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Characterization of Leachate from Lead Free Alloys

Caroline Michael[a] and R.Wilfred Sugumar[b]

a – Department of Physics, Madras Christian College (Autonomous), Tamabaram, Chennai 600 059
b – Department of Chemistry, Madras Christian College(Autonomous), Tambaram, Chennai 600 059, India.
E-mail: wilfmcc@rediffmail.com

Abstract

In the eco-design strategy of developing lead free alloys to replace lead in soldering, evaluating the life-cycle environmental impacts and occupational toxicity of lead-free solders were given importance. One of the evaluating parameters was the potential environmental impact of the solders through leaching when disposed in the landfill. In the present study, the commercially available tin based lead free SAC 305 series and the conventional leaded alloy Sn63Pb37 were allowed to leach in different water samples. The amount of lead and tin from leaded alloy and the amount of copper and tin from the lead free alloys were determined. Leaching of lead and copper for the particle sizes lying between 0.241 to 0.416 mm was found to be more. 12ppm and 26ppm lead had leached at pH 7 and at pH 6 respectively for the same sample. In bore well water, lead had leached to a level of 0.100ppm and 0.318ppm when the leaded alloy was in contact for 7 days and 21 days respectively. During the same contact period of 21 days, 0.115 ppm and 0.318 ppm lead had leached in distilled water and bore well water respectively. Tin did not leach from any of the samples. The amount of lead, leached from leaded alloy in all the water samples was observed to be always greater than that of copper. Use of Lead free alloys in soldering has thus proved to be eco-friendly.

Keywords: Leacheate, Toxicity Characteristics, lead free alloys, Environmental impact.

Introduction

In the fast growing electronics industry, the environmental and health hazards due to the usage of lead started becoming a global concern. Lead-containing solder alloys are cheap and possess desirable properties like of melting point, wettability, strength, creep, corrosion resistance and so they have been used in the microelectronic packaging industry. Among them, lead (Sn-37Pb) solder had been a dominant material for interconnection and packaging of modern electronic components and devices. In countries like India, the conventional eutectic Sn63Pb37 is mostly used even now due to their low cost.

But the introduction of RoHS (Restriction of Hazardous Substances) Directive on 1 July 2006, proved to be a turning point in the manufacturing techniques of the electronic industry and the lead-free solder (LFS) alloys have been developed during the past decade to replace conventional Pb-Sn alloys. Though it involved greater cost and increased risk to industry, many industries have been emerged to accommodate the newly developed LFS alloys with improved performance, reliability and to reduce toxicity.

In the eco-design strategy of developing such new materials to replace lead, while extensive research have been progressing in determining the solder alloys' physical, mechanical, thermal and electrical properties, evaluating the life-cycle environmental impacts and occupational toxicity of lead-free solders were also given importance. In the life cycle assessment (LCA), one of the evaluating parameters was the potential environmental impact of the solders when disposed in the landfill. Several different leaching procedures such as Toxicity Characteristic Leaching Procedure – TCLP (US EPA), Synthetic Precipitation Leaching Procedure – SPLP (UE EPA), 7-day Deionized Water Test (State of Texas), 7-day Groundwater Test (State of Texas modified) and Waste Extraction Procedure – WET (State of California) were adopted domestically and internationally to assess the environmental hazards and a detailed survey and comparative studies were also done on these procedures and their applications. TCLP [1] was one of the mostly used procedures done to evaluate metal leaching from computers, [2, 3] printed circuit boards, [4, 5], cellular phones[6], discarded Electronic equipment in MSW in many countries have been reported.[7-12]Periodic monitoring of leachate quality had been carried out at two large dumpsites in Chennai, India and a few smaller dumpsites from Sri Lanka. Various studies in this field have revealed that the leachate quality may vary from time to time and site to site due to variables such as waste composition, temperature, moisture content, climatic changes etc. [13-15 The landfill leachate pollution can also be quantified in terms of Leachate Pollution Index (LPI), a technique developed by Kumar and Alappat. LPI higher than 7.5 indicates a polluting leachate. [16]Comparative studies were also done with that between Woodrow and TCLP and Woodrow and Smith [17].

