

Study on Fractional Recovery of Phosphorus from Incinerated Ash and Anaerobically Digested Sludge

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ABSTRACT

In this study, acidic solubilization of phosphorus and its alkaline fractional recovery were attempted, using incinerated ash and anaerobically digested sludge that were originated from sewage sludge. For acidic solubilization, chemical leaching with sulfuric acid was employed for ash, and bacterial leaching for digested sludge. The ash showed higher solubilization of phosphorus (72%), while the digested sludge exhibited higher solubilization of heavy metals (87-100%). The recovery of phosphorus from the acidic solution by ferric chloride and alkali addition revealed that, at the pH of 2 – 2.3, relatively pure ferric phosphate can be precipitated, and that higher percent recovery of phosphorus from the acidic solution is possible with the ash (96%) than digested sludge (81%). Also, heavy metals in the acidic solutions were successfully removed as precipitates at the pH of 8.6 – 8.8. The separation of heavy metals from ferric phosphate precipitates was easier with the digested sludge, because of its lower element concentrations and chelating ability of heavy metals by soluble organic substances.

1. INTRODUCTION

All living matter requires phosphorus as an essential nutrient. Phosphorus is thus inevitable to be used as fertilizers in agriculture. However, phosphate rock, the main phosphorus source containing high amounts of phosphate, is likely to be depleted within several decades. Recovery and recycling of phosphorus from wasted materials are now of importance for constructing the sustainable society.

All of phosphorus used in Japan has been imported from foreign countries. It is reported that about 10% of the imported phosphorus flows into sewage (Ministry of Land, Infrastructure, Transport and Tourism, 2007). Phosphorus in sewage thus represents a renewable resource in Japan. Sewage sludge also contains a significant amount of toxic heavy metals, which tend to hinder the use of sewage sludge as a phosphorus source.

In Gifu City, Japan, a full-scale plant has been constructed which recovers phosphorus from incinerated ash of sewage sludge (Nakagawa, 2007). The plant employs sodium hydroxide to elute phosphate at an alkaline pH and recovers the

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phosphate as a calcium phosphate salt. The percent phosphorus recovery is typically in the range 50 – 60%.

In this study, acidic solubilization of phosphorus and its fractional recovery were examined and evaluated using the sewage sludge oriented wastes, incinerated ash and anaerobically digested sludge. The use of both incinerated ash and anaerobically digested sludge is for a comparative purpose, since the former is mostly in an inorganic and oxidized form, and the latter in an organic and reduced form. Cu and Zn were chosen in this study to elucidate the behavior of heavy metals.

2. METHODS

All the experiments were performed in the laboratory at the room temperature of 22 – 25 °C. Acids used were those for heavy metal analysis (Wako Pure Chemical Industries), and other chemicals were the guaranteed grade. Laboratory apparatus used were washed with HCl (1+1) prior to experiments. Hereafter, both chemical and bacterial leaching are commonly called acidic solubilization, and the filtered solution obtained after the acidic solubilization is called acidic solution.

2.1. Wastes

Incinerated ash was produced at an incineration plant in Fukui City, Japan, which largely deals with anaerobically digested sludge collected from the surrounding areas. Anaerobically digested sludge was taken from a mesophilic anaerobic digester in a wastewater treatment plant located in Fukui City, Japan.

2.2. Chemical leaching of incinerated ash

100 g of incinerated ash was added with 1 L of 0.25 mol/L sulfuric acid (the liquid-to-solid ratio of 10), and mixed at 300 rpm for 4 hours. The resultant pH was 2 or less. These experimental conditions were based on Takahashi et al. (1998), under which they reported phosphorus solubilization from ash is maximized and completed in 1 hour.

