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EXAFS and ^{27}Al NMR Studies of $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$ Structural Changes Due to Heat Treatments

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Abstract. At low temperature ($T < 10^\circ\text{C}$), $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$ is formed by hydration of high-alumina cements (HACs). HACs are used for refractory applications; heat treatments then lead to thermal decomposition of $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$, which first dehydrates to $\text{CaAl}_2\text{O}_4\cdot\text{H}_{2x}$ ($x < 10$) and finally to the anhydrous phase CaAl_2O_4 . In $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$, aluminium atoms are 6-coordinated, whereas they are 4-coordinated in CaAl_2O_4 . Materials heat-treated between 120°C and 900°C are amorphous and, therefore, only short-range order techniques can be used to study the environment of ions, in particular calcium. Solid-state NMR cannot be used due to low natural occurrence of the isotope ^{43}Ca . Our innovation is then to study the changes in calcium and aluminium environments during $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$ dehydration by X-ray absorption spectroscopy (EXAFS and XANES). Ca K-edge EXAFS spectra show a decrease in Ca-O distance and a reduction of the number of oxygen neighbours in the first coordination shell. Al K-edge XANES spectra indicate an important distortion of the aluminium sites when amorphisation occurs. The relative contents of Al^4 and Al^6 are determined by ^{27}Al MAS NMR.

1. INTRODUCTION

High-alumina cements (HACs) are a range of cements in which calcium aluminate are the main constituents. Because of their ability to gain strength rapidly and withstand aggressive environments and high temperatures, HACs have found applications in civil engineering and refractories industry. Hydration of cements (and especially of the main phase CaAl_2O_4) results in the formation of different hydrates, depending on the temperature [1]. Doubts subsist concerning the structures of $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$ and $\text{Ca}_2\text{Al}_2\text{O}_3\cdot\text{H}_{16}$ which are formed at temperatures below 10°C and 30°C , respectively. Cubic $\text{Ca}_3\text{Al}_2\text{O}_7\cdot\text{H}_{12}$ and monoclinic $\text{Al}(\text{OH})_3$ are the stable phases formed at temperatures higher than 30°C .

Dehydration of HACs is accompanied by a stepwise removal of water. The dehydrated products of $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$ and $\text{Ca}_2\text{Al}_2\text{O}_3\cdot\text{H}_{16}$ are amorphous, whilst dehydration of $\text{Ca}_3\text{Al}_2\text{O}_7\cdot\text{H}_{12}$ gives rise to crystallised products. The study of the dehydration behaviour of $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$, investigated in this paper, is important for at least two reasons. First, a major use of HACs is for making refractory concrete, and it is useful to understand what happens to the hydrates during the first stages of heating. Second, the phenomenon of conversion (transformation of $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$ into $\text{Ca}_3\text{Al}_2\text{O}_7\cdot\text{H}_{12}$ and $\text{Al}(\text{OH})_3$) is of practical importance because it can lead to a strong decrease in mechanical properties.

Most dehydrated phases being badly crystallised, the knowledge of the short-range order is of prime importance. Nuclear magnetic resonance (^{27}Al NMR) is useful for characterising the environment of aluminium; for calcium, however, the use of ^{43}Ca NMR encounters the problem of the very low natural abundance of ^{43}Ca (0.145 %).

In the present study, X-ray absorption spectroscopy (XAS) at the Al and Ca K-edges is used for the first time to study the changes in calcium and aluminium environments during $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$ dehydration. X-ray powder diffraction shows that dehydration leads to an amorphous material at 120°C , and that CaAl_2O_4 crystallises at 930°C . During dehydration, the coordination of aluminium atoms changes from an octahedron (Al^6) to a tetrahedron (Al^4). Additional information obtained by ^{27}Al MAS and Al-H CP-MAS NMR is then reported.

2. EXPERIMENTAL

2.1 Materials

After the dissolution of a Fondu cement (*Lafarge*, $\text{CaO}:\text{Al}_2\text{O}_3 = 1:1$ in molar ratio) in distilled water at 10°C , the liquor obtained was kept at 5°C in CO_2 -free air, and $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$ precipitated. X-ray fluorescence together with thermogravimetric analysis gave a formula of $\text{CaAl}_2\text{O}_{13.4}\text{H}_{18.8}$, due to a partial dehydration during storage at 4°C . $\text{CaAl}_2\text{O}_4\cdot\text{H}_{20}$ was then subjected to dehydration at the temperature T_0 , for 24 hours, in a thermogravimetric apparatus in which the weight losses and the temperature were recorded. After the heat treatment, the resulting product was controlled by DTA-TGA and XRD. All samples have been kept sealed under inert atmosphere before use.

2.2 X-ray absorption spectroscopy

The experiments at the Ca and Al K-edge were performed at LURE (Orsay, France), using the DCI and the SuperACO storage rings, respectively. Spectra were recorded in the transmission mode, for the Ca K-edge and in the total electron yield mode for the Al K-edge.

