

Analytical Technologies for Steel Slag

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Abstract

Analysis of steel slag is significant to control the steelmaking process and to maintain/expand the ways to reuse steel slag firmly. Especially to create new features for the steel slag, the chemical characteristics should be revealed. For that purpose, information about not only chemical composition and elution analysis of trace elements, but also chemical structure of steel slag is required. We NSSMC have established a series of techniques to analyze chemical structure of steel slag by using Nuclear Magnetic Resonance spectroscopy (NMR) and Fourier-Transform Infrared spectroscopy (IR). To elucidate the relationship between the chemical structure and actual physical (and chemical) properties of steel slag, e.g. expansibility and alkaline pH, provides quantitative understanding of the characteristic features of steel slag.

1. Introduction

In the steelmaking process, it is not only necessary to purify the molten steel but also to accurately grasp and control the composition of steel slag in order to properly monitor and control the refining reaction and meet the quality requirements of the customer. To that end, it is indispensable to rapidly analyze the chemical composition of steel slag. In addition, because positive efforts have been made to effectively utilize steel slag as a raw material for cement, aggregate, roadbed material, etc., it is important to conduct a thorough quality control of the steel slag before shipment, which includes appropriate analyses of steel slag for management and conservation of the environment, as a social responsibility of all steelmakers, including Nippon Steel & Sumitomo Metal Corporation.

On the other hand, in view of the changing steel slag supply-demand structure reflecting various recent changes in the social situation, it is necessary to continue the development of technologies for finding new uses of steel slag. In this context, in addition to the analysis of steel slag chemical composition and environmental management mentioned above, a quantitative analysis of the crystal structure, or the chemical state, that determines the properties of steel slag needs to be conducted to clarify why and how many of the physical properties of steel slag manifest themselves. In this technical report, we shall describe the representative analysis methods and quality control of steel slag that are employed at Nippon Steel & Sumitomo Metal and its affiliated companies, together with our newly-developed analytical methods for studying the chemical state

of steel slag.

2. General Methods of Analysis of Steel Slag for Quality Control and Environmental Management

2.1 Method of composition analysis for controlling the steelmaking process

In the analysis conducted at the steelmaking site for feeding back the chemical composition, basicity, etc. of the steel slag to the process, X-ray fluorescence spectrometry (XRF)¹⁾ that enables analysis in the solid phase is widely employed because of its speed and simplicity. The slag sample for XRF analysis is prepared by the powder briquette method in which the slag is dried and ground into coarse and fine powders, which are then press-formed into specimens of suitable size. With this method, the analysis takes only about 15 minutes from specimen preparation to the preparation of the analysis report. Therefore, the XRF is used as a very effective and efficient tool for process control.

It should be noted that in the XRF analysis the information about the chemical composition is given in the form of signals from the individual elements detected. For denoting the chemical composition of a specific slag sample, it is a common practice to show the content of each component element converted in terms of equivalent oxides, because it is difficult to detect oxygen by XRF due to its light weight. In addition, when analyzing trace elements, it is necessary to reduce background noise and correct the measurements using a suitable coexisting element. It is also possible to apply the fun-

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damental parameter method for quantitative analysis, in which the X-ray intensity is theoretically calculated with due consideration given to its absorption and excitation effects by using the appropriate measuring conditions and fundamental parameters are compared with the measured X-ray intensity.

2.2 Method of analysis for controlling the product shipment

For the use of steel slag, quality requirements of slag are determined in various standards as “environmentally sound qualities” with special attention paid to the environmental impact of slag in specific applications and under specific ambient conditions. Nippon Steel & Sumitomo Metal ships slag products that meet all these quality requirements and standards. There are established methods for the composition analysis of slag aggregate for concrete²⁾ and blast furnace slag fine powder for concrete.³⁾ When steel slag is used, the composition of effluent from the slag becomes a problem because it can adversely affect the quality of groundwater, etc. Incidentally, it is known that steel slag, which remains in molten state under high temperatures, contains little amounts of harmful organic chlorides and elements with low boiling point (Hg, As, Cd, etc.). Therefore, in the steel slag standards used in civil engineering works,⁴⁾ for example, only five species, i.e., Pb, Cr⁶⁺, Se, F, and B, are specified as environmentally hazardous.

