

Recovery of Manganese and Phosphorus from Dephosphorization Slag with Wet Magnetic Separation

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Abstract

The dephosphorization slag has a great potential as the secondary resources of manganese and phosphorus, while quite a large amount of slag is landfilled and simply reused such as cement. The objective of this study is to investigate the recovery of manganese and phosphorus by wet magnetic separation technique. The hot metal pretreatment slag (dephosphorization slag) generally contains a $\text{Ca}_3\text{P}_2\text{O}_8\text{-Ca}_2\text{SiO}_4$ (phosphorus enriched phase) and FeO-MnO (manganese enriched phase) solid solutions together with FeO-CaO-SiO_2 matrix phase. Since the difference in their magnetic properties is significant, it is possible to separate each phase with the aid of wet magnetic separation. By applying strong magnetic field to the crushed slag ($<32\mu\text{m}$), 31% of phosphorus enriched slag and 14% manganese enriched slag could be successfully recovered.

1. Introduction

Security of resources becomes more important than ever due to the recent trend in commodity prices for minerals and natural resources. Manganese and phosphorus are important resources for many advanced countries like Japan and South Korea. More importantly, they are not produced in the countries, although domestic use of each is increasing.¹⁻³⁾ Manganese is an indispensable element in industrial and consumer products, and phosphorus is in global demand, particularly for mainly fertilizer production. However, in the steel industry, phosphorus is typically recognized as a harmful element for high-quality steel, whereas manganese is considered to be an important alloying and deoxidizing element in the steelmaking process. Because of its ability of desulfurization and deoxidation for steel, manganese plays a key role in the steelmaking. Manganese and phosphorus exist in coal, iron ore, and limestone,⁴⁾ which are essential raw materials for iron- and steel-making processes. Since manganese and phosphorus are less noble in chemical nature, they are easily oxidized and mostly distributed into the steelmaking slag, particularly hot metal pretreatment slag (dephosphorization slag). Because total amount of crude steel production in Japan and South Korea is huge, the amount of manganese and phosphorus transferred to steelmaking slag is also huge.

The recovery of valuable mineral resources such as manganese and phosphorus from steelmaking slag is

important for several reasons. First, reserves of high manganese and phosphorus content resources are very limited. Second, industrial processes for mining, producing, and distributing can cause environmental and uneconomical problems. Therefore, as a secondary resource, steelmaking slag could be an important alternative because of high manganese and phosphorus content.

Despite the economic and ecological importance, however, only a few researchers have paid attention to recovering valuable elements from slag.⁵⁻⁸⁾ In general, dephosphorization slag can be divided into three major phases in its solidified micro-structure: a FeO-free phosphorus-rich phase ($\text{Ca}_3\text{P}_2\text{O}_5\text{-Ca}_2\text{SiO}_4$), a phosphorus-free manganese-enriched phase (mangano-wustite phase), and a phosphorus-free matrix phase (FeO-CaO-SiO_2) containing minor part of manganese. Therefore, in principle, it is possible to recover mangano-wustite using a weak first magnetic separation followed by a relatively strong second magnetic separation to recover phosphorus as calcium phosphate from residues. With such a background, the authors have developed a new process to recover manganese and phosphorus from steelmaking slag by wet magnetic separation.

2. Manganese and phosphorus material flows through steel industry

Different forms of phosphorus are widely used in industry and other human activities; common uses include fertilizers, soaps, detergents, and surface preparation agents. In these situations, phosphorus is viewed as an important but limited natural resource that should be used efficiently, economically, and in environmentally friendly ways. However, in the steel industry, phosphorus is known as a typical harmful element for high-quality steel products. Phosphorus is thus removed from hot metal (molten pig iron) to slag. Since the total crude steel production in Japan and South Korea is extremely huge (118 and 53 million tons in 2008 respectively)⁹⁻¹⁰⁾, the amount of phosphorus removed to steelmaking slag must also be large. The authors have found by material flow analysis¹¹⁻¹⁵⁾ that phosphorus removed to the steelmaking slag shares a significant part of total phosphorus flow in Japan and South Korea. The amount of phosphorus transferred to steelmaking slag is estimated to be 96.4 and 35.7kt-P/year in Japan and South Korea, respectively.

