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ESTABLISHMENT OF A RECOVERY PROCESS OF HEAVY METALS FROM MUNICIPAL SOLID WASTE INCINERATION ASH

(都市ごみ焼却灰から重金属類回収プロセスの構築に関する研究)

A Thesis

Submitted to the Graduate School of Engineering

at

Osaka University

by

Masafumi Tateda

in a fulfillment of the

requirements for the degree

of

Doctor of Philosophy

in

Engineering

January 1998

Don't cry, just revenge.

The best revenge is to live well.

Dedicated to

my parents and Miho

for their love

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ABSTRACT

It has been reported that incineration or combustion ash contains remarkable amounts of metallic elements. Considering the fact, management of the waste can be said to be inappropriate and a doubt about attaining sustainable social development remains because of the current tendency of abandonment and release of the metallic elements into environment, for example, most of the waste is directly dumped into landfill sites or is recycled into second products without element recovery. In this study, based on the hypothesis that the metallic element recovery from the waste is essential for the sustainable social development, importance of the recovery was emphasized and experimental research was performed for establishment of a recovery process.

This study consisted of five phases. In the first phase, basic information of virgin and secondary metallic elements was obtained. Results of the stage showed that depletion of many metallic elements would be close, and lead, in particular, would be depleted in less than 20 years. Total annual generation amounts of municipal waste incineration ash, thermal power station coal ash, and sludge incineration ash from wastewater treatment facilities were approximately 3.7 million tons, 1.0 million tons, and 4.4 million tons, respectively, and the total metallic element loss associated with ash disposal was approximately 0.7 million tons per year for aluminium.

In the second phase, a new recycling concept was proposed and defined. The new recycling or first stage recycling was described to be effective for as natural resource conservation, soil environment protection, and reduction of toxic metal exposure.

In the third phase, social impacts associated with ash disposal were discussed. It was found that monetary loss from lost aluminium had reached approximately 800 million dollars per year. Amounts of metallic elements recovered by final stage recycling were estimated as approximately 30 %, 22%, and 45 % of the aluminium, lead, and zinc, respectively, that were recycled by front stage recycling.

In the fourth phase, municipal solid waste incineration fly ash (MSWFA) was selected for the research, and evaluation and comparison of heavy metal recovery processes, that is, hydrochloric acid leaching, chloride evaporation, acetic acid leaching, and biological leaching, were done. Results indicated that biological leaching process had a huge potential for heavy metal recovery although hydrochloric acid leaching was evaluated as the most balanced process.

In the final phase, a laboratory experiment of heavy metal extraction using a sulfur oxidizing bacterium was performed for establishment of a new heavy metal recovery process from MSWFA. Six types of MSWFAs were used for the experiment, and results showed that cadmium, copper, and zinc were successfully extracted at the ranges of 55.3-68.5 %, 57.4-84.6 %, and 38.8-56.4 %, respectively. On the other hand, the extraction percentage of lead was relatively low, 2.2-19.6 %. Use of sulfur free culture, whose purposes were microbe recycling and prevention of second environmental pollution, showed no significant differences in heavy metal extraction from that of the culture with elemental sulfur.

CHAPTER I

INTRODUCTION

I-1) Background

Japan was on the track of prosperity for 50 years after the end of World War II or 1945. Economy reached its zenith during the period, and the society has been full of merchandises and enjoyed mass consumption. The words of reuse and recycle of products have been eliminated from mind of people who live in one of the most unfortunate countries on natural resources. Japanese government enforced laws for general recycling in 1991 and for container and wrap recycling in 1997 in order to reduce waste production and enhance a sense of recycling (1). "Seeds" of recycling have been just planted, and some times will be required for flower blooming.

On the way of pursuing prosperity, Japan experienced terrible environmental disasters. Minamata disease (see Appendix I) spread in an area in 1956 and was recognized as a disease caused by environmental pollution (DCEP) in 1968 (1) (2). In spite of the fact that it had been seen since the beginning of the 1940s Itai-itai disease (see Appendix I) was recognized as a DCEP one year from Minamata disease (3). The disasters cost the country a lot of victims lives and freedom and extremely expensive lessons. Japan was not the only country to have such a sever experience, and other industrialized countries has also suffered irreversible loss of precious nature. Love Canal incident (see Appendix I), for example, is notorious for a hazardous chemical disaster (4).

After 24 year suspension of local fishing, Minamata Bay was declared to be pollution free and to have regained the initial condition in which it used to be (5). News of the safety of the bay implies that it takes more than several decades for an environment to recover fully from deterioration once it gets polluted. Those miserable experiences should not fade out from people's memory, and we absolutely need to care environments and to watch not to take the same trace as people in the previous era did.

Environmental disasters always keep silence for a while, and progress of the disasters usually does not come under people's notice. It is too late to take actions against excessive damages when symptoms comes to appear on biota. There are always some potentials for exposure to another environmental threat, and even at this moment the thread may been growing at a place close to human's society.

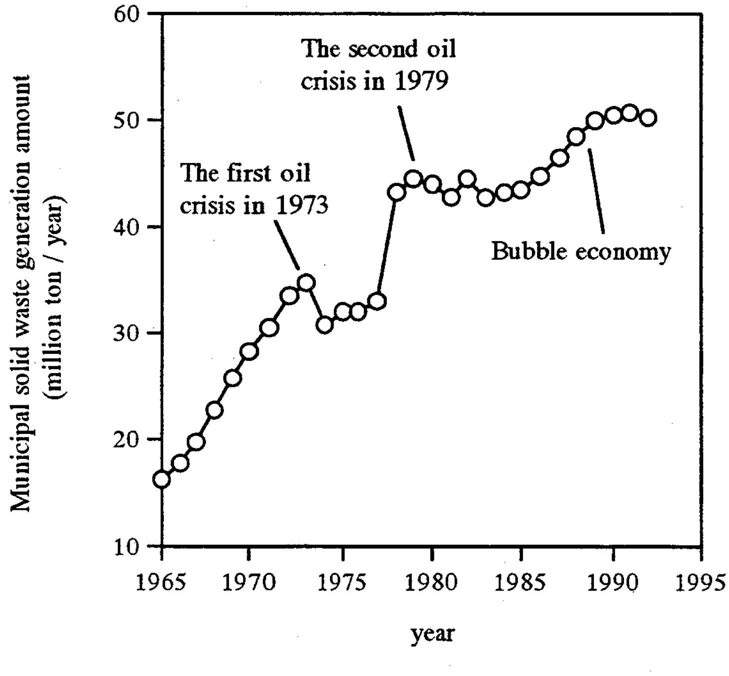

Figure I-1 Annual Total Municipal Solid Waste Generation Amount in Japan

One of the potentials in Japan, at this decade, may be effects of municipal solid waste incineration. As seen in Figure I-1$^{(6)}$, an annual waste generation amount in Japan has constantly increased since 1965 though there were several drops led mainly by the oil crises, and it is expected to stay high for another decade. Approximately 75 % of the total generation amount (1.6 % in Korea (7) and 14 % in the US (8)) depends on incineration as a treatment (6), so it can be said that Japan is a unique country.

In Japan, incineration for municipal solid waste originally started for the purpose of elimination of pathogenic microorganisms against prevalent cholera, dysentery, and pest in the beginning of the 1890s (9). Incineration is a quick treatment, and benefits of it is concluded into four aspects: reduction of volume, elimination of odor, degradation of harmful chemical and biological materials, and electricity and hot water distribution to local areas by thermal recycling (9). The atmosphere became polluted by fly ash, hydrogen chloride gas, SOx, and NOx as a sacrifice, however, the headaches of pollutants got almost solved by state of the art exhaust gas treatment technology.

When the pollutants went under control and people started relaxing from burden of environmental concern about municipal solid waste incineration plants, detection of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from the plants was made public in Japan in 1983 for the first time (10), and civilians were shocked again by another silent development of an environmental disaster. Almost 15 years having passed after the first detection, the PCDDs and PCDFs release now is likely expected to become controllable by installing the first legal regulation in the near future.

Waste materials changes their forms into either air or solid bodies at incineration plants. Since release of fly ash to the air was regulated in 1962 (9), they have been collected in solid states. Besides polychlorinated chemical materials' release, there is a primary problem concerning municipal solid waste incineration such as treatment and disposal of incineration ash. High toxic heavy metal content in the ash being recognized, selected kinds of intermediate treatments are obligated for disposal under the current regulation. However, current major ash treatments leave huge anxiety about natural resources and silent development of environmental disasters, which have not been discussed in public. It is very important to emphasize the points which people have not noticed and discuss the potential effects of the continuous treatment in order to prevent civil life from suffering from another environmental disasters and natural resources from being abused.

Incineration (combustion) ashes, which are potentially hazardous and need intensive observation, were selected as the topic of this study, and their total annual generation amounts and total losses of metallic elements by disposal were estimated. Then potential social effects by the heavy metal release to the environment were considered, leading the proposal of a new concept of recycling in the sense of social benefits. Fly ash from municipal solid waste incineration plants was chosen among the wastes for development of a new heavy metal recovery process, whose feasibility study was performed by conducting laboratory experiments.

I-2) Objectives

Objectives of this study can be summarized as follows:

1) to investigate quantitative assessment on generation of incineration ashes and loss of metallic elements associated with disposal of the ashes;

2) to propose a new concept of recycling;

3) to discuss expected social impacts associated with disposal of the ashes;

4) to evaluate and compare heavy metal removal processes proposed in literature in order to obtain a clue for establishment of a better process; and

5) to examine feasibility of the new heavy metal extraction process.

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CHAPTER II

LOSS OF METALLIC ELEMENTS ASSOCIATED WITH ASH DISPOSAL

II-1) Introduction

Consumption of natural resources provides a convenient way of living to human beings. None of the natural resources, however, are inexhaustible, and they are limited in reserve. There are two types of natural resources: recyclable ones such as metallic elements, and non-recyclable ones such as oil, coal and natural gas. Fossil fuels are consumed as thermal energy and decompose to basic compounds via the process of oxidation reactions. On the other hand, metallic elements are permanent and neither decompose nor cease to exist, which implies they are recyclable.

Municipal solid waste incineration ash (MSWA), sludge incineration ash from wastewater treatment facilities (WTSA), and thermal power station coal ash (PSA) contain considerable amounts of elements, especially, heavy metals (1) (2) (3). Waste treatment plants such as municipal solid waste incineration plants and wastewater treatment facilities can be considered as secondary mining sites because compared to in consumer products, entropy of metallic elements becomes minimized in the ash.

The purpose of this chapter is to address the importance of natural resource conservation and estimate losses of elements associated with disposal of the ashes. First, amounts of the metallic elements available world-wide as natural resources were estimated. Next, the annual generation of the ashes and total amounts of the elements in the ashes were calculated using conservative values for metallic element contents.

II-2) Availability of Metallic Elements (4) (5)

Table II-2-1 is made based on the report of the Agency of Natural Resources and Energy, Director-General's Secretariat Mining Division (4), and shows basic information for some metallic elements. World availability for the elements is calculated basically as world reserve divided by world production, and in the case of no data available for world production, world reserve is divided by the world consumption instead of world production. The years of drain are obtained as those results added to 1993. The data of the elements with an asterisk(*) are obtained from Tominaga (5). In the case of arsenic, for instance, the world consumption is an accumulated datum for seventeen years, that is, 1983 to 2000, and was estimated assuming a 1.5 percent yearly averaged world economic growth rate during these years. The world reserve shows a prospective amount of the mineral that will be reserved in 2000.

According to world availability, metallic elements can be classified into four groups, which are Group I made of the elements with need of urgent reactions, Group II of those with need of careful watches, Group III of those with a limit in reserve and Group IV of those with no limit, based on the years of drain of 2000-2049, 2050-2199, 2200-2499, more than 2500, respectively (Table II-2-2). According to the table, there are thirteen metallic elements classified into Group I. Among them, mercury, arsenic and lead should be given special attention because of their highly strained situations. On the other hand, beryllium, hafnium and gallium can be called limitless resources and need less attention for a while because of their huge world reserves.

Considering the continuation of economic growth, world availability will not be lengthened unless mines are newly discovered. In sum, the approximate numbers of

Table II-2-1
World Reserve, Production and Consumption of Metallic Elements (4)

Constituent		World Reserve in 1993	unit	World Production in 1993	unit	World Consumption$^{\Delta}$	unit	Year of Drain
Ag	Silver	4.20x10^{5}	ton	1.49x10^{4}	ton	1.98x10^{4}	ton	2021
Al†	Aluminium	2.80x10^{10}	ton	1.96x10^{7}	ton	1.83x10^{7}	ton	2351
As*	Arsenic	4.10x10^{5}	ton			5.90x10^{5}	ton	2012
Au	Gold	5.70x10^{4}	ton	2.29x10^{3}	ton	2.99x10^{3}	ton	2018
B	Boron	6.30x10^{8}	ton	5.30x10^{6}	ton			2112
Ba	Barium	5.00x10^{8}	ton	5.20x10^{6}	ton	5.40x10^{6}	ton	2089
Be	Beryllium	7.42x10^{5}	ton	2.91x10^{5}	kg	2.85x10^{2}	kg	4543
Bi	Bismuth	2.50x10^{5}	ton	2.70x10^{3}	ton	3.71x10^{3}	ton	2086
Cd	Cadmium	9.70x10^{5}	ton	1.93x10^{4}††	ton	1.91x10^{4}	ton	2043
Co	Cobalt	8.80x10^{6}	ton	1.74x10^{4}	ton	2.75x10^{4}	ton	2499
Cr	Chromium	6.70x10^{9}	ton	1.00x10^{7}	ton	1.16x10^{7}	ton	2663
Cs*	Cesium	1.09x10^{5}	short ton			5.20x10^{2}	short ton	5563
Cu	Copper	5.90x10^{8}	ton	1.16x10^{7}	ton	9.28x10^{6}	ton	2044
Fe	Iron	2.30x10^{11}	ton	9.40x10^{8}	ton			2238
Ga	Gallium	1.65x10^{5}	ton	2.80x10^{4}	kg	6.00x10^{1}	ton	7886
Hf	Hafnium	8.50x10^{5}	ton			1.90x10^{5}	lb	11847
Hg*	Mercury	3.10x10^{5}	flask			3.69x10^{6}	flask	2001
In	Indium	5.70x10^{3}	ton	1.45x10^{5}	kg	1.29x10^{2}	ton	2032
Li	Lithium	8.40x10^{6}	ton	5.50x10^{3}	ton	5.14x10^{3}	ton	3520
Mn	Manganese	4.80x10^{9}	ton	2.04x10^{7}	ton	2.20x10^{7}	ton	2228
Mo	Molybdenum	1.20x10^{7}	ton	9.59x10^{4}	ton	7.94x10^{4}	ton	2118
Nb	Niobium	4.20x10^{6}	ton	1.46x10^{4}	ton	2.04x10^{4}	ton	2281
Ni	Nickel	9.98x10^{7}	ton	8.31x10^{5}	ton	7.49x10^{5}	ton	2113

