Chapter 13

Phosphorus Extraction from Sewage Sludge Ash by the CO_2 Blowing Method

Takeshi Toyama

Abstract Sewage sludge ash (SSA) often contains high levels of phosphorus (P) and has been considered as one of important secondary P resources. However, SSA also contains toxic heavy metals such as Cd, As, and Hg which can cause contamination problems in the recovery of P from SSA. Alkaline earth metal phosphate salts, which are present in SSA, can be preferentially dissolved by blowing CO_2 into the aqueous suspension of SSA. The dissolution mechanism involves the formation of soluble hydrogen carbonate by the CO_2 blowing which allows alkaline earth metal phosphate salts to form bicarbonate salts having high solubility in water. This chapter describes the selective extraction of phosphate from SSA using the CO_2 blowing method.

Keywords Alkaline earth metal phosphate · CO_2 blowing · Selective dissolution · Hydroxyapatite

13.1 Introduction

The raw material for phosphoric acid, which is widely used for chemical fertilizer, livestock feed, and various industrial products, is phosphate (P_i) rock. The global distribution of P_i rock is uneven, and its reserve is concentrated in a limited number of countries. Japan is most entirely dependent on imported P_i rock and is, therefore, vulnerable to the price volatility in the global market. For example, in the summer of 2008, China raised the tariff on P_i rock and restricted the export of phosphorus (P) products. This caused the price surge of P_i in Japan and greatly affected not only the industrial production but also food supply (Cordell and White 2014).

Municipal sewage contains relatively high levels of P_i which eventually ends up in sewage sludge at wastewater treatment plants (WWTP). In Japan, more than 70%

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of sewage sludge is incinerated at WWTP. Sewage sludge ash (SSA) from mono-incinerators contains high levels of P_i and has been considered as one of the most important secondary P resources (Shiroyama et al. 2015; Takahashi et al. 2004). However, SSA also contains toxic heavy metals which are harmful to plants when applied to farmland (Soma et al. 1989; Chatterjee and Dube 2005). Although various technologies are potentially available for P_i recovery from SSA, their implementation has been hampered mainly by economic reasons. It is, therefore, critical to develop a simple, low-cost technology for recovering P_i from SSA.

The author of this chapter has been conducting research on the morphological control of calcium carbonate and calcium phosphate crystals. The morphological control is a technique to increase the added value of materials by controlling the particle size, shape, and distribution. The basis of this method is the dissolution-deposition reaction, and it is critical to prepare a highly concentrated salt solution. Recently, the author has developed the CO_2 blowing method which is effective for dissolving alkaline earth metal phosphate salts. This chapter describes the selective extraction of P_i from SSA using the CO_2 blowing method.

13.2 The CO_2 Blowing Method

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp), which is a main component of P_i rock, is insoluble in water and chemically stable. On the other hand, alkaline earth metal carbonates such as $CaCO_3$ is dissolved in water by the CO_2 blowing and form highly soluble bicarbonate salts (Langmuir 1968; Segnit et al. 1962). HAp is decomposed into soluble $Ca(HCO_3)_2$ and H_3PO_4 by blowing CO_2 into an aqueous suspension of HAp according to the formula (13.1) (Toyama et al. 2012).

$$Ca_{10}\left(PO_4\right)_6\left(OH\right)_2 + 20CO_2 + 18H_2O \rightarrow 10Ca\left(HCO_3\right)_2 + 6H_3PO_4 \tag{13.1}$$

Figure 13.1 exemplifies the time-course of HAp decomposition after the start of CO_2 blowing into an aqueous suspension of HAp. No significant release of Ca^{2+} from HAp is observed in deionized water without CO_2 blowing. However, the concentration of Ca^{2+} increases soon after the start of CO_2 blowing and reached about 80 mg/L in 1 h. Thus, it is possible to prepare a highly concentrated calcium phosphate solution from insoluble HAp by simply blowing CO_2 gas to the aqueous suspension.

