

Available online at www.sciencedirect.com**ScienceDirect**

Procedia Environmental Sciences 31 (2016) 345 – 350

Procedia
Environmental Sciences

The Tenth International Conference on Waste Management and Technology (ICWMT)

Feasibility of using natural fishbone apatite on removal of Pb from municipal solid waste incineration (MSWI) fly ash

Yue Mu^{a,*}, Amirhomayoun Saffarzadeh^b, Takayuki Shimaoka^b^a*Dept. of Urban and Environmental Engineering, Graduate School of Engineering, Kyushu University, West 3-916, 744, Motooka, Nishi-ku, Fukuoka 819-0395, Japan*^b*Dept. of Urban and Environmental Engineering, Faculty of Engineering, Kyushu University, West 3-916, 744, Motooka, Nishi-ku, Fukuoka 819-0395, Japan*

Abstract

Fishbone, a common waste generated in coastal areas, especially from the fish processing industry, is known as the natural resource of hydroxyapatite (HAP). Researchers have investigated the removal of heavy metals from the contaminated environments based on the exchange capacity of Ca in HAP with heavy metal ions, while there are limited numbers of researches on the effect of natural HAP on municipal solid waste incineration (MSWI) residues. This work is an attempt to ascertain the feasibility of fishbone used for stabilizing Pb in lime-treated MSWI fly ash via leaching process. Lime-treated MSWI fly ash and ground fishbone of Japanese horse mackerel (aji in Japanese) were used during the whole experiment. The result from X-ray fluorescence on fly ash indicated that Ca and Cl are the two main elements, and Zn and Pb take the first two places among heavy metals. Based on X-ray diffractometry analysis, HAP is the only mineral phase in aji fishbone. The effects of fishbone on Pb immobilization of fly ash under different fishbone doses and various contact times were investigated by batch leaching test at room temperature, and Pb concentration in leachates was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Different fishbone/fly ash ratios were examined; 0 (control group), 5%, 10%, 15%, and 20% (test groups) by weight, and the tests were run for different periods; 3, 6, 24, and 72 h. The results indicated that higher dosage of fishbone and longer contact time were more effective for Pb sequestration from the leachate and the highest removal efficiency of Pb in leachate under the given conditions reached to 24.76% after 72 h leaching process at fishbone dosage of 20%. Although the effectivity of fishbone on Pb removal was not as expected, the preliminary experiments provided promising results regarding the possibility of using low-cost waste fishbone as an environmental-friendly alternate for the stabilization of Pb in MSWI fly ash.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

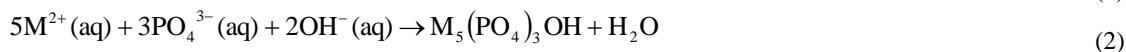
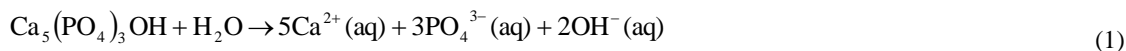
Peer-review under responsibility of Tsinghua University/ Basel Convention Regional Centre for Asia and the Pacific

* Corresponding author. Tel.: +81-92-802-3431; fax: +81-92-802-3432.
E-mail address: mu-y@doc.kyushu-u.ac.jp / etsumuch@126.com

Keywords: Fishbone; natural hydroxyapatite; MSWI fly ash; Pb removal; Leaching test.

1. Introduction

Fishbone is a common waste generated in coastal areas, especially from the fish processing industry. For such communities, fish waste management is becoming a pressing issue, because there is a large amount of fishbone waste daily exhausted¹. This type of waste needs to be managed properly in a short period of time in order to avoid environmental risks due to the rapid corruptibility of the organic fractions². As a kind of bio-waste, treated fishbone and other fish waste have been utilized in food industry, biogas production and other fields³. Fishbone is also known as the natural resource of P and Ca, and actually is the natural supply of hydroxyapatite (HAP), whose Ca possesses the exchange capacity with heavy metal ions⁴⁻⁶. The mechanism was assumed as a dissolution-precipitation mechanism (Eq.1 and 2). Metal ions are referred to the divalent ones including Pb^{7,8}:



Where M^{2+} is a divalent metal.

