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Development of Analytical Methods for Free-MgO in Steelmaking Slag†

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Abstract:

Steelmaking slags have been widely used as aggregate for roadbeds and civil engineering. However, when used as aggregate, slag sometimes expands as a result of hydration, resulting in the evolution of cracks at the surface of roads. Because free magnesium oxide (free-MgO) as well as free calcium oxide in the slag are potential causes of this expansion, analytical methods to determine the free-MgO in slag for accurate evaluation of expansion are required. Based on a combination of chemical extraction and thermogravimetry (TG), an accurate method to determine the free-MgO in steelmaking slag was developed. In this method, the free-MgO and magnesium hydroxide ($Mg(OH)_2$) in the steelmaking slag are dissolved in an ethyleneglycol solution containing iodine and ethanol when heated. The amount of the magnesium species dissolved in the solution is determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The amount of ($Mg(OH)_2$) in the slag is determined separately by TG, and the result is then subtracted from that of the magnesium species dissolved in the ethyleneglycol to obtain the amount of free-MgO. The newly-established method enables determination of free-MgO in steelmaking slag at the 0.1 mass% level.

1. Introduction

Steelmaking slag, which is a byproduct of the steel manufacturing process, is used as a concrete aggregate, roadbed material, etc. Roadbed material made from steelmaking slag is used based on adequate consideration of the expansion of the slag[1)]. Hydration of free calcium oxide (free-CaO), free magnesium oxide (free-MgO), etc. in the slag is considered to be the main cause of this expansion[2,3)].

In order to understand the expansion mechanism of slag, it is important to determine the free-CaO and free-MgO in the slag. The analytical method by ethyleneglycol (EG) extraction[4–7)] is widely known as a determination method for free-CaO. As determination methods that do not use chemical extraction, determination by X-ray diffraction (XRD)[8,9)], calculation from infrared spectroscopy after hydration with heavy water[10)] and others have been reported. Reported methods for determination of free-MgO in slag include extraction by using ammonium nitrate[11)], the solid-state ^{25}Mg nuclear magnetic resonance (NMR) spectroscopy[12)], calculation from infrared spectroscopy after hydration with heavy water[13)], etc. Determination of free-MgO by ammonium nitrate extraction has the problems that Mg compounds other than MgO are also extracted or MgO is not extracted completely, leading to poor in repeatability. The ^{25}Mg NMR spectroscopy is not a general-purpose method, as high performance NMR apparatus are necessary, and requires a long measurement time. The method of calculation from infrared spectroscopy after heavy water hydration also lacks practicality, since MgO must be changed completely to $Mg(OH)_2$ by hydration, and considerable time is required.

On the other hand, determination of CaO and MgO using I_2-EG solution and measuring the electrical conductivity before and after addition has been reported as an analytical method for CaO and MgO in cement clinker[14)]. The I_2-alcohol dissolution method is known as a standard method for extraction of oxides in steel[15,16)].

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From the above, an I_2-alcohol-EG solution was considered to be a possible solvent for extraction of free-MgO in slag. However, there were no cases in which this solvent was studied as an analytical method for MgO in slag. Therefore, the authors investigated fractional determination of free-MgO in slag by chemical extraction using an I_2-alcohol-EG solution, and determined the optimum conditions for dissolution of free-MgO and $Mg(OH)_2$ by using standard reagents and actual slags. We also found that thermogravimetric analysis can be used in determination of $Mg(OH)_2$ that is dissolved together with MgO. This paper reports a determination method for free-MgO in slag which was developed based on the study outlined above.

2. Experimental

2.1 Reagents and Sample Materials

2.1.1 Reagents

The MgO used in this study was a high purity reagent manufactured by Kanto Chemical Co., Inc. The $Mg(OH)_2$ was a high purity reagent manufactured by Kojundo Chemical Laboratory Co., Ltd. As Al complex oxides, Si complex oxides and Fe complex oxides for use in investigation of the melting behavior of Mg oxides, $Mg(AlO_2)_2$, $Mg_2Si_3O_8 \cdot 5H_2O$ and $MgFe_2O_4$ manufactured by Wako Pure Chemical Industries, Ltd. and Kojundo Chemical Laboratory were used.