Materials and Methods

One of the commercially available potential candidates in the present consumer world is tin based Lead Free SAC 305 series. In countries like India, even today the conventional leaded alloy with eutectic composition Sn63Pb37 is mostly used. Hence four compositions of lead free alloys [LF1- LF4] and the eutectic Sn63Pb37 lead alloy were chosen for the present study.

Sample Preparation

The commercially available samples were in the form of bars and they were sawed to small particles and sieved to four different sizes. Size 1 < 0.241 mm; Size 2 + 0.241 to - 0.416 mm; Size 3 + 0.416 to -0.995 mm and Size 4 slightly greater than 0.995mm and << .995cm. Of the different particle size of the sample, 84.37% could pass through 850 micron sieve, 37.51% through 425 micron sieve and 11.39% through 250 micron sieve.

Sample media

Water samples were collected from a Bore Well [BW] 150 feet deep located at Selaiyur in the southern part of Chennai (12^{o}57' North), capital of Tamil Nadu state, India, from two rivers namely Vaigai [RW1] and Kaveri [RW2] in Tamil Nadu [18, 19] and from sea water from three different places namely Tarangambadi [SW1], Pulicat [SW2] and Marina Beach [SW3] in Tamil Nadu.[20-24]

Leachate Characterization

The different sizes of the samples were allowed to digest at 40% concentration in the water sample BW for seven days and were filtered using a 40 micron Whatman filter paper. Leachate samples were analyzed for copper, lead and tin using Inductively Couple Argon Plasma Spectroscopy (ICP-OES). The amount of lead and tin in ppm leached from leaded alloy and the amount of copper and tin in ppm leached from the lead free alloys at pH 7 for four different particle sizes and at pH 6 for two different particle sizes are reported in Table 1.

One of the lead free alloys LF1 and the leaded alloy Sn/Pb belonging to different particle sizes were allowed to digest at 40% concentration in different water samples for 21 days with periodic shaking and were filtered using a 40 micron Whatman filter paper and the leachate samples were analyzed for copper, lead and tin and the results reported in Table 2.The number inside the bracket indicating the size of the particle

Table 1 - Leaching of lead and copper in Bore well water

pH - Particle size	Leaching period - 7 days				
	Leaching of copper in ppm From lead free [LF] alloys				Leaching of Lead in ppm from leaded alloy
	LF 1	LF 2	LF 3	LF 4	Sn/Pb
7-1	14	4	11	10	10
7-2	18	6	5	10	12
7-3	nil	nil	nil	0.005	0.4
7-4	0.037	nil	0.01	0.003	0.1
6-2	20	nil	nil	nil	26
6-4	0.02	0.015	0.003	0.015	0.5

Table 2- Leaching of lead and copper in different water samples

Water samples	Leaching period – 21 days	
	Lead from VAC [ppm]	Copper from SAC [ppm]
Distilled WaterDW	0.115[4]	0.032[4]
Bore well BW	0.318[4]	0.035[4]
Tarangambadi SW1	0.720 [4]	0.056[4]
Pulicat sea SW2	1.170 [4]	0.016[4]
Marina seaSW3	2.200[3]	0.035[3]
Vaigai RiverRW1	0.135[3]	0.098[3]
Kaveri RiverRW2	0.400[3]	0.024[3]

Results and Discussion

The leaching effect of lead from the leaded alloy and copper from the Pb free alloys were studied, with respect to size of the particles, medium of leaching and the leaching period.

Table 1 highlight that the leaching effect is less for the particle sizes 3 and 4 when compared to that for sizes 1 and 2 and particle size 2 has the best response. [Fig1] Lead has leached to the maximum of 12ppm and copper 18ppmfrom the sample LF 1.[Fig.2] For the particle sizes 3 and 4 copper has not leached much from all the samples when compared to lead.

