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# Mössbauer study of synthetic and extracted brownmillerite from sulfate resisting Portland cements

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**Key words:** industrial brownmillerite, Portland cement clinker, <sup>57</sup>Fe Mössbauer spectroscopy, X-ray diffraction, iron site occupation

## Abstract

This paper investigates the quantitative distribution of iron between the two crystallographic sites of brownmillerite isolated in a previous study from four sulfate resisting (SR) Portland cement clinkers. <sup>57</sup>Fe Mössbauer spectroscopy was combined with powder X-ray diffraction (XRD) in order to determine the balance between Fe<sup>3+</sup> and Al<sup>3+</sup> ions in the tetrahedral and octahedral sites of the orthorhombic structure. Synthetic samples covering the whole composition range were studied for protocol validation.

## 1 | INTRODUCTION

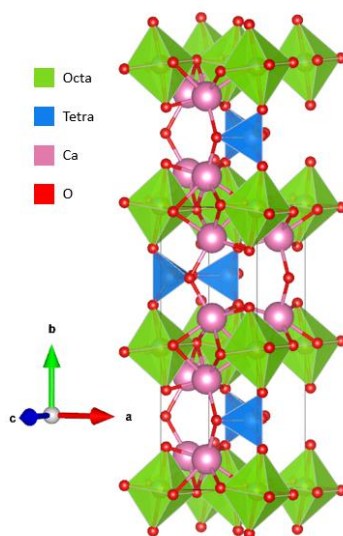
Brownmillerite, Ca<sub>2</sub>Fe<sub>2-x</sub>Al<sub>x</sub>O<sub>5</sub>, also referred to as calcium aluminoferrite, is the main iron-containing phase in Portland clinker, accounting for up to more than 20 wt.% of clinker in sulfate resisting cement. The study of the crystal chemistry of brownmillerite is therefore essential for understanding why C<sub>3</sub>A<sup>a</sup>-free and low-C<sub>3</sub>A cements (Sulfate Resisting Cement SR0 and SR3) exhibit underperformance in a sulfate medium. This study aims to find the key parameters that drive the durability of cement in sulfated medium. Until now, only the content of C<sub>3</sub>A was taken into account for defining the sulfate resistance class of a cement, SR5, SR3 or SR0.<sup>1</sup> However, poor performances of cements without C<sub>3</sub>A have occurred in natural sulfated environment. Then, the unique Al-bearing remaining phase is brownmillerite. However, brownmillerite is a solid solution with variable aluminum content. The Al<sup>3+</sup> and Fe<sup>3+</sup> occupancy, which depends on the aluminum content, is an indicator of brownmillerite's reactivity.<sup>2</sup> Consequently, we hypothesized that there could be a threshold value of the Al/Fe ratio triggering swellings. This is the reason why the solid solution domain from Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> (Al/Fe = 0) to Ca<sub>2</sub>AlFeO<sub>5</sub> (Al/Fe = 1) was investigated and compared to industrial SR brownmillerites. Mériot et al.<sup>3,4</sup> have recently investigated by X-ray diffraction (XRD), electron probe microanalysis, and X-ray fluorescence spectroscopy the crystal chemistry of synthetic and extracted brownmillerite from SR cements studied, establishing that Al/Fe ranges between 0.7 and 0.9 compared to 1–2 in more common Portland cements. This is where this study comes-in, by quantifying the aluminum and iron sites occupancy by Mössbauer spectroscopy and XRD.

Brownmillerite crystallizes in the *Pnma* space group for  $x < 0.6$  and in the *Ibm2* space group for  $0.6 < x < 1.4$ . Its crystal structure is composed of layers of oxygen octahedral occupied by Fe<sup>3+</sup> or Al<sup>3+</sup>

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<sup>a</sup> C = CaO; S = SiO<sub>2</sub>; A = Al<sub>2</sub>O<sub>3</sub>; F = Fe<sub>2</sub>O<sub>3</sub> in abbreviated oxide notation.