The data were fitted using the program FITEX [2] which utilised the single scattering plane wave method to calculate EXAFS. The spectra recorded at the Al K-edge showed a large damping of the EXAFS modulations; information was then limited to the first-coordination shell.

2.3 ^{27}Al MAS and CP-MAS NMR

All the NMR spectra have been recorded at room temperature, after the heat treatments. A *Bruker DSX 400* (9.4 T, $\nu(^{27}\text{Al}) = 104.2$ MHz) was used for one pulse experiments and a *Bruker DSX 300* (7.0 T, $\nu(^{27}\text{Al}) = 78.2$ MHz) for Al-H cross polarization (CP). All samples were spun at 15 kHz in a commercial Bruker double bearing magic angle spinning (MAS) probe. The spectra were referenced to a 1 M aqueous solution of $\text{Al}(\text{NO}_3)_3$.

3 RESULTS

3.1 Al XANES

The Al XANES spectrum of $\text{CaAl}_2\text{O}_4\cdot\text{H}_2\text{O}$ presented in fig. 1 consists of three resonances. Previously reported XANES spectra suggested that Al XANES spectra could differentiate tetrahedrally Al^4 from octahedrally Al^6 coordinated aluminium atoms, since spectra of Al^4 show a strong single edge maximum at 1566 eV whereas Al^6 yields two distinct maxima at 1568 and 1572 eV, and a weak pre-edge feature at about 1566 eV [3,4]. However, the overlap of the low pre-edge feature for Al^6 and the main absorption feature for Al^4 causes a difficulty in estimating the Al^4/Al^6 ratio.

Fig. 1 shows a significant progression of the Al XANES spectra with increasing temperature of the heat treatment. Especially evident is the development of the shoulder at 1565 eV, which corresponds to Al^4 . It must be reminded here that the anhydrous phase CaAl_2O_4 contains Al^4 , but the hydrate $\text{CaAl}_2\text{O}_4\cdot\text{H}_2\text{O}$ contains only Al^6 . Due to the difficulty to quantify, by Al XANES, the aluminium atoms with the different coordinations, ^{27}Al NMR has been investigated.

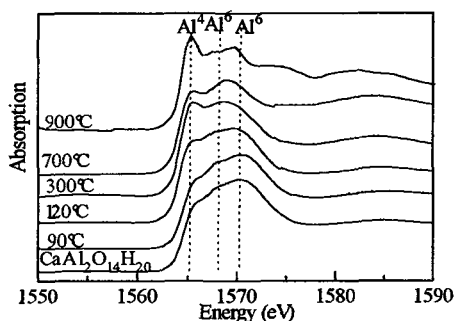


Fig. 1: Evolution of the Al XANES spectra of $\text{CaAl}_2\text{O}_4\cdot\text{H}_2\text{O}$ with heat treatment.

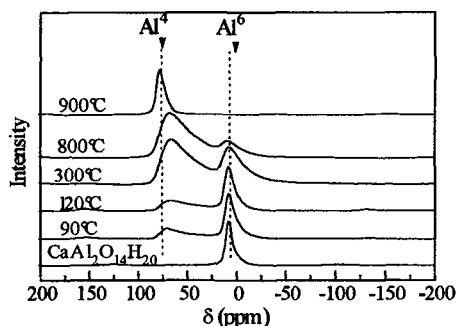


Fig. 2: Changes in the ^{27}Al MAS NMR spectra of $\text{CaAl}_2\text{O}_4\cdot\text{H}_2\text{O}$ with the temperature of heat treatment.

3.2 ^{27}Al MAS and CP-MAS NMR

NMR spectrum have been recorded at room temperature, after the heat treatments (Cf. fig. 2). From 90 to 800 °C, the spectra show two distinct peaks around 10 and 70 ppm, and a shoulder around 50 ppm, which are related to Al^6 , Al^4 and Al^5 , respectively. The procedure used to quantify the aluminium atoms with the different coordinations is described elsewhere [5]; the accuracy of the quantitative results is about $\pm 5\%$.

The changes in the environment of aluminium atoms during heat treatments occur in three stages :

- for $T < 300^\circ\text{C}$, the subhydrate contains mainly Al^6 , which are subjected to an important modification between 150 and 300°C : the peak related to Al^6 becomes broader whereas peaks related to Al^4 and Al^5 do not change; the dispersion of the quadrupolar coupling frequency of Al^6 site also increases, which shows that the symmetry of the Al^6 site decreases;
- for $300^\circ\text{C} \leq T < 800^\circ\text{C}$, the phase contains mainly Al^4 ;
- for $800^\circ\text{C} < T$, only Al^4 are present.