Table II-2-1 (continued)

Constituent		World Reserve in 1993	unit	World Production in 1993	unit	World Consumption$^{\Delta}$	unit	Year of Drain
Pb	Lead	1.30×10^{8}	ton	5.44×10^{6}	ton	5.06×10^{6}	ton	2017
Re	Rhenium	1.00×10^{4}	ton	2.40×10^{4}	kg	4.00×10^{4}	lb	2410
Sb	Antimony	4.70×10^{6}	ton	3.61×10^{4}	ton			2123
Se	Selenium	1.30×10^{5}	ton	1.80×10^{3}	ton			2065
Sn	Tin	1.00×10^{7}	ton	2.06×10^{5}	ton	2.03×10^{5}	ton	2042
Sr	Strontium	1.20×10^{7}	ton	2.83×10^{5}	ton	1.64×10^{5}	ton	2035
Ta	Tantalum	3.50×10^{4}	ton	2.90×10^{5}	kg	9.37×10^{2}	kg	2114
Te	Tellurium	3.80×10^{4}	ton	2.59×10^{5}	kg	2.20×10^{2}	kg	2140
Ti†	Titanium	1.65×10^{8}	ton	3.65×10^{6}	ton	2.08×10^{6}	ton	2020
Tl	Thallium	6.40×10^{5}	kg	1.45×10^{4}	kg			2037
V	Vanadium	2.70×10^{7}	ton	2.80×10^{4}	ton	7.50×10^{7}	lb	2957
Zn	Zinc	3.30×10^{8}	ton	7.11×10^{6}	ton	6.65×10^{6}	ton	2039
Zr	Zirconium	5.80×10^{7}	ton	7.03×10^{5}	ton	8.27×10^{5}	ton	2076
W	Tungsten	3.30×10^{6}	ton	2.55×10^{4}	ton	3.79×10^{4}	ton	2122

†Defined as data including oxidized compounds in world reserve. 0.25 and 0.6 are applied as ratios of aluminium/bauxite and Ti/TiO2 to estimates, respectively.

††Defined as a 1992 datum

*Defined as data from the reference (5). Assumed yearly world economic growth rates, As:1.5, Cs:3.0 and Hg:1.4.

$^{\Delta}$Defined as data from different years. 1993:Ag, Al, Au, Cu, Pb, Sn and Zn. 1992:Cd, Cr, Mo, Nb, Ni, Ti and V. 1991:Co, In, Mn, Re and W. 1990:Sr.
1989:Ba, Bi, Te and Zr. 1988:Be and Li. 1987:Ga and Ta. 1983:Hf.

years left for the metallic elements reminds people that none of the elements are limitless.

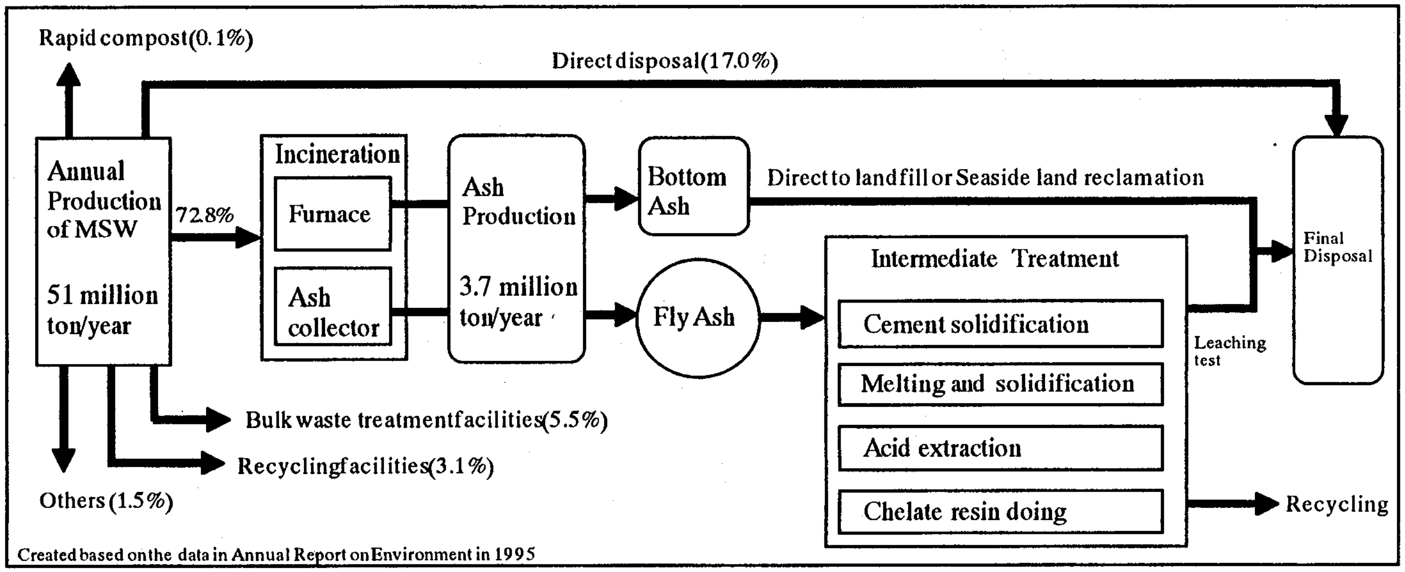
Table II-2-2
Classification of Metallic Elements Based on Year of Drain in Table II-2-1

Group I	(2000 - 2049)	Hg, As, Pb, Au, Ti, Ag, In, Sr, Tl, Zn, Sn, Cd, Cu
Group II	(2050 - 2199)	Se, Zr, Bi, Ba, B, Ni, Ta, Mo, W, Sb, Te
Group III	(2200 - 2499)	Mn, Fe, Nb, Al, Re, Co
Group IV	(more than 2500)	Cr, V, Li, Be, Cs, Ga, Hf

II-3) Ash Production and Fate

II-3-1) MSWA

Total generation of municipal solid waste amounted to approximately 50 million tons in 1991, which means that 1.18 kg of waste was discharged per capita, and 17.0%, 3.1% and 72.8% of the total amount of solid waste were managed as direct dumping, recycling and incineration, respectively (6). A typical flow chart of the municipal solid waste treatment process (self-treatment is no included) is shown in Figure II-3-1. According to the figure, approximately 36 million tons of municipal waste was incinerated that year. Incineration has been, at the present time, the most technically and financially dependable treatment scheme to cope with the tremendous production of waste in Japan. Ash generation amounts from the incineration process are usually estimated as one tenth of the amount of solid waste incinerated, which was in this case 3.7 million tons in 1991. Furnace bottom ash can be disposed to final disposal sites directly without any intermediate treatment. Fly ash, on the other hand, is a specially designated type of waste, which is controlled by the waste disposal law having been revised in 1992, and has to be treated before final disposal. Four types of treatments are suggested: 1) cement solidification, 2) melting-and-solidification, 3) acid



Created based on the data in Annual Report on Environment in 1995

Figure II-3-1 Flow of MSWA in Japan

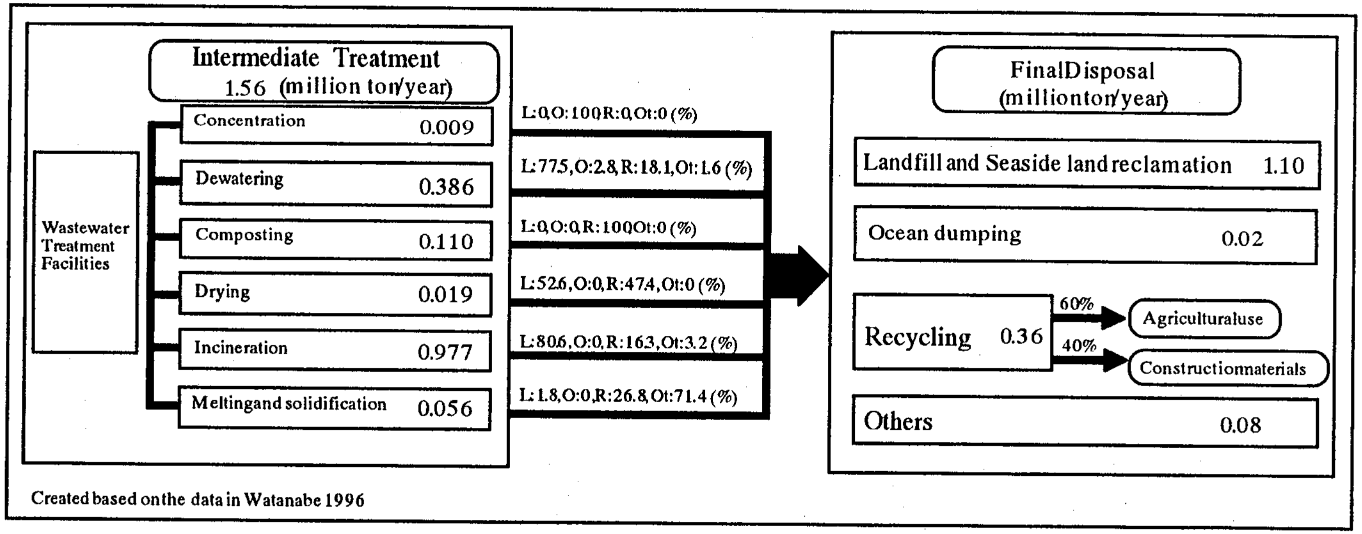


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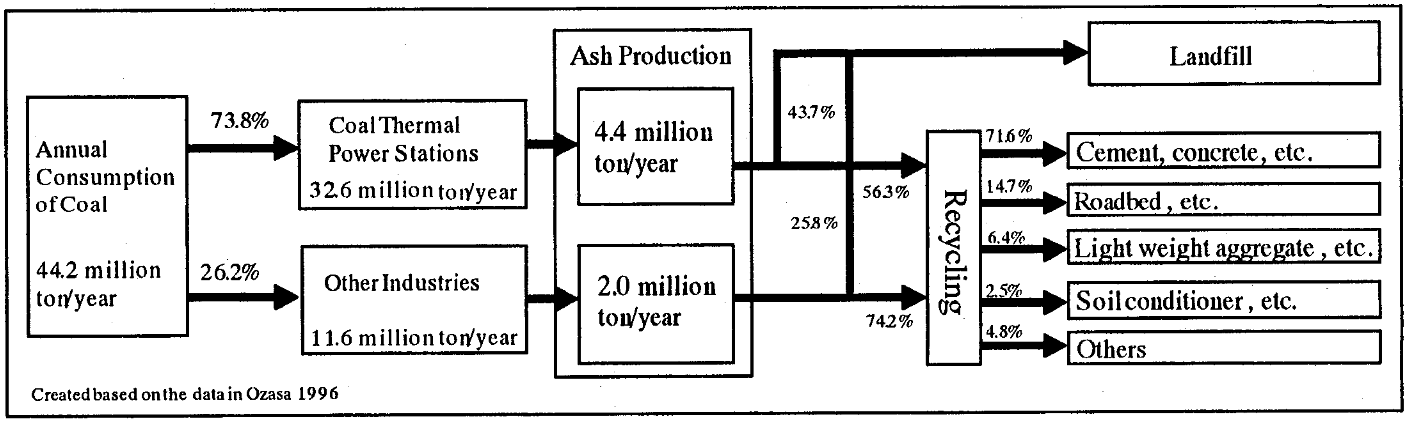
Figure II-3-2 Flow of WTSA in Japan



Created based on the data in Ozasa 1996

Figure II-3-3 Flow of PSA in Japan

leaching and 4) chelate resin dosing. Because of economical and technical advantages, cement solidification may be the most frequently employed treatment scheme among these. After intermediate treatment, dissolution tests should be conducted and fly ash is disposed to final dumping sites when results of dissolution tests satisfy final disposal criteria.

II-3-2) WTSA

There are approximately 930 wastewater treatment facilities in Japan and 1.56 million tons (dry weight) of wasted sludge were intermediately treated in fiscal year 1993 (7). The typical wasted sludge flow is shown in Figure II-3-2. According to the figure, incineration was the most frequently employed scheme for intermediate treatment and approximately 63 percent of total dried based sludge or 0.98 million tons were treated in 1993. The notations, L, O, R and Ot along the arrows shown in the center of the figure represent landfill and seaside land reclamation, ocean dumping, recycling, and others, respectively. In case of incineration, for example, the L, O, R and Ot were 80.6 %, 0 %, 16.3 % and 3.2 %, respectively, and it is shown that the most frequently employed wasted sludge management was the combination of incineration and landfill and seaside land reclamation. There is a plan of an increase in the percentage of sewered population, from 47 percent in 1993 (8) to 70 percent by 2000 (9). The generation of sludge is expected to be increased in the coming century.

II-3-3) PSA

Coal may be one of the primary resources for power generation, and total electric generation by coal thermal plants is expected to increase from 21 million kilowatts in 1995 to 30 million kilowatts by 2000 (10). Ash production is also expected to rise and will be 10 million tons at the beginning of the twenty first century, up from the current 6.4 million tons in 1993 (11). A typical coal ash flow is shown in Figure II-3-3. Approximately 14 percent of coal consumed became ash and 2.4 million tons of ash went to dumping sites in 1993.