The potential of the CO_2 blowing method was further examined using various phosphate salts (Fig. 13.2). The P_i release from Na_3PO and K_3PO_4, which are alkaline metal phosphate salts, was not enhanced by CO_2 blowing. P_i salts such as $Fe_3(PO_4)_2$ and $AlPO_4$, which were insoluble in water, showed no significant P_i release even after 30-min CO_2 blowing. On the other hand, alkaline earth metal phosphates such as $Mg_3(PO_4)_2$ and $Ca_3(PO_4)_2$ showed a distinct release of P_i by CO_2 blowing as in the case of HAp. This is attributable to the fact that alkaline earth

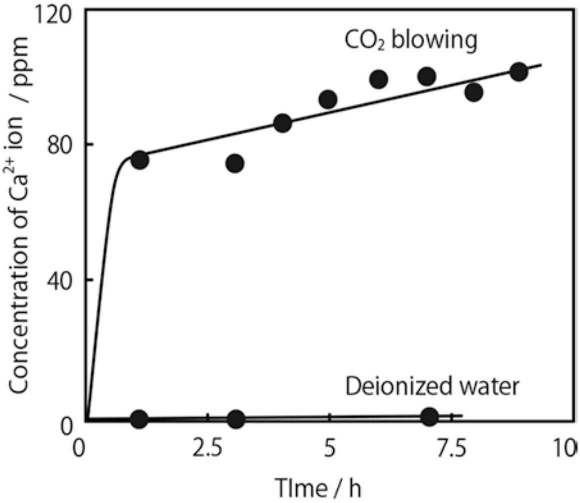


Fig. 13.1 The release of Ca^{2+} from HAp by CO_2 blowing

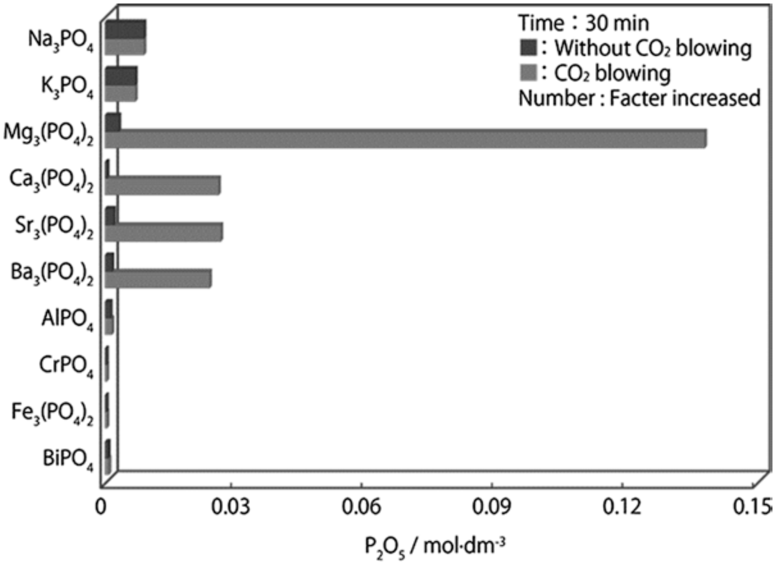


Fig. 13.2 P_i release from various P_i salts by CO_2 blowing

metal phosphate salts can react with CO_2 to form water-soluble bicarbonate salts. Thus, the CO_2 blowing method is able to dissolve alkaline earth metal phosphate salts selectively from a mixture of P_i salts.