When a steel slag product is used in a land area, its environmental safety is evaluated by the elution test specified in the Quality Standards for Soil Environment. As an analysis method applied to steel slag, the elution test method prescribed in JLT (Japanese Environmental Agency)-46 can be cited. The test procedure is as follows. First, dry and crush the sample. Next, pass it through a sieve with a mesh 0.5 to 2 mm. Then, mix the crushed sample in a solvent (pure water added with hydrochloric acid to obtain a solution of pH 5.8 to 6.3) in such a manner that the mass/volume ratio of the sample becomes 10% and the volume of the mixed liquid is 500 ml or more. Using a shaker (shaking frequency: 200 times/min, shaking stroke: 4 to 5 cm), continuously stir the mixed liquid at room temperature for six hours. After that, the composition of elute in the test solution is analyzed.⁵⁾

Another method of analysis prescribed in JLT-19 is based on an elution test presupposing the risk of taking in a specific hazardous substance. In this method, the extraction solvent differs according to the target element to be extracted. When the target element is fluorine, for example, the sample and the solvent (1 mol/l HCl) are mixed in a mass/volume ratio of 3%, and then the mixture is shaken (shaking frequency: 200 times/min, shaking stroke: 4 to 5 cm) at room temperature for two hours. The solution is left undisturbed for 10 to 30 minutes and then filtered to obtain the test liquid. In case the target element is Cr⁶⁺, alkali buffer solution is used as the solvent for elution, although the elution method and the procedure for test liquid preparation are the same as with fluorine.

In 2005, analytical methods exclusively applicable to slags were included in JIS.⁶⁾ Specifically, an elution test based on the tank leaching method was prescribed. In this method, the sample is immersed in the solvent (pure water added with hydrochloric acid to obtain a solution of pH 5.8–6.3) in a mass/volume ratio of 10%. The solution is stirred with a stirring blade at a rate of 200 rpm for six hours. Then, the liquid solvent is filtered and the environmentally hazardous substances in the eluate are analyzed. The abovementioned JIS also prescribes the elution method based on Quality Standards for Soil Environment (JLT-46) and the analytical method for the contents of target elements (JLT-19). Roadbed materials are analyzed by the abovementioned analytical method.⁷⁾

When a steel slag product is used in a sea area or on reclaimed ground, the elution test method prescribed in JLT-14 is applied to ensure that product safety is evaluated in accordance with the Japanese sediment quality guidelines based on the Marine Pollution Prevention Law. Slag disposal by landfill is subject to the elution test prescribed in JLT-13 in accordance with “the method of testing metals, etc. contained in industrial waste specified in the Waste Disposal and Public Cleansing Law” applied to “the cinder, sludge, slag, soot, or dust, or any other material treated to dispose such industrial waste that is to be disposed of by landfill or the inorganic sludge to be dumped into the sea.”

Nippon Steel & Sumitomo Metal controls the qualities of its slag products using the appropriate analytical methods specified in various standards with special emphasis on environmental protection to only ship the slag products that can be used safely and securely.

2.3 Analysis method for understanding the chemical state of steel slag

Steel slag contains various types of elements. As mentioned in 2.1, the analysis results obtained by XRF represent the concentration of each component element converted to their respective oxides. In many cases, each of the component element forms a composite oxide, which is expected to vary in chemical state according to differences in the refining process and cooling treatment. In addition, depending on the condition of slag application, the physical properties of certain component elements change as they undergo hydration and/or carbonation. The physical and chemical properties of steel slag itself are significantly influenced not only by the chemical composition of the slag but also by the crystallinity of slag and the type of mineral phase formed. To grasp and control the properties of steel slag and widen the application scope of steel slag, it is indispensable to understand the chemical state of steel slag.

For identifying the crystal phase of air-cooled blast furnace slag and steelmaking slag, X-ray diffraction (XRD) is a simple and effective method. However, when the slag contains more than one composite oxide, the identification is not always easy because of overlapping diffraction angle. The micro chemical structure of slag is estimated via elemental analysis using a scanning electron microscope or an electron-beam microanalyzer or by examining the X-ray absorption fine structure. Granulated blast furnace slag or any other slag that rapidly cools in the manufacturing process is vitreous and solidifies easily. With XRD, therefore, it is difficult to obtain detailed information about the chemical structure of the slag because the diffraction pattern becomes wide. Therefore, nuclear magnetic resonance spectroscopy (NMR) with ²⁷Al or ²⁹Si as the target is used to clarify the chemical structure of slag. For example, it has been noted that ²⁷Al in simulated granulated slag exists in the form of four coordinated oxygen.⁸⁾ In regards to technology development utilizing NMR positively, an example is given in 3.1.

The species that have been attracting attention as the targets of chemical state analysis are free-CaO (f-CaO),⁹⁾ which are simple calcium oxide (CaO) existing as an unreacted oxide in steelmaking slag, and/or crystallized or precipitated from calcium oxide compounds in the cooling process. These species are important indexes of the degree to which the input lime is slagged in the refining reaction. However, for using steelmaking slag as a roadbed material, earthwork material, etc., f-CaO poses a difficult problem because it is highly alkaline and becomes nearly double in volume because of the hydration reaction ($\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2$). Therefore, determining its content is very important from the standpoint of properly controlling steel slag.