In recent decades, some researchers focused on the application of fishbone for the immobilization of heavy metals in contaminated environments with emphasis on the effectiveness of fishbone on decreasing the concentration of heavy metals⁹⁻¹¹. These researches were mainly conducted^{12,13} using standard metal solutions or in low metal concentrations^{14,15} under a relatively controlled condition. The problem of heavy metal contamination does not only occur in aqueous environments, but also in solid waste management field.

An enormous amount of municipal solid waste is generated every year, and incineration treatment is adopted as a common technology in many countries in order to effectively reduce the volume and mass of solid waste and to generate electricity¹⁶. Bottom ash and fly ash are the main residues from the incineration of municipal solid waste, and fly ash is classified as a hazardous waste due to containing much higher concentration of leachable heavy metals than that of bottom ash¹⁷. Many technologies are employed for inhibiting the environmental risk brought by fly ash during its disposal, like sintering¹⁸, vitrification¹⁹, transforming into a harmless material by a combination of chemical and thermal processes²⁰ or immobilizing through a solidification by cement, and so on. But some of these technologies are very costly or may not be technically viable in some countries. Accordingly, the exploration and development of low-cost and more environmental-friendly techniques should also be considered.

Therefore, the possibility of using fishbone for immobilizing Pb in municipal solid waste incineration (MSWI) fly ash was taken into account in the present research. Instead of using standard metal solutions, this work was an attempt to ascertain the potential of natural fishbone apatite on the immobilization of Pb in lime-treated MSWI fly ash via leaching process, in which the relationship between Pb removal efficiency and fishbone dosage or contact time was investigated. Additional experimental scenarios are underway to evaluate the capacity of fishbone for the immobilization of toxic heavy metals and to examine the effect of other parameters on the interaction of fishbone with MSWI fly ash.

2. Material and methods

2.1. Sample collection and preparation

Lime-treated MSWI fly ash was obtained from an incineration plant (K) in Japan. The sample used in this study was collected from the air pollution control system. The original fly ash sample was in dry state, the moisture content of which was 1.5-2% tested in an oven at 105 °C for 24 h. Thus, the original samples were directly used in the

experiments except for X-ray diffractometry (XRD) measurement. To avoid mineral phase change, the fly ash sample was freeze-dried before XRD analysis for efficient drying.

The fresh fishbone of Japanese horse mackerel (aji in Japanese) was collected from the market in Fukuoka city, Japan. Aji is a kind of common commercial fish that is daily supplied to the Japanese customers with or without bone. To improve the fishbone quality, the fresh aji fishbone, which was almost free from soft tissues, was pre-treated before the experiments. The fresh fishbone was boiled for 5 min, and then cleaned by brush to exclude all soft tissues. The cleaned fishbone was dried in an oven at 40 °C in order to obtain hard and friable fishbone meal. The dried fishbone was ground into powder state and stored in the tight containers.

2.2. Batch leaching test

Batch leaching tests were conducted in 250 ml polypropylene bottles at room temperature. All bottles were shaken at a speed of 200 rpm with leak-proof lid during the leaching process. Every experimental set consisted of 5 bottles each containing 10.00 g of fly ash, 100 ml of distilled water as leachant and different doses of fishbone. The following doses of fishbone were supplied to each bottle: 0, 0.5, 1.0, 1.5, 2.0 g in order to maintain various fishbone/fly ash ratios at 0 (control group), 5%, 10%, 15%, and 20% (test groups) by weight. Contact times of 3, 6, 24, and 72 h were investigated. To obtain leachate after each test, bottles were centrifuged at 3000 rpm for 20 min, then solid and liquid parts were separated by vacuum filtration through 0.45 µm pore-size membrane. The leachate was stored in a polypropylene bottle for elemental analyses.

2.3. Bulk compositional analysis

The fly ash sample was dried in an oven at 105 °C, and then ground by mechanical milling machine for 1 min, the elements of which were determined by X-ray fluorescence (XRF, ZSX Primus II, Rigaku). The elemental composition of aji fishbone was determined by a compact XRF apparatus (EDX-7000, Shimadzu) using standardless measurement technique. The concentration of Pb in leachate from batch leaching tests was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.4. Mineral phase detection

The mineral phases of aji fishbone and freeze-dried fly ash sample were determined by X-ray diffractometry (XRD, Rigaku) using CuK α radiation at 44 kV and 30 mA. Specimens were scanned from 2-75 deg (2 θ) by 0.02 deg (2 θ)/step, and the X-ray irradiation time was 2 s/step.