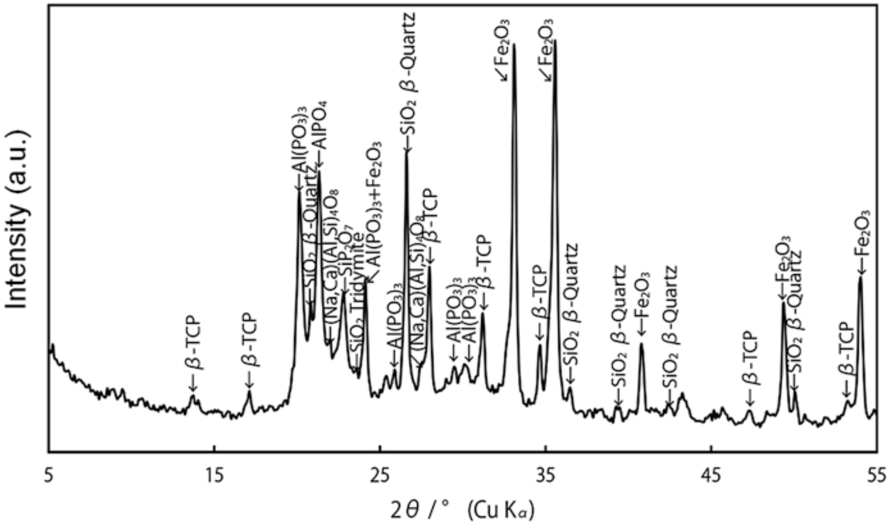


Fig. 13.3 X-ray diffraction pattern of a SSA sample

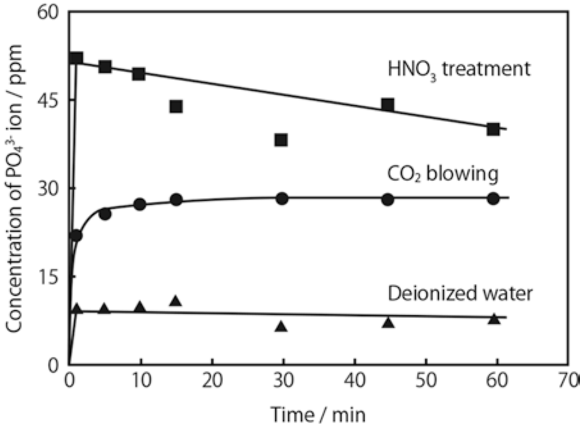
13.3 Morphologies of P_i Salts in SSA

SSA often contains P_i at levels similar to those of mined P_i rock. When extracting P_i from SSA using the CO_2 blowing method, it is necessary to know the morphologies of P_i salts in SSA. Ozaki et al. (2005) have analyzed the morphologies of P_i salts in SSA in detail using energy dispersive X-ray (EDX) spectroscopy and have detected various P_i salts in SSA. Figure 13.3 shows the X-ray diffraction pattern of a SSA sample taken from WWTP in Japan. The SSA sample, which was brownish in color, exhibited a strong diffraction peak corresponding to Fe_2O_3 in the X-ray diffraction pattern. In addition to the peaks corresponding to quartz (SiO_2), the peaks of P_i salts such as $Al(PO_3)_3$, $AlPO_4$, SiP_2O_7, and β-$Ca_3(PO_4)_2$ were clearly detectable. Among them is β-$Ca_3(PO_4)_2$ that can be efficiently dissolved by the CO_2 blowing method as shown in Fig. 13.2.

13.4 P_i Release from SSA

To examine the performance of CO_2 blowing on the release of P_i from SSA, SSA samples were suspended in deionized water at a concentration of 0.5 mass%. Then, the CO_2 gas was blown into the suspension at a rate of 1 L/min for 60 min at room temperature. Then, the suspension was filtered with a glass filter to obtain the leachate. Figure 13.4 shows the time-course data on P_i release from SSA by CO_2 blowing. The data were also compared with those obtained with HNO_3 treatment. The P_i concentration reached approximately 10 mg/L soon after suspending SSA in

Fig. 13.4 The release of PO_4^{3-} form SSA



deionized water. However, there was no significant increase in P_i concentration in deionized water without CO_2 blowing. By contrast, the concentration of P_i rapidly increased up to 50 mg/L when HNO_3 was added to the suspension of SSA. Then, the P_i concentration gradually decreased down to 40 mg/L at 60 min. The P_i concentration of deionized water increased up to 30 mg/L by CO_2 blowing. Importantly, pH was about 5.3 even 60 min after the start of CO_2 blowing. The level of P_i release from SSA by CO_2 blowing was about 70–80% of that observed with HNO_3 treatment.

The time-course data on the release of Na^+, Mg^{2+}, and Ca^{2+} from SSA were shown in Fig. 13.5. The release of these cations was low in deionized water without CO_2 blowing. HNO_3 could enhance the release of Na^+, Mg^{2+}, and Ca^{2+} from SSA. Interestingly, there was no significant difference in the release of Na^+ from SSA in deionized water with and without CO_2 blowing (Fig. 13.5a). This suggests that alkaline metal P_i salts are not dissolved by CO_2 blowing. By contrast, Mg^{2+} and Ca^{2+} were significantly released by CO_2 blowing (Fig. 13.5b, c), suggesting that alkaline earth metal P_i salts could be dissolved by the CO_2 blowing method. Figure 13.6 shows the time-course data on the release of Fe ions (mainly Fe^{3+}) from SSA. The release of Fe ions was remarkable by HNO_3 treatment, but the elution of Fe ions was not enhanced by CO_2 blowing. This is likely attributable to the fact that trivalent Fe^{3+} ion is difficult to form bicarbonate salts.

