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Acid Leaching of Indium-Lead-Tin Alloy Wire Scrap

by

M.A. Barakat† and K. Koike††

ABSTRACT

Acid leaching of indium-lead-tin alloy wire scrap has been studied. An experimental study was excuted to produce leaching liquor for subsequent separation of the concerned metals from the scrap material. Two leaching solutions were investigated ; hydrochloric acid and hydrochloric-nitric acid oxidation leaching. Parameters affecting leaching processes such as time, temperature, acid concentration and acid : scrap stoichiometric ratio have been evaluated. Results obtained revealed that hydrochloric acid failed to extract metals completely, the maximum extraction efficiency was in the order of indium 97.1, lead 94.1 and tin 89.2% by using 5M HCl for 6 hours at 95℃, HCl : scrap ratio was 5. Addition of nitric acid as oxidizing agent resulted in complete extraction for metals, the optimum leaching conditions were conducted by addition of 0.6 ml of 1 : 1 HNO_3／g scrap to the leachate of 5M HCl for 1.45 hours at 80℃ with HCl : scrap ratio of 2.5. Another advantage for using of HCl-HNO_3 leaching was that about 71% of the lead content was separated as pure crystals of $PbCl_2$ on cooling the resulting solution.

Key Words : Alloy scrap, Metals extraction, HCl-HNO_3 acid leaching

1. INTRODUCTION

Different hydrometallurgical processes have been proposed for the leaching of indium, lead and tin from their secondary resources.

Extraction of indium from alloy scrap using mineral acid leaching has been reported [1-3]. Hydrochloric acid (pH 1.2-1.4) was used [4, 5]. Yoshimura [6] used HCl-NH_4Cl solution for dissolving indium scrap to remove tin after adjusting pH to (2.5-4.2). A fine fraction of scrap was leached with aqueous solution of HCl containing H_2O_2 as oxidizing agent at pH (0.5-1.5) to recover indium [7]. Takahashi [8] and Abevova [9] investigated the recovery of indium from slag by using H_2SO_4-H_2O_2 and NaCl-H_2SO_4-H_2O_2-H_2O systems respectively as leaching agents. Sulphuric acid leaching was used to extract indium from Zn-leach residue and In-scrap [10, 11]. Goryachkin [12] used H_2SO_4 acid leaching in an autoclave with heating under pressurized oxygen to extract indium from wastes. Alkaline leaching with NaOH was reported for recovery of indium and tin from a flue dust containing Zn, As, Sb, Sn, Pb and In. [13]

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† Extractive Metallurgy Dept.,CMRDI, P.O.Box 87 Helwan, Cairo, Egypt

†† Mining College, Akita University, Akita 010, Japan

Chloride leaching for lead extraction from wastes as $PbCl_2$ has been reported. Sahoo [14] used brine solution, Mulak [15] used $FeCl_3$-NaCl solution while Ignat'eva [16] used aqueous solution of NaCl after convertion of lead to $PbSO_4$ for leaching. Both of HCl and H_2SO_4 leaching for lead recovery from a waste containing 37.2% Pb and 52.2% Zn has been investigated [17], the dissolution of lead was 5.5 and 22% after leaching with HCl at 20℃ for 24h, and with H_2SO_4 at 20℃ for 0.5h respectively.

Extraction of lead and tin from dust was studied, H_2SO_4 acid leaching was applied [18, 19], Adamski [20] used 30-60% acetic acid for 6-15 h at 50-80℃, while Jackson [21] used a solution contains HNO_3, Fe (NO_3), anthranilic acid and a tenside. Various extractants were tested for selective tin extraction from leachates ; HCl and HCl-$CuCl_2$ mixture were used [22, 23]. Vizsolyi and Forward [24] used H_2SO_4 with a slight oxygen over-pressure, while Lazarova [25] used both of H_2SO_4 and HCl.

The aim of this work was to study the optimum leaching conditions such as acid concentration, temperature and time for extraction of indium, lead and tin from alloy wire scrap material. The work considered saving the energy consumption and economic expenses via simple extraction procedure and low temperature application.

