

## ALKALI – SILICA REACTION IN QUARTZITE TREATED BY A SILANE ANALYZED BY NUCLEAR MAGNETIC RESONANCE

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### Abstract

Methyltrimethoxysilane (MTMS,  $\text{Si}(\text{OCH}_3)_3\text{CH}_3$ ) is a new potential material to prevent or mitigate the development of Alkali-Silica Reaction (ASR) in reactive quartzite aggregate. In this work, the structure at atomic level of silicate phases in quartzite aggregates subjected to KOH attack, with or without MTMS treatment, was analyzed using solid-state  $^{29}\text{Si}$  Nuclear Magnetic Resonance (NMR). For the reactive quartzite samples,  $^{29}\text{Si}$ -NMR revealed an amorphous structure for the silicate network, with potentially reactive silicon species on the surface of a silica-like matrix. In samples attacked with KOH solutions, to simulate the conditions of ASR, the resulting product is an amorphous network with a strong reduction in the fraction of reactive silicon species. In contrast, quartzite samples exposed to solutions of MTMS prior to the KOH attack preserve the original silicate structure to a greater extent, demonstrating the potential of MTMS to influence the structure at atomic level of the resulting product.

**Keywords:** quartzite, ASR, reactivity, expansion, nmr,

### 1 INTRODUCTION

The interventions and treatments of a concrete structure compromised by the alkali-silica reaction (ASR) are still challenges in Civil Engineering. The efficiency of these practices varies widely, depending on the degree of advance and the nature of the materials involved in the process, requiring specific analysis on the field and in the laboratory.

The available treatments to mitigate the expansive phenomenon associated to the ASR can be classified as those aiming to the symptoms or those addressing the causes of the process. Many of the former methods are expensive, and their effect may be only temporary in those situations where the ASR last for longer periods, due to the availability of materials involved in the process. The treatments addressing the causes of the ASR, seek to reduce the concentration of key components (reactive minerals, alkali ions, humidity) or, alternatively, to act chemically on the development of the reaction [1]. With the same objective, solutions based on lithium nitrate have been proposed for treatments of concretes [2]. It has been demonstrated that Li is able to modify the characteristics of the silicates resulting from the ASR, producing compounds with less capacity of expansion [3,4]. Nevertheless, the effective capabilities of these processes have to be evaluated in real structures along time. On the other hand, the application of hydrophobic agents based in silanes/siloxanes, which allow the evaporation of water in concrete, has also been proposed to reduce the expansion from ASR [1].

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The objective of this work is to describe a potentially preventive treatment of the ASR expansion of a quartzitic aggregate with well known reactivity on the field, responsible for damages in concrete structures of the hydroelectric power plant of Furnas (Brazil) [5]. The proposed product for treatment is methyltrimethoxysilane ( $\text{Si}(\text{OCH}_3)_3\text{CH}_3$ ), MTMS) a bifunctional molecule with organic and inorganic groups, which is less expensive than products based on Li. In the present communication, the effect of MTMS on the products of the alkaline reaction of quartzite was analysed using the technique of Nuclear Magnetic Resonance (NMR).  $^{29}\text{Si}$  NMR Spectroscopy is able to detect the presence of different silicate products and provide information about their structures at atomic level. Therefore, differences between the amorphous silicates resulting from KOH reaction of quartzite aggregates, with or without previous MTMS treatments, can be revealed.

## 2 MATERIALS AND METHODS

### 2.1 General

Samples of quartzite aggregate used in this work were collected at the site of the Furnas Hydroelectric Dam (MG, Brazil). The chemical composition of these samples is shown in Table 1. A set of four samples were analyzed by  $^{29}\text{Si}$ -NMR: quartzite aggregate without any treatment (QA), quartzite aggregate attacked with KOH (QK), quartzite aggregate treated with MTMS (QM), and a treated sample of quartzite aggregate subsequently attacked with KOH (QMK). The corresponding treatments are described in Section 2.2.

### 2.2 Materials and reaction conditions

#### *Treatment with MTMS*

Powdered samples of quartzite aggregate (mesh  $53\mu$ ) were immersed in a previously prepared solution of 3% MTMS in deionised water (pH 4.92) during 72 hours at  $80^\circ\text{C}$  within closed polyethylene vessels. After this period, samples were left to dry for 24 hours at  $80^\circ\text{C}$  in air atmosphere. The resulting material was packed in polyethylene vial and stored inside a desiccator until the time of the NMR analysis, when they were grinded in agate mortar.

