J. of Korean Inst of Resources Recycling
Vol.1, No.1, December 1992, 86-93

≫ 技術解說 ≪

The Recovery of Metals from Secondary Sources
-A Review-

K.N. Han
Department of Metallurgical Engineering South Dakota School of Mines and Technology

1. TREND IN METAL PRODUCTION IN U.S.

Scrap from various sources represents an important component of the domestic supply of various materials especially metals. When we look back the history of the mankind, we see that the major type of metals used by the humankind has changed as the civilization has developed new taste and needs. As we are ready to enter the twenty-first century, such behavior seems to be repeating itself. Although the major metal currently used most is still the iron-based alloys, it has been the trend that light and strong metals or materials are gradually replacing the heavy use of iron. It is remarkable to note that the use of so called "advanced materials" is increasingly frequent and the rate of use of more traditional materials is declining. Since the 70's energy crisis, the size of various household machines and equipment has been continually reduced. The reduction in size of automobiles is a good example.

Table 1 lists the annual growth rate of U.S. demand in selected materials including basic metals, agriculture materials, building materials and advanced materials. As can be seen in the table, the growth rate of the traditional metals such as iron and lead is declining rapidly, while that of advanced materials such as gallium and germanium is increasing sharply.

As can be seen in the above table, the growth rate of more traditional metals such as iron and lead is continually declining and that of so called High-Tech metals such as Gallium and Germanium is incredibly high.

Prior to the recent trend in the popular demand in electronic materials, the wealth and strength of a nation

Table 1. Annual Growth Rate of U.S. Demand in Selected Materials(1971-1985)[1]

Basic Metals	% growth rate
Al	2.3
Cu	0.7
Fe Ore	-3.6
Iron & Steel	-0.7
Pb	-1.2
Zn	-1.2
Agriculture Materials	
Phosphate rock	2.7
Potash	2.0
Sulfur	1.8
Building Materials	
Cement	0.4
Sand and Vravel	-0.8
Advanced Materials	
Co	1.1
Ga	8 7
Ge	4 9
Plastics	6.2

Table 2. Non-ferrous Metals Consumption Dollars per Capita[1).

	1962	1973	1984
Total World	6.0	9.6	8.7
U.S.	32 5	50.7	39 9
USSR	11 8	17.5	21.1
Japan	10.7	43.5	44 0
OECD	17.8	26.6	26.6
Developing Nations	0.8	1.4	1.9

was judged based on the consumption rate of non-ferrous metals. As can be seen in the following table, the consumption of non-ferrous metals by the so called advanced nations, notably the U.S. is declining or stagnant at best in recent years.

It is important and informative to examine the trend of the use of various common metals by the U.S.

1.1. Iron and Steel

▶The Production of Iron in the U.S.(10^6 long tons)[2]

	1987	1988	1989	1990	1991
Production	47.6	57.5	59.0	56.4	53.7
Imports	16 8	20.2	19.6	18 1	13.1

Iron is regarded traditionally as the most important metal in the U.S The consumption of this metal represents about 90% of the total value of metal consumption in the U S. However, the iron and steel industry sufferd a severe setback since 1970. The competition against less developed countries such Taiwan and Korea has been increasingly sever. In addition, this industry has been greatly affected by the recent trend of the use in energy efficient materials by many industries.

1.2. Aluminum

The aluminum industry is one of few which have been adversely affected too much by the 70's energy crisis. However, it also has been going through a similar hardship due to the downsizing trend in the 80's by

▶The Production of Aluminum in the U.S.(1,000 long tons)[2]

	1987	1988	1989	1990	1991
Production					
Primary	3343	3944	4030	4048	4100
Scrap	852	1045	1011	1359	1300
Imports	1850	1620	1470	1514	1400

numerous industries such as the electronic industry. The production of aluminum was negatively affected in mid 80's as seen in the above figure. However, there is a positive growth in the production in the recent years primarily due to the increase sales in the beverge industry, which uses aluminum cans. Due to the excellent ratio of strength/mass, the use of aluminum in car and airplane industries helps the productivity of aluminum in the U.S.

