Chapter 7
Industrial-Scale Manufacturing of Phosphoric Acid Using Sewage Sludge Ash

T. Mochiyama

Abstract Nippon Phosphoric Acid Co. Ltd. (NPA) started to use sewage sludge ash (SSA) for the industrial manufacturing of phosphoric acid (PA) in 2013. NPA purchases SSA from wastewater treatment plants (WWTP) equipped with a Bio-P process to remove phosphate (P_i) from sewage. In the NPA's manufacturing plant, SSA is blended with roller-milled P_i rock and is dissolved in concentrated sulfuric acid to generate phosphogypsum slurry. Then the slurry is filtered to separate PA from gypsum which is recycled for the manufacture of plasterboard and cement. Currently, NPA accepts a total of 1300 t/a of SSA for the manufacture of PA and gypsum. In full operation, the manufacturing plant has the capacity to accept 3000 t/a of SSA. The blend ratio of SSA with roller-milled P_i rock is currently limited to a maximum of 2.5% (<97.5% P_i rock). This is needed to guarantee the quality of both PA and by-product gypsum for customers. NPA could accept SSA from WWTP without the need to modify its existing facilities and save material costs by partially replacing P_i rock with SSA.

Keywords Sewage sludge ash · Phosphoric acid · Wet acid process · Phosphogypsum

7.1 Introduction

In Japan, only two companies produce phosphoric acid (PA) from phosphate (P_i) rock on industrial scale. Nippon Phosphoric Acid Co. Ltd. (NPA), which was established in 1967, is the principal supplier of PA for agricultural purposes. This company has produced approximately 90 kt/a of PA as P_2O_5 using approximately 250 kt (10^3 tons)/a of P_i rock. In the NPA's manufacturing process, PA has been

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extracted from P_i rock with sulfuric acid. Gypsum ($CaSO_4$) is generated as a by-product, whose market is an indispensable prerequisite for the economic viability of the P_i industry in Japan. NPA has used P_i rocks imported mainly from Morocco, China, and Jordan. They need to be mixed together before use to reduce the contamination of cadmium and radioactive materials, whose levels are relatively high in Morocco's P_i rock.

In 2009, NPA began a feasibility study to accept sewage sludge ash (SSA) from a wastewater treatment plant (WWTP) for the manufacture of PA. This was triggered by the surge in P_i rock price in 2007–2008. NPA needed to diversify phosphorus (P) sources, thereby minimizing the risk associated with the volatility of P_i rock price. NPA saw the possibility of using SSA as a substitute for P_i rock, because P_i-rich SSA was abundantly available from WWTP. In Japan, the total amount of P_2O_5 in SSA was estimated to be approximately 67 kt/a which is essentially equivalent to the amount of imported P_2O_5 as P_i rock. Additionally, the Ministry of Land, Infrastructure, Transport and Tourism (MLITT) encouraged NPA to use SSA as a secondary P resource for the manufacture of PA. At present, NPA purchases a total of 1300 t/a of SSA from WWTP for the manufacture of PA. In full operation, the manufacturing plant has a capacity to accept 3000 t/a of SSA. This paper describes NPA's experience to realize the industrial manufacturing of PA using SSA as a substitute for P_i rock.