Manganese material flow for the steel industry in both countries is shown in Fig. 1. In the ironmaking process, pig iron (hot metal) is produced as the main product and BF slag is generated from the blast furnace (BF) as a by-product. The input of manganese to the ironmaking process is iron ore, ferruginous manganese ore, and steel scrap. The manganese output to pig iron and ironmaking slag is evaluated to be 95.1 kt-Mn/year and 15.9 kt-Mn/year, respectively.¹⁵⁾ In the case of Japan, the manganese output to pig iron and slag are estimated to be 208.9 kt-Mn/year and 55.4 kt-Mn/year.¹⁴⁾ In the steelmaking process, crude steel is produced as the main product and steelmaking slag is generated as a by-product from the basic oxygen furnace (BOF) and electric arc furnace (EAF) processes. Steelmaking slag is generally classified into some categories depending on the refining processes such as desiliconization, dephosphorization, desulfurization, BOF and EAF slags while manganese flow in each slag has been summarized as a whole “steelmaking slag” in Fig. 1. It should be noted that, among these slags, our major target to recover manganese and phosphorus is the hot metal dephosphorization slag⁸⁾ because manganese and phosphorus tend to be highly concentrated into the slag. The sources of manganese in the steelmaking

process are hot metal, steel scrap, ferro-manganese, silico-manganese, and manganese metal. The manganese outputs from the steelmaking process were evaluated to be 260.0 kt-Mn/year in crude steel and 146.0 kt-Mn/year in slag in South Korea while in the case of Japan the manganese outputs are 590.3 kt-Mn/year in crude steel and 530.7 kt-Mn/year in slag, respectively. It should be noted that the amount of manganese loss into steelmaking slag is almost equivalent to that of manganese input into steelmaking process as ferro-manganese etc. in both countries. The results of material flow analysis suggest that a significant ripple effect can be expected if the recovery of manganese and phosphorus from iron- and steel-making slag becomes possible.

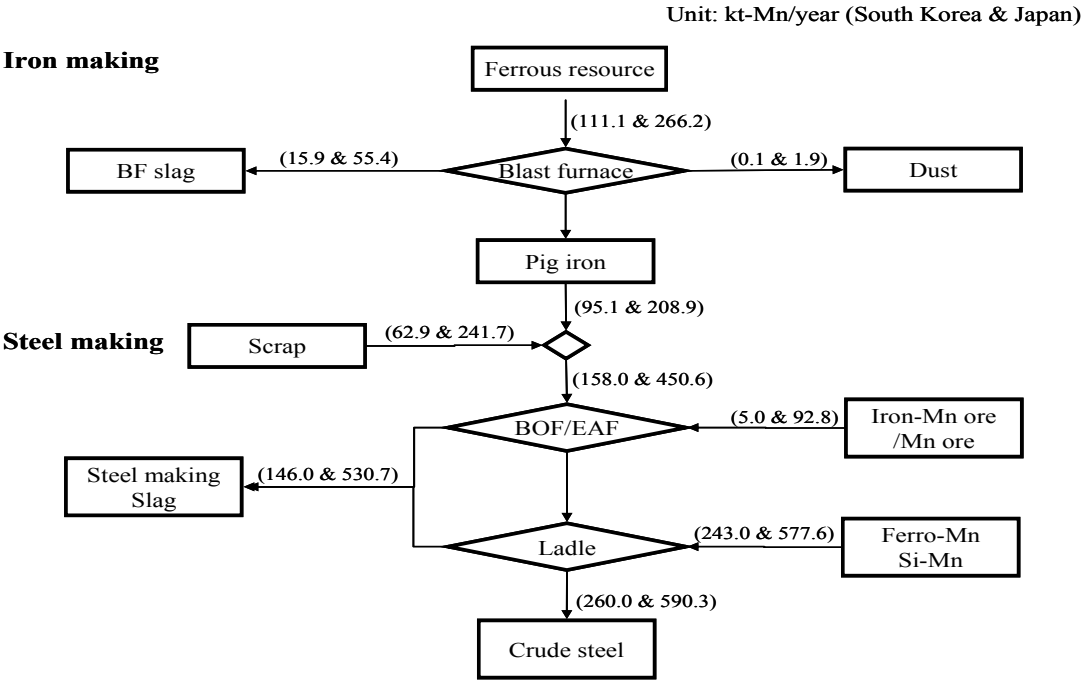


Figure 1 Material flow of manganese in Japanese and South Korean steel industries (2005)