2. EXPERIMENTAL

In-Pb-Sn alloy wire scrap was obtained from a Sealing Company, Chemicals used in this work were of chemically pure grade. Leaching experiments were carried out in a multi-neck 0.5 ℓ cylindrical glass reaction vessel, immersed in a thermostatically controlled water bath. A 100 ml volume of HCl was used for leaching.

One stoichiometric ratio of HCl : scrap was calculated according to the reaction of HCl with the alloying metals as follows : -

$$In + 3HCl \longrightarrow InCl_3 + 1.5H_2 \quad (1)$$

$$Sn + 2HCl \longrightarrow SnCl_2 + H_2 \quad (2)$$

$$Pb + 4HCl \longrightarrow H_2(PbCl_4) + H_2 \quad (3)$$

Metal content of the sample and extracted metals in solution were determined spectroscopically using ICP spectrometer and Atomic Absorption spectrometer. Extraction percentage of metals was evaluated according to the following equ. : Extraction % of metal

= (metal content in extracted solution／metal content in scrap) x 100

3. RESULTS AND DISCUSSION

Table (1) shows the chemical composition of the studied scrap. Figure (1) shows the effect of leaching time on the extraction percentage of indium, lead and tin from the wire scrap using 2M HCl with acid volume of 20 ml／g scrap at 80 and 95℃. It can be seen that indium extraction

Table 1 : Chemical composition of the used wire alloy scrap

Constituent	Indium	Lead	Tin
Mass %	42.3	8.5	49.2

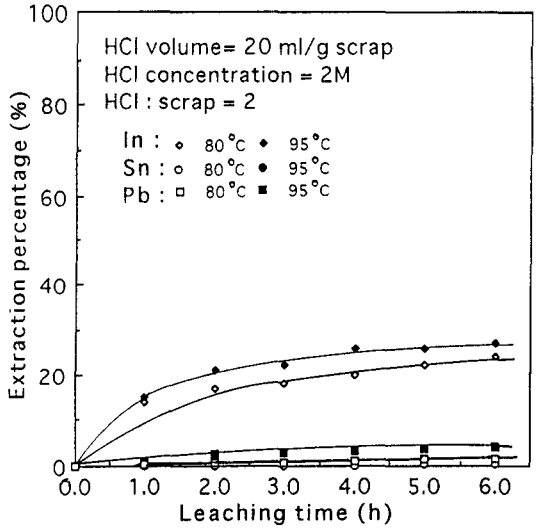

Fig. (1) : Effect of leaching time on extraction percentage of indium, tin and lead from wire alloy scrap using 2M HCl at different temperatures

increases gradually with time and temperature reaching a maximum after 6h with values of 24 and 27% at 80 and 95℃ respectively, lead extraction increases slowly reaching a little significant value of 4% after 6h at 95℃ while tin is nearly disaffected. It is clear that there are different rates for metals extraction in increasing order of tin, lead and indium respectively, however more amount of the acid is required for all metals. Figures (2 & 3) show the effect of leaching time on extraction % of metals by using 5M and 6M HCl with acid : scrap ratio of 5 and 6 respectively (20 ml/g scrap) at 80 and 95℃. In figure (2) with 5M HCl, it is seen that the extraction % of metals is directly proportional to leaching time approaching a maximum after 6h at both of 80 and 95℃, maximum values were attained in decreasing order of In, Pb and Sn with values of 97.1, 94.1 and 89.2 % at 95℃, and of 85.3, 79.4 and 76.1 % at 80℃ respectively. This may indicate that the ability of the acid to extract the metals increases with time and temperature, this ability decreases in the order of In, Pb and Sn respectively. This behaviour can be explained as follows, the general level of the metals reactivity may be evaluated from their positions in the electromotive series of elements, where the standard potential values of the elments (E°) are :

	E° / V	
$In \dashrightarrow In^{3+} + 3e^-$	−0.3382	(4)
$Pb \dashrightarrow Pb^{2+} + 2e^-$	−0.126	(5)
$Sn \dashrightarrow Sn^{2+} + 2e^-$	−0.137	(6)

