A Material Flow Analysis of Phosphorus in Japan

The Iron and Steel Industry as a Major Phosphorus Source

Kazuyo Matsubae-Yokoyama, Hironari Kubo, Kenichi Nakajima, and Tetsuya Nagasaka

Keywords:

industrial ecology
input–output analysis (IOA)
phosphate
slag
substance flow analysis (SFA)
steelmaking

Summary

The demand for biofuels has recently increased because of rising prices of fossil fuels and diversification of energy resources. As a result, the demand for sugarcane and corn has been increasing, not only for food production, but also as sources of energy. In this context, securing supplies of phosphorus, required as an essential nutrient in agricultural production, has considerable implications that extend beyond food and agricultural policy. It is therefore important to consider the quantity and availability of phosphorus resources that remain untapped, because the demand and supply of phosphate ore is currently becoming very tight, and Japan has no domestic phosphorus resources.

To identify potential phosphorus resources, we have investigated the material flow of phosphorus within Japan, including that in the iron and steel industry, on the basis of statistical data for 2002. Our major finding is that the quantity of phosphorus in iron and steelmaking slag is almost equivalent to that in imported phosphate ore in terms of both the amount and concentration. We also found, by means of a waste input–output analysis and a total materials requirement study, that the phosphorus potentially recoverable from steelmaking slag by a new process that we have proposed has considerable environmental and economic benefits. Concerning the restricted supplies of phosphorus resource, it is important to consider the quantity and availability of phosphorus resources that currently remain untapped. From that viewpoint, steelmaking slag would be expected to be a great potential resource for phosphorus.

Address correspondence to:
Dr. Kazuyo Matsubae-Yokoyama
Graduate School of Environmental Studies
Tohoku University
Sendai, 980-8579, Japan
matsubae@m.tains.tohoku.ac.jp
www.kankyo.tohoku.ac.jp/en/index.html

DOI: 10.1111/j.1530-9290.2009.00162.x

Volume 13, Number 5

Introduction

Phosphorus is present only as a trace element on the Earth but is one of the important strategic resources for agricultural food production and for the chemical industry, where it used in fire retardants, glues, food additives, detergents, and so on. Natural phosphate ore (phosphate rock) is traded worldwide, mainly as a raw material for fertilizer. Approximately 147 × 10^3 kilotons (kt)[1] of phosphate ore was mined in the world during 2005. Of this, 24.7% (36.3 × 10^3 kt) was produced in the United States, 20.7% (30.4 × 10^3 kt) in China, and 17.1% (25.2 × 10^3 kt) in Morocco, while there are essentially no deposits of phosphate ore in Japan or the European Union (USGS 2007). In the case of Japan, all phosphate ore is imported from China, South Africa, Morocco, Jordan, and so on. Imports from the United States stopped in 1998, and the total amount of phosphate ore imported into Japan is decreasing year by year (from approximately 14.0 × 10^2 kt in 1993 to 8.5 × 10^2 kt in 2002) (Ministry of Finance 2004). It is of concern that, due to growing world demand for fertilizers, deposits of high-grade phosphate ore could be exhausted within the next 100 years (Abelson 1999; Christen 2007), and the average price of the ore in 2002 was approximately 1.5 times that in 1993. Furthermore, we faced an extraordinary price increase of P ore and its derived fertilizer in 2008. Since 2007, in terms of the rising production costs and strong demands, the price of phosphate fertilizer has increased sharply. Meanwhile, the price of phosphorus ore and phosphorus chemical products also increased. To maintain a sustainable supply of phosphorus to meet domestic demand, new sources of phosphorus need to be developed. Sewage sludge is one candidate as a potential source of phosphorus, and some research workers are attempting to develop new technologies for recovering phosphorus from it (Christen 2007).

Coal and iron ore are essential raw materials for the production of iron and steel, and they contain very small amounts of phosphorus. Because phosphorus has detrimental effects on the mechanical properties of steel, it is removed from molten iron in the steelmaking process by slag treatment. A flux based on calcium and iron oxides ($CaO–Fe_tO$) is added to or injected into liquid pig iron (hot metal) or molten steel,[2] and the phosphorus in the molten metal is removed in the slag phase as phosphate ion, according to the oxidation reaction.

$$4P(\text{in iron}) + 5O_{2(g)} + 6(O^{2-}) = 4(PO_4)^{3-} \quad (1)$$

Where, (O^{2-}) and $(PO_4)^{3-}$ denote free oxygen ion and phosphate anion in the slag, respectively. Because phosphate anion is well stabilized by calcium oxide (CaO) in the slag in the form of calcium phosphate, phosphorus can be efficiently removed from liquid iron to give a slag of high basicity. That is, one of the most important roles of steelmaking slag is dephosphorization of molten steel, and the slag after the dephosphorization contains approximately 2 to 10 mass% of phosphorus pentoxide (P_2O_5), together with Fe_tO, CaO, and silica (SiO_2). As a result, steelmaking slag is unavoidably generated as a by-product in the steelmaking industries, and the amount produced is approximately 15.0 × 10^3 kilotons per year (kt/yr) in Japan, where 120 × 10^3 kt/yr of crude steel was produced in 2007 (Nippon Slag Association 2003). Some steelmaking slag is used as a road-construction material, but most is merely a waste product that has to be disposed of. Therefore, steelmaking engineers and researchers are investigating new technologies for reducing the amount of steelmaking slag that is produced, and they are examining ways to develop new demand for the remaining slag as a valuable resource from the environmental and economic viewpoints. In short, although phosphorus is a very important and strategic resource, it is an impediment to the production of high-quality steel products.

We do not know exactly how much phosphorus passes through our society. Although Smil (2000) performed a detailed study of natural reservoirs of phosphorus and its flow, the author did not take into consideration the phosphorus flow associated with iron and steel production. A considerable amount of phosphorus passes through the steel industry and is accumulated in steelmaking slag and not used as a phosphorus resource.

With this as a background, we are developing a new process for recovering calcium phosphate from steelmaking slag as a new phosphorus

Table 1 Sector classifications

Agriculture, livestock, and fishery sectors		
Crops	Livestock	Meat and oils
Marine products	Farms and ranches	
Industrial sectors		
Mineral resources	Chemical industry	Fertilizer industry
Iron- and steelmaking industry	Other industry	
Waste treatment and environmental sectors		
Human excrement treatment	Wastewater	Sewage and sludge
River and marine	Landfill	

resource. Our process is based on the precipitation of various separate crystalline phases in the slag during cooling and the differences in the magnetic properties of these phases. The basic principle of this process and the results of some trials made by using practical steelmaking slags are introduced in this article.

We discuss the flow of phosphorus in Japan, introduce our new technology for phosphorus recovery, and evaluate the environmental and economic impacts of phosphorus recovery by means of a waste input–output analysis. This article presents the phosphorus flow on the basis of sectoral data, our new technology for phosphorus recovery from steelmaking slag, the total substance flow of phosphorus in Japan, and the results of an environmental assessment of phosphorus recovery.

Material/Substance Flow of Phosphorus in Japan

Phosphorus is a reactive element and tends to diffuse into the environment in nature, so that accurate material-flow accounting is not very easy to achieve. To simplify matters, we evaluated the total phosphorus flow by considering 15 sectors, as shown in Table 1. We estimated the inputs and outputs for each sector and connected the various sectors, taking into account the total mass balance.

Agriculture, Livestock, and Fishery Sectors

First, we will examine the phosphorus flow in the agriculture and fishery sectors. The activities of these sectors are strongly related to the production of food and feed, such as crops and livestock, and they have an economic impact on human activity and, in particular, the food-processing industry.

Crops and Livestock

Figure 1 shows the phosphorus flow related to crops and livestock. The crops sector deals with the flow of phosphorus associated with the production of agricultural products, classified into grains, potatoes, peas, vegetables, fruit, and other agricultural products. The quantity of each agricultural product that is distributed and its phosphorus content are taken from the *Food Balance Sheet* (MAFF 2004a) and the *Food Composition Database* (MEXT 2004), respectively. Phosphorus inputs to the crops sector are divided into two categories, and the output is divided into eight categories. When plants grow, they obtain their nutrients from sources such as fertilizer, plant nutrients, and soil-accumulated nutrients. Phosphorus in the developed plant is mainly consumed by human activity and by livestock, or it passes into the oil industry in raw materials for vegetable oils and biofuels. Note that "Import" means imported crops and "Farm/Ranch" denotes the domestic production of crops.

