Dissolution Behaviour of Hazardous Materials from Steel Slag with Wet Grinding Method

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Abstract. Steel slag is a by-product from steel industry and it contains variety of hazardous materials. In this study, the dissolution behaviour and removal potential of hazardous materials from steel slag with the wet grinding method was investigated. The slag was wet ground in the CO_2 atmosphere and the slurry produced was filtered using centrifugal separator to separate the liquid and solid sediments. Then, the concentrations of dissolved metal elements in the liquid sediment were analyzed by ICP-MS. The changes of pH during the grinding were also investigated. It was found that the pHs were decreased immediately after the CO_2 gas introduced into the vessel. The pHs were ranging from 6.8 to 7.6 at the end of grinding. The dissolved concentration of Zn and Cr were ranging from 5~45 [mg/dm^3] and 0.2~2.5 [mg/dm^3] respectively. The ratios of Zn removal for stainless steel oxidizing and reducing slag were very high, but those from normal steel oxidizing and reducing slag were very low. It is assumed that the Zn dissolved as $ZnOH^+$ from $Zn(OH)_2$ that formed due to the reaction between ZnO and water. Dissolution of Cr also occurred but in very low quantity compared to the dissolution of Zn. The dissolution of Cr occurred due to the grinding process and small amount of $Cr(OH)_3$ was formed during the grinding. This small formation of $Cr(OH)_3$ resulted to the low dissolved concentration of Cr in the form of $Cr(OH)_2^+$. According to the XRD analysis, the Cr mostly existed in the slags as Cr(III) in the form of $MgCr_2O_4$ and $FeCr_2O_4$.

1. Introduction
The steel industry is one of the key industries in the world due to the high demand especially from building construction, automotive and machinery sectors. Based on the World Steel Association (WSA) report, the world crude steel production in 2008 was approximately 1326.5 million tons [1]. Along with the production of steel, the steel industry also generates steelmaking slag as a by-product. These slags can be broadly divided into blast furnace slag and steel slag. In the blast furnace (BF), constituents other than iron in the iron ore are melted and become slag together with the ash of coke,

and the slag was separated from the pig iron and recovered. This BF slag has components similar to those of natural rocks, and about 290 kg is generated per ton of pig iron. On the other hand, the steelmaking process which consists of refining pig iron, scrap and other material to produce steel leads to the production of steel slag. It can be divided into basic oxygen furnace (BOF) slag and electric arc furnace (EAF) slag with generation amounts of 110 and 120 kg per ton of crude steel respectively [2]. The EAF steel slag consisted of two different types of slag which are the oxidizing and reducing slag, with generation amounts of 70 and 50 kg per ton of crude steel respectively.

Steelmaking slag contains heavy metals such as chromium and zinc. The ingestion of these heavy metals beyond permissible quantities causes various chronic disorders in human beings [3-8]. The excessive ingestion of this substance into human body can affect several serious disorder such as genotoxicity, mutagenicity, and cell transformation, and lung cancer [3]. Alok Prasad Das et al. and Gibb H.J. et al. has reported that the risk of lung cancer among workers of the chromate industry in US increased compared to the general population and a positive correlation between duration of exposure and lung cancer death was found [4, 5].

Therefore, the removal of chromium and zinc from steelmaking slag has received a great deal of attention for recovery and elimination of those metals [9-12]. N.K. Hamadi et al. have investigated about the batch removal of hexavalent chromium (Cr(VI)) from wastewater under different experimental conditions using economic adsorbents [9]. The adsorbents were produced from the pyrolysis and activation of the waste tyres (TAC) and from the pyrolysis of sawdust (SPC). They found that the removal was favoured at low pH, with maximum removal at pH=2 for all types of carbon. All sorbents were found to efficiently remove Cr(VI) from solution.

In the previous studies, we have conducted several experiments especially in investigating the potential of slag as a sorbent for CO_2 and investigating the dissolution behavior of slag in pure water [13-15]. The wet grinding method was found to be applicable in dissolving and removing heavy metals inside the slag such as zinc and chromium. Therefore, our current research objective is to investigate the dissolution behavior and the removal potential of chromium and zinc with the wet grinding method.