ions, separated by chains of oxygen tetrahedral, also occupied by  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  ions<sup>3</sup> (FIGURE 1). Synthetic brownmillerite and its solid solution have already been intensively studied using XRD.<sup>5</sup>  $^{57}\text{Fe}$  Mössbauer spectroscopy is another powerful tool for investigating iron-containing compounds, to identify the crystallographic sites of iron, their quantitative site occupancy, and their oxidation state ( $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ ). It is still used today for cementitious materials.<sup>6</sup> Numerous authors have already studied synthetic brownmillerite using  $^{57}\text{Fe}$  Mössbauer spectroscopy.<sup>5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17</sup> The solid solution  $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$  ( $0 < x < 1.4$ ) exhibits different magnetic behaviors as a function of the aluminum content and the temperature. At room temperature, brownmillerite is antiferromagnetically ordered for a value of  $x$  between 0 and 1.06, which results in a Mössbauer spectrum composed of two sextuplets, one for each crystallographic site of iron (octahedral and tetrahedral). For higher values of  $x$  ( $x > 1.06$ ), brownmillerite becomes paramagnetic<sup>14</sup>, which results in a Mössbauer spectrum composed of two doublets, corresponding again to the two crystallographic sites of iron. The Néel temperature of brownmillerite, which is the temperature at which an antiferromagnetic material becomes paramagnetic, depends on the value of  $x$  in the solid solution  $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ . Geller and Grant estimated the Néel temperature of several members of the brownmillerite solid solution, varying from 730K for  $x = 0$  to 333K for  $x = 1$ .<sup>7, 18, 19</sup>



**FIGURE 1** Brownmillerite ( $\text{Ca}_2\text{AlFeO}_5$ ) crystal structure from Colville and Geller<sup>20</sup>. The graphic was drawn using the VESTA software<sup>21</sup>.

Brownmillerite from cement was also studied to a lesser extent in clinkers, without extracting brownmillerite.<sup>22, 23, 24, 25, 26</sup> To our knowledge, only one article has studied extracted brownmillerite by Mössbauer spectroscopy at room temperature.<sup>10</sup> At this temperature, industrial brownmillerite exhibits a paramagnetic behavior, which can be due to high alumina content and the presence of  $\text{Si}^{4+}$  ions perturbing the iron environment.<sup>10</sup>

The aim of this paper is to investigate the quantitative sites occupancy of iron in brownmillerite by Mössbauer measurements, compared to XRD, in industrial isolated brownmillerite together with synthetic compounds. All samples were systematically studied with the same experimental protocol (elaboration and analysis) and the same instruments. The singularity of this study lies in the removal of the other main phases of clinker in order to avoid iron as impurities in those phases, using selective dissolution techniques, as described in a previous paper.<sup>3</sup>

## 2 | MATERIALS AND METHODS

### 2.1 | Materials

Seven synthetic and four industrial samples were used. The Al/Fe ratio of our synthetic brownmillerite samples<sup>4</sup> were: 0, 0.1, 0.5, 0.6, 0.7, 0.9, 1. Synthetic ferrite was obtained by firing a stoichiometric mixture of Al<sub>2</sub>O<sub>3</sub> (≥ 98 %, Sigma-Aldrich), Fe<sub>2</sub>O<sub>3</sub> (≥ 95 %, Sigma-Aldrich, > 99.4% measured by X-ray fluorescence spectroscopy) and CaCO<sub>3</sub> (AnalaR NORMAPUR, VWR) for 2 h at 1350°C in a platinum crucible, and then quenched in air. The product was manually ground in an agate mortar and re-fired at 1350°C for two additional hours. All the samples were investigated using X-ray diffraction in order to inspect the material purity. The industrial brownmillerite samples, extracted from commercial clinkers, are referred to as A, B, C, D, owing to their various origins. The samples and the extraction protocols are described in detail in <sup>3</sup>. In the following, the designation “SAM” stands for insoluble residue of industrial samples obtained by Salicylic Acid Methanol dissolution.<sup>27</sup>

### 2.2 | Methods

#### 2.2.1 | Mössbauer spectroscopy

Based on the Mössbauer effect, which is a nearly recoilless nuclear resonance absorption spectroscopy, Mössbauer spectroscopy is a non-destructive characterization method for solid materials. It allows the precise determination of oxidation state, bonding properties (covalency, symmetry), and magnetic properties (ferro & antiferromagnetism) of an atomic species in a solid. Although iron (Fe) and tin (Sn) are by far the most studied elements, the technique can be used on around 40 different chemical elements<sup>28</sup>.

The qualitative and quantitative studies of both the valence and the coordination of iron were performed using <sup>57</sup>Fe Mössbauer spectroscopy. Mössbauer spectra were measured at 10K in a transmission geometry and constant acceleration mode. We chose to study brownmillerite at low temperature in order to have a better contrast between the contributions of the octahedral and tetrahedral iron sites. The velocity scale was calibrated with <sup>57</sup>Co in Rh matrix source and a metallic iron foil. The evaluation of the Mössbauer spectra was performed by the least-square fitting of lines using the WinNormos-for-Igor (version 7, Wissel) program. Experimental error for the <sup>57</sup>Fe Mössbauer spectra was ±0.1 mm.s<sup>-1</sup>.