3. Experimental procedures

3.1 Morphology of dephosphorization slag

The FeO-CaO-SiO₂-P₂O₅(-MgO-MnO) system is the typical dephosphorization slag. The morphology of solidified dephosphorization slag has been discussed in a number of previous studies. According to the report of Futatsuka et al.,¹⁶⁾ dephosphorization slag after solidification generally consists of (1) iron free crystalline phase that contains phosphorus (herein-after “phosphorus enriched phase”) and (2) phosphorus free another phase that contains iron. The authors have made more detail analysis on the manganese and phosphorus morphology in the practical dephosphorization slag to develop a manganese and phosphorus recovery process from the slag. It was found that the above-mentioned phosphorus free another phase can be further divided into two kinds of phases; FeO-CaO-MnO based mangano-wustite phase (herein-after “manganese enriched phase”) and FeO-CaO-SiO₂ phase which contains manganese as minor component (herein-after “matrix phase”). Figure 2 shows the examples of element mapping image in the dephosphorization slag by EPMA.

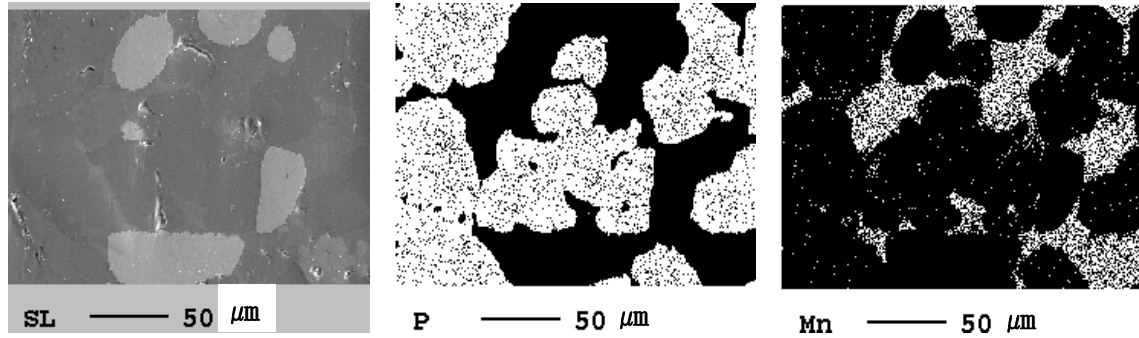


Figure 2 Examples of microstructures of dephosphorization slag C

Though the composition and morphology widely vary in general depending on the produced steel categories and operating conditions, most of dephosphorization slag approximately consists of three major phases as it was explained earlier. Table 1 gives the compositions of dephosphorization slag supplied for the present experimental runs. The authors measured the magnetic properties of FeO-CaO-MnO based slag with a vibrating sample magnetometer (VSM) as part of a quantitative investigation of the possibility of magnetic separation of manganese enriched phase from slag.

Table 1 Chemical composition of the steelmaking slag

Slag		Composition (%)				
		FeO	CaO	SiO ₂	P ₂ O ₅	MnO
A	average	22.51	42.36	11.05	2.24	3.49
	phosphorus enriched phase	2.79	61.96	27.41	6.82	0.28
	manganese enriched phase	63.75	2.33	0.04	0.01	9.00
B	average	22.85	32.30	21.80	6.85	9.90
	phosphorus enriched phase	0.99	56.32	12.31	32.65	1.69
	manganese enriched phase	76.68	0.26	0.07	0.01	16.98
C	average	40.40	24.20	12.70	7.85	6.05
	phosphorus enriched phase	1.53	55.95	10.78	35.08	1.11
	manganese enriched phase	64.54	4.74	4.04	0.69	15.48