2. Experimental

2.1. Samples

EAF oxidizing and reducing slag from normal and stainless steelmaking process were used in this experiment. The chemical compositions of the slag used are shown in Table 1. The "Oxi" and "Red" indicate oxidizing and reducing respectively. The Oxi C and Red B slag are the EAF normal steelmaking slag, while the others are the stainless steelmaking slag. Oxi A, Oxi B, Red A and Red B are rich with CaO and SiO_2, while Oxi C rich with FeO. The content of Cr_2O_3 in Oxi A, Oxi B, Oxi C and Red A were high but in Red B was very low. The content for Zn were low in all type of slags.

Table 1. Chemical compositions of the used slag [mass%].

Slag type	Size [mm]	Chemical composition [mass%]											
		CaO	SiO₂	Al₂O₃	MgO	CaS	Cr₂O₃	MnO	TiO₂	FeO	NiO	CuO	ZnO
Oxi A	<10	35.4	36.3	13.5	6.9	0.2	2.1	3.3	2.0	0.23	0.03	0.06	0.01
Oxi B	<10	33.0	44.1	5.4	7.7	0.3	3.3	1	1.0	0.7	0.06	0.2	0.01
Oxi C	<10	20.5	20.2	20.1	6.2	0	1.7	4.1	0	26.8	0.03	0.03	0.07
Red A	<5	47.1	30.5	10.5	5.8	2.5	1.3	0.47	0.4	1.2	0.06	0.01	0.01
Red B	<5	50.3	21.1	18.7	4.1	4.0	0.2	0.6	0	0.9	0.02	0.07	0.01

According to the XRD analysis as in the previous works [13-16], Cr is mostly exists in the slag as Cr(III) in the form of $MgCr_2O_4$ and $FeCr_2O_4$. While, the compounds of Zn were not detected by XRD assumed to be due to its content which are too small. The example of cross section of the slag used is shown in Figure 1. Figure 1 shows the cross section of the EAF stainless steelmaking oxidizing slag (Oxi A). Whitish phases as in Figure 1(a); ①, ③, ⑤, and (b); ③, ⑤, are the phases that rich with Cr and Mg. The compositions of these elements are equivalent to that in $MgCr_2O_4$. The dark whitish phases as in Figure 1 (a)④ and (b)② are rich with the Cr and Fe, and the compositions of them are equivalent to that in $FeCr_2O_4$.
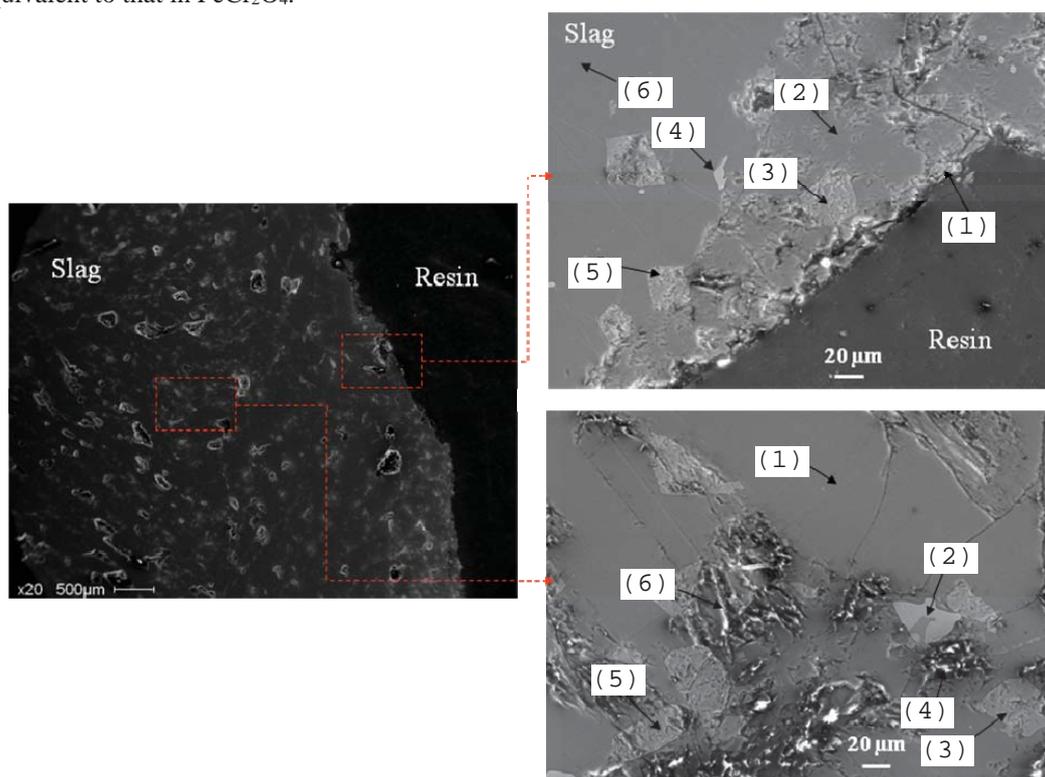

