1 **Hidden phosphorus flows related with non agriculture industrial activities:**

2 **A focus on steelmaking and metal surface treatment**

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45

46 **Abstract**

47 Due to the impact of increasing global demand for high-grade steel for a variety of applications
48 at a time when high grade iron ore reserves are becoming depleted, the removal of impurities,
49 and especially phosphorus, has become essential. Demand in the rapidly growing car industry,
50 in particular, is increasing pressure on steelmakers to provide high quality steel. The
51 dephosphorization step presents new opportunities to steelmakers: besides producing
52 high-quality steels not prone to cracking or corrosion, and improving production efficiency,
53 steelmakers are presented with the opportunity to recover phosphorus and market it as a
54 value-added product. Another industry with potential to recover P as a secondary product is
55 the surface treatment industry. Surface treatment and the galvanization of metal products
56 requires phosphoric acid and generates waste containing phosphorus, which is typically not well
57 recovered or recycled. In this study, we focus on the potential of steelmaking slag and waste
58 sludge from nickel plating and metal surface treatment processes as non-traditional phosphorus
59 resources. An MFA on the hidden phosphorus flow behind global iron ore trade showed that,

60 that the hidden flow of phosphorus from the three major iron ore export countries to China
61 alone was 331 kt in 2013, which is equivalent to 1.7% of the global consumption of P in
62 fertilizers consumed that year. In 2013, 3.6 kilo ton of phosphorus was wasted in acid waste
63 from the metal surface treatment industry.

64

65 Keywords: hidden phosphorus flow, steelmaking slag, iron ore, metal surface treatment, plating
66 bath

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70 **1. Introduction**

71 The strategic importance of phosphorus for agricultural food production and the chemical
72 industry cannot be overstated. While phosphorus is currently used extensively as food
73 additives in the food processing industry, as a dopant in the semiconductor industry, in the
74 production of detergents, anti-corrosive paints and medicine, it may well be that one day an
75 alternative may be found for these applications. We are absolutely sure, however, that there
76 will never be a substitute for phosphorus in food production. Along with nitrogen and potassium,
77 phosphorus is an absolutely essential nutrient in plant growth. Commercial food production is
78 largely dependent on fertilizers and all speculation about the world's ability to feed itself in the
79 future assumes plentiful supplies of phosphorus in the years to come. As such, the increased
80 demand for food as global population increases must also be understood as an inevitable
81 increase in demand for phosphorus over time (Tilman, Cassman et al. 2002, Elser and Bennett
82 2011, Wyant, Corman et al. 2013). Considering that just six countries are responsible for some
83 80% of the phosphate ore traded internationally, to ensure a reliable supply of phosphorus for
84 the global production of agricultural products in the future, the status quo will need to be
85 challenged with a new approach not only to the flow of phosphorus between countries, but also
86 to the recovery and recycling of phosphorus domestically (Scholz 2014). Nature provides us
87 with easy access to many of the essentials for life: light from sunshine, oxygen, nitrogen and
88 CO₂ in the air that surrounds us, and water in the rivers, lakes and oceans. While equally
89 important to life, phosphorus is much harder to come by. Accumulated manure can certainly be
90 considered a phosphorus supply for small-scale agriculture, but most of the P-supply used in
91 commercial farming is an underground resource which takes thousands of years to form in a
92 marine sedimentary environment from phosphorus rich materials. The rest comes in the form
93 of igneous rock or guano. It follows, then, that the potential for phosphate ore to become

94 depleted at a time when population is racing towards the 10 billion mark has raised concerns
95 (Abelson 1999, Vaccari 2009).

96 In recent years, analyses of the flow of phosphorus from the perspectives of economical use
97 and recycling have appeared in the literature (Neset, Bader et al. 2008, Matsubae-Yokoyama,
98 Kubo et al. 2009, Yuan, Sun et al. 2011). The knowledge gained through these studies has
99 provided a strong basis for the belief that a combination of good management strategies and
100 better resource recycling has the potential to bring about an end to the linear path that
101 phosphorus takes in society since the phosphorus loop has been broken. As noted by Scholtz
102 et al , improving efficiency is one option: a significant amount of phosphorus loss occurs behind
103 the mining and beneficiation processes (Scholz 2014), and preventing this avoidable loss of
104 phosphorus to the environment is highly desirable. The phosphorus dissipated in mining and
105 beneficiation, however, is not a target for recovery and recycling. In fact, there are few
106 concentration paths of phosphorus offered to us from the waste streams of human activity.
107 Much attention has been given to the recovery of phosphorus from sewage sludge and
108 wastewater (Wyant, Corman et al. 2013, Scholz 2014). Two other options for the
109 concentration and recovery of phosphorus in industry are provided by steelmakers who utilize
110 iron ore with a significant P-content, and the industrial sludge from metal surface treatment.
111 The amount of steelmaking slag and industrial waste from which phosphorus can be recovered
112 and reutilized is expected to increase significantly over time as high grade iron ore supplies
113 become further depleted and steelmakers are forced to utilize iron ore with a higher P-content
114 (Matsubae 2015). The research and development challenge to stop the avoidable phosphorus
115 loss from these industries has been taken up in earnest in Japan in particular
116 (Matsubae-Yokoyama, Kubo et al. 2010, Yamasue, Matsubae et al. 2013), and the requirement
117 for social innovation to enable a change in the status quo regarding the use of the recovered