2.3. Bacterial leaching of anaerobically digested sludge

Bacterial leaching was employed for anaerobically digested sludge to solubilize both phosphate and heavy metals. Erlenmeyer flasks with a working volume of 500 mL were used as the leaching reactors, and operated semi-continuously at 5 day HRT and 100 rpm. 0.5 – 0.75 mL of sulfuric acid per 100 mL of influent digested sludge was added to reduce the pH to about 2 or lower. According to Couillard and Mercier (1990) and Kitada et al. (1999), bacterial leaching is affected by several factors such as HRT, pH and Fe(II) addition. Here, a longer HRT and lower pH were employed for efficient leaching. Composite effluent samples for 2 days were used to increase the sample volume for analyses.

2.4. Behavior of major elements in acidic solution with alkali addition (alkali titration)

In order to gain an insight into the behavior of major elements at various pH, alkali titration was performed with the acidic solutions. 50 mL of acidic solution was transferred to nine polyethylene bottles, and each added with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Ca/P

molar ratio of 1) to increase the cation concentration and precipitate all phosphate. The bottles were adjusted to the pH between less than 2 to about 10 with 10 mol/L NaOH, and shaken at 100 rpm for 24 hours. After that, the final pH was measured, and filtrates were prepared by centrifugation (15,000 rpm, 5 min) and membrane separation (0.45 μm). The concentration of phosphate and heavy metals in the filtrates were analyzed, as described later.

In this experiment, a chemical equilibrium calculation program, MINEQL+ (Ver 4.5, Environmental Research Software), was applied to theoretically estimate soluble concentrations of major elements in the wide pH range.

2.5. Fractional recovery of phosphorus with a ferric salt

Ferric salt addition was attempted to recover phosphorus fractionally from other metals, based on the results of the alkali titration. First, acidic solution was added with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Fe/P molar ratio of 1.1), adjusted to about pH 2 with 10 mol/L NaOH, and shaken at 100 rpm for 4 hours to precipitate ferric phosphate. Filtrates were prepared as written above. Then, the filtrate was adjusted to pH 8 – 9 with 10 mol/L NaOH, and shaken at 100 rpm for 4 hours to precipitate heavy metals.

To analyze the composition, the ferric phosphate precipitates were dried at 110 $^\circ\text{C}$ for 1 night, resolubilized with a few mL of nitric acid, and adjusted to 1 g DS/L and to 0.3 mol/L nitric acid.

2.6. Analytical procedures

Most of the analyses were performed in accordance with Standard Methods (APHA/AWWA/WEF, 1998). The pH was measured with a pH meter (HM-60G, TOA/DKK) connected to a pH probe (GST-5711C, TOA/DKK). Phosphate was measured by the ascorbic acid method (Standard Methods 4500-P E) using a spectrophotometer (DR/4000U, Hach) with appropriate dilution.

SO_4 and NO_3 ions were analyzed with an ion chromatograph (DX-120, Dionex), NH_3 with an ion meter (720A, Thermo Scientific) connected to an ammonia electrode (9512BN, Thermo Scientific), and total organic carbon (TOC) with a TOC analyzer (TOC-Vcsh, Shimadzu).

The concentration of metals was determined by the flame atomic adsorption method using a polarized Zeeman atomic adsorption spectrometry (Z-5010, Hitachi). The ash and sludge samples for total metal concentration were prepared by microwave-assisted digestion (Standard Methods 3030 K; Model 7195, O.I.Analytical).

3. RESULTS AND DISCUSSION

3.1. Acidic solubilization

The characteristics of ash and digested sludge are summarized in Table 1. The results of acidic solubilization of those wasted materials are shown in Table 2. The percent solubilization expresses the percent of soluble phosphate or metal concentration against the corresponding total concentration.