For the determination of f-CaO, the tribromophenol and the ethylene glycol extraction methods have long been used,¹⁰⁻¹³⁾ although the latter method is used more widely. First, a uniformly sized slag sample is put into ethylene glycol solvent for extracting f-CaO at a certain temperature for a certain time. Then, Ca concentration in the filtrate is determined by atomic absorption spectrometry or ICP atomic emission spectroscopy. With this method, however, the result of determination varies widely from laboratory to laboratory or from one steel slag sample to another. For the steel industry to solve this problem, the Iron and Steel Institute of Japan, with the support of Nippon Slag Association, organized a society for the “standardization of technology for characterization of f-CaO in steel slag,” which strove to standardize the analytical method for obtaining highly accurate results for the period 2008–2012. The society first identified the problems involved in the conventional analytical methods; not only CaO but also a part of Ca(OH)₂ is extracted at the same time and the result of analysis depends more or less on the particle size of the slag and the duration of extraction and filtration. Finally, the society standardized the method of analysis for f-CaO (it prepared a written analytical procedure as the method recommended by the Iron and Steel Institute of Japan), thereby reducing the variation of analysis result from one steelmaking plant to another.¹⁴⁾

3. Development of Technology for Evaluating Steel Slag

In this section, examples of the steel slag analytical techniques developed by Nippon Steel & Sumitomo Metal are presented. The company has been paying attention to the chemical state of steel slag for long. For example, for solving the problem of yellow water caused by sulfur (S) elution to the environment from air-cooled blast furnace slag, the company developed a method of quantitative analysis for each of the chemical states of sulfur, i.e., S⁰, S in thiosulfuric acid, and S in sulfuric acid in air-cooled blast furnace slag.¹⁵⁾ Now, we shall describe in a topical manner the analytical techniques the company has developed in recent years.

3.1 Quantitative analysis of hydrate in air-cooled blast furnace slag by using NMR

Air-cooled slag used as a roadbed material (hydraulically and mechanically stabilized slag, HMS) is required to have a certain level of strength, which is secured by hydration, i.e., the reaction between steel slag and water. Therefore, we considered it necessary to have a method of quantitative analysis of hydrates, specifically ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O). Hence, we established a new analytical method using NMR.¹⁶⁾ Ettringite is a hydrate that aids in the initial hardening of a roadbed material and cement. To predict the strength of the material and the possibility of cracking and other harmful effects of excessive hydration, it is necessary to implement the quantitative analysis of ettringite.

With NMR, it is possible to obtain: (1) information regarding chemical state by element (nuclide), (2) local information at the molecular level, and (3) information regarding chemical state of the entire sample. Thus, the quantitative analysis using NMR has these advantages: information on only the target element can be extracted from steel slag comprising multiple elements; the chemical state of even vitreous materials can be analyzed; and the chemical states of both the exterior and interior parts of the material can be detected. Among the nuclides making up ettringite, ⁴³Ca, ²⁷Al, ³³S, and ¹⁷O have a nuclear spin that can be measured by NMR. However, with the exception of ²⁷Al, the natural abundance of those nuclides is so low that the detection of their chemical shifts is almost impossible

with NMR. Therefore, determining ettringite with these three nuclides is virtually impossible.

On the other hand, because ²⁷Al has the natural abundance of 100%, it allows a high-sensitivity measurement. It should be noted, however, that like the other three nuclides, ²⁷Al has a quadrupolar nucleus (i.e., nucleus whose nuclear spin is other than 1/2) and hence, there is a possibility that the peak of spectrum measured widens because of the secondary interaction between quadrupolar nuclei, which makes it difficult to detect ²⁷Al. Moreover, if the peak of the ²⁷Al NMR spectrum obtained from the ettringite overlaps with a peak attributed to the Al of some other chemical states, it becomes difficult to accurately determine ettringite.

Therefore, to accurately determine ettringite using ²⁷Al NMR, author et al. considered it important to: (1) clarify the degree of peak widening caused by the interaction between quadrupolar nuclei, (2) ensure that the ettringite peak does not overlap with the matrix peak, and (3) use an Al-containing compound giving a unique peak as the internal standard test specimen for both the ettringite and matrix. **Figure 1** shows the ²⁷Al magic-angle-spinning (MAS) NMR spectrum for aged air-cooled blast furnace slag added with a suitable amount of potash alum (AlK(SO₄)₂·12H₂O). It can be seen that Al in the blast furnace slag framework shows a peak at 60–70 ppm due to four coordination. It can also be seen that the peak is asymmetrical and very wide as a result of the secondary interaction between quadrupolar nuclei mentioned above.