3. Results and discussion

3.1. Elemental composition of MSWI fly ash and fishbone

Major, minor and trace elements of MSWI fly ash K analyzed by XRF are presented in Table 1. Ca, Cl, Na, Si, K, Mg, Al and S were the major elements, the contents of which were over 1%. Due to lime treatment, Ca was found in an overwhelming high concentration (55 wt%). Among heavy metals, Zn and Pb are the most abundant elements. Besides the elements mentioned above, the other elements were in lower concentrations that were counted as minor and trace constituents.

Table 1. Elemental composition of MSWI fly ash K.

Compositio n (wt%)	CaO	Na ₂ O	SiO ₂	K ₂ O	MgO	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	TiO ₂	MnO	Cl	S	LOI
Fly ash K	54.8 1	4.37	4.03	2.83	2.44	2.12	0.80	0.72	0.58	0.03	19.9 0	1.56	4.60
Compositio	Zn	Pb	Sb	Cu	Sr	Ba	Cd	Cr	Sn	Ni	As	Co	V

n (ppm)													
Fly ash K	9461	1874	537	503	311	250	180	151	50	36	12	9	2

Elemental composition of aji fishbone analyzed by XRF is presented in Table 2. Ca and P took over 95 wt%, which provided an evidence that fishbone is the natural resource of Ca and P. Besides these two elements, the other elements presented considerably lower concentrations. Especially there were rare heavy metals in fishbone, which indicated that fishbone could be an appropriate substance for heavy metal immobilization.

Table 2. Elemental composition of aji fishbone.

Composition (wt%)	Ca	P	K	S	Sr	Fe	Si	Zn	Cu	Br
Aji fishbone	79.19	16.75	1.52	1.46	0.65	0.16	0.15	0.07	0.04	0.01

3.2. Mineral phase detection of fishbone and MSWI fly ash

The mineral phases of aji fishbone and fly ash K were both identified by XRD, the patterns of which are shown in Fig. 1. For the aji fishbone, hydroxyapatite (HAP) was detected as the only main phase (Fig. 1a), indicating that fishbone might suggest a reasonable potential to be used as an alternate material for the immobilization of heavy metals including Pb in MSWI fly ash. In the fly ash sample, sylvite (KCl), halite (NaCl) and calcium chloride hydroxide (CaClOH) were the major mineral phases (Fig. 1b). Besides, the other detected phases were essentially Ca-rich minerals such as anhydrite, calcite, lime, portlandite, and mayenite. The XRD results of the both samples are consistent with the elemental composition results as shown in Table 1 and 2. Not all detected elements were matched with the corresponding peaks in the XRD patterns, as some of which might be present in the amorphous phase, or the weak peaks of the minor phases could have been overlapped by the stronger peaks of the major mineral phases that obscured their identification by XRD.

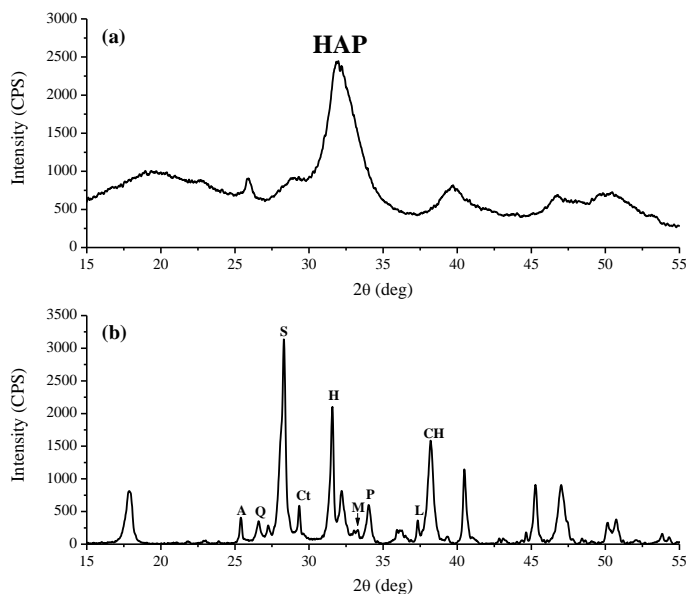


Fig. 1. (a) XRD pattern of aji fishbone; (b) XRD pattern of fly ash K. (a) HAP: hydroxyapatite; (b) A: anhydrite, Q: quartz, S: sylvite, Ct: calcite, H: halite, M: mayenite, P: portlandite, L: lime, CH: calcium chloride hydroxide. The X-axes was set at 15-55 deg (2θ) to reveal the main peaks obviously. Only the first peak of each mineral phase is marked in the patterns due to peak position overlap.