The phosphorus flows associated with cattle, pigs, chickens, horses, sheep, goats, and other livestock are considered in the livestock sector. Input data are derived from the *Yearbook of Fertilizer Distribution* (MAFF 2004b) and the *Food Balance Sheet* (MAFF 2004a), because we consider feed as the input to this sector: meats and livestock manure are considered as outputs. The production data for meats are obtained from the *Food Balance Sheet* (MAFF 2004a), and the phosphorus contents of various meats are obtained from the *Food Composition Database* (MEXT 2004). Flows of phosphorus in livestock manure (PL) are calculated by means of the following equation:

$$PL = N \times M \times PC \qquad (2)$$

where N is the number of livestock, M is the amount of manure produced per head of livestock,

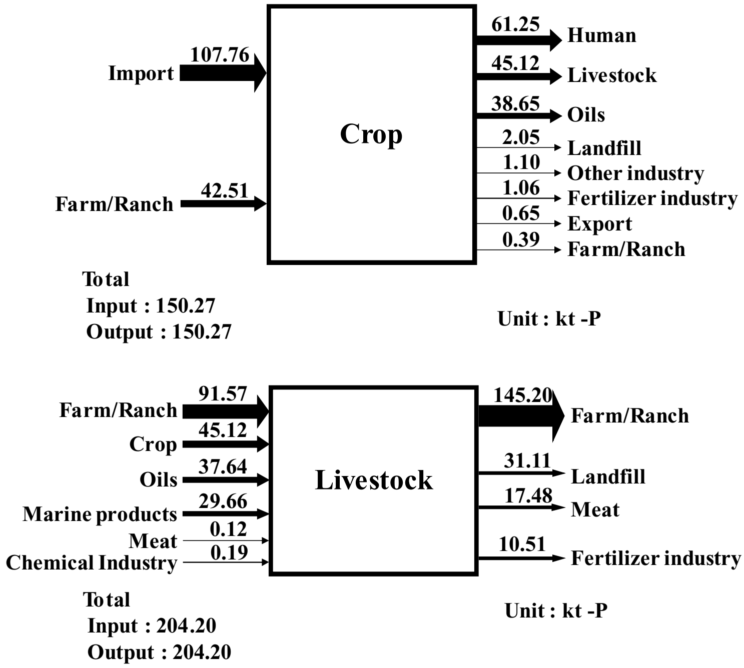


Figure 1 Phosphorus flows associated with crops and livestock in kilotons of phosphorus (kt-P).

and PC is the phosphorus concentration in the livestock manure. Input paths to the livestock sector are crops, meat, oils, farms/ranches, marine products, and the chemical industry, through feedstuff. As output paths, we consider meat, farms and ranches, sewage, fertilizer, and waste disposal. In terms of disposal of livestock manure, 10% goes to open-air storage, 80% is utilized as an organic fertilizer in farms and ranches, and the rest is disposed of as sewage or recycled as compost. The phosphorus input from organic fertilizer from farms and ranches amounts to 42.51 kt/yr for the crops sector and 45.12 kt/yr for the livestock sector, as shown in figure 1. Approximately 78% of the phosphorus in livestock manure is directly utilized as fertilizer in the farm and ranch sector, 17% is used as the resource of fertilizer production sector, and the phosphorus in the residues is assumed to be treated in well-managed landfill sites.

Meat, Oils, and Marine Products

The meat sector deals with meat, chicken eggs, and milk and dairy products, as defined in the *Food Balance Sheet*. Input paths to the meat sector are from imports and from the livestock sector, and output paths are to livestock, fertilizer, disposal, human activity, and exports (figure 2). Starch, sugar, oils and fats, soybean paste, and soy sauce are considered in the oils sector, and the phosphorus flow in the oil sector is taken as entering from imports and crops and leaving in the form of fertilizer, human activity, livestock, exports, and disposal. Phosphorus from the meat sector and oil sector consumed in human daily life amounts to 21.28 kt/yr and 4.55 kt/yr, respectively.

Marine products comprise fishery products and seaweed, as defined in the *Food Balance Sheet*. Phosphorus enters the sector from fisheries and imports, and leaves through livestock, fertilizer, human activity, and exports. As shown in figure 3, the main consumers of these products, in the form of food and feed, are humans and livestock. The total amount of phosphorus passing through this sector is 56.9 kt.

Human Activity and Farming and Ranching

Figure 4 shows the phosphorus flow related to human activity and to farming and ranching. The farm/ranch sector deals with phosphorus flow associated with agricultural fields in Japan, taking

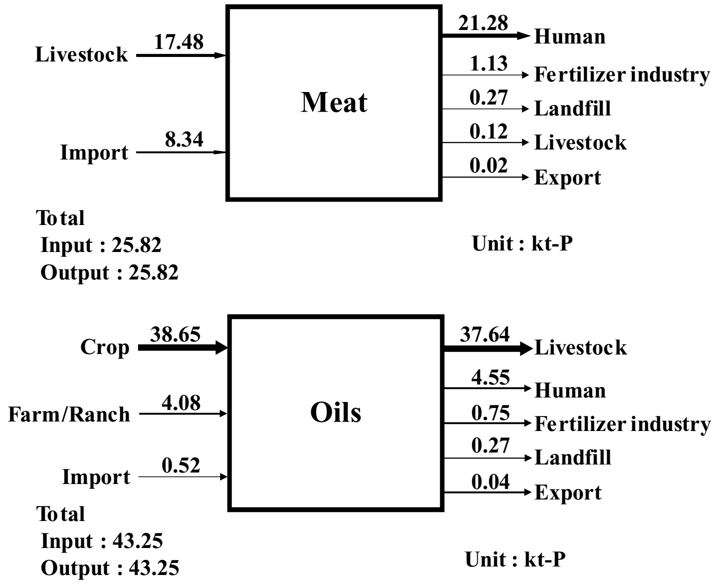


Figure 2 Phosphorus flows associated with meat and oils in kilotons of phosphorus (kt-P).

into consideration fertilizer, compost, and livestock manure as input paths, and crops, livestock, rivers, and soil accumulation as output paths. Soil accumulation is calculated as the difference between inputs and all the remaining outputs. It is hard to define the boundaries of farms and ranches. In particular, the accumulation capacity of farms and ranches differs from region to region because it is strongly dependent on the properties of the underlying soils. We estimate the phosphorus passing through this sector to be 546.8 kt/yr.

All the phosphorus inflow associated with food consumption in the human sector is not translated to phosphorus in human excrement. A part of the phosphorus is not consumed but just ends up in the garbage. Here we estimated the amount of phosphorus in human excrement and landfilled waste on the basis of the surveyed data. The remaining part of the phosphorus is assumed to go to the sewer sector.

Summary of the Agriculture, Livestock, and Fishery Sectors

Figure 5 summarizes the phosphorus flows related to the agriculture, livestock, and fishery sectors. In Japan, waste transfer across the border between prefectures is regulated by law. Utilization of phosphorus from compost and livestock manure requires onsite management, and manure is thus unsuitable for off-site utilization as a phosphorus source. Thus it is difficult to ensure the

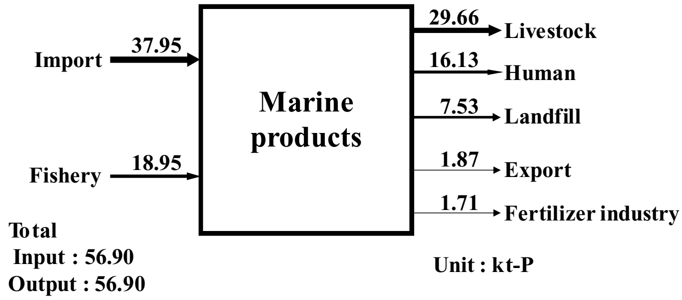


Figure 3 Phosphorus flows associated with marine products in kilotons of phosphorus (kt-P).