II-4) Estimated Element Loss

In this section, total losses of the metallic elements in ash are calculated. The treatment and disposal process of each kind of ash is described and annual amounts of ash generation are shown in previous section. Reasonable values for the amounts of metallic elements contained in ash are developed from references and are used for estimates of total amounts of elements.

Table II-4-1 shows metallic element contents. The data for PSA and WTSA are obtained from Theis (1), however, data for MSWA are from actual incineration plants in Japan. The reason that the data in Japan, instead of those of Theis, are used for MSWA is that it is reasonable to think that characteristics of the solid waste strongly depend on life style in the country, so that more reasonable values could be obtained in the estimates when domestic data are used. Maximum and minimum values are available and values shown in the table are mean values between the two, because it is judged that the means give more conservative estimates.

The individually referenced data, for instance, those of barium in MSWA, beryllium in WTSA and cerium in PAS, are collected from Theis, Itou (3) and Berg (2), respectively. Metallic elements such as tungsten, thallium and germanium are not found in these three kinds of ash. On the other hand, high amounts of aluminium, iron and silicon are commonly present. The table indicates kinds of elements which may be

Table II-4-1
Metallic Element Contents in the Ash

Constituent	MSWA†(mg/kg)	WTSA(1)(mg/kg)	PSA†(1)(mg/kg)
Al	79,500	58,600	87,000
As	36.5	11.0	603
B		16.5	305
Ba	4,544(1)	2,868	587
Be	0.75	0.82(3)	
Cd	243	452	25.6
Ce		72.8(3)	210(2)
Co	39.5(1)	386	20.7
Cr	515	3,455	458
Cs		6.3(3)	
Cu	3,615	4,250	208
Fe	31,350	172,850	142,000
Ga		12.5(3)	230(3)
Hg	22.0	5.6	0.07
In			520(3)
La		45.9(3)	
Li	14.7(3)	19.3(3)	1,400(3)
Mn	1,215	3,000	550
Mo		152	20.7
Nb			14.0(3)
Ni	132	2,085	7.4
Pb	5,220	1,085	406
Rb		45.4(3)	
Rh		0.42(3)	
Sb	1,120	56.1(2)	101(2)
Se	2.3	4.0	383
Si	119,450	256,500	150,050
Sn	8,858(2)	9.0	184(2)
Sr	179(3)	214(3)	1,300(3)
Ta			66.0(3)
Te	0.75		
Ti	363	110(3)	6,600
V	138(1)	515	165
Zn	3,150	12,350	4,525
Zr		11.6(3)	330(3)
Y		13.3(3)	

†Defined as data of fly ash

Table II-4-2
Total Amounts of Metallic Element in the Ash

Constituent	MSWA (ton/year)	WTSA (ton/year)	PSA (ton/year)	Total (ton/year)
Al	294,150	57,428	382,800	734,378
As	135	10.8	2,653	2,799
B		16.2	1,342	1,358
Ba	16,813	2,810	2,583	22,206
Be	2.8	0.80		3.6
Cd	900	443	113	1,456
Ce		71.3	926	997
Co	146	378	90.9	615
Cr	1,904	3,386	2,013	7,303
Cs		6.2		6.2
Cu	13,376	4,165	915	18,456
Fe	115,995	169,393	624,800	910,188
Ga		12.3	1,012	1,024
Hg	81.5	5.5	0.3	87.3
In			2,288	2,288
La		45.0		45.0
Li	54.4	18.9	6,160	6,233
Mn	4,496	2,940	2,420	9,856
Mo		148	90.9	239
Nb			61.6	61.6
Ni	488	2,043	32.6	2,564
Pb	19,314	1,063	1,784	22,162
Rb		44.5		44.5
Rh		0.41		0.41
Sb	4,142	55.0	444	4,641
Se	8.7	3.9	1,687	1,700
Si	441,965	251,370	660,220	1,353,555
Sn	32,775	8.8	810	33,593
Sr	662.3	210	5,720	6,592
Ta			290	290
Te	2.8			2.8
Ti	1,343	108	29,040	30,491
V	511	505	724	1,739
Zn	11,655	12,103	19,910	43,668
Zr		11.4	1,452	1,463
Y		13.0		13.0

found in ash and shows reasonable content levels. However, it should be noted that these elements may not always be found in all ash. There is variability; one kind of ash might contain fewer elements and another might contain more.

The ash generation processes from municipal solid waste incineration plants, thermal coal power stations and wastewater treatment facilities are shown in Figures II-3-1 to II-3-3. The values in Table II-4-1 are multiplied with the total annual amounts of ash generated in order to estimate the metallic element contents in ash. For example, in the case of aluminium, according to Table II-4-1, the content in MSWA is about 79,500 mg/kg and the total annual MSWA generation was 3.7 million tons in 1991, which means approximately 294,150 tons of aluminium content was found in MSWA in 1991. The same manner of calculations is applied for metal contents in PSA and WTSA and results are summed in order to estimate total amounts of elements (Table II-4-2).

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CHAPTER III

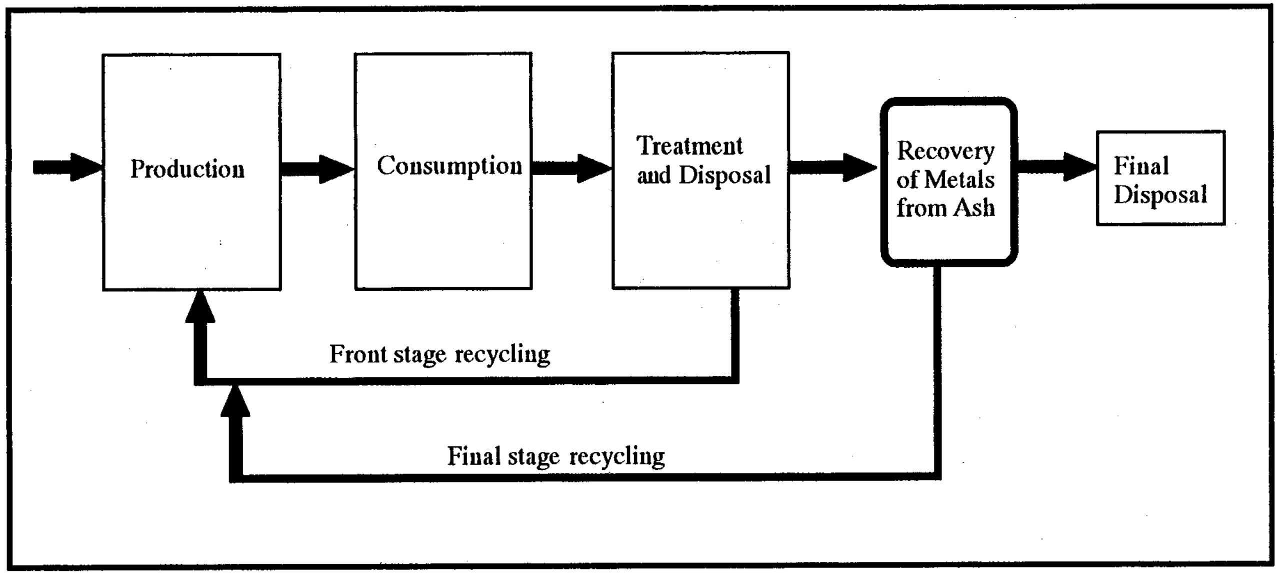
PROPOSAL OF FINAL STAGE RECYCLING

III-1) Introduction

The current social waste management system which was built to deal with mass consumption has abandoned most of wasted materials although some of them could be recycled. For maintaining social development, recycling is the primal agenda to be considered. Japan, whose natural resource supplies heavily depend on countries overseas, may be the first country to take the agenda seriously. In this chapter, a new recycling concept was defined and proposed. This is the time for people to understand the true meaning of the concept and to take a brave action of installation of a new recycling process into the social system for the future of human being and nature.

III-2) Concept of Final Stage Recycling (1)

"Recycling", in this study, has two meanings: one is recycle and the other is recovery. The former is recycling of waste material, such as recycling of aluminium and steel cans. The later is use of valuable materials recovered from waste such as activated carbon from wasted tires and coal ash for cement (2). Recycling is thought to be performed by two kinds of processes, namely, front stage recycling and final stage recycling. Front stage recycling may be mainly performed at civic level without any special skills and knowledge such as recycle of aluminium cans mentioned above. Final stage recycling may be mainly explained as recovery of metallic elements from waste. Unlike the former recycling, this recycling requires highly specialized skills and knowledge. It can be also called engineering recycling. This is a very important



Fugure III-2 Concept of Final Stage Recycling

recycling process in terms of mineral availability and environment. The concept of final stage recycling is described in Figure III-2.

If metallic elements are recovered from MSWA, WTSA or PSA, in other words, if the final stage recycling is made, social benefits can be expected in many ways. Currently, ash is dumped directly into final disposal areas or is carried through intermediate treatment such as concrete solidification and melting-and-solidification to final disposal sites. Recycling of ash has been done for purposes of construction (3) and commerce (4). Not only direct dumping to landfills but also intermediate treatment and even current recycling schemes, however, have been ruling out recovery. Final stage recycling must be taken more seriously, because there are considerable losses of the metallic elements and this may pose a serious threat to the environment without their recovery.

III-3) Appication of Final Stage Recycling

Application of the final stage recycling process into the social metallic material flow is required to manage a continuously growing, large amount of ash generated. According to the Ministry of Health and Welfare, there are more than 1,600 incineration facilities in Japan (5). It will be a very difficult task to apply final stage recycling into each facility because small ones do not have sufficiently continuous ash production in terms of the metallic element recovery. A large city like Tokyo might be a candidate for application of a final stage recycling process due to the large amount of municipal solid waste continuously generated (4.7 million tons or 9 percent of the total municipal solid waste produced in Japan in 1991 (6)). If the ash is collected from each facility into designated sites instead of treating the waste at each facility individually, metallic element recovery would be more meaningful and more realistic.

The realization of reduced potential hazards and the recovery of metallic elements from ash prior to the final disposal are very important for ash treatment. Recovering metallic elements from ash has the following advantages: it can assist the conservation of natural resources, reduce soil toxicity and reduce the potential risk of toxic metal exposure. In sum, metallic element recovery or final stage recycling should be given more attentions as a more elaborate system for protecting and conserving the whole environment.

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CHAPTER IV

SOCIAL IMPACTS ASSOCIATED WITH ASH DISPOSAL AND BENEFITS FROM FINAL STAGE RECYCLING

IV-1) Introduction

Considering size of the land and annual trash production, incineration as an intermediate treatment of municipal solid waste probably cannot be substituted by any other treatment processes in Japan, and it will be the main scheme for coping with the tremendous amount of generated trash in the coming century. Cement solidification and melt-and-solidification also may be social main streams for MSWA treatment in Japan in the future. The amounts of generated PSA and WTSA are also expected to increase in the future because of the expected increase in the amount of electric power generation and the planned increase of sewage treatment. Under the circumstances, social impacts by abandonment and release of metallic elements in the wastes may be inevitable in near future. In this chapter, monetary loss of the elements, environmental deterioration, and possible exposure to humans in the future are discussed, supposing the current treatment scheme will continue to be the social main stream for dealing with ash in the coming century. The social meaning of the recovery or benefits of final stage recycling are also discussed.

IV-2) Economic Impacts

Using international prices reported in December 1993 (1), total monetary losses are estimated for the metallic elements. The considerable losses calculated are shown in Table IV-2. With the accumulation of lost metallic elements, this will be a tremendous amount in 10 years and 50 years. This trend is expected to increase along with social prosperity unless the social main waste treatment and disposal scheme becomes more elaborate through the inclusion of final stage recycling into the management of material flow.

Table IV-2
Estimates of Monetary Loss

Constituent	International Price on December of 1993(1)	Total Monetary Loss (million dollar/year)
Al	1,094 $/ton	803
As	0.6 $/lb	3.7
B	192.5 $/lb	576
Be	225 $/lb	1.8
Cd	0.5 $/lb	1.6
Co	18.0 $/lb	24.4
Cr	3.4 $/lb	54.7
Cs	260 $/lb	3.5
Cu	†190,800 ¥/ton	32.0
Ga	500 $/lb	1,128
Hg	173 $/flask	0.44
In	150 $/kg	343
Li	31.8 $/lb	437
Mn	1,380 $/ton	13.6
Mo	135 $/kg	32.3
Nb	80.0 $/lb	10.9
Ni	5,121 $/ton	13.1
Pb	471 $/ton	10.4
Sb	1,604 $/ton	7.4
Se	4.9 $/lb	18.3
Sn	†523,000 ¥/ton	160
Ta	†73,000 ¥/kg	193
Te	30.0 $/lb	0.18
Ti	4.25 $/lb (sponze)	285
V	1.45 $/lb($V_2O$)	5.6
Zn	†107,900 ¥/ton	42.9
Zr	12.0 $/lb (sponze)	38.7

†Average exchange rate of December in 1993: 109.90¥/$.

In the case of aluminium, 69 percent of the total consumption or 2.53 million tons were recycled by front stage recycling in 1992 (2). On the other hand, final stage recycling could put back approximately 0.73 million tons of aluminium per year in the process according to Table II-4-2. If aluminium had been recovered by final stage recycling and returned into the aluminium material flow, the total amount of recycled aluminium would have reached, instead of 64 percent, more than 80 percent of the supply as raw material (3.95 million tons) (Figure IV-2-1). The life cycles of copper, lead and zinc with their final stage recycling processes are shown in Figures IV-2-2 through IV-2-4 (2). According to the figures, approximately one quarter and one half of lead and the zinc recycled by front stage recycling, respectively, could have been recovered by final stage recycling in 1991.

It should be noted that these values may change greatly because the estimates are made using the values in Table II-4-1 for the metallic element contents in MSWA, WTSA and PSA and are mean values of a maximum and a minimum. Therefore, actually obtainable recovery amounts by final stage recycling might be larger or smaller than shown in Figures IV-2-1 to IV-2-4.