Table 2 Experimental condition

Slag	Run No.	Size (μm)		Air pump	Remark
		<32	<52		
A	1	O		X	slag: 10g water: 200ml
B	2		O	X	
	3	O		X	
C	4		O	X	
	5	O		X	
	6	O		O	

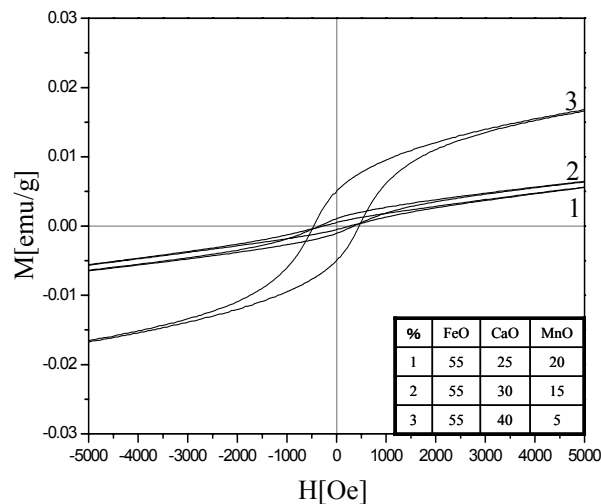


Figure 3 The magnetization curves for FeO-CaO-MnO based slag

The VSM sample was made by mixing and premelting reagent grade chemicals at desired ratios as shown in Fig. 3. A MoSi₂ heater electric furnace was used for preparing VSM sample. The result is shown in Fig. 3 in terms of magnetization as a function of the magnetic field. The magnetization curves of FeO-CaO-MnO based phase, that is manganese enriched slag, seem to be ferromagnetism or paramagnetism depending on MnO composition. On the other hand, the magnetic property of phosphorus enriched phase has been found as an antimagnetism.⁸⁾ Since the magnetic property of each phase has found to be significantly different, the authors have tried wet magnetic separation process to recover manganese enriched phase and phosphorus enriched phase from the dephosphorization slag as a new manganese and phosphorus resource.

3.2 Magnetic separation

A magnetic separation experiment was carried out using a Wet High Intensity Magnetic Separators (Eriez Series L Model 4 Laboratory). Three kinds of dephosphorization slag as shown in Table 1 were prepared for the experiments. The hot metal dephosphorization slag specimen was provided from JFE steel. This slag was crushed in zirconia ball mills (ball size: 10mm diameter) under 32 μ m and 52 μ m. Table 2 gives the experimental condition.