Figure 1. Cross section of EAF oxidizing slag (a) outer part, (b) inner part.

2.2. Procedure

The experimental apparatus used is as shown in Figure 2. Certain amount of slag and the alumina balls were placed in the grinding vessel. After the air in the vessel was evacuated to less than 1.3 Pa by a rotary pump, CO_2 gas was introduced into the vessel. This vacuum displacement was repeated twice to assure that all air in the vessel was fully replaced by CO_2. After that, pure water was poured into the vessel under a CO_2 gas flow. Finally, CO_2 gas was introduced until the internal pressure reached the desired value. Subsequently, the grinding was started.

The slag and the water became slurry under the grinding process. The pH of the slurry was measured with a pH meter. The slurry was then separated into the solid products and the aqueous solution using a centrifugal separator (HSIANGTAI Centrifuge, CN-820) at 1,500 rpm for 10 minutes. After the separated solid product was dried in air, it was characterized by SEM (JSM 6300, JEOL) and XRD (RINT 2500, Rigaku). The concentrations in the supernatant liquid were measured by ICP-AES

(P-4010, Hitachi). Finally, the liquid was vaporized, and the obtained sediments were dried in a laboratory dryer for one hour at 420 K. The sediments were then characterized by SEM and XRD.
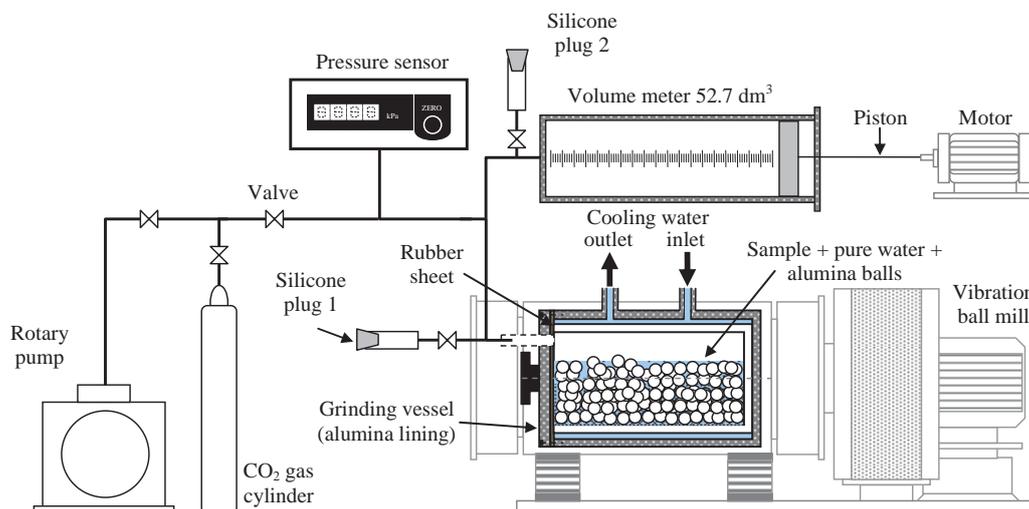

Figure 2. Schematic of the experimental apparatus.