The role of scrap in the overall procuction of aluminum is very notable in the figure. For example, in 1990, about 25% of aluminum production came from recycling of scrap.

1.3. Copper

▶The Production of Copper in the U.S.(1,000 metric tons)[2]

	1987	1988	1989	1990	1991
Prpoduction					
Primary	1127	1406	1477	1577	1590
Scrap	498	518	548	535	545
Imports	469	332	300	262	260

The consumption of copper over the period of 72—82 showed a decline of about 20%. This trend was attributed to remarkable improvement in energy efficiency in the equipment used in energy related areas such as air-conditioning and heating Furthermore, the replacement of aluminum for copper in areas such as automobile and high voltage power industries as well as in fiber optics. In recent years however, due to attrac tive price, U.S domestic copper refineries have been activated in production.

In the case of copper too, the role of scrap on the overall production is notable. In 1990, about 25% of the copper production was derived form scrap.

1.4. Lead

▶The Production of Lead in the U.S.(1,000 metric tons)[2]

	1987	1988	1989	1990	1991
Production					
Primary	336	371	379	386	330
Scrap	658	691	842	874	840
Imports	188	152	122	97	110

As the case of copper, the consumption of lead too has been declining. In 1988, only a 65% capacity of lead refinery was in operation. The restriction in the use of lead in automobile gasoline and the downsizing of car batteries could be the main reason of this decline. Besides, replacement of titanium and iron oxide for lead in the pigment industry has added the declination of lead usage in the U.S.

It should be noted that about 69% of the lead production in 1990 was coming from scrap

1.5. Zinc

▶The Production of Zinc in the U.S.(1,000 metric tons)[2]

	1987	1988	1989	1990	1991
Production					
Primary	261	241	263	262	260
Scrap	82	97	117	109	120
Imports	694	665	724	775	820

The use of zinc over the 72—82 period was decreased by 50% due to the oil crisis in the 70's. The reasons for this decline are similar to those of the lead case. In addition, zinc is being replaced by aluminum and plastics in many industries.

The contribution of scrap to the total production in 1990 was about 29%.

1.6. Gold

▶The Production of Gold in the U.S.(1,000 metric tons)[2]

	1987	1988	1989	1990	1991
Production					
Primary	112	138	184	205	190
Scrap	109	134	164	168	190
Imports	120	93	153	98	190

Unlike any other metals, the production of gold in the U.S. is continually growing. In 1975 there were only 120 gold mines existed in the U.S. but in 1985 the number increased to 210. About 58% of gold use is found in jewelry and arts, 35% in electronic industry and 7% in dental application.

In 1990, about 45% of gold was produced from scrap.

2. CHARACTERISTICS OF SCRAP RECYCLE

It is very obvious that recovery of metals from scrap is becoming important as the primary source of these metals becomes scarce. For example, over 30 million vehicles are scrapped annually, one third being in the U.S. It has been estimated that about one ton of iron and steel, 30—50 kg of aluminum and more than one kg of lead, copper, zinc and other minor metals can be recovered per car[3].

Table 3 shows annual scrap values produced in the U.S[4]. It is interesting to see that added value of steel is $\$6 \times 10^9$, that of aluminum $\$2 \times 10^8$ and that of copper is $\$1.5 \times 10^8$. Furthermore, values of less common metals such as germanium, titanium and gallium are also significant.

Table 4 presents comparative economics of metal production costs for the recovery from scrap and from

Table 3. Scrap Metal Values Produced in the U.S.[4)]

▶ Large Streams-Low-prices Metals

	Annual Amt. Millions of S Tons	Annual Growth, Pct	Value, Millions of Dollars	Added Value Millions of Dollars
Steel	3 5	2	10,000	6,000
Aluminum	1.5	2.5	1,200	200
Copper	1.4	1.5	700	150

▶ Small Streams-High-priced Metals

	Annual Amt. Millions of pounds	Annual Growth, Pct	Value, Millions of Dollars	Added Value Millions of Dollars
Superalloys	20	15	200	30
Germanium	0.2	6	100	10
Titanium	20	10	50	10
Gallium	0.02	50	6	3

Table 4 Economics of Metal Production Costs(cents/pound)[4)].