#### *Reaction in KOH solution*

To simulate the conditions leading to the ASR, samples were exposed to a 1M solution of KOH during 72 hours. To obtain a significant fraction of reacted material, the reaction was accelerated carrying out the process at  $80^\circ\text{C}$ . After the reaction period, samples were dried for 24 hours at  $80^\circ\text{C}$  in air atmosphere. The resulting material was packed in polyethylene vial and stored inside a desiccator until the time of the NMR analysis, when they were grinded in agatha mortar. This procedure was carried out on a powdered quartzite sample and on a quartzite sample previously treated with MTMS.

### 2.3 Methods for analysis

#### *Quartzite reactivity*

Reactivity of quartzite was studied through petrographic analysis [6], chemical method (ASTM C-289) [7], accelerated method in mortar bars (ASTM C-1260) [8], and concrete prisms (ASTM C-1293) [9]. In methods involving mortar and concrete, a standard free-of-admixtures cement was used with the following oxide composition:  $\text{SiO}_2$  20.75wt%,  $\text{CaO}$  64.65wt%,  $\text{Al}_2\text{O}_3$  4.52wt%,  $\text{Fe}_2\text{O}_3$  2.56wt%,  $\text{MgO}$  1.16wt%,  $\text{SO}_3$  2.44wt%, with 1.32wt% and 0.83wt% total and soluble alkali, respectively. Cement fineness was equal to  $3,110\text{ cm}^2/\text{g}$  and autoclave expansion of 0.1%. In the concrete tests, natural non-reactive sand of quartz was used. The expansions corresponding to this sand were less than 0.10% in the accelerated mortar bar test and equal to 0.07% at 16 days.

### *Nuclear Magnetic Resonance (NMR)*

High-resolution NMR experiments were performed on a magnetic field of 9.4T with a Varian Unity INOVA spectrometer, using magic angle spinning (MAS) up to 7KHz. Samples were powdered immediately before the analysis and packed in 7mm zirconia rotors. The  $^{29}\text{Si}$  spectra were obtained from single pulse experiments with  $\pi/2$ -pulse duration of 4.0 $\mu\text{s}$ , and recycle delays between 200s and 300s. Up to 400 signals were typically averaged in these experiments. A kaolinite sample was used as secondary standard for  $^{29}\text{Si}$  chemical shift (resonance at -91.5 ppm with respect to tetramethylsilane, TMS).

## **3 RESULTS**

### *Quartzite reactivity*

According to optical microscopy, quartzite is 90% quartz, 5-10 % muscovite, and less than 5% of opaque mineral. Rocks shows fine granulation, granoblastic texture and strong metamorphic foliation, which is determined by preferred orientation of the laminar flakes of muscovite and by the elongated strained quartz with sutured boundaries between adjacent quartz grains. Quartz crystals measure 0.10mm in average and show undulatory extinction due to rock strain. Muscovite occurred as small oriented flakes lined among quartz grains. Opaque minerals occurred disseminated throughout the rock, but preferentially around the micaceous minerals. Mineralogical composition associated with texture indicates that this rock was originated after metamorphism over arenitic sediments.

The reactivity parameters determined by the chemical method correspond to those considered deleterious [7], with an average dissolution of silica of 64.2mmoles/l and a reduction in alkalinity of 27.2mmoles/l.

The expansive potential of the quartzite aggregate is revealed by the mortar and the concrete methods. The average results of the tests indicate 0.24% expansion at 16 days in mortar and 0.09% in one year in concrete. In both cases, the values are higher than the limits established by the ASTM C-33 standard, 0.20% in 16 days and 0.04% in one year respectively for mortar and concrete. Other studies also show the potential for residual expansion of this aggregate in samples extracted from concrete structures in the dam and tested in laboratory [5].