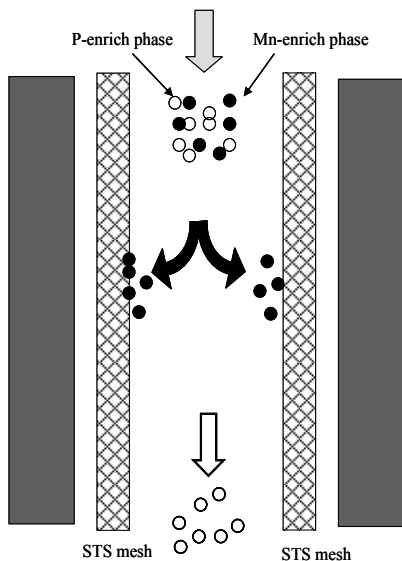


Figure 4 Schematic of the experimental magnetic field

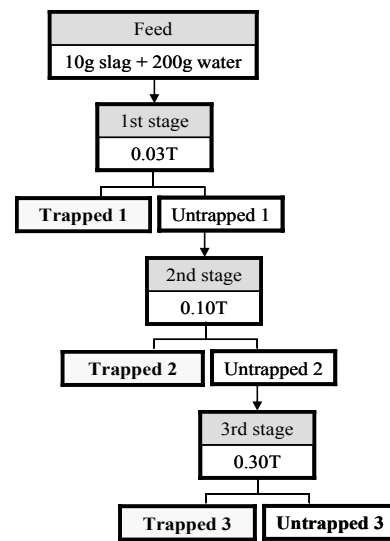


Figure 5 Magnetic separation steps

10g of the sample was dispersed in approximately 200ml of ion exchanged water to avoid coagulation and poured the sample into constant surface magnetic field strength in a controlled separation cell. 11 pieces of stainless steel mesh filters which were magnetized were inserted in the cell, and these mesh filters themselves also contributed to separation. The magnetized particles in the charged samples were magnetically trapped by the filters, and then, the particles which were not magnetized were untrapped from the cell by opening the valve equipped at the lower part of the cell as shown in Fig. 4. Magnetically trapped and untrapped particles were respectively collected and analyzed their compositions by ICP. Figure 5 shows the magnetic separation process and applied magnetic intensity. At first, a sample was separated at magnetic field strength of 0.03T and, the magnetically trapped sample in the cell was collected. The

untrapped sample from the cell without magnetization was supplied into a new cell with stronger magnetic field. This procedure was repeated for several times up to maximum 0.3T. In some experimental runs, air was injected into the cell by air pump to promote homogeneous dispersion of particles in the water.

4. Experimental results

Figure 6 shows the experimental result of the magnetic separation in Run No. 1. The manganese concentration in the recovered sample becomes smaller at higher intensity of the magnetic field. On the contrary, the phosphorus concentration in the recovered sample increased with higher magnetic field strength. In other words, because the concentration of manganese and phosphorus recovered has indicated opposite tendency, separating manganese and phosphorus individually by magnetic field from dephosphorization slag could be possible. According to the morphology study of dephosphorization slag and element mapping image by EPMA, manganese coexisted with FeO in most cases. That is, relatively small crystalline phase of manganese enriched phase dispersed on the matrix phase. Therefore, manganese tends to be collected at higher intensity of the magnetic field. Due to such reason, individual separation of manganese enriched phase and matrix phase was not well done in the present experimental condition. The phosphorus content at untrapped 3 of 0.30T becomes almost double of the average composition in spite of low phosphorus concentration of tested slag. However, it is not satisfactory for the usage of phosphate fertilizer. P_2O_5 content in natural phosphate ore for phosphate fertilizer is over 25~30wt%.¹⁷⁾ Phosphorus segregation in slag A was not remarkable and suitable. Therefore, other slag which had higher manganese and phosphorus segregations were used for magnetic separation.

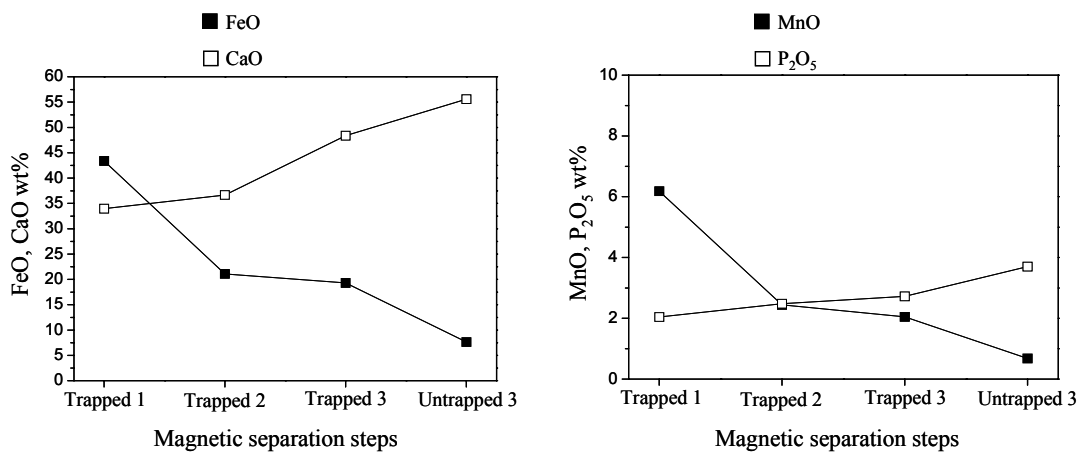


Figure 6 Magnetic concentration of slag A in Run No. 1

Run No. 2 and 3 were carried out for magnetic separation with slag B. The average composition of this slag was MnO 9.9% and P₂O₅ 6.9%, and MnO and P₂O₅ contents in manganese and phosphorus enriched phases were respectively MnO 17.0 and %P₂O₅ 32.7% as shown in Table 1. The particle size prepared was 32 μ m (Run No.3) and 53 μ m (Run No.2). Figure 7 shows the influence of the particle size to recovery efficiency of manganese and phosphorus. Manganese and phosphorus recovery efficiencies somewhat increased with smaller particle size, indicating that the population density of the isolated manganese and phosphorus enriched phases would be increase in the charged slag powder if the particle size is smaller and