On the other hand, ettringite shows a very sharp peak at approximately 13 ppm. The Al in ettringite six-coordinated (each Al atom is surrounded by six O atoms). Therefore, it shows a peak in a region of chemical shift different from that for the peak of four-coordinated Al in the slag framework. In addition, because the structure around Al has a solid symmetry, Al shows a sharp and symmetric peak without being influenced by the secondary interaction between quadrupolar nuclei. Therefore, the abovementioned two peaks do not overlap. As an internal standard test specimen for the determination of ettringite, author et al. studied potash alum. Consequently, potash alum was found to be a suitable internal standard test specimen for NMR analysis, because it shows a very sharp peak as ettringite and the peak does not overlap with the peaks of slag framework and ettringite.

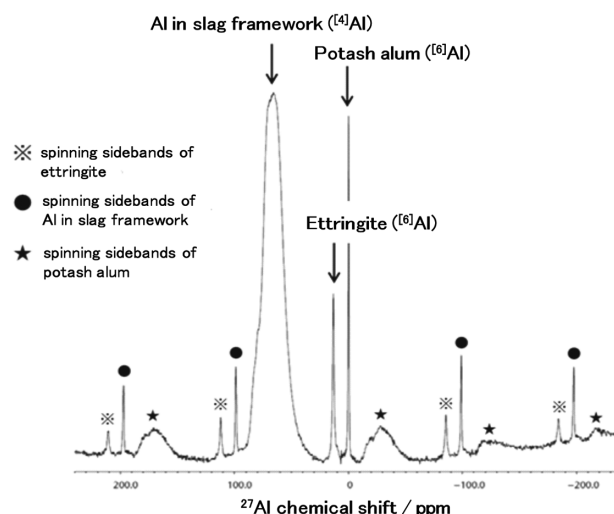


Fig. 1 ²⁷Al MAS NMR spectra for the mixture of steel slag and potash alum

Then, author et al. optimized the static magnetic field intensity and specimen rotating speed for accurate determination of ettringite. As a result, for example, it was found that the specimen rotating speed needs to be set at 17 kHz or more (for measurement with 16.4 T). In actual determination, the amount of ettringite in slag can be calculated using the following equation.

$$\begin{aligned} & \text{Ettringite in slag (mass\%)} \\ & = 50 \cdot (W_{\text{alum}}/W_{\text{slag}}) \cdot (M_{\text{ett}}/M_{\text{alum}}) \cdot (S_{\text{ett}}/S_{\text{alum}}) \end{aligned} \quad (1)$$

where W_{alum} and W_{slag} denote the mass (g) of potash alum and the mass (g) of slag, respectively, each is put in a solid NMR specimen tube, M_{ett} and M_{alum} are the molecular weight (g/mol) of ettringite and potash alum, respectively, and S_{ett} and S_{alum} are the integral intensity, considering the intensity of spinning sidebands at the peak in ^{27}Al NMR spectrum for ettringite and potash alum, respectively.

For validating the determination of ettringite in slag using the abovementioned method, the author et al. performed an NMR determination using reagent-based mixed specimens—several types of matrices with each added with pure ettringite of prescribed concentration—and compared the measured ettringite concentrations with the nominal concentration. The results are shown in Fig. 2. The horizontal axis represents the nominal concentration of ettringite and the vertical axis shows the concentration of ettringite obtained by NMR. The nominal and measured concentrations show an almost linear relationship. Thus, it was confirmed that as long as the concentration of ettringite is within 0.3–10 mass%, the determination by NMR is sufficiently reliable.

As another method of determining ettringite, the powder XRD method has been known and employed by Nippon Slag Association. In this method, several levels of mixtures—the specimen added with varying amounts of ettringite—are subjected to XRD and an analytical curve showing the relationship between the integral intensity of (100) diffraction peak of ettringite is observed in the neighborhood of $2\theta = 9^\circ$, and the concentration of ettringite added is prepared (standard addition method). With this method, it is possible to easily determine ettringite even when its concentration in the specimen is unknown. It should be noted, however, that the diffraction peak intensity in XRD varies with particle size and crystal orientation of the specimen. In contrast, NMR is a highly reliable determination method because it is, in principle, an absolute quantification method.

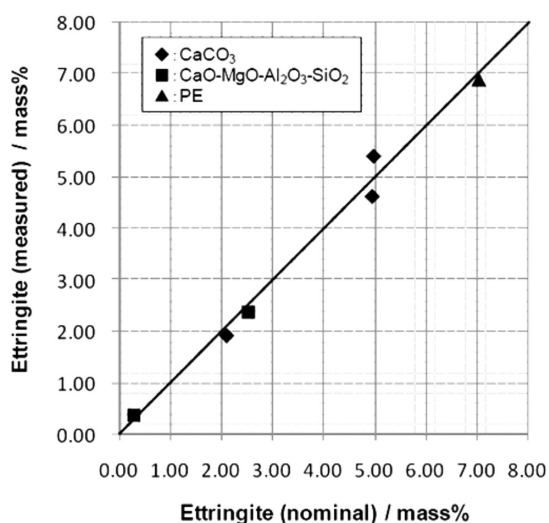


Fig. 2 Relationship between nominal and measured concentration of ettringite in a variety of matrix