2.1.2 Slags

The steelmaking slags (Slag A-D) shown in **Table 1** were used in the study of free-MgO analysis. When used in analysis, the slags were crushed in advance to 0.075 mm or smaller.

2.2 Experimental Method

2.2.1 Melting and determination method for MgO+Mg(OH)$_2$ in slag

A 0.1 g sample of slag crushed to 0.075 mm or smaller is weighed in a conical flask (100 m*l*), and 17 m*l* of ethyleneglycol and 8 m*l* of 25 mass% I_2 ethanol are added to the flask. The flask is placed in a hot water bath adjusted to 80±5°C and heated for 60 min while stirring with a stirrer. After heating for 60 min, the flask is cooled to room temperature in running water. Using a syringe with a tube attached to its tip, approximately 5 m*l* of extraction liquid is aspirated and discharged, and the syringe and inside of the tube are rinsed. After taking 5 m*l* or more of the extract, the tube is removed, a membrane filter (pore size: 0.45 μm) is attached, and filtration is performed. After discarding the first approximate 1 m*l*, the filter is rinsed. The following 1 m*l* of the filtrate is separated and transferred to a 100 m*l* volumetric flask. 10 m*l* of hydrochloric acid (1+1), 3 m*l* of ethanol, and 5 m*l* of internal standard solution Y (100 μg/m*l*) are added to the flask, and the contents are adjusted to a constant volume of 100 m*l* with water. The intensity of emission of Mg and Y in a calibration curve solution and in the sample solution is measured by an inductively coupled plasma-atomic emission spectrophotometer (ICP-AES), and the concentration of Mg in the sample solution is calculated by the Y internal standard method. Here, the obtained results take Mg as ($MgO+Mg(OH)_2$).

2.2.2 Determination of Mg(OH)$_2$ in slag

The $Mg(OH)_2$ contained in slag is determined by the following procedure.

(1) Removal of $Ca(OH)_2$

A 0.15 g sample of slag crushed to 0.075 mm or smaller is weighed in a conical flask (100 m*l*), and 25 m*l* of ethyleneglycol is added. The flask is placed in a hot water bath adjusted to 70±5°C and heated for 60 min while stirring with a stirrer. After heating for 60 min, the flask is cooled to room temperature in running water. The slag after filtration is rinsed with ethanol, and is then dried in a vacuum desiccator.

(2) Thermogravimetric analysis (TG)

The slag from which $Ca(OH)_2$ has been removed by the above-mentioned method is measured by TG under the following conditions.

Sample weight: 0.1 g
Atmosphere: Ar
Heating conditions: Room temperature to 500°C (10°C/min)

The weight changes in the temperature ranges of 350–415°C and 285–350°C are obtained (denoted as TG-a (%) and TG-b (%), respectively).

Table 1 Composition of slag samples [17]

(mass%)

	Ca	Fe	Si	Mn	Mg	Al	P	S
Slag A	32.0	21.5	6.3	3.2	1.4	1.6	0.8	N. D.
Slag B	29.9	22.9	6.5	2.8	3.6	1.5	0.9	N. D.
Slag C	30.6	22.4	6.2	2.4	3.8	1.7	1.0	N. D.
Slag D	30.8	21.7	5.9	2.3	3.6	1.2	1.1	N. D.

N. D.: Not detected

(3) Calculation of amounts of MgO and $Mg(OH)_2$

The amounts of $Mg(OH)_2$ and free-MgO are calculated from the results obtained by TG measurements by the following equations.

-Calculation of $Mg(OH)_2$
$Mg(OH)_2$=TG-a (%)−TG-b (%)
Mg as $Mg(OH)_2$ is obtained.
-Calculation of free-MgO
[Mg as free-MgO]
=[Mg as ($MgO+Mg(OH)_2$)]−[Mg as $Mg(OH)_2$]

3. Results and Discussion

3.1 Form of Existence of Mg in Slag

In order to clarify the Mg compounds contained in slag, a microstructural analysis was performed by a scanning electron microscope (SEM)-energy dispersive X-ray spectrometer (EDX). The Mg in the slag was detected at the same positions as O, Fe, Si and Al. From this, the main forms of Mg in steelmaking slag were estimated to be complex oxides compounded oxides or hydroxides of Mg with Fe, Si and Al. As Mg was not detected at the same positions as P or S in the samples used here, it is thought that phosphates, sulfides and sulfates were virtually nonexistent. Based on these results, the reagents shown in section 2.1.1 were selected as substances for use in study of an chemical extraction method for Mg compounds in slag.