For the particle size 2, leaching of lead is 12ppm for pH7 but has increased to 26 ppm for pH 6.But Cu has leached only 18ppm for pH7and 20ppm for pH 6.[Fig 3]

Lead has leached only 0.100ppm when the leaded alloy was allowed to leach for 7 days in bore well water and 0.318 ppm when allowed to leach for 21 days. Copper from LF1 has leached almost the same 0.037ppm and 0.035 ppm when allowed to leach for 7 days and 21 days respectively in bore well water. [Fig 4]

During the same leaching period of 21 days, lead has leached only 0.115 ppm in distilled water but 0.318ppm in bore well water. For the same leaching period of 21 days, Cu has leached almost the same 0.032ppm and 0.035 ppm respectively in distilled water and bore well water respectively. [Fig 5] It was also observed that tin has not leached from any of the samples.

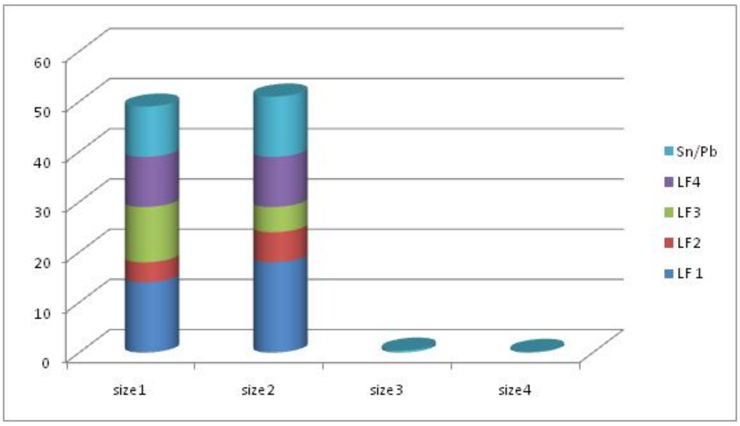

Fig.1 Leaching of Cu from LF alloys and Pb from Sn/Pb with respect to size of the particles

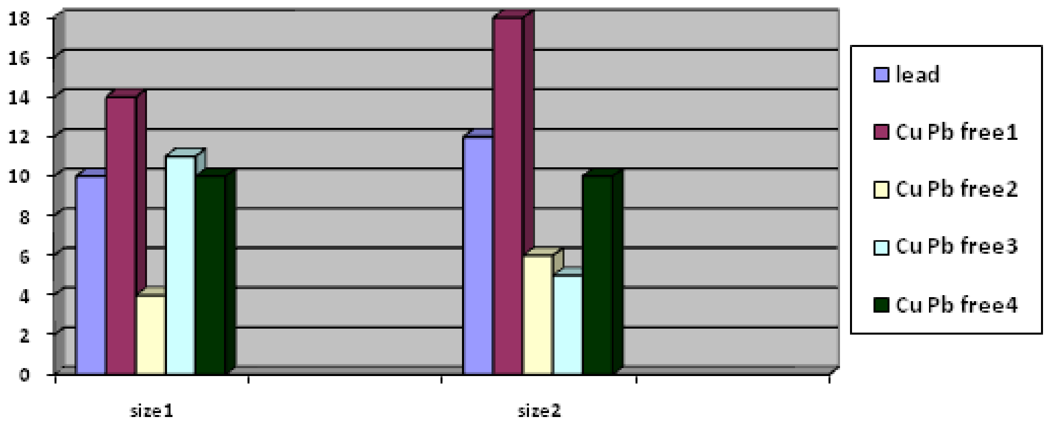

Fig.2 Comparison of Leaching of Cu from LF alloys and Pb from Sn/Pb for size1 and size2