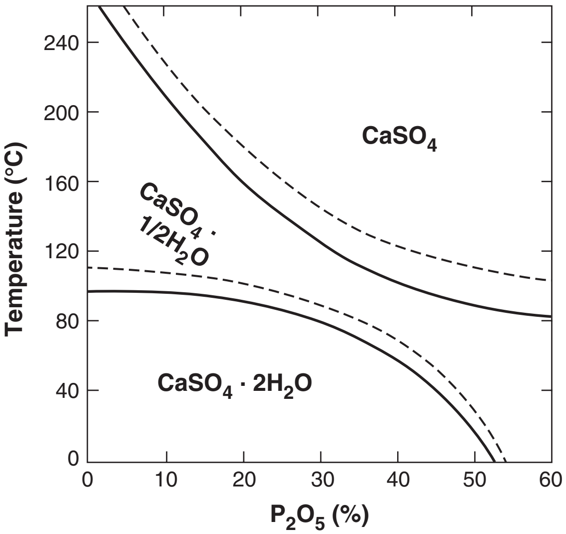
7.2 Wet Acid Process

There are two different processes (i.e., dry and wet processes) for the industrial manufacturing of PA. In the dry process, PA (called thermal PA) is obtained by oxidation of elemental P that is generated by the carbothermal reduction of P_i rock in an electric furnace (Slack 1968). Since the purity of thermal PA is high, it has a wide range of industrial applications. However, the manufacture of elemental P is energy-intensive and dependent on access to low-cost, locally sourced electricity, P_i rock, and coal. Therefore, it is prohibitively difficult to generate elemental P in Japan because of energy shortage and lack of P_i rock reserve. On the other hand, in the wet process, PA (called wet PA) is extracted from P_i rock with strong acids such as hydrochloric acid, nitric acid, and sulfuric acid. Among them is sulfuric acid commonly used worldwide.

$$\underset{\text{P}_\text{i}\text{rock}}{\mathrm{Ca_5F(PO_4)_3}} + \underset{\substack{\text{Sulfuric}\\\text{acid}}}{\mathrm{5H_2SO_4}} + \underset{\text{Water}}{\mathrm{5nH_2O}} \rightarrow \underset{\text{PA}}{\mathrm{3H_3PO_4}} + \underset{\text{Gypsum}}{\mathrm{5(CaSO_4{\cdot}nH_2O)}} + \underset{\substack{\text{Hydrofluoric}\\\text{acid}}}{\mathrm{HF}}$$

By-product gypsum is separated from the slurry (called phosphogypsum slurry) by filtration, while metallic impurities of P_i rock mostly move to the filtrate. Although the filtrate itself cannot meet technical-grade requirements for PA because of impurities such as metals, hydrofluoric acid, and sulfate, it is marketable as a

Fig. 7.1 Equilibrium diagram for the system $CaSO_4$-P_2O_5-H_2O (Slack 1968)



fertilizing material for agricultural purposes. Recovered gypsum contains unreacted P_i rock and silica which is not dissolved with sulfuric acid. Hence, the purity of gypsum relies primarily on the quality of P_i rock used as a raw material. Dewatered gypsum (called phosphogypsum) with the purity of 93–98% can be used for cement, plasterboard, and soil improvers.

Gypsum can take three different forms (i.e., anhydrous, hemihydrate, or dihydrate forms) in phosphogypsum slurry, depending on the PA content and temperature (Fig. 7.1). Based on the form of gypsum generated, wet processes can be further classified into (i) (direct or indirect) dihydrate, (ii) hemihydrate, and (iii) dihydrate-hemihydrate processes. PA-manufacturing plants located near to P_i rock mines mostly adopt either direct dihydrate or hemihydrate processes, giving the priority to the cost performance rather than the quality of gypsum. The direct dihydrate process generates gypsum with the P_2O_5 content of about 1 wt% and the purity of 90–95%. The gypsum is mostly disposed of landfilling or dumped into the ocean. By contrast, the PA-manufacturing plants operating in Japan adopt either indirect dihydrate process (Nissan "H" process) or dihydrate-hemihydrate process (Central-Prayon process). These Japanese original processes consist of multistage reaction steps for the manufacture of PA and thus are more complex than direct dihydrate processes. However, by promoting the crystal transition between hemihydrate and dihydrate forms, they can produce larger gypsum crystals with a lower P_2O_5 content compared to those from the direct dihydrate process. These processes can lower the PA content of gypsum, thereby increasing the extraction efficiency of PA from P_i rock. The generation of low-PA gypsum is critical to guaranteeing the demand from the manufacturers of cement and plasterboard and is therefore essential for the economic viability of the PA manufacturing in Japan.