3.2 MgO and $Mg(OH)_2$ Dissolution Method

In the analytical method of CaO and MgO in cement clinker[14)], 2.5 mass% of I_2 is added to EG, and CaO and MgO are determined from the change in electrical conductivity. In analysis of inclusions in metals[15,16)], a 10–20 mass% I_2-alcohol solution is used; however, depending on the kinds of metal, the optimum I_2 concentration, solvent composition, dissolution temperature and dissolution time differ, and solubility also changes. Therefore, first, the possibility of chemical extraction of MgO by an I_2-ethanol (C_2H_5OH) solution was studied by using reagents of MgO, $Mg(OH)_2$ and various complex oxides, which are the main forms of Mg in slag.

3.2.1 Dissolution of Mg compounds using reagents

The dissolution rate of MgO was determined by stepwise addition of a saturated I_2-C_2H_5OH solution (25 mass% I_2-C_2H_5OH) to EG. In this study, 10 mg of the MgO reagent was used. The dissolution rate was investigated by adding a solution, in which the combined I_2-C_2H_5OH solution and EG were adjusted to a constant 25 m*l*, to the MgO reagent. The heating conditions were 80°C × 60 min. The results are shown in **Fig. 1**.

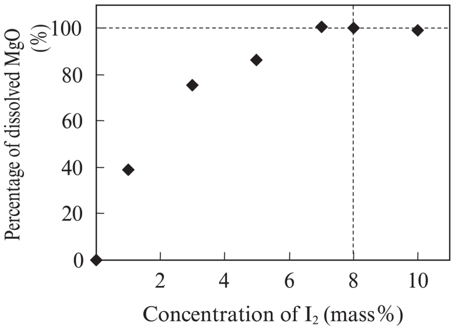


Fig. 1 Effect of concentration of I_2 for dissolution of MgO (MgO: 10 mg, Solvent: 25 m*l* of I_2-C_2H_5OH-ethyleneglycol, Temperature: 80°C, Heating time: 60 min)[17)]

Because 100% of the MgO was dissolved when the I_2 concentration of the solution was 7 mass% or more, the necessary solution concentration for dissolution of MgO was decided to be 8 mass% I_2-24 mass% C_2H_5OH-EG. The solubility of Mg compounds was investigated using this solution. As a result, it was found that MgO and $Mg(OH)_2$ are almost completely dissolved by the above-mentioned solution, whereas complex oxides of Mg compounded with Fe, Si and Al, which are the other main forms of Mg in slag, are substantially not dissolved. Based on this, 8 mass% I_2-24 mass% C_2H_5OH-EG was adopted as the solution for dissolution of $MgO+Mg(OH)_2$ in steelmaking slag.

3.2.2 Optimization of dissolution conditions for MgO and $Mg(OH)_2$ by using simulated slag

A simulated slag for use in study of MgO dissolution was prepared. The simulated slag was prepared by melting a mixture of reagents of $CaCO_3$, SiO_2, Al_2O_3 and MgO, and cooling and crushing the resulting material. The total Mg content in the synthesized simulated slag was 10.6 mass%. Using this simulated slag, the optimum temperature and time for dissolution of MgO in slags in the 8 mass% I_2-24 mass% C_2H_5OH-EG solution was studied. The results are shown in **Fig. 2**.