The experimental conditions are shown in Table 2. The experiments were performed by changing the diameter of alumina ball, the initial pressure of CO_2, weight of the slag, and the volume of water. All of the grinding experiments were carried out at room temperature.

Table 2. Experimental conditions.

Condition	Value/Item
Sample	Oxi A, Oxi B, Oxi C, Red A, Red B
Diameter of alumina ball, d_b [mm] ( ) : number of ball	20 (180)
Partial pressure of CO_2, PCO_2 [kPa]	101.3
Weight of sample, W_s [kg]	0.2
Volume of water, V_w [dm^3]	0.4

3. 3. Results and Discussion

3.1. Change of pH with Grinding Time
Figure 3 shows the change in pH of the slurry for all samples during grinding in the CO_2 atmosphere. The initial pH indicates the pH of mixture of slag and water right after they had been mixed together. The initial pH ranging from 8 to 11.5 and it seemed to depend on the content of CaO in the slag. The higher the content, the higher the initial pH was. The pHs were decreased immediately after the grinding was started and almost unchanged in the latter stage of grinding for all samples. The pHs were ranging from 6.8 to 7.6 at the end of grinding. The decrease in the pH might occurred due to the dissolution of CO_2 gas into water, hydration of aqueous CO_2 and the ionization of hydrated CO_2, forming either carbonate or bicarbonate ions which can be summarized by the following equation:

$$CO_{2(g)} + H_2O \rightarrow HCO_3^- + H^+ \tag{1}$$

$$CO_{2(g)} + H_2O \rightarrow CO_3^{2-} + 2H^+ \tag{2}$$
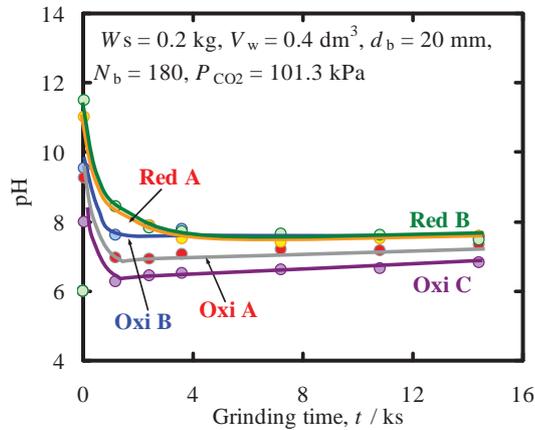
**Figure 3**. Change of pH during grinding process for all samples.
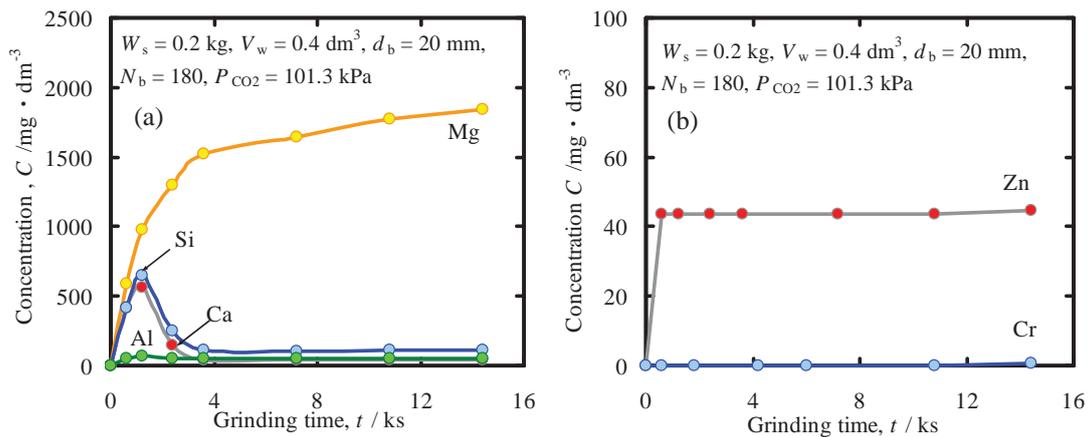
Figure 4. Dissolution behavior of (a) Ca, Mg, Si and Al, (b) Zn and Cr, during grinding. (Sample : Oxidizing A)

