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# Novel attempts for the synthesis of calcium sulfate hydrates in calcium chloride solutions under atmospheric conditions

Jen-Chang Yang [a,b,1], Hong-Da Wu [c,1], Nai-Chia Teng [c], Dian-Yu Ji [c], Sheng-Yang Lee [b,c,d,*]

[a] *School of Dental Technology, College of Oral Medicine, Taipei Medical University, Taipei, Taiwan, ROC*
[b] *Center for Teeth Bank and Dental Stem Cell Technology, Taipei Medical University, Taipei, Taiwan, ROC*
[c] *School of Dentistry, College of Oral Medicine, Taipei Medical University, Taipei, Taiwan, ROC*
[d] *Dental Department of Wan-Fang Hospital, Taipei Medical University, Taipei, Taiwan, ROC*

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## Abstract

The medical grade calcium sulfate is widely used in clinical applications for treating bone defects. A high-purity and predictable calcium sulfate (CS) synthesis process is desirable in the medical industry. The objective of this study was to develop a one-pot method for the direct preparation of calcium sulfate hemihydrates (CSHs; such as the α- and β-forms) in a $CaCl_2$ solution. CS was synthesized by mixing $K_2SO_4$ and $Ca(NO_3)_2{\cdot}4H_2O$ under various $CaCl_{2(aq)}$ concentrations and reaction temperatures under atmospheric pressure. The calcium sulfate dihydrate (CSD) was found to be an intermediate phase that converts to CSH during the synthesis process, and α-CSH was gradually transformed from β-CSH over time. Moreover, the kinetic of CSD conversion to CSH was strongly accelerated by increasing the $CaCl_2$ concentration. As the reaction temperature was fixed in 90 °C, the form of the CS reactant with an increase in the $CaCl_2$ concentration was in the following sequence: CSD → CSD + β-CSH → CSD + β-CSH + α-CSH → α-CSH. In this study, the synthesis processing window of the CS reactant was established according the test results, and it is worth noting that all phases of CS hydrate could be synthesized with this system and well predicted by the constructed processing window.

*Keywords:* Calcium sulfate; Calcium chloride; Dehydration; Processing window

## 1. Introduction

Calcium sulfate (CS) is the subject of much research due to its multifaceted clinical applications for treating bone defects [1,2]. Good control of biodegradation is essential for CS to achieve satisfactory clinical outcomes. It is desirable for CS to have a dissolution rate close to the rate of new bone growth as a bone substitute [3]. The resorption rate of CS can be governed by its particle size and crystalline structure. Medical use CS hydrate can be further classified as dihydrate (CSD, $CaSO_4{\cdot}2H_2O$), β-hemihydrate (β-CSH, β-$CaSO_4{\cdot}0.5H_2O$), and α-hemihydrate (α-CSH, α-$CaSO_4{\cdot}0.5H_2O$) based on the crystal structure and crystalline water content. Unlike β-CSH (microcrystalline crystal), α-CSH is a long and regular needle-like macrocrystalline crystal and requires less hydration water but produces gypsum with greater strength and a longer resorption period [4,5].

According to ASTM F2224-03 standard specifications for high-purity CSH or CSD for surgical implants, the upper limit of heavy metal contents (such as mercury, arsenic, lead, and cadmium) is 10 ppm, and that of iron content is 100 ppm. Generally, CS can be obtained from natural rock mines or industrial by product (e.g., flue gas desulfurization (FGD) gypsum), however, heavy metal elements or impurities are usually present in FGD gypsum and nature gypsum [6], which is not suit for medical application. For this reason, medical industry usually direct synthesis high quality CSD with wet-precipitation method, however the produced CSD still need a process to convert into CSH. Transformation of CS hydrate phases is influenced in a complex manner by temperature, pressure, dissolved electrolytes or organics, and the presence of nuclear seeds [7]. Among them, an autoclaving (high pressure

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* Corresponding author. Permanent address: School of Dentistry, College of Oral Medicine, Taipei Medical University, 250 Wu-Hsing Street, Taipei City, Taiwan 110, ROC.
*E-mail address:* seanlee@tmu.edu.tw (S.-Y. Lee).

[1] Jen-Chang Yang and Hong-Da Wu contributed equally to this work.

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steam) method is the typical way to convert CSD to α-CSH [8]. Recently, an alternative approach to transform CSD into α-CSH gypsum with inorganic salts or sulfuric acid under atmospheric pressure without an autoclaving step is possible [9], and the process is relatively milder than the autoclave method [10], moreover the crystal dimensions also can be controlled by electrolyte concentration [11].

To combine the synthesis and conversion process, this paper reports a systematic study that was recently undertaken to seek the one-pot direct synthesis of various CS hydrates by providing $Ca^+$ and $SO_4^-$ ions in a $CaCl_2$ solution at a suitable temperature, and identified the residue heavy metal content. We also tried to construct a processing window of the design process to provide an alternative for producing medical-grade CSs.