7.3 Bench-Scale Tests

Although considerable attention has been paid to the potential of using SSA as a secondary P resource, the application in full-scale PA-manufacturing processes has been hampered mainly by its impurities (Table 7.1). For agricultural use, levels of heavy metals and other harmful substances in fertilizers are regulated by the Fertilizer Regulation Act in Japan. Since the PA manufactured by NPA is used as a fertilizing material, the priority target was given to minimizing the contamination of toxic heavy metals from SSA and P_i rock. Chemical analysis was carried out to examine the levels of toxic heavy metals in SSA samples collected from different WWTP (Table 7.1). Except lead, levels of heavy metals in SSA were essentially the same as those of P_i rock. Since lead moves to gypsum solids in the wet process, it could be effectively removed from phosphogypsum slurry by filtration.

Then, PA solution was prepared by varying the blend ratio between SSA and P_i rock. Table 7.2 shows the quality of diammonium phosphate (DAP) prepared using

Table 7.1 The main components of SSA and P_i rock

		SSA		P_i rock	
		Min	Max	Min	Max
P_2O_5	[wt%]	21	35	32	38
CaO	[wt%]	4	14	48	53
Al_2O_3	[wt%]	5	33	0.2	0.8
Fe_2O_3	[wt%]	2	30	0.2	0.7
MgO	[wt%]	1	6	0.2	1
SiO_2	[wt%]	22	46	2	11
As	[mg/kg]	2	44	2	20
Cd	[mg/kg]	1	20	0.1	15
Hg	[mg/kg]	0.01	2	0.01	1
Pb	[mg/kg]	20	100	1	15

SSA samples were collected from six different WWTP. P_i rock was sampled from those used in the PA-manufacturing process of NPA

Table 7.2 Characteristics of DAP generated by varying the blend ratio of SSA and P_i rock

	The SSA/P_i rock blend ratio (wt%)					Marketable DAP
	0	2.5	5.0	10.0	20.0	(wt%)
SP	46.90	47.20	46.50	46.96	45.41	46
WP	45.70	44.60	42.60	38.47	34.88	40
AN	19.10	18.10	18.80	17.50	17.18	18
Fe_2O_3	0.43	0.59	0.75	1.10	1.55	–
MgO	0.78	0.95	1.13	1.33	1.66	–
Al_2O_3	0.54	0.89	1.23	1.81	2.90	–
Total metal	1.75	2.43	3.11	4.24	6.11	–

SP citrate-soluble P_2O_5, *WP* water-soluble P_2O_5, *AN* ammoniacal nitrogen (N), Total metal: Fe_2O_3 + MgO + Al_2O_3. The standard of marketable DAP is given to SP, WP, and AN

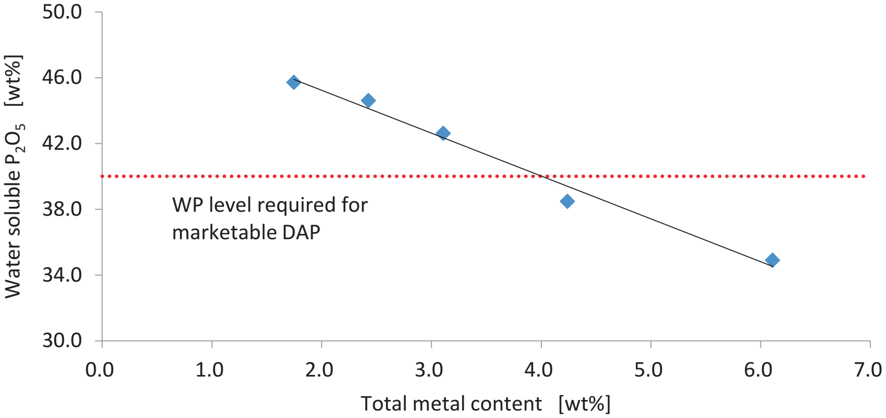
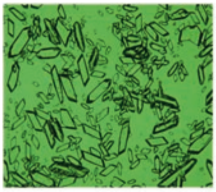