thus the recovery efficiency becomes higher. It should be noted that, however, the suitable particle size depends on the initial morphology of slag. That is, if the crystal sizes of manganese and phosphorus enriched phases were initially large in the supplied slag, the relatively large particle size even after crushing would result in sufficient recovery. The morphology of slag strongly depends on the operating conditions, in particular, slag cooling conditions.

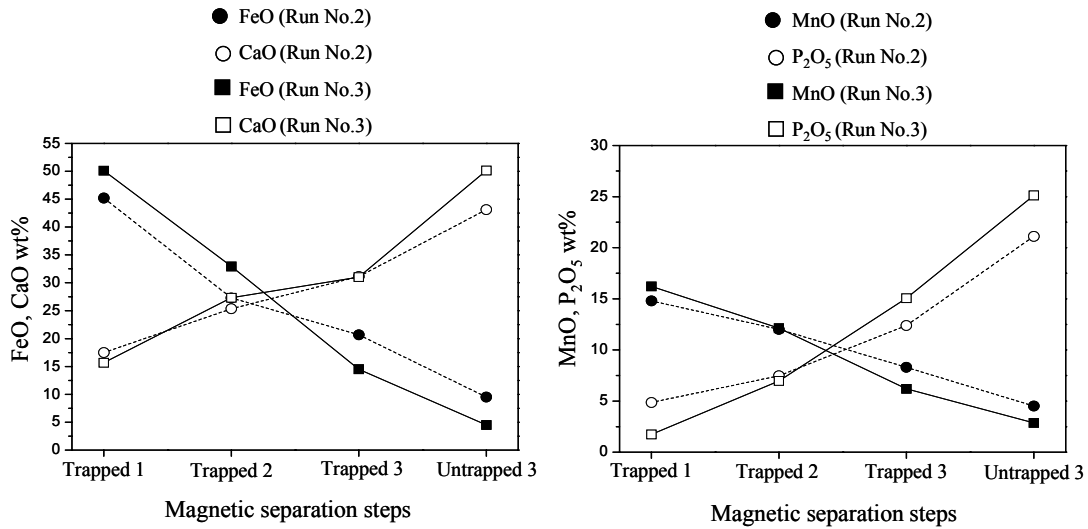


Figure 7 Magnetic concentration of slag B in Run No. 2&3

Run No. 4, 5 and 6 were carried out for the magnetic separation with slag C. The average composition of this slag was MnO 6.1% and P₂O₅ 7.9%, and MnO and P₂O₅ contents in manganese and phosphorus enriched phases were respectively MnO 15.5% and P₂O₅ 35.1% as shown in Table 1. Figure 8 shows the influence of the particle size after crushing on the recovery efficiency of manganese and phosphorus. On the basis of this result, the following experiment was made under 32 μ m.

