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Novel process for recycling valuable elements from steelmaking slag

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Abstract

Steelmaking slag can be considered as a domestic resource of alloying elements, e.g. Mn and Cr. The amount of Mn and Cr contained in steelmaking slag is roughly equal to the amount of the annual import of these elements in Japan. Although Mn and Cr can be easily separated from slag by means of reduction reactions, the ratio of Mn and Cr to Fe is too low and the P content is too high for the use as Mn and Cr ferroalloys. This paper proposes a novel process for the recycling of Mn and Cr from steelmaking slag.¹ The process consists of two important steps: (1) formation of a molten sulphide phase (matte) from the slag to separate P from Mn and (2) water treatment of the residual oxide phase after sulphurisation to separate P, which is contained in the water soluble phase, from Cr. From the results of fundamental sulphurisation experiments, the separation of P from Mn was confirmed. Further, the distribution ratio of Mn and Fe between slag (oxide phase) and matte (sulphide phase) was investigated. In addition, the difference between the water solubility of the P enriched phase and the remaining matrix phase was clarified.

Introduction

Because most of the metals used in Japan are imported from foreign countries, a stable supply of these metals is a very important issue. The reasons for instability in the metal resource supply can be attributed to the following: the countries that produce these metals are very limited, the amount of metals produced in these countries is affected by their political situation, and they are objects of speculation. Based on these considerations, the Japanese government has designated Ni, Cr, W, Co, Mo, Mn, and V as the national stockpile elements (Table 1) and initiated a research programme named 'Element Strategy'. It is well known in the steelmaking industry that the various characteristics of steel products are controlled by the addition of alloying materials. As the demand for high-grade steel increases, the production of special steel and high alloy steel increases accordingly. In addition,

various elements are added to the plain carbon steel for micro-alloying. This implies that the steel properties become highly dependent on the non-ferrous metals. In the recycling of steel as steel scrap, the value of the added alloying elements is not considered and the scraps are reused in the production of low-grade steel. In this sense, steel can be considered as a place where the elements play an active role but also as a graveyard for the elements. Nonetheless, steelmaking slag contains many valuable elements. Steelmaking slag can be considered as a domestic resource of the alloying elements, especially Mn and Cr. These elements can be easily separated from slag by means of reduction reactions; however, the ratio of Mn and Cr to Fe in the resulting ferroalloy is too low and the P content is too high to use this ferroalloy in the steelmaking process. This paper proposes a novel process for the recycling of Mn and Cr from steelmaking slag and presents the results of fundamental experiments.

Table 1: Element storage target in Japan

	60-Day Storage Target (kt)	Conversion to Annual Quantity (kt)
Nickel	19.505	117.03
Ferro-Chromium Alloy	94.853	569.12
Tungsten Ore	0.579	3.47
Cobalt	0.251	1.51
Molybdenum Ore	1.771	10.63
Ferro-Manganese	43.183	259.10
Ferro-Vanadium	0.641	3.85

Mass flow of Mn and Cr in Japan

Manganese

Manganese is an important alloying element in high-grade steel production. Nowadays, manganese is used not only in the production of heavy plates and pipes but also as an additive for various grades of coil and sheet, due to the increasing demand for high tensile strength steel for the automotive use. Figure 1 shows the mass flow of Mn in Japan.² Approximately 440 kt of Mn is imported as the ferroalloy of metallic Mn, and more than 95% of this amount is consumed as an alloying material for steel. In addition to this, about 255 kt of the imported Mn is contained in iron ore. This Mn is reduced in a blast furnace, and its content in the hot metal is approximately 0.3%. Almost all of the Mn in the hot metal is oxidised in a BOF and discarded as slag. After the steel is tapped from the BOF, imported ferromanganese