IV-3) Environmental Impacts

Recycling of metals has been considered important for prolonging life of metallic element reserves. Currently, metallic elements in ash go directly to final disposal sites without any recovery. As shown in Table II-4-1, considerable amounts of metallic elements are contained in the ash, which means that a great loss of elements has accumulated. The removal of all metallic elements in ash may be impossible. However, if current social trends for waste treatment were changed and metallic elements were recovered from ash prior to final disposal and recycled in their social

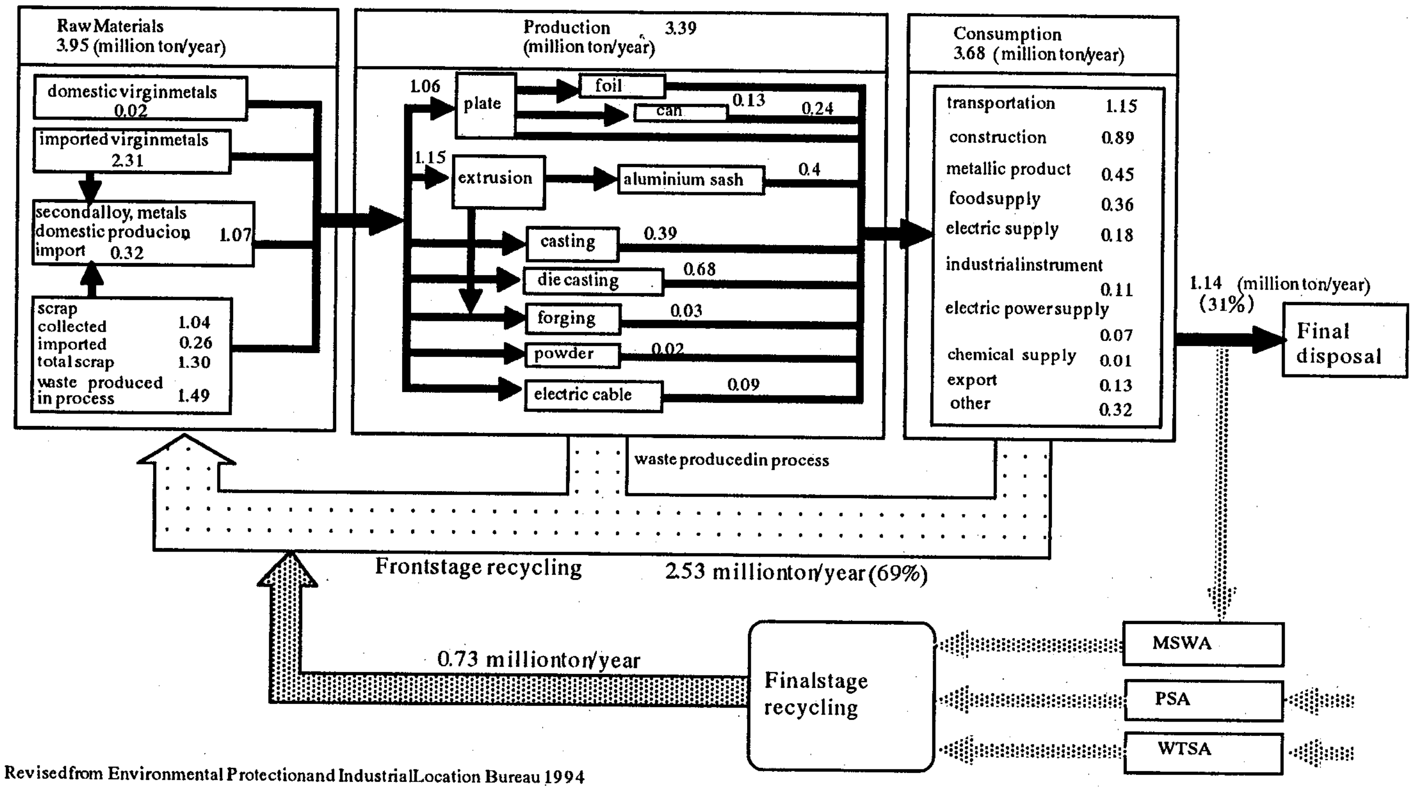

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Figure IV-2-1 Life Cycle of Aluminium and Final Stage Recycling

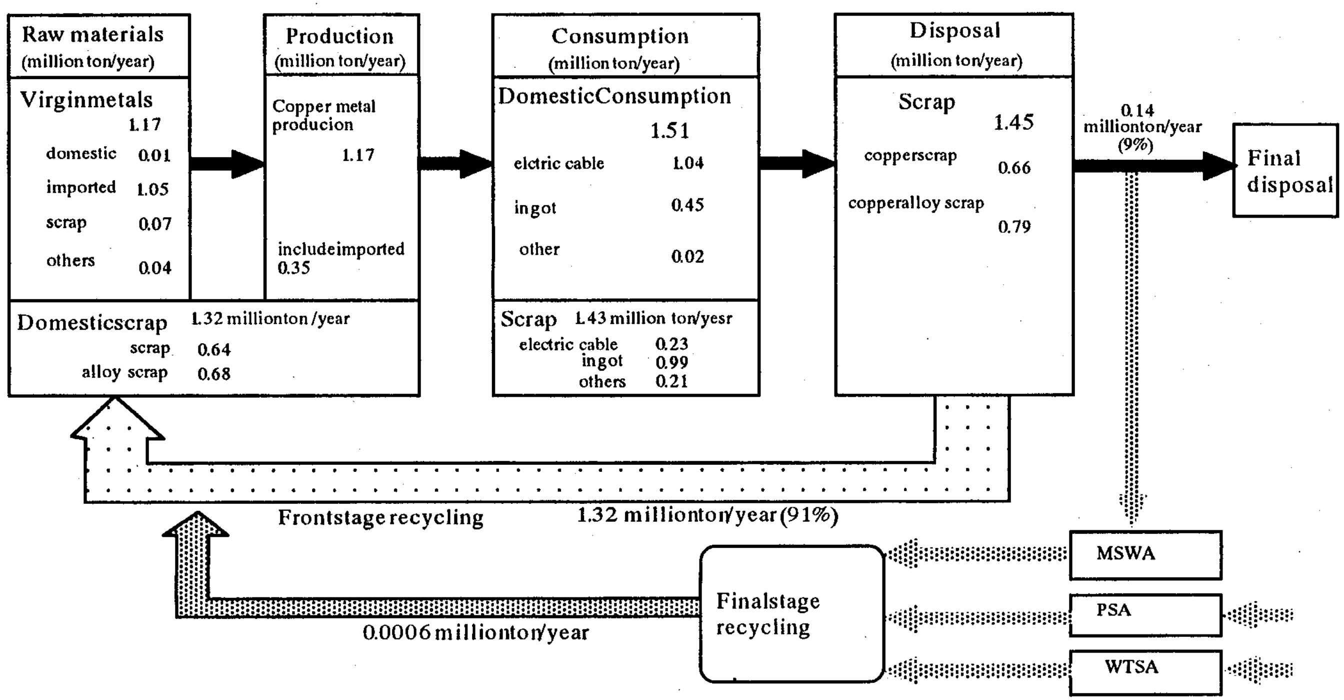

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Figure IV-2-2 Life Cycle of Copper and Final Stage Recycling

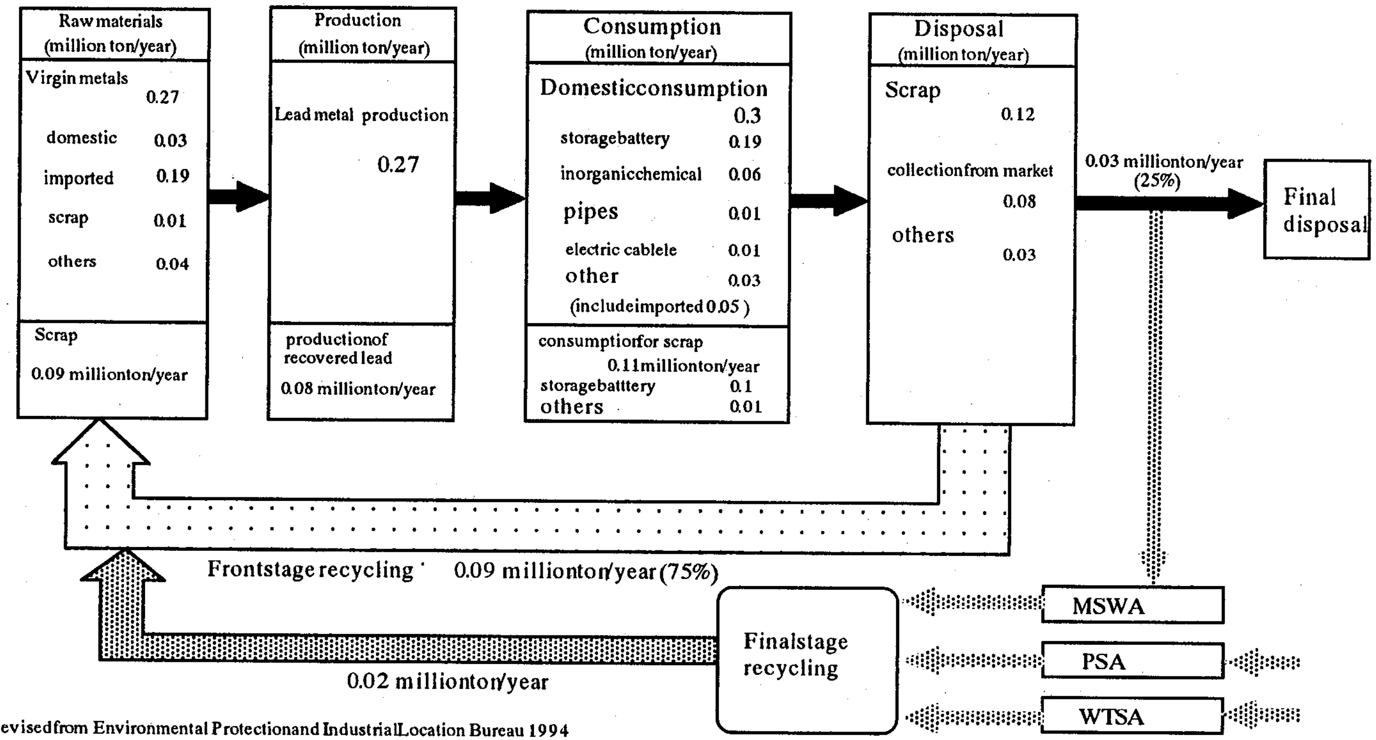

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Figure IV-2-3 Life Cycle of Lead and Final Stage Recycling

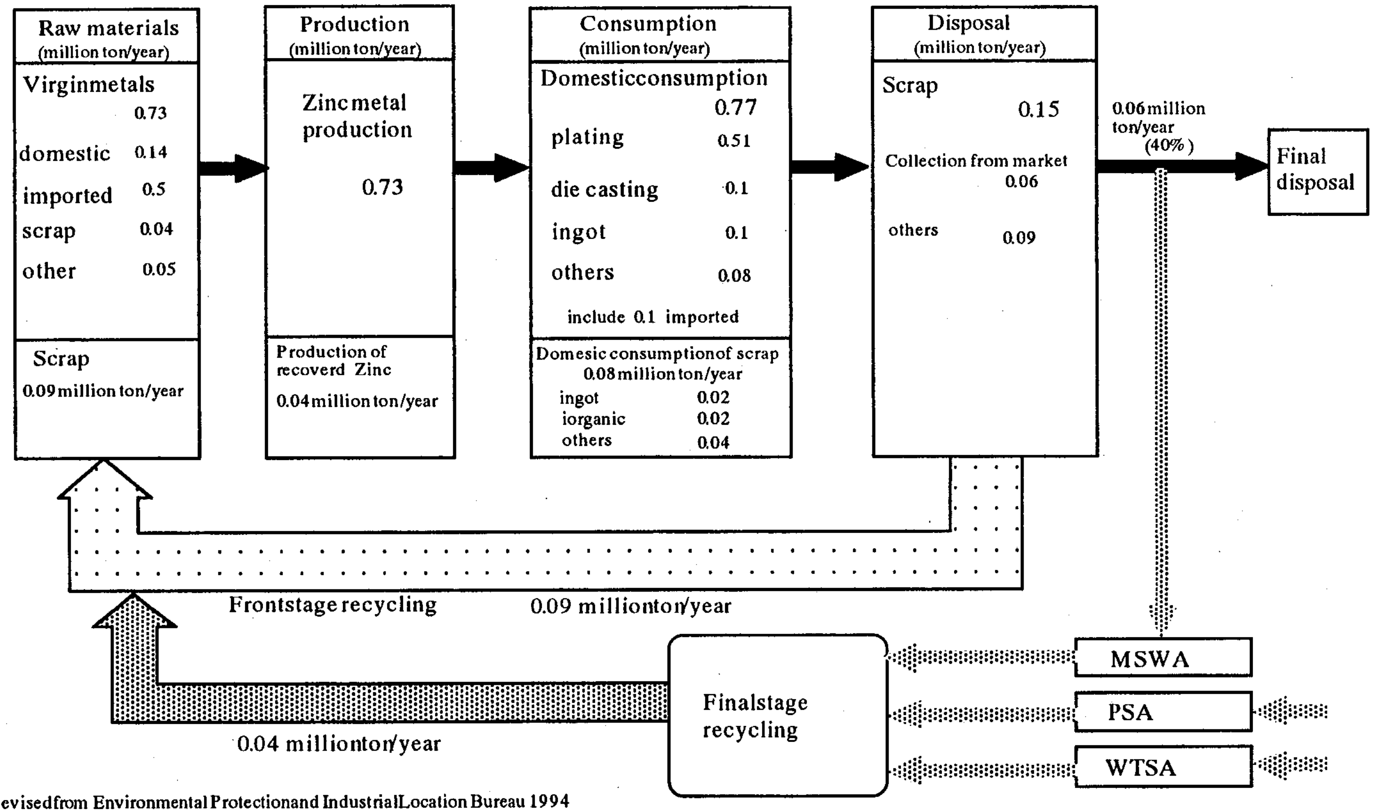

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Figure IV-2-4 Life Cycle of Zinc and Final Stage Recycling material flow, it would promote conservation objectives and prevent maximum loss of metallic elements.

