hydrous calcium aluminum sulfate mineral in cementitious matrices, for effective removal of  $^{14}\text{C}$  from simulated waste solutions present as bicarbonate and carbonate anion species at intermediate pH (~ 8.5) and high pH (~11.5), respectively. Ettringite has been widely applied for removal and immobilization of various hazardous anions [4]. Solution route approach was applied for synthesis of ettringite powder. After synthesis, the material was analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM), and Fourier transform infrared (FT-IR) spectroscopy. Thereafter, the synthesized ettringite was used for sequestration of bicarbonate and carbonate anions from simulated waste solution at different testing conditions, including time as well as concentrations of sorbent and sorbate.

### 2. Materials and methods

#### 2.1. Materials

The chemicals were used in this study without their further treatments. The reagents ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHCO}_3$ ,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ,  $\text{KCl}$ ,  $\text{NaNO}_3$ , and  $\text{NaOH}$ ) were mainly procured from Sigma-Aldrich and Junsei chemicals. The ultrapure “Milli-Q” water was used for preparing the needed solutions.

#### 2.2. Synthesis and characterization of ettringite

The material was synthesized via solution route approach. The calculated amount of calcium nitrate tetrahydrate was suspended in the desired volume of boiled deionized water (DIW) in a polypropylene bottle (PPB). Similarly, two other aqueous solutions of aluminum sulfate octadecahydrate and  $\text{NaOH}$  were prepared in two different PPBs. The prepared solutions of calcium nitrate tetrahydrate and aluminum sulfate octadecahydrate were mixed and stirred at room temperature (RT). Later, the  $\text{NaOH}$  solution was poured in the above mixture solution and stirred for ~5 minutes at RT. Finally, the resultant solution mixture was kept for 24 hour under static condition at RT. Next day, the precipitate was filtered, washed with ammonia solution, and dried at 40 °C for overnight. Subsequently, the ettringite samples (powder) was obtained.

The synthesized ettringite powder was characterized via XRD, SEM, and FT-IR spectroscopy to identify its phase, morphology, and presence of different functional groups, respectively.

#### 2.3. Removal of bicarbonate and carbonate anions

The experiments for removal of bicarbonate and carbonate anions were performed at intermediate pH (~8.5) high pH (~11.50) conditions, respectively, at RT. Typically, 2g/L solid (ettringite powder) to solution (100 ppm  $\text{NaHCO}_3$  (simulated) waste solution in DIW) was used in a polypropylene tube (PPT) and kept for defined contact times in dynamic batch conditions. After the predefined contact time intervals, the suspensions were separated via filtration and the inorganic carbon content was determined using total carbon analyzer. The sequestration % of bicarbonate and carbonate anions were calculated using the following equation.

$$\text{Sequestration (\%)} = ((I_c - E_c)/I_c) \times 100$$

where  $I_c$  and  $E_c$  represent the initial and equilibrium concentrations of  $\text{HCO}_3^-/\text{CO}_3^{2-}$  anions in waste solutions, respectively.

### 3. Results and discussion

The wide angle XRD pattern of synthesized material confirmed the presence of different signature peaks of ettringite. Fig.1 depicts the obtained typical XRD pattern of synthesized ettringite powder.

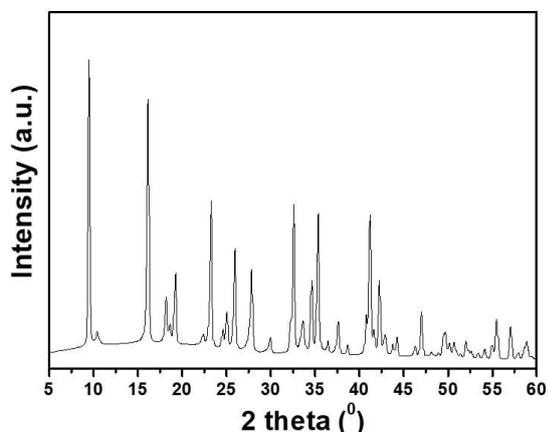


Fig. 1. Wide angle X-ray diffraction pattern of synthesized ettringite powder.

The SEM analysis suggested the successful synthesis of needle-shaped uniform ettringite crystals (Fig.2). The presence of signature FT-IR peaks for Al-O bending and Si-O stretching at  $850\text{ cm}^{-1}$  and  $1110\text{ cm}^{-1}$ , respectively, indicated the ettringite material.

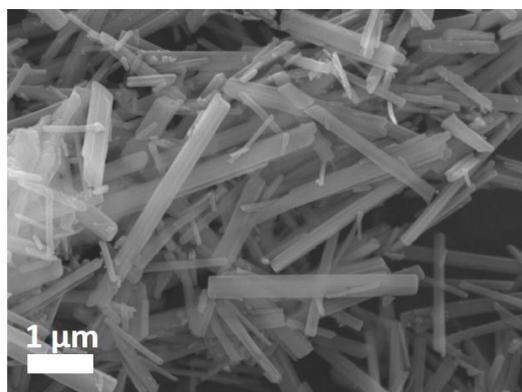


Fig. 2. SEM image of synthesized ettringite powder.

The effect of contact time (10 minutes to 72 hour (h)) on removal of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  anions onto ettringite were performed at pH 8.5 and 11.50, respectively. Table 1 summarizes the optimized removal % of both anions onto ettringite at the defined experimental conditions. The obtained results suggested that the efficient sequestration of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  anions onto ettringite was achieved within 48 h and 8 h, respectively. The removal of carbonate anions onto ettringite was followed by pseudo second order kinetic. Moreover, the characterization results (XRD and SEM) of ettringite after removal of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  anions suggested that the synthesized materials was highly stable at high pH (11.50) and vice versa at lower pH (8.5) experimental conditions.

Table 1. Performance of ettringite for sequestration of bicarbonate and carbonate anions

Experimental outcome	$\text{HCO}_3^-$ (pH = 8.5)	$\text{CO}_3^{2-}$ (pH = 11.50)
Removal saturation time ( $T_{\text{max}}$ )	48 h	8h
Kinetic modeling	Pseudo 2 <sup>nd</sup> order	Pseudo 2 <sup>nd</sup> order
Sequestration performance	~ 93 %	~ 92 %
Ettringite structure	Unstable	Stable

#### 4. Conclusions

This study demonstrated the synthesis of ettringite via solution route method. Synthesis of the desired material was confirmed via XRD and SEM analyses. The synthesized material exhibited efficient sequestration affinity for both  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  anions. We believe that this work would enable us to interpret the potential application of ettringite for removal and immobilization of the bicarbonate and carbonate anions (as analogous of radioactive  $\text{H}^{14}\text{CO}_3^-$  and  $\text{CO}_3^{2-}$ ) in aqueous environment.

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