118 phosphorus, as well as for industries to improve their recycling portfolio is being discussed
119 widely (Ulrich and Schnug 2013, Shiroyama 2015).

120 The phosphorus challenge has been described as the need to put an end to the “once-through
121 mode of societal phosphorus metabolism” which remains predominant today (Liu, Villalba et al.
122 2008). The global demand for high-grade steel is increasing to meet the demands from the car
123 industry and for applications in high chloride ion environments, where corrosion proceeds
124 rapidly, and in other harsh environments, like those encountered by pipelines, etc. The
125 dephosphorization step required to produce high-quality steels resistant to cracking and
126 corrosion, improves production efficiency, and provides steelmakers with a new opportunity: to
127 become urban phosphorus ore producers and to market this value-added product and improve
128 resource efficiency. This applies especially to the Asian steelmakers and to the steelmakers of
129 the next emerging economies who will be utilizing iron ore with a significant phosphorus
130 content.

131 The phosphorus-containing waste produced by the surface treatment industry is also not well
132 recovered or recycled as a secondary phosphorus resource. With the increasing number of
133 automobiles being produced around the world, there is potential to recover phosphorus from the
134 waste from the metal-surface treatment, which utilizes high-grade phosphoric acids. It is
135 important to note that the supply of the yellow phosphorus used to produce these acids to the
136 international market is restricted to just a few countries, including China, Vietnam and
137 Kazakhstan. The time has come for more careful attention to be paid to the recycling of
138 P-containing secondary waste, not only for the sake of P-resource conservation but also to
139 ensure a better geopolitical risk-aversion strategy for the many countries and regions who
140 depend on the imported phosphorus resources for their own economic activities.

141 In this study, our focus is on the potential of steelmaking slag and waste sludge from nickel

142 plating and metal surface treatment processes as non-traditional phosphorus resources. These
143 processes are connected in that much of the steel produced in Japan is used in car production,
144 and that this steel is subjected to metal surface treatment procedures in the production line. The
145 potential of these secondary phosphorus resources is evaluated, and the bottlenecks and benefits
146 of advancing the utilization of these resources from a socio-economic perspective is discussed.

147

148 **2. Phosphorus in steelmaking slag**

149 **2.1. Global flows of Phosphorus in traded iron ore**

150 On addition to the phosphate ore imports used in the chemical and fertilizer industries, a
151 significant amount of phosphorus flows into our society as hidden phosphorus in other forms.
152 One example is the phosphorus which enters steelmaking nations as an element accompanying
153 the iron ore it imports. Many of these sources of this phosphorus are not regarded as phosphorus
154 resources: rather, they are regarded as impurities in more useful materials, and most of them
155 flow out from our economic sphere with little or no effort to tap the phosphorus which enters
156 the waste stream.

157 With regard to the phosphorus in iron ore, the international phosphorus flow accompanying the
158 trade of iron ore was estimated, and is shown in Fig.1. Here we assumed that P content of
159 Australian ore was 0.061%, and ones from Brazil and South Africa were 0.031%. Of the 287 kt
160 of phosphorus traded in 2005 in the ten largest steelmaking resource transactions, 2 71 kt was
161 traded in the top-ten transactions of iron ore. That is, almost 95% of the phosphorus traded in
162 these transactions can be attributed to the trade of bulk and powdered iron ore, with exports
163 from Australia and Brazil accounting for 49.2% and 30.8% of that trade, respectively. China and
164 Japan respectively account for 58.7% and 24.3% of the imports of phosphorus in steel-making
165 resources of all the top-ten transactions (over 80%). Of all the phosphorus traded in the top-ten

166 transactions of iron ore, the largest three quantities of phosphorus traded in iron ore were 69
167 kt-P imported by China from Australia, and 48 kt-P by Japan from Australia, and 43 kt-P
168 imported by China from India, respectively. The dramatic increase in steel production in China
169 since 2005 has resulted in an increase in the phosphorus flow into China as an accompanied
170 element of iron ore from Australia, from 68 kt in 2005 to 254 kt in 2013. The second largest
171 trade flow of iron ore was from Brazil to China in 2013, while the trade of iron ore decreased
172 from India to China since 2009. If we define the hidden phosphorus flow as the phosphorus
173 flow which is not well-recovered or recycled as a secondary phosphorus resource, it can be
174 estimated that the hidden flow of phosphorus from the three major iron ore export countries to
175 China alone was 331 kt in 2013, which is equivalent to 1.7% of the global consumption of P in
176 fertilizers consumed that year(USGS 2014).