In addition to conservation of mineral reserves, one of the goals in final stage recycling, recovery of the metallic elements from ash would bring another advantageous goal, the residual waste can be recycled into soil after satisfying soil conservation criteria. The disposal of untreated ash into landfills may result in contamination of soil by its leachate and may cause groundwater contamination. Contamination of the marine environment should also be considered when ash is disposed into sea land reclamation sites. Final stage recycling offers not only the advantage of virgin mineral conservation but also that of soil and marine environment conservation, making environmental impacts stay at minimized levels.

IV-4) Health-related Impacts

Denison (3) (4) has discussed the exposure risk of toxic metals in ash. The utilization of ash in road building and construction activities by incorporating toxic metals into ash-derived products by solidification merely postpones exposure risks. Roads constructed by ash-derived products may get torn and worn and concrete buildings made with ash-derived products will be demolished in the future and may produce a tremendous amount of toxic dust. Results of short term extraction tests (continuous shakings for six hours within a near neutral pH range) may give safety levels for avoiding near term effects to the environment. However, they do not address the long term environmental effects.

The threat of secondary pollution by utilization of ash-derived products in city construction projects always exists because the toxicity of metals in the ash is always there. The environment after ten years, twenty years and even more than a century being foreseen, ash treatment schemes that leave room for doubt for the occurrence of second pollution, such as cement solidification and melt-and-solidification, should be reviewed and more environmentally elaborate processes should be installed. Final stage recycling is one of the selections.

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CHAPTER V

COMPARATIVE EVALUATION OF PROCESSES FOR HEAVY METAL REMOVAL FROM MSWFA

V-1) Introduction

Finding a better process for heavy metal recovery from MSWFA is now taken into consideration because introduction and installation of the final stage recycling into society is urgent for conservation of natural resources and reduction of environmental effects. 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 (1) and biological adsorption (2) (3) are available for the process.

In this chapter, literature review was done, and evaluation and comparison of four processes, namely, hydrochloric acid leaching, chloride evaporation, acetic acid leaching, and biological leaching, for heavy metal removal from MSWFA were made by six factors, that is, energy consumption, process efficiency, process handling, process cost estimation, cost reduction potential, and study progress in order to find out their advantages and disadvantages and to help develop a better recovery process. Cost estimation has been the main factor to strongly influence selection of a process in the system of society, leading 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 recommended to install a process whose chemicals used are highly risky to human health and environment. Then, the proposal of balancing weights of factors should be necessary for relative evaluation to select or construct most balanced process.

V-2) Selection of MSWFA as a Target Waste

Incineration or combustion ash can usually be devided into two kinds of ash, namely, bottom ash and fly ash. The former always accumulates at the bottom of furnaces and directly goes to ash pits, but the latter flies away from furnaces and is gathered in fly ash collecters. MSWA, PSA, and WTSA have also bottom ash and fly ash for each. Among six type of ashes, removal of heavy metals from municipal solid waste incineration fly ash (MSWFA) was paid attention to. Environmental threats by MSWFA have been great concern in Japan because of tremendous amounts of annual municipal solid waste generation and the social system of extremely high dependence on incineration treatment for municipal solid waste management. However, very few studies on heavy metal extraction from MSWFA have been reported until now (4) (5) (6) (7) (8) (9) (10). It has been recognized that heavy metals contained play a major role in the threats and that development of a recovery process is essential for reality of installing the final stage recycling process into social current material flow.

V-3) 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 V-3.

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 (11).

Table V-3
Representative Heavy Metal Removal Processes Selected by Literature Review

Reference	Method	Process symbol
Legiec et.al. 1989	Acid Leaching (HCl)	L
Takeda et.al 1994	Chloride Evaporation	T
Fukunaga et.al. 1996	Acid Leaching (HAc)	F
Bosshard et.al. 1996	Biological Leaching	B

V-3-1) Physico-chemical Process

Legiec et al. (4) investigated removal percentages of heavy metals from MSWFA by chemical extraction using 1.0N NaCl solution acidified with hydrochloric 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. (10) also conducted leaching 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.

Takeda et al. (6) investigated chloride evaporation process for removing heavy metals from 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 ^{O}C, 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 ^{O}C, evaporativities of the elements were 48%, 5%, 18%, and 10% in the same atmosphere. Jakob et al. (7) (9) also performed evaporation experiment for the same kinds of heavy metals in MSWFA and investigated on much wider conditions such as 670 to 1300 ^{O}C for temperature and air, argon/hydrogen, and argon for atmosphere. The paper by Takeda, 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. (8) 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.

V-3-2) Biological Process

Bosshard et al. (11) 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 extracted 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.

Table V-4-1a
Summary of Process Operations

Process Symbol		L	T	F	B
Reactor Type		semicontinuous - pilot	batch	batch	batch
Operational Conditions	temperature	ambient	600 - 900 (°C)	ambient	ambient
	duration	2 (hrs)	20 (min)	3 (hrs)	22 days (one-step) 24 hrs (two-step)
	fixed pH	1.59 (CF3) 2.65(MF)	-	4.4	-
	aeration	mechanical stirrer	-	rotary shaker	rotary shaker
Treatable Amount		5% (w/v) ash feed:1kg/hr extractant solution feed:20kg/hr	5g / operation	10% (w/v)	5% (w/v) (up to 7.5%)
Extraction Chemicals		NaCl, HCl	5% HCl gas (4*l* /min)	acetic acid (1:1)	*Aspergillus niger* • gluconate (one-step) • citrate (two-step)
Other Requirements		1N NaCl	electric oven (13.2kVA)	caustic soda	sucrose, $NaNO_3$, KH_2PO_4, $MgSO_4 \cdot 7H_2O$, KCl, and yeast extract

Table V-4-1a (continued)

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 CF3	• complete destruction of toxic organic compounds • considerable difference in extraction efficiency between at 600 C and at 900 C	• high buffering capacity of acetic acid; capability of maitaining pH value stable	• one-step : treatment of ash with microbes • two-step : treatment of ash with organic acid after microbe removal

V-4) Process Evaluation

Tables V-4-1a and b show summary of operations of the selected four 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.

Table V-4-1b
Summary of Process Operations (Heavy Metal Removal Percentage)

Process Symbol		L		T		F	B	
	Condition	MF	CF3	600	900		one-step	two-step
Percentage of removal	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

For instance, MF instead of CF3 as a kind of ash, temperature of 900 ^{o}C from the range of 600 to 900 ^{o}C, and two-step treatment instead of one-step treatment were used for evaluation of Processes L, T, and B, respectively (see Table V-4-2).

Table V-4-2
Cost Estimation for Processes

Process Symbol	L	T	F	B
Chemicals Needed and Prices	• 35% HCl (12N): 15-17yen/kg† (density = 1.2) • NaCl: 40-42yen/kg†	• electricity basic charge 1,660yen/kW/mo† charge for use 14.5yen/kW/h†	• HAc: 180-200yen/kg† (density = 1.1) • 48% NaOH(18N): 40yen/kg† (density = 1.49)	• sucrose: 29.11yen/kg§† • $NaNO_3$: 108yen/kg† • KH_2PO_4: 800yen/kg† • $MgSO_4 \cdot 7H_2O$: 65yen/kg† • KCl: 32.2yen/kg† • yeast extract: 13,600yen/kg†
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	1N HCl 81 ml 1N NaCl 119 ml Experiments' results 1. Neutralization to pH 1.59 1N NaCl = 100 ml 1N HCl = 68 ml 2. Calculations x = 1N HCl y = 1N NaCl $x/y = 0.68$ $x+y = 200$ $x = 81, y = 119$	13.2 kW 2 operations---> 20min x 2	(1:1) HAc 90.4 ml 18N NaOH 9.6 ml Experiments' results 1. Neutralization to pH 4.4 (1:1) HAc = 100 ml 18N NaOH = 10.6 ml 2. Calculations x = HAc y = NaOH $y/x = 0.106$ $x+y = 100$ $x = 90.4, y = 9.6$	200ml ---> 4.23g citrate (110mM citrate needed)

Table V-4-2 (continued)

Calculations for Cost Estimation	• HCl - for water consumption 17yen/kg x 1.2 =20.4yen/*l* 1N->81ml, 12N->6.8ml 20.4yen/*l* x 6.8ml =0.14yen - for ash consumption assuming approx. 4,000ppm HCl needed. -->0.05yen • NaCl 58.5g/*l* x 119ml = 7.0g 7g x 42yen/kg =0.29yen 0.48yen/10g	• Basic charge 1,660x13.2 kW/(30d•24hr) =30.4yen/hr =20.3yen/40min • Charge for use 14.5x13.2 kWx(2/3)hr =127.6yen/40min 147.9yen/10g	• HAc 90.4/2 x 1.1 = 50g 50 x 200 =10yen • NaOH 9.6 x 1.49 = 14.3g 14.3 x 40 =0.6yen 10.6yen/10g	• sucrose 100g/*l*x29.11 =0.58yen • $NaNO_3$ 1.5g/*l*x108 =0.032yen • KH_2PO_4 0.5g/*l*x800 =0.08yen • $MgSO_4 \cdot 7H_2O$ 0.025g/*l*x65 =0.00033yen • KCl 0.025g/*l*x32.2 =0.00016 • yeast extract 1.6g/*l*x13,600 =4.35 5.04yen//10g
Cost for 1g Ash Treatment	0.048yen	14.79yen	1.06yen	0.50yen

§Price of unrefined sugar.
†Obtained by Personal Communication.

V-4-1) Energy Consumption

Electricity was a main energy consumed by processes due to an electric muffle, a stirrer 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 °C 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.

V-4-2) Process Efficiency

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

V-4-2-1) 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.

V-4-2-2) 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 5 g in one operation, ash amounts of the other processes were chosen to be 5 g, 10g, and 5g for Processes L, F, and B, respectively, which were treatable ash amounts when solution was 100 ml. 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 Processes 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.

V-4-3) 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.

V-4-3-1) pH adjustment necessity

Processes L and F required pH adjustment. NaCl solution was adjusted to pH 2.65 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 in 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.

V-4-3-2) Wastewater treatment operation

Use of organic acids such as HAc and citrate acid was 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.

V-4-3-3) 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.

V-4-3-4) Liability of chemical 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.

V-4-4) Process Cost Estimation

Expense estimation for treating 1 g of ash was done for each process based on estimated costs of chemicals used (12) and electricity consumed for a muffle (Table V-4-2). According to Table V-4-2, the lowest treatment cost was 0.048 yen 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 stirrer 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. 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 treating 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.

V-4-5) 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 if 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.

V-4-6) Study Progress

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

V-5) Results and Discussion

Evaluation of processes on factors is shown in Table V-5. 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 their 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

Table V-5
Process Evaluation Summary

Factor	Sub factors	Total evaluation
Energy Consumption	-	L = F > B > T
Process Efficiency	reaction duration : T>L>F>B removal efficiency : F>T=B>L	T > F > L > B [§]
Process Handling	pH adjustment necessity : T=B>L>F wastewater treatment necessity : T>L>F=B liability of process operation : L=F=B>T liability of chemicals used : B>F=L>T	B > T = L > F [†]
Process Cost Estimation	-	L > B > F > T
Cost Reduction Potential	-	B > F > L = T
Study Progress	-	L > B = F = T

[§] Between Processes T and L, relation of "T > L" was obtained since Process T was better than Process L for both sub factors. 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. Likewise, 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.

[†] The same manner was applied for making the total evaluation with respect to process handling.

cost reduction potential. Processes were compared individually on process efficiency and process cost estimation.

Process T showed superiority only on 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. However, the process showed disadvantage by appearing on the very right of sides in Total Evaluation of Table V-5 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 alone 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 was 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 given 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.

V-6) References

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CHAPTER VI

HEAVY METAL EXTRACTION FROM MSWFA USING A SULFUR OXIDIZING BACTERIUM

VI-1) Introduction

Although, unlike chemical and physical processes, biological processes might have advantages of low running cost for large amounts of waste and of simplicity of their operation, there has been only one using the biological means among the studies on the metal extraction. Bosshard et.al. (1) employed *Aspergillus niger*, which produces citric acid or gluconic acid for heavy metal extraction. Since the fungus is a heterotrophic microorganism and no organics are found available in ash for microbe growth, supply of organics as a carbon source is necessary. Although substitution of wastewater containing organics which are necessary for microbe growth as media can be a remedy for anticipated running cost increase when commercial sucrose used as a carbon source, undesirable addition of organics into the ash which is in an inorganic nature may leave a disadvantage in wastewater treatment after metal recovery.

Unfortunately no paper has reported bioleaching of heavy metals from MSWFA using sulfur oxidizing bacteria, yet employment of the microbes may be one of the alternatives for development of heavy metal extraction from MSWFA. They are very unique microorganisms and easy to obtain from anywhere because of widely spread habitats. Hashimoto et.al. (2) successfully obtained *Thiobacillus* spp. by screening 14 samples taken from pond waters, sediments, hot spring sites, ground soils, and return and digested sludges of sewage treatment plants, and they concluded that the microbe which had been collected from a hot spring site showed the fastest growth rate. Sulfur oxidizing bacteria have extremely acidophilic characteristics and no need of organic material supply as a carbon source due to autotrophic (chemolithotrophic) characteristics, for which they fix carbon dioxide from air.

Table IV-1
Classification of Organisms Nutritionally (3)

Class	Carbon Source	Energy Source	Electron Donors	Examples
Photolithotrophs	CO_2	Light	Inorganic compounds (H_2O, H_2S, S)	higher plants, blue-green algae, Photosynthetic bacteria
Photoorganotrophs	Organics (and CO_2)	Light	Organic compounds	nonsulfur purple bacteria
Chemolithotrophs	CO_2	Redox reactions	Inorganic compounds (H_2, S, H_2S, Fe^{2+}, NH_3)	nitrifiers hydrogen, sulfur, iron, bacteria
Chemoorganotrophs	Organics	Redox reactions	Organic compounds	higher animals, most microorganisms, nonphotosynthetic plants

The microbes have been actively used in industrial applications, especially in mining industries of copper and uranium (4), and in recycling applications such as heavy metal leaching from sewage sludge (5) (6) (7) (8) (9) (10) (11) (12) (13). Most of sulfur oxidizing bacteria oxidize elemental sulfur and produce a sulfuric acid as a consequence of metabolism described following reactions (14):

Reaction for electron donor ;

$$1/6\ S + 2/3\ H_2O = 1/6\ SO_4^{2-} + 4/3\ H^+ + e^- \qquad (a)$$

Reaction for electron acceptor ;

$$1/4\ O_2 + H^+ + e^- = 1/2\ H_2O \qquad \text{(b)}$$

(a) + (b) ;

$$2S + 3O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2H_2SO_4.$$

Extraction of heavy metals from the ash can be proceeded and the metals are allowed to be soluble in water, under the condition of low pH and high oxidation reduction potential (ORP) which are led by the microbe activities.

