Technical Report

Quantitative Analysis of Compounds Causing Slag Expansion by Solid-state NMR

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Abstract

Steel slag is utilized as cement materials and base course materials. Since some compounds composed of steel slag cause slag expansion, reliable analytical techniques for the quantification of such compounds are strongly desired. In this report, a novel approach to the quantification method for compounds causing slag expansion is proposed by solid-state NMR. This method is applied to the quantification of ettringite in slow-cooled blast furnace slag and free magnesium oxide in steel making slag.

1. Introduction

Blast furnace slag and steel making slag are by-products produced massively in the iron and steel making process. To control the iron making process and the steel making process correctly, and to promote the reuse of slag, it is very important to analyze the chemical composition and the chemical structure of slag. In particular, to promote the effective use of blast furnace slag and steel making slag as a cement material and/or a subbase course material, it is very important to conduct with high accuracy the quantitative analysis of the compounds (i.e. ettringite in blast furnace slag and free lime (f-CaO) and free magnesia (f-MgO) in steel making slag) possibly contained in such slag that induce slag expansion.

Ettringite is a hydrate with the composition of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$, and is a compound that is involved in the initial hardening of a subbase course material and/or cement. The reason of the hydration swelling caused by ettringite is considered to be the expansion of boundaries of cement particles by the growth pressure of ettringite needle crystals.[1]

In steel making slag, f-CaO and/or f-MgO that were not molten in the refining process and remained unreacted in slag, and f-CaO and/or f-MgO that were crystalized during the cooling process of molten slag are present. Formation of calcium hydroxide $(Ca(OH)_2)$ and magnesium hydroxide $(Mg(OH)_2)$ by the hydration of these f-CaO and f-MgO induces volume expansion, which causes deformation and/or fracture of a formed body of slag occasionally.

A number of analytical methods have been proposed for quantifying ettringite, f-CaO and f-MgO contained in slag and cement. For quantifying ettringite, the solvent extraction method (ethylene glycol-methanol)[2,3], X-ray diffraction (XRD)[2,4–7] and thermogravimetry/differential thermal analysis (TG/DTA)[2] are used. As for f-CaO, the solvent extraction method (ethylene glycol)[8] is employed as the standard method in the iron and steel industry. As for f-MgO, the solvent extraction method (e.g. iodine-ethanol-ethylene glycol[9], acetic acid-methyl acetate[10], carbonate buffer solution[11]) and hydration reaction (light water and heavy water)[10,12,13] are employed.

The solvent extraction method is listed as commonly applicable to all the compounds described above. This is a method of conducting element analysis by solving only the object compound selectively. Quantification analysis by the solvent extraction method reveals that the obtained extraction ratio varies depending on the changes in slag particle size, extraction time and temperature. Accordingly, it becomes difficult to obtain the "true" values of the object compound contained in slag.

Therefore, it is important to analyze slag as it is in the solid state to solve the problems of solvent extraction methods. Application of the instrumental analysis method capable of measuring solid-state samples is considered to be effective. Although XRD is a comprehensive apparatus and is relatively easy to operate, and has been used for the quantification analysis of ettringite and f-MgO, it has a possible shortcoming that diffraction peak intensity changes depending on crystallinity and crystal orientation.

Then, attention was focused on the solid-state nuclear magnetic resonance (NMR) spectroscopy method. In principle, the ratio of peak intensity (integral) is proportional to the ratio of the number of atoms, and therefore, NMR provides quantitative information not dependent on the crystallinity and orientation of the compound. However, NMR sensitivity and spectral resolution strongly depend on target nuclides. This article reports the effectiveness and the is-

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sues of the application of solid-state NMR to the quantification of ettringite in slow-cooled blast furnace slag[14, 15] and f-MgO in steel making slag[16, 17].

2. Main Discourse

2.1 Experimental

2.1.1 Samples

Chemical compositions of Slag A (slow-cooled blast furnace slag) and Slag B (steel making slag) determined by fluorescence X-ray analysis are shown in **Table 1**. The internal standard samples of aluminum potassium sulfate dodecahydrate ($AlK(SO_4)_2 \cdot 12H_2O$) and magnesium silicide (Mg_2Si) for quantifying ettringite and f-MgO were purchased from Kanto Chemical Co., Inc. and Sigma-Aldrich Co. LLC respectively, and were used as they were. MgO and $Mg(OH)_2$ were purchased from Sigma-Aldrich, and were used as they were.