3.3. The effect and efficiency of fishbone on Pb immobilization of MSWI fly ash via leaching process

The effect of fishbone on the immobilization of Pb in MSWI fly ash under different fishbone dosages and various contact times was identified by the concentration of Pb in leachates, the results of which are shown in Fig. 2. Batch leaching tests were conducted under different aji fishbone/fly ash ratios as 0 (control group), 5%, 10%, 15% and 20% (test groups) by weight and various contact times as 3, 6, 24, and 72 h. The results shown in Fig. 2 indicated that higher dosage of fishbone and longer contact time were more effective for Pb sequestration from the leachate. Because of lime treatment, the pH of all leachates were quite high (about 12) regardless of the existence of fishbone. The efficiency of Pb removal by fishbone was estimated by the concentration of Pb in the leachate of each experimental set, which was calculated as the percentage of the sequestered portion of Pb in the leachate of the test group relative to the Pb concentration in the leachate of its control group (Eq. 3). The highest Pb removal efficiency under the given conditions of the present experiment reached 24.76% after 72 h leaching process when fishbone/fly ash ratio was 20%.

$$\text{Pb removal efficiency (\%)} = \left(1 - \frac{C(\text{Pb in test group})}{C(\text{Pb in control group})} \right) \times 100 \quad (3)$$

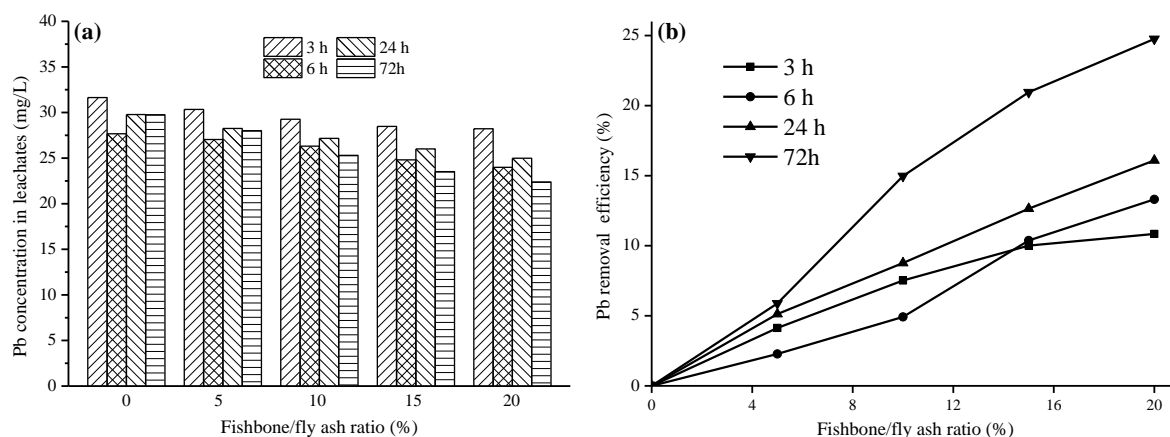


Fig. 2. The effects of aji fishbone on Pb immobilization of fly ash under different fishbone dosages and various contact times. (a) Pb concentration in the leachates under different conditions; (b) Pb removal efficiency under different conditions.

4. Conclusions

Natural fishbone apatite has been considered as an alternative material for the immobilization of heavy metals in the contaminated media such as water and soil. The idea of using fishbone for heavy metal stabilization in fly ash residues derived from waste incineration process is an innovative and eco-friendly approach that has been proposed in the present research. The fresh fishbone of Japanese horse mackerel (aji) was selected as one of the available types of fish in the market for carrying out this research. Fishbone products were pretreated in the laboratory and interacted with MSWI fly ash in the leaching process to verify the efficiency of fishbone on Pb sequestration from fly ash. Different fishbone/fly ash ratios were examined; 0, 5%, 10%, 15%, and 20% by weight, and the tests were run for different periods; 3, 6, 24, and 72 h. Higher dosage of fishbone and longer contact time were more effective for Pb sequestration from the leachate, and the highest removal efficiency reached 24.76% after 72 h leaching process at the fishbone dosage of 20% in the present work.