3.2 Quantitative analysis of f-CaO and f-MgO in steel slag

The importance of analysis of f-CaO in steelmaking slag was explained in section 2.3. On the other hand, in the application of steelmaking slag in a land area, free magnesium oxide (f-MgO) which behaves like f-CaO is also important. At present, however, there are no standard methods of analysis for f-MgO. Therefore, it is urgent to establish a reliable method of f-MgO analysis in steel slag.

First, in an infrared (IR) absorption spectrum, we obtain constant k for the oscillatory force of O-H of $\text{Ca}(\text{OH})_2$ from the frequency (wavenumber) ($= 3643 \text{ cm}^{-1}$) of O-H of $\text{Ca}(\text{OH})_2$ and $m_1 = 16(\text{O})$ and $m_2 = 1(\text{H})$. Next, using k we calculate the frequency of O-D of $\text{Ca}(\text{OD})_2$. The frequency is calculated to be 2651 cm^{-1} . In the same manner, calculate O-D of $\text{Mg}(\text{OD})_2$ from O-H ($= 3696 \text{ cm}^{-1}$) of $\text{Mg}(\text{OH})_2$. The frequency of O-D is found to be 2689 cm^{-1} . Thus, both are expected to show an isotope shift of about 1000 cm^{-1} . Therefore, an attempt was made to obtain deuterates by reacting heavy water (D_2O) with CaO and MgO and analyze them separately from hydrates.^{17, 18)}

The reagents used were: 99.9% CaO of Wako Pure Chemical, special-grade $\text{Ca}(\text{OH})_2$ of Wako Pure Chemical, special-grade MgO (heavy) of Wako Pure Chemical, 95+% $\text{Mg}(\text{OH})_2$ of Wako Pure Chemical, deuterium oxide D_2O (99.9 atom% D) of Isotech, and H_2O for high-speed liquid chromatography of Wako Pure Chemical. CaO and MgO were first heated to 1000°C in argon atmosphere and then cooled to normal temperature. Immediately after that, they were immersed in D_2O and H_2O . $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ were directly immersed in D_2O and H_2O , respectively. All the specimens were recovered by filtration after immersing for 24 hours. They were then vacuum-dried at 100°C for two hours. The KBr disk method was used to measure IR spectra. Each specimen weighing 0.5 mg was mixed with 300 mg KBr to prepare a disk. To evaluate the degrees of hydration, thermogravimetric (TG) equipment was used. The conditions for TG measurement were: temperature range: 40°C to 1000°C , heat-up rate: $10^\circ\text{C}/\text{min}$, and atmosphere: argon 200 ml/min.

Figure 3 shows the IR spectra obtained with CaO and $\text{Ca}(\text{OH})_2$ which were first immersed in H_2O and D_2O , respectively, and then dried. For CaO and $\text{Ca}(\text{OH})_2$ immersed in H_2O , an O-H stretching vibration of $\text{Ca}(\text{OH})_2$ is observed at 3643 cm^{-1} . For CaO immersed in D_2O , an O-D stretching vibration of $\text{Ca}(\text{OD})_2$ is observed at 2685 cm^{-1} . In addition, O-H is slightly observed because of the residue of $\text{Ca}(\text{OH})_2$ caused by insufficient preliminary dehydration or the hydration of $\text{Ca}(\text{OH})_2$ in air during the treatment after dehydration. For $\text{Ca}(\text{OH})_2$ immersed in D_2O , an O-D peak is observed at 2685 cm^{-1} probably because $\text{Ca}(\text{OH})_2$ was partly replaced by OD in D_2O . In all the spectra, (a)–(d), the absorption of CO_3^{2-} is observed at 1460 – 1440 cm^{-1} . This is considered to have come from basic carbonate.

Figure 4 shows the IR spectra obtained with MgO and $\text{Mg}(\text{OH})_2$ which were first immersed in H_2O and D_2O , respectively, and then dried. When MgO is immersed in H_2O , $\text{Mg}(\text{OH})_2$ is formed. When it is immersed in D_2O , $\text{Mg}(\text{OD})_2$ is formed. The O-D of $\text{Mg}(\text{OD})_2$ is observed at 2722 cm^{-1} . However, note that MgO immersed in H_2O and D_2O is weaker in peak intensity than $\text{Mg}(\text{OH})_2$ immersed in H_2O , suggesting that the hydration/deuteration of MgO is insufficient. It should also be noted that the solubility of $\text{Mg}(\text{OH})_2$ is significantly smaller than that of $\text{Ca}(\text{OH})_2$ and hence, even when $\text{Mg}(\text{OH})_2$ is immersed in D_2O , only a small amount of $\text{Mg}(\text{OD})_2$ is formed.