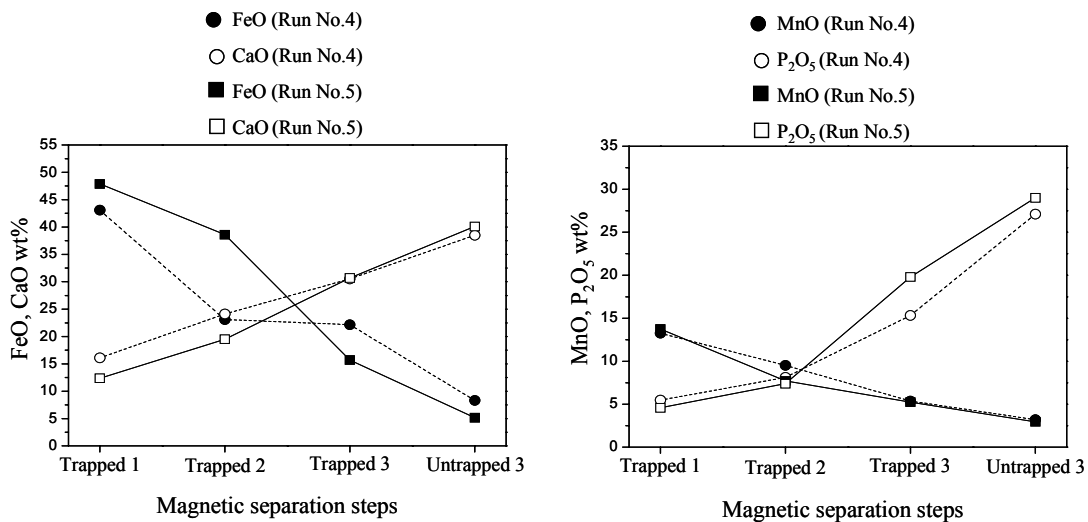


Figure 8 Magnetic concentration of slag C in Run No. 4&5

Run No. 6 was conducted for magnetic separation with physical agitation with slag C. The sample was sufficiently agitated by injecting air into the cell. The flow rate of air was controlled by the flow meter at 0.03L/min. Figure 9 shows the influence of air agitation. The results of Run No. 4, 5, and 6 indicated that the effect of the particle size and physical agitation could improve the recovery efficiency significantly. In the present experimental conditions, about 31% P_2O_5 could be recovered as “untrapped 3” of 0.30T, and about 14% MnO can be recovered as “trapped 1” of 0.03T where particle size was less than $32\mu m$ with air agitation, which was the best result. Figure 10 shows the rate of consisted phases in each recovery step. The higher magnetic field intensity resulted in the higher P_2O_5 recovery ratio. The P_2O_5 concentration of 31% at untrapped 3 is good enough to use for phosphate fertilizer. In addition, it is possible to reduce other phase contamination under 5%. The results obtained in Run No.6 are also summarized in Fig. 11. Separation efficiency should be improved in the future work, but sufficiently high P_2O_5 content was achieved in Untrapped 3 in the present work.