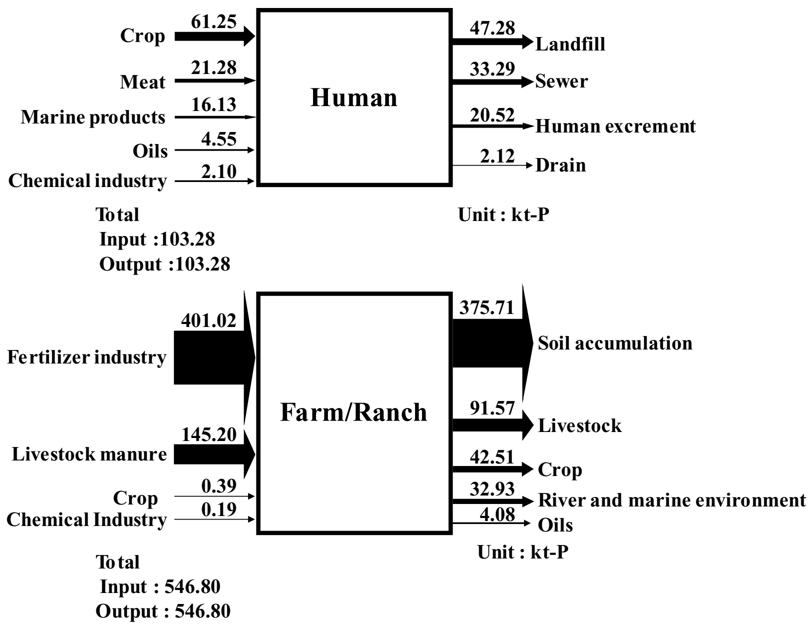


Figure 4 Phosphorus flows associated with human activity and farms/ranches in kilotons of phosphorus (kt-P).

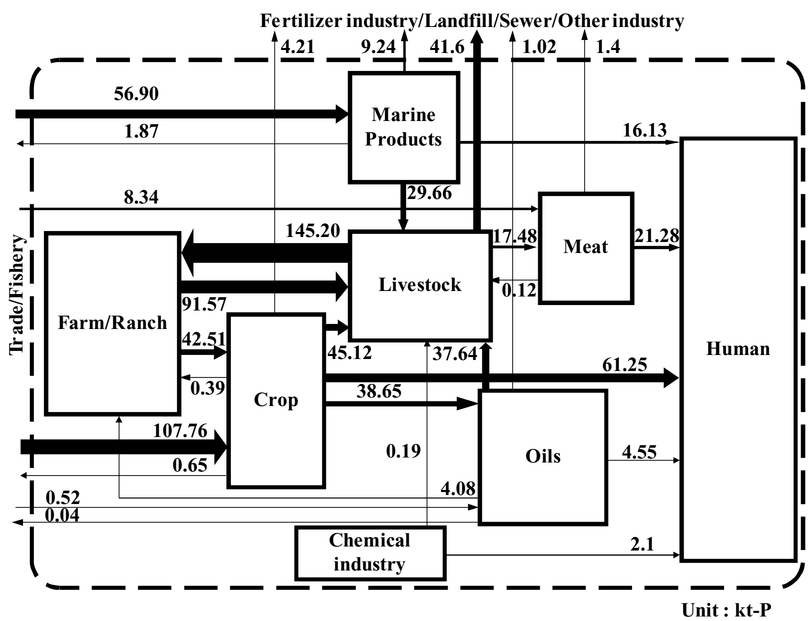


Figure 5 Overall phosphorus substance flows related to the agriculture, livestock, and fishery sectors, in kilotons of phosphorus (kt-P).

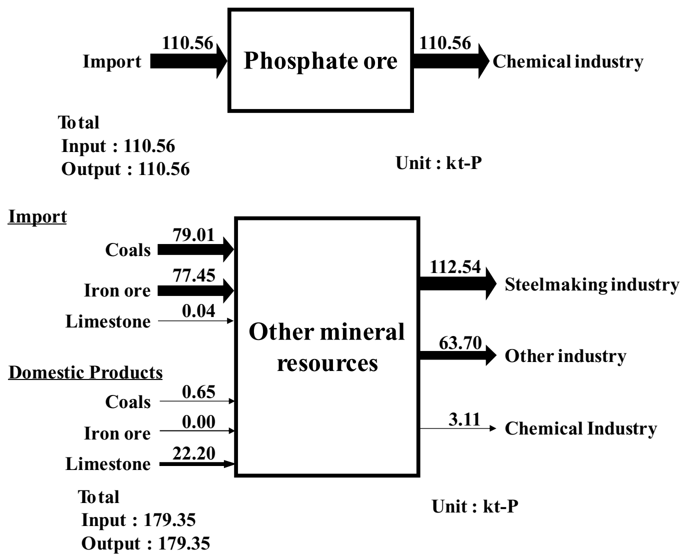


Figure 6 Phosphorus flows associated with phosphate ore and other mineral resources, in kilotons of phosphorus (kt-P).

accuracy of the estimation based on the Japan-wide statistics. We therefore consider that the real contribution of compost and manure to the quantity of phosphorus in circulation in Japan is less than that calculated on the basis of the gross weight in circulation. Inedible materials and process wastes from agricultural products are used mainly as raw materials for organic fertilizer. The main path for return of phosphorus from the economy to farms and ranches is in the form of compost and livestock manure, and its amount is evaluated at 145.20 kt/yr.

Industrial Sectors

Secondly, we examine the phosphorus flow with a focus on industrial sectors, especially the chemical industry, as a main supplier of phosphorus fertilizer, and the steelmaking industry, which consumes huge amounts of mineral resources and generates large quantities of slag.

Mineral Resources

Phosphorus flow related to phosphate ore is a significant starting point for phosphorus-related products in Japan (figure 6). Japan does not have any domestic mineral resources of phosphorus, so all the ore is imported and almost all the imported ore is used in the chemical industry as a raw material: This amounts to an estimated 110.56 kt/yr of phosphorus.

Iron ore, coal, and limestone are considered separately from phosphate ore as mineral resources, and these provide 179.35 kt/yr of phosphorus. Although input paths from imported and domestic mineral resources are considered separately, most of the phosphorus input in this sector comes from imported minerals, more than half the total amount of which is used in the steelmaking industry.

The Chemical Industry

Here we consider the phosphorus flow associated with the chemical industry, which produces phosphorus-containing inorganic compounds, fertilizers, and commodity chemicals. Figure 7 shows the phosphorus flow with respect to the chemicals sector. As products of the chemical industry, we considered the following nine commodities: phosphoric acid, phosphorus trichloride, phosphoryl chloride, ammonium phosphate, calcium phosphate, sodium phosphate, sodium tripolyphosphate, phosphate fertilizer, and compound and mixed fertilizers. The flow of phosphorus into foods and medical services is considered as a direct input for human activity, and output to the iron and steel industry

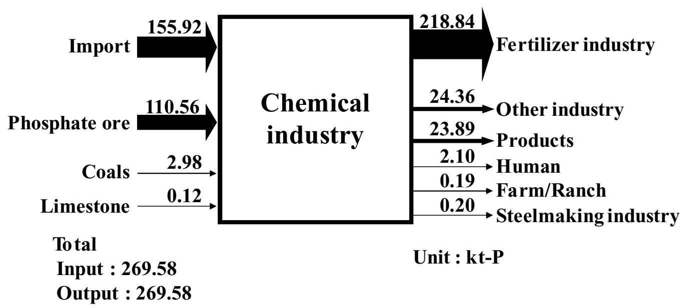


Figure 7 Phosphorus flows associated with the chemical industry in kilotons of phosphorus (kt-P).

is in the form of chemical agents for plating sheet steel.

The Fertilizer Industry

The fertilizer industry produces commercial and special fertilizers by using raw materials and commodity chemicals produced by the chemical industry, and its phosphorus throughput is reported as 218.84 kt/yr (figure 8). We assumed that all the fertilizer produced, except for a proportion that is exported, goes to farms. We also assumed that all the phosphorus contained in the fertilizer is spread and absorbed in farms and ranches.