177

178 **2.2. Destination of Phosphorus in iron ore**

179 Slag is a molten material comprised mostly of oxides produced during the smelting of molten
180 metal. Like water (molten metal) and oil (slag), the mutual solubility of slag in molten metal is
181 low. Slag can be defined as the smelting byproduct retained as an additional layer on top of
182 molten metal, and is much like the bubbles formed from detergent while washing. Perhaps the
183 most important characteristic of this slag layer is that functions like a sponge and absorbs
184 impurities. As shown in Fig.2, steelmaking slag can be subdivided depending on the refining
185 method: desulfurization slag, dephosphorization slag, desiliconizing slag, and decarburization
186 slag. While all the Japanese steelmaking companies and a few other Asian steelmaking facilities
187 include the three steps marked A, B and C in Fig. 2 in their steelmaking processes,
188 dephosphorization tends to be carried out by a combination of the steps marked A and C (Jeong,
189 Matsubae-Yokoyama et al. 2009, Matsubae-Yokoyama, Kubo et al. 2009).

190 Steel-making dephosphorization slag is largely comprised of the $\text{CaO-SiO}_2\text{-FeO-P}_2\text{O}_5$ system.
191 From a thermodynamic perspective, dephosphorization is more efficient at lower temperatures.
192 With that in mind, to respond to the increasing need for high-grade steel, such as automotive
193 steel sheets and high-toughness/high-strength steel, an oxidizing agent (oxygen or iron oxide)
194 and a dephosphorization material (lime) are added between the blast-furnace and the converter
195 stages, when the molten metal is in a temperature range between 1300–1400 °C. This is known
196 as the hot-metal dephosphorization treatment. In this temperature range, not all of the
197 $\text{CaO-SiO}_2\text{-FeO-P}_2\text{O}_5$ system slag melts: rather, the result is solid suspension similar to mud, i.e.,
198 a solid–liquid coexistence state.

199 To determine the form of phosphorus that occurs within this hot-metal dephosphorization slag,
200 domestic blast-furnace makers provided samples of the actual slags after cooling for
201 microstructure analysis. The results showed that the constituent phases of slag can be classified
202 as follows: (1) a phosphorus-rich phase (P-content approx. 10%) consisting of a $\text{CaO-SiO}_2\text{-P}_2\text{O}_5$
203 system, and almost no iron; and (2) an iron-rich phase consisting mostly of the $\text{CaO-SiO}_2\text{-FeO}$
204 system, and little phosphorus. The phosphorus-rich phase is a product of the dephosphorization
205 reaction, and is presumed to have remained solid during the dephosphorization treatment.
206 Depending on the dephosphorization-treatment conditions, this phase can contain a small
207 amount of SiO_2 . Of more interest is the crystalline phase in this phosphorus concentrated slag:
208 it is P_2O_5 , the principal component of phosphorus rock. The iron-rich phase is presumed to have
209 been liquid during dephosphorization and to have functioned as the transfer medium for
210 phosphorus during the reaction. Since the iron-rich and phosphorus-rich phases can be separated
211 once the slag is cooled, it is technically possible to recover phosphorus as an urban resource
212 (Matsubae-Yokoyama, Kubo et al. 2009, Diao, Xie et al. 2012, Yang, Wu et al. 2012, Yamasue,
213 Matsubae et al. 2013, Lin, Bao et al. 2014).

214

215 **3. Phosphorus in waste sludge**

216 **3.1. Nickel plating waste**

217 Phosphorus compounds are used in metal-surface treatment processes to improve the functional
218 performance of material surfaces. They are used in degreasing, chemical conversion, and nickel
219 plating. The utilization and waste forms of the phosphorus compounds of each of these
220 processes are described below.

221 The degreasing process removes mineral and vegetable oils as a pre-treatment for the
222 nickel-plating process. Because the chlorinated organic solvents that were used in the past are
223 toxic in the environment, they are gradually being replaced by alkaline aqueous solutions. In
224 phosphorus-based alkali degreasing, sodium tertiary phosphate (Na_3PO_4) is used as a degreasing
225 liquid for iron and steel materials and zinc/zinc alloy materials. The degreasing process
226 generates three types of waste, each of which contains phosphorus: as the wastewater from
227 washing, the excess solution, and a sludge type byproduct.