Figure 5 shows the TG patterns for CaO/ $\text{Ca}(\text{OH})_2$ and MgO/ $\text{Mg}(\text{OH})_2$ which were first immersed in H_2O and D_2O , respectively,

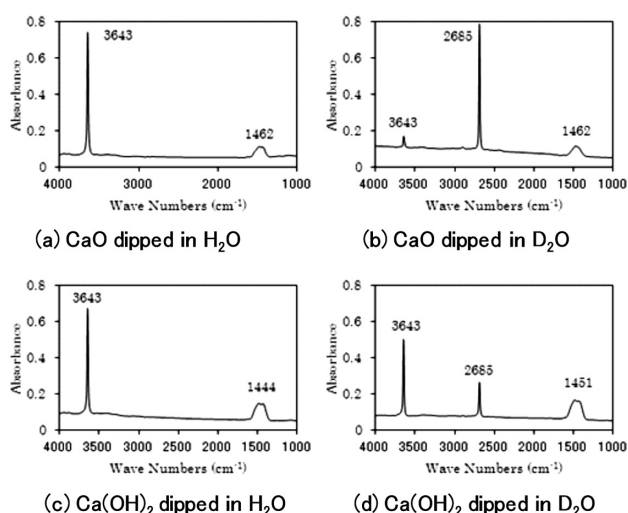


Fig. 3 IR spectra for the CaO/Ca(OH)₂ after dipped in H₂O/D₂O

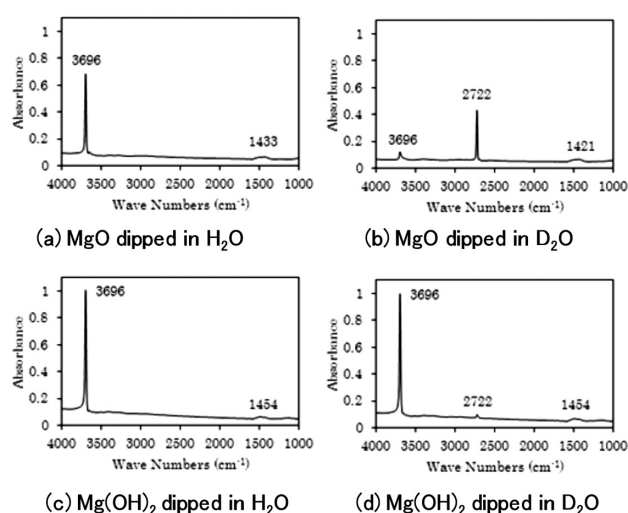


Fig. 4 IR spectra for the MgO/Mg(OH)₂ after dipped in H₂O/D₂O

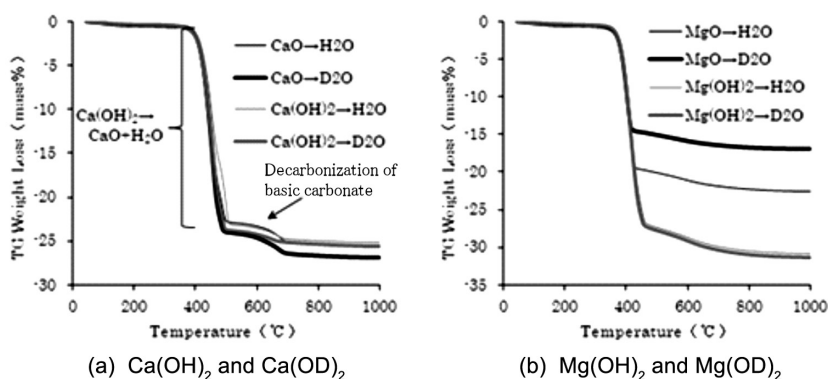


Fig. 5 TG patterns for (a) Ca(OH)₂ and Ca(OD)₂; (b) Mg(OH)₂ and Mg(OD)₂

and then dried. In Fig. 5(a), the weight losses observed in the temperature range 350°C to 500°C are probably due to the dehydration/dedeuteration of Ca(OH)₂ and Ca(OD)₂, and those in the temperature range 500°C to 700°C are probably due to the decarbonation of basic carbonate. As shown in Fig. 5(b), the dehydration of Mg(OH)₂ and Mg(OD)₂ occurs most conspicuously in the temperature range 320°C to 480°C, although a small weight loss continues till the temperature reaches about 800°C. It is said that Mg(OH)₂ becomes MgO when it is heated until red-hot. To dehydrate Mg(OH)₂ completely, it is considered necessary to heat it from 800°C to 1000°C. Weight loss based on stoichiometry is 24.3 mass% for Ca(OH)₂, 26.3 mass% for Ca(OD)₂, 30.9 mass% for Mg(OH)₂, and 33.2 mass% for Mg(OD)₂.