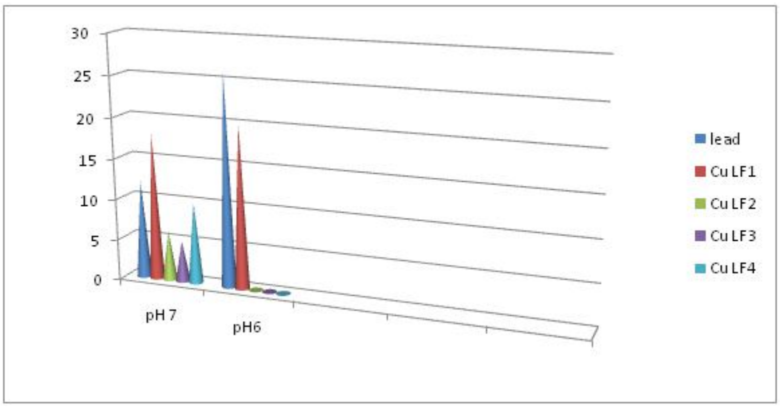

Fig.3 Leaching of Lead from Sn/Pb and leaching of Cu from LF alloys for different pH

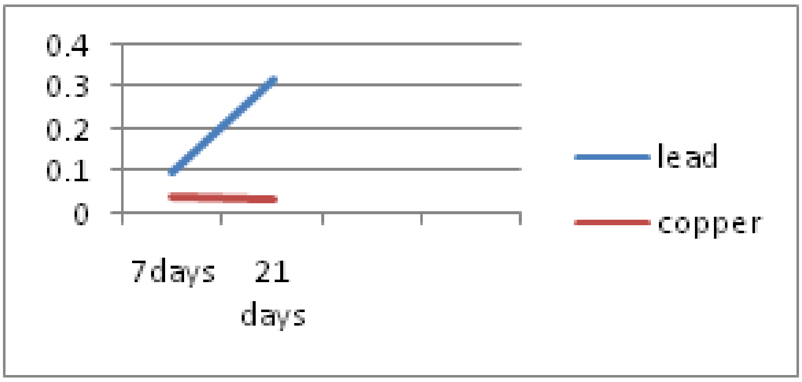

Fig 4 Same media – Bore well water

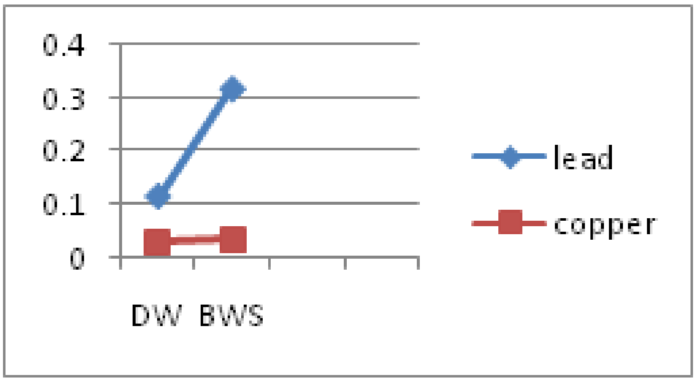

Fig 5 Same Leaching period – 21 days

During the same leaching period of 21 days, from Sn/Pb alloy, lead has leached 0.115 ppm in distilled water, 0.318ppm in bore well water, 0.72 ppm in the sea water at Tarangambadi (SW1) and 1.170 ppm in the sea water at Pulicat (SW2). For the same leaching period of 21 days, from LF1 alloy, Cu has leached 0.032ppm in distilled water, 0.035 ppm in bore well water, 0.056ppm from SW 1 and 0.016ppm from SW 2 .[Fig 6.]

For the same leaching period of 21 days for a different size particle it was observed that 0.135ppm of lead has leached from Vaigai River (RW1), 0.400ppm from Kaveri River (RW 2) and 2.200ppm from the sea water in Marina Beach.(SW3) and Cu has leached 0.098ppm, 0.024ppm and 0.035ppm from RW 1, RW 2 and SW3 respectively. [Fig7]