2.1.2 Solid-state NMR

The experimental conditions of solid-state NMR for the quantification analysis of ettringite in slow-cooled blast furnace slag and f-MgO in steel making slag are summarized in **Table 2**. ^{27}Al (spin $I=5/2$) and ^{25}Mg ($I=5/2$) were selected as the target nuclides for the quantification of ettringite and f-MgO, respectively. In the quantification of ettringite, dependence of the obtained signals on the external magnetic field strength (7.0–16.4 T) and on the MAS (magic angle spinning) rate (15–18 kHz) were examined.

2.2 Results and discussion

2.2.1 Quantification of ettringite in slow-cooled blast furnace slag

An ^{27}Al MAS spectrum of slag A with a small amount of $AlK(SO_4)_2 \cdot 12H_2O$ is shown in **Fig. 1**. Three main peaks accompanied by spinning side bands (SSB) are observed. The broad peak between 40–90 ppm is assigned to four-coordinated (tetrahedral) Al of the slag framework. The sharp peaks observed at 13.2 ppm and −0.2 ppm are due to six-coordinated (octahedral) Al of ettringite in slow-cooled blast furnace slag and $AlK(SO_4)_2 \cdot 12H_2O$, respectively. The difference in line width of these peaks is due to the difference in the quadrupolar coupling constant P_Q of ^{27}Al; P_Q of the slag framework is about 7–8 Hz, whereas that of ettringite and $AlK(SO_4)_2 \cdot 12H_2O$ are almost zero.

Figure 1 reveals the following two important findings.

(1) The peak of the slag framework and the peak of ettringite are completely separated owing to the difference in coordination numbers.

(2) Ettringite and $AlK(SO_4)_2 \cdot 12H_2O$ show very sharp peaks, and are completely separated from each other.

Based on the result of (1), because the ettringite peak can be observed without interference from any other peaks, the quantification of ettringite can be performed by comparing its integration value with that of an appropriate internal standard sample. When selecting an internal standard sample, to avoid interference from other peaks, and to enhance quantification accuracy, the selection of an internal standard sample is desirable that shows a sharp peak without influence of the second-order quadrupolar interaction. The result of (2) above shows the appropriateness of the selected $AlK(SO_4)_2 \cdot 12H_2O$ as the internal standard sample for quantifying ettringite in slow-cooled blast furnace slag.

Next, the optimization of ^{27}Al NMR experimental conditions was performed to enhance the accuracy of the quantification of ettringite. **Figure 2** shows ^{27}Al MAS spectra of slag A with a small amount of $AlK(SO_4)_2 \cdot 12H_2O$ with different external magnetic field strength. The MAS rate was fixed at 18 kHz. At 16.4 T, ^{27}Al peaks of the slag framework, ettringite and $AlK(SO_4)_2 \cdot 12H_2O$ are completely separated. However, the peak of the slag framework becomes broadened and the center of gravity of the peak approaches the peaks of ettringite and $AlK(SO_4)_2 \cdot 12H_2O$ (shifting to the lower frequency side) by decreasing the external magnetic field. This is because the line width and the deviation from the isotropic chemical shift are inversely proportional to the external magnetic field strength.[18]