The Iron and Steel Industry

Inputs of phosphorus into iron and steel industry considered are iron ore, coal, limestone, steel scrap, and chemicals (figure 9). Iron- and steelmaking slag and steel products are accounted for as outputs. Moreover, iron- and steelmaking slags are divided into three groups and five categories, depending on the dephosphorization procedure that is used, as shown in table 2.

The input–output data are taken from some available references (METI 2002; JISF 2003; JIE 2004; Japan Coal Energy Center 2007; MIAC 2007) and from our own fieldwork. The total amount of iron- and steelmaking slag produced in Japan in 2002 was reported to be 12,168 kt, including 3,329 kt from electric arc furnaces (EAFs). Of the remaining 8,839 kt (12,168 minus 3,329) of iron- and steelmaking slag, approximately 40% is generated after dephosphorization in torpedo cars and basic oxygen furnaces (BOFs). The average phosphorus contents of these two slags are approximated 5.0 and 3.0 mass% of P_2O_5, respectively, according to operational data. Calculated conditions, assumptions, and detailed

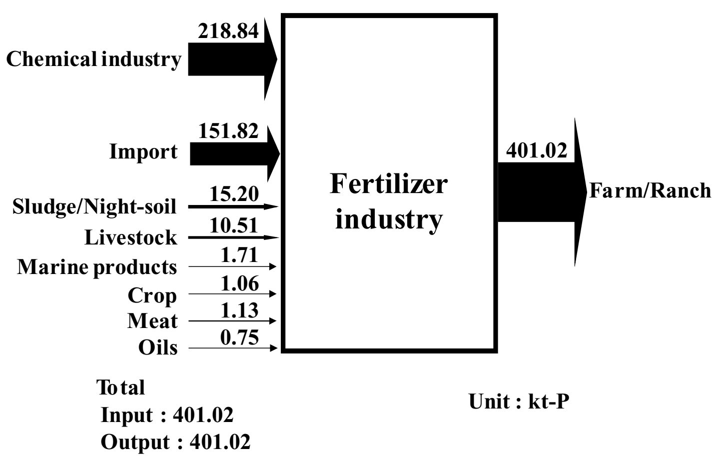


Figure 8 Phosphorus flows associated with the fertilizer industry in kilotons of phosphorus (kt-P).

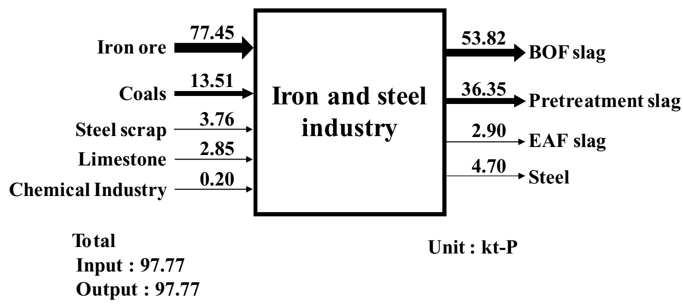


Figure 9 Phosphorus flows associated with the iron and steel industry, in kilotons of phosphorus (kt-P). BOF = basic oxygen furnace; EAF = electric arc furnace.

results on the material flow of phosphorus in the steel industry are summarized in table 3.

Other Industry

"Other industry" deals with products that are not directly related to phosphorus as a main component, but which contain phosphorus as a secondary component (figure 10). Here we deal with mineral resources, coal, limestone, and their residuals as commodities of this category. Phosphorus from coal moves into coal ash, which is utilized as a secondary material for the production of cement products and ends up becoming diffuse. Seventy percent of limestone products are used in the cement industry or civil engineering sector, and the phosphorus content of limestone is ultimately diffused.

Summary of Industrial Activity

Figure 11 shows a summary of phosphorus material flow related to industrial activity. From this figure, we can see that the major share of phosphorus flow is related to fertilizer, and almost all of this is used in farms and ranches. Although there is a considerable flow of phosphorus associated with steelmaking activity that accumulates in steelmaking slag, this has never been utilized as a phosphorus resource.

Waste Treatment and Environmental Sectors

In this subsection, we discuss phosphorus flows in the waste treatment and environmental sectors. We consider human excrement treatment, wastewater, sewage treatment,[3] and solid wastes as waste-treatment sectors, and we consider rivers, the marine environment, and soil accumulation as environmental sectors. Phosphorus is an indispensable element for plant growth and human life. Conversely, excess phosphorus has negative environmental impacts on ecosystems, for example, in causing red tides through eutrophication of lakes. Therefore, for reasons of ecosystem protection and public health, phosphorus flows related to waste treatment have been the subject of investigation for many years.

Table 2 Phosphorus related to iron and steel slags, in kilotons of phosphorus (kt-P)

Total 93.07 kt-P				
BOF slag		*EAF slag*	*Hot-metal pretreatment slag*	
Slag A	*Slag B*	*Slag C*	*Slag D*	*Slag E*
without HM de-P	with HM de-P		de-Si/de-S slag	de-P slag
24.9 kt-P	29.0 kt-P	2.9 kt-P	2.5 kt-P	33.9 kt-P
(av. P_2O_5 = 3.0%)				(av. P_2O_5 = 5.0%)

Note: HM de-P = hot-metal dephosphorization; de-Si = desiliconization; de-S = desulfurization; BOF = basic oxygen furnace; EAF = electric arc furnace.

Table 3 Calculated conditions for phosphorus material flow

Coal/coke		*Iron ore*		*Limestone*	
Consumption	62,210 kt	Consumption	113,858 kt	Consumption	22,419 kt
%P in mass	0.05	%P in mass	0.06	%P in mass	0.01
Steel scrap		*EAF slag*		*Crude steel*	
Input	38,000 kt	Output	3,329 kt	Production	107,745 kt
%P in mass	0.01	%P in mass	0.17	%P in mass	0.004

Note: EAF = electric arc furnace.

Human Excrement Treatment Sector

Figure 12 shows the flow of phosphorus through the waste-treatment sector. Phosphorus from human excrement is estimated separately for regions with nonflush and flush toilets. The phosphorus flow for regions with nonflush toilets (Pns) is calculated by the following equation:

$$\text{Pns} = \text{Pop} \times \text{NS} \times \text{R} \tag{3}$$

where Pop is the population, NS is the human excrement per head, and R is the average unit contents of phosphorus in human excrement (R).

The phosphorus flow in regions with flush toilets is estimated from the amount of drainage multiplied by its average unit phosphorus content. Discharge into sewers is considered as an output flow from the human excrement treatment sector, and utilization of human excrement in farms and disposal in rivers or oceans are considered as output flows to the environmental sectors.

Wastewater Sector

The wastewater sector deals with phosphorus contained in wastewater from miscellaneous drainage and human excrement treatment plants, and in discharged water after treatment. Phosphorus passing through this sector is disposed of in rivers or in the ocean.

Actually, a part of the discharged treated water is not directly diffused into the environment but is utilized for melting snow, in agriculture, or in flush toilets. However, we estimated the flow on the assumption that all the discharged water finally ends up in rivers or the ocean.

Sewage Treatment and Sludge Sector

Sewage implies the discharged water that comes from the human activities, in particular from regions with flush toilet, industrial plants, and wastewater-treatment facilities, and ends up in sludge or wastewater. The flow of phosphorus from human activity is estimated from the user population of the public sewerage system multiplied by the phosphorus content of miscellaneous drainage. Output flow is estimated from the amount of treated water (13,019,790 kiloliter[4]) multiplied by its average phosphorus content (1.0 milligrams per liter). The difference between the output and the input flow is taken to be the amount concentrated in sludge generated by sewage-treatment plants. Note that local conditions relating to the phosphorus content of treated sewage are not considered in this study. Part of the sludge is utilized as a raw material for civil engineering and its phosphorus content is regarded as being diffused into the environment.