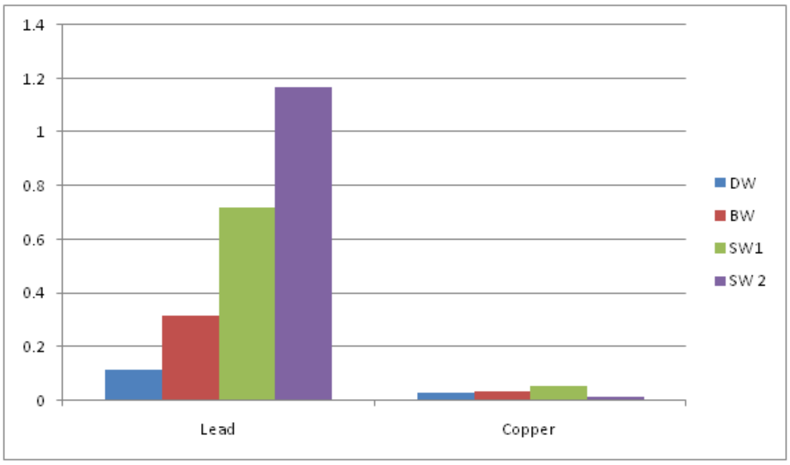

Fig 6 Leaching of lead from Sn/Pb and Cu fromLF1 [4] in different water samples

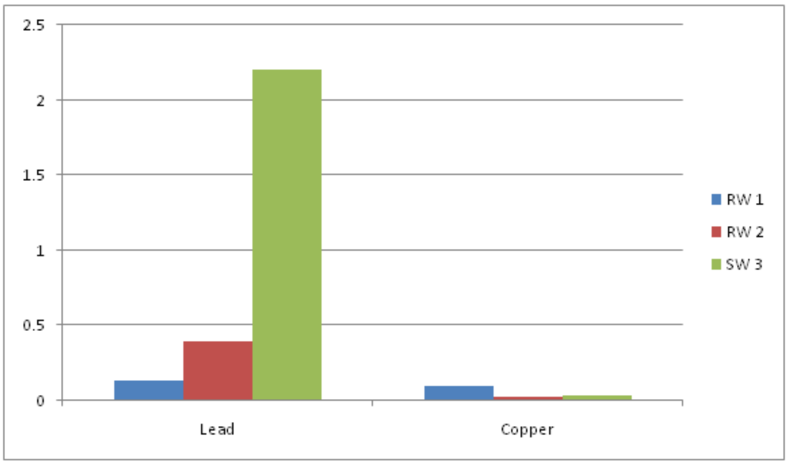

Fig 7 Leaching of lead from Sn/Pb and Cu from LF1[3] in different water samples

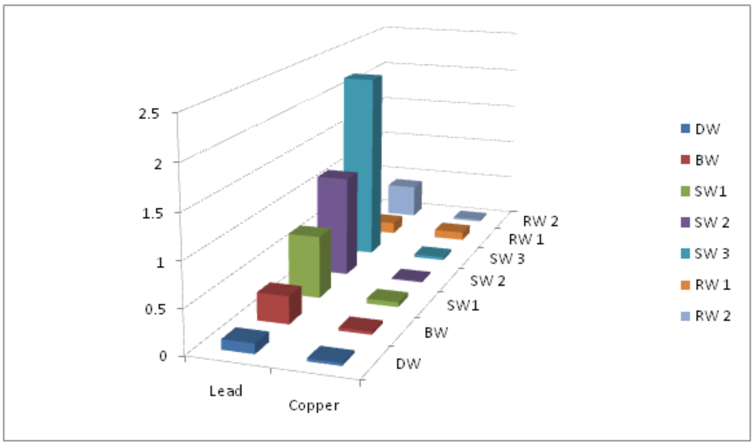

Fig 8 Comparison between leaching of lead and Copper

Several leaching tests were conducted by Woodrow with boards that contained lead solder and lead-free solder. While TCLP required 100 g of waste (size < 9.5mm) per 2000g (2L) of leaching fluid acid digested prior to analysis, Woodrow used a 500ml sample vessel with the sample at an appropriate liquid to solid ratio and shaked at 2 cycles per second and analyzed on an as-received basis. In order to demonstrate mimic waste streams from circuit board fabrication and assembly operations, Smith adopted different procedures to evaluate the metal leaching from lead free solder in different forms such as wire solder, solder solids, solder paste with flux, and solder dross and also tested to Lead/tin solder for comparison.[16]

