Fuel 203 (2017) 445–451

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full length article

Retarding effect of impurities on the transformation kinetics of FGD gypsum to α-calcium sulfate hemihydrate under atmospheric and hydrothermal conditions

Hailu Fu [a,*], Jianshi Huang [a], Linwan Yin [a], Jie Yu [b], Wenbin Lou [c], Guangming Jiang [d,*]

[a] *College of Quality & Safety Engineering, China Jiliang University, Hangzhou 310018, China*
[b] *Faculty of Architectural, Civil Engineering and Environment, Ningbo University, Ningbo 315211, China*
[c] *School of Materials and Chemical Engineering, Ningbo University of Technology, Ningbo 315021, China*
[d] *Engineering Research Center for Waste Oil Recovery Technology and Equipment, Ministry of Education, Chongqing Technology and Business University, Chongqing 400067, China*

HIGHLIGHTS

- This paper confirms the retarding effect of the impurities in the FGD gypsum that inhibits the transformation to α-HH.
- $CaSO_3$ proves to be the main retarding factor in comparison with $CaCO_3$.
- $CaSO_3$ impedes the transformation by depressing the driving force and probable occupation of the α-HH nucleation sites.
- Several possible solutions are proposed to overcome the retarding effect.

ARTICLE INFO

Article history:
Received 30 December 2016
Received in revised form 19 March 2017
Accepted 30 April 2017
Available online 6 May 2017

Keywords:
FGD gypsum
α-Calcium sulfate hemihydrate
Impurities
$CaSO_3$
Transformation kinetics

ABSTRACT

The influence of impurities in FGD gypsum (>90% $CaSO_4·2H_2O$) on the kinetics of its transformation to α-calcium sulfate hemihydrate (α-HH, $CaSO_4·0.5H_2O$) has been seldom investigated. This work demonstrates that $CaCO_3$ and $CaSO_3$ in FGD gypsum retard the transformation kinetics under hydrothermal conditions at atmospheric pressure, while SiO_2 produces little effect. The induction time elapsed to initiate the transformation is significantly prolonged mainly because of $CaSO_3$, which origins from its ability to decrease the driving force and simultaneously block α-HH nucleation sites on gypsum crystals. Transformation of FGD gypsum to α-HH can be significantly boosted by washing away the $CaSO_3$. Enlarging the driving force via regulating temperature, salt solution concentration and acidity can also accelerate the transformation. The results indicate FGD process optimization, especially by a complete oxidation of $CaSO_3$, would advance the utilization of FGD gypsum for α-HH production.

1. Introduction

Large quantities of flue gas desulfurization (FGD) gypsum are produced by about 70–80 million tons per year in China [1], raising the risk of secondary environmental pollution (such as soil contamination) and land occupation [2,3]. Utilization of FGD gypsum as road sub-base, building materials, cement retarders, fire resistant material, etc., has been widely investigated [4–7]. Of them, transforming FGD gypsum into α-calcium sulfate hemihydrate (α-HH) presents a high value-added utilization way because of its excellent cementitious property and biocompatibility [1,8–11].

Autoclave-free method is commonly employed to transform FGD gypsum into α-HH, which usually occurs in inorganic or organic media [11–14]. During this transformation, the main component calcium sulfate dihydrate (DH, $CaSO_4·2H_2O$, >90 wt%) in FGD gypsum dissolves firstly followed by α-HH crystallization [15,16]. Previous study shows the transformation kinetics is mainly influenced by driving force and DH crystal surface characteristics [16,17]. The driving force created by the solubility difference between DH and α-HH depends heavily on temperature and water activity [18,19]. Surface characteristics of DH crystals mainly work by influencing the nucleation sites of α-HH [17,20]. However, the effect of impurities existing in FGD gypsum on the transformation kinetics has been seldom studied.

The impurities in FGD gypsum mainly come from the flue gases and desulfurization agent. SiO_2, $CaCO_3$ and other inorganic

---

* Corresponding authors.

E-mail addresses: hlfu@cjlu.edu.cn (H. Fu), jiangguangming@zju.edu.cn (G. Jiang).

http://dx.doi.org/10.1016/j.fuel.2017.04.143
0016-2361/

elements (i.e. K, Na, Mg, Al and Fe) are commonly found [1,21]. $CaSO_3$, the initial reaction product of $CaCO_3$ and SO_2, may also be detected if the forced oxidation doesn't proceed thoroughly. Intensive work has been conducted to clarify the role of inorganic ions played in calcium sulfate phase transformation, which provides guidance to regulate the conversion rate and the crystal habit [6,22,23]. K^+, Mg^{2+} and Al^{3+} show both retarding and promotion effects on calcium sulfate nucleation depending upon their concentrations [13,24,25]. Acidity benefits the DH-α-HH conversion via enlarging the driving force [15,26]. Besides, Mg^{2+} and Al^{3+} were also found to be effective crystal modifiers regulating the length/width ratio of HH crystals [27–29].

In this work, the transformation kinetics using FGD and analytical reagent (A.R.) gypsums as precursors are compared, and the results demonstrate the retarding effect of impurities. The chemical composition and compound species of impurities were determined and the retarding effect was further confirmed by single factor experiments. Possible retarding mechanism was explored, based on which optimization measures are proposed to alleviate the retarding effect.