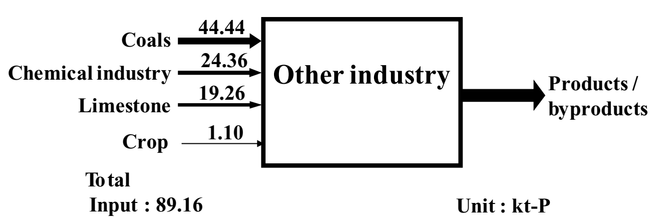


Figure 10 Phosphorus flows associated with other industry, in kilotons of phosphorus (kt-P).

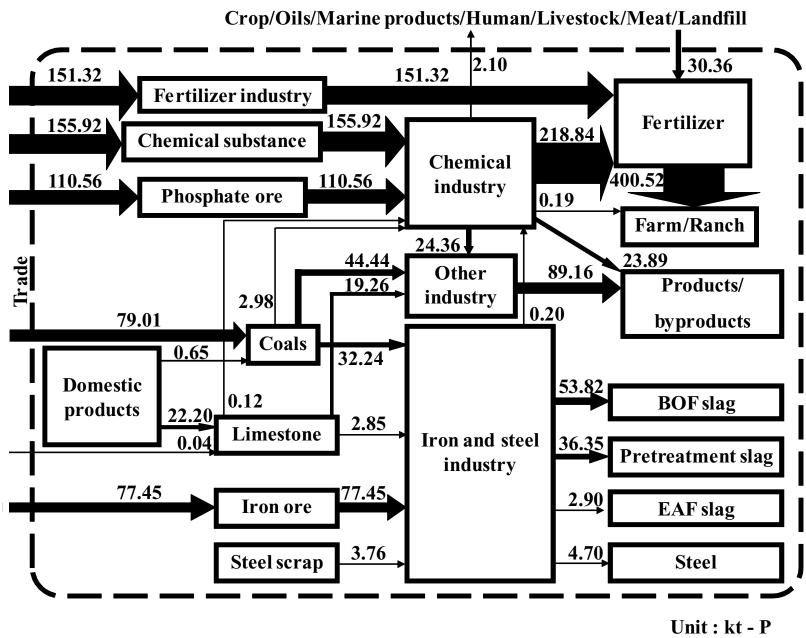


Figure 11 Overall phosphorus substance flow for various industrial sectors, in kilotons of phosphorus (kt-P). BOF = basic oxygen furnace; EAF = electric arc furnace.

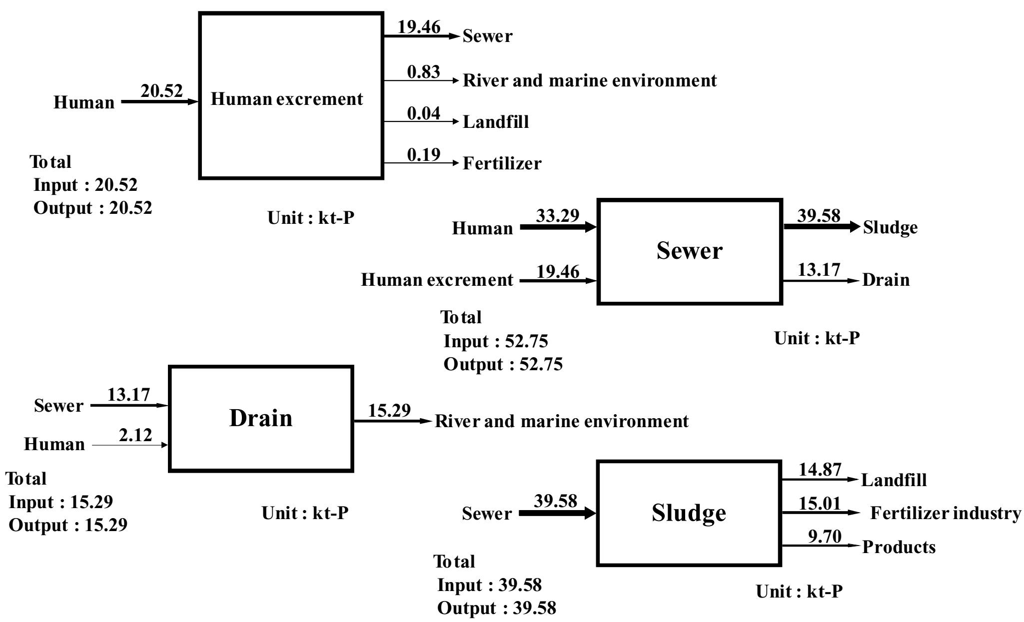
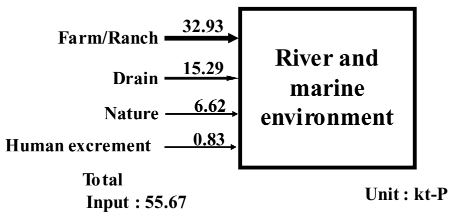


Figure 12 Phosphorus flows associated with waste-treatment sectors, in kilotons of phosphorus (kt-P).



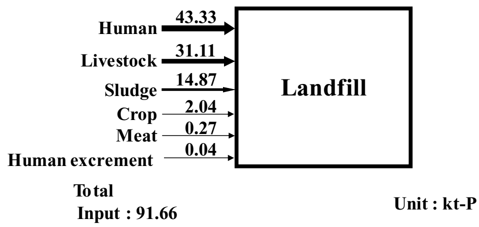


Figure 13 Phosphorus flow associated with environmental sector, in kilotons of phosphorus (kt-P).

Environmental Sectors

Phosphorus flows related to rivers and the marine environment include phosphorus emitted to the water environment by disposal in rivers or seas, and phosphorus leached from the soil of farms and ranches (figure 13). The landfill sector accepts final waste generated by the various industrial and waste-treatment sectors. Figure 13 also shows that the phosphorus in the various kinds of final wastes goes into landfill sites, and 91.66 kt of phosphorus is estimated to be diffused by this route.

Summary of the Waste-Treatment and Environmental Sectors

Figure 14 shows the overall phosphorus flows for the waste-treatment and environmental sectors. As shown in figure 14, the main flow in the waste treatment and environment sector arises from human activity, and the amount of phosphorus in sludge reaches 50% of the amount of the domestic flow related to phosphate ore, which means that it may potentially be a good secondary resource for phosphorus.

Domestic Substance Flow of Phosphorus in Japan

Finally, we developed a domestic substance flow of phosphorus in Japan, illustrated in figure 15. The total input of phosphorus into Japanese society is estimated to be 747.82 kt/yr. Of this, 417.8 kt is supplied to the economic

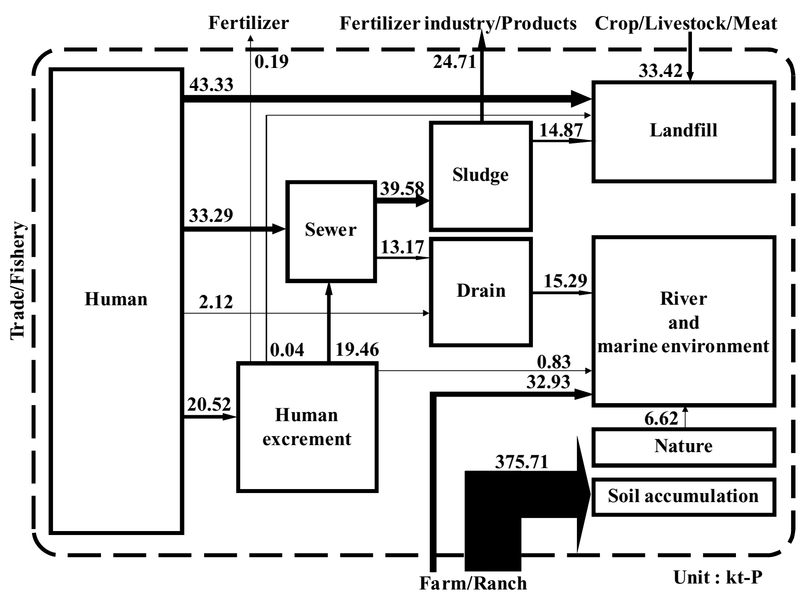


Figure 14 Overall Phosphorus substance flows related to the waste-treatment and environment sector, in kilotons of phosphorus (kt-P).