In the present study, the composition of one of the tin based LF alloys SAC 305 (LF1) is 96.5Sn3Ag0.5Cuquite close to one of the eight solder types Smith evaluated96.3Sn3.2Ag0.7Cu. While the next two solder alloys of Smith do not contain Cu, (96.5Sn3.5Ag, 98.0Sn2.0Ag), the alloys LF2 and LF3 considered in the present study involve both copper as well as silver. (99.0Sn0.3Ag0.5Cu, 99.2Sn0.1Ag0.7Cu) and LF 4 contains 99.3Sn and 0.7 Cu and that of Smith 99.3 Sn and 0.7 Ag as indicated in Table 3. The maximum size of the samples involved in the present study (size 4 > 0.995 mm but << .995cm) were quite less than that was used by Smith 3/8 inch solid spheres (.9525cm) for TCLP.

Table 3 Choice of samples in the present study and Smith study

Present Study				Remarks	Smith study			Remarks
Lead free	Sn	Ag	Cu		Sn	Ag	Cu	
LF 1	96.5	3.0	0.5	Nearer to Smith	96.3	3.2	0.5	Nearer to LF1
LF 2	99.0	0.3	0.7	Sn increasing Ag decreasing, Cu same	96.5	3.5		Sn increasing Ag decreasing No Cu
LF 3	99.2	0.1	0.7		98.0	2.0		
LF 4	99.3	-	0.7	Tin and copper	99.3	0.7		Tin and Silver

Following Woodrow's pattern, the liquid to solid ratio was chosen to make up a 40% concentration [50g of solid in 125ml of the water sample] in a 500ml beaker with periodic shaking. Short-term extractions (18 and 48 h) which used MSWLs from a variety of California landfills and long-term sequential extractions (48−84 days) which simulated longer term leaching that might occur in MSW landfills and similar studies in other countries like Nigeria[9], Australia[11]have been carried out. While Smith has used 7–day Deionized water and 7-day ground water procedures, in the present study, 7-day distilled water, and 7day ground water, 21 day distilled water and 21 day ground water procedures were adopted. Ground water sample was chosen from a bore well. The water sample BW [Bore Well South] was collected during June - August

2011 before monsoon from a Bore well 150 feet deep located at Selaiyur in the southern part of Chennai (12°57' North), capital of Tamil Nadu state, India.

While TCLP required 100 g of waste (size < 9.5mm) per 2000g (2L) of leaching fluid acid digested prior to analysis, in the present study, the samples were also digested in pH 6 to study the leaching behavior of lead free alloys and leaded alloys.

TCLP and SPLP tests seem to maintain their credibility - the TCLP representing worse case MSW landfill conditions, and the SPLP representing rainwater. But the results of Woodrow and Smith could not be compared because one leached the circuit boards and the other considered the solder material, yet from a regulatory perspective, both the studies show that lead leaches to levels above the RCRA toxicity characteristic under the TCLP (5 mg/l) which was true for both solder and circuit boards.

The potential human health risk associated with exposure to silver-contaminated groundwater from 96.3Sn/3.2Ag/0.7Cu lead-free solder leachate has been assessed and the results show that in the worst-case scenario, silver concentrations may exceed drinking water standards at nearby wells after roughly 100 years. [25]Woodrow found no silver leach from the circuit boards under the TCLP, Smith found silver to leach to hazardous waste levels in solder spheres but not in solder paste. The maximum silver concentration reported was 11.5 mg/l for the 3.5% silver/96.5 % tin solder in 3/8 inch solder spheres using TCLP[16]and in the present study leaching of silver was not considered for analysis.

