Comparative evaluation of processes for heavy metal removal from municipal solid waste incineration fly ash

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Abstract—Hydrochloric acid leaching, chloride evaporation, acetic acid leaching, and biological leaching were evaluated and compared as processes of heavy metal removal for municipal solid waste incineration fly ash(MSWFA). Six factors, namely, energy consumption, process efficiency, process handling, process cost estimation, cost reduction potential, and study progress, were used in order to find out their advantages and disadvantages and to help develop a better recovery process of heavy metals from MSWFA in terms of treatment of the waste material. Hydrochloric acid leaching process was found to be most balanced among the evaluated processes. It showed superiority on energy consumption, process cost estimation, and study progress. On the other hand, despite of its excellency in process efficiency, chloride evaporation process was most unfavorable mainly due to heavy energy dependence. Biological process, with huge potential of cost reduction, was concluded to be the second best process.

Keywords: municipal solid waste; incineration fly ash; heavy metal removal process; process evaluation.

1 Introduction

It has been reported that municipal solid waste incineration fly ash (MSWFA) contains considerable amounts of heavy metals(Berg, 1993; Theis, 1990). Plus, waste treatment plants including municipal solid waste incineration plants can be considered as secondary mining sites because entropy of heavy metals becomes minimized in the ash(Tateda, 1997). Hence, Japan, which has highly depended on incineration for municipal solid waste treatment, can improve natural resource conservation, environmental conservation, and health risk reduction by developing a process of heavy metal recovery from MSWFA or the final stage recycling, whose importance was fully discussed in the author's previous paper(Tateda, 1997).

In general, heavy metal recovery from ash is done by two processes, namely heavy metal removal and heavy metal collection. Removal is a process which moves heavy metals from ash to a free state of solution or atmosphere, and extraction (leaching) and evaporation can be classified into this process. Collection is a process which collects heavy metals which are in a free state, and chemical precipitation (Larsson, 1992) and biological adsorption(Darnall, 1986; Subramanian, 1994) are available for the process.

In this research, removal of heavy metals from MSWFA was paid attention to because of constantly high amounts of ash generation expected in coming future, high heavy metal contents in MSWFA (Theis, 1990), and few intentional research papers on heavy metal recovery from the waste. Literature review was done, and evaluation and comparison of the above heavy metal removal processes were made by six factors, that is, energy consumption, process efficiency, process handling, process cost estimating, cost reduction potential, and study progress. Cost estimation has been the main factor to strongly influence selection of a process in the system of society, leaching minimizing cost to be the primary goal in process operation. However, not only cost estimation but also other factors should be taken into consideration. For instance, it is not

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recommended to install a process whose chemicals used are highly risky to human health and environment. We propose, then, that balancing weights of factors should be necessary for relative evaluation to select or construct most balanced process.

2   Proposed heavy metal removal processes in literature

Literature review was done using on-line search services such as the Japan Information Center of Science and Technology(JICST) and DIALOG® from 1974 to 1995 with keywords of heavy metals and recovery, bioleaching, heavy metals and extraction, and incineration ash and reuse. The searches resulted in a list of 374 papers. Papers after 1996 were checked manually. Up to now, very few studies on recovery of heavy metals from MSWFA have been done, and the representatives are shown in Table 1. Removal methodologies that have been previously investigated are categorized into physico-chemical and biological processes; the former dominates, and the latter has been reported only in one paper(Bosshard, 1996).

2.1   Physico-chemical process

Legiec *et al.* (Legiec, 1989) investigated removal percentages of heavy metals from MSWFA by chemical extraction using 1.0 mol/L NaCl solution acidified with hydrocloric acid(HCl). Their pilot plant experiment achieved removal percentages of 81% Cd, 51% Cr, 8% Cu, 10% Ni, 51% Pb, and 56% Zn. Kim *et al.* (Kim, 1997) also conducted leaching

Table 1   Representative heavy metal removal processes selected by literature review

References	Methods	Process symbol
Legiec et al., 1989	Acid leaching(HCl)	L
Tateda et al., 1994	Chloride evaporation	T
Fukunaga et al., 1996	Acid leaching (HAc)	F
Bosshard et al., 1996	Biological leaching	B

experiment using inorganic acids (HCl, H_2SO_4, and HNO_3), and HNO_3 showed best removal percentages. However, this process was not counted as a representative one since details of the experiment were not available. Also, they emphasized collection process of heavy metals more than removal process.