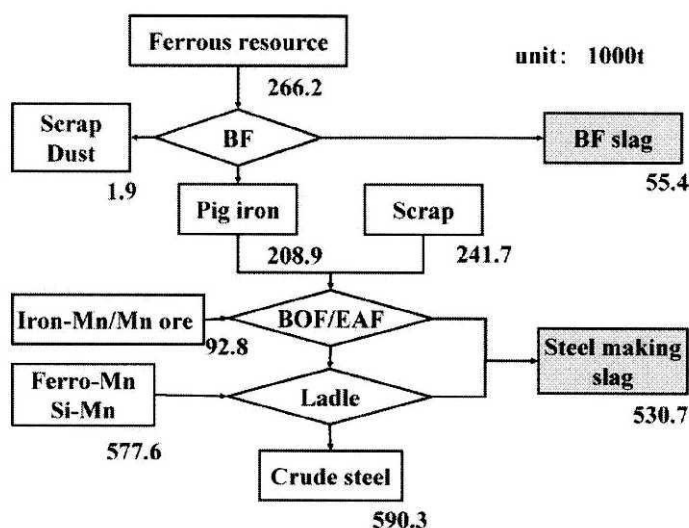


Figure 1: Elemental flow of manganese in 2005²

alloy is added into the secondary steelmaking process. As shown in Figure 1, the total amount of manganese in steelmaking slag is close to the amount imported. Therefore, steelmaking slag may be considered to be a valuable source of manganese. Although the ferromanganese alloy can be produced through the reduction of steelmaking slag, it is not suitable for use as an alloying material in the steelmaking process because the phosphorous content in the alloy is too high and the manganese content too low. Based on a mass balance calculation, the manganese content is found to be less than 20% whereas the phosphorus content is found to reach up to 7% by use of a simple reduction process.¹

Chromium

Chromium is also one of the national stockpile elements in Japan. The mass flow of Cr in Japan is shown in Figure 2.³ Chromium is mainly used as an alloying material to produce stainless steel. Stainless steel is divided into two types based on the metallography, *i.e.* austenitic stainless steel and ferritic stainless steel. Most of the austenitic stainless steel contains Cr and Ni. Typical austenitic stainless steel is the grade 304, which contains 18% Cr and 8% Ni; the grade 316, which contains 18% Cr, 12% Ni, and 2% Mo, is also popular. Typical ferritic steel, on the other hand, is the grade 430, which contains 18% Cr, and does not contain Ni.

This difference in metallography has very important implications for the recycling of stainless steel. Most of the steel scrap, which includes ferritic stainless steel, has the ferritic structure and exhibits magnetic properties. Conversely, stainless steel, which has the austenitic structure, is non-magnetic. Consequently, austenitic stainless steel scrap is easily separated from other steel scrap. For this reason, the values of the

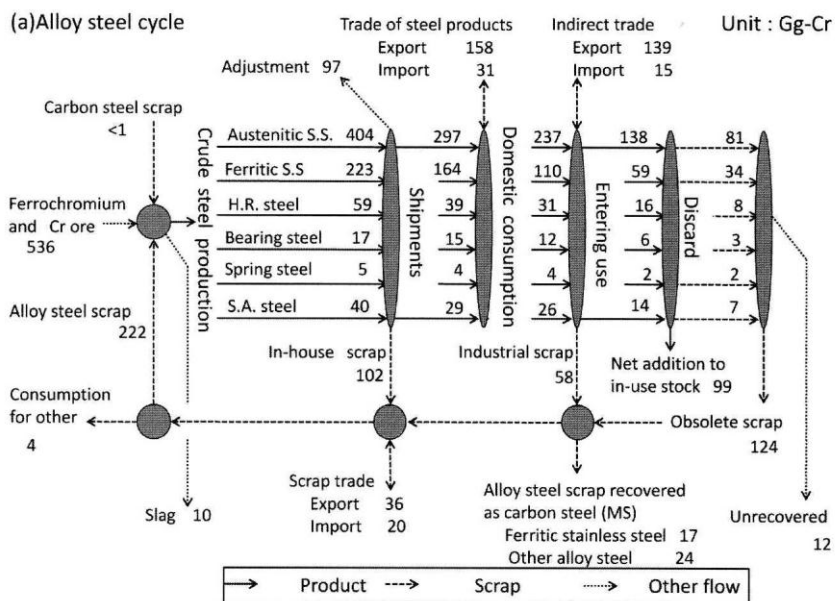


Figure 2: Substance flow of Cr in 2005 associated with alloy steel³

alloying elements, *i.e.* Ni, Cr, and Mo are reflected in the scrap price and the austenitic stainless steel scrap is a major resource in the production of steel of the same grade in EAF. This unique case in which the scrap is recycled not as low-grade but same-grade products is very important. In the process of recycling austenitic stainless steel scrap, Cr, and Mo are also recycled.