However, the bonding characteristics of indium influence the apparent reactivity of it, where the bond of trivalent form of indium is relatively nonionic or covalent [26]. On the other hand with tin and lead, the high hydrogen overvoltage at the metal surface inhibits further acid attacking with both of Sn and Pb which require relatively vigorous conditions to occur, this explains the little

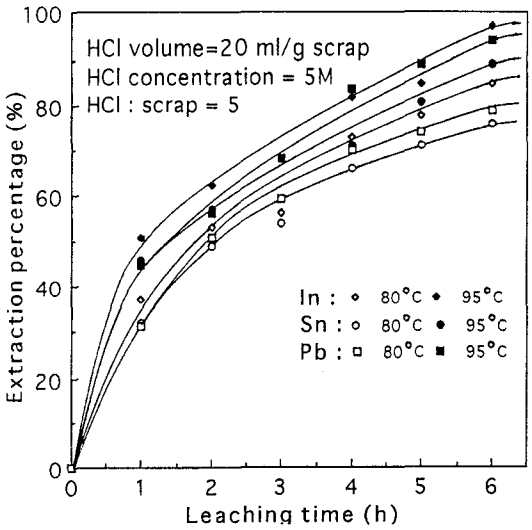

Fig. (2) : Effect of leaching time on extraction percentage of indium, tin and lead from wire alloy scrap using 5M HCl at different temperatures

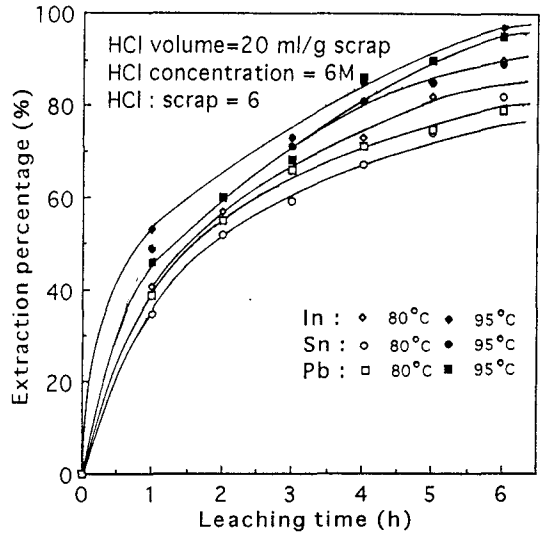

Fig. (3) : Effect of leaching time on extraction percentage of indium, tin and lead from wire alloy scrap using 6M HCl at different temperatures

increasing in extraction % with increasing the temperature from 80 to 95℃. In figure (3), the change in extraction % of metals by using 6M HCl is insignificant comparing to that with 5M HCl specially at higher temperature and time. Figure (4) demonstrates the extraction % as a function of time by using 1M HCl, the used acid volume (100 ml／g scrap) corresponds to HCl : scrap ratio of 5 which is equivalent to that ratio of 5M HCl used in figure (1). It is obvious that the extraction efficiency of metals is nearer to that obtained with 2M HCl (figure 1) which is very low with respect to that of 5M, this indicates that the leaching processes depend mainly on the acid concentration rather than volume. Figures (5 & 6) illustrate the extraction % as affected by HCl concentration with constant volume of the acid (20 ml／g scrap) at 80 and 95℃ after leaching for 3 and 6h respectively. It can be seen that the extraction %

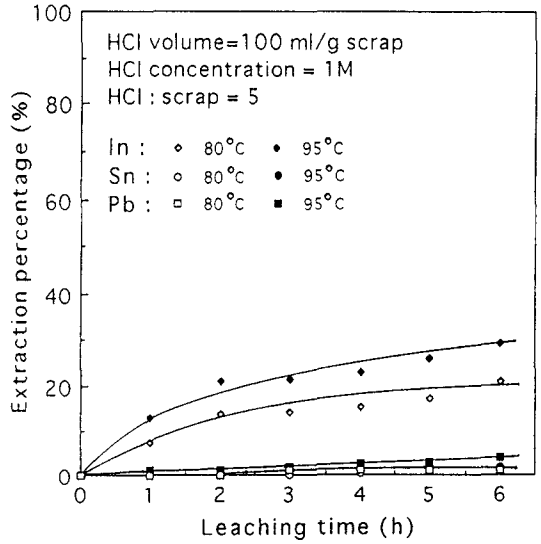

Fig. (4) : Effect of leaching time on extraction percentage of indium, tin and lead from wire alloy scrap using excess of 1M HCl at different temperatures