Although the effectiveness of fishbone on Pb removal was not as expected, the preliminary experiments provided promising results regarding the possibility of using very low-cost waste fishbone as an environmental-friendly method for the stabilization of Pb in MSWI fly ash. Therefore, additional experiments have been designed in order to evaluate

the influence of fishbone products on Pb stabilization in MSWI fly ash and to optimize the parameters for achieving higher efficiency. The experiments are in progress, and their results will be published upon completion.

Acknowledgements

The authors are thankful to the executives and staff of the incineration plant who permitted sampling and material collection for the present research.

References

1. Ozawa M, Suzuki S. Microstructural development of natural hydroxyapatite originated from fish-bone waste through heat treatment. *J Am Ceram Soc* 2002; **85**: 1315-17.
2. Bin MI, Dara A, Sontang M, et al. Fish bone waste utilization program for hydroxyapatite product : a case study of knowledge transfer from a university to coastal communities. *J Environ Res Develop* 2013; **7**: 1274-81.
3. Arvanitoyannis IS, Kassaveti A. Fish industry waste: treatments, environmental impacts, current and potential uses. *Int J Food Sci Technol* 2008; **43**: 726-45.
4. Narasaraju TSB, Phebe DE. Some physico-chemical aspects of hydroxylapatite. *J Mater Sci* 1996; **31**: 1–21.
5. Tan E, Kizilkaya B, Ucyol N, et al. Surface modification with P-aminohippuric acid on biogenic apatite (fish bones) particles. *Mar Sci Tech Bull* 2014; **3**: 45-50.
6. Vila M, Sánchez-Salcedo S, Vallet-Regí M. Hydroxyapatite foams for the immobilization of heavy metals: from waters to the human body. *Inorg Chim Acta* 2012; **393**: 24-35.
7. Admassu W, Breese T. Feasibility of using natural fishbone apatite as a substitute for hydroxyapatite in remediating aqueous heavy metals. *J Hazard Mater* 1999; **69**: 187-96.
8. Mavropoulos E, Rossi AM, Costa AM, et al. Studies on the mechanisms of lead immobilization by hydroxyapatite. *Environ Sci Technol* 2002; **36**: 1625-29.
9. Xu Y, Schwartz FW. Lead immobilization by hydroxyapatite in aqueous solutions. *J Contam Hydrol* 1994; **15**: 187-206.
10. Ozawa M, Satake K, Suzuki R. Removal of aqueous chromium by fish bone waste originated hydroxyapatite. *J Mater Sci Lett* 2003; **22**: 513-14.
11. Ozawa M, Kanahara S. Removal of aqueous lead by fish-bone waste hydroxyapatite powder. *J Mater Sci* 2005; **40**: 1037-38.
12. Kizilkaya B, Tekinay AA, Dilgin Y. Adsorption and removal of Cu (II) ions from aqueous solution using pretreated fish bones. *Desalination* 2010; **264**: 37-47.
13. Lim HK, Teng TT, Ibrahim MH, et al. Adsorption and removal of zinc (II) from aqueous solution using powdered fish bones. *APCBEE Procedia* 2012; **1**: 96-102.
14. Oliva J, De Pablo J, Cortina J-L, et al. The use of Apatite IITM to remove divalent metal ions zinc(II), lead(II), manganese(II) and iron(II) from water in passive treatment systems: column experiments. *J Hazard Mater* 2010; **184**: 364-74.
15. Oliva J, De Pablo J, Cortina J-L, et al. Removal of cadmium, copper, nickel, cobalt and mercury from water by Apatite IITM: column experiments. *J Hazard Mater* 2011; **194**: 312-23.
16. Lam CHK, Ip AWM, Barford JP, et al. Use of incineration MSW ash: A review. *Sustainability* 2010; **2**: 1943-68.
17. Ferreira C, Ribeiro A, Ottosen L. Possible applications for municipal solid waste fly ash. *J Hazard Mater* 2003; **96**: 201-16.
18. Mangialardi T. Sintering of MSW fly ash for reuse as a concrete aggregate. *J Hazard Mater* 2001; **87**: 225-39.
19. Park YJ, Heo J. Vitrification of fly ash from municipal solid waste incinerator. *J Hazard Mater* 2002; **91**: 83-93.
20. Vehlow J, Braun H, Horch K, et al. Semi-technical demonstration of the 3R process. *Waste Manag Res* 1990; **8**: 461-72.