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CHROMIUM(III)-ETTRINGITE FORMATION AND ITS THERMAL STABILITY

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Abstract

Attempts have been made to replace aluminium(III) by chromium(III) in the ettringite structure because of practical importance of a waste treatment technology. The optimum conditions of $Ca_6[Cr(OH)_6]_2(SO_4)_3{\cdot}26H_2O$ formation and its thermal stability are reported.

Keywords: Cr(III)-ettringite, ettringite, thermal stability of $Ca_6[Cr(OH)_6]_2(SO_4)_3{\cdot}26H_2O$

Introduction

Ettringite, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$, is as a naturally occurring mineral. It appears in the technology of cements [1–3] and also as a hydrated product of the reaction of calcium sulphate with aluminium from the fuel ash on landfilled fluidized bed combustion solid wastes [4–6].

The crystal structure of ettringite has been determined [7–9] and found to be of the form $Ca_6[Al(OH)_6]_2(SO_4)_3{\cdot}26H_2O$. Part of the ettringite structure is shown in Fig. 1. The molecule is based upon columns of $[Al(OH)_6]^{3-}$ octahedra linked together through Ca^{2+} ions between which SO_4^{2-} ions and remaining H_2O molecules lie. These columns centre upon the lines (0, 0, z) and have the composition $\{Ca_6[Al(OH)_6]_2{\cdot}26H_2O\}^{6+}$ per pseudo-

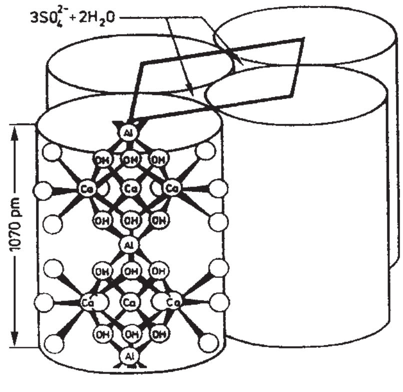

Fig. 1 Part of a single column of the ettringite structure (after [8])

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cell. Each $[Al(OH)_6]^{3-}$ octahedron is linked to each of its neighbours through three Ca^{2+} ions, which are 8-co-ordinated by four OH^- groups and four H_2O molecules, and each shares two edges with different $[Al(OH)_6]^{3-}$ octahedra.

It is worth considering that the aluminium can be replaced by any trivalent metal (M) ion that can give suitable $[M(OH)_6]^{3-}$ octahedra without destroying the ettringite structure, e.g. Cr(III), Fe(III), Mn(III) and Ti(III). These metal ions have comparable ionic radii and third ionization potentials, which could account for their ability to form the ettringite derivatives [9–11].

Substitution of Al(III) in ettringite by Cr(III) has important implications in a waste treatment technology because it is possible for the ettringite phase to accommodate chromium(III) ion if present in the wastes. It means that it might be applied to purifying wastewaters containing Cr-compounds using e.g. fly ashes [12, 13], and subsequently, the solid wastes formed could be utilized in a Na_2CrO_4 process production. This can be the achievement of a new ecological technology [14, 15].

The aim of the present work is to estimate the optimum conditions of chromium(III)-ettringite formation and to determine the $Ca_6[Cr(OH)_6]_2(SO_4)_3\cdot 26H_2O$ thermal stability.

Experimental

Materials

$Cr_2(SO_4)_3\cdot 18H_2O$, $CaCO_3$, (p. a. POCh Gliwice) were used for the syntheses of $Ca_6[Cr(OH)_6]_2(SO_4)_3\cdot 26H_2O$. Readily hydratable quicklime was obtained by $CaCO_3$ calcination at 1000°C during 3 h.

Equipment and methods of measurement

Thermogravimetric analyses (TG/DTG curves) of the samples were carried out on a Mettler thermobalance TG-50 in a Mettler TA-4000 System. Records were obtained with samples heated at a rate of 12°C min^{-1}, up to 800°C, in an open platinum crucible. The sample size was about 10 mg. DSC curves were obtained using a Mettler DSC-30 differential scanning calorimeter operated by the same Mettler System.

The samples of Cr(III)-ettringite were calcined isothermally at 200, 400, 600 and 800°C in a ceramic furnace.

X-ray powder diffraction patterns were obtained using a Philips X'Pert Diffractometer (CuK_α) in the 2θ range of 10–60°.

IR spectra over the range of 4000–400 cm^{-1} were recorded by means of UR-20 Spectrometer (Zeiss Jena) using KBr pellets.

pH measurements were carried out using an ELMETRON CP-315M pH-meter.

The procedure of Cr(III)-ettringite syntheses

$Ca_6[Cr(OH)_6]_2(SO_4)_3 \cdot 26H_2O$ has been synthesized at room temperature under different, definite conditions (pH, Cr^{3+} concentrations and Cr^{3+}/CaO proportions) by two methods:

- by mixing water solution of chromium sulphate with $CaO_{(S)}$,
- by mixing water solution chromium sulphate with super-saturated solution of $Ca(OH)_2$ according to Murdie's method [16].