Fig. 7.2 The relationship between the water-soluble P_2O_5 and total metal contents in PA

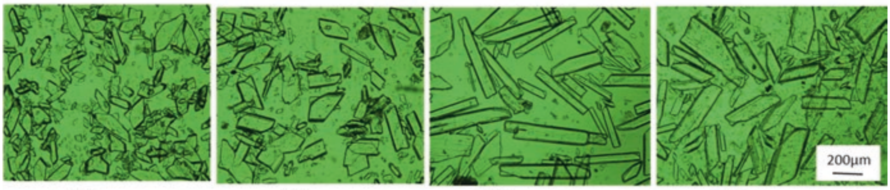
the PA solutions. The commercially available DAP needs to guarantee the amounts of 46 wt% citrate (ammonium citrate)-soluble PA, 40 wt% water-soluble PA, and 18 wt% ammoniacal nitrogen. A remarkable reduction was observed with the water-soluble PA as the blend ratio of SSA increased up to 20%. When the blend ratio exceeded 10%, the content of water-soluble PA failed to meet the requirement for marketable DAP. This reduction was attributable to the increase in the amounts of Fe, Al, and Mg ions in PA solution.

In the literature, it has been reported that Fe^{3+}, Al^{3+}, and Mg^{2+} can form insoluble salts such as (Fe, Al)$NH_4HF_2PO_4$ and $MgNH_4PO_4$ when PA solution is neutralized by ammonia for fertilizer production (Akiyama 1980). Figure 7.2 shows the relationship between the contents of total metal ($Fe_2O_3 + Al_2O_3 + MgO$) and water-soluble PA. Obviously, the content of water-soluble PA decreased with increasing the total metal content. When the total metal content exceeded 4 wt%, the level of water-soluble PA declined below 40 wt% which is the minimal requirement for marketable DAP. Therefore, provided that the total metal content of SSA is 25 wt%, the allowable blend ratio needs to be 8% or lower.

The blend ratio between SSA and P_i rock can affect the crystal morphology of gypsum generated (Fig. 7.3). When the blend ratio exceeded 10%, gypsum showed a needle-shaped crystal structure. The needle-shaped gypsum requires more water in the kneading process, thereby consuming more energy for the manufacture of plasterboards compared to gypsum having a rhombic plate crystal structure. Consequently, the blend ratio needs to be lower than 5% to avoid the formation of needle-shaped gypsum. It has also been reported that F^- can react with Al^{3+}, thereby forming a complex AlF_n^{3-n} in PA solution (Jun et al. 1997). This complex is known to precipitate on gypsum, thereby inhibiting its crystal growth in the long axis direction. Similarly, silica is likely to react with F^- in PA solution to generate a complex SiF_6^{2-}. This reaction may competitively inhibit the formation of AlF_n^{3-n}, thus allowing the elongation of gypsum crystal. It has also been shown that the addition of



Gypsum for P_i rock



2.5 5.0 10.0 20.0

Fig. 7.3 The crystal morphology of gypsum generated from the mixture of SSA and P_i rock. The SSA/P_i rock blend ratio was varied from 0.0 to 20.0. *Bar* = 200 µm

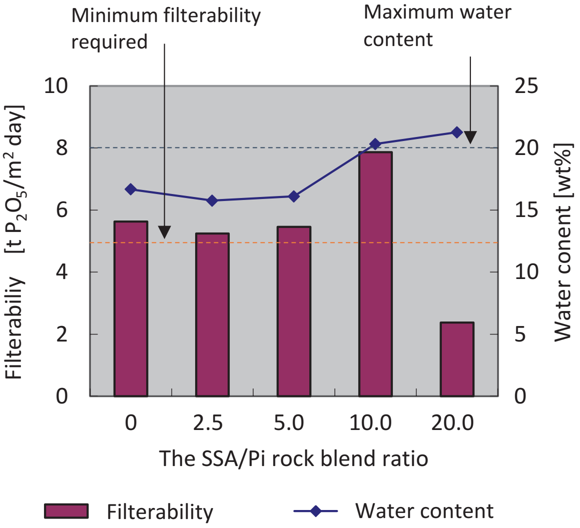


Fig. 7.4 The effect of the SSA/P_i rock blend ratio on the filterability of phosphogypsum slurry and the water content of gypsum cake

fluorine compounds such as fluorite to PA solution is likely effective in allowing gypsum to form the rhombic plate crystal structure (Mochiyama et al. 2017).