On the other hand, the line width and the peak position of ettringite and $AlK(SO_4)_2 \cdot 12H_2O$ do not change in accordance with the change in the external magnetic field strength because the second-order quadrupolar interaction is negligible. Based on the above experimental result, a higher external magnetic field is desired to avoid the interference of the slag framework peak to quantify ettringite in a slow-cooled blast furnace by using solid-state ^{27}Al NMR.
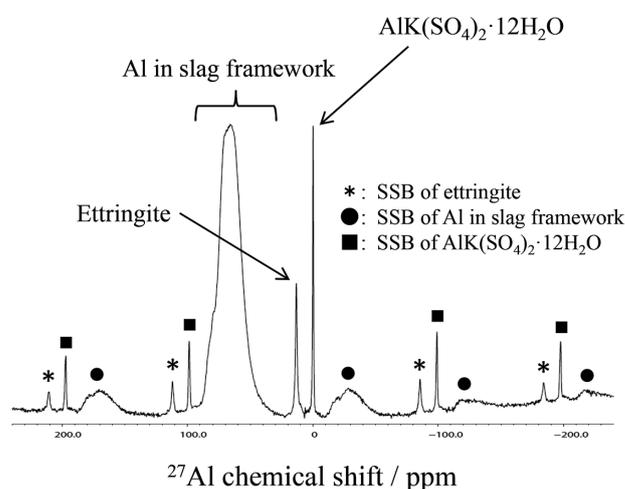

Fig. 1 ^{27}Al MAS spectrum of slag A with small amount of $AlK(SO_4)_2 \cdot 12H_2O$
External magnetic field: 16.4 T, MAS rate: 18 kHz, by permission of the Japan Cement Association[15]

Table 1 Chemical compositions of slag

(mass %)

	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3
Slag A	39.3	33.2	13.1	5.8	
Slag B	47.6	9.36	22.1	14.6	6.69

Table 2 Soild-state NMR parameters

Sample	Target	Nuclide	Magnetic field (T)	Resonant frequency (MHz)	Pulse sequence	MAS rate (kHz)	Flip angle (deg)	Pulse repetition time (s)	Experiment time (h)
Slag A	Ettringite	^{27}Al	7.0–16.4	78.11–182.30	Single pulse	15–18	18	0.5	0.2
Slag B	f-MgO	^{25}Mg	11.7	30.599	Single pulse	10	30	40	100

Following the above, dependence of the ^{27}Al spectrum on MAS rates was investigated (**Fig. 3**). SSBs were observed for all three peaks in a wide frequency range, caused by the first-order quadrupolar interaction. As SSBs are observed periodically at the positions apart from the main peak by integer time of the MAS rate, they approach more closely to main peaks with the decrease in the MAS rate. As shown in Fig. 3, when the MAS rate becomes lower than 17 kHz, the first SSB (SSB nearest to the main peak) of $AlK(SO_4)_2 \cdot$
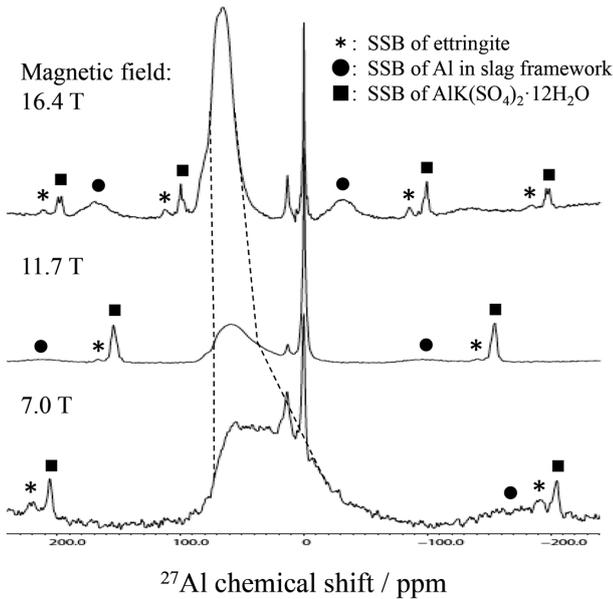