### *Nuclear Magnetic Resonance (NMR)*

Figure 1 shows the  $^{29}\text{Si}$ -NMR spectra of the four samples. The spectrum of the quartzite aggregate QA shows a narrow peak centred at -107.7ppm which corresponds to silicon in quartz environments ( $\text{Q}^4$ ) [10]. The relatively narrow line-width (3.5ppm) of this resonance indicates that these silicon environments are structurally well defined, and may be associated with crystalline or quasi-crystalline quartz domains. There is also a very broad component in the spectrum, encompassing values of  $^{29}\text{Si}$  chemical shifts from sites  $\text{Q}^n$  with all possible degree of Si-O-Si connectivity ( $n=0, 1\dots4$ ). The individual  $\text{Q}^n$  resonances are not resolved due to spectral broadening caused by structural disorder around these silicate groups. The  $\text{Q}^n$  species with  $n<4$  are responsible for the signal observed between -60ppm and -100ppm. These species corresponds to silicon establishing at least one covalent bond with a silanol (Si-OH) or an ionic bond with other cationic species (Si-O- $\text{X}^+$ ). According to the results in Table 1, the concentration of available cations is too low, which led us to conclude that most of the  $\text{Q}^n$  sites with  $n<4$  observed in this aggregate correspond to the potentially reactive Si-OH sites. A least-square fitting of Gaussian line-shapes to the spectrum yields the fraction of silicon in ordered  $\text{Q}^4$  quartz sites as 11%. The remaining 89% population corresponds to silicon in amorphous environments.

Figure 1.b shows the  $^{29}\text{Si}$ -NMR spectrum from the sample QK. The resonances from  $\text{Q}^n$  ( $n<3$ ) species are extremely weak in this sample, indicating that these sites reacted almost completely in the presence of the KOH solution. The main resonances observed corresponds to amorphous  $\text{Q}^3$  (around -100ppm) and

Q<sup>4</sup> (peak at -114ppm). The narrow resonance from quartz sites is essentially invariant. These results reveal that the product of reaction is an amorphous material with a very high degree of Si-O-Si connectivity, and crystalline quartz domains with low reactivity in the time scale and conditions of these experiments.

Figure 1.c shows the <sup>29</sup>Si-NMR spectrum from the sample QM. This spectrum shows resonances characteristic of two silicon species with one Si-C bond: the D silicon (-56.3ppm) forming two Si-O-Si bridges and the T silicon (-58.2ppm) forming three Si-O-Si bridges. These silicon species can be traced to the MTMS molecule, in which two or three of the original Si-OCH<sub>3</sub> bonds reacted with other Si-O bonds. The rest of the spectrum is very similar to the observed one in the untreated quartzite sample.

Figure 1.d shows the <sup>29</sup>Si-NMR spectrum from the sample QMK, corresponding to quartzite aggregate treated with MTMS before exposure to KOH attack. The spectrum shows the resonance from D sites and a broad component associated to a distribution of Q<sup>n</sup> sites from an amorphous silicate. Superposed to this broad line, there are peaks at -78.7ppm, -86.0ppm and -93.7ppm indicating the presence of silicate sites with less disordered structural environments. Two of these peaks, -78.7ppm and -86.0ppm, are compatible with hydrated potassium silicates. The spectral region corresponding to amorphous Q<sup>4</sup> is essentially invariant with respect to the QM sample. The line from crystalline quartz in this sample is weaker than in QM, indicating some degree of reactivity to KOH. The line from T sites is not clearly observed, indicating conversion to Q<sup>n</sup> sites.

#### 4 DISCUSSION

From the mineralogical analysis, quartzite is potentially reactive for ASR due to the presence of strained and elongated quartz [11,12]. As a concurrent factor, the fine granulometry enhances the dissolution of silica in the rock, as indicated by the chemical method. In the presence of the cement-based composites this aggregate caused expansions above the acceptable limits, revealing its reactivity.