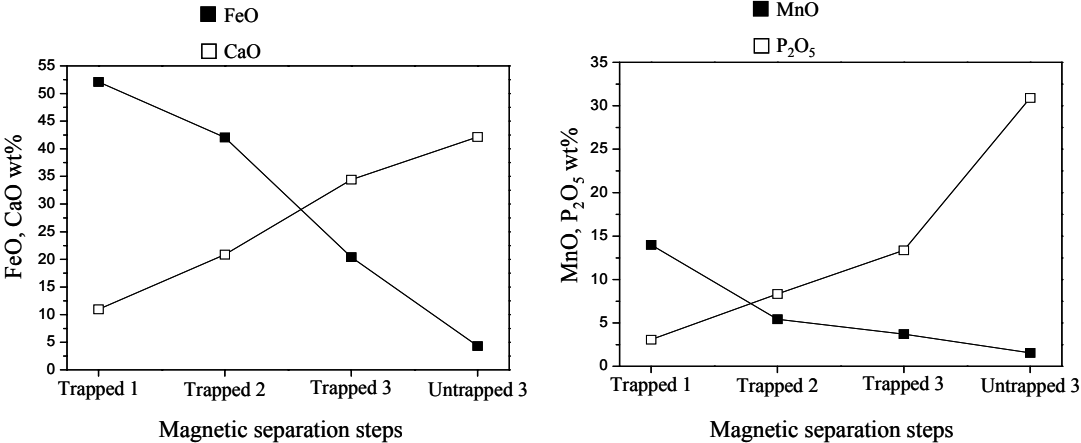


Figure 9 Magnetic concentration of slag C in Run No. 6

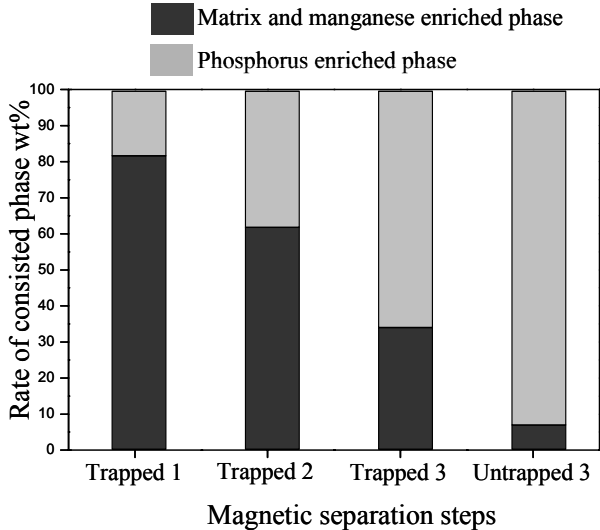


Figure 10 Rate of phosphorus enriched phase and other phase

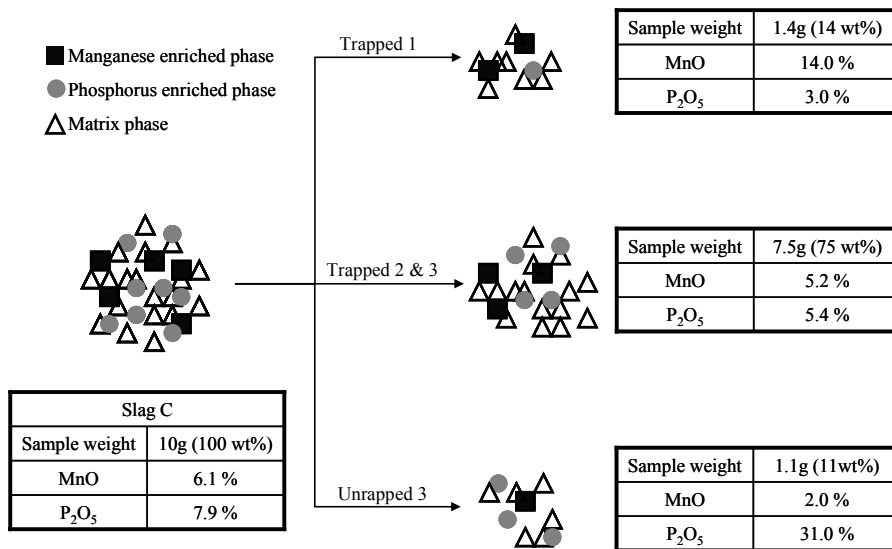


Figure 11 Concentration and weight in recovered slag

5. Conclusion

The quantity of recyclable manganese and phosphorus from slag waste in Japanese and South Korean steel industries has been evaluated with the methodology of the material flow analysis. In the case of Japan, manganese and phosphorus contained in steelmaking slag was 530.7 kt-Mn/year and 96.4 kt-P/year respectively in 2005. The recovery of manganese and phosphorus from steelmaking slag could have a significant impact on a national mineral strategy and on the environment. In the case of South Korea, the amount of manganese and phosphorus contained in steelmaking slag was estimated to be 146.0 kt-Mn/year and 35.7 kt-P/year respectively in 2005.

Magnetic separation was applied to the recovery of manganese and phosphorus from dephosphorization slag. Dephosphorization slag consists of phosphorus enriched phase and manganese enriched phase together with matrix phase. The magnetic property of each phase has found to be significantly different. In the present experiment, about 31% of phosphorus enriched slag could be recovered with less than 10% of matrix and manganese enriched phase contamination at untrapped 3 of 0.30T and about 14% of manganese enriched slag could be recovered with less than 20% of phosphorus enriched phase contamination at trapped of 0.03T, particle size of less than 32 μ m with physical agitation. For better recovery of manganese and phosphorus, it is emphasized that compositions and morphology of slag should be controlled for easier magnetic separation for manganese and phosphorus recovery. The steelmaker should be encouraged to produce not only high quality steel but also good slag as the secondary resources of manganese and phosphorus, while they basically don't care the slag quality in the view point of its recovery. However, the present authors believe that it is possible to convert "steelmaking slag" to "secondary resources of manganese and phosphorus" with additional small technologies like slow cooling and composition control. The present authors call such concept as "Slag-making technology".

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