The percent solubilization of phosphate from the ash was 71.7% at pH 1.5 on average. According to Ohshita et al. (2003), acidic solubilization of ash is dependent on $[\text{H}^+]/[\text{P}]$ ratio, where $[\text{P}]$ is the molar of phosphorus originally present in ash, and

Table 1 Characteristics of ash and digested sludge

	Water	TS	VS	SS	VSS	T-P	T-Cu	T-Zn	T-Fe	T-Al	T-Ca	T-Mg	T-K	T-Na
Ash	(wet %)					(mg/wet g)								
	35.6	64.4	13.6	—	—	53.0	0.752	1.92	38.4	39.6	43.5	6.95	2.92	4.38
Digested sludge	(g/L)					(mg/L)								
	—	23.6	14.1	21.6	14.0	627	9.06	24.7	1,090	507	414	102	114	54.8

*Average of duplicate for ash and of triplicate for digested sludge.

Table 2 Results of acidic solubilization

	Total conc. in waste			Soluble conc. in acidic solution				% solubilization		
	P (mg/L)	Cu (mg/L)	Zn (mg/L)	pH	PO ₄ -P (mg/L)	Cu (mg/L)	Zn (mg/L)	PO ₄ -P (%)	Cu (%)	Zn (%)
Ash	5,300	75.2	192	1.5	3,800	44.9	93.6	71.7	59.7	48.8
Digested sludge	627	9.06	24.7	2.3	266	7.87	24.5	42.4	86.9	99.2
				1.8	340	8.70	24.8	54.2	96.0	100.4
				1.5	413	8.28	22.5	65.9	91.4	91.1

*Average of triplicate for ash and single analysis for digested sludge.

[H⁺] is the molar of hydrogen ion added. Their equation estimates 73.0% of phosphate solubilization under these conditions, close to the value obtained here. The percent solubilization of Zn and Cu were between 49 and 60%.

The pH in the bacterial leaching of digested sludge was purposely varied between 1.5 and 2.3, because phosphate solubilized was found to be dependent on the pH even in this narrow range. The percent phosphate solubilization was 42.4% at pH 2.3, 54.2% at pH 1.8 and 65.9% at pH 1.5. Wild et al. (1997) reported that 31% of phosphorus was in the organic fraction of anaerobically digested sludge. Thus phosphorylation of organic phosphorus might proceed at the lower pH. The heavy metals in the bacterial leaching were solubilized very efficiently, 87 – 96% and 91 – 100% of percent solubilization for Cu and Zn, respectively. This is attributable to the longer detention time and lower pH.

The reported heavy metal leaching from digested sludge has varied widely, depending on the type of heavy metal, sludge characteristics, operating conditions and so on. (Babel and Dacera, 2006; Pathak et al., 2009). It is generally observed that Cu is more difficult to be leached than Zn, and that chemical methods using acids solubilize only as much as 50% of Cu from digested sludge (Tyagi et al., 1988). It is therefore apparent that the biological leaching method is superior to chemical leaching methods for heavy metals.

According to Kato et al. (2007), phosphorus in ash is present as phosphates of Al, Fe and Ca or is associated with Si crystals, whereas phosphorus in wastewater sludge is mainly in the forms of organic phosphorus and polyphosphates. Heavy metals exist primarily as oxides in ash, and as sulfides in digested sludge. The different results of acidic solubilization appear to reflect the forms of those elements. In short, for phosphorus, inorganic forms are easier to be leached than in organic forms. For heavy

metals, although oxides can be solubilized quickly according to the Tessier extraction method (Tessier et al., 1979), sulfides appear to be solubilized easily when sulfur oxidizing bacteria function well.

3.2. Behavior of major elements in acidic solution with alkali addition (alkali titration)

The concentration of major elements in acidic solution is listed in Table 3. The behavior of major elements in acidic solution with alkali addition is plotted in Fig. 1.

The majority of PO₄, Fe and Al were precipitated at the pH of 1.5 – 2.5. For Zn and Cu, the corresponding pH became higher, around 4. The soluble Ca concentration was relatively constant in the whole pH range, probably because an extra amount of Ca was present in the acidic solution.