The change of pH during grinding affected the dissolution behavior of each element inside the slag. Figure 4 shows the example of dissolution behavior of elements inside the slag into water for oxidizing A. The dissolution of elements such as Ca, Mg, Si and Al were quite high. One of the Ca and Mg phases exist in the slag was $2CaO \cdot MgO \cdot 2SiO_{2(s)}$ [14, 15]. This phase might reacted with the following equation:

$$2CaO \cdot MgO \cdot 2SiO_{2(s)} + 5H_2O \rightarrow 2Ca^{2+} + Mg^{2+} + 2H_2SiO_{3(s)} + 6OH^- \tag{3}$$
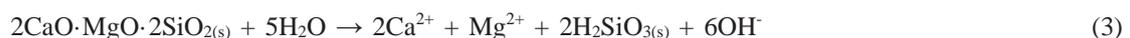
Along with the dissolution of these elements, the dissolutions of Zn and Cr were also occurred during the grinding as in Figure 4 (b). The concentration of dissolved Zn was higher than that of Cr. The concentration of Zn for all samples is shown in Figure 5. The concentrations of Zn were instantly

increased as the grinding started. However, they did not increase further and almost unchanged afterward except that for the reducing A. The concentration of Zn for reducing A increased for the second time after 10.8 ks before decreased back after that. In general, the dissolved concentrations of Zn from the oxidizing A, oxidizing B and reducing A which were the EAF stainless steelmaking slag were higher than those from the oxidizing C and reducing B slag which were the EAF steel slag from normal steelmaking process.
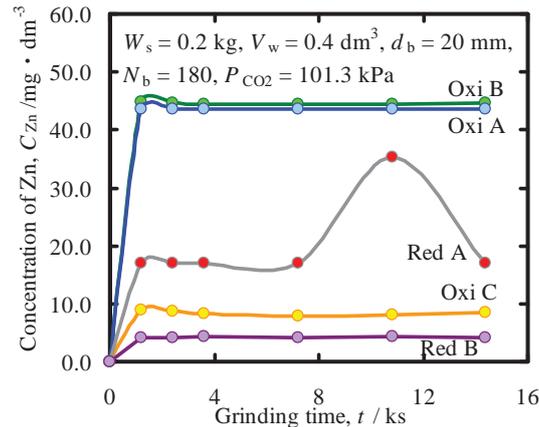

Figure 5. Dissolution behavior of Zn during grinding for all samples.

Using the composition of Zn inside each sample, m_{Zn} [mass%], weight of sample used, W_s [g], dissolved concentration of Zn, C_{Zn} [mg/dm^3] from Figure 5 and volume of water used, V_w [dm^3], the extraction rate of Zn, ER_{Zn} [%] can be defined as follows:

$$ER_{Zn} = \{[(C_{Zn} \times V_w) / 10^3] / (m_{Zn} \times W_s)\} \times 100 \tag{4}$$

Table 3 shows the removal ratio of Zn during grinding under CO_2 atmosphere. The ratios for Oxi A, Oxi B and Red A were very high, but those from Oxi C and Red B were very low. It can be concluded that Zn can be removed from slag using the mechanical grinding in CO_2 atmosphere. However, in the case of Oxi C and Red B, further investigation is needed to verify the reason for low removal ratio. $Zn(OH)_2$ that was assumed to be formed due to the reaction between ZnO and water dissolved as $ZnOH^+$ into the water as the following reaction:

$$ZnO_{(s)} + H_2O = Zn(OH)_{2(s)} \tag{5}$$
$$Zn(OH)_{2(s)} + H^+ = ZnOH^+ + H_2O \tag{6}$$

Table 3. Removal ratio of Zn [%].