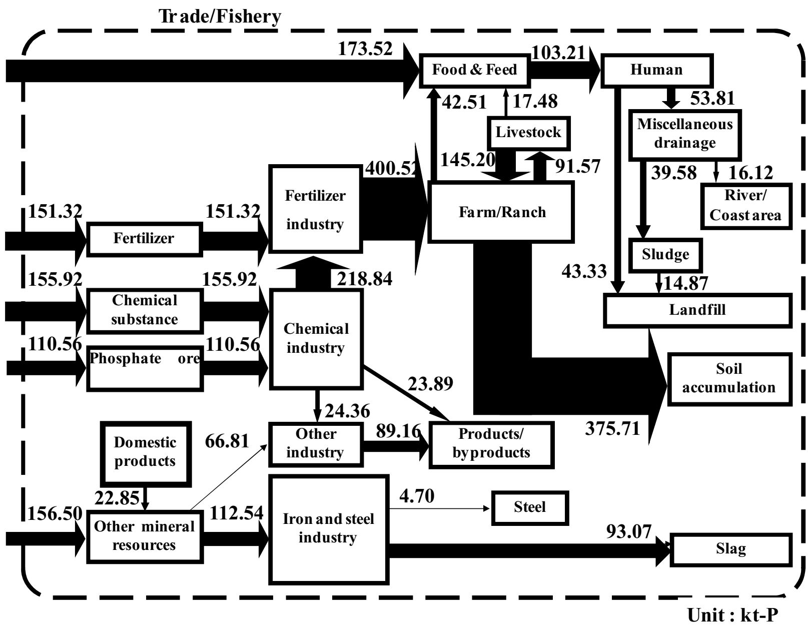


Figure 15 Overall domestic material flows of phosphorus in Japan, in kilotons of phosphorus (kt-P).

activities as a valuable resource, but the remainder is not recognized as a resource flow. Most of the phosphorus resources are used in fertilizers. Though approximately 130–150 kt/yr of the phosphorus cycle is involved in the farm/ranch sector, the remaining phosphorus diffuses into the environment. The phosphorus flow into the steel industry is estimated to be 97.77 kt/yr, most of which is accumulated in steelmaking slag (93.07 kt, 95.2%) through the dephosphorization of molten iron. The main flows of phosphorus finally reach the soil, river, sea, sludge, steelmaking slag, and waste sectors. The phosphorus concentrations in these sectors are quite low, except for sludge and steelmaking slag. As shown in figure 15, the domestic phosphorus flow related to mineral resources other than phosphate ore provides a parallel flow to that related to phosphate ore.

This figure has very important implications concerning the domestic flow of phosphorus in Japan. That is, the country has considerable potential secondary phosphorus resources in terms of quantity and quality as a raw material for fertilizers and other chemical products.

Environmental Effects of Phosphorus Recovery

Recovery of Phosphorus from Iron and Steelmaking Slag

Figure 16 is a schematic process-flow diagram for a conventional BF (blast furnace)–BOF (basic oxygen furnace) steelmaking process. The present authors are currently developing a new process for recovering phosphorus from steelmaking slag (particularly dephosphorization slag, which has a high phosphorus content) as a new phosphorus resource (Yokoyama et al. 2007). The main components of dephosphorization slag are CaO, FeO, SiO_2, and P_2O_5. Figure 17 shows the structure and phosphorus distribution among the phases precipitated in a practical dephosphorization slag, as observed by energy-dispersion type electron-probe microanalysis (EPMA). The slag was supplied by a major Japanese steelmaking company. The white parts in upper right-hand picture have high concentrations of phosphorus but no FeO. It is known that phosphorus in slag generally shows remarkable segregation as solid solutions of calcium phosphate and dicalcium

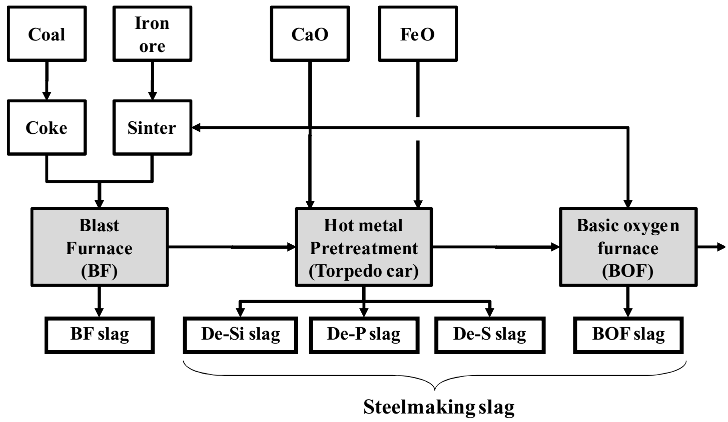


Figure 16 Schematic process flow diagram of the conventional BF–BOF steelmaking process, where silicon, phosphorus, and sulfur in molten pig iron (hot metal) are removed by the hot-metal pretreatment process before charging to the BOF. BF = blast furnace; BOF = basic oxygen furnace; De-Si = desiliconization; De-P = dephosphorization; De-S = desulfurization; CaO = calcium oxide; FeO = iron oxide.

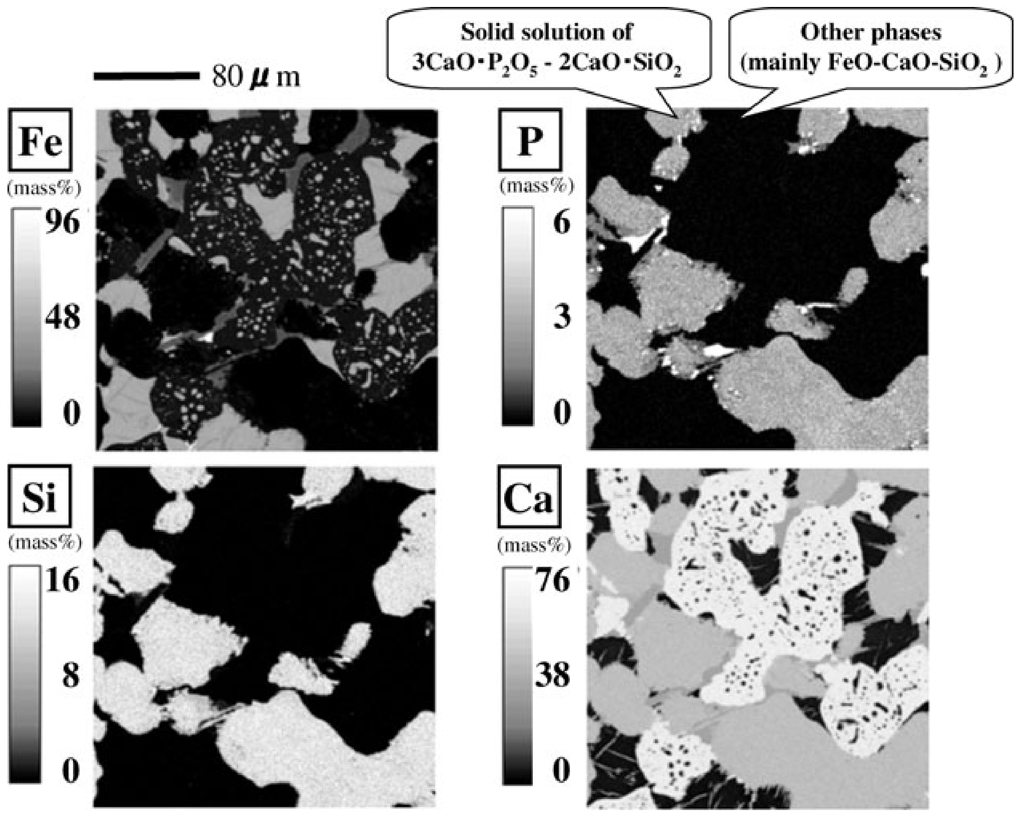


Figure 17 EPMA (energy-dispersion type electron-probe microanalysis) mapping image of a dephosphorization slag (Fe_tO = 19%, CaO/SiO_2 = 4.4%, P_2O_5 = 2.8%) supplied by a Japanese steelmaking company.