Cu and Pb were the most leachable heavy metals in WPCBs according to TCLP andSPLP[5].Theleaching level of copper has not exceeded 25mg/L according to California state WET (STLC) limit for hazardous waste classification and the leaching level of lead is 5mg/L according to California state WET (STLC) limit for hazardous waste classification and federal TCLP limit for hazardous waste .While copper has not exceeded its limit in all the samples, lead has crossed the limit when allowed to leach in the bore well water.

The leachate studies performed with lead-containing components found in electronic devices from Florida landfills, US using the TCLP, California's Waste Extraction Test (WET) and the Synthetic Precipitation Leaching Procedure showed that the lead concentrations in the extractions using MSW landfill leachates were lower than those by the TCLP. Lower the pH of the leaching solution greater the amount of lead leached in TCLP and WET. [7]In the present study, lead has leached more in pH 6 than in pH7.

Recovery of tin from a fresh solder of composition 52.6% Sn and 47.3% Pb could be done by varying the acid concentration, temperature, mixing time and pulp density. The Pb from the leach residue was removed by using 0.1 M nitric acid at 90 °C in mixing time 45 min and pulp density 10 g/L.[26].The maximum tin concentration reported by Smith was 63.2 mg/l for the 3.5% silver/96.5 % tin solder in 3/8 inch solder spheres using the WET.[16] In the present study tin has not leached in most of the samples.

Conclusions

The present study has modified the techniques adopted by Woodrow and Smith but has restricted the samples only to the commercial raw alloys to study their leaching behavior in different water media. The most leachable heavy metals lead and copper had been analyzed. Leaching of silver may not be prominent when used in a small quantity. The leaching level of lead was more when compared to that of copper in the same environment. The leaching effect could depend on the size of the particles. The results highlight that the leaching of lead from a leaded alloy in an acidic environment of low pH can be higher and it strongly supports that fact that when acid rain occurs, lead will leach into environment quite strongly and abundantly when compared to copper from lead free alloys. Tin which is not toxic was least leaching from any of the alloys and this characteristic of tin material is a boost for the lead free alloys which are mostly tin based. The technique used in the present study has proved to be a successful method to understand the leaching of heavy metals from raw alloys in ground water resources. This study confirms that the use of lead free alloys is eco friendly.

References

[1] Lincoln J.D., Ogunseitan O.A ., Shapiro A.A., 2006“Meta-analysis of Hazard Criteria Designation for Electronic Waste”In :Proceedings of the 2006 IEEE International Symposium on Electronics and the Environment, pp. 89 - 94

[2] Yong-ChulJ., TownsendT., HyunmyungY., 2006 “ Evaluation of metal leaching from end-of-life laptop computers using the TCLP and other standard leaching tests, ” In: Proceedings of the 2006 IEEE International Symposium on Electronics and the Environment, pp. 309-314.

[3] LiY.D., RichardsonJ.B., WalkerA.K., YuanP.C., 2006 “ TCLP heavy metal leaching of personal computer components”, J. Environ. Eng., 132, pp. 497-504.

[4] Xiaoyu Zhou, JieGuo, Kuangfei Lin, Kai Huang, Jingjing Deng, 2013“Leaching characteristics of heavy metals and brominated flame retardants from waste printed circuit boards”, J. Hazard. Mater., 246 -247, pp.96 -102

[5] XiaojunNiu, Yadong Li, 2007 “Treatment of waste printed wire boards in electronic waste for safe disposal”, J. Hazard. Mater., 145(3), pp.410 – 416

[6] John D. Lincoln, Oladele A. Ogunseitan, Andrew A. Shapiro and Jean-Daniel M. Saphores, 2007“Leaching Assessments of Hazardous Materials in Cellular Telephones” *Environ. Sci. Technol.*, 41 (7), pp. 2572–2578

[7] JangY.C., TownsendT.G., 2003 “Leaching of lead from computer printed wire boards and cathode ray tubes by municipal solid waste landfill leachates”, Environ. Sci. Tech., 37, pp. 4778- 4784.