Because of advantages of autotrophic microorganisms, a number of successful applications for industries, and a history of using biological treatment for huge scale applications, it is very meaningful to evaluate feasibility of heavy metal extraction from MSWFA using sulfur oxidizing bacteria for development of a new heavy metal recovery process. In this chapter bioleaching of MSWFA using a sulfur oxidizing bacterium of *Thiobacillus* spp. strain TM-32, which was isolated from soil at a hot spring site, is presented. Six MSWFA samples were obtained from actual incineration plants. The four heavy metals, namely Cd, Cu, Pb, and Zn, were selected for leaching tests. First of all, characteristics of each ash were investigated. Then, leaching tests were performed to investigate effects of ash sources on heavy metal extraction percentages. Moreover, an effect of sulfate accumulation on heavy metal extraction was investigated. Also, regarding sulfur recovery and concern of secondary environmental pollution led by unused sulfur in the ash in a postleaching state, extraction tests were performed using sulfur free culture, and the extraction percentages were compared to original ONM culture's. Finally, cost reduction for making a medium was investigated for reality of the process.

VI-2) Materials and Methods

VI-2-1) MSWFAs

Samples of MSWFA were obtained from six municipal solid waste incineration plants in Japan based on furnace types, exhaust gas treatment processes, and dust collector types. Table VI-2-1 shows a profile of fly ash samples. It is very important to show production sources and conditions of MSWFA because characteristics of the ash were considerably affected by them and were different from each other, although classification of waste collection rules is not strictly kept. Each ash was directly used for experiments without any pretreatment made. Many prohibited waste and materials which were not supposed to be found in bottom ash were observed when sampling was conducted. Total Heavy Metal Contents in MSWFAs were obtained following the procedure proposed by Japan Sewage Works Association (15).

VI-2-2) Media and Culture Conditions

ONM media (16) were used in this study (Table VI-2-2). With a half and a tenth of the ONM in concentration, 1/2 ONM and 1/10 ONM, respectively, were prepared by simply reducing inorganic salt concentration with purified water. Tap water medium was prepared, containing 10 g of elemental sulfur in 1000 ml of tap water, and pH was adjusted to near 3.9 with 0.5 N HCl. The A medium (2) was used for isolation of the bacterium. Liquid cultures were prepared in 300 ml flasks containing 97 ml of the ONM medium and 3 ml of inoculation unless otherwise stated. After having been autoclaved at 105 °C for 45 minutes, liquid cultures were incubated on a rotary shaker.

Table VI-2-1
Profile of MSWFA

MSWFA	Population of Town	Classification of separate collection	Type of furnace	Type of exhaust gas treatment	Type of dust collector	Density (g/cm^3)
A	less than 50,000	burnable, nonburnable and bulk wastes, batteries, cans and glasses	continuous-feed traveling-grate stoker	dry scrubber	electrostatic precipitator	2.7
B	less than 50,000	burnable and nonburnable wastes	mechanical batch	dry scrubber	fabric filter	3.0
C	more than 50,000 less than 100,000	burnable, nonburnable and bulk wastes and glasses	continuous-feed traveling-grate stoker	dry scrubber	fabric filter	3.0
D	more than 100,000 less than 150,000	burnable, nonburnable and bulk wastes, cans, fluorescent lights and batteries	continuous-feed fluid-bed	wet scrubber	electrostatic precipitator	2.7
E	more than 150,000 less than 500,000	burnable, nonburnable and burnable bulk wastes	continuous-feed traveling-grate stoker	wet scrubber	electrostatic precipitator	3.0
F	more than 1,000,000	burnable and nonburnable wastes	continuous-feed traveling-grate stoker	wet scrubber	electrostatic precipitator	2.7

Table VI-2-2

Constituents of ONM Medium (16)

Constituents	Amount (g)
$(NH_4)_2SO_4$	0.2
$MgSO_4 \cdot 7H_2O$	0.03
$CaCl_2 \cdot 7H_2O$	0.03
$FeSO_4 \cdot 7H_2O$	0.001
KH_2PO_4	0.4
Elemental Sulfur	1.0
Distilled water	100 ml

VI-2-3) Isolation and Identification of Strain TM-32

A soil sample from a hot spring site of Aso in Kyushu Island, Japan was used for isolation of a sulfur oxidizing bacterium. 5 grams of the soil was placed into 100 ml of the ONM medium and incubated by a rotary shaker at 150 rpm and 30 °C. Approximately 10 ml of the culture was transferred from enriched culture into new ONM medium. After the procedure was repeated 14 times, aliquots of the resultant enriched culture were plated onto the A agar plates, which resulted in formation of uniform whitish yellow colonies 8 days later. A colony was transferred into the ONM medium, causing pH reduction along with sulfate production, and the typical strain was designated as TM-32. As a result of morphological and physiological investigations, the strain TM-32 was found to be gram(-), short rod-shaped (approx. 1.0 x 1.5 μm), single, paired, chained, motile, capable of sulfate production from elemental sulfur, acidophilic (< pH 0.5), and autotrophic. Hence, the strain was identified as *Thiobacillus* spp. following Bergey's Manual (17) (see Appendix III).

VI-2-4) Heavy Metal Extraction Percentage

Heavy metal extraction percentage was obtained by the following calculation;

$$\begin{aligned}\text{Extraction }\% &= (m_t / M_t)(100) \\ &= \{C_t \bullet V_t / (M_{t-1} - C_{t-1} \bullet v)\}(100)\end{aligned}$$

where, m_t = amount of heavy metal in solution at time = t (mg), M_t = total amount of heavy metal in system at time = t (mg), C_t = heavy metal conentration at time = t (mg/*l*), V_t = volume of the system at time = t (*l*), M_{t-1} = total amount of heavy metal in system at previous sampling or time = t-1 (mg), C_{t-1} = heavy metal conentration at previous sampling or time = t-1 (mg/*l*), and v = volume of aliquot for heavy metal measurement (*l*).

VI-3) Experimental Procedures

VI-3-1) Leaching Tests

Each ash sample was added into 100 ml of the 5 day-culture with the strain TM-32 and continuously incubated on a rotary shaker at 122 rpm and 27.8 °C. For a heavy metal extraction test by sulfur free culture, the ONM culture was filtered by a Whatman type C glass fiber paper for removal of powdered elemental sulfur, and then ash was added into the sulfur free culture. 7 ml of aliquots were taken from the culture at intervals and filtered by the Whatman paper for preparation of heavy metal measurement. All procedures were performed under nonsterilized conditions, and the culture touched air outside when the aliquots were taken. Effect on the microbe's activities of culture contamination was not considered because of extremely acidic environment.

VI-3-2) Sulfate Production

For a sulfate production experiment, 3 ml ONM cultures were centrifuged at 15,000x*g* for 10 minutes, and pellets of the strain TM-32 were inoculated into the test media whose volumes were 100 ml in 300 ml flasks. Incubation was performed at 122 rpm and 27.8 °C. 1.2 ml of aliquots of the cultures were taken at intervals and centrifuged at 15,000x*g* for 10 minutes. 1.0 ml supernatants were taken and used for sulfate measurement.

VI-3-3) Analytical Procedures

Heavy metal concentrations were determined by an atomic adsorption spectrophotometer (AAS; Seiko instruments, Chiba, Japan, SAS7500A system equipped with an AT100A autosampler). Sulfate was determined by an ion chromatography (IC; Dionex Corp., California, U.S.A., DX-300 system with a CDM-3 conductivity detector) with an Ion Pac® AG4A-SC guard column, an AS4A-SC column, an ASRS-I suppressor, and a DAS-80 autosampler.

VI-4) Results and Discussion

VI-4-1) Ash Charateristics

Six ash samples were collected for heavy metal extraction in this study. It is very important to use and observe more than one sample for extraction tests because each ash has different characteristics and the obtained extraction percentage of a heavy metal from a sample is not necessarily the same as the one of the same metal from a different sample.

Table VI-4-1
Total Heavy Metal Contents in MSWFA

MSWFA	Total contents of heavy metal (mg/kg)			
	Cd	Cu	Pb	Zn
A	39.8	454	1,089	4,917
B	28.7	456	641	1,764
C	72.1	391	1,120	4,981
D	7.7	4,727	1,655	6,310
E	190	1,574	7,804	27,293
F	87.7	521	1,913	9,715

Table VI-4-1 shows results of analysis on total heavy metal contents from each ash sample. Among six ash samples, Sample D was the only one which was taken from a fluid-bed type of furnace and the others were taken from stoker types of furnace. According to Table VI-4-1, throughout all samples except the D, the descending order of metal contents was Zn, Pb, Cu, and Cd. The highest content of Cu and lowest content of Cd among the samples were observed from the D. Table VI-4-1 also shows Cd content tended to be low and Cu content tended to be high in fluid-bed types of furnace (18). The contents of Zn and Pb in Sample E were significantly higher than those of the others. This might have been attributed to characteristics of incinerated municipal waste.

VI-4-2) Effects of Ash Sources on Heavy Metal Extraction

Trends of pH and ORP changes during the extraction tests using the strain TM-32 for Samples A, B, C, D, E, and F are shown in Figures VI-4-2-1a and b. Initial decreases in pH and increases in ORP from time 0 to 115.5 hours indicate the sulfate accumulation and oxidation reaction progress by the microbe growth. 0.7 % (w/v) ash were added into the cultures on the 5th day (115.5 hours) and rapid increases in pH and decreases in ORP were observed in the samples. Degrees of pH changes reciprocally corresponded to those of ORP changes. Samples A, B, and C from dry scrubber processes showed larger pH increases than Samples D, E, and F from wet scrubber processes. Sample A, especially, showed the largest pH increase to 3.67 and the lowest ORP decrease to 192 ml. Degrees of pH increases corresponded to contents of alkaline components such as $Ca(OH)_2$ in the samples. The graph shows that Samples A, B, and C contained large amounts of alkaline components and Samples D, E, and F did small amounts .

Despite of different degrees of the pH and ORP changes, the ash samples showed very similar trends on the four heavy metals during the next 10 days of extraction, and extraction percentages at the end of the period were 55.3-68.5 %, 57.4-84.6 %, 2.2-19.6 %, and 38.8-56.4 % for Cd, Cu, Pb, and Zn, respectively (Figures VI-4-2-2a to d). Results show that heavy metal extraction from the ash was proceeded in two mechanisms, which are called in this paper initial extraction and secondary extraction. Initial extraction must have occurred the right after the ash was added at Time 115

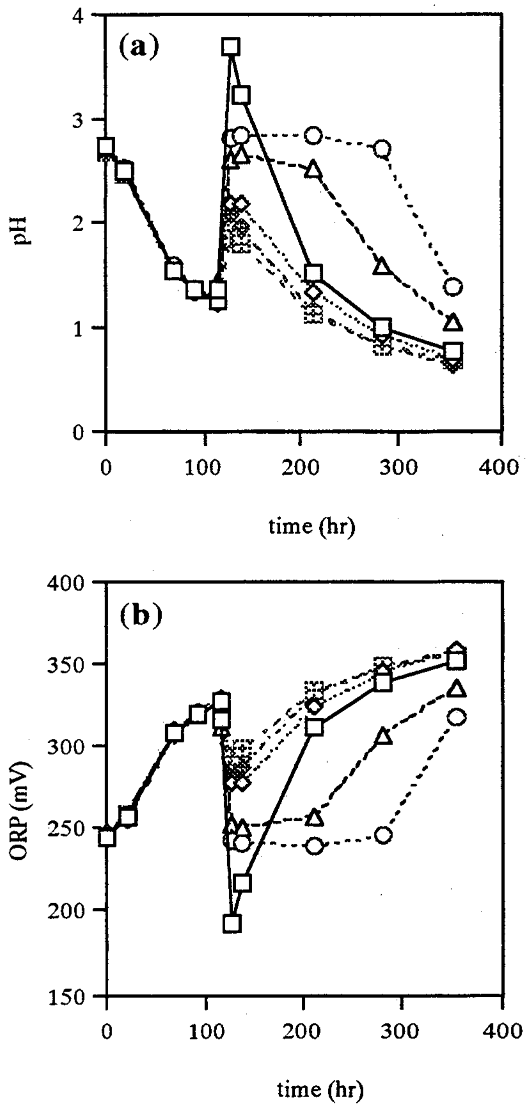


Figure VI-4-2-1
(a) pH Change of Ash Samples, (b) ORP Change of Ash Samples.

—□— A, ----○---- B, ----△---- C, ---⊞--- E,
·······◇······· D, -·-·◆-·-· F.

because no of the extraction percentages were 0 at Time 115. Secondary extraction took place gradually as time passed.