Fig. 2 ^{27}Al MAS spectra of slag A with small amount of $AlK(SO_4)_2 \cdot$ 12H$_2$O with different external magnetic field strength
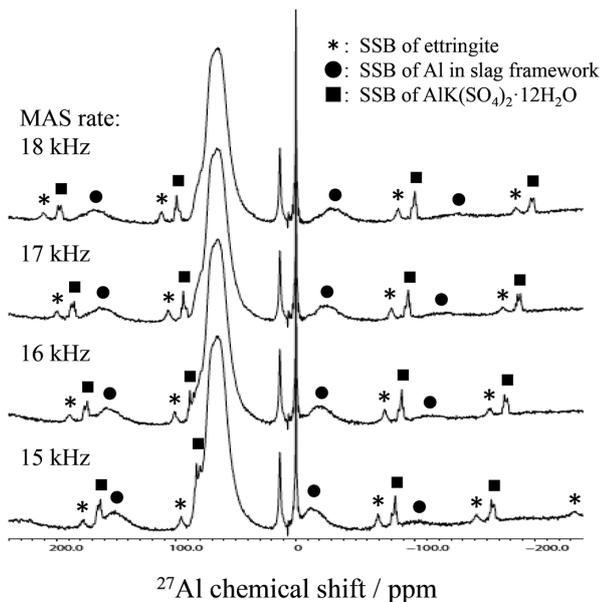MAS rate: 18 kHz, by permission of the Japan Cement Association[15]

Fig. 3 ^{27}Al MAS spectra of slag A with small amount of $AlK(SO_4)_2 \cdot$ 12H$_2$O with different MAS rate
Magnetic field: 16.4 T, by permission of the Japan Cement Association[15]

12H$_2$O on the high frequency side is overlapped by the main peak of the slag framework, making it difficult to obtain a highly reliable quantified value under 16.4 T. In actual measurement, depending on the applied external magnetic field strength, it is important to select the MAS rate in such a way that will not allow all observable peaks including SSB to interfere or be interfered with mutually.

As described above, based on the ^{27}Al NMR spectrum obtained under an optimized measurement condition (e.g. Fig. 1), ettringite in slag can be quantified according to the following formula (1).

Ettringite (mass%) = 50 $(W_{ref}/W_{sample}) (M_{ett}/M_{ref}) (S_{ett}/S_{ref})$ (1)

Where W_{ref} is the weight of $AlK(SO_4)_2 \cdot 12H_2O$ (g),

W_{sample} is the weight of slag (g),

M_{ett} is the molecular weight of ettringite (=1 255.11) (g/mol),

M_{ref} is the molecular weight of $AlK(SO_4)_2 \cdot 12H_2O$ (=474.39),

S_{ett} is the integral of ettringite peak including SSBs (arbitral unit),

S_{ref} is the integral of $AlK(SO_4)_2 \cdot 12H_2O$ peak including SSBs (arbitral unit).

In the case of Slag A (W_{sample}=64.24 mg, W_{ref}=2.90 mg, S_{ett}=40.52 and S_{ref}=60.83) shown in Fig. 1, ettringite concentration was calculated as 3.98 mass%. It was confirmed that this method (^{27}Al NMR) provided highly reliable ettringite concentration in the range of 0.3–10 mass% by comparison of the calculated value using formula (1) with nominal concentration.[15]

2.2.2 Quantification of f-MgO in steel making slag

When quantifying f-CaO in steel making slag by the ethylene glycol extraction method, the obtained value is the sum of CaO and Ca(OH)$_2$. Therefore, to quantify only CaO that induces expansion, the combination with other techniques (e.g. thermogravimetry analysis) is needed.[8] Therefore, whether MgO and Mg(OH)$_2$ can be separately quantified was investigated in the ^{25}Mg NMR spectrum. **Figure 4** shows a ^{25}Mg MAS spectrum of the mixture with MgO : Mg(OH)$_2$=1:1 (molar ratio). The very sharp peak observed at 26.4 ppm is derived from MgO. Since MgO has a cubic crystal structure with high structural symmetry, P_Q is negligible and the sharp symmetric peak is obtained without influence of the second-order quadrupolar interaction.