#### 2.2.2 | XRD

XRD data were collected in previous studies<sup>3, 4</sup> using a powder X-ray diffractometer (D8 Advance, Bruker AXS, Karlsruhe, Germany) in the Bragg-Brentano geometry ( $\theta/\theta$ ) equipped with a copper tube. The instrument was operated in step-scan mode, between 5° and 90° (2 $\theta$ ) with 0.005° (2 $\theta$ ) per step and 1s per step. In order to minimize preferential orientation, the powder is “backloaded” by means of a special sample holder.

Phase identifications were performed using the DIFFRAC.EVA software (version 5, Bruker-AXS, Karlsruhe, Germany, 2010–2020). Rietveld refinements were performed using the TOPAS software (version 6, Bruker-AXS, Karlsruhe, Germany, 1999–2016) based on the fundamental parameters approach.<sup>29</sup> The starting structural data used for the phases are listed in TABLE 1. For the brownmillerite phase, the refined parameters were a strain parameter (referred to as strain G) and the occupancy factors of aluminum and iron on tetrahedral and octahedral sites.

**TABLE 1** Structural data for the brownmillerite phase. For each phase, the ICSD code (Inorganic Crystal Structure Database, web version 1.1.0) and the PDF number (International Centre for Diffraction Data (ICDD) PDF, release 2002) are given. The PDF numbers in brackets correspond to the experimental data.

Phase/mineral name	Formula	Symmetry	Space group	PDF file	ICSD	Reference
C <sub>4</sub> AF Brownmillerite	Ca <sub>2</sub> AlFeO <sub>5</sub>	Orthorhombic	<i>Ibm2</i> (46)	01-071-0667 (00-030-0226)	9197	20
C <sub>2</sub> F Srebrodolskite	Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	Orthorhombic	<i>Pcmm</i> (62)	01-071-2108 (00-038-0408)	14296	30

### 3 | RESULTS AND DISCUSSION

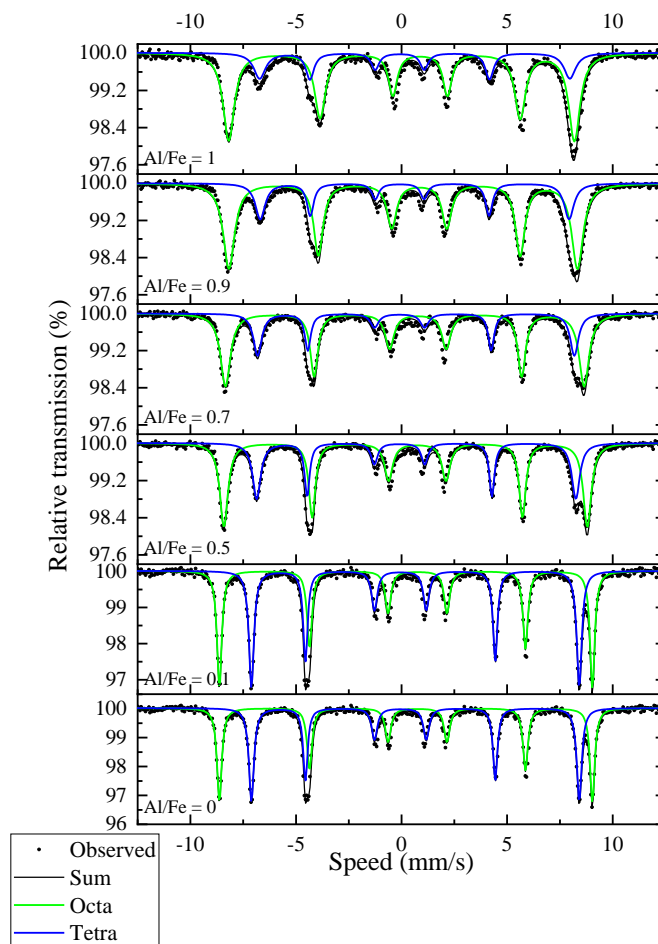
In brownmillerite, Fe<sup>3+</sup> and Al<sup>3+</sup> ions are distributed in the same atomic positions with either tetrahedral or octahedral site symmetry. The question is now to discuss the distribution of the two types of ions as a function of the Al/Fe ratio.