In both cases the crystallization products were filtered off rapidly and dried at room temperature in a desiccator prior to examinations, so that contamination from atmospheric carbon dioxide might be avoided.

Results and discussion

X-ray diffraction, IR absorption measurements and chemical analyses of Ca^{2+}, Cr^{3+} and SO_4^{2-} for solids and solutions were carried out to identify and to estimate semi-quantitatively the phases present in solids isolated from Cr(III)-ettringite.

Phase analysis of the solid products synthesized in some definite crystallization conditions is given in Table 1. The phase identification shows that Cr(III)-ettringite was formed in some cases along with the other reactants, such as $Ca(OH)_2$, $Cr(OH)_3$ and $Ca(SO_4)_2 \cdot 2H_2O$. It seems that the pH value during synthesis has a particularly important effect in promoting formation of chromium(III)-ettringite. Alkalinity influences the chromium(III) hydroxocomplex formation ($Cr^{3+}+6OH^- \rightarrow [Cr(OH)_6]^{3-}$), the presence of which is essential for Cr(III)-ettringite to be formed. Moreover, the equilibrium state of this reaction depends on the concentration of Cr^{3+}. The appropriate choice of both alkalinity and reagent concentrations in the solution is responsible for the fact whether the sole $Ca_6[Cr(OH)_6]_2(SO_4)_3 \cdot 26H_2O$ will appear or not. In general, relatively high concentrations of reagents cause co-precipitation of $Ca(SO_4)_2 \cdot 2H_2O$ and moreover unsuitable pH values of the solutions have effect on $Ca(OH)_2$, and/or $Cr(OH)_3$ formation.

Table 1 Experimental conditions used in Cr(III)-ettringite syntheses and phase composition of the products obtained

Sample	pH	Cr^{3+} concentration/ mol dm^{-3}	Phase composition
1.1	11.29	0.003	Cr(III)-ettringite, $Cr(OH)_3$
1.2	12.15	0.050	Cr(III)-ettringite, $CaSO_4 \cdot 2H_2O$
1.3	12.20	0.100	Cr(III)-ettringite, $CaSO_4 \cdot 2H_2O$, $Ca(OH)_2$
2.1	9.55	0.015	Cr(III)-ettringite
2.2	9.57	0.014	Cr(III)-ettringite
2.3	11.09	0.037	Cr(III)-ettringite, $CaSO_4 \cdot 2H_2O$
2.4	11.14	0.036	Cr(III)-ettringite, $CaSO_4 \cdot 2H_2O$

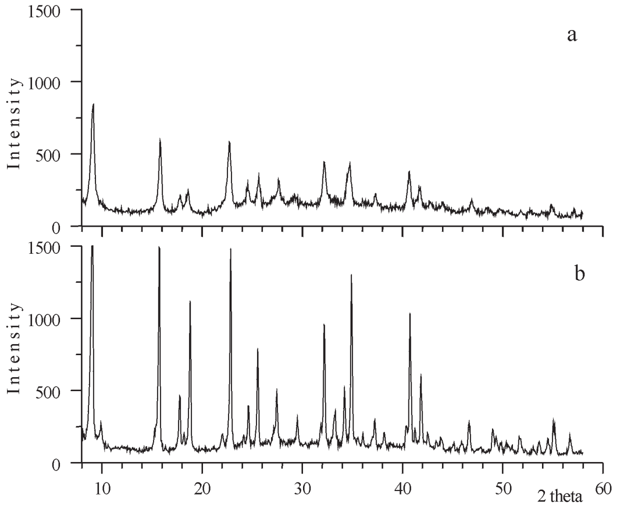

Fig. 2 X-ray diffraction patterns: a – $Ca_6[Cr(OH)_6]_2(SO_4)_3{\cdot}26H_2O$, b – $Ca_6[Al(OH)_6]_2(SO_4)_3{\cdot}26H_2O$

For comparison, in Figs 2a and 2b the X-ray diffraction patterns for Cr(III)-ettringite and ettringite are presented, respectively. The similarity in the results suggests that these two compounds have similar crystal lattices. Hence it is obvious that the X-ray diffraction results are in accord with the results of the IR spectroscopic studies. The main wavenumbers obtained for Cr(III)-ettringite are shown in Table 2, where they have been compared with those given by ettringite.

