NUCLEAR MAGNETIC RESONANCE

EMPA Materials Science & Technology

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Introduction

Solid-state nuclear magnetic resonance (NMR) spectroscopy becomes a popular tool in studying the chemistry of cement based materials. .

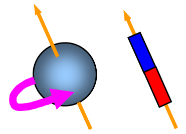
NMR permits to investigate the local environment of a selected nucleus (as ^{27}Al, ^{29}Si) in **crystalline and/or amorphous** systems.

NMR can provides **quantitative information** about the degree of reactivity of OPC, slag and formation of ettringite, AFm during hydration.

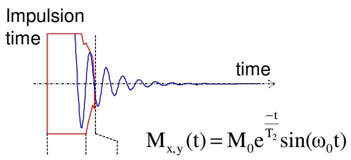
NMR can be combined with XRD to obtain qualitative and quantitative information on the both crystalline and amorphous phases.

Measurement Principle

The nucleus and the spin

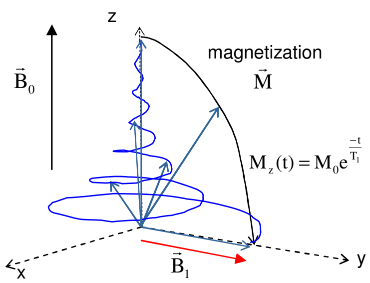


Free induction decay (fid)



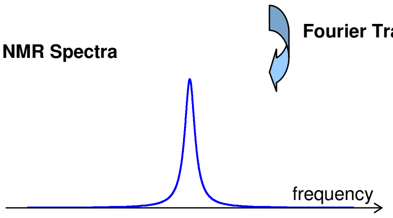
$$M_{x,y}(t) = M_0 e^{\frac{-t}{T_2}} \sin(\omega_0 t)$$

Experiment



Fourier Transform

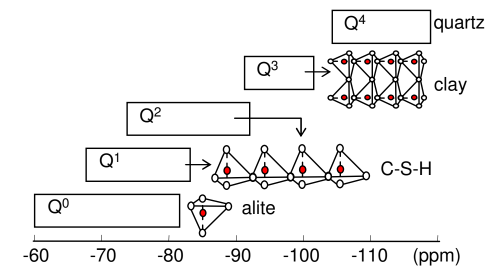
NMR Spectra



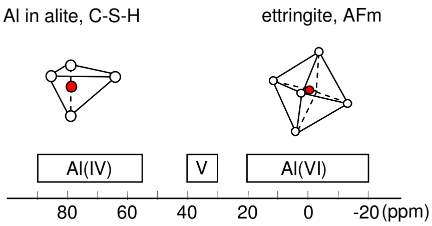
Unity: chemical shift $\delta = \frac{10^6(\upsilon_{sample} - \upsilon_{ref.})}{\upsilon_{ref.}}$ in ppm

Relevance for Our Field

^{29}Si chemical shift ranges of silicates

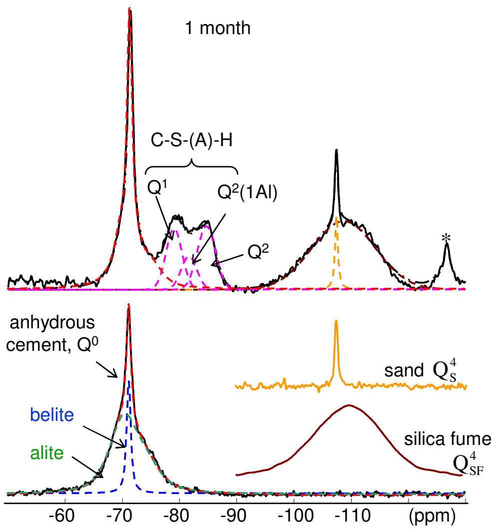


^{27}Al chemical shift ranges of aluminates



Example

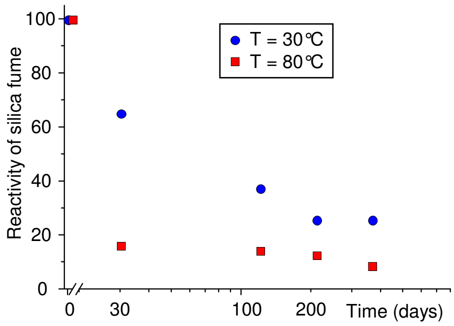
Reactivity of silica fume [1]



The reactivity of silica fume is calculated according to

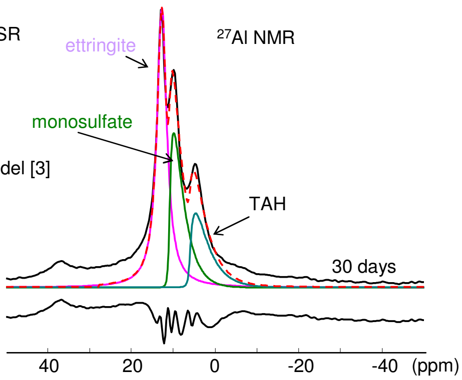
$$P_{Silica\ Fume} = \frac{100 * I_{Silica\ Fume}(t)}{I_{Silica\ Fume}(t=0)}$$

where the intensity represents the number of mole of Si



Applications & Potentials

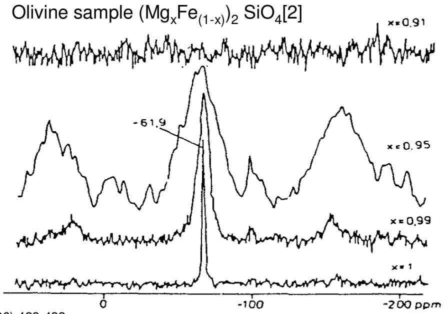
- Quantitative analysis: Reactivity of silica fume, OPC, slag, ASR
- Characterizations of the C-S -(A)-H (mean chain length)
- Quantification of the ettringite and AFm using the Czjzek model [3]
- Investigation of substituting ions in the silicate structure
- Others nuclei can be investigated (^{33}S, ^{31}P, ^{17}O…)
- Investigation of the porosity with ^{1}H NMR



Limitations

- Quantitative analysis depend on the relaxation time T_1
- Modeling may be problematic especially for quadrupolar nuclei (^{27}Al)
- Problem of paramegnetic species (ex: iron)

Olivine sample $(Mg_xFe_{(1-x)})_2\ SiO_4$[2]



[1] G. Le Saout, E. Lécolier, A. Rivereau, H. Zanni, Chemical structure of cement aged at normal and elevated temperatures and pressures, Cement and Concrete Research 36 (2006) 428-433.
[2] A.-R. Grimmer in: Application of NMR spectroscopy to cement science, Gordon and Breach Science Publishers, 1994, pp. 113- 150.
[3] J.-B. d'Espinose de Lacaillerie, C. Fretigny, D. Massiot, MAS NMR spectra of quadrupolar nuclei in disordered solids: The Czjzek model, J.Magn Res., 192 (2008) 244-251