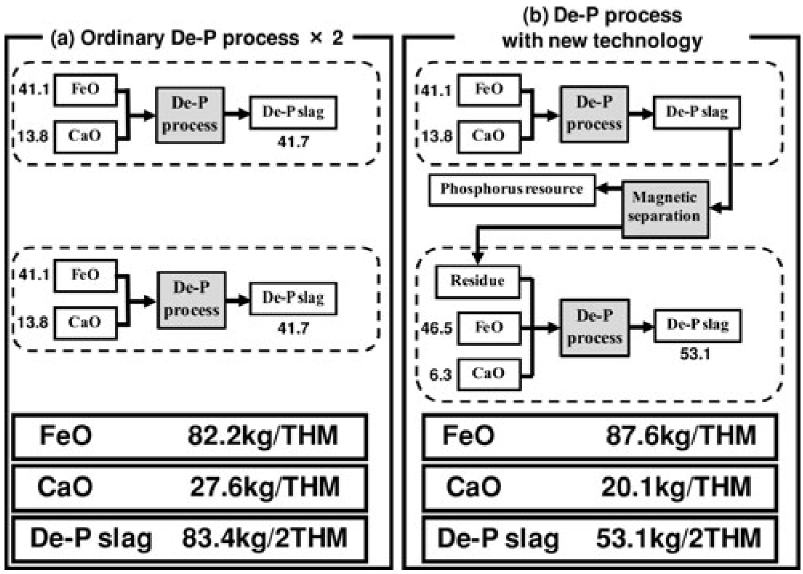


Figure 18 Recovery of phosphorus by magnetic-separation technology, in kilograms per ton hot metal (kg/THM). CaO = calcium oxide; FeO = iron oxide; De-P = dephosphorization.

silicate, which depends on the total slag composition (Futatsuka et al. 2004). This phosphorus-enriched crystal phase generally contains approximately 3 to 10 mass% depending on the operating conditions. The black parts in this picture consist mainly of $FeO–CaO–SiO_2$, an almost phosphorus-free phase. Because these two phases have totally different magnetic properties, they can be separated by applying a strong magnetic field. Another benefit of this process is that the residues could be returned to the sintering, hot-metal desiliconization and hot-metal dephosphorization processes, and this recycling process enables a reduction of the total input of new resources such as CaO.

We evaluated the effects of phosphorus recovery and slag utilization on the steelmaking process. The detail of the mass balance calculation is described elsewhere (Matsubae-Yokoyama et al. 2009; Kubo et al. 2009). The typical dephosphorization process requires an input of 13.8 kilograms[5] per ton of hot metal (kg/THM) of CaO and 41.1 kg/THM of FeO, and discharges 41.7 kg/THM of dephosphorization slag.

Because it is hard to achieve perfect magnetic separation, we estimated the amounts of CaO and FeO required as dephosphorization agents and the amount of slag generated on the assumption that 60% of the phosphorus-rich phase and 10% of the residual slag are recovered as phosphorus resources, and that the residues that are formed from the remaining 40% of phosphorus-rich phase and 90% of residual slag are utilized in the dephosphorization process. From the estimated result, 29.78 kg/THM is generated as the residue and the phosphorus concentration is approximately 3.1 mass% as P_2O_5. On the basis of estimated results, we evaluate the amounts of CaO and FeO required to achieve the dephosphorization level (0.02 mass%) permitted as the final phosphorus concentration in liquid pig iron after treatment. Finally, the new process requires 6.3 kg/THM of CaO and 46.5 kg/THM of FeO as additional inputs and generates 53.1 kg/THM of slag. The results are summarized in figure 18. In this figure, (a) shows the estimated result for iteration of the existing dephosphorization process and (b) shows the case of phosphorus recovery and the utilization of residues in the dephosphorization process. A 36% reduction in slag generation should be realized by the (b) process.

This new process is still being tested on the laboratory scale. However, because steelmaking slag has the greatest potential as a secondary resource of phosphorus as indicated in previous sections, the new process would have great environmental and economic impacts if it can be successfully done.

Waste Input–Output Analysis

We need some discussion about the repercussion effects from the environmental and economic perspective. On the basis of the results discussed in the section on the domestic substance flow of phosphorus in Japan, we evaluated the environmental and economic effects of phosphate recovery from slag by applying the waste input–output (WIO) model (Nakamura and Kondo 2002), which considers the circulation between the production and waste-treatment sectors.

A WIO table shows the flow of waste material between sectors, and describes interrelationships between production sectors and waste-treatment sectors. The WIO model is as follows:

$$\begin{bmatrix} X_1 \\ X_2 \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} \\ SA_{21} & SA_{22} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} + \begin{bmatrix} F_1 \\ F_2 \end{bmatrix} \quad (4)$$

where X_j is the total output vector, A_{ij} is the technical coefficient matrix, and F_j is the final demand vector. Here, the subscript notation $i,j = 1$ implies a flow related to industrial activity, and $i,j = 2$ implies a flow related to waste-treatment activity. Note that the waste-allocation matrix S represents the share of waste treated by waste treatment. Environmental emissions E are evaluated by using this model in the following equation:

$$E = [e_{o:1}\ e_{o:2}] \begin{bmatrix} A_{11} & A_{12} \\ SA_{21} & SA_{22} \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \end{bmatrix} + [e_{f:1}\ e_{f:2}] \begin{bmatrix} F_1 \\ F_2 \end{bmatrix} \quad (5)$$

where $e_{i:j}$ is an emission coefficient, corresponding to the amount of emissions associated with a unit of industrial or waste-treatment activity. The subscript notation $i \in \{o, f\}$, o, f, implies emissions associated with production of intermediate goods and final demand; $j \in \{1, 2\}$ 1,2 implies industrial and waste-treatment activity, respectively. The WIO table is a hybrid type of conventional input–output table (Leontief 1986) that is built from economic and physical data on waste generation and recycling. The use of the input–output approach can significantly reduce the degree of arbitrariness in the definition of the boundaries of the relevant systems. The WIO table is a database that contains the year 2000 input–output table for Japan and the statistics of waste generation and secondary material recycling in each industry and household sector. We can therefore discuss environmental effects by applying the WIO approach.

The environmental and economic effects of recovery of phosphorus, as discussed in a previous section, were estimated by using the WIO model. For the estimation, we assumed that the recovery of phosphorus from slag results in an equivalent reduction in imports of phosphate ore and that the recovered phosphorus is used as a raw material by the chemical industry for fertilizer production.

Our evaluation was based on the amount of steelmaking slag generated in 2005, during which the existing dephosphorization process generated 1,745 kt of slag. We assumed that 60% of the phosphorus recovered from concentrated phases would contribute a reduction of 634 kt/yr of slag; we also assumed that slag utilization would increase FeO input by 6.6% and decrease CaO input by 27.2%. For these conditions, half the phosphorus in steelmaking slag could be recovered by the new process, corresponding to 12,184 t/yr of phosphorus, which is equivalent to 93,066 t/yr of phosphate ore, assuming that the P_2O_5 concentration is 32.0 mass%.

Our other assumptions are as follows:

1. the imported phosphate ore contains 32 mass% of P_2O_5;
2. the price of phosphate ore is 50,834 yen per ton of P_2O_5;
3. the reduction in the cost of transporting phosphate ore cancels out the additional cost of transporting recovered phosphorus from the slag yard to the chemical industry; and
4. there is no change in the production process or in environmental emissions from a change in input material.