The comparison of the <sup>29</sup>Si-NMR spectra of the quartzite aggregate after the attack with KOH solution, reveals major structural differences in the reaction products depending on whether the sample was previously treated with MTMS (Figure 1.d) or not (Figure 1.b). The structure of the amorphous silicate found in the QK sample is composed of a high fraction of Q<sup>4</sup> and Q<sup>3</sup> units, and very low fractions of Q<sup>n</sup> (n<3). This silicate is very different from the quartzite aggregate, which has a large fraction of the latter silicate groups. In the quartzite sample QMK, treated with MTMS prior to reaction with KOH, the amorphous silicate shows a wide distribution of Q<sup>n</sup> sites, completely different from the observed one in the QK sample. The higher intensity occurs in the chemical shift range attributable most likely to Q<sup>2</sup> groups. Potassium seems to be incorporated in structures resembling hydrated potassium silicates. These properties reveal fundamental differences with respect to the structure of ASR gel, with prominence of Q<sup>3</sup> species and incorporation of K in the amorphous structure [13]. Therefore, the presence of MTMS influences critically the development of the reaction and the structure of the products. The structural difference observed between the amorphous products may be significant with respect to their expansion properties upon hydration. A structure with dominance of Q<sup>2</sup> groups is mostly composed by chains of silicate tetrahedra, which is less prone to host water molecules than a sheet-like structure of Q<sup>3</sup> groups.

#### 5 CONCLUSIONS

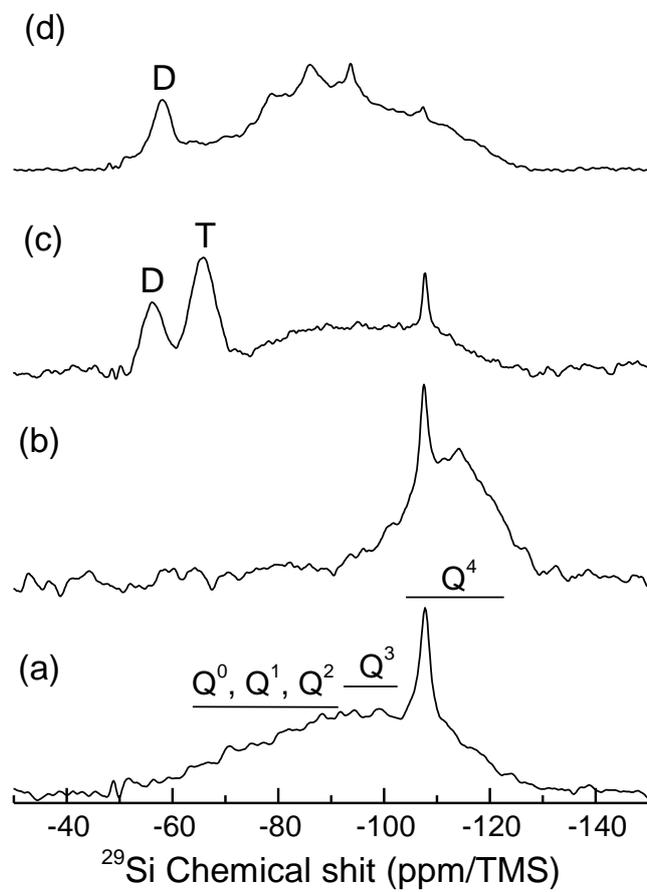
A new chemical treatment acting on the development of the ASR was presented. Through the analysis with <sup>29</sup>Si-NMR, it was demonstrated the potential of MTMS to interfere in the ASR on a highly reactive quartzite responsible for damages in concrete structures. The treatment of reactive quartzite aggregate with MTMS influences critically the structure and the types of the amorphous silicates obtained after the reaction with KOH.

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TABLE 1: Chemical analysis of the reactive quartzite aggregate.	
<i>main elements</i>	Mole %
Na <sub>2</sub> O	0,18
K <sub>2</sub> O	0,54
CaO	0,14
MgO	0,18
Fe <sub>2</sub> O <sub>3</sub> -total	1,19
Al <sub>2</sub> O <sub>3</sub>	1,15
SiO <sub>2</sub>	92,06
LOI	0,35
SUM total	95,79

Other elements identified but not quantified:  
Ti, P, Mn, Rb, Zr, Sr. CO<sub>2</sub> is already comprised in LOI determined at 950°C.



**Figure 1:**  $^{29}\text{Si}$ -NMR spectra from (a) quartzite aggregate without any treatment (QA), (b) quartzite aggregate attacked with KOH (QK), (c) quartzite aggregate treated with MTMS (QM), (d) treated sample of quartzite aggregate subsequently attacked with KOH (QMK).