Table 13.1 summarizes the data on the release of various ions from SSA. The release of P_i (PO_4^{3-}) by CO_2 blowing was about 75% of that observed with HNO_3 treatment. However, the release of K^+ and Na^+ was not enhanced by CO_2 blowing. As shown in Fig. 13.2, aluminum phosphate salts ($AlPO_4$) in SSA was not efficiently dissolved by CO_2 blowing. By contrast, the release of alkaline earth metal ions was greatly enhanced by CO_2 blowing. Hence, β-$Ca_3(PO_4)_2$ in SSA could be selectively dissolved by the CO_2 blowing method. Importantly, though heavy metal ions such as Fe^{3+}, Cu^{2+}, and Mn^{2+} can be eluted by HNO_3, their release from SSA was

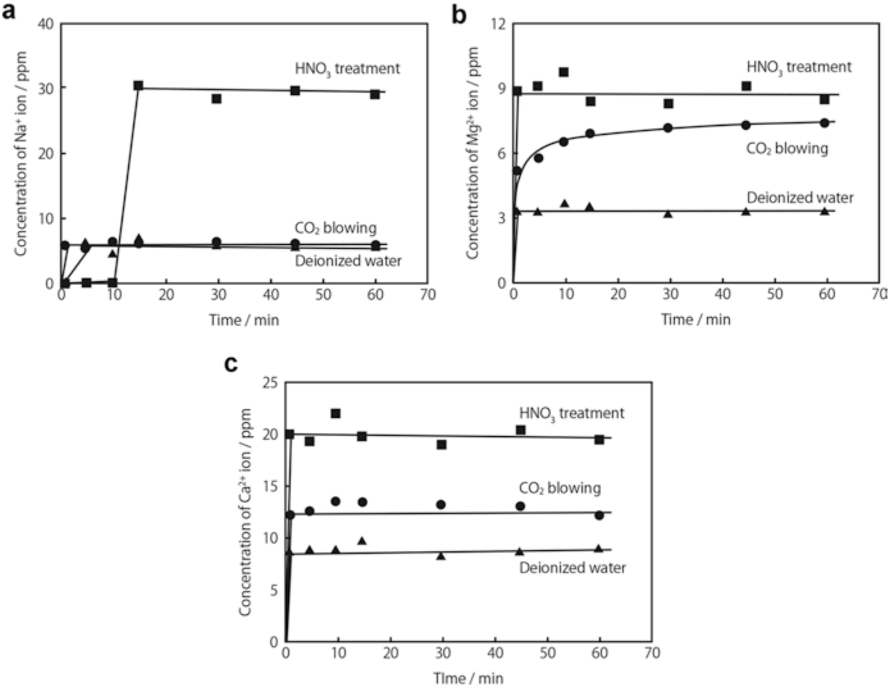


Fig. 13.5 The release of Na^+ (A), Mg^{2+} (B), and Ca^{2+} (C) by CO_2 blowing

Fig. 13.6 The release of Fe ions (Fe^{2+} plus Fe^{3+}) by CO_2 blowing

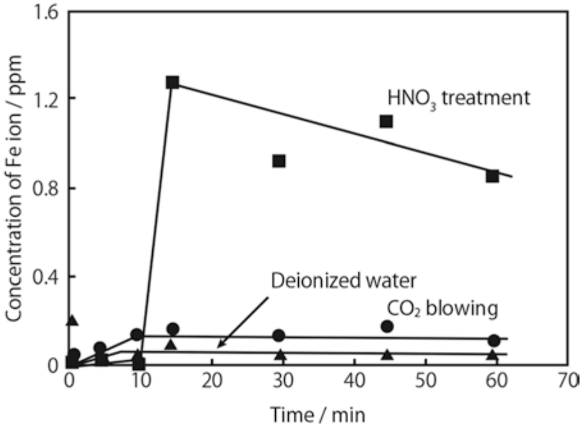


Table 13.1 The release of various ions from SSA (Unit: ppm)

Component	HNO_3 treatment	CO_2 blowing	Deionized water
PO_4^{3-}	40	30	7
Mg^{2+}	9	8	3
Ca^{2+}	20	12	8
Na^{2+}	30	6	6
K^{+}	24	4	3
Fe^{3+}	1.3	0.2	0.1
Cu^{2+}	2.0	0.3	N.D.
Mn^{2+}	2.0	N.D.	0.3

insignificant by CO_2 blowing. Consequently, it is likely possible to release P_i from SSA by CO_2 blowing, while minimizing the contamination by toxic heavy metals.

13.5 Conclusions

SSA often contains a large amount of P_i and can serve as a promising secondary P resource. The CO_2 blowing method is potentially a simple, low-cost technology for releasing P_i from SSA, since it requires only water and CO_2 gas for releasing P_i from SSA. Needless to say, CO_2 is unlimitedly available from a sludge incinerator in WWTP. The CO_2 blowing method can release P_i from SSA at room temperature and without needing to adjust pH to low or high values. Further study is needed to examine the performance and cost effectiveness of this technology at a full scale.

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