A chemical equilibrium calculation by MINEQL+ is also shown in Fig.1. The behavior of Al was simulated best, while that of Fe was least. Accordingly, the agreement of the MINEQL+ calculation with the measured values is dependent on the element, and could be influenced by many factors, such as equilibrium constants and chelation effects by organic substances.

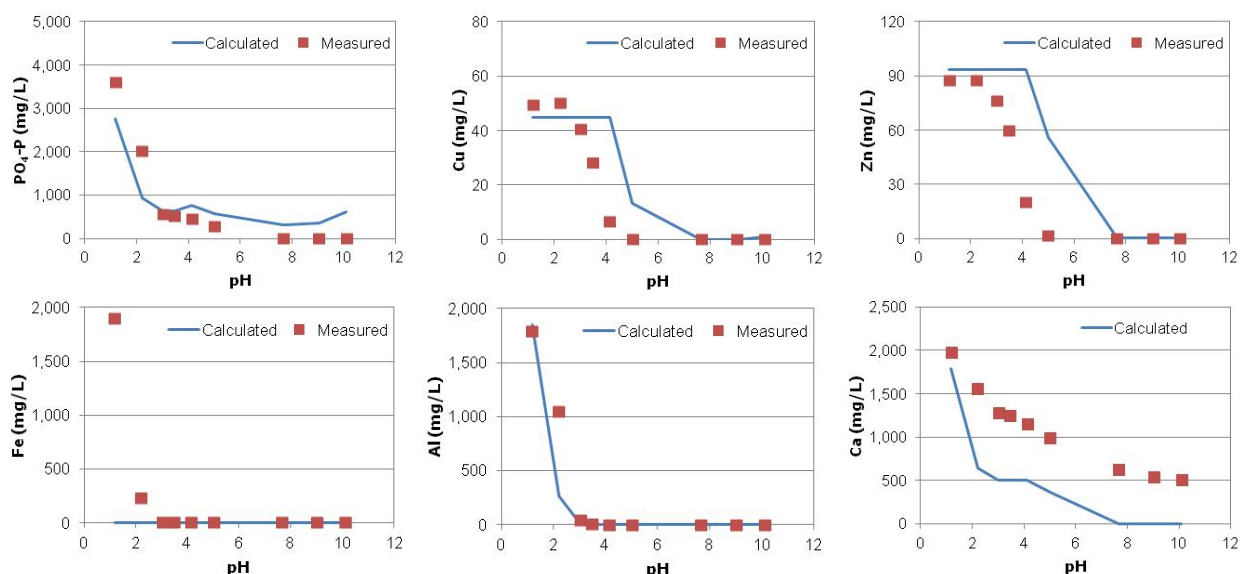
Based on the results of the alkali titration of acidic solutions, the separation of PO₄, Fe and Al precipitates from Cu and Zn appears to be possible to a considerable extent. The optimum pH for the separation is somewhere between 3 – 3.5 for ash, while it is 4 – 4.5 for digested sludge. This shift of about 1 pH unit for the digested sludge is due to the lower concentration of the elements as well as the chelation by soluble organic substances. In fact, TOC in the acidic solution for digested sludge (262 mg/L) was 24 times higher than that for ash (11mg/L).

Furthermore, the pH range to separate PO₄ and Fe precipitates from Al is very narrow, but relatively purified phosphorus as FePO₄ · 2H₂O can be obtained by the precipitation at around pH 2. MINEQL+ estimation of predominant PO₄ precipitates, shown in Table 4, supports this, as FePO₄ · 2H₂O predominantly exists up to about pH 2, while AlPO₄ and Ca₅(PO₄)₃OH from pH 2 or higher.

