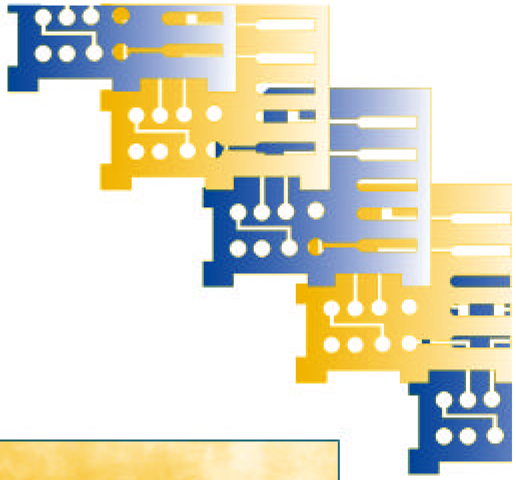

Lead Free Solders - A Push in the Wrong Direction?

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Lead Free Solders - A Push in the Wrong Direction?

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Abstract

The United States Environmental Protection Agency ("USEPA"), along with other environmental regulators worldwide propose to limit the use of lead in manufactured products. In response to these actions, the electronic manufacturing community has developed several lead free solder blends. The Printed Circuit Board ("PCB") fabrication industry has also moved toward tin, silver, nickel, and gold plating of surface mount pads and through holes. While there has been research with regard to the electrical and mechanical properties of lead free solders, there has been little published research on the environmental effects of the available lead free formulations. This paper gives the results of the study of five lead free solder alloys: Tin/Silver/Copper, Tin/Silver, Tin/Copper, and Tin/Antimony when leached according to USEPA methods. These methods are designed to simulate waste disposal and groundwater contact with both lead free solder solids and dross waste.

History/Background

The European Union proposes to ban all lead in electronic products by the year 2004[1]. Japan is also taking similar regulatory stance[2]. While the toxic effects of lead are well known, a literature search revealed no evidence that there has been research into the environmental effects of lead free solders.

Hazardous waste is defined as any waste that may "pose a substantial present or potential threat to human health and the environment when improperly treated, stored, transported, or otherwise managed." The USEPA identified four characteristics of hazardous waste: 1) toxicity, 2) corrosivity, 3) reactivity, and 4) ignitability. EPA also developed standardized procedures and criteria for determining whether a waste exhibits one of these characteristics. These characteristics and criteria are codified at 40 CFR Part 261. Testing procedures are detailed in SW-846.[3]

When waste is disposed it is weathered by rainfall and reactions with other wastes. This weathering process allows metal elements and their salts to be leached from the metal surfaces of the waste. Heavy metals leached from waste then dissolve into the liquid leachate that collects in landfills. If the landfill is breached, metal bearing leachate may migrate into the local groundwater and contaminate it. The USEPA interest in lead free solders derives from this concept, as well as lead's toxicity when absorbed into the skin or ingested. As these exposures are difficult to imagine from electronic products (few people eat printed circuit boards), the disposal/leachate problem becomes the USEPA primary focus for lead regulation.

Development of the Extraction Procedure

The Toxicity Characteristic Leaching Procedure (TCLP) was developed by USEPA for determining whether a waste was hazardous by virtue of its toxicity. The law defines a hazardous waste as a waste that presents a threat to human health and the environment when "improperly managed," thus the USEPA has developed a set of assumptions that describe possible ways in which a waste can be disposed improperly. The USEPA intended this so-called "mismanagement scenario" to simulate a "plausible worst case" of mismanagement. Under this worst case scenario, USEPA assumes that potentially hazardous wastes would be co-disposed with municipal solid waste in a landfill with actively decomposing material overlying a groundwater aquifer.

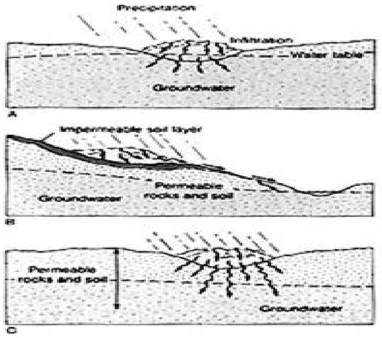

Figure 1 - Three Methods for Waste Leachate to Contaminate Groundwater [P1]

The TCLP itself was developed specifically based on these assumptions regarding waste mismanagement. Assuming that potentially hazardous waste could be disposed in a landfill containing actively decomposing municipal waste, the USEPA reasons that the most likely pathway for human exposure to toxic constituents would be through drinking water contaminated by leachate from the landfill. Thus, the TCLP defines the toxicity of a waste by measuring the potential for the toxic constituents present in the waste to leach out and contaminate groundwater and surface water (and by extension, drinking water sources) at levels of health or environmental concern. Electronic devices containing tin/lead solders are disposed in municipal landfills. These landfills allow lead to leach from the disposed items.

Specifically, the TCLP requires analyzing a liquid waste or liquid waste extract to determine whether it contains unacceptably high concentrations of any of eight toxic metal constituents identified in the National Interim Primary Drinking Water Standards. These are:

Arsenic	Barium
Cadmium	Chromium
Lead	Mercury
Selenium	Silver

Some States have added copper, nickel, and zinc to this list. Consistent with the mismanagement scenario, the liquid extract is obtained from solid waste by exposing the waste to organic acids (the acids likely to be found in a landfill containing decomposing municipal wastes).

Seven Day Leach Methods

The State of Texas, as well as other environmental regulators, publish a seven day, less aggressive leach method than the TCLP. These methods are used to demonstrate the contamination potential to drinking water and groundwater from a waste that comes into contact with drinkable water. Stormwater contamination potential can also be predicted using the seven day leach method. In this method, a portion of the material under study is mixed with four times its weight in distilled or deionized water, shaken or tumbled for five minutes, then allowed to leach undisturbed for seven days. The leachate is then filtered and analyzed for the constituents of interest. In jurisdictions where this test is used, if the leachate shows constituents of interest higher than the USEPA or local drinking water standards, the material is considered to have failed the test. In the study outlined in this paper, both deionized and local groundwater are used to leach constituents of interest. Properties of the waters are:

Tables 1 and 1a - Properties of Leach Waters

Parameter	Groundwater
pH	7.56
Total Dissolved Solids, mg/L	310
Chloride, mg/L	106
Carbonate/Bicarbonate, mg/L	158
Sulfate, mg/L	44
Parameter	Deionized Water
pH	7.05
Total Dissolved Solids, mg/L	<5
Chloride, mg/L	<5
Carbonate/Bicarbonate, mg/L	<5
Sulfate, mg/L	<5

Both the deionized water and the groundwater were tested for ambient metal concentrations as part of the "blank" quality control analyses.

Metal Toxicity[4]

Extensive research has been conducted on the toxicological effects of lead; and there are also toxicity concerns with the use of the so-called lead replacement metals.

Tin and tin compounds can cause biological effects such as severe digestive tract irritation with abdominal pain, nausea, vomiting, diarrhea, and permanent tissue destruction of the esophagus and digestive tract. Tin salts may cause systemic toxic effects on the nervous system, heart, and liver. Tin may interact with the absorption of biologically essential metals such as copper, zinc, and iron and can inhibit various enzymes and metabolism. Ecotoxicity, reproductive effects, and mutagenicity have been observed in laboratory studies.

Silver and silver compounds can cause biological effects such as digestive tract irritation and agryria, which is characterized by a permanent blue-gray pigmentation of the skin, eyes