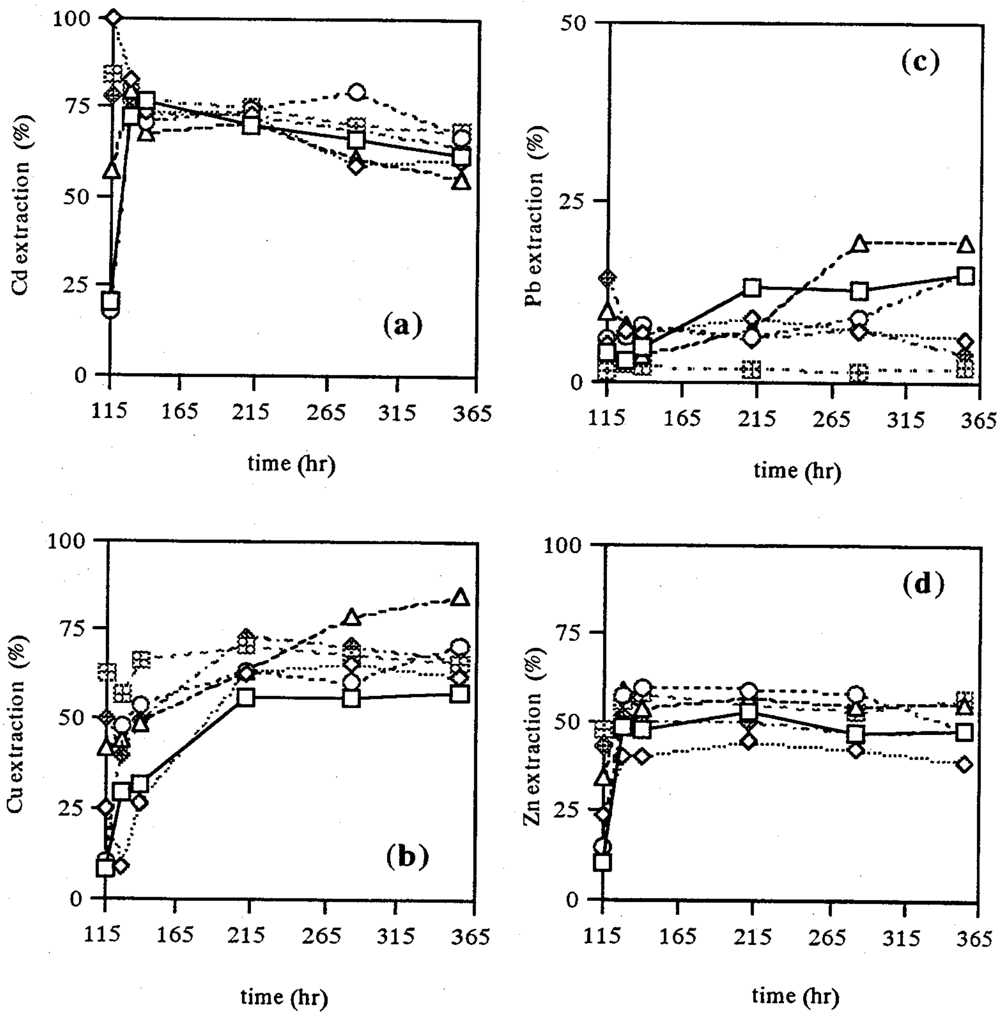


Figure VI 4-2-2 (a) Cd Extraction Percentage, (b) Cu Extraction Percentage, (c) Pb Extraction Percentage, (d) Zn Extraction Percentage. —□— A, ----○---- B, ----△---- C, ·······◇······· D, ---⊞--- E, ---◈--- F.

The two extraction mechanisms can be attributed to locations of heavy metals. Fukunaga et.al. (19) stated that there are two locations where heavy metals exist; one is surface of the ash and the other is inside of the ash. The former case occurs in heavy metal extraction from metal salts such as $PbCl_2$. Metals form salts and are in their gas state in combustion, and then come to attach to surface of the ash as temperature decreases. The heavy metals can be easily extracted in acidic conditions. Regarding the latter case the extraction is not easy but can be done in only highly acidic conditions. Seen in the figures, extraction of Cd and Zn might have been done mainly by initial mechanism so the maximum extraction was reached at the early stage of the experimental period. On the other hand, secondary mechanism might have dominated in Cu extraction because gradual extraction was seen as in Figure VI-4-2-2b.

There was no significant difference on Cd, Cu, and Zn extractions between dry scrubber processes and wet scrubber processes. In case of Pb, extraction percentages were generally very low, which was attributed to low solubility of lead sulfate production (7). At the end of the period, the ash from dry scrubber processes showed relatively higher extraction percentages than that from wet scrubber processes did and the percentages were 15.0-19.6 % and 2.2-6.2 %, respectively.

VI-4-3) Effects of Sulfate Accumuration on Heavy Metal Extraction Percentages

Two experiments were performed to observe extraction percentages and microbial conditions. For sulfate accumulation effect on the extraction percentages, Sample A was selected because it was most influential to pH increase and ORP decrease of culture, as shown in Figures VI-4-2-1a and VI-4-2-1b.

In one experiment, after 1.5 % (w/v) ash had been added into 5 day ONM culture, extraction percentages of Cd, Cu, Pb, and Zn were observed for five days. During the first 12 hours, a rapid increase in pH and decrease in ORP occurred, and 1.33 and 325 mV became 9.38 and -131 mV for pH and ORP, respectively (Figure VI-4-3-1).

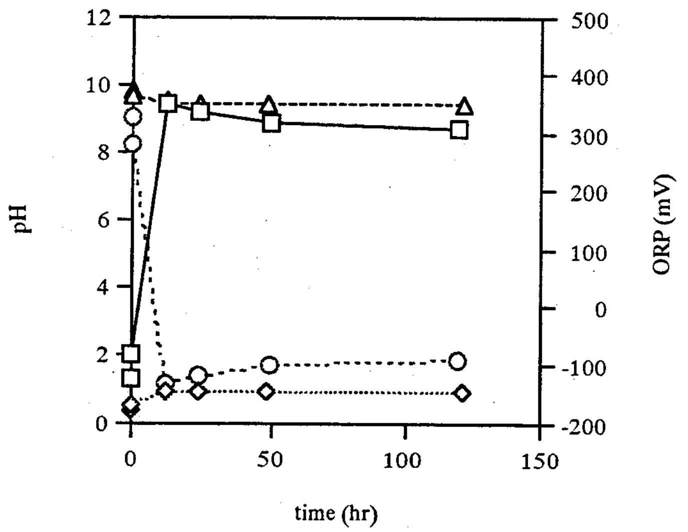


Figure VI-4-3-1 pH and ORP Changes with 1.5 and 3.0% Ash Addition

—□— pH (1.5% Ash), ----○---- ORP (1.5% Ash),

·········◇········· pH (3.0% Ash), ----△---- ORP (3.0% Ash).

The results of heavy metal extraction are shown in Figures VI-4-3-2a to d. The amounts of alkaline components in the ash exceeded the amount of sulfate produced, which was approximately 5,000 ppm, resulting in large increases in pH and negative values of ORP. Under the conditions, the heavy metals extracted by initial mechanism could not maintain soluble forms in the solution and settled down into ash solid layer after changing the forms to insoluble ones. Also, since the strain TM-32 did not survive and the sulfate production ceased when pH of culture reached about 6, secondary extraction did not occur. As a result, unlike with the 0.7 % ash, no extraction was observed for the four metals.

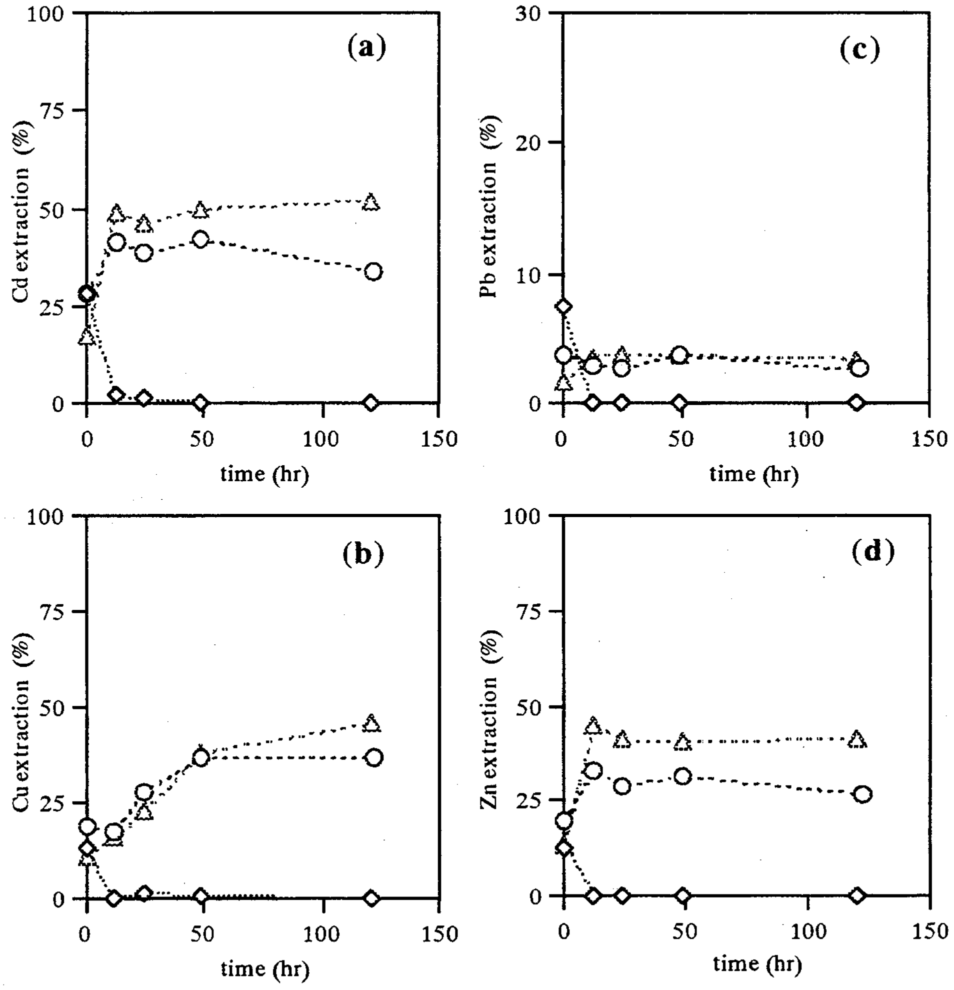


Figure VI-4-3-2 (a) Cd Extraction with Ash Addition, (b) Cu Extraction with Ash Addition, (c) Pb Extraction with Ash Addition, (d) Zn Extraction with Ash Addition.

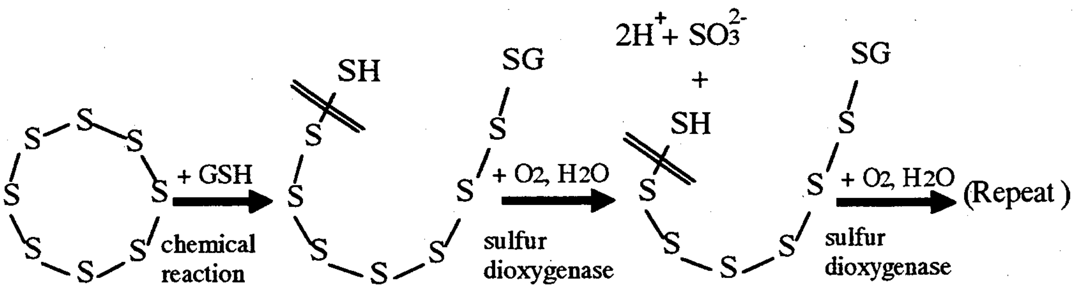
········◇······· ONM(1.5%), ----○--- ONM(3.0%), ----△--- Sulfur free culture(3.0%).

In the other experiment, 3.0 % (w/v) ash was added into 73 day incubated ONM culture. pH and ORP changes are shown in Figure VI-4-3-1. The pH and ORP were not affected during the 5 day period of the experiment even though twice as much ash as the 1.5 % was added, and pH and ORP were settled to 0.92 and 350 mV at the end of the experiment, changing from 0.38 and 372 mV at Time 0. This can be explained that, unlike the experiment stated above whose incubation time was 5 days, enough sulfate concentration to maintain low pH and high ORP levels lasted and the strain TM-32 survived even after alkali components in the ash consumed sulfate at the early stage, because sulfate was accumulated during the long period of incubation (approximately five times more of 5,000 ppm). The extraction was proceeded under the suitable conditions for heavy metal extraction, and the results are in Figures VI-4-3-2a to d.

Consequently, it can be said a long incubation time and large accumulation of sulfate are essential for providing suitable conditions for heavy metal extraction, when ash amounts are increased. Comparing with the test of 0.7 % ash addition, extraction of heavy metals from ONM containing more ash seems to have a disadvantage, since the extraction percentages of the 3.0 % test were relatively lower than the one of the 0.7 % test; 61.9 and 33.9 % for Cd, 57.4 and 37.1 % for Cu, 15.0 and 2.6 % for Pb and 47.4 and 26.6 % for Zn from the 0.7 and 3.0 % ash addition tests, respectively. However, in terms of extraction efficiency, much more of the heavy metals were extracted in the 3.0 % ash addition test than in the 0.7 % test except for Pb. The extracted amounts were Cd; 0.016 and 0.038 mg, Cu; 0.170 and 0.470 mg, Pb; 0.106 and 0.079 mg, and Zn; 1.52 and 3.65 mg for the 0.7 % and 3.0 % ash tests, respectively.

VI-4-4) Heavy Metal Extraction by Sulfur Free Culture

Sulfur free culture, for which powdered elemental sulfur was removed, was used for the heavy metal extraction tests on sulfur recovery and concern of secondary environmental pollution such as reacidification of soil environment in the postleaching stage (13). Sulfur that was used as an electron donor was not consumed completely even during 2 month incubation, and some of it was left on the bottom of culture. It is exceedingly wasteful to dispose ash with unused sulfur, though. Sulfur oxidizing bacteria metabolize elemental sulfur in two steps (20). They, first, attach to surface of elemental sulfur by using reductive glutathion and, then, start oxidizing the sulfur by using sulfur dioxygenase.



$$S_n + GSH \text{ -------> } GSS_nH$$

$$GSS_nH + O_2 + H_2O \text{ -----------> } GSS_{n-1}H + SO_3^{2-} + 2H^+$$

Figure VI-4-4 Oxidation Mechanism of Elemental Sulfur (20)

Introduction of adopted microbes which are already attached to surface of elemental sulfur into new culture will require a short time for sulfate production, and direct ash addition into culture makes it impossible for the sulfur to be recovered. Use of sulfur free culture can provide not only an advantage of sulfur recovery but also an advantage of microbe recovery, because many of the microbes colonize on surface of sulfur.

The results of heavy metal extraction are in Figures VI-4-3-2a to d. According to the figures, the extraction percentages in sulfur free culture were better than those of the original ONM culture except Pb even though the sulfur free culture was incubated for 9 days less than the other one. It suggests that employment of sulfur free culture for heavy metal extraction from MSWFA could be a very useful method for pursuing high extraction percentages, operational cost reduction and environment conservation .