The weight losses at 500°C and 1000°C shown in Fig. 5 are summarized in **Tables 1** and **2**. For CaO immersed in H₂O and D₂O, respectively, the weight loss is about 23 mass% at 500°C and about 26 mass% at 1000°C. When CaO is immersed for 24 hours, it is considered to be almost hydrated, although it partly turns into basic carbonate. For MgO immersed in H₂O or D₂O, on the other hand, the measured weight loss is smaller than the weight loss based on stoichiometry. It ranges from 50% to 70% of the stoichiometric value. The peak intensity of the IR spectrum shown in Fig. 4 is also weak, suggesting that the 24-h immersion is insufficient for complete hydration/deuteration.

Table 1 Weight loss of Ca(OH)₂ and Ca(OD)₂

Sample	Weight loss (mass%)	
	500°C	1000°C
CaO → H ₂ O	22.8	25.6
CaO → D ₂ O	24.0	26.9
Ca(OH) ₂ → H ₂ O	21.4	25.2
Ca(OH) ₂ → D ₂ O	23.8	25.7

Table 2 Weight loss of Mg(OH)₂ and Mg(OD)₂

Sample	Weight loss (mass%)	
	500°C	1000°C
MgO → H ₂ O	20.0	22.5
MgO → D ₂ O	15.1	16.9
Mg(OH) ₂ → H ₂ O	27.4	30.9
Mg(OH) ₂ → D ₂ O	27.7	31.3

When CaO is immersed in D₂O, Ca(OD)₂ is readily formed. When Ca(OH)₂ is immersed in D₂O, it partly turns into Ca(OD)₂ as well. The solubility of Ca(OH)₂ is 0.16 g/100 g water (at 20°C). Thus, Ca(OH)₂ slightly dissolves in water. It is considered, therefore, that when Ca(OH)₂ is immersed in D₂O, it partly dissolves in

D_2O (in the form of Ca^{2+}) and, as it re-precipitates, it takes in OD^- which is abundant. In order to restrain $Ca(OH)_2$ from turning into $Ca(OD)_2$, it is necessary, for example, to lower the solubility of $Ca(OH)_2$ by increasing its pH value. When MgO is immersed in D_2O , $Mg(OD)_2$ is formed. However, MgO is not sufficiently hydrated merely by immersing it in D_2O . The solubility of $Mg(OH)_2$ is 9.8 mg/saturated solution 1 dm^3 (at 18°C), which is lower than that of $Ca(OH)_2$.

It is considered that the hydration/deuteration progresses as MgO dissolves and turns into Mg^{2+} , which forms hydroxides with OH^- and OD^- . In the case of Mg, the solubility of hydroxide is extremely low. Therefore, it is considered that only the surface of MgO is smoothly hydrated/deuterated, whereas the interior of the MgO particles is hardly hydrated/deuterated. To promote the hydration/deuteration of MgO, it is necessary, for example, to increase the solubility of MgO or reduce the size of MgO particles. In doing so, it will become possible to implement an accurate quantitative analysis.

It is said that f-MgO shows delayed expansion more conspicuously than f-CaO. Because details on the phenomenon are unknown, the Iron and Steel Institute of Japan has conducted "development and standardization of methods of analysis of free MgO in steel slag" through industry-academy cooperation. It is a three-year project that started in fiscal year 2014. Nippon Steel & Sumitomo Metal also engages in the development of f-MgO analytical techniques utilizing NMR¹⁹⁻²¹⁾ described in 3.1 and in the study of new analytical methods using powder XRD²²⁾ as well as the heavy water hydration/deuteration method. Thus, the company is positively progressing with the standardization of f-MgO analytical methods.

4. Conclusion

We have so far reviewed various methods of steel slag analysis that have already been established and put into practical use in slag control, that are now discussed in earnest by the steel industry, and the methods being developed at Nippon Steel & Sumitomo Metal. In the quantitative analysis of ettringite using NMR, a sample tube was filled with prescribed amounts of the sample to be determined (e.g., slag) and potash alum (internal standard test specimen), and the integral intensity ratio of the ettringite peak to the potash alum peak was then measured from the obtained ^{27}Al NMR spectrum. As a result, the ettringite could be determined accurately. In the deuteration method, it was found that when CaO and MgO were immersed in D_2O , $Ca(OD)_2$ and $Mg(OD)_2$ were formed. In the IR spectra obtained, the O-D absorption peak was observed at 2685 cm^{-1} for $Ca(OD)_2$ and 2722 cm^{-1} for $Mg(OD)_2$. They both showed a shift in the low-frequency side by approximately 1000 cm^{-1} as compared with O-H, making it possible to discriminate them from O-H easily. In the range 2800 to 2500 cm^{-1} , there was very little interfering absorption. Therefore, it was considered that as long as the deuteration conditions are optimized, the abovementioned method using D_2O is effective to evaluate oxides.