Table 2 Infrared spectroscopic data (wavenumber/cm^{-1})

Ettringite	Cr(III)-ettringite	Assignment
855 w	–	M–O–H bending
1120 vs	1120 vs	ν_3SO_4
1640 m,b	1640 b,m	ν_2H_2O
1675 s,b	1675 b,s	
2190 vw	–	$2\nu_3SO_4$
3420 vs,b	3420 vs,b	ν_1 and ν_3 H_2O; $\nu OH_{assoc.}$
3635 m	3610 m	νOH_{free}

vw – very weak, w – weak, m – medium, s – strong, vs – very strong, b – broad, *M* – metal

The thermal stability of Cr(III)-ettringite

Figure 3 shows TG/DTG and DSC curves for $Ca_6[Cr(OH)_6]_2(SO_4)_3{\cdot}26H_2O$ samples. Cr(III)-ettringite is thermally stable merely up to ~100°C. Its thermal transformations are complex. Many structural, physical and chemical processes are occurring simultaneously including the oxidation/reduction reactions of chromium compounds

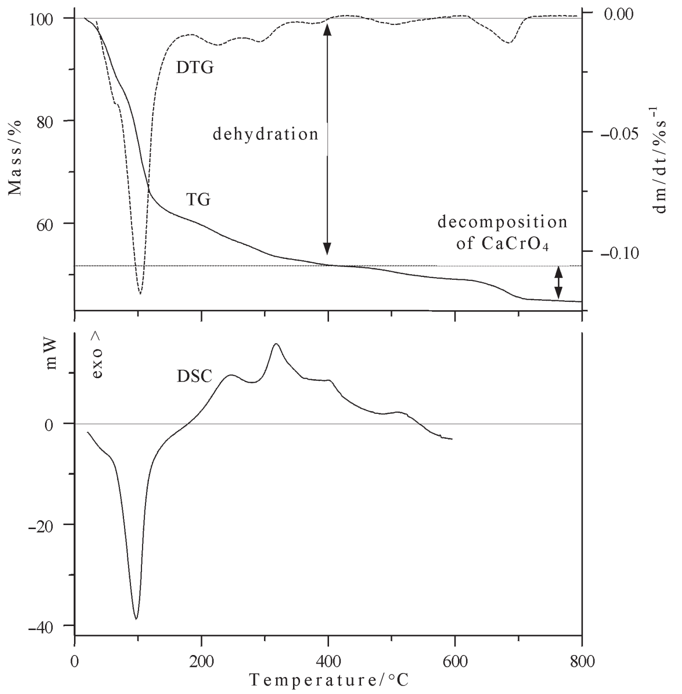

Fig. 3 TG/DTG and DSC curves for Cr(III)-ettringite

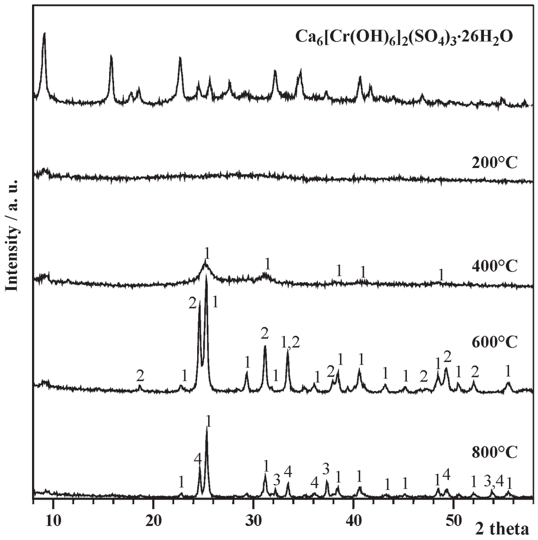

Fig. 4 X-ray diffraction patterns for Cr(III)-ettringite samples before and after thermal treatment at different temperatures: 200, 400, 600 and 800°C, 1 – $CaSO_4$, 2 – $CaCrO_4$, 3 – CaO, 4 – Cr_2O_3

formed as a decomposition products of $Ca_6[Cr(OH)_6]_2(SO_4)_3{\cdot}26H_2O$. The confirmation of the phenomena mentioned are visual observations of changes in colour of solid samples (different Cr valences). The dehydration is a multistep process which occurs up to 400°C. With regard to the phase analyses the thermoanalytical results are in good agreement with the diffraction patterns for samples calcined at different temperatures. The solid crystalline resulted from the thermal treatment of Cr(III)-ettringite at higher temperatures are $CaSO_4$, $CaCrO_4$, CaO and Cr_2O_3, as shown in Fig. 4.

Conclusions

It has been found that the formation of sole $Ca_6[Cr(OH)_6]_2(SO_4)_3{\cdot}26H_2O$ requires both suitable reagent concentrations and a suitable alkaline medium. Otherwise $Ca(SO_4)_2{\cdot}2H_2O$, $Ca(OH)_2$, and $Cr(OH)_3$ co-precipitation may take place. Moreover, even Cr(III)-ettringite formation may not proceed. The estimation of the conditions for chromium(III)-ettringite formation is of practical value.

The phenomena during the thermal treatment of ettringite Cr-derivative are very complicated and further detailed investigation is in progress.

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