228 The chemical-conversion process is a preparation treatment for painting surfaces, lubrication in
229 deformation processing, and anti-rust treatment. When treating iron and steel materials, and also
230 zinc materials, a solution with phosphate and zinc ions as the principal components is used.
231 There are also other treatments that involve the use of phosphate iron, phosphate manganese, or
232 phosphate calcium for use on various target materials for various purposes. These treatments
233 result in the formation of a thin film of metal salt on the material surface. The liquid waste from
234 these processes includes the residues from the generation of these films.

235 In the nickel-plating process, phosphorus compounds are used as raw materials for
236 nickel-phosphorus (Ni-P) alloy plating. One common usage of these compounds is as a reducing
237 agent in electroless Ni-P-alloy plating. In the Ni-P alloy-plating process, a surface film of Ni-P

alloy is obtained by reducing and depositing nickel ion, using sodium hypophosphite (NaH_2PO_2) as the reducing agent. The byproduct of this process is a liquid waste which contains mainly the oxidized byproduct, inorganic phosphite (H_3PO_3).

Table 1 shows the typical composition of plating solutions (baths) and their main applications. Both types of plating baths contain P: the gold–nickel-plating alkali baths and electroless nickel-plating baths. In order to estimate the phosphorus material flow for high production volumes involving electroless nickel plating, the following process was used, assuming a volumetric relationship in each process:

- Neither the manufacturing nor the disposal of the nickel-plating solution is a complete process in itself. The circulation of materials is assumed, with new solution added and a portion disposed of in each cycle. Since it is difficult to estimate the amount of plating solution used in Japan, it is not possible to consider the amount of phosphorus contained in the plating solution already in circulation. Instead, only the input and output of the plating process can be estimated.

- In the plating process, the input value of phosphorus is assumed to be the amount of plating solution supplied as new solution. The flow volume was estimated from the statistical values of the nickel used in plating.

- Phosphorus removed from the plating process is assumed to be the phosphorus contained in the liquid waste from partial-solution renewal and in the plates.

The composition of an electroless nickel plate is Ni: 90–92% and P: 8–10%. Thus, we assumed that there is 10% phosphorus in the plate, and the weight ratio of phosphorus/nickel is defined as 0.059. Based on these assumptions, in 2005 the amount of phosphorus flow was estimated to be 2034 t-P in the plating solution, 193 t-P in the plate, and 1840 t-P in the liquid waste in Japan.

260

261 3.2. Surface treatment sludge

During chemical conversion, nonmetal films such as oxide and hydroxide are chemically formed on the metal surface. This provides functionalities such as corrosion resistance, abrasion resistance, lubricity, and paint adhesion. Chromium oxide films are formed by chromate treatment, and phosphate films are formed from phosphate treatment. These include phosphate zinc films, phosphate manganese films, and phosphate calcium films. Phosphate treatment is standard practice in the fabrication of automobile bodies (and other parts which are prone to corrosion), to improve the adhesion of coating films. The thickness, the adhesion with the coating film, and corrosion resistance are standardized properties of phosphate film, and appear in the Japanese standards JIS K3151. The thickness is defined within the range of 1.5–6.0 g/m² or larger depending on usage. The reactions which occur in phosphate zinc treatment are as follows:

Zinc dihydrogen phosphate (Zn(H₂PO₄)₂), which is soluble in water, follows the equation below within a solution; it is in the state of equilibrium with insoluble zinc (II) phosphate (Zn₃(PO₄)₂) crystal and phosphate (H₃PO₄).

If iron is immersed in this solution, phosphate and iron trigger the following reaction: soluble iron (II) dihydrogen phosphate (Fe(H₂PO₄)₂) is generated while producing hydrogen gas (H₂), and dissolving iron. In this reaction, phosphate is consumed; thus, the above parallel reaction shifts to the right-hand side, and generation of crystalline zinc (II) phosphate progresses to form a film:

To enhance the reaction, small amounts of oxidant and other metals such as nickel are added.

Here, we estimate the phosphorus flow in the automotive industry, assuming that phosphate is used in all automotive-related surface treatments.

Zinc-plated steel plates are commonly used in automobiles. The zinc on the surface is dissolved to induce the above reaction. Thus, by referring to the LCA database(JEMAI), from the amount of phosphorus used to treat 1 m² of product it can be estimated that 0.000963 g/m² of phosphorus is contained in the zinc dihydrogen phosphate (Zn(H₂PO₄)₂) used, the iron (II) dihydrogen phosphate (Fe(H₂PO₄)₂) emitted contains 0.000642 kg/m² of phosphorus, and the film contains 0.000321 kg/m² of phosphorus..