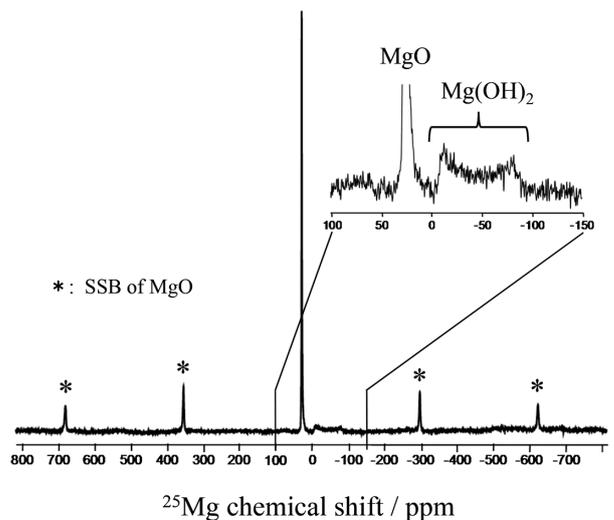On the other hand, as P_Q of Mg(OH)$_2$ is about 3.0 MHz,[19–21]

Fig. 4 ^{25}Mg MAS spectrum of the mixture with MgO: Mg(OH)$_2$=1:1 (molar ratio), by permission of the Iron and Steel Institute of Japan[17]

$Mg(OH)_2$ displayed a typical second-order quadrupolar line shape. The peak intensity of $Ca(OH)_2$ is considerably weak in spite of the high concentration of 59.1 mass% (50 mol%) because the peak of $Ca(OH)_2$ is very broad. For the real slag samples containing much lower $Ca(OH)_2$ concentration than Fig. 4, the $Mg(OH)_2$ peak is buried in spectral noise. As a result, the MgO peak is selectively observed.

Although other Mg-containing compounds (e.g. $CaMgSi_2O_6$) are present in steel making slag, these compounds are also affected by the second-order quadrupolar interaction of ^{25}Mg as with MgO, showing very broad peaks. Therefore, the MgO peak in slag can be observed without interference from other peaks.

The idea of quantifying f-MgO in steel making slag by solid-state NMR is fundamentally the same as that of quantifying ettringite in slow-cooled blast furnace slag as shown in 2.2.1. f-MgO can be quantified by comparing the peak integral of MgO to that of the internal standard sample. An internal standard sample that shows the sharp peak is preferable for precise quantification of f-MgO. Mg_2Si and MgS were found as appropriate for the internal standard sample. These compounds exhibited sharp peaks at the positions (frequency) apart from the peak of MgO.

f-MgO concentration is calculated from formula (2).

$$MgO (mass\%) = 100 R (W_{Ref}/W_{Slag}) (M_{MgO}/M_{Ref}) (S_{MgO}/S_{Ref}) \quad (2)$$

Where R is the molar number of the Mg atom present in 1 mol of the internal standard sample (2 for Mg_2Si, 1 for MgS),

W_{Slag} is the weight of slag (g),

W_{Ref} is the weight of the internal standard sample (g),

M_{Ref} is the molecular weight of the internal standard sample (g/mol),

M_{MgO} is the molecular weight of MgO (=40.305) (g/mol),

S_{Ref} is the integral of the internal standard sample peak including SSBs (arbitral unit),

S_{MgO} is the integral of the MgO peak including SSBs (arbitral unit).

In the actual measurement of steel slag, due to the influence of the magnetic substance such as Fe in the slag, it become difficult for stable sample spinning in the NMR magnet. To solve this problem, dilution of the sample with a non-magnetic substance like NaCl is effective. However, this reduces the amount of slag filled in the test tube and causes deterioration in sensitivity.

A ^{25}MAS spectrum of Slag B added with a small amount of Mg_2Si as an internal standard sample and diluted with NaCl is shown in **Fig. 5**. The main peak assigned to MgO is observed with SSBs, indicating the presence of f-MgO in Slag B. In the case of Slag B (W_{Slag}=422.04 mg, W_{Ref}=10.08 mg, M_{Mg_2Si}=76.696, S_{MgO}/S_{Ref}=2.97) shown in Fig. 5, the f-MgO concentration was calculated as 7.5 mass%, corresponding to 51% to total Mg concentration (Table 1).