	Capital			Operating Cost		
	Scrap	Virgin	Ratio	Scrap	Virgin	Ratio
Steel	*10−20*	*20−25*	2 : 1	4−5	10−15	3 : 1
Aluminum	20−30	200−300	10 : 1	18−22	40−60	3 : 1
Copper	20−30	200−400	12 : 1	16−20	45−60	3 : 1

virgin source[4)].

As can be seen in the above table, capital and operating costs of scrap are much more economical than those of virgin ores. In general, the capital cost for scrap processing is about one tenth of that for primary sources, While the operating cost for scrap is one third of that for primary sources

It should be pointed out that the recovery strategy of metals from scrap and that from the primary sources are quite different. There is an inherent major differenece in *the physical and chemical association between metals* and their environment in scrap and primary sources.

Metals occur in nature as sulfides or oxides, while their occurrence in secondary sources is quite differnet in that they are frequently associated with other metals to form alloys.

A number of investigators have been working on the effective recovery of metals from electronic scrap[5−15)]. Most of these investigations have focused on hydrometallurgical treatments rather than pyrometallurigical approaches. Some important reasons for the hydrometallurgical process instead of the pyrometallurgical process are ' hydrometallurgical processes are environmentally more acceptable, easier separation of multi-components, and lower production cost.

As noted earlier, in most scrap metals occur not as a single component but as parts of alloys. The extraction behavior of a metal from alloys is much different from that of the individual metal from its natural ores. Unfortunately, there is little information available in the literature on the extraction behavior of the individual metal element from various alloys.

3. LEACHING BEHAVIOR OF ALLOYS

Researchers at the South Dakota School of Mines and Technology have been working on a systematic study on the leaching behavior of gold, silver and copper alloys [16–20]. Some typical examples will be given below.

Fig. 1 represents dissolution behaviors of copper and gold from an alloy consisting of 52% gold and 48% copper. The leaching was carried out at 25℃ with 5% nitric acid, 5% sulfuric acid and 5% hydrochloric acid in the presence of 0.45% sodium hypochlorite as an oxidant[19]. As can be seen in this figure, copper is extracted much faster than gold. As a matter of fact, gold practically does not dissolve out into the solution until copper is dissolved nearly in completion.

The leaching rate of silver and copper from silver/copper alloys was studies in a solution containing 0.1 M sulfuric acid and 0.004 M ferric sulfate at 35℃ [16–18]. As can be seen in Fig. 2, the dissolution rate of copper increases as the silver content in the alloy increases, while the dissolution rate of silver drops sharphy with increase of the copper content in the alloy. This is

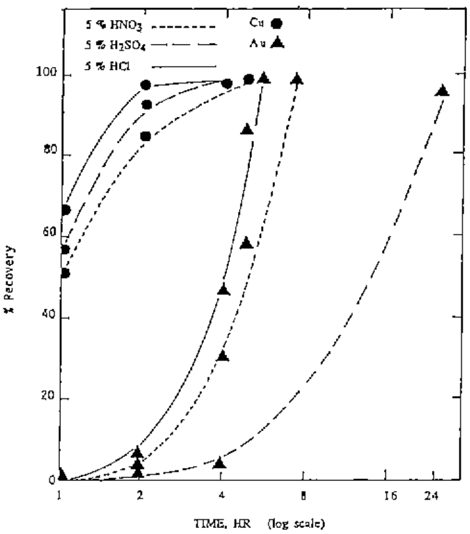

Fig. 1. Leaching behavior of gold and copper from an Au/Cu alloy in various acid solutions at 25℃ [19].