Spectra for $\text{CaAl}_2\text{O}_4\cdot\text{H}_2\text{O}$ heated at 120 and 300°C have also been recorded using Al-H cross-polarisation (CP-MAS); only aluminium atoms surrounded by hydrogen atoms then contribute to the spectra. ^{27}Al -H CP NMR indicates that all the

hydrogen atoms belong to the environment of Al^6 . Moreover, the mean number of hydroxyl ions in this coordination shell decreases as temperature increases.

3.3 Ca EXAFS

The amorphisation of the dehydrated products suggests that the structural disorder σ increases; furthermore, a change in the calcium coordination number N with the temperature is expected. As N and σ are strongly correlated, a "classical" fit could not be applied; the "amplitude ratio method" was therefore used. It consists in considering a reference phase ($\text{CaAl}_2\text{O}_4\text{H}_{20}$), and calculating:

$$\ln\left(\frac{A_i}{A_{\text{CaAl}_2\text{O}_4\text{H}_{20}}}\right) = \ln\left(\frac{N_i R_{\text{CaAl}_2\text{O}_4\text{H}_{20}}^2}{N_{\text{CaAl}_2\text{O}_4\text{H}_{20}} R_i^2}\right) - 2k^2(\sigma_i^2 - \sigma_{\text{CaAl}_2\text{O}_4\text{H}_{20}}^2) - \frac{2(R_{\text{CaAl}_2\text{O}_4\text{H}_{20}} - R_i)}{\lambda(k)} \quad (1)$$

where A_i is the amplitude of the EXAFS function related to a given shell, for the phase i . Since the third term can be neglected ($R_{\text{CaAl}_2\text{O}_4\text{H}_{20}} - R_i \ll \lambda$), the plot of $\ln(A_i / A_{\text{CaAl}_2\text{O}_4\text{H}_{20}})$ versus k^2 gives the Debye-Waller factor σ_i (slope) and the number of neighbours N_i , provided the distance R_i had been obtained by the fit. Results are presented in fig. 3.

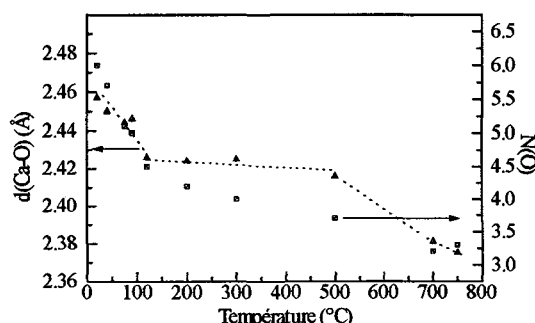


Fig. 3: Changes in the Ca-O distance and the number of neighbours, versus heat treatment, for $\text{CaAl}_2\text{O}_4\text{H}_{20}$.

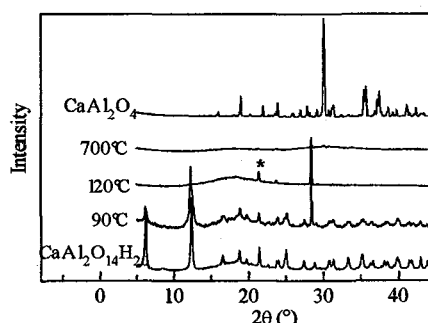


Fig. 4: Evolution of the X-ray diagram of $\text{CaAl}_2\text{O}_4\text{H}_{20}$ versus heat treatment.

4 DISCUSSION

The X-ray absorption spectroscopy, together with the ^{27}Al NMR, allowed the understanding of the dehydration of $\text{CaAl}_2\text{O}_4\text{H}_{20}$; the different steps observed could be related to the structural model detailed elsewhere [6]. The elimination of the first four water molecules does not affect the structure ($T < 75^\circ\text{C}$). The loss of some OH^- ions belonging to the $\text{Al}(\text{OH})_6^{3-}$ octahedra leads to broadened peaks on the XRD diagram (Cf. fig. 4), and the appearance of $[\text{AlO}_4]^{5-}$ tetrahedra ($T = 90^\circ\text{C}$), whereas the Ca environment is less affected. As amorphisation occurs ($T = 120^\circ\text{C}$), the distortion of the Al sites increases, and the second peak of the radial distribution function around Ca disappears. At 800°C , the local environment around Ca is analogous to the one in the crystallised CaAl_2O_4 , which is formed only at 900°C ; the Al environment is however still strongly distorted.

5 CONCLUSION

The study of $\text{CaAl}_2\text{O}_4\text{H}_{20}$ dehydration illustrated the necessity to combine different techniques to follow the structural changes. The subhydrates becoming rapidly amorphous, the XRD could not be applied anymore. XAS was then well suited to determine the calcium environment; concerning the aluminium environment, it was necessary to combine ^{27}Al NMR and XANES, which allowed respectively the quantification of Al^4 and Al^6 , and the description of the Al sites distortion.

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