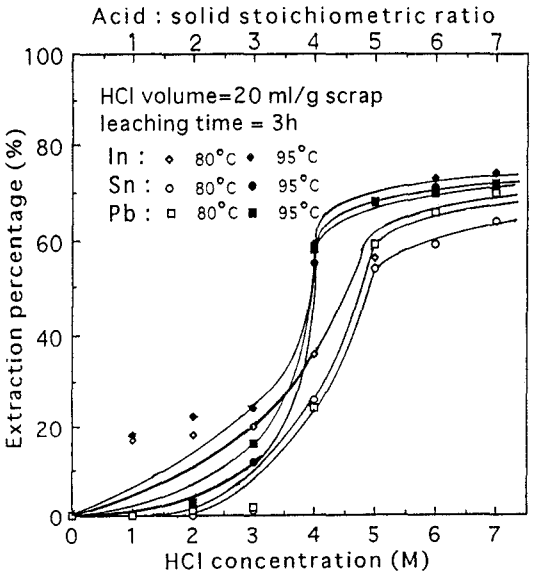

Fig. (5) : Extraction percentage of indium, tin and lead from wire alloy scrap as affected by HCl concentration after 3 hours leaching at different temperatures

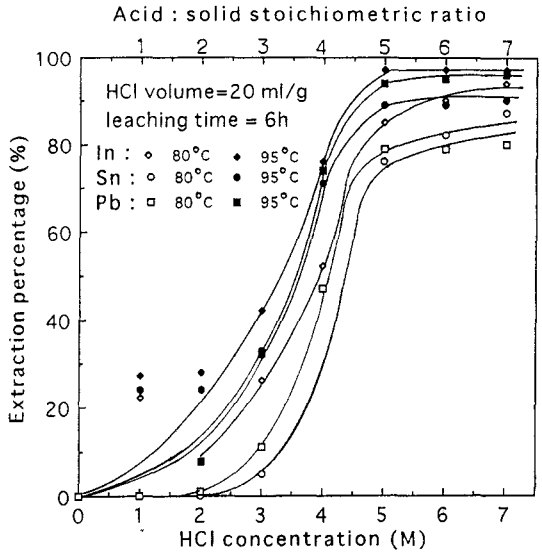

Fig. (6) : Extraction percentage of indium, tin and lead from wire alloy scrap as affected by HCl concentration after 6 hours leaching at different temperatures

increases gradually with HCl concentration up to 3M, while after that a sharp increasing in the extraction % is attained up to 5M HCl with both of 3 and 6h leaching. It is also clear that there is no remarkable change in the extraction with acid concentration more than 5M, maximum and constant values for In, Pb and Sn extraction were attained with 5M HCl at 95℃ for 6h leaching. The drastic increasing in the extraction with HCl concentration more than 3M may be attributed to that the dilute acid can not resist the higher hydrogen overvoltage due to presence of large number of hydrogen bonds in the formed hydration sphere in solution and so the intermolcular distances between the molcules increase, consequently the attacking of the acid to the metals is low. With increasing the concentration, the intermolcular distances decrease and consequently the probability of chloride ions attacking to the metals increases. However complete attacking for the metals was not varied which indicates that more vigorous leaching conditions are required. Figure (7) shows the effect of leaching temperature on the extraction % of metals at the optimum conditions of HCl leaching, it can be seen that temperature increasing favours the extraction % of In, Pb and Sn reaching their maximum values at 95℃, also it is clear that the rate of metals extraction increases in the order of Sn, Pb and In respectively at any leaching temperature which proves the different affinities of acid attacking to the concerned metals.