## 2. Experimental procedures

All reagents used in the study were obtained from Sigma–Aldrich (Seelze, Germany) with no further purification. The synthesis process is summarized in Fig. 1. The CS reactant was prepared by mixing 0.1 mole $K_2SO_4$ and 0.1 mole $Ca(NO_3)_2 \cdot 4H_2O$ in a beaker containing 100 ml of the designed concentration of a $CaCl_2$ solution (0–5 M) at each preset temperature (25–110 °C) for various reaction times (1–240 min) under atmospheric pressure. The temperature of the system was controlled using an oil bath. All reaction conditions are listed in Table 1. The stoichiometric CS precipitates were harvested by filtration, washed with 95% ethanol, and dried in a freeze-dryer (Christ Co., Osterode am Harz, Germany) overnight to preserve the CS phases without causing undesired rehydration or phase transformation during sample handling.

The crystalline phases of the CS products were investigated by wide-angle X-ray diffraction (WAXD, MaxRC, Rigaku, Japan). The wavelength of the monochromatic X-ray beam was 1.54 Å for CuKα radiation, and the range of the $2\theta$ scan was 5–60° at a scanning rate of 10°/min. The diffraction peaks of various CS phases were analyzed according to the American mineralogist crystal structure database. Thermal analysis and SEM observations were conducted to distinguish the crystalline structure between α-CSH and β-CSH. Samples, of 10 mg each, were loaded in onto an aluminum disc and placed in an oven of a differential scanning calorimeter (DSC, TA-Q100, New Castle, DE, USA). The heating rate was 10 °C/min from 20 to 350 °C. CS specimens were sputter-coated using an ion sputter (E-1010, Hitachi, Tokyo, Japan), and the crystal morphology was examined by scanning electron microscope (SEM) (S2400, Hitachi, Tokyo, Japan) at 15 kV with a magnification of 1000×. The content of heave metal was identified by inductively coupled plasma optical emission spectrometer (ICP/OES) (Perkin Elmer Optima 3000 ICP-OES, Waltham, MA, USA)

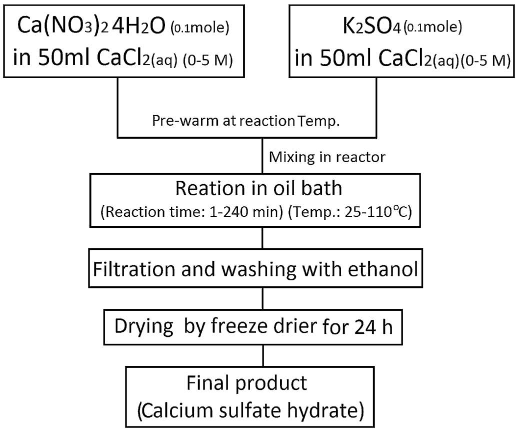

Fig. 1. Schemtic flow chart of the direct synthesis of calcium sulfate (CS) hydrates.

## 3. Results and discussion

### 3.1. Synthesis of CSH in a $CaCl_2$ solution

CSD can be synthesized by a wet precipitation method. The precipitation process involved three stages of supersaturation, nucleation, and crystal growth. We added $CaCl_2$ to this wet precipitation system to regulate the crystalline phases of the CS reactant. In this reaction, 0.1 mole $K_2SO_4$ and 0.1 mole $Ca(NO_3)_2 \cdot 4H_2O$ were respectively dispersed in the $CaCl_2$ aqueous solution, and the solutions were agitated on a stirring plate to prevent $K_2SO_4$ aggregation in the $CaCl_2$ solution. When the ratio of $K_2SO_4$ (mole)/$CaCl_{2(aq)}$ (L) exceeded 3, the reactant slurry was too viscous to react. For operational convenience, the ratio of $K_2SO_4$ (mole)/$CaCl_{2(aq)}$ (L) of the following experiment was kept constant at 2. According to the solubility of the material and boiling point of the solution, the reaction analysis produced the following conditions: $CaCl_2$ of 0–5 M, a reaction temperature of 25–110 °C, and reaction time of 1–240 min; all conditions are listed in Table 1. As previously reported, CSD could be completely transformed to α-CSH in an over 35% (about 3.15 M) $CaCl_2$ solution at near the boiling point [11,12], thus the reaction temperature and concentration of $CaCl_2$ were controlled to 3.5 M and 90 °C. The effect of the reaction time on the synthesis of CSH was evaluated first. Since the WAXD pattern could only be used to identify the crystalline phases for CSD and CSH, each resulting CS reactant had to be further analyzed by DSC and SEM to distinguish β-CSH and α-CSH.

### 3.2. Effect of reaction time on the synthesis of CSH

The time effect of CSH synthesis (1, 15, 60, 120, and 240 min) was evaluated by WAXD measurements. The characteristic peaks of CSD located at 11.64°, 20.75°, 23.41°, and 29.14° were correlated with the crystal planes of (0 2 0), (0 2 1), (0 4 0), and (0 4 1), while the characteristic peaks of CSH located at 14.75°, 25.66°, 29.76°, and 31.91° were associated with the crystal planes of (1 1 0), (3 1 0), (2 2 0), and (−1 1 4), respectively. Typical characteristic peaks of AH usually located at 25.47°, 31.37°, 38.66°, and 40.83° were attributed to the crystal planes of (2 0 0), (1 0 2), (0 2 2), and (1 2 2). According to the WAXD results (Fig. 2A), only the