Tateda *et al.* (Tateda, 1994) investigated chloride evaporation process for removing heavy metals form MSWFA. In this experiment, heavy metals in the ash were chlorinated, and boiling points of the compounds became lower than those of any other oxygen and sulfur compounds, therefore, evaporation of the heavy metals was relatively easy and efficient. At the heating temperature of 900 ℃, evaporativities of 96%, 21%, 90%, and 86% were observed in HCl atmosphere within 20 minutes for Cd, Cu, Pb, and Zn, respectively. When the temperature was 600℃, evaporativities of the elements were 48%, 5%, 18%, and 10% in the same atmosphere, respectively. Jakob *et al.* (Jakob, 1995; 1996) also performed evaporation experiment for the same kinds of heavy metals in MSWFA and investigated on much wider conditions such as 670 to 1300 ℃ for temperature and air, argon/hydrogen, and argon for atmosphere. The paper by Tateda *et al.* was used for evaluation and comparison because they made a whole process open and came to publication faster than the other.

Fukunaga *et al.* (Fukunaga, 1996) reported relationship between pH and heavy metal removal percentages in chemical extraction process. They removed metallic elements from MSWFA by chemical extraction using acetic acid (HAc) and caustic soda, and results showed that lower pH values led higher extraction concentrations of heavy metals. Removal percentages were as follows : 0% Cu, 68% Cd, 30% Pb, and 39% Zn at pH 9.4, and 50% Cu, 97% Cd, 75% Pb, and 80%

Zn at pH 4. 4. They used HAc as extraction chemical because it had higher buffering capacity than other acids, and pH values remained relatively stable during metal extraction.

2.2 Biological process

Bosshard *et al* . (Bosshard, 1996) reported the first experiment for removal of heavy metals from MSWFA by bio-extraction using a fungal microorganism, *Aspergillus niger* . They investigated heavy metal removal percentages using one step and two step processes. The former exacted heavy metals with microbes and proceeded the extraction by gluconate, and the latter used microbe free culture for extraction and achieved the following extraction percentages after one day of leaching; 81% Cd, 66% Zn, 57% Cu, 52% Pb, 32% Mn, 27% Al, and less than 10% Cr, Fe and Ni.

3 Process evaluation

Table 2 shows summary of operations of the selected for processes L, T, F, and B, and evaluation was done with six factors as stated earlier. Experimental results varied depending on operational conditions, but the conditions which brought better results on average were used for evaluation. For instance, MF instead of CF_3 as a kind of ash, temperature of 900°C from the range of 600 to 900°C , and two-step treatment instead of one-step treatment were used for evaluation of processes L, T, and B, respectively(Table 3).

Table 2   Summary of process operations

Process symbol		L	T	F	B
Reactor type		Semicontinuous pilot	Batch	Batch	Batch
Operation conditions	Temperature	Ambient	600—900°C	Ambient	Ambient
	Duration	2h	20min	3h	22days (one-step) 24 h (two-step)
	Fixed pH	1. 59(CF_3) 2. 56(MF)	—	4. 4	
	Aeration	Mechanical stirrer	—	Rotary shaker	Rotary shaker
Treatable amount		5% w/v ash feed: 1kg/h extractant solution feed : 20kg/h	5g operation	10% w/v (up to 7.5%)	5% w/v
Extraction chemicals		NaCl, HCl	5% HCl gas 4L/min	Acetic acid(1:1)	Aspergillusn iger Gluconate(one-step) Citrate(two-step)
Other requirements		1mol/L NaCl	Electric oven (13.2kVA)	Caustic soda	Sucrose, $NaNO_3$, KH_2PO_4, $MgSO_4 \cdot 7HO$, KCl, yeast extract
Advantages/ disadvantages		Existence of the process in a pilot scale along with collection process Practicality High chemical cost Liability of hazardous chemical handling	Treatment of ash without water;no requirement of wastewater treatment High electricity consumption	High chemical cost Liability of hazardous chemical handling	Self acid production; no cost for acid supply Requirement of a certain degree of temperature for microbes' cultivation
Remarks		Better average extraction efficiency from MF than CF_3	Complete destruction of toxic organic compounds acid; Considerable difference in extraction efficiency between at 600°C and at 900°C	High buffering capacity of acetic capability of maintaining pH value stable	One-step: treatment of ash with microbe Two-step:treatment of ash with organic acid after microbe removal