The amount of Mg dissolution from the simulated slag became constant when the dissolution temperature

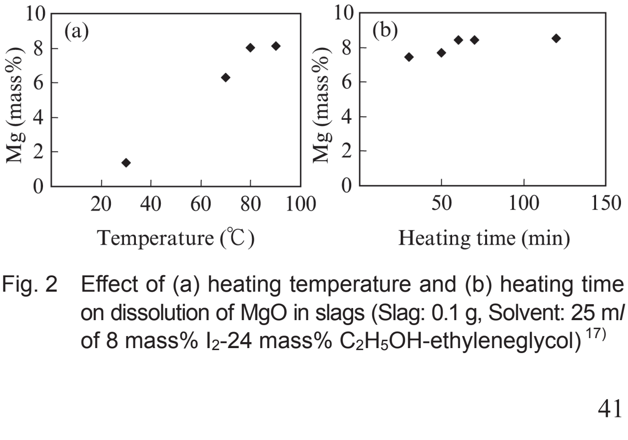


Fig. 2 Effect of (a) heating temperature and (b) heating time on dissolution of MgO in slags (Slag: 0.1 g, Solvent: 25 m*l* of 8 mass% I_2-24 mass% C_2H_5OH-ethyleneglycol)[17)]

was 80˚C or higher and the dissolution time was 60 min or longer. The conditions for dissolution of MgO and $Mg(OH)_2$ in 8 mass% I_2-24 mass% C_2H_5OH-EG were set at 80˚C and 60 min.

3.3 Determination of $Mg(OH)_2$ by Thermogravimetric Analysis

The sum of the concentrations of MgO and $Mg(OH)_2$ can be determined by ICP-AES analysis of the Mg in the solution dissolved with 8 mass% I_2-24 mass% C_2H_5OH-EG. Although direct determination of MgO is difficult by this method, the content of MgO can be determined by subtracting the amount of $Mg(OH)_2$ from sum of the concentrations of MgO and $Mg(OH)_2$. Therefore, a method for determination of $Mg(OH)_2$ by TG was studied. Because the amount of $Ca(OH)_2$ in steelmaking slag is generally larger than the amount of $Mg(OH)_2$, the existence of $Ca(OH)_2$ is an influence to accuracy when measuring $Mg(OH)_2$ in slag by TG. In steelmaking slag, a decrease in weight occurs accompanying thermal decomposition of $Ca(OH)_2$ at 400–460˚C, as shown by the dotted line in **Fig. 3**. The pyrolysis temperature of $Mg(OH)_2$ is 350–415˚C, which overlaps the decomposition temperature of $Ca(OH)_2$. In order to reduce the influence of $Ca(OH)_2$ on determination of $Mg(OH)_2$, it is possible to use a sample from which $Ca(OH)_2$ has been removed from the slag sample in advance in the TG analysis. Therefore, for this measurement method, we examined the possibility of using samples from which $Ca(OH)_2$ is removed by EG, conforming to the method of dissolving CaO in slag[5)]. The TG curve after EG treatment is shown by a solid line in Fig. 3.

Because the weight decrease which accompanies pyrolysis of $Ca(OH)_2$ is no longer observed when the slag is treated with EG, it can be understood that $Ca(OH)_2$ has been removed. As a result, highly accurate determination of $Mg(OH)_2$ in slag by TG is possible by measuring the weight reduction at 350–415˚C with an EG treated sample, and simultaneously with this, performing compensation by treating the weight loss at 285–350˚C as background. The average of three analytical values of $Mg(OH)_2$ in actual slag C was 0.054 mass%, and the standard deviation (σ) was 0.008 mass%, showing sufficient accuracy for practical purposes.

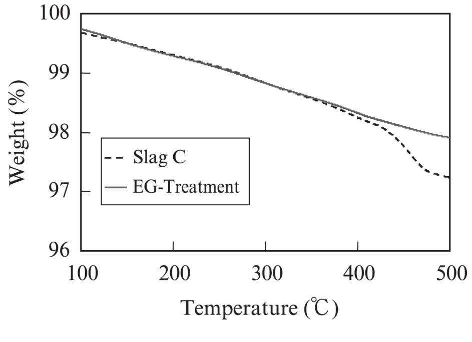
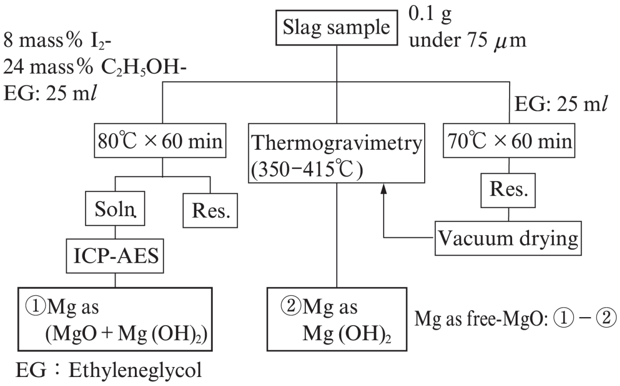