As opposed to austenitic stainless steel scrap, the scrap of ferritic stainless steel is magnetic, which makes it difficult to separate it from the scrap of plain carbon steel. This situation results in an increase of the Cr content in the scrap used to produce plain carbon steel and also an increase in the Cr content of EAF slag due to the fact that Cr is oxidised in the refining process. As shown in Figure 3,³ about 80% of Cr is

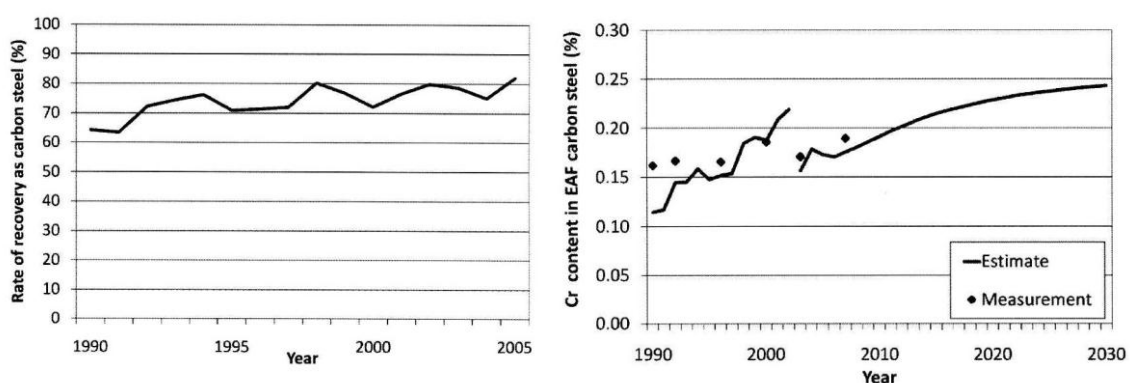


Figure 3: Recovery rate of alloy steel as plain carbon steel scrap (a), and Cr content in the plain carbon steel produced by EAF (b)³

recovered as plain carbon steel scrap and the Cr content in the scrap used to produce plain carbon steel is increasing.

Outline of the recycling process

The slag recycling process consists of two steps: (1) formation of a molten sulphide phase (matte) from the slag in order to separate P from Mn and (2) water treatment of the residual oxide phase after the sulphurisation process, to separate P, that is contained in the water-soluble phase, from Cr. The schematic diagram of this process is shown in Figure 4. In the first stage, steelmaking slag is sulphurised and a FeS-MnS matte is formed. The matte is then oxidised in order to increase the Mn/Fe ratio, thereby forming an intermediate slag whose composition is adjusted to increase the activity coefficient ratio of $\gamma_{\text{FeO}}/\gamma_{\text{MnO}}$. Finally, this intermediate slag is reduced to produce the ultra low P ferromanganese alloy. The residual slag from the first stage is used as a starting material in the second stage. This residual slag is ground and immersed in water. Selective dissolution of the solid solution phase, which has a high P content, can then be achieved by adjustment of the pH and the other conditions. The residual oxide is then reduced to produce the ultra low P ferrochromium alloy. In this step, the partial pressure of oxygen has to be controlled precisely in order to achieve the increase in the Cr/Fe ratio of the alloy.