VI-4-5) Culture Substitute for Cost Reduction

Figure VI-4-5 shows sulfate production in different culture media. The strain TM-32 yielded the approximately same production rates in the three media, ONM, 1/2 ONM and 1/10 ONM. On the other hand, although the sulfate production in tap water culture showed approximately the same trend as in the three cultures in 48 hours, it became considerably slow later on. Since specific growth rates of sulfur oxidizing bacteria have proportional relationship with pH decreasing rates (2), the rates are very useful to get to know the microbes' activities (see Appendix II).

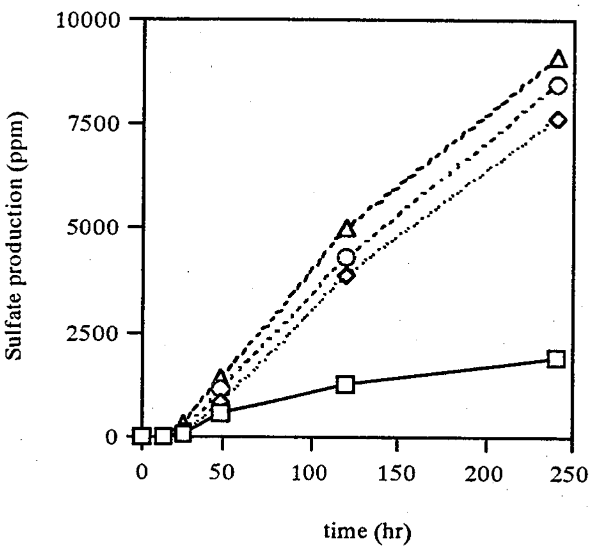


Figure VI-4-5 Sulfate Production in Different Cultures

—□—	tap water,	·····◇·····	1/10 ONM,
----○----	1/2 ONM,	----△----	ONM.

They were calculated by applying a linear regression to pH decreasing curves (Table VI-4-5). In the period of 0-48 hours, the pH decreasing rates were not considerably different among the four cultures, however, the rate of tap water culture became a half of the other three cultures' after 48 hours. This implies that there were nutrient limitations in tap water culture, and some nutrients were needed to be added.

Generally, elementary composition of microbial cells is said to be nitrogen for 10-15 % and phosphorus for 1-3 %, and the amount of nitrogen is required to be more than five times that of phosphorus (14). The slow sulfate production in the tap water culture might have been attributed to the nitrogen limitation.

Table VI-4-5
pH Decreasing Rates on Culture Types

culture type	pH decreasing rate (day^{-1})	
	0 - 48 hrs.	48 - 240 hrs.
tap water	0.96	0.048
1/10 ONM	1.01	0.096
1/2 ONM	1.03	0.096
ONM	0.98	0.12

In this study, ONM media, containing 0.91 g/l of phosphorus and 1.13 g/l of potassium, were used for microbial growth. However, supply of the elements into a medium might not be required since contents of P and K in MSWFA are usually reported to be 5,000-6,000 mg/kg and 2.5-5.5 %, respectively (18), which reduces operational costs. Effluent from sewage treatment plants also could be one of the possible contributors to inexpensive medium making. Moreover, a process that combines the strain TM-32 with another sulfate oxidizing bacterium such as *Thiobacillus ferrooxidans* should be considered in order to use tailings from mines such as sulfide minerals as a source of sulfur. However further studies are needed for confirmation of the possibilities.

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CHAPTER VII

CONCLUSIONS

The following conclusions were drawn from this study:

1. Considering to world availability of metallic elements, there are many elements which are classified into the group with need of urgent reaction. Mercury, arsenic, and lead especially need special attention.

2. The total annual generation amount of municipal solid waste incineration ash (MSWA), thermal power station coal ash (PSA), and sludge incineration ash from wastewater treatment facilities (WTSA) was estimated as approximately 9.0 million tons / year. Total amounts of metallic elements in the ashes were also estimated, and loss of metallic elements, especially heavy metals, associated with ash disposal was found to be considerably large. Environmental deterioration by the metals was concerned.

3. The final stage recycling was defined and proposed. Importance of the recycling process was emphasized, and benefits by the process were concluded to be conservation of natural resources, reduction of soil toxicity, and reduction of the potential risk of toxic metal exposure.

4. Economic, environmental, and health-related impacts were discussed concerning the loss of metallic elements associated with the disposal of ash. It was found that, in amount, approximately 30 %, 22 %, and 45 % of the aluminium, lead, and zinc,

respectively, that were recycled by the front stage recycling could have been recovered by the final stage recycling. Importance of recognition of the metallic element recovery from ash was pointed out in order to reduce impacts to the environment and human beings.

5. Processes of heavy metal removal from MSWFA, that is, hydrochloric acid leaching, chloride evaporation, acetic acid leaching, and biological leaching, were evaluated and compared with six factors, namely, energy consumption, process efficiency, process handling, process cost estimation, cost reduction potential, and study progress. Hydrochloric acid leaching process was found to be most balanced among the 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 and was expected for further improvement.

6. To develop a better bioprocess than the one of Bosshard et.al., tests of heavy metal extraction from municipal solid waste incineration fly ash (MSWFA) were conducted using *Thiobacillus* spp. strain TM-32, isolated from soil at a hot spring site. Six types of MSWFAs were collected from actual incineration plants. Despite of the different ash sources, the samples showed approximately the same percentages by heavy metal extraction. They were 55.3-68.5 % , 57.4-84.6 %, 2.2-19.6 %, and 38.8-56.4 % for Cd, Cu, Pb, and Zn, respectively. Pb extraction percentages were generally very low because of production of lead sulfate which had a low solubility to water.

7. It was found that amounts of treatable ash depended on sulfate accumulation in cultures. To treat large amounts of ash, large sulfate accumulation was essential. Sulfur free culture, which does not contain powdered elemental sulfur, was employed for the tests and showed a higher extraction percentage than original ONM culture. For cost reduction of medium preparation, it was discovered that nutrients which were in some concentration were required for expecting high microbe growth rates. Nutrient concentration could be reduced to a tenth of that of the ONM medium, containing 0.21 *g/l* of nitrogen.

8. Despite of the fact that, on some elements such as Cd and Pb, lower heavy metal extraction percentages were yielded in the process with *Thiobacillus* spp. than in the one with *Aspergillus niger*, results from laboratory experiments indicated that the former process had more feasibility than the latter, especially in terms of process operation cost reduction.

CHAPTER VIII

RECOMMENDATIONS AND ENGINEERING CONSIDERATIONS

1. Influence on Front Stage Recycling by installation of Final Stage Recycling should be investigated, which may be very important for balancing the two recycling processes in social material flow.

2. Qualitative and quantitative investigations may be needed for environmental and health-related impacts by ash disposal and recycling in order to strength the arguments.

3. Study on biological process for heavy metal removal from MSWFA has just begun, and employment of different types and species of microorganisms should be also examined. Bioprocess has huge potential for development and should be encouraged more for heavy metal recovery from waste.

4. Improvement of the Pb extraction percentage needs further investigation. One possible strategy for the achievement may be use of consortium culture for extraction of the metal.

5. Construction of reactors should be considered, and feasibility of shortening reaction duration should be investigated. Not only physico-chemical and biological processes are applied independently but also combination of the two should be considered for recovery of metallic elements from MSWFA.

6. For pursuing more reduction of running cost, substitution of elemental sulfur should be investigated. Tailings from mines such as sulfide minerals might be used as alternatives by combining the strain TM-32 with other sulfur oxidizing microbes.

7. In the case of wastewater treatment facilities, only WTSA, which accounts for 63 percent of generated waste, was discussed in Chapter II. However, wasted sludge carries considerable amounts of metallic elements and accounts for the other 37 percent. The final stage recycling also should be applied to this type of waste as well as incineration ash for the purpose of reducing environmental impacts.

8. Landfill sites in Japan should be given function of reactors instead of dumping sites. Bioleaching process might be suitable for large scale applications, for example, direct heavy metal leaching process for controlled landfill sites rather than reactor process. A waste treatment system more elaborate than the current one should be proposed and developed for mutual benefits between the human and nature .

APPENDICES

Appendix I

Minamata disease (1) (2):

Around 1956, a disease of central nervous system was seen often in the area of Minamata Bay of Kumamoto Prefecture in Kyushu Island, and it was officially recognized as Minamata disease. The disease started being seen after around 1953. In 1963, Kumamoto investigation team reported that the disease had been caused by methyl mercury compounds, which were discharged by a chemical company. Acetaldehyde was produced from acetylene with inorganic mercury catalyst used. The production completed when the catalyst became organic compounds, and methyl mercury, produced as a by-product as a result of depleted reaction of the catalyst, was mixed with wastewater and discharged into the river. Because of bioaccumulation of the chemical and the food chain, people who had eaten fish and shells of the bay caught the disease. A similar disease was found in Niigata Prefecture in 1963 and, two years later, also recognized as Minamata disease, caused by the same pollutant discharged by another company.

In 1973, compension was agreed upon with consolation money and medical treatment costs paid to the patients (2,260 in Kyushu, 690 in Niigata). Reconciliation between the patients, the companies, and governments was made in both Minamata cases in 1996. The number of patients' applications for registration reached more than 6,000 in 1978.

Itai-itai disease (3) (4):

The symptom of the disease at the first stage was femoral pain or lumbago. Pains gradually spread to the entire bodies, and patients at the final stage were disturbed in sleeping and limited in taking breathes. The name of "itai-itai (ouch-ouch)" came from the fact that the patients always appealed for their pains. The disease expanded along the Jintsu River in Toyama Prefecture of the main land of Japan, and the cause was attributed mainly to cadmium (Cd) contained in discharges from a mine which was located up the river. Cd reached to human via fish, domestic animals, rice, and vegetables and softened of bones (osteomalaia) by loss of calcium (Ca) and imbalance of internal Ca in consequence of kidney urethral disorder. The number of registered patients were 210 by 1978, and more than 661 patients are under intensive observation.

Love Canal incident (5) (6):

In 1978, approximately 400 families were evacuated from the Love Canal in New York, US due to contamination of the area by carcinogenic and hazardous materials such as dioxin, where strange diseases and deaths of inhabitants with unknown cause had been often seen. Back in the US history, Colonel William Love who had a plan to build chemical plants decided to make a canal at the upstream of the Niagara Rivers for electricity generation. The plants and the electric power plant were better to be close since direct current was used at that time and most of electricity was lost during transmission. However, shortly after the canal construction started, a new way of use the form of electricity, alternating current, was invented, and electricity came to be transmitted with modest loss. Then, the power generator did not need to be constructed next to the plants, and the partly completed canal suddenly became meaningless. The canal was used as a dump site and filled with chemical wastes. Years later, residential subdivision was built along both sides of the canal, and people moved in without knowing previous figure of the area. They began to be harmed by the chemicals that oozed up from the ground.

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Appendix II

RELATIONSHIP BETWEEN GROWTH RATE OF SULFUR OXIDIZING BACTERIA AND pH DECREASING RATE (1)

A basic relationship for microorganisms is defined as follows;

$$\mu = (1/X)(dX/dt) = Y(1/X)(dS/dt) - d \qquad (1)$$

where, μ = specific growth rate (day^{-1}), X = concentration of microorganism (mg/l), Y = yield coefficient (mg/mg), S = concentration of substrate utilized (mg/l), d = endogenous decay coefficient (day^{-1}), and t = time (day). Sulfur oxidizing bacteria obtain energy by oxidizing sulfur, and consequently sulfuric acid is produced. Therefore, the following relationship can be drawn;

$$(1/X)(dX/dt) = h(1/X)(dH/dt) - d \qquad (2)$$

where, h = proportional constant and H = concentration of hydrogen ion (mol/l). Considering the relationship of $\mu >> d$ in exponential growth stage, Eq. (2) becomes;

$$dX/dt = h(dH/dt). \qquad (3)$$

Eq. (3) can be rewritten by a integration;

$$X - X_o = h(H - H_o) \qquad (4)$$

where, X_O = initial concentration of microorganism (mg/l) and H_O = initial concentration of hydrogen ion (mol/l). When $X >> X_O$ and $H >> H_O$ are considered, Eq (4) can be expressed as

$$X = h(H). \tag{5}$$

Substitution of Eq. (3) for h, Eq. (5) becomes;

$$(1/X)(dX/dt) = (1/H)(dH/dt) = d(\ln H)/dt. \tag{6}$$

Since pH = - log H, the following relationship is finally obtained;

$$\mu = -(2.3)\{d(pH)/dt\}. \tag{7}$$

Eq. (7) shows that pH decreasing rate (- d(pH)/dt) is proportional to specific growth rate (μ).

Reference

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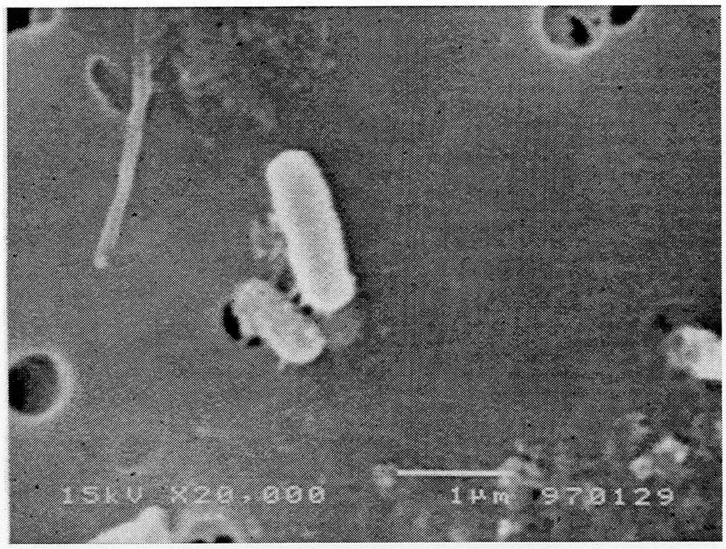
Appendix III



Thiobacillus sp. Strain TM-32