Table 2 shows the automobile production in 2013, with 65 million units of cars and 21 million

units of trucks and buses produced globally that year. Approximately half of these were produced in the Asia pacific region, and the EU and North America produced 19% and 16% respectively. The weight of the body of an automobile is assumed to be 204 kg, and the production volume of automobiles in one year is as shown in the table. The thickness of the steel plates used in the automobile is assumed to be 0.6 mm. If the iron density is taken as $7.89 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$, the area of steel plates used in one automobile can be calculated as 43.1 m^2 . Since both sides of steel plates are treated, the treatment area is actually doubled (86.2 m^2). From this estimate, the phosphorus material flow associated with the phosphorus-based zinc treatment of automobile bodies is shown in Table 3. It is estimated that 5,371 ton of phosphorus was required for zinc phosphate coating solution, and 3,583 ton of phosphorus was wasted in acid waste. In the Asia-Pacific region alone, an estimated 2 kt of phosphorus was wasted from the surface treatment of new cars in 2013.

While 2 kt of phosphorus is a small figure when considered in the context of the entire phosphorus flow is considered, it must be remembered that the phosphorus used in plating is produced from yellow phosphorus. It is also small when we consider that surface treatment is also routinely carried out on cars already in circulation as part of their regular servicing. Another likely significant loss of phosphorus in the automobile industry is that which occurs due to the etching of the liquid crystal panels. This process utilizes high grade phosphoric acid as the etching solution. Due to the lack of statistical data, however, it is difficult to assess the hidden phosphorus flow due to the etching process.

High-purity phosphoric acid produced from yellow phosphorus requires careful attention due to the geopolitical risks involved in acquiring this resource. China is the biggest supplier of yellow phosphorus in the world, and many countries in the Asia-Pacific region heavily rely on China to meet their demand (E. Webeck , Webeck 2014a). Europe, which does not produce large quantities of phosphorus ore, relies on the second largest producer and exporter of yellow phosphorus, Kazakhstan. It should be noted that suppliers of yellow phosphorus are very few.

3.3. Case study: Japan

As Gantner et al. suggested the accurate figure for non-fertilizer usage were not available(Gantner O 2014), thus here we focus on Japan, and the P-demand for the non-agricultural industry in Japan was analyzed on the basis of the 2005 year dataset.

The 2005 statistics were chosen because they are the most recent set of full trade data and

325 Japanese Input Output Table available. The national P flow was estimated from the statistical data
326 based on the above-mentioned 2005 data in Matsubae-Yokoyama et al.(2009). The Material Flow
327 Analysis (MFA) reveals estimates of the domestic stock and flow of phosphorus in Japan. The
328 total input of phosphorus into Japan is estimated to be 616 kt. Of this input, 40% (251.1 kt) is
329 used in fertilizers and 26% (163.1 kt) is consumed by humans and livestock; the phosphorus
330 through both routes finally ends up in either sewage sludge or animal manure. In addition, 16%
331 (100.5 kt) of phosphorus is utilized in the steel industry as a mineral resource, most of which is
332 condensed in steelmaking slag. The remaining phosphorus (approximately 45.4 kt) is used in
333 industrial chemical products (excluding fertilizers), accounting for 7.4 % of the total phosphorus
334 input. The use and amount of phosphorus in chemical industrial products varies. As yet, no clear
335 data has been extracted with regard to the amount of phosphorus in the various products of the
336 chemical industry. However, by using the statistics available and data supplied from interviews,
337 the phosphorus flows of the non-agricultural industry were estimated.

338 The result is given in Table 4. As can be seen from the table, the phosphorus flow and usage in
339 the compounds used for various purposes suggests that more phosphoric acid is consumed for the
340 production of the phosphorus compounds used in metal surface processing and surfactants in the
341 etching solutions than any other compounds. The production of the calcium phosphates used as
342 food additives and the phosphorus chloride used in surfactants, plasticizers, and pesticides
343 account for the second and third highest consumption of phosphoric acid. In fourth position is the
344 production of the sodium phosphates used as food additives, and metal surface processing soaked
345 in electroless nickel plating.

346 The production ratios for each purpose indicate that the main purpose of 69.9 kt of phosphoric
347 acid used in the chemical industry was metal surface processing (26.5%), and that the production
348 of food additives and surfactants followed at 21.2% and 12.4%. respectively. Since no other data

349 details the amount of phosphoric acid consumed in the non-agricultural industrial areas in Japan,
350 it was difficult to judge the validity of the results. However, it is clear that a significant amount of
351 phosphorus contained in industrial chemical products is being dissipated as sludge waste from the
352 metal surface treatment industry in Japan (approximately 32 kt-P). In particular, some of the
353 waste generated from metal surface treatment has potential to be recovered and utilized as a
354 secondary phosphorus resource. One such example is the solution generated from the electroless
355 nickel plating bath, which contains approximately 20 % P in the dry state.