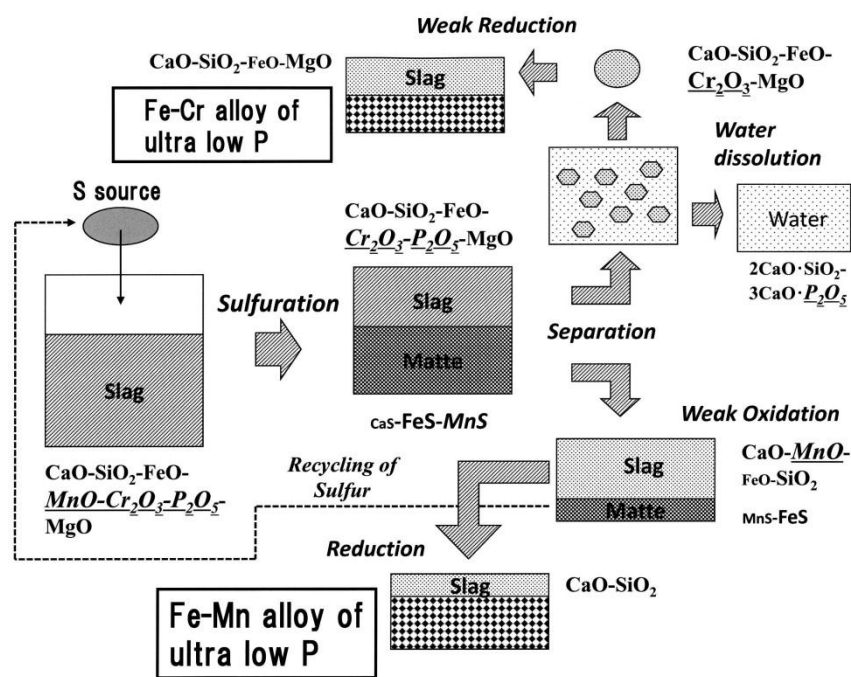


Figure 4: Schematic diagram of the proposed novel recycling process.

Formation of Matte

The relationship between the oxides and sulphides of Mn and Fe is expressed in equation (1):



The activity coefficients of FeO and MnO have been previously determined for steelmaking slag. The activity ratio of a_{MnS} to a_{FeS} can be calculated from the typical steelmaking slag composition and the relationship between the temperature and the activity ratio of $a_{\text{MnS}}/a_{\text{FeS}}$, as shown in Figure 5. If the activity coefficients of γ_{MnS} and γ_{FeS} are equal in value, this figure implies that the ratio of MnS and FeS contents is more than 1.0 in the matte formed by the sulphurisation of steelmaking slag for temperatures below 1830 K. In addition, based on the phase diagram of the FeS–MnS system, the maximum MnS/FeS in liquid sulphide is 1.0 in wt% at 1773 K. Therefore, based on both of these considerations, the MnS/FeS ratio is estimated to be approximately 1.0.

An increase in the Mn/ Fe ratio is imperative in the production of ferromanganese alloy, and this can be achieved by oxidation of the matte formed by the sulphurisation of the steelmaking slag. Based on the relationship presented in equation (1), the MnO/FeO ratio of a slag in equilibrium with the matte was calculated for various basicities of the slag. In this case, the activity ratio of $a_{\text{MnS}}/a_{\text{FeS}}$ was set as 1.4, which was obtained by the previous calculation. As shown in Figure 6, when choosing the optimum basicity and temperature conditions, the mass percentage ratio of MnO/FeO can be as high as 3.0. These calculation results indicate that a ferromanganese alloy containing more than 75% Mn can be produced using the present process.

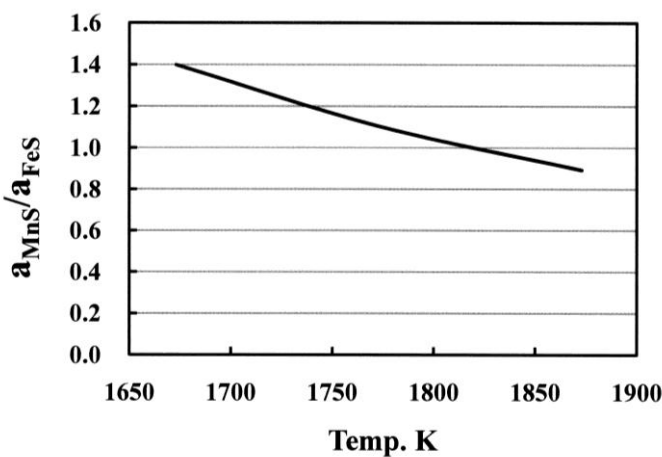


Figure 5: Influence of temperature on the activity ratio of a_{MnS} to a_{FeS} in a matte at equilibrium with steelmaking slag.