Element	Oxi A	Oxi B	Oxi C	Red A	Red B
Zn	100.0	81.4	3.2	88.2	9.6

*3.2. Dissolution behavior of Cr from slag*
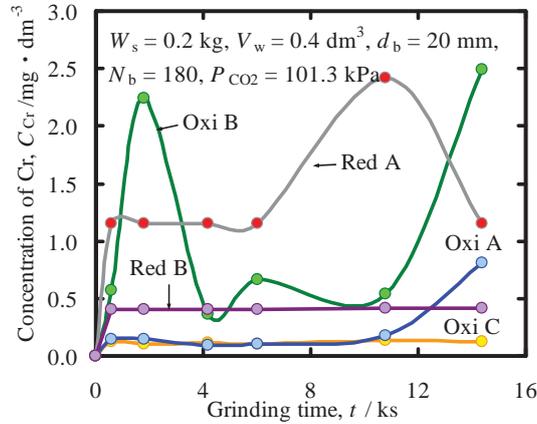
Figure 6. Dissolution behavior of Cr during grinding for all samples.

Figure 6 shows the dissolution behavior of Cr during grinding for each sample. The concentration of dissolved Cr for oxidizing A and reducing B increased slightly as the grinding started and almost unchanged afterward. The oxidizing A also increased slightly after the grinding was started but increased after 14.4 ks. The concentration of dissolved Cr from oxidizing B and reducing A were higher than the others. However, in comparison to the dissolved concentration of Zn shown in Figure 5, the concentrations of Cr from all samples were very small. Using the composition of Cr inside each sample, m_{Cr} [mass%], weight of sample used, W_s [g], dissolved concentration of Cr, C_{Cr} [mg/dm^3] from Figure 6 and volume of water used, V_w [dm^3], the extraction rate of Cr, ER_{Cr} [%] can be defined as follows:

$$ER_{Cr} = \{[(C_{Cr} \times V_w) / 10^3] / (m_{Cr} \times W_s)\} \times 100 \tag{7}$$

From this equation, the maximum extraction rates of Cr for oxidizing A, oxidizing B, oxidizing C, reducing A and reducing B were found to be 0.00023%, 0.00044%, 0.000044%, 0.0011% and 0.0014% respectively.

It is assumed from the concentration-pH diagram that the Cr dissolved into the aqueous solution as $Cr(OH)_2^+$ ion. It might be occurred according o the following reaction:

$$Cr_2O_3 + 3H_2O \rightarrow 2Cr(OH)_{3(s)} \tag{8}$$
$$Cr(OH)_{3(s)} + H^+ = Cr(OH)_2^+ + H_2O \tag{9}$$
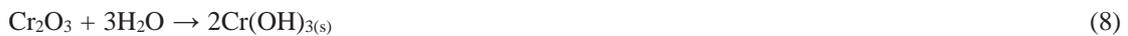
This reaction occurred due to the grinding process and the amount of $Cr(OH)_3$ formed must be very small. This small formation of $Cr(OH)_3$ resulted to the low dissolved concentration of Cr in the form of $Cr(OH)_2^+$. According to the XRD analysis, the Cr mostly exists in the slags as Cr(III) in the form of $MgCr_2O_4$ and $FeCr_2O_4$.

4. Conclusion

From the results above, it can be concluded that:

1. The pHs were decreased immediately after the grinding was started and almost unchanged in the latter stage of grinding for all samples. The pHs were ranging from 6.8 to 7.6 at the end of grinding.

2. Extraction rate for Zn was high by this method. $Zn(OH)_2$ that was assumed to be formed due to the reaction between ZnO and water dissolved as $ZnOH^+$ into the water.

3. Dissolution of Cr occurred by the wet grinding method, but the dissolved concentrations were very low. It is assumed to be dissolved as $Cr(OH)_2^+$ ions from $Cr(OH)_3$ that was produced during the grinding.

5. Acknowledgements

6. References

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