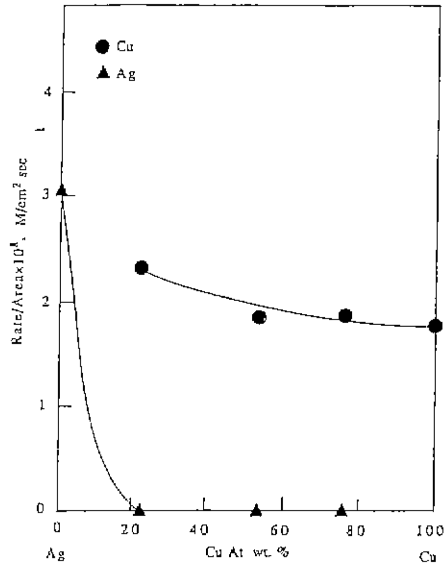

Fig. 2. Effect of composition on the dissolution rate of silver and copper from Ag/Cu alloys at 35℃. H_2SO_4, 0.1 M ; $Fe_2(SO_4)_3$, 0.0004 M[16].

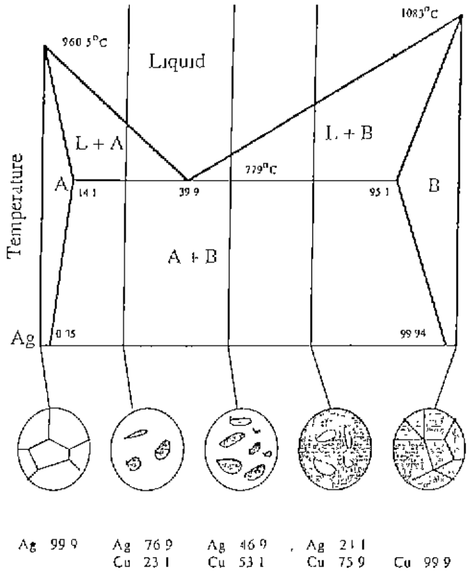

Fig. 3. Phase diagram for the silver-coper system. Also shown micrographs of alloys with varing compositions. Shaded region represents the phase B[16].

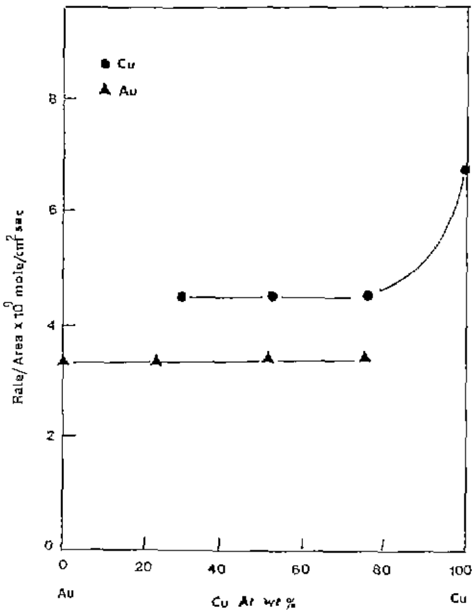

Fig.4. Effect of composition on the dissolution rate of gold and copper from Au/Cu alloys at 35℃. NaCN, 0.02 M[20].

definitely a galvanic effect on the rate of dissolution of these two metals. Since silver is more noble than copper, copper dissolves readily into the solution, while the rate of dissolution of silver is affected adversely. Such a galvanic effect is usually pronounced when the distribution of metals in the alloy is characterized by a distinctive grains as shown in the phase diagram in Fig. 3. The size of these grains were found by a scanning electron microscope to be 50−100 microns[16].

On the other hand, when two metals in the alloy are of solid solution, namely these metals are uniformly mixed at the molecular level, the dissolution rates of two metals involved in the alloy will not behave according to the galvanic couple. The dissolution of gold and copper from gold/copper alloys was investigated[20] in 0.02 M cyanide solutions with oxygen as the oxidant at 35℃. The results are shown in Fig. 4. The dissolution of gold was not affected at all by the presence of copper in the matrix of the alloy, while the rate of dissolution of copper was adversely affected from pure copper to alloy. This is believed to be due to the chemical bond strength of Cu-Cu, Au-Au and Au-Cu. The chemical bond strengths of Cu-Cu, Au-Cu and Au-Au are about 176 kJ/mole, 228 kJ/mol and 225 kJ/mole, respectively[21].