Furthermore, likewise the case in 2.2.1, pertaining to a sample made of a free-of-MgO matrix added with a reagent MgO to a prescribed concentration and added with Mg_2Si, by comparing the quantified value of MgO obtained from the result of ^{25}Mg MAS spectrum with the prescribed MgO concentration, the validity of the quantified value obtained by this method was examined. As matrix, Fe-free model slag ($40CaO-40SiO_2-10MgO-10Al_2O_3$ glass) in which f-MgO does not exist was used. It was confirmed that this method provides high quantification accuracy in the MgO concentration range of below 5 mass%.[17]

In addition, as to other steel slag, the quantified value of f-MgO obtained by this method was compared with the results obtained by
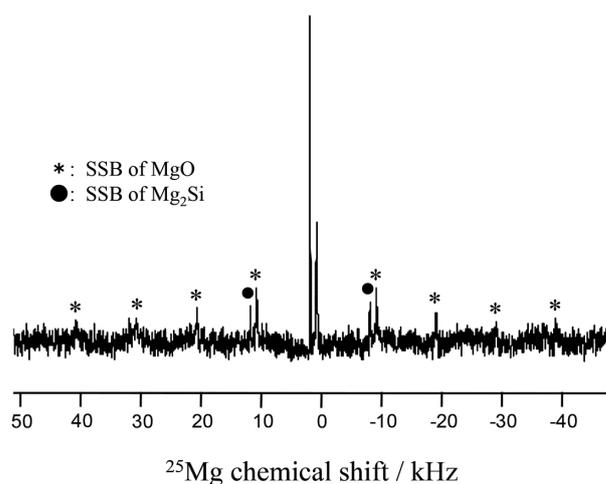

Fig. 5 ^{25}Mg MAS spectrum of the slag B with Mg_2Si and NaCl, by permission of the Iron and Steel Institute of Japan[17]

conventional analysis methods. Both of the quantified values obtained by the carbonate buffer solution extraction method and acetic acid extraction method stayed below the quantified value obtained by solid-state-NMR, the relative values of which were 26.5–61.7 %.[17] This is probably because, in the above solvent extraction methods, f-MgO enclosed in slag particles (not exposed on the surface of slag particles) has not been sufficiently extracted. On the other hand, solid-state NMR is capable of detecting entire f-MgO regardless of whether they stay inside or outside of a slag particle.

3. Conclusion

Novel techniques for quantifying the compound of ettringite and f-MgO in slag that induce slag-expansion have been established by using solid-state NMR. When quantifying ettringite and f-MgO, although the target nucleus for NMR measurement differs (^{27}Al and ^{25}Mg, respectively), the idea of quantification is common. Although ^{27}Al and ^{25}Mg are both of quadrupole nuclei, the ^{27}Al peak of ettringite and ^{25}Mg peak of MgO show very sharp signals because of high symmetry of the crystal structure. Therefore, by selecting an appropriate internal standard sample that also exhibits a sharp peak, quantification of ettringite and f-MgO based on the peak integral ratio becomes possible. When quantifying ettringite contained in slow-cooled blast furnace slag, within less than ten minutes, a peak with a high signal/noise ratio (S/N) can be obtained. However, to separate the peak derived from the slag framework from the ettringite peak, optimization of the external magnetic field strength and MAS rate is required.

In particular, the peak of the slag framework under a low magnetic field is broadened and overlaps the ettringite peak, therefore, measurement under a relatively high magnetic field is required. On the other hand, in the quantification of f-MgO in steel making slag, as the sensitivity of ^{25}Mg is quite low as compared to that of ^{27}Al, the broad peaks of Mg-bearing compounds are not detected due to poor sensitivity. Accordingly, measurement under a low magnetic field is possible as there's no interference of other peaks. However, in many cases, wherein dilution with a non-magnetic substance is required to avoid the influence of the magnetic substance present in steel making slag, and to improve the S/N ratio as well, measurement under a high magnetic field and/or with the use of a large-diameter sample rotor are desired. In particular, the latter case is effec-

tive not only from the viewpoint of improving sensitivity, but also from the viewpoint of reducing the variation of quantified values due to heterogenous slag structures and compositions.

Although the quantification method by solid-state NMR can overcome the problems of solvent extraction methods, solid-state NMR (with high magnetic field in particular) is not a versatile method. Especially, in the quantification of f-MgO in steel making slag, as the sensitivity is very low and several days are needed for measurement, it is considered that this method can be effectively used to confirm true values and is helpful in the pursuit of other more comprehensive analysis methods.

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