Table 2　Summary of process operations

Process symbol		L		T		F	B	
Percentage of extraction	Condition	MF	CF₃	600	900		One-step	Two-step
	Al						30	27
	Cd	81	90	48	93	97	57	81
	Cr	51	100				7	7
	Cu	8	0	5	26	50	33	57
	Fe						12	9
	Mn						41	32
	Ni	10	0				5	3
	Pb	51	47	18	85	75	52	52
	Zn	56	—	10	57	80	52	66

Table 3　Cost estimation for processes

Process symbol	L	T	F	B
Chemicals needed and prices	35% HCl(12mol/L) 15—17 yen/kg[b] (density = 1.2) NaCl: 40-42yen/kg[b]	Electricity basic charge 1660yen/kW/mo[b] Charge for use 14.5yen/kw/h[b]	HAc: 180-200 yen/kg[b] (density = 1.1) 48% NaOH(18mol/L) 40yen/kg[b] (density = 1.49)	Sucrose: 29.11yen/kg[a,b] NaNO₃: 108yen/kg[b] KH₂PO₄: 800yen/kg[b] MgSO₄.7H₂O : 65yen/kg[b] KCl: 32.2yen/kg[b] Yeast extract: 13600yen/kg[b]
Amount of solution and numbers of operations for 10g ash treatment	10g→200ml solution	10g→2 operations	10g→100ml solution	10g→200ml solution
Amounts of chemicals and time of operation needed	1mol/L HCl 81ml 1mol/L NaCl 119ml Experiments' results 1. Neutralization to pH 1.59 1mol/L NaCl = 100ml 1mol/L HCl = 68ml 2. Calculations x = 1mol/L HCl y = 1mol/L NaCl x/y = 0.68　$x + y$ = 200 x = 81,　y = 119	13.2 kW 2 opes→20min x 2	(1:1) HAc 90.4ml 18mol/L NaOH 9.6ml Experiments' results 1. Neutralization to pH 4.4 (1:1) HAc = 100ml 18mol/L NaOH = 10.6ml 2. Calculations x = HAc　y = NaOH y/x = 0.106　$x + y$ = 100 x − 90.4, y − 9.6	200ml→4.23 g citrate (110 mmol citrate needed)
Calculations for cost estimation	HCl for water consumption 17yen/kg × 1.2 = 20.4yen/L 1mol/L→81ml, 12mol/L→6.8ml 20.4 yen/L × 6.8ml = 0.14yen for ash consumption assuming approx. 4000ppm HCl needed →0.05yen NaCl 58.5g/L×119ml=7.0g 7g×42yen/kg = 0.29yen 0.48yen/10g	Basic charge 1660×13.2kW(30d.24h) = 30.4 yen/h = 20.3yen/40min Charge for use 14.5×13.2kW×(2/3)h = 127.6yen/40min 147.9yen/10g	HAc 90.4/2×1.1=50g 50×200 = 10yen NaOH 9.6×1.49 = 14.3g 14.3 × 40 = 0.6yen 10.6yen/10g	Sucrose 100g/L × 29.11=0.58yen NaNO₃ 1.5g/L × 108 = 0.032yen KH₂PO₄ 0.5g/L × 800 = 0.08yen MgSO₄.7H₂O 0.025g/L×65 = 0.00033yen KCl 0.025g/L×32.2 = 0.00016 Yeast extract 1.6g/L×13600 = 4.35 5.04yen/10g
Cost for 1g ash treatment	0.048yen	14.79yen	1.06yen	0.50yen

a: price of unrefined sugar; b: obtained by personal communication

3.1　Energy consumption

Electricity was a main energy consumed by processes due to an electric muffle, a stirred used for mixing and aeration, and a heater used for optimal microbe growth. All extraction processes but

process T operated at ambient temperature. Operating at ambient temperature had a great advantage because no electric energy consumption was required. On the other hand, process T had a disadvantage compared to the other ones since the operation temperature range was from 600 to 900℃ and it was highly electricity dependent.