Effect of nitric acid addition (to different volumes of 5M HCl leachate) on the extraction % is shown in figure (8), the leaching processes were carried out for 3h at 80℃. It is seen that with HCl

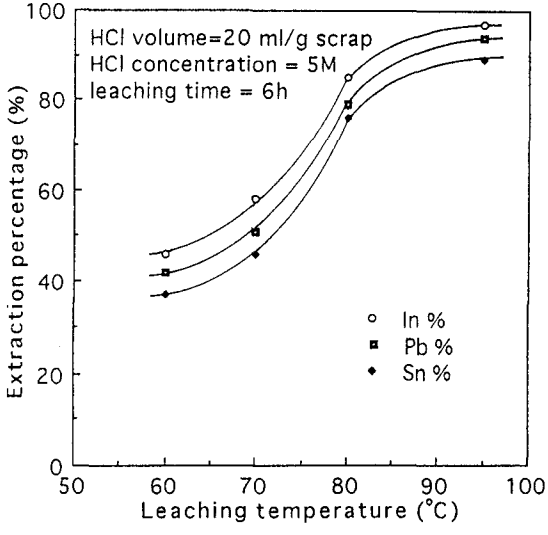

Fig. (7) : Effect of temperature on extraction percentage of indium, tin and lead from wire alloy scrap at the optimium conditions of HCl leaching

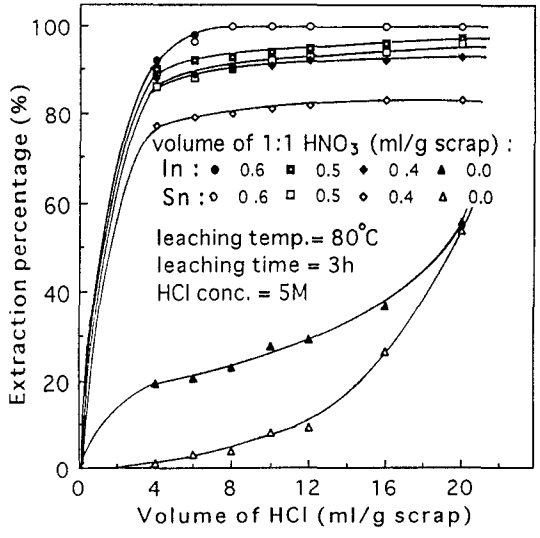

Fig. (8) : Extraction percentage of indium and tin from wire alloy scrap as affected by volume of both of HCl and HNO_3 in their solution mixture at constant time and temperature

solution, the extraction % gradually increases with increasing HCl volume attaining maximum values of 56.3 and 54.1 % for In and Sn with acid volume of 20 ml/g scrap. On the other hand a drastic increasing in the extraction % is achieved by adding a little amount of HNO_3 to the HCl leachate. This is attributed to the oxidizing effect of HNO_3 which overcome the hydrogen overvoltage at the metal surface, and consequently a rapid attacking is achieved between the chloride ions and metals in solution. The extraction % of indium and tin increases with increasing the volume of both of HCl and HNO_3 reaching a complete extraction for the metals with leaching solution composition of 8 ml of 5M HCl and 0.6 ml of 1 : 1 HNO_3/g scrap. A complete extraction for lead also is attained at these conditions, however on cooling the resulting solution, pure crystals of $PbCl_2$ are settled in solution and this considered the first step of lead separation process. According to that at the conditions of partial extraction, the extraction of lead selectively is difficult due to contamination of the insoluble residue of scrap with the produced precipitate of $PbCl_2$ in solution which starts to appear on hot.

$$\underset{\text{complex solution}}{H_2(PbCl_4)} \xrightarrow[\text{cooling}]{} \underset{\text{ppt}}{PbCl_2} + 2HCl \qquad (7)$$

Figure (9) shows the time of complete metals extraction as a function of volume of 5M HCl containing a constant amount of 1 : 1 HNO_3 (0.6 ml/g scrap) at 80 and 95℃. It can be seen that the time of complete extraction decreases rapidly to 103 minutes with increasing HCl volume up to