The filterability of phosphogypsum slurry is critical to the operability of downstream process in the PA-manufacturing plant. Figure 7.4 shows the dependence of slurry filterability on the SSA/P_i rock blend ratio. When the blend ratio exceeded 20%, the filterability of phosphogypsum slurry remarkably deteriorated. This was caused due to the formation of fine silica particles in the slurry.

Regarding the toxicity of DAP generated using SSA, plant cultivation tests were conducted using the leaf vegetable komatsuna (*Brassica rapa* L. var. *perviridis*) as

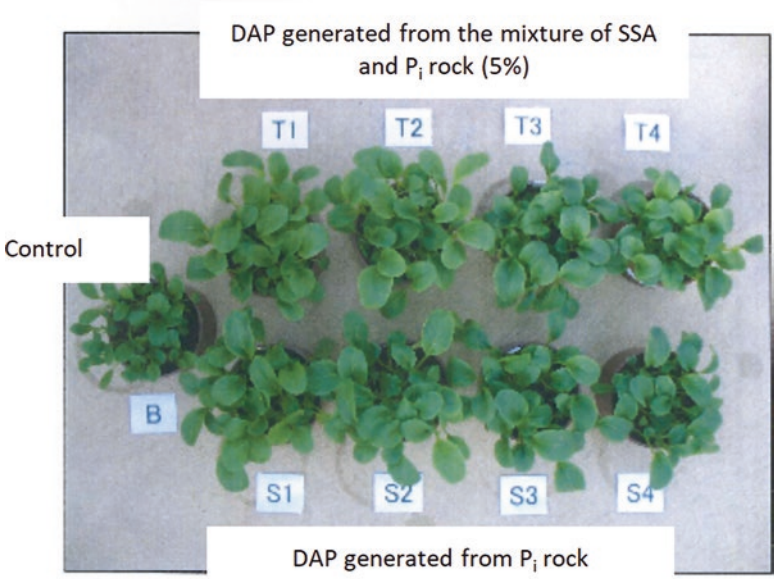


Fig. 7.5 The toxicity test of DAP generated from the mixture of SSA and P_i rock (5%) using the leaf vegetable komatsuna as a test plant

a test plant. As can be seen in Fig. 7.5, no significant toxicity was detected with the DAP compared to commercially available DAP samples.

Another problem regarding gypsum quality is the contamination of lead, which can move from P_i rock to gypsum in a wet acid process. Lead can react with sulfate, thereby precipitating onto gypsum in the PA-manufacturing process. The elution test of lead from gypsum was conducted using samples prepared from SSA having different lead contents (Fig. 7.6). The results showed that if the lead content of SSA is higher than 60 mg/kg, the blend ratio should be lower than 3% to prevent lead leakage which may cause health and environmental issues.

7.4 Industrial PA Manufacturing

In April 2010, NPA conducted a full-scale plant test for the manufacture of PA using 70 t of SSA at the blend ratio of 2.5%. The SSA used for the plant test fulfilled the following specifications:

- P_2O_5, 30 wt% or greater
- SiO_2, 30 wt% or lower
- Lead, 60 mg/kg or lower
- Metals (i.e., Fe_2O_3+ Al_2O_3+ MgO), 20 wt% or lower