Stirring was required for the other three processes, which stimulated leaching in processes L and F and caused aeration in process B. Besides stirring, electricity for heating was required in process B in order to keep a certain degree of temperature for microbe growth.

3.2　Process efficiency

Process efficiency was evaluated based on two aspects, that is, reaction duration and removal efficiency.

3.2.1　Reaction duration

Process T had a great advantage on this aspect, and the duration necessary for one operation was 20 minutes. Processes L and F required 2 and 3 hours, respectively, which were not remarkably short reaction durations but still reasonable as actual operation times. On the other hand, process B required 24 hours for the same purpose, and it might be a severe disadvantage of biological treatment.

3.2.2　Removal efficiency

Cd, Cu, Pb, and Zn were the only common metallic elements that were removed throughout the four processes. Removal efficiency was evaluated by removed heavy metal amounts, which were obtained by removal percentages times treatable ash quantities in one operation.

Based on the fact that the treatable ash amount of process T was fixed at 5g in one operation, ash amounts of the other processes were chosen to be 5g, 10g, and 5g for processes L, F and B, respectively, which were treatable ash amounts when solution was 100ml. Relative coefficients were employed for indicating amounts treatable in one operation in ratio, that is, $1:1:2:1$ for process L: process T: process F: process B by initial amounts.

For Cd, removal efficiency of processes of L, T, F and B were expressed as 0.81, 0.93, 1.94 and 0.81, respectively. In case of Cu, process F resulted in 1.0, which was the best removal efficiency, followed by 0.57 of process B, 0.26 of process T, and 0.08 of process L. 1.5 of Pb removal efficiency was obtained from process F, and for the same element 0.52, 0.85 and 0.51 were shown in process B, T and L. For Zn removal, 0.80, 0.66, 0.57 and 0.56 were resulted for processes of F, B, T and L. Consequently, process F showed the best extraction efficiency among the four processes. Processes T and B were evaluated to possess the same efficiency as a whole; better Cd and Pb efficiency percentages by process T and vice versa for Cu and Zn. Process L yielded lowest values for all elements.

3.3　Process handling

Process handling considers simplicity of plant operation and safety of process, namely, pH adjustment necessity, wastewater treatment necessity in the post-removal stage, liability of process operation, and liability of chemicals used.

3.3.1　pH adjustment necessity

Processes L and F required pH adjustment. NaCl solution was adjusted to pH 2.56 by HCl in process L, and caustic soda was used for adjusting HAc solution to pH 4 in process F. It was very difficult to adjust the pH process F, and a large volume of caustic soda was consumed because of HAc's high buffering capacity. No pH adjustment was required for processes B and T.

3.3.2　Wastewater treatment necessity

Use of organic-acids such as HAc and citric acid were required for wastewater treatment in the

post removal stage. Biological process can solve the concern but produce waste sludge disposal concern. In case of process L with inorganic acid, COD concern was not a problem, but neutralization was necessary, and salinity had to be considered. Since process T did not involve water, it did not require wastewater treatment.

3.3.3 Liability of process operation

Attention and highly operational skill were required for process T because of extremely high operational temperature. Unlike chloride evaporation, chemical and biological extractions were very simple processes.

3.3.4 Liability of chemicals used

Acid leaching process required acid solution, and HCl and HAc were used in processes L and F, respectively. Those chemicals needed to be handled with good care when they were stored and used because they were harmful and might have led to a serious accident. Bioleaching was the process that extracted heavy metals by acid, which was produced as a result of metabolism of microorganisms. In this process, acid storage and handling were not required, therefore, risk liability was comparatively low, and the condition of appropriate temperature was the only consideration for microbial growth. Process T used HCl gas, and highly careful handling was necessary.