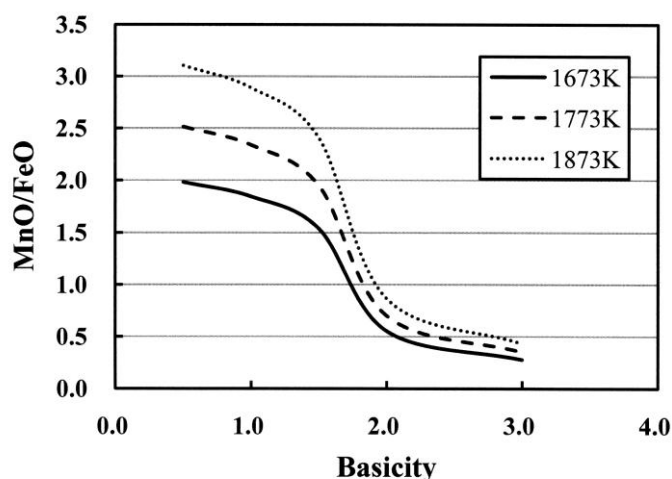


Figure 6: Influence of basicity on the ratio of MnO to FeO at equilibrium with a matte formed by the sulphurisation of steelmaking slag.

Some fundamental experiments were carried out to verify the results of the calculations. In this experiment, the equilibrium distributions of Fe, Mn, and P between the FeS-MnS matte and FeO-MnO-CaO-SiO₂-MgO-P₂O₅ slag was measured under a controlled CO/CO₂/SO₂ atmosphere. A reagent mixture of approximately 5 g of slag was charged on a reagent mixture of approximately 5 g of matte in a fused magnesia crucible. The sample was heated to 1673 K under a suitable CO/CO₂/SO₂ atmosphere in a furnace. In this experiment, $\log p_{O_2}$ and $\log p_{S_2}$ were set as -13.0 and -6 . Based on thermodynamic calculations, under these conditions the sulphide is more stable than the oxide when the activity of each component is unity. The