2. Materials and methods

2.1. Phase transformation

The FGD gypsum was obtained from Jiaxing power plant (Ningbo Zhejiang, China). A.R. gypsum was commercially purchased from Shanghai Silian Industrial Co., Ltd. The transformation of gypsum to α-HH was performed in $CaCl_2$ solutions at 95.0 °C. Specifically, $CaCl_2$ stock solutions were prepared by dissolving A.R. anhydrous $CaCl_2$ into deionized water, and preheated in a 1 L double-wall glass reactor by flowing oil in the jacket. The temperature was monitored with a thermometer and kept within ±0.2 °C. Gypsum was mixed into the solution when the desired temperature was reached. Then, hot suspensions were sampled at certain time intervals, and immediately filtrated. The filtration cake was washed with boiling water for 3–4 times and rinsed by acetone for 1–2 times before drying in an oven at 45 °C. Phase transformation was investigated by tracking the composition of the solid phase along with time. To make clear the retarding effect, certain amounts of the impurities were mixed into the A.R. gypsum and the transformation was investigated in a same way as mentioned above.

To optimize the transformation, the FGD gypsum was purified by washing with solid/water (S/W) ratios of 1:10, 1:20, 1:30 and 1:40, and the solids after treatment are named as J.X.-W1, J.X.-W2, J.X.-W3 and J.X.-W4, respectively. Certain amount of FGD gypsum was mixed into 2 L deionized water in a glass tank and the slurry was stirred with a 200 rpm impeller for 1.0 h. Then, the slurry was vacuum filtered and the cake was dried in an oven at 45 °C.

2.2. Chemical composition analysis and solid characterization

The chemical compositions (CaO, SO_3, SO_2, SiO_2, K_2O, Na_2O, MgO, Al_2O_3 and Fe_2O_3) of the FGD gypsum were analyzed referring to the Methods for Chemical Analysis of Gypsum (China National Standard, GB/T 5484-2012). Particularly, the contents of CaO, MgO and Al_2O_3 are determined by a titration method using disodium ethylenediamine tetraacetate (EDTA-Na); the content of SO_2 is tested according to the idometric method; and the contents of SiO_2 and Fe_2O_3 are analyzed based on ultraviolet–visible (UV-VIS) spectrophotometry. The CO_2 was determined by inorganic carbon (IC) measured by TOC analyzer (TOC-L, SHIMADZU).

The particle size distributions (PSDs) of the gypsums were determined by a laser particle size analyzer (Mastersizer 2000, Malvern, England), through which the specific surface area data can be obtained. Before testing, the solids were dispersed in anhydrous ethanol facilitated with ultrasonic bath. Infrared analysis (IR, Affinity-1, SHIMADZU) was performed to identify the impurity structure, and spectra were collected at 4 cm^{-1} resolution over the frequency of 500–4000 cm^{-1}. X-ray diffraction (XRD, D/Max-2500pc, Rigaku Inc.) analysis was carried out with Cu-Kα radiation at a scanning rate of 8 $°min^{-1}$ in the 2θ range from 10 to 80° to further determine the impurity structure. The solid component and crystal water content characterizing the transformation progress were revealed by thermogravimetry and differential scanning calorimetry (TG-DSC, STA-409PC, NET-ZSCH, Germany). About 8 mg solid was sealed in a lidded Al_2O_3 crucible and heated to 350 °C at a rate of 10 $°C\ min^{-1}$ under N_2 gas atmosphere. The mole fraction evolution of the A.R. gypsum transformation can be calculated on the basis of crystal water content.

2.3. Effect of $CaSO_3$ on the gypsum solubility

To clarify the effect of $CaSO_3$ on the driving force, the solubilities of A.R. gypsum ($c(SO_4^{2-})$) with or without $CaSO_3$ were determined. Excess solids composed by A.R. gypsum and $CaSO_3$ were dissolved in a 2.50 m $CaCl_2$ solution at 95.0 °C. The hot slurry was withdrawn at different time intervals (up to equilibrium), and immediately micro-filtered through 0.22 μm membrane. Then, the concentration of SO_3^{2-} ions ($c(SO_3^{2-})$) in the liquid was tested according to the iodometric method. The total concentration of SO_4^{2-} ions ($c(SO_4^{2-})_T$) was tested after SO_3^{2-} ions were oxidized by H_2O_2, and the $c(SO_4^{2-})$ is calculated by $c(SO_4^{2-})_T - c(SO_3^{2-})$. The $c(SO_4^{2-})$ is tested according to the turbidity method using $PC_{Multidirect}$ COD Vario Moving Labs (ET99731, Tintometer GmbH Germany) [30].

3. Results and discussion

3.1. Transformation kinetics of different gypsums to α-HH

The conversion rates of A.R. and J.X. FGD gypsums to α-HH in 3.5 m $CaCl_2$ solutions at 95.0 °C are shown in Fig. 1. The crystal water of solid changes slowly/little during the initial period (i.e. induction time for α-HH nucleation) before a sharp decrease occurs (from 19.0 wt% to 6.21 wt%, main conversion/dehydration time). Apparently, A.R. gypsum finishes the transformation much earlier than J.X. FGD gypsum. The difference mainly lies in the induction time (11.0 h for J.X. FGD gypsum and 2.0 h for A.R. gypsum). J.X.

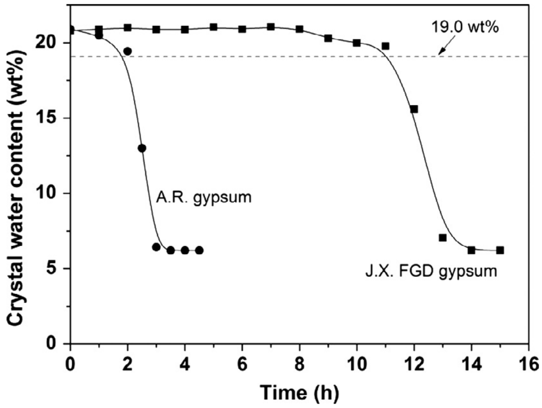

Fig. 1. Transformation kinetics of A.R. and J.X. FGD gypsums into α-HH in 3.50 m $CaCl_2$ solutions at 95.0 °C.