356

357 **4. Discussions**

358 **4.1. Bottlenecks and benefits of P recovery from steelmaking slag**

359 The potential for steelmaking slag to serve as a new urban supply of phosphorus has been
360 considered with the idea of developing better phosphorus management strategies in industry and
361 utilizing as-yet-untapped phosphorus resources. At first glance, the low phosphorus content in
362 steelmaking slag would rule it out as a P resource: the P content of steelmaking slag is in the
363 range of 1-2.2%-P, whereas that of phosphate ore is in the range of 8-15% P. On closer
364 inspection, however, steelmaking slag presents some very attractive options as a source of
365 phosphorus. One of the most compelling factors is that steelmaking slag currently does not
366 include any naturally occurring radioactive materials (NORMs). Since steelmakers are able to
367 use NORM free steel resources, including iron ore, coal and limestone, the slags produced by
368 the steel industry are also NORM free. In the event that steelmakers have to use NORM
369 contaminated iron source, the slag would not be a NORM free P resource. While it must be
370 acknowledged that there is no consensus on the effect of NORMs on the human body and that
371 research is ongoing, the urgency of investigating new non-NORM phosphorous resources is
372 widely felt.

373 Another compelling argument for the use of steelmaking slag as a P resource is rooted in the
374 sheer quantity of phosphorus generated by the steelmaking industry. Despite not having any
375 phosphate deposits, our previous research showed that Japan generated nearly the same amount
376 of phosphorus in the form of steelmaking slag in 2005 (104 kt-P) that it imported as phosphate
377 rock (101.4 kt-P)(Matsubae, Kajiyama et al. 2011). This implies that the effective separation of
378 phosphorus from steelmaking slag would significantly reduce Japan's reliance on imports of
379 phosphorus in the form of phosphate ore and fertilizer. This of course offers the many benefits
380 that come with reduced dependency on imports, and the phosphorus itself would be both
381 NORM-free and uncontaminated by heavy metals.

382 At present, however, it should be noted that steelmaking slag is used not as a valuable
383 phosphorous resource, but mainly as road material and in other civil engineering applications.
384 As yet, no significant work has been carried out to evaluate the recyclability of phosphorus from
385 steelmaking slag, even in Japan where a phosphorus-removal step is standard in the steelmaking
386 process. As a major steel-producing nation with a standard phosphorus-removal step in the
387 steelmaking process already in place, and a steel industry with a strong commitment to
388 employing environmentally sustainable processes, Japan stands to serve as a valuable case study,
389 providing lessons that may be applied globally.

390 It should be noted that the benefits of a dephosphorization step in the steelmaking process have
391 been well documented. The mechanical properties of steel are considerably improved by the
392 inclusion of this process: high-phosphorus steels are known for their hot shortness, temper
393 embrittlement, lower ductility, and high corrosivity, while low-phosphorus steel has excellent
394 ductility and low corrosivity. Breakouts in continuous casting have also been attributed to P
395 contamination, indicating that low-P steel not only has better mechanical qualities, but also
396 makes more sense in terms of production efficiency. The global demand for high-grade low-P

397 steel is rising to meet the demands from the car industry and for applications in severe
398 environments. In addition to producing high-quality steels that are not prone to cracking and
399 corrosion (and improving production efficiency), a dephosphorization step also provides
400 steelmakers with the option of producing phosphorus and marketing it as a value-added
401 product(Matsubae 2015).

402

403 **4.2. Bottlenecks and benefits of P recovery from surface-treatment sludge**

404

405 The byproducts from plating processes include three types of phosphorus containing waste: two
406 types of liquid-waste and a solid sludge. Both of the liquid wastes have potential as a
407 secondary resource of phosphorus: one is rich in phosphorus and the other is not.
408 Technologies for recovering useful resources from the liquid waste of electroless nickel plating
409 are currently being developed (Ayuzawa, Suzuki et al. 1991, Okada 2010, Kamimoto, Ichino et
410 al. 2013, Li, Wang et al. 2014, Liu, Li et al. 2014); these include the recovery of nickel sulfate
411 through the solvent-extraction method, and the effective use of phosphorus components from
412 the residual liquids. However, there are still issues in the implementation and distribution of
413 such methods within society. The recovery of liquid waste, and its use as a resource, is
414 influenced by the price of nickel. However, currently, treatment is conducted from the
415 perspective of water-pollution prevention, and very few policies encourage recovery and reuse
416 with the intent of nickel and phosphorus resource dissipation.