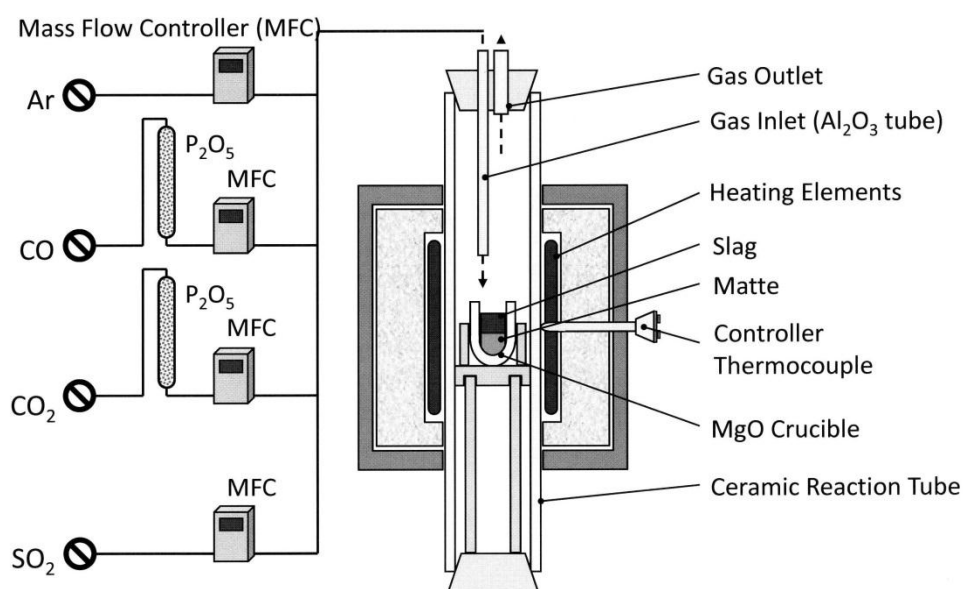


Figure 7: Experimental setup¹

preliminary experiment confirmed that the reaction achieved equilibrium after 24 h. Therefore, the sample was removed from the furnace after 24 h and then quenched by blowing He gas on the sample. The content of each element in the sample was analysed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The experimental setup is shown in Figure 7, and the results of this experiment are listed in Table 2. The matte was composed of FeS and MnS, with a very low CaS content. The P content was also very low, and it was confirmed that P can be separated from Fe and Mn through the matte production. Approximately 2% S was observed in the slag phase. Suspended sulphide particles were observed in the microstructure, and the high S content in the slag may have been caused by the presence of suspended matte. The ratio of Mn/Fe in the matte was less than 0.3, which is significantly lower than the activity ratio of a_{MnS} to a_{FeS} calculated based on the thermodynamics shown in Figure 5. This indicates that the activity coefficient of γ_{MnS} is much higher than that of γ_{FeS} in this system. Based on the equilibrium relationship shown in equation (1), the equilibrium constant (K) is described in equation (2), where N is the mole fraction and γ is the activity coefficient:

$$\{N_{FeS}/N_{MnS}\} \times (N_{MnO}/N_{FeO}) \times \{\gamma_{FeS}/\gamma_{MnS}\} \times (\gamma_{MnO}/\gamma_{FeO}) = K \tag{2}$$

The activity coefficient of each oxide in the slag can be calculated by the regular solution model.⁴ Therefore, the activity coefficient ratio of sulphides can be calculated using the concentration of each component in the slag and matte listed in Table 2. The result of these calculations is shown in Figure 8, and it is found that the activity coefficient of γ_{MnS} is two to three times larger than that of γ_{FeS} .

Table 2: Experimental results

	Slag (mass%)							Matte (mass%)				
	(Fe)	(Mn)	(Mg)	(P)	(Ca)	(Si)	(S)	{Fe}	{Mn}	{Ca}	{Mg}	{P}
1	7.3	9.8	10.8	2.1	15.6	18.4	1.4	54.5	13.5	1	0.5	0.1
2	6	6.8	10.2	2.2	21.1	14.4	2.2	53.9	16.1	1.9	0.2	< 0.1

This indicates that even though P can be separated by the formation of the matte, successive oxidation treatment of the matte is necessary to increase the ratio of Mn/Fe in the matte.

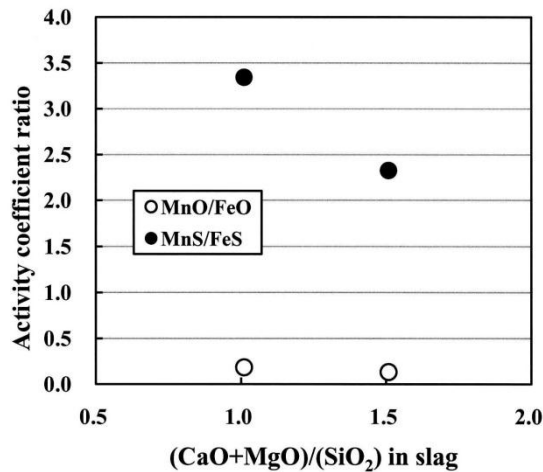


Figure 8: Activity coefficient ratio of Mn and Fe as sulphides and oxides

Water Treatment

In most cases, steelmaking slag is saturated with dicalcium silicate (C_2S), and it is well known that dicalcium silicate forms a solid solution with tricalcium phosphate (C_3P) and the partition ratio of P between the solid solution and liquid slag is large.⁵ Therefore, most of the P in slag goes into forming the solid solution and the P content in the other matrix phase is low. Some methods have been proposed for the removal of P from the other oxide phases by using the difference in density,⁶ and magnetic properties.⁷