#### 3.1 | Synthetic brownmillerites

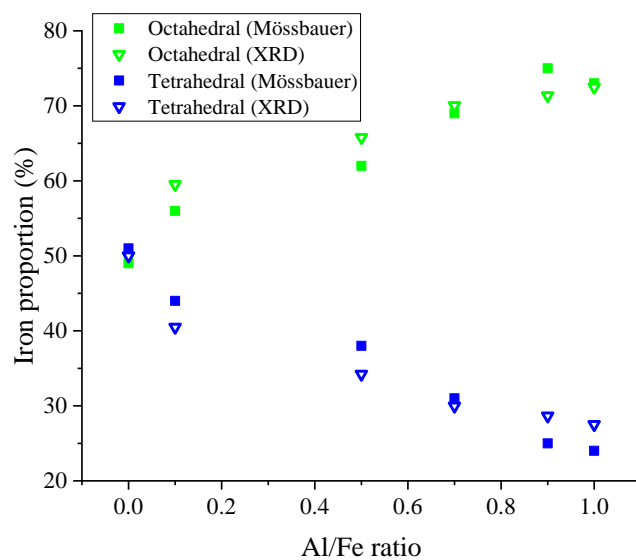
Mössbauer spectra of synthetic brownmillerites were recorded at 10K (FIGURE 2). At this temperature, brownmillerite is antiferromagnetically ordered, which splits the spectrum into sextuplets.

The hyperfine parameters and the XRD refinement parameters are given in TABLE 2. The typical values of Fe<sup>2+</sup> Isomer Shift (IS) are between 0.7 and 1.5 mm.s<sup>-1</sup>, which are far from the typical values of Fe<sup>3+</sup> Isomer Shift, from 0.1 up to 0.6 mm.s<sup>-1</sup>.<sup>28</sup> The difference of isomer shift between Fe<sup>3+</sup> and Fe<sup>2+</sup> is much higher than the measurement error of 0.1 mm.s<sup>-1</sup>, which confirms that iron only exists under the form Fe<sup>3+</sup> in our samples. The quadrupole splitting (QS) depends on the local environment of iron and allows us to distinguish between octahedral and tetrahedral sites. The hyperfine parameter values are similar to those in the literature.<sup>5, 14</sup> They are strongly linked to the iron proportion in crystallographic sites. TABLE 2 shows a decreasing of the isomeric shift (IS) and quadrupole splitting (QS) along with the iron proportion.

In the case of srebrodolskite (Al/Fe = 0), the iron ions are equally distributed between the two types of sites, as previously seen in <sup>7</sup>. With an increasing Al/Fe ratio, the iron content linearly increases in octahedral sites (FIGURE 3), until 70% of iron ions are in the octahedral site versus 30% in the tetrahedral sites, in line with the results of <sup>5, 14</sup>. Aluminum substitutes iron preferentially in tetrahedral site, increasing the iron fraction in octahedral site. This configuration, Fe<sup>3+</sup> in octahedral site and Al<sup>3+</sup> in tetrahedral site, minimizes the Gibbs free energy of brownmillerite, as shown by Tao et al.<sup>31</sup> The site populations were determined by Mössbauer spectroscopy using the ratio of the relative areas (designated as “I”) of each site contribution. Populations determined by Mössbauer spectroscopy are consistent with populations estimated by XRD.



**FIGURE 2** Mössbauer spectra of synthetic brownmillerites at 10K.



**FIGURE 3** Fraction of Fe in octahedral and tetrahedral sites for synthetic samples.

**TABLE 2** Isomer shift (IS), quadrupole splitting (QS), magnetic field (B) and relative areas (I) for synthetic brownmillerites at 10K; the occupation is also determined by XRD.