417 Wasted solution, wastewater from washing, and sludge are qualitatively and quantitatively
418 unattractive as potential secondary phosphorus resources, and markets for accepting such
419 recycled materials have not been established. Since these “resources” are waste byproducts, the
420 quality of the phosphorus contained in them and the purity of the recovered phosphorus is

421 difficult to guarantee using existing economically feasible technologies. The optimization of
422 processes that use mineral resources and their processed goods as primary raw materials is
423 ongoing in the fields of chemical engineering, and in fertilizer manufacturing, etc. One major
424 challenge which needs to be overcome in order for secondary urban phosphorus resources to be
425 utilized in various industries is the lack of knowledge regarding the safety of these resources.
426 Another consideration is that for the many largely small and medium-sized businesses which
427 engage in nickel plating, the economic benefit of recovering such a small amount of materials
428 from the byproducts their businesses create is insufficient to justify engaging in the recovery
429 process. That is, the high costs of transportation and the recovery process itself make it difficult
430 to ensure the phosphorus in the byproducts is recovered and then distributed for further
431 consumption.

432 In the recycling of phosphate as a resource, both the quality and the supply must be stabilized
433 for the separation recovery of nickel and other plating metals. In one pre-treatment technology,
434 nickel is recovered from aging liquid waste via the solvent-extraction method (Tanaka, Huang et
435 al. 2008, Tanaka, Narita et al. 2010). In other processes, nickel is recovered from the liquid
436 waste from washing, by separation (Qin, Wai et al. 2004, Qin, Oo et al. 2006),
437 recovery/neutralizing precipitation (Robotin, Coman et al. 2012), and the ion-exchange resin
438 method (Karrs, Buckley et al. 1986). These technologies have proven to be useful in the
439 utilization of recycled materials through the demonstration of test facilities. The accumulation
440 of data and the knowledge of process optimization accompanying the distribution of such
441 technologies will contribute to an expanded market for secondary urban phosphorus resources,
442 and this will translate into a stable supply, both qualitatively and quantitatively. Among the
443 many technologies already developed, the sulfide precipitation technique (Okamoto, Miyamoto
444 et al. 2012) and the dry-melting furnace methods, which involve significant infrastructure costs,

445 are capable of providing a stable supply and the quantity and quality that an expanded market
446 will require, and will be cost-effective in the long-term.

447 Given the enormous increases projected in the phosphorus requirements for accommodating the
448 changing diets of these nations over time (Webeck 2014b), it is foreseeable that the prudent use
449 of all phosphorus resources will soon become a matter of national security. Aside from reducing
450 geopolitical risks, and contributing to more efficient resource use, the removal of phosphorus
451 from surface-treatment sludge would serve to improve the surface-treatment process, which is
452 primarily required in the commodities of the automobile industry and other machinery-related
453 industries, by means of reducing waste-treatment costs.

454

455 **4.3. Encouraging phosphorus resource use efficiency**

456 The vast majority of the demand for phosphorus resources is for use in fertilizers. Soil diagnosis
457 methods are required to improve the efficiency of fertilizer use, and to allow farmers to control
458 the agricultural nutrient salts on their land (Socolow 1999, Wyant, Corman et al. 2013, Scholz
459 2014). The necessary data for improving soil science needs to be assembled, the information
460 needs to be made available to farmers, and incentives for better management need to be offered.

461 At present, the following serve as bottlenecks slowing down the actualization of these goals:

- 462 1. Lack of maintenance for circulated-resource markets, based on appropriate management and
463 regulation.
- 464 2. Lack of incentives associated with the use of circulated resources.
- 465 3. Mismatch in the price and cost involved in introducing long term economically beneficial
466 technologies.

467 The key to improving the efficiency of phosphorus-resource utilization in society is the recovery
468 and recycling of dissipated phosphorus. Wastewater-treatment facilities provide an important

469 infrastructure since they can remove and concentrate the phosphorus that is thinly spread
470 throughout society. As yet, however, phosphorus recovery is not widespread in the wastewater
471 industry. The concentration processes that can recover phosphorus resources in the waste
472 stream are still not underway in the plating and steel industries. Attention should be paid to
473 ensuring that plating sludge and wastewater are subject to phosphorus removal and
474 concentration techniques, and that the phosphorus recovered is recycled. If it is difficult to
475 recover and recycle, it might be another option to promote adapting new techs including
476 phosphate free coating technology(Zirm 2015).