3.4 Process cost estimation

Expense estimating for treating 1g of ash was done for each process based on estimated costs of chemicals used (personal communication, 1997) and electricity consumed for a muffle (Table 3). According to Table 3, the lowest treatment cost was 0.048 yen(Japanese) per g ash for process L and the highest one was 14.79 yen per g ash for process T, which showed a difference of more than 300 times.

Costs of water and electricity for a stirred and a heater for microbe cultivation were not considered for processes B, F and L because it was assumed that the expenses were approximately equal. In cost estimation for process B, price of unrefined sugar was used instead of sucrose's and cost of yeast extract for laboratory use was used since price of that for industrial use did not exist. Both L and F were chemical process, however, treatment costs were considerably different between the two processes. Organic acids such as HAc have been more expensive than inorganic acids, and HAc cost over ten times more than HCl, whereas there was no difference in price between caustic soda and sodium chloride. The estimation showed a difference of approximately twenty-two times in cost of testing 1 g of ash between the two processes. In process T, cost estimation was done only for electricity consumption of the muffle, and cost of atmospheric gas was not included because no information was obtained. The estimation was, therefore, expected to be lower than the actual cost.

3.5 Cost reduction potential

Since processes L and F were chemical process, chemical acid solution played a role of active agent for heavy metal extraction. Therefore, expense for acid solution was inevitable. Unlike chemical process, bio-process could have reduced costs of suitable conditions for microbe growth had been supplied because acid was self-produced by microbes and the production of acid continued as long as the microbes were alive. In process B, commercial chemicals were needed for making media, and they could have been substituted by wastewater such as sewage treatment effluent because wastewater contains essential nutrients for growth. Therefore, if suitable wastewater had been found and used as a medium, supply of sucrose, $NaNO_3$, KH_2PO_4, $MgSO_4 \cdot 7H_2O$, KCl, and yeast extract might not have been necessary, and operation cost would have been greatly reduced.

Process B had a great potential in this regard.

3.6 Study progress

Research progress in process is also one of considerations. Process L has been developed on a pilot scale. On the other had, process T, F, and B are still at their beginning states. For constructing process on an actual scale, it should be evaluated whether batch process or continuous process is better for an operation.

4 Results and discussion

Evaluation of processes on factors is shown in Table 4. Evaluation by accumulating points assigned to processes for each factor was not employed since process comparison in that manner was not appropriate. The point system may simply result in heavy dependence on numbers without solid definitions, and there is still no criterion for granting points to processes.

A process which had superiority to other processes is shown by a sign of inequality, and a sign of equality indicates no significant difference between processes. According to the table, the four processes were grouped into two blocks for the factor of study progress, and three groups were made for energy consumption, process handling, and cost reduction potential. Processes were compared individually on process efficiency and process cost estimation.

Process T showed superiority only process efficiency. Remarkably short reaction time was a great advantage of this process and, moreover, it showed good heavy metal removal efficiency in spite of the reaction time. Howevere, the

Table 4 Process evaluation summary

Factor	Sub factors	Total evaluation
Energy consumption	L = F > B > T	
Process efficiency	Reaction duration: T > L > F > B	T > F > L > B[a]
	Removal efficiency: F > T = B > L	
Process handling	pH adjustment necessity	
	T − B > L > F	
	Wastewater treatment necessity	
	T > L > F = B	B > T = L > F[b]
	Liability of process operation	
	L = F = B > T	
	Liability of chemicals used	
	B > F = L > T	
Process cost estimation	—	L > B > F > T
Cost reduction potential	—	B > F > L = T
Study progress	—	L > B = F = T

a: Between processes T and L, relation of T > L was obtained since process T was better than process L for both subfactors. Similarly, processes T and B and processes F and B were found to hold orders of T > B and F > B, respectively. Then, by comparison of processes T and F, relation of T > F was concluded because of process T's superiority on reaction duration by two degrees and process T's inferiority in terms of removal efficiency by a degree. Likelywise, relations of L > B for processes L and B and F > L for processes F and L were found. Process T seemed to be the best process according to results of T > L, T > B, and T > F, and outcomes of L > B and F > L led to relation of F > L > B, which was confirmed by remained relation of F > B. Hence, relation of T > F > L > B was finally acquired as the whole evaluation on process efficiency.

b: The same manner was applied for making the total evaluation with respect to process handling.

process showed disadvantage by appearing on the very right of sides in total evaluation of Table 4 for the rest of the factors but process handling. It could be said that process T was less attractive than the others.