The results of the analysis are listed in table 4. A 0.014% reduction in carbon dioxide (CO_2) emissions and a 1.68% reduction in the consumption of landfill space can be expected in comparison with the present conditions. From

Table 4 Estimated effects of phosphorus recovery

(A) Monetary effects on industrial sectors		
Unit	*Industrial sector*	*Change rate (%)*
Million yen	Nonmetallic ores	−5.998
Million yen	Basic inorganic chemical products	−0.047
Million yen	Coal products	−0.005
Million yen	Cement and cement products	−0.010
Million yen	Pottery, china, and earthenware	−0.008
Million yen	Other ceramic, stone and clay products	−0.005
Million yen	Pig iron and crude steel	−0.005
Million yen	Steel products	−0.005
Million yen	Cast and forged steel products	−0.019
Million yen	Metal products for construction and architecture	−0.010
Million yen	General industrial machinery	−0.007
Million yen	Other transportation equipment and repair of transportation equipment	−0.020
Million yen	Other civil engineering	−0.027
Million yen	Self transport by private cars	−0.005
Million yen	Repair of motor vehicles and machine	−0.005
(B) Carbon dioxide emission and landfill effects		
Unit	*Environmental effects and others*	*Change rate (%)*
Ton-CO_2	Carbon dioxide emissions	−0.014
Square meter	Landfill volume	−1.680

the viewpoint of employment in the whole economic system, a negative effect is predicted as a result of a shrinkage in activity in the sectors "materials for ceramics," "chemical fertilizer," and "waste treatment: landfill activity." However, the predicted negative effect on employment is relatively insignificant in comparison with the reductions in CO_2 emissions and landfill consumption. In addition, a larger saving in input resources and reduction of environmental burden would be achieved if the slag residue after phosphorus recovery could be returned to the blast furnace or BOF. Therefore, we can conclude that the phosphorus-recovery process proposed here would have considerable economic and environmental benefits.

Discussion and Conclusion

First, to identify potential phosphorus resources that are currently untapped, we investigated domestic phosphorus material flows in Japan, including the iron and steel industry, on the basis of statistical data for 2002. Our major finding was that the quantity of phosphorus in iron and steelmaking slag is almost equivalent to that in imported phosphate ore, both in terms of the amount and the concentration. Second, we assessed the amount of phosphorus that could be recovered from steelmaking slag by the application of a strong magnetic field. By means of a waste input–output analysis and a study of total materials requirements, we found that the recovery of phosphorus by this new process would have considerable environmental and economic benefits. As Christen (2007) mentioned, the main problem lies in the economic situation and cost of recovering phosphorus: the world market price for phosphorus is still below the current cost of its recovery. However, the recovery cost could decrease through introduction of a commercialized process.

Concerning the restricted supplies of phosphorus resource, it is important to consider the quantity and availability of phosphorus resources that currently remain untapped. Because of this situation, advanced efforts have been made by some leading groups in the EU (BAM 2005; BMBF/BMU Funding Programme 2008; Johansson et al. 2008), and Asia (Yokoyama et al. 2007;

Ohtake et al. 2008; Phosphorus Recycling Promotion Council 2008).

For further discussions, with greater accuracy, it will be necessary to carry out a more detailed investigation of not only domestic phosphorus flows, but also global ones. It also is important to consider differences in phosphorus accumulation in various steelmaking slags and to examine the possibility of recovering phosphorus resources.

Acknowledgments

The authors wish to thank Messrs K. Mori, K. Kato, and K. Yoshimoto, Graduate students of Tohoku University, for their experimental assistance. The present work is financially supported as a Contract Research Program for 2003's Study on Sustainable Society, Research Institute of Science and Technology for Society, JST and Grant-in-Aid for Scientific Research from Ministry of Education, Sports and Culture, Japan, as contract number 18360433 (2006 to 2008). Special thanks are due to the late Mr. S. Takeuchi, former General Manager of JFE Steel Co. Ltd., for his useful comments and great encouragement.

Notes

1. The tons used in this article are metric tons. One metric ton = 10^3 kilograms (SI) ≈ 1.1 short tons.
2. Fe_tO is a nonstoichiometric oxide formed with the oxidation of iron at high temperature.
3. Due to a statistical technicality, we considered the sewer, human excrement, and waste water separately.
4. One liter ≈ 1.06 quarts.
5. One kilogram (SI) ≈ 2.2 pounds.

References

Abelson, P. H. 1999. A potential phosphate crisis. *Science* 283(5410): 2015.

BAM (Federal Institute for Materials Research and Testing). 2005. Sustainable and safe re-use of municipal sewage sludge for nutrient recovery – SUSAN. <http://www.susan.bam.de/index.htm>. Accessed February 2009.

BMBF/BMU (Bundesministerium für Bildung und Forschung/ Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit) Funding Programme. 2008. Recycling management of plant nutrients, especially phosphorus. <http://www.phosphorrecycling.de>. Accessed February 2009.

Christen, K. 2007. Closing the phosphorus loop. *Environmental Science and Technology* 41(7): 2078.

Futatsuka, T., K. Shitogiden, T. Miki, T. Nagasaka, and M. Hino. 2004. Dissolution behavior of nutrition elements from steelmaking slag into seawater. *ISIJ International* 44(4): 753–761.

Japan Coal Energy Center Home Page. 2007. <http://www.ccuj.or.jp/jcis/index.htm>. Accessed July 2007.

JIE (Japan Institute of Energy). 2004. *Coke note 2004* (in Japanese). Tokyo.

JISF (Japan Iron and Steel Federation). 2003. Handbook of iron and steel statistics (in Japanese). Tokyo.

Johansson, K., M. Perzon, M. Frölingb, A. Mossakowska, and M. Svanström. 2008. Sewage sludge handling with phosphorus utilization – Life cycle assessment of four alternatives. *Journal of Cleaner Production* 16(1): 135–151.

Kubo, H., K. Matsubae-Yokoyama, and T. Nagasaka. Forthcoming. Magnetic separation of phosphorus enriched phase from dephosphorization multiphase flux. *ISIJ International* 49.

Leontief, W. 1986. *Input–output economics*. 2nd. ed. Oxford, UK: Oxford University Press.

MAFF (Ministry of Agriculture, Forestry and Fisheries). 2004a. *Food balance sheet* (in Japanese). Tokyo.

MAFF (Ministry of Agriculture, Forestry and Fisheries). 2004b. *Handbook of commercial feed* (in Japanese). Tokyo: Association of Agriculture and Forestry Statistics.

Matsubae-Yokoyama, K., H. Kubo, and T. Nagasaka. 2009. Forthcoming. Recycling effect of solid residue of magnetic separation process for dephosphorization multiphase flux. *ISIJ International* 49.

MEXT (Ministry of Education, Culture, Sports, Science and Technology). 2004. *Food Composition Database* (in Japanese). Tokyo.

METI (Ministry of Economy, Trade and Industry). 2002. *Yearbook of Mineral Resources and Petroleum Products Statistics* (in Japanese). Tokyo: Research Institute of Economy, Trade and Industry.

MIAC (Ministry of Internal Affairs and Communications). Statistics Bureau Home Page. <http://www.stat.go.jp/english/index.htm>. Accessed June 2007.

Ministry of Finance. *Trade statistics of Japan*. 2004. Tokyo.

Nakamura, S. and Y. Kondo. 2002. Input–output analysis of waste management. *Journal of Industrial Ecology* 6 (1): 39–63.

Nippon Slag Association. 2003. *Production and Uses of Blast Furnace Slag in Japan*. <http://www.slg.jp/e/statistics-e.htm>. Accessed May 2007.

Phosphorus Recycling Promotion Council, Japan. 2008. <http://www.jora.jp/rinji/rinsigen/index.html> Accessed February 2009.

Smil, V. 2000. Phosphorus in the environment: Natural flows and human interferences. *Annual Review of Energy and the Environment* 25: 53–88.

USGS (U.S. Geological Survey). 2007. *Minerals Information*. <http://minerals.usgs.gov/minerals/>. Accessed June 2007.

Yokoyama, K., Kubo, H., Mori, K., Okada, H., Takeuchi, S. and Nagasaka, T. 2007. Separation and recovery of phosphorus from steelmaking slags with the aid of a strong magnetic field. *ISIJ International* 47(10): 1541–1548.

About the Authors

Kazuyo Matsubae-Yokoyama is associate professor of eco-material design and process engineering division in the Graduate School of Environmental Studies at Tohoku University in Sendai, Japan. **Hironari Kubo** is a former graduate student at Tohuku University and is now a researcher for Asahi Pretec Corporation in Kobe, Japan. **Kenichi Nakajima** is a special researcher at the National Institute for Environmental Studies in Tsukuba, Japan. **Tetsuya Nagasaka** is professor of the eco-material design and process engineering division in the Graduate School of Environmental Studies at Tohoku University in Sendai, Japan.