Although this was not considered in the text, in the analysis of steel slag, it is extremely important to collect a representative sample of steel slag. The amount of sample that can be analyzed is several grams for chemical composition analysis, tens of grams for elution testing, and tens of milligrams for the NMR/IR analyses described in the text. On the other hand, steel slag from a certain steel-making process is not always homogeneous. Therefore, it is impor-

tant to know how to collect a sample having a high level of representation and reduce the sample for preparing it for the analysis without impairing its representativeness. For an analytical chemist, it is difficult to tackle on a consistent basis in cooperation with a slag engineer.

Considering the standardization of analytical methods, in general, the steel industry has advanced remarkably. It must be noted, however, that the methods of analysis of steel slag have not been standardized sufficiently. This is not only due to the problems with analytical methods, such as the one associated with f-CaO described in 2.3, but also due to the difficulty involved in securing and controlling standard reference materials. Standard reference materials must be composed of homogeneous in major and trace elements, should be readily available, and their composition and chemical state should remain unchanged for a long period of archive time. Steel slag is not homogeneous and is subject to time-serial changes caused by hydration, carbonization, etc. In particular, if steel slag is finely crushed with the aim of facilitating its analysis, its surface area increases, causing a radical change of chemical states.

Steel slag exists together with the steel industry, which has long been controlled by applying analytical chemistry. Nevertheless, with respect to the various properties of steel slag discussed in this special issue, such as the change in strength of steel slag with time, there are still several uncertainties about the chemical changes that influence these properties. From the viewpoint of analytical chemistry, steel slag is a very attractive and challenging material embracing many problems that remain to be solved.

References

- 1) JIS K 0119: 2008 General Rules for X-ray Fluorescence Analysis
- 2) JIS A 5011: 2003 Slag Aggregate for Concrete
- 3) JIS R 5202: 2010 Methods for Chemical Analysis of Cements
- 4) JSTM H 8001: 2008 Crushed Steelmaking Slag for Civil Engineering Works
- 5) For Example, JIS K 0102: 2008 Testing Methods for Industrial Wastewater
- 6) JIS K 0058: 2005 Test Methods for Chemicals in Slags
- 7) JIS A 5015: 2013 Iron and Steel Slag for Road Construction
- 8) Kanehashi, K., Hatakeyama, M., Saito, K., Matsumiya, T.: *Tetsu-to-Hagané*. 89, 27 (2003)
- 9) Suito, H., Yokomaku, T., Hayashida, Y., Takahashi, Y.: *Tetsu-to-Hagané*. 63, 2316 (1977)
- 10) Schlapfer, P., Bukowski, R.: *Rep. Swiss Fed. Lab. Test Mater. Zurich*, 63 (1933)
- 11) Javellana, M. P., Jawed, I.: *Cement and Concrete Research*. 12, 399 (1982)
- 12) JCAS I-01: 1997 Method for Determination of Free Calcium Oxide
- 13) The Japan Iron and Steel Federation, Committee for Utilization of Slag and Expert Committee on Steel Slag: *Tentative Method of Analysis of Free Lime in Converter Slag and Electric Furnace Slag*. 1980
- 14) The Iron and Steel Institute of Japan: *Standardization of Techniques for Characterization of Free CaO in Steel Slag*, Final Report. 2013
- 15) Ono, A., Kuroki, H., Adachi, A.: *Tetsu-to-Hagané*. 72, 1287 (1986)
- 16) Kanehashi, K., Aimoto, M.: *Cement Science and Concrete Technology*. 66, 266 (2012)
- 17) Fujioka, Y., Aimoto, M., Nishifuji, M.: *CAMP-ISIJ*. 22, 325 (2009)
- 18) Nishifuji, M., Aimoto, M., Fujioka, Y.: *Annual Meeting of the Japan Society for Analytical Chemistry*. 62, 2013, p. 3120
- 19) Kanehashi, K., Aimoto, M.: *CAMP-ISIJ*. 25, 351 (2012)
- 20) Kanehashi, K., Aimoto, M.: *Discussion Meeting on Analytical Chemistry of the Japan Society for Analytical Chemistry*. 72, 2012, p. 40
- 21) Kanehashi, K., Aimoto, M.: *Tetsu-to-Hagané*. 99, 543 (2013)
- 22) *Journal of Technical Disclosure of the Japan Institute for Promoting Invention and Innovation* 2013-501411

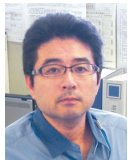
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