477 Similarly, infrastructure improvements in the iron-steel industry that improve the
478 dephosphorization process and make it possible to concentrate phosphorus are highly desirable.
479 At present, however, the infrastructure currently in place in most of the iron and steel producing
480 countries is not optimized to conduct phosphorus resource recovery. Because the lifespan of
481 such infrastructures is long, it is difficult to introduce new
482 phosphorus-resource-recovery/recycling technology unless new furnaces are built or the
483 operation of existing furnaces is shutdown or stopped for maintenance and upgrades. Because
484 bringing the steelmaking process to a halt represents a significant economic loss, the
485 implementation of new technology to improve resource efficiency once a furnace is put into
486 operation is difficult. It is clear, however, that the importance of phosphorus resource recovery
487 is now recognized by the steel industry.

488 To ensure a stable supply of phosphorus and that sustainable phosphorus resource management
489 is a future reality, it is important to introduce efficient technology and equipment in conjunction
490 with conducting phosphorus resource recovery. Mechanical and chemical methods have been
491 developed for isolating the concentrated phase and separating and recovering phosphorus in
492 iron–steel slag; this presents enormous potential for large quantities of recovered phosphorus.

493 Fundamentally, chemical separation is a reduction recovery procedure, and is described in Refs.
494 (Hassall, Jackaman et al. 1991, Matsui, Nakase et al. 2011, Fisher-White, Lovel et al. 2012).
495 However, no economically feasible methods have been well established for the concentration,
496 separation and recovery of the phosphorus remaining in the slags and sludge mentioned in this
497 study. Further developments are expected which will provide efficient
498 resource-recovery/recycling technology for dealing with these secondary urban phosphorus
499 resources. Further effort also needs to be made to establish the economic and social conditions
500 required for this transition in industrial practices. In addition, to ensure that waste which
501 contains phosphorus is used effectively, the transition from wastes to value-added products
502 needs to be promoted, the quality of the recycled materials must be ensured, and a stable supply
503 needs to be established. Finally, it is important to manage the quantitative and qualitative data of
504 the byproducts with a comprehensive view of the phosphorus life cycle throughout the supply
505 chain.

506

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511

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624

Fig. 1 Phosphorus content accompanied with traded iron ore

Fig. 2 Schematic diagram of a typical steel production process including pre-treatment process

Table 1 Composition of typical solutions used in plating

Plating solution	Bath Composition
Gold electroplating	Gold potassium cyanide 1~12 g/L Potassium cyanide 70~90 g/L Dipotassium hydrogen phosphate 10~40 g/L
Electroless nickel plating	Nickel sulphate 25 g/L Sodium hypophosphite 20 g/L Sodium acetate 10 g/L Sodium citrate 10 g/L

Table 2 Automobile production in 2013 year

Year 2013	Automobile	Track and bus	Sum
EU	14,613,286	1,570,560	16,183,846
CIS	2,099,134	306,986	2,406,120
North America	5,312,149	8,113,559	13,425,708
South America	5,112,131	2,598,474	7,710,605
Asia Pacific	37,196,603	8,554,005	45,750,608
Africa	409,589	226,930	636,519
Total	64,742,892	21,370,514	86,113,406

[Japan Automobile Manufactures Association, Inc.](http://www.jama.or.jp/world/world/world_t2.html)

http://www.jama.or.jp/world/world/world_t2.html [Access: 20141201]

Table 3 Phosphorus flow related to zinc phosphate coatings in the automobile body
(Unit: ton-P/Year)

	EU	CIS	North America	South America	Asia Pacific	Africa	World
Zinc Phosphate Coating solution	1,212	174	441	424	3,086	34	5,371
Zinc Phosphate Coatings	404	58	147	141	1,029	11	1,791
Acid waste	809	116	294	283	2,059	23	3,583

Table 4 Phosphorus flow for non-agricultural purpose in Japan
(Unit: ton-P/Year)

	Injection (t-P)	Amount by use (t-P)								
		Food additive	Plasticizer	dye	Medicine	Surface acting agent	Cosmetics	Pesticide	Metal-surface treatment	Other Product
Phosphoric acid	35683.2	1591.5		71.4	1613.1	6088.0			16477.6	9841.6
Sodium phosphate	6832.2	2933.4		16.2	743.8				2011.5	1127.3
Anhydrous phosphoric acid	2269.7				290.9	216.6		1475.0		287.3
Phosphorus chloride	9753.5		1999.7		131.9	2337.8		1504.8		3779.2
Ammonium phosphate	968.4	140.6		54.5						773.3
Potassium phosphate	1241.9	917.8								324.1
Calcium phosphate	12036.2	9781.8			566.9		566.9			1120.6
Red phosphorus	261.4								25.8	235.7
Other	865.7							60.4		805.3
Total	69912.3	15365.2	1999.7	142.1	3346.6	8642.4	566.9	3040.2	18514.8	18294.3
Proportion by use(%)	100.0	22.0	2.9	0.2	4.8	12.4	0.8	4.3	26.5	26.2