Processes L and F removed heavy metals by chemical acid extraction. The major differences between the two processes were extraction chemicals, HCl and HAc, and reactor types, which were semi-continuous stirred tank reactor with recycle and batch reactor, for processes L and F, respectively. Among six factors, process L showed superiority to process F with respect to process handling, process cost estimation, and study progress. Process F was better than process L in terms of process efficiency and cost reduction potential, however, it was not ranked as the best process along for any factor. With leaching process, removal durations were reasonable, although

they could have been improved by increasing concentration of acids used, as well as removal percentages. However, material of reactor would have been made should have been considered if highly concentrated acids had been used, and cost of the chemicals would have been high and total process cost estimation would correspondingly have become higher.

Process B was bioleaching treatment process and evaluated to be the best for process handling and cost reduction potential factors. As results showed, the process had disadvantage in process efficiency. A considerable disadvantage of this process was 24 hours of removal duration, which removal very long compared with 2 or 3 hours of chemical leaching process. Lower removal percentages also resulted because of limitation of biological leaching process under the give conditions. A long leaching test of up to 23 days had been conducted, however, the results had not shown that longer had been better. The process had, however, potential of further improvement in ash treatment because of acid self-production nature and high potential of cost reduction.

5　Conclusion

HCl chemical leaching process was found relatively balanced compared to processes of HAc chemical leaching, chloride evaporation, and biological leaching. The chemical process was approximately 10 times more cost effective than the biological process, which was probably the second best. However, it may not be the final conclusion. The inferiority of process B can be overcome by further study since it had advantage of cost reduction potential. Study on biological process have just begun with one type of microorganism, and employment of different types of microorganisms can be also expected for investigation. Bioprocess has a huge potential for development and should be encouraged for heavy metal recovery from MSWFA.

Unlike sewage treatment sludge, research on recovery of heavy metals from MSWFA has collected a little attention. Not only physico-chemical and biological processes but also combination for the two should be considered for finding a better process because introduction and installation of the final stage recycling into society is urgent for conservation of natural resources and reduction of environmental effects. Research on recovery of heavy metals from MSWFA should receive more attention and active involvement in this subject is desperately needed.

References

Berg I, Schlüer T, Gercken G. Journal of Toxicity and Environmental Health, 1993, 39;341
Bosshard P P, Bachofen R. Brandle H. Environmental Science and Technology, 1996, 30(10);3066
Darnall D W, Greene B, Hosea M, McPherson R A, Henzl M, Alexander M D. Special publication /Royal Society of Chemistry, 1986, (61);1
Fukunaga I, Itou H, Sawachi M. Waste Management Research, 1996, 7(1);28
Jakob A, Stucki S, Kuhn P. Environmental Science and Technology, 1995, 29(9);2429
Jakob A, Stucki S, Struis R P W J. Environmental Science and Technology, 1996, 30(11);3275
Kim J H, Yang J G, Kunugita E, Kagaku Kougaku Ronbunshu, 1997, 23(1);47
Larsson S, Gunneriusson E, Lindström E B. Biorecovery, 1992, 2;107
Legiec I A, Hayes C A, Kosson D S. PB report, 1989. 253
Subramanian V V, Sivasubramanian V, Gowrinathan K P. Journal of Environmental Science and Health, 1994, A29(9);1723
Tateda N, Okajima S, Nagasawa S, Mine K. Environmental & Sanitary Engineering Research, 1994, 8(3);185
Tateda M, Ike M, Fujita M. Resources, Conservation and Recycling, 1997, 19;93
Theis L T, Kevin H G. Critical Reviews in Environmental Control, 1990, 20(1);21