High Field ^{33}S MAS NMR of Sulphate Mineralogy in Cement-Related Chemical Systems

J.-B. d'Espinose de LaCaillerie, C.-N. Chao (Ecole Supérieur de Physique et de Chimie Industrielle de la Ville de Paris, Laboratoire de Physico-chimie des Polymères et des Milieux Dispersés); Z. Gan (NHMFL)

Introduction

Our previous study of natural abundance ^{33}S solid-state MAS NMR showed a strong potential for the quantitative analysis of sulphate mineralogy in cement-related chemical systems. This method could be helpful to gain a better understanding of the durability of cementicious materials [1]. However, in order to extend our knowledge on solid-state ^{33}S NMR related to those materials, there is a need to study phases more representative of the actual sulfate speciation in cement paste.

Results and Discussion

We report here on ^{33}S solid-state MAS NMR one-pulse spectra obtained at 46.05 MHz and 5 kHz spinning speed of different sulfate compounds present in cement-related chemical systems. The use of high field (14.1 T) revealed that the sulfate compounds resulting from the hydration of the cement paste (thaumasite, monosulfoaluminate, ettringite) spectra (Fig. 1) correspond simply to a single second-order central transition quadrupolar lineshape. Although they present isotropic chemical shifts similar within 2 ppm, their quadrupolar line shapes are very different and we think that they could be distinguished in actual cement pastes on this basis.
We also studied the gypsum present in the cement before hydration. $CaSO_4$ and $CaSO_4$•$2H_2O$ spectrum (Fig. 2) can also be fit by a single quadrupolar lineshape. However, differences in their crystal structure lead to a reduction in an asymmetry parameter (η) from 1 ($CaSO_4$•$2H_2O$) to 0.5 ($CaSO_4$) and thus a different quadrupolar line shapes signature. For a hydration degree equal to $CaSO_4$•$0.5H_2O$, the structure is still debated but NMR reveals that at least three different environments must be present for sulfate (Fig. 3).

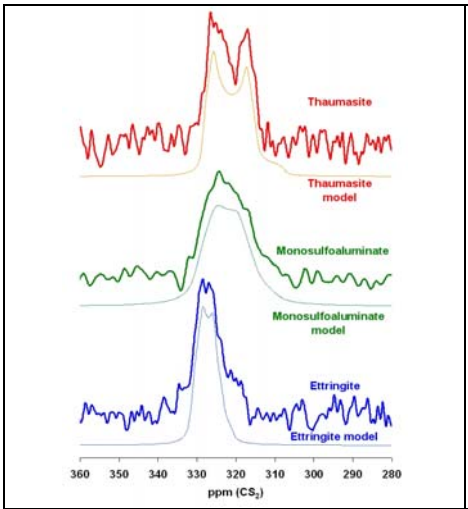

Figure 1 : Powder ^{33}S MAS NMR of different hydrates sulphate compound

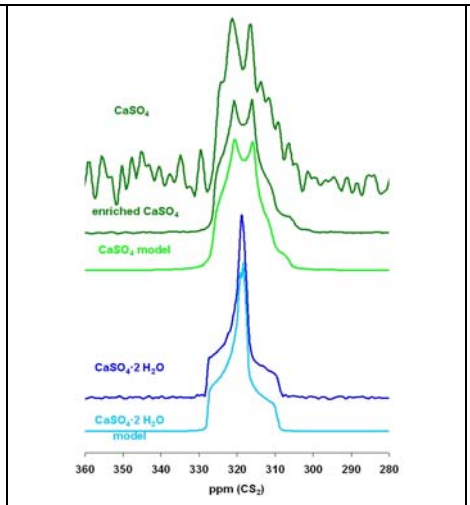

Figure 2 : Powder ^{33}S MAS NMR of $CaSO_4$ and $CaSO_4$•$2H_2O$

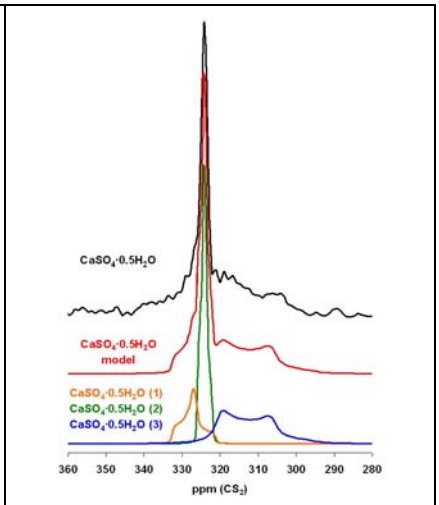

Figure 3 : Powder ^{33}S MAS NMR of $CaSO_4$•$0.5H_2O$

Conclusions

Thanks to the dissimilar ^{33}S signature of sulphate groups between different anhydrous and hydrated compounds, this will allow us to identify and improve quantitative analysis of sulphate mineralogy in cement-related chemical system.

References

[1] Jean-Baptiste d'Espinose de la Caillerie, *et al.*, Cement and Concrete Research, **36**, 1781-1783 (2006).