4. EXTRACTION OF METALS FROM MUNICIPAL SEWAGE

In the United States, about 9.3 million dry tons[22] of municipal sewage sludge is generated annually, of which 20−35 percent is incinerated. The metro plant in the Minneapolis-St. Paul area processed 195 tons of sludge per day which resulted in 58 tons of incinerated ash in 1985[23]. Gabler[22] determined the chemical composition of the incinerated sewage ash for 14 plants in 11 U.S. cities. Typical results of these studies contains a variety of metal elements including industrially valuable metals with varying quantity. In the list, it can be seen that this ash contains a substantial amount of gold, in the order of 0.02−1.0 oz/ton. This amount of gold is sufficient enough to regard this ash as a gold ore.

As we enter the 21st century, the ever increasing technology demands better management of resources and waste. The U.S. government is reacting to the call for resource and waste consciousness in the private and industry sector. The Environmental Protection Agency has issued recently guidelines for stringent permit requirements for sewage sludge[24].

It is imperative and timely to study the most effective and efficient method of extraction important metal values in view of resource recovery as well as removal of hazardous elements to make the sewage ash a safe product. In order to extract metal elements from any source materials, it is desirable to identify the associt tion of these metals with the surrounding environment. Studies have been carried out to identify the mineralogical status of various elements in the sludge[25].

Gabler[22] studied the extraction behavior of silver, bismuth, cadmium, cobalt, chromium, copper, manga

Table 5. Chemical Composition of Incinerated Sewage Sludges[22].

Major elements	wt %
Al	1 2 — 7.05
Ca	.79 — 27.60
Fe	1 59 — 15.16
Mg	.28 — 10.06
P	1 15 — 5.68
Si	9.29 — 42.01
Na	.061 — 2.3
Ti	.20 — 1.45
LOG	.18 — 15.66
Trace elements	**ppm**
Ba	1,200 — 8,700
Bi	58 — 150
B	3 — 30
Cd	6 — 96
Cr	52 — 3,600
Co	11 — 290
Nb	3 — 30
Cu	210 — 7,300
Ga	10 — 1,000
Pb	160 — 1,700
Li	7 — 66
Mn	260 — 2,400
Mo	3 — 100
Ni	19 — 1,500
K	1,300 — 14,100
Rb	30 — 3,000
Ag	24 — 575
Sr	12 — 950
Sn	30 — 1,000
V	30 — 1,000
Zn	570 — 5,000
Zr	30 — 1,000
Au	0.02 — 1.0 oz/ton

nese, nickel, phosphorus, lead and zinc in acidic media. He used rather a high concentration of sulfuric(25 wt%), nitric(25 wt%) and hydrochloric(conc.) acids and found reasonable recoveries of these metal elements. There has also been a study on the leaching behavior of metals including gold and silver using thiourea with reasonable recovery values for these metal elements. However, these methods required a high reagent consumption resulting in high cost of the treatment.

The study carried out using the conventional cyanide leaching at the author's laboratory indicated that the extraction recovery of gold is over 85% after 24 hours of leaching. However, the extraction of silver was shown to be a mere 10%[26,27].

It is apparent that there needs to be a systematic research to be conducted to identify the best way to extract valuable metal elements from the sewage ash which could then be disposed to a safe product. Recently, researchers in the author's laboratory have developed an extraction of gold and silver using ammonia solutions [28,29]. This technology has been tested on an incinerated ash of industrial sewage and the results showed very encouraging. The advantages of this technology over other acid based techniques include low reagent consumption, and very efficient recovery of valuable metals such as gold, copper, silver, zinc and nickel.

REFERENCES

1. H.Enzer, *Miner. Proc. Ext. Met. Rev.*, **3**, 11—28(1988).
2. Anon, "Mineral Commodity Summaries," U.S. Bureau of Mines, 1992, 204p.
3. H.spoel, *Journal of Metals*, April. 38—41(1990).
4. N Jarrett. *Met. Trans. B.*, **18B**, 289—313(1987).
5. B.W. Dunning, Jr. et al., USBM, RI 8788(1983) 17p.
6. R.C. Horton, in "Materials Substitution and Recycling," Proc. of 57th Meeting of Structures and Materials Panel in Vimeiro, Portugal. 1983, 24p.
7. B.W, Dunning, Jr and F. Ambrose, USBM, RI 8499 (1980) 20p
8. H.E Hillard et al , USBM, RI 8757, 1983, 15p.
9. R.Newell et al., USBM, RI 8940, 1985, 20p.
10. H E. Hillard et al., USBM, RI 8940, 1985, 20p.