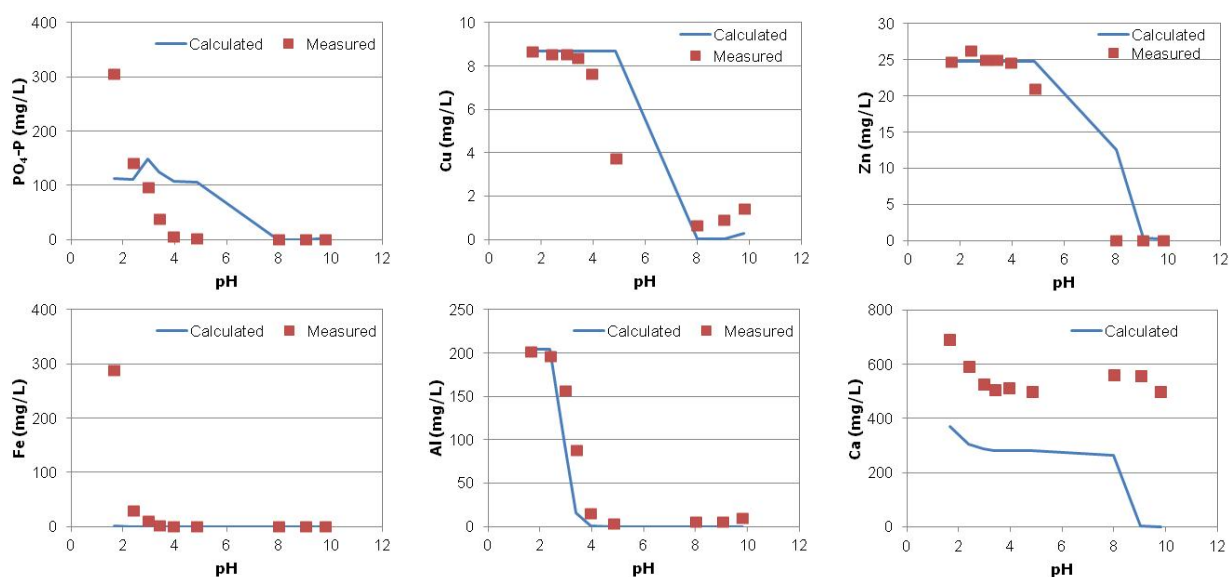
Table 3 Concentration of major elements in acidic solution

		Al ³⁺	Ca ²⁺	Cl ⁻	Cu ²⁺	Fe ³⁺	K ⁺	Mg ²⁺
Ash	mg/L	1,850	6,780	96.0	44.9	1,880	155	308
	mol/L	6.84x10 ⁻²	1.84x10 ⁻¹	2.70x10 ⁻³	7.06x10 ⁻⁴	3.37x10 ⁻²	3.97x10 ⁻³	1.27x10 ⁻²
Digested sludge	mg/L	204	1,150	161	8.70	414	101	58.8
	mol/L	7.56x10 ⁻³	4.08x10 ⁻²	4.54x10 ⁻³	1.37x10 ⁻⁴	7.41x10 ⁻³	2.57x10 ⁻³	2.42x10 ⁻³
		Na ⁺	NH ₄ ⁺ -N	NO ₃ ⁻ -N	PO ₄ ³⁻ -P	SO ₄ ²⁻ -S	Zn ²⁺	
Ash	mg/L	411	—	97.0	3,800	6,770	93.6	
	mol/L	1.79x10 ⁻²	—	6.93x10 ⁻³	1.22x10 ⁻¹	2.12x10 ⁻¹	1.43x10 ⁻³	
Digested sludge	mg/L	43.3	900	94.0	340	3,640	24.8	
	mol/L	1.88x10 ⁻³	6.43x10 ⁻²	6.71x10 ⁻³	1.10x10 ⁻²	1.14x10 ⁻¹	3.79x10 ⁻⁴	

*Ca²⁺ is the concentration after CaCl₂ · 2H₂O addition.