[8] Townsend T.G., Musson S.E., 2006 “Assessing the landfill disposal implication of discarded electronic equipment”, In: Proceedings of the 2006 IEEE International Symposium on Electronics and the Environment, pp. 298-301

[9] Aluko O.O., Sridhar M.K.C. and Oluwande P.A., 2003 "Characterization of leachates from a municipal solid waste landfill site in Ibadan, Nigeria", J. Environ. Health Res., 2 (1), pp.32-37
[10] El-Fadel M., Bou-Zeid E., Chahine W. and Alayli B., 2002 "Temporal variation of leachate quality from pre-sorted and baled municipal solid waste with high organic and moisture content", Waste Mgt., 22, pp.269–282
[11] Jorstad L.B., Jankowski J. and Acworth R.I., 2004 "Analysis of the distribution of inorganic constituents in a landfill leachate-contaminated aquifer Astrolabe park, Sydney, Australia", Environ. Geol., 46, pp.263-272
[12] Reinhart D.R. and Grosh C.J., 1998 "Analysis of Florida MSW landfill leachate quality", Florida center for solid and hazardous waste management, Report # 97-3
[13] Kim Hooper, MiladIskander, GurmailSivia, Fatima Hussein, John Hsu, Merlyn DeGuzman, ZenaidaOdion, ZaidaIlejay, Fred Sy, MyrtoPetreas, and Barton Simmons, 1998 "Toxicity Characteristic Leaching Procedure fails to extract Oxoanion-Forming elements that are extracted by Municipal Solid Waste leachates" Environ. Sci. Technol., 32 (23), pp. 3825–3830
[14] Esakku1S., Obuli P. Karthikeyan, Kurian Joseph, NagendranR., PalaniveluK., Pathirana K.P.M.N., KarunarathnaA.K. and BasnayakeB.F.A., 2007 "Seasonal variations in leachate characteristics from MunicipalSolid Waste dumpsites in India and Srilanka", Proceedings of the International Conference on Sustainable Solid Waste Management, 5 - 7 September, Chennai, India. pp.341-347
[15] KurniawanT.A., 2009"Landfill Leachate: Persistent Threats to Aquatic Environment", http://www.scitopics.com/Landfill_Leachate_Persistent_Threats_to_Aquatic_Environment.html
[16] Kumar D. and Alappat B.J., 2003 "A Technique to quantify landfill leachate pollution", Proc. Sardinia 2003, 9th International Landfill Symposium, Italy, pp.6-10,
[17] Thomas Woodrow, Boeing and Edwin Smith, "Reliability and Leachate Testing of Lead Free Solder Joints", KTEC Electronics, http://leadfree.ipc.org/files/RoHS_16.pdf
[18] http://en.wikipedia.org/wiki/Vaigai_River [last accessed in October 2012]
[19] http://en.wikipedia.org/wiki/Kaveri [last accessed in October 2012]
[20] http://en.wikipedia.org/wiki/Tharangambadi [last accessed in October 2012]
[21] http://en.wikipedia.org/wiki/Pulicat_Lake [last accessed in October 2012]
[22] Pulicat lake: Ecologically Important Areas of Andhra Pradesh Coast" [last accessed in October 2012].
[23] At Pulicat Lake, an ecological turnaround". *The Hindu*, (Chennai, India). 2007-04-17
[24] http://en.wikipedia.org/wiki/Marina_Beach [last accessed in October 2012]
[25] Masanet, 2002 "Assessing public exposure to silver-contaminated groundwater from lead free solder: an upper bound, risk-based approach", Conference Record 2002 IEEE International Symposium on Electronics and the

Environment, Dept. of Mech. Eng., California Univ., Berkeley, CA pp.174-179

[26] Choubey, Pankaj K and Jha, Manis K and Kumar, Vinay and Jeong, Jinki and Lee, Jae-chun, 2010" *Leaching studies for the recovery of tin from the solder of waste printed circuit boards"* In: Proceedings of the XI International Seminar on Mineral Processing Technolog NML Jamshedpur, India.