11. H.B. Salsbury et al., USBM, RI 8561, 1981. 16p

12. R.W. Dunning, Jr., USBM, IC 9059. 1986, 13p.

13 S.O. Heimala et al., U.S. Patent 4,002,544, 1977.

14. B.Kolodziej and Z. Adamski, *Hydromet.*, **12**, 117 (1984).

15. W. Kunda, *Hydromet.*, **7**, 77(1981).

16. Y.U. Choi, "Dissolution Behavior of Silver and Copper from Silver-Copper Alloys," Ph.D. Thesis, South Dakota School of Mines and Technology, 1990, 155p.

17. Y.U. Choi, E.C. Lee and K.N. HaN, *Met. Trans. B*, **22B**, 755−764(1991).

18. Y U. Choi, and K.N. HaN, *Min. Proc. Ext. Met. Rev* , **9**, 43−60(1992).

19. P.Pupanthong, "Leaching Behavior of Copper, Silver and Gold from Alloy, "Leaching Behavior of Copper, Silver and Gold from Alloys," M.S. Thesis, South Dakota School of Mines and Technology. 1989, 67p.

20 Y. Guan and K.N. Han, "The Dissolution Behavior of Gold and Copper from Gold and Copper Alloys," 121st AIME Annual Meeting, Phoenix, AZ, February 24−27, 1992. Preprint 10p.

21. D.R. Lide, Handbook of Chemistry and Physics, 71st ed., CRC Press, Inc., 1990−1991

22. R.C. Gabler, Jr., "Incinerated Municipal Sewage Sludge as a Potential Secondary Resource for Metals and Phosphorus," USBM, RI 8390, 1982, 23p.

23. H.C. Grounds, "Combining Waste Treatment and Mining Technologies for Incinerator Ash Management," Prepared for presentation at WASTECH ' 87, San Francisco, CA, October 27, 1987, 12p.

24. Anon, "Guidance for Writing Case-by-Case Permit Requirements for Municipal Sewage Sludge," Office of Water Enforcement and Permits, U.S. Environmental Protection Agency, Washington, D.C , EPA/505/8−90/001, May 1990, 243p.

25. S.P. Brandom, E.J. Fregeau and R.T. Brandom, "Mineralogy of Municipal Sludge Ash," MRRC, Univ. of Minn., 1987, 40p.

26. K.N. Han, *Final Report to Governor's Economic Dvelopment Offices*, Pierre, South Dakota, October 31, 1989, 49p.

27. K.N. Han, "Chemical and Physical Treatment of the Sewage Ash at Edgemont," Final Report to Department of Water & Natural Resources, State of South Dakta, January 26, 1989, 15p

28. K.N. Han, X.Meng. Proceedings of Randol Gold Forum, Randol International (1992), 213-218.

29 K.N. Han and X.Meng, U.S. Patent 5,114,687, May 19,1992

먼지제거기 국산화－작업장 개선

－<환경>작업장 먼지제거기 국산화…한국신동공업－

수입에 의존해 오던 공장내 유해가스 및 먼지 제거기가 최근 국내 기술진들에 의해 1백% 국산화 개발에 성공했다.

(주) 한국신동공업(손익주)은 15일 "공장내 생산설비로부터 발생하는 각종 유해가스와 먼지를 제거할 수 있을 뿐 아니라 열 손실을 극소화해 에너지 효율을 높일 수 있는 한국형 집진기를 개발했다"고 밝혔다.

한국신동공업측이 개발한 집진기는 분진원을 발생 시점에 빨아들여 마스크 없는 작업환경을 가능케 할 것으로 기대되고 있다.