



## Precipitation of calcium carbonate during direct aqueous carbonation of flue gas desulfurization gypsum

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### HIGHLIGHTS

- ▶ Direct carbonation of FGD gypsum was studied.
- ▶ Direct carbonation produced a mixture of vaterite and calcite.
- ▶ Vaterite/calcite increased with carbonation time.
- ▶ Impurity-free calcite was obtained in direct carbonation.

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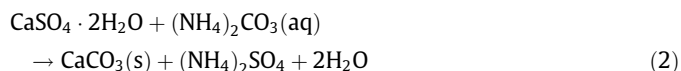
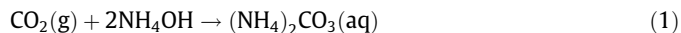
### ABSTRACT

The precipitation of calcium carbonate during the direct aqueous carbonation of flue gas desulfurization (FGD) gypsum, an industrial waste product, was investigated. For comparison, two-step carbonation was also attempted. Calcite was the dominating phase produced in the two-step carbonation, while the direct carbonation produced a mixture of vaterite and calcite phases under all conditions. The relative amounts of each phase were determined by comparing their X-ray diffraction peak intensities. The amount of vaterite phase in the mixture was found to increase with carbonation time for a fixed CO<sub>2</sub> flow rate. An induction period before the precipitation of physically detectable calcium carbonate crystals was assessed using X-ray photoelectron spectroscopy (XPS) and field-emission scanning electron microscopy (FE-SEM). For the CO<sub>2</sub> flow rate of 1 L/min, the C1s peak of CaCO<sub>3</sub> became clear after carbonation took place for longer than 15 min. Virtually impurity-free, single-phase calcite crystals were precipitated from the solution extracted during the induction period. The amount of calcite obtained was typically 5.3% of the amount that can be obtained in the case of the complete reaction. However, further elaboration of this method may allow for the preparation of pure calcite crystals from industrial by-product FGD gypsum.

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### 1. Introduction

Flue gas desulfurization (FGD) gypsum is the main product of the desulfurization system used to remove SO<sub>x</sub> from coal combustion products. One established utilization of waste gypsum has been the production of the fertilizer ammonium sulfate [1–3]. At the same time, calcium carbonate is produced as a byproduct which might have commercial value depending on the purity, morphology, etc. Its application ranges from the conventional fields such as paper or cosmetics to drug industries [4]. The process conventionally consists of the two following consecutive reactions:



The above reactions are characterized by the high yield and purity (up to 99%) of the ammonium sulfate produced [2]. Burnett et al. [3] clearly demonstrated that the purity of the ammonium sulfate could be guaranteed because most contaminants of FGD gypsum remained in the solid residue. If impurities exist in solid form, they can be easily separated from the ammonium sulfate solution by filtration. Considering the solubilities of ammonium sulfate and calcium carbonate, the former, with high solubility (74 g/100 mL of H<sub>2</sub>O at 20 °C), should exist in solution and most of the comparatively insoluble latter (0.15 g/100 mL H<sub>2</sub>O at

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