The authors have proposed another method to separate P using the difference in the water solubility of the solid solution and that of the residual matrix phase. Based on the solubility of various calcium silicate and calcium phosphate compounds in sea

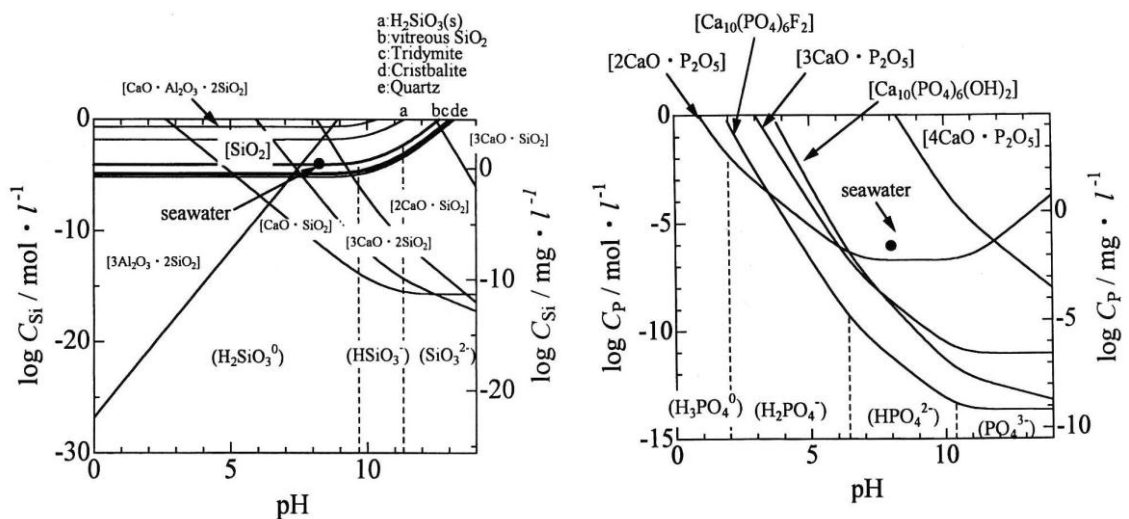


Figure 9: Solubility of silicon and phosphorus in sea water at 298 K⁷

water shown in Figure 9,⁸ it is found that the solubility of C_2S is larger than that of C_3P and the solubility is affected by the pH of the water. The water solubility of the solid solution with various ratios of C_2S to C_3P and the solubility of the remaining matrix phase was investigated using fundamental experiments. In the experiments, a solid solution was made by pressing a mixture of reagents with a target composition to form a tablet followed by sintering for 48 h at 1873 K. The ratio of C_2S and C_3P was changed. The synthetic matrix slag was melted at 1673 K in an iron crucible and rapidly quenched. Both samples were ground into powders with diameter less than 57 μm . About 1 g of the powdered sample was immersed in 0.4 L of water, which was stirred by an impeller under Ar bubbling condition, at room temperature. The experimental setup is shown in Figure 10. The pH of the water was automatically controlled by the addition of HNO_3 . The water was sampled at 10–60 min intervals for 180 min and the concentration of the various elements in the water was analyzed using ICP. The result when the solid solution ($C_2S:C_3P = 7:3$) was immersed in water at pH = 7 is shown in Figure 11(a). In this figure, the dissolution ratio indicates the ratio of the weight of each element dissolved in the water to that in the immersed powder sample. It can be seen that dissolution of Ca and Si increased gradually to reach a maximum dissolution ratio of 0.30–0.35 at 180 min. This indicates that about 35% of Ca and Si is dissolved. In contrast, the dissolution ratio of P shows an initial increase for the first 30 min followed by a gradual decrease to dissolution ratio of about 0.1. Analysis of the residual materials after the filtration confirms the formation of hydroxyapatite. In order to enhance the dissolution of P, the formation of this compound must be suppressed. Figure 11(b) shows the dissolution ratio of the matrix phase (CaO: 33.4%, SiO_2 : 33.6%, FeO: 27.1%, P_2O_5 : 5.9%). It is clear that the dissolved Ca and Si content in the water is 10 times smaller than the values shown in Figure 11(a). These results show the possibility that the C_2S - C_3P solid