(a) Ash



(b) Digested sludge

Fig. 1 Soluble concentration of major elements in acidic solution at various pH. The MINEQL+ calculation was conducted under the following conditions: CO₂ is in the open system, and pH is 1.2, 2.2, 3.0, 3.5, 4.1, 5.0, 7.7, 9.0 and 10.1 for ash, and 1.6, 2.4, 3.0, 3.4, 4.0, 4.9, 8.0, 9.0 and 9.8 for digested sludge.

Table 4 Predominant precipitates at various pH calculated by MINEQL+

pH	1.2 – 1.6	2.2 – 2.4*	3.0 – 5.0	7.7 – 10.1
Predominant precipitate	FePO ₄ · 2H ₂ O	AlPO ₄ or FePO ₄ · 2H ₂ O	AlPO ₄	Ca ₅ (PO ₄) ₃ OH

*Only at this pH, AlPO₄ for ash or FePO₄· 2H₂O for digested sludge is predominant.

3.3. Fractional recovery of phosphorus and heavy metals with a ferric salt and alkali

In this experiment, the acidic solutions were added with ferric chloride and sodium hydroxide to demonstrate fractional recovery of phosphorus and heavy metals. The experimental results for the soluble element concentrations before and after the addition are shown in Table 5. Also, the composition analysis of the ferric phosphate precipitates recovered is shown in Table 6.

The resultant pH for the phosphate recovery was 2.0 and 2.3, and the percent phosphate recovery was 96.1% and 81.4% for ash and digested sludge, respectively. Higher phosphate concentration in the acidic solution of ash is considered to be advantageous for the phosphate recovery. At these pH, almost all of Zn and Cu were left in the acidic solutions, and thus excluded from the precipitates. For ash, the heavy metal recovery was performed at pH 8.8, and 99.9% of those metals was recovered from the acidic solution. For digested sludge, lower recovery of heavy metal precipitates was observed at pH 8.6. Particularly, 1.4 mg/l of soluble Cu was still left in the acidic solution, and the percent Cu recovery was as low as 84.4%. The chelation effect by soluble organic substances is presumed to deteriorate the Cu precipitation.

As shown in Table 6, the elemental composition of the precipitates obtained at pH 2.0 – 2.3 were close to that of pure ferric phosphate dihydrate ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$). On the basis of P content, 84.4% and 79.6% of the precipitate were estimated to be ferric phosphate for ash and digested sludge, respectively, indicating relatively high purity of the precipitates. For digested sludge, it was easier to exclude heavy metals from the

Table 5 Soluble concentration before and after the fractional recovery of phosphate and heavy metals

		pH	PO ₄ -P (mg/L)	Fe (mg/L)	Al (mg/L)	Ca (mg/L)	Zn (mg/L)	Cu (mg/L)
Ash	Acidic solution	1.5	3,620	7,070	1,790	571	88.0	49.5
	PO ₄ recovery	2.0	140	305	1,450	545	85.9	49.0
	Heavy metal recovery	8.8	0.14	0.05	1.3	387	0.003	0.005
Digested sludge	Acidic solution	1.8	340	638	204	484	24.8	8.70
	PO ₄ recovery	2.3	63.4	46.1	198	451	27.5	9.04
	Heavy metal recovery	8.6	0.28	0.08	1.0	416	0.05	1.41

*Fe in the acidic solution is the concentration after ferric chloride addition.

Table 6 Composition of ferric phosphate precipitates recovered

(%)	Fe	P	Al	Ca	Zn	Cu	Others
Ash	27.3	14.0	1.62	0.090	0.024	0.015	57.0
Digested sludge	27.2	13.2	0.61	0.089	0.015	0.006	58.8
FePO ₄ · 2H ₂ O as reference	29.9	16.6	—	—	—	—	53.5

precipitate, but impure components other than heavy metals were contained more.

At least, it is worth to obtain the relatively pure phosphorus-containing precipitates from both ash and digested sludge. Although ferric phosphate has not been used as a fertilizer, it recently has found wider applications such as an electrode for lithium iron phosphate batteries and a pesticide for organic agriculture.