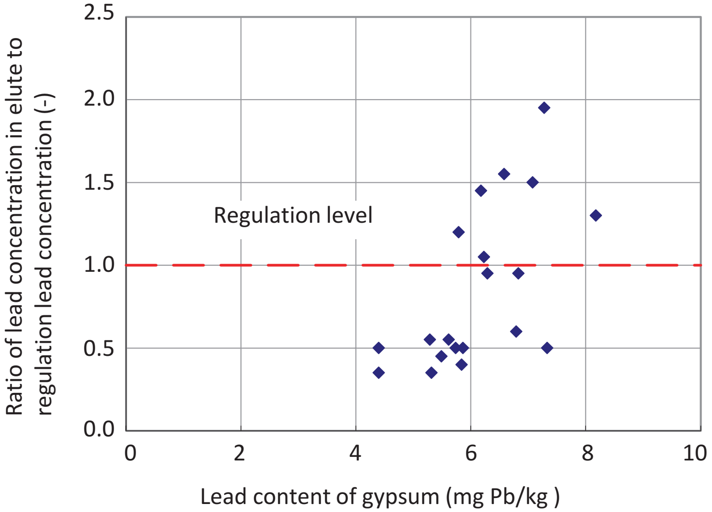


Fig. 7.6 Elution of lead from gypsum prepared from SSA having different lead contents

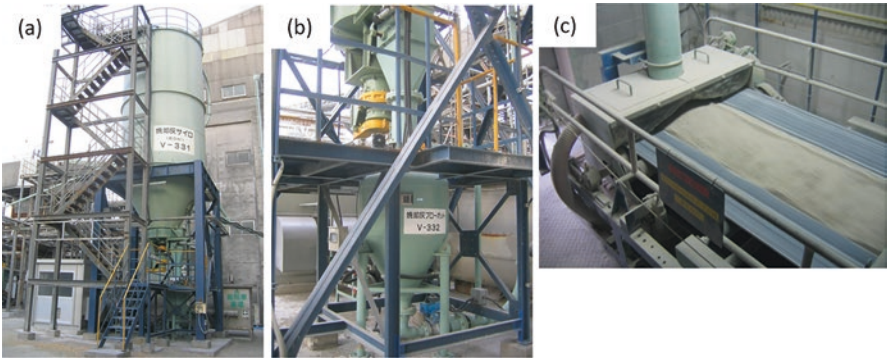


Fig. 7.7 SSA storage tank and weighing equipment implemented in the existing PA-manufacturing plant. **a** Storage tank, **b** weighing equipment, **c** unit for mixing SSA with P_i rock

The results convincingly showed that the use of SSA caused no significant problem on plant performance, product quality, and pollution prevention under the conditions tested. Based on the results, NPA decided to accept SSA for the commercial production of PA in November 2012. Since the control of blend ratio of SSA was critical to guaranteeing the product quality, SSA storage tanks and weighing equipment were newly implemented in the existing PA-manufacturing plant (Fig. 7.7). In addition, NPA acquired an industrial waste disposal business license from the government to purchase SSA from WWTP. This was absolutely needed because SSA was regarded as industrial waste by the Waste Management Law. The existing

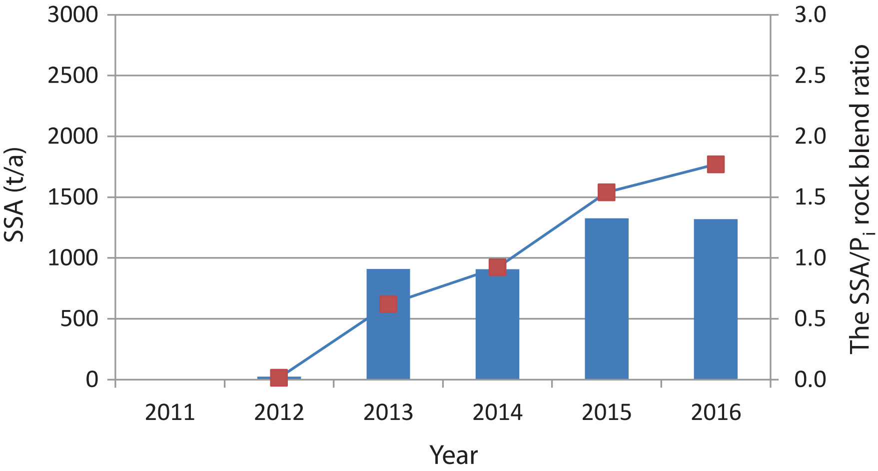


Fig. 7.8 Year-to-year changes in the amount of SSA accepted by NPA (*bar*) and the SSA/P_i rock blend ratio for the manufacture of PA (broken line)