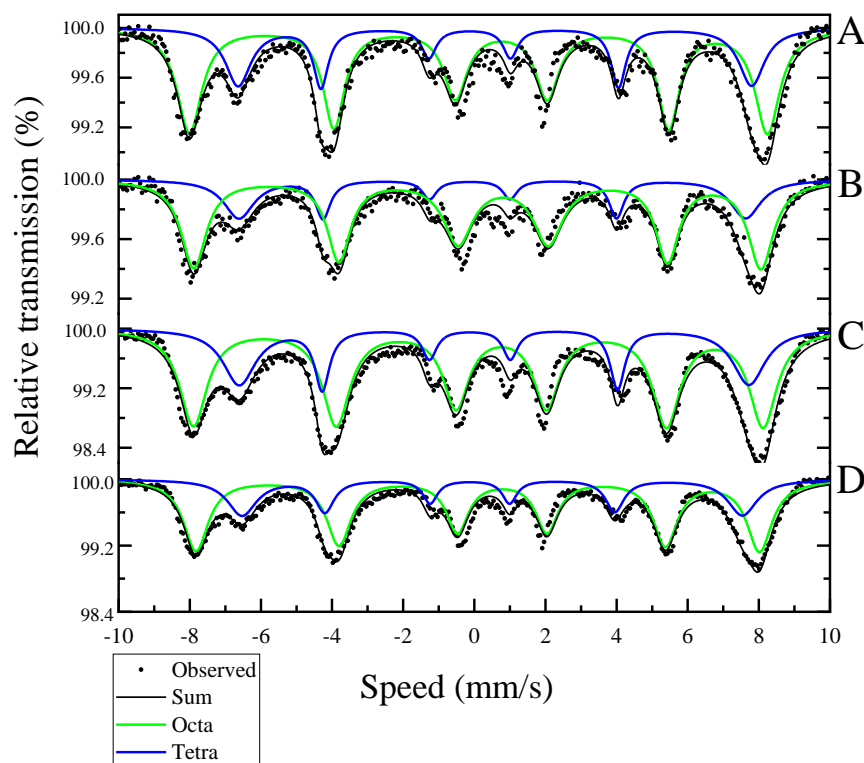
Al/Fe	Site	Mössbauer			XRD	
		IS (mm/s)	QS (mm/s)	B (T)	Occupation (% of iron)	
0	Octahedral	0.47	-0.54	54.8	49	50
	Tetrahedral	0.29	0.72	48.1	51	50
0.1	Octahedral	0.47	-0.57	54.4	56	60
	Tetrahedral	0.30	0.77	48.0	44	40
0.5	Octahedral	0.47	-0.55	53.4	62	66
	Tetrahedral	0.29	0.78	47.0	38	34
0.7	Octahedral	0.46	-0.62	52.5	69	70
	Tetrahedral	0.29	0.77	46.5	31	30
0.9	Octahedral	0.45	-0.76	51.2	75	71
	Tetrahedral	0.26	0.72	45.5	25	29
1	Octahedral	0.44	-0.87	50.9	73	72
	Tetrahedral	0.27	0.71	45.4	24	28

### 3.2 | Industrial brownmillerites

The Mössbauer spectra are deconvoluted in two sextuplets, which indicates that the iron ions are located in the two octahedral and tetrahedral crystallographic sites (FIGURE 4). Isomer shift values are typical of Fe<sup>3+</sup> ions.

The hyperfine parameters extracted from the data are reported in TABLE 3. Their values are in line with those in the Mössbauer literature on brownmillerite at low temperature.<sup>12, 15</sup> The values of the relative areas correspond to the occupancy estimated by Rietveld refinements, with a large majority of iron in the octahedral site (70%).

It can be seen that the quadrupole splitting of industrial brownmillerite is lower than that of synthetic samples for equivalent Al/Fe ratios. This phenomenon is due to the Si<sup>4+</sup> ions in the industrial brownmillerite which affect the spin state of Fe<sup>3+</sup> ions.<sup>10</sup>



**FIGURE 4** Mössbauer spectra of industrial brownmillerites at 10K.

**TABLE 3** Isomer shift (IS), quadrupole splitting (QS), magnetic field (B) and relative areas (I) for industrial brownmillerites at 10K; the occupation is also determined by XRD.

	Al/Fe	Site	Mössbauer				XRD
			IS (mm/s)	QS (mm/s)	B (T)	I (%)	Occupation (% of iron)
SAM A	0.71	Octahedral	0.45	-0.64	51	67	72
		Tetrahedral	0.22	0.68	45	32	28
SAM B	0.87	Octahedral	0.47	-0.72	50	72	75
		Tetrahedral	0.20	0.65	44	28	25
SAM C	0.69	Octahedral	0.45	-0.61	50	64	72
		Tetrahedral	0.23	0.64	44	36	28
SAM D	0.95	Octahedral	0.44	-0.66	50	64	74
		Tetrahedral	0.22	0.61	44	36	26

## 4 | CONCLUSION

This paper shows a high concordance in the determination of site populations of  $\text{Fe}^{3+}$  in calcium aluminoferrites, as derived from two independent analytical techniques: Mössbauer spectroscopy and XRD. The results also demonstrate the complementarity between Mössbauer spectroscopy and the conventional laboratory-based powder XRD technique. Two series of samples were studied: synthetic and industrial brownmillerite.

In the Al/Fe range between 0 and 1, each tetrahedral and octahedral site is statistically populated by either  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  ions. For synthetic brownmillerites, the percentage of iron located in each site varies linearly along with the Al/Fe ratio. For industrial brownmillerites, impurities probably affect the chemical environment of the iron site. Only  $\text{Fe}^{3+}$  was detected in industrial samples.

The need to extract the brownmillerite from other main phases of industrial clinker is the key factor for success of this kind of study of such complex multiphase material.

## 5 | ACKNOWLEDGMENTS

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