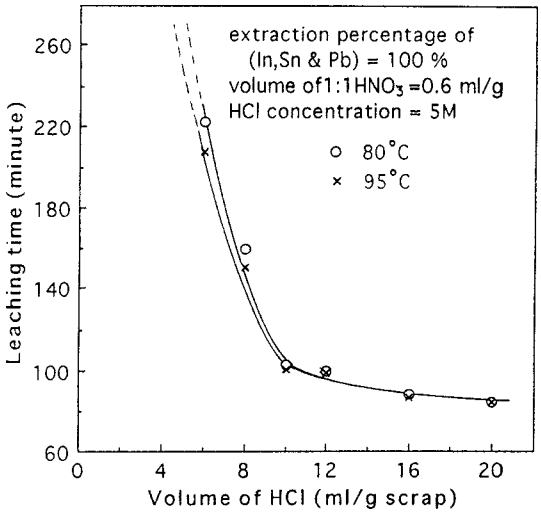

Fig. (9) : Time of complete extraction of indium, tin and lead as affected by volume of HCl solution containing a constant amount of HNO_3 at different temperatures

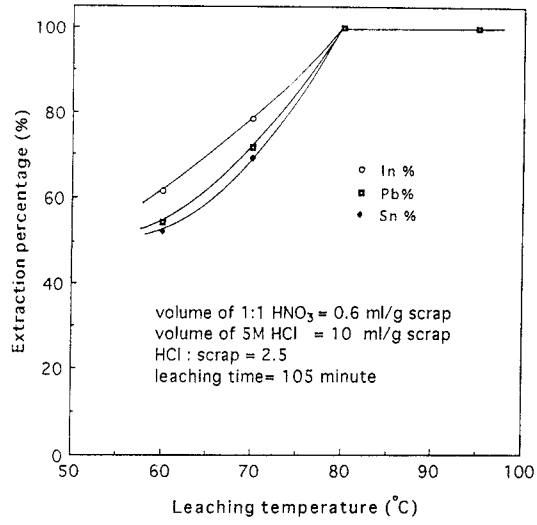

Fig. (10) : Effect of temperature on extraction percentage of indium, tin and lead from wire alloy scrap at the optimium conditions of HCl-HNO_3 leaching

10 ml/g (which is equivalent to HCl : scrap ratio of 2.5) and then with increasing HCl volume, no remarkable change in time is recognized. Also it is clear that increasing temperature from 80 to 95 ℃ is insignificant. Figure (10) shows the effect of leaching temperature on the extraction % of metals at the optimum conditions of HCl-HNO_3 leaching. It is shown that the extraction % increases with temperature increasing reaching a complete extraction for the three metals at 80℃. At lower temperatures than 80℃, the extraction rate of metals increases in the order of Sn, Pb and In respectively.

4. CONCLUSION

The output of this work reveals that indium, lead and tin can be extracted from alloy wire scrap using simple acid leaching technique.

With hydrochloric acid leaching, the maximum extraction efficiency was 97.1, 94.1 and 89.2% for In, Pb and Sn respectively by using 5M HCl for 6h at 95℃ with HCl : scrap ratio of 5. With HCl-HNO_3 oxidation leaching, complete extraction for the metals (100%) is achieved. The optimum leaching conditions are conducted by adding of 0.6 ml of 1 : 1 HNO_3/g scrap to the leachate of 5M HCl for 1.45 h at 80℃ with HCl : scrap ratio of 2.5. The latter leaching solution insures the low cost of the extraction processes via saving acid consumption, time and temperature. Pollution hazards associating pyrometallurgical treatment disappeared.

