HIGH-FIELD ^{33}S, ^{35}Cl AND ^{25}Mg MAS NMR IN CEMENTITIOUS MATERIALS: DESCRIPTION OF PHASES, STABILITY AND REACTIVITY

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The upgrading of temporal and chemical durability of cementitious materials is one of the priorities for construction departments. Different attacks can occur considering the environment of the material. For instance, marine structures (bridge, barrage …) are considerably degraded by salt water damage to the structure of the cement. Sulphates, chlorides, carbonates naturally present in the water react with the hydrates and can completely change the structure and obviously the mechanical characteristics of the structure.

Using ^{35}Cl MAS NMR experiments, different samples have been explored. Figure 1 represents are example of a 30 days old cement paste mixed with sodium chloride and a 2 year old ordinary concrete put in contact with a saline solution. The cement paste spectrum is a superposition of two contributions: one near 0 ppm coming from ionic chloride and the other one near 30 ppm corresponding to solid or adsorbed chloride. On the other hand, since no capillary water and no free ionic chloride are present, the concrete spectrum reflects only the solid or adsorbed chloride contribution. This spectrum can plausibly be attributed to Friedel's salt and adsorbed chloride and will be evaluated further to confirm these results.

The first ^{33}S MAS NMR spectra of cementitious materials have been realized on both enriched and natural abundance samples (Figure 2). The ^{33}S enriched calcium sulphate sample became a reference sample since its acquisition was highly simplified on the NHMFL 830 MHz spectrometer. The natural abundance ettringite spectrum was more difficult to obtain and the result is surprisingly excellent showing a clearly different NMR signature between the two samples. This is very encouraging for further NMR determination of sulphate phases in cementitious materials.

Finally, ^{25}Mg MAS NMR feasibility experiments have been realized on commercial brucite sample. Brucite is one of the most important compounds in leached materials. The obtained spectrum is very encouraging to provide further experiments on leached concrete.

This work has been presented at national and international congresses and will be published in *Magnetic Resonance Imaging*.

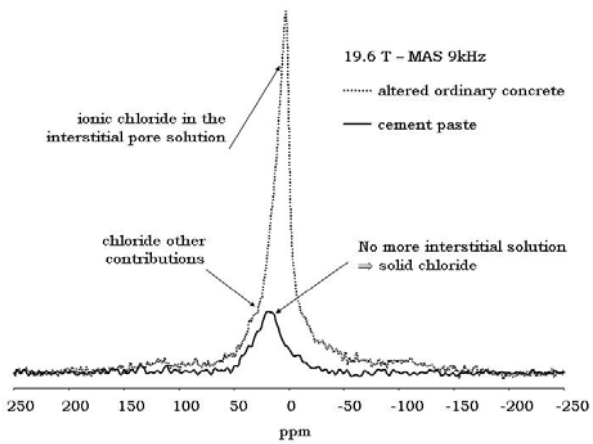

Figure 1: ^{35}Cl spectra of the ordinary concrete chloride-exposed sample (dash line) and the cement paste (full line) at 19.6 Tesla. The cement paste spectrum is the superposition of one peak near 0 ppm (ionic chloride) and another one near 30 ppm (solid or adsorbed chloride). The concrete spectrum exhibits only the solid (attributed to Friedel's salt) and the adsorbed chloride contribution

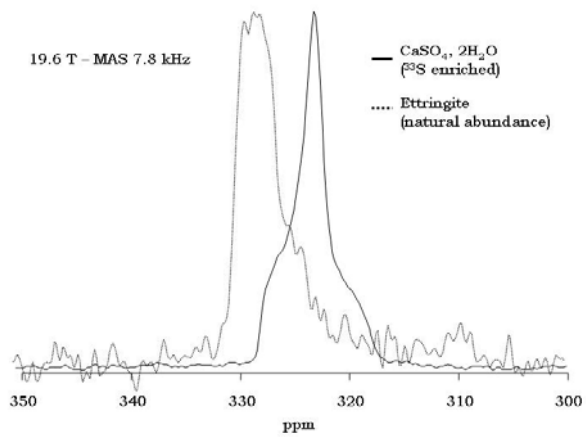

Figure 2: First ^{33}S MAS NMR spectra of ^{33}S enriched calcium sulphate $CaSO_4,2H_2O$ (full line) and natural abundance ettringite (dash line). These two compounds are fundamental in the comprehension of sulphate reactions in a cementitious material