Fig. 3 Thermogravimetry curves of slag C before and after the treatment with ethyleneglycol (Slag: 0.1 g, Heating rate: 10˚C/min, Atmosphere: Ar)[17)]



EG : Ethyleneglycol
ICP-AES : Inductively coupled plasma atomic emission spectrometry

Fig. 4 Scheme of analytical methods for free-MgO in slags[17)]

3.4 Scheme of Developed Free-MgO Analysis Methods

Figure 4 shows an outline of the analytical methods for free-MgO in steelmaking slag developed as a result of the study described above.

3.5 Determination of Free-MgO in Steelmaking Slag

Table 2 shows the results of determination of the MgO content in three sample slags by the developed method. The three slags shown here are slag A, which is an actual slag, and slag A’ and slag A”, which were prepared by adding 1 mass% and 5 mass% of reagent MgO, respectively, to slag A.

The free-MgO in slag A was determined to be 1.10 mass% by this analytical method. The analytical value of MgO in slag A’, which was prepared by adding 1 mass% of MgO to slag A, was 2.12 mass%, and the value for slag A”, containing 5 mass% of added MgO, was 6.06 mass%. Thus, the rates of recovery from the added MgO were 102% and 99%, respectively. It can be understood that a known amount of MgO added to slag can be determined with good accuracy. These results demonstrate that determination of free-MgO in slag is possible by the developed method.

The free-MgO contents in slags B, C and D were also

Table 2 Analytical results of free-MgO in slag A[17)]

	Total Mg (mass%)	Added MgO (mass%)	$Mg(OH)_2$ (mass%)	free-MgO (mass%)	Recovery (%)
Slag A	1.42	—	< 0.01	1.10	—
Slag A’		1.0	< 0.01	2.12	102
Slag A’		5.0	< 0.01	6.06	99

Table 3 Analytical results of free-MgO in slags [17)]

(mass%)

	Total Mg		① Mg as (MgO + $Mg(OH)_2$)	② Mg as $Mg(OH)_2$	Mg as free-MgO
Slag B	3.6_4	Ave.	0.43_4	< 0.01	0.43
		σ	0.03_3	—	
Slag C	3.8_3	Ave.	0.48_7	0.05_4	0.43
		σ	0.00_5	0.00_8	
Slag D	3.5_6	Ave.	0.27_4	< 0.01	0.27
		σ	0.01_3	—	

determined by the developed method. The results are shown in **Table 3**.

The table shows the average (Ave.) and standard deviation (σ) of the analytical results when analysis of each sample was performed repeatedly three times. With all the samples, the relative standard deviation of the repeatability of the analytical values of Mg as ($MgO+Mg(OH)_2$) was 10% or less, showing satisfactory analytical precision. It can be said that highly accurate determination of $MgO+Mg(OH)_2$ and MgO in slag at the 0.1 mass% level is possible by this method. Moreover, although there was virtually no difference in the total Mg in slags B-D, analysis by the developed method revealed a large difference in the contents of free-MgO in slags B and C and in slag D.

4. Conclusion

An analytical method for free-MgO in steelmaking slag was studied, and a method for determination of $Mg(OH)_2$ was developed based on a combination of a fractional dissolution method for [$MgO+Mg(OH)_2$] by dissolution with I_2-ethyleneglycol (EG), and thermogravimetric analysis of the sample after EG treatment. The content of free-MgO is obtained from the difference between the two results. This method enables evaluation of free-MgO in slag. It is possible to apply this technique to studies of aging treatment conditions, indexes of criteria for judging that shipment of slag is possible, and other fields.

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