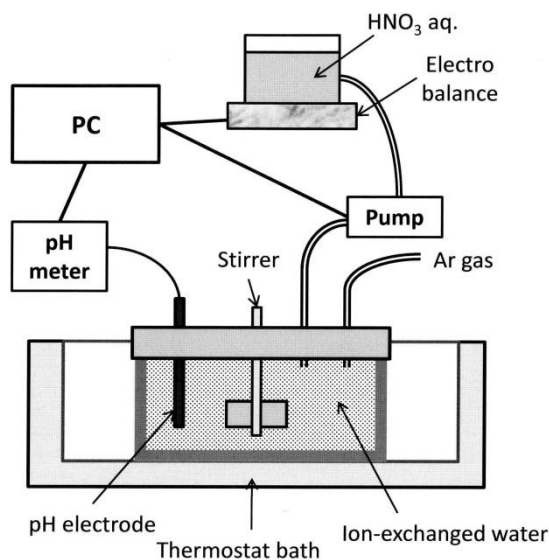


Figure 10: Experimental setup to measure dissolution behaviour

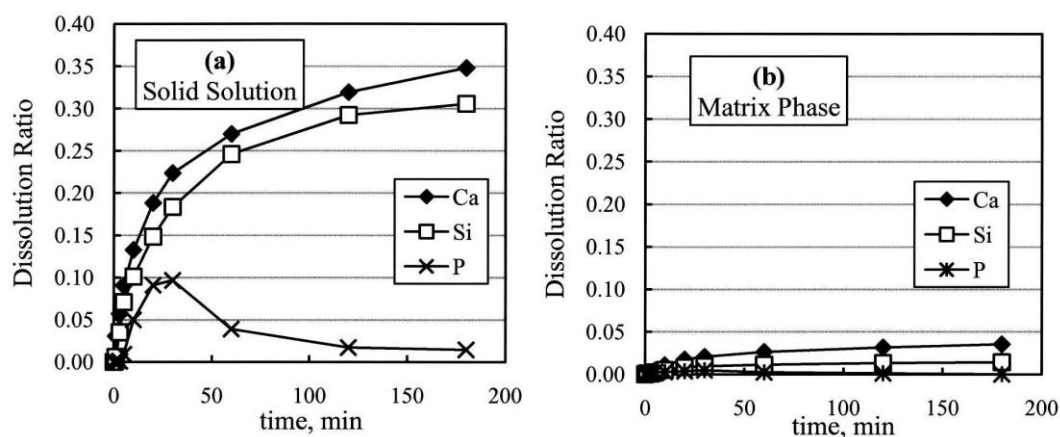


Figure 11: Dissolution ratio of each element in solid solution (a) and matrix phase (b) in water at pH = 7

solution may be selectively dissolved in water. However further investigations on that are necessary.

Conclusions

Steelmaking slag can be considered as a domestic resource of alloying elements, *e.g.* Mn and Cr. The amount of Mn and Cr contained in the steelmaking slag is roughly equal to the amount imported annually. Although these elements can be easily separated from slag by reduction reactions, the ratio of Mn and Cr to Fe is too low and the P content is too high for use as the ferroalloy in the steelmaking process. This paper proposes a novel process for the recycling of Mn and Cr from steelmaking slag.¹ The process consists of two important steps: (1) formation of a molten sulphide phase (matte) from slag to separate P from Mn and (2) water treatment of the residual oxide phase after the sulphurisation, to separate the P contained in the water soluble phase from Cr. Fundamental sulphurisation experiments confirm the effective separation of P from Mn and the distribution ratio of Mn and Fe between slag and matte was investigated. In addition, the difference in the water solubility of the P enriched phase and the remaining matrix phase was clarified.

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