PA-manufacturing plant was therefore designated as an intermediate treatment facility for industrial waste. After a 5-month trial, the commercial production of PA using SSA commenced on April 2013 (Fig. 7.8). Currently, the blend ratio of SSA remains around 1.5% because of the shortage of SSA supply from WWTP. NPA has made efforts to develop collaborations with WWTP, advocating mutual economic benefits brought by the valorization of SSA. Although WWTP need to pay SSA shipping costs, they can not only earn revenue from selling SSA but also save sludge disposal costs.

7.5 Conclusions

NPA has realized the industrial use of SSA, which is purchased from WWTP, without modifying the existing PA-manufacturing process. Since SSA is available at costs considerably lower than P_i rock, the use of SSA has allowed NPA to reduce the net cost of PA production on industrial scale. At present, SSA needs to be mixed with P_i rock at a blend ratio of 2.5% or less before being subjected to the wet acid process. Although PA is readily released from SSA with sulfuric acid, it also inevitably dissolves metals from SSA, thereby contaminating PA solution. Metals such as Al, Fe, and Mg can form insoluble salts with PA in fertilizer-manufacturing processes, lowering the quality and value of fertilizer. To overcome this problem, it is necessary to develop a cost-effective technology capable of effectively removing metals from PA solution. Although various technologies have been potentially applicable to metal removal from PA solution, no technology has been successfully applied to industrial wet acid processes mainly due to economical reasons. Further study is needed to develop cost-effective technology for removing metals from PA solution.

In industrial PA-manufacturing processes, by-product gypsum is generated about 1.5 times more than P_i rock input as a raw material. Since the revenue from selling by-product gypsum is critical to the economic viability of industrial PA production, NPA makes every effort to guarantee the quality of not only PA but also gypsum to end users. Importantly, this effort can make a contribution to the improvement of resource efficiency by turning waste in a resource. In Japan, however, the wastewater treatment sector still gives the priority to P_i removal rather than P_i recycling. The precipitation of P_i with Al^{3+} or Fe^{3+} is a cost-effective, commonly used technology for removing P_i from sewage. The chemical precipitation of P_i with Al^{3+} or Fe^{3+} leads to the increase of metal contents, making the application of SSA to PA manufacturing difficult. Hence, it would be desirable to adopt biological P_i removal (known as Bio-P process) in WWTP rather than chemical P_i precipitation. In addition, to reduce the contents of silica, aluminum, and lead in SSA, it seems effective to avoid the mixing of primary and secondary sludge before incineration. Primary sludge generally contains more silica, aluminum, and heavy metals compared to secondary sludge (Kanjou and Sone 2017).

References

Akiyama T (1980) Formation and reaction of mineral constituents in compound fertilizer (in Japanese). Japan Phosphatic and Compound Fertilizers Manufactures' Association, Tokyo

Jun L, JianHua W, YunXiang Z (1997) Effects of the impurities on the habit of gypsum in wet-process phosphoric acid. Ind Eng Chem Res 36:2657–2661

Kanjou T, Sone K (2017) Reuse Recycl (in Japanese) 41(154):64–69

Mochiyama T, Morita K, Oishi Y (2017) Influence of fluorine and aluminum ion on crystal habit of gypsum in production of phosphoric acid by wet-process (in Japanese). J Soc Inorg Mater Jpn 24:3–8

Slack A (1968) Phosphoric acid. Marcel Dekker, New York