4. CONCLUSIONS

1) The chemical leaching of incinerated ash with sulfuric acid showed phosphorus solubilization of 72% and heavy metal solubilization of 49 – 60%, while 42 – 66% of phosphorus and 87-100% of heavy metals were solubilized by the bacterial leaching of anaerobically digested sludge.

2) The addition of a ferric salt and alkali to the acidic solutions was capable of precipitating relatively pure ferric phosphate at the pH of 2 – 2.3. Higher recovery of phosphorus from the acidic solution was possible with the ash (96%) than digested sludge (81%). On the other hand, the separation of phosphorus from heavy metals was easier with the digested sludge.

3) Heavy metals were successfully removed from the acidic solutions at the precipitating pH of 8.6 – 8.8. The removal efficiency was in the range of 84.4 – 99.9%, showing lower values with the digested sludge due to the presumed chelation by soluble organic substances.

4) Modeling with a chemical equilibrium program, MINEQL+, was partially successful for predicting the remaining concentration of soluble phosphate and heavy metals in the acidic solutions at various pH.

In summary, it is possible to recover phosphorus as relatively pure ferric phosphate from incinerated ash and anaerobically digested sludge with low heavy metal contents. Furthermore, it may be possible to fractionally collect heavy metals for recycle. The economy associated with this procedure is left to be solved.

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REFERENCES

APHA, AWWA and WEF (2000), *Standard methods*.

Babel, S. and Dacera, D.D.M. (2006), "Heavy metal removal from contaminated sludge for land application: A review," *Waste Management*, Vol. **26**, 988-1004.

Couillard, D. and Mercier, G. (1990), "Optimum residence time (in CSTR and airlift reactor) for bacterial leaching of metals from anaerobic sewage sludge-bioreactors comparison," *Environ. Pollut.*, Vol. **66**, 237-252.

Ito, A., Umita, T., Aizawa, J. and Kitada, K. (1998), "Effect of inoculation of iron oxidizing bacteria on elution of copper from anaerobically digested sewage sludge," *Wat. Sci. Tech.*, Vol. **38** (2), 63-70.

Kato, F., Takaoka, M., Oshita, K. and Takeda, N. (2007), "Present state of phosphorus recovery from wastewater treatment," *JSCE Journal G*, Vol. **63**, 413-424.

Ministry of Land, Infrastructure, Transport and Tourism (2007), *Material flow of mineral resources 2007*.

Oshita, K., Iwashita, M., Takaoka, M., and Takeda, N. (2003), "Basic study on wet extraction process of phosphorus from sewage sludge ash," *Environmental engineering Research*, Vol. **40**, 395-404, 2003.

Pathak, A., Dastidar, M.G. and Sreekrishnan, T.R. (2009), "Bioleaching of heavy metals from sewage sludge: A review," *J. Environmental Management*, Vol. **90**, 2343-2353.

Takahashi, M., Kato, S., Onari, Y. and Enjyoji, H. (2002), "Study on technology to recover various elements from incineration ashes (V) – technology for recovering phosphorus salt from incinerated ash of sewage treatment sludge," *Annual report of Mie Prefectural Environmental Science Center*, No. **47**, 27-31.

Tessier, A, Cambell, P.G.C. and Bisson, M. (1979), "Sequential extraction procedure for the speciation of particulate trace metals," *Analytical Chemistry*, Vol. **51**, 844-851.

Tyagi, R.D., Couillard, D. and Tran, F. (1988), "Heavy metals removal from anaerobically digested sludge by chemical and microbiological methods," *Environmental Pollution*, Vol. **50**, 295-316.

Wild, D., Kisliakova, A. and Siegrist, H. (1997), "Prediction of recycle phosphorus loads from anaerobic digestion," *Water Research*, Vol. **31**, 2300-2308.