REFERENCES

1. Nishiyama,Yutaka ; Kimura,Etsuji and Shibazaki,Takeyoshi, "Separation and recovery of indium", Jpn. Kokai Tokkyo Koho JP 63 89,635 (1988) ; 6pp.
2. Molnar,Istvan ; Feher,Ivan ; Vigvari,Mihaly and Vitanyi,Pal, "Processes for enrichment and recovery of indium and gallium components of waste material", Hung. Teljes HU 44,810 (1988) ; 11pp.
3. Yoshimura,Ryoji ; Ogawa,Nobuhiro and Mori,Takashi, "Recovery of indium oxide", Jpn.Kokai Tokkyo Koho JP 03,199,122 (1991) ; 6pp.
4. Kusuhashi,Hiroshi ; Tanaka,Nobuhiro and Minami,Chiaki, "Recovery of indium from residue in zinc-cadmium purification", Jpn.Kokai Tokkyo Koho JP 61,257,438 (1986) ; 4pp.
5. Odo,Shuichi and Yamaki,Tetsuo, "Recovery of indium from acid solution", Jpn.Kokai Tokkyo Koho JP 63,140,047 (1988) ; 2pp.
6. Yoshimura,Ryoji ; Ogawa,Nobuhiro and Mori,Takashi, "Recovery of indium", Jpn.Kokai Tokkyo Koho JP 03,82,720 (1991) ; 7pp.
7. Kubota,Harutoshi ; Minami,Chiaki and Takei,Kazuhiko, "Recovery of indium from scrap", Jpn.Kokai Tokkyo Koho JP 06,65,658 (1994) ; 4pp.
8. Takhashi,Katsuto, "Recovery of indium from slags", Jpn.Kokai Tokkyo Koho JP 05,311,267 (1993) ; 4pp.
9. Abevova,T.A. et al., "Recovering rare metals in treatment of slag sublimates", Proc. Int. Miner. Process. Symp., 5th (1994), 387—91.
10. Matsuda,Masaaki and Aoi,Masahiro, "Separation,recovery and purification of indium...", Nippon Kagaku Kaishi (1990), (9), 976—81.
11. Sakano,Takeshi and Nemoto,Naotoshi. "Recovery of indium from scrap", Jpn.Kokai Tokkyo Koho JP 03,153,526 (1991) ; 3pp.
12. Goryachkin,Vladimir I. et al.,"Processing of zinc sulfide ores and wastes by acid leaching with indium recovery", U.S.S.R. SU 1,822,439, Izobreteniya (1993), (22), 168.
13. Milner,Edward and Perri,Roland, "Recovery of indium and tin", Can. CA 1,214,045 (1986) ; 21pp.
14. Sahoo,P.K. and Das,S.C., " Recovery of lead from zinc plant waste", Trans. Indian Inst. Met. (1986), 39(6), 604—8.
15. Mulak,W. and Wawrzak,D., "Ferric chloride leaching of lead sulfide concentrate", Proc. Int. Miner. Process. Symp., 5th (1994), 373, 7.
16. Ignat'eva,N.I. et al., "Lead recovery by leaching", U.S.S.R. SU 1,355,613 Otkrytiya,Izobret. (1987), (44), 99.
17. Visan,Sanda et al., "Recovery of zinc and lead from metallic wastes", Mine, Pet. Gaze (1987), 38(7), 330—3.
18. Nyitrai,Zoltan et al., "Hydrometallurgical recovery of lead and zinc from flue dust", Rom.RO 92,110 (1987) ; 3pp.
19. Myerson,Allan S.and Cudahy,Michael W.,"Leaching for metal recovery from...", U.S. US 5,431,713 (1995) ; 16pp.
20. Adamski,Zbigniew et al., "Recovery of tin and lead from oxide dust", Pol. PL 129,966 (1985) ;

2pp.
21. Jackson,Brian and Barnett,Gary, "Solution for removal of tin, lead or Pb-Sn alloy deposits from...", Ger. Offen. DE 3,941,524 (1990) ; 7pp.
22. Marshall J.E.F. et al., British Patent 1 278 207 (1972).
23. Burdon R,G.,"Extraction of tin by...",Min. Mag., Land., 110, (1964), 314—5.
24. Vizsolyi A. and Forwaro F.A.,"A process for the extraction and purification of tin by sulfate solutions", In 7th Int. Mineral Process.
25. Lazarova,Z. and Schuegeri,Karl,"Selective extraction of tin from...", Chem.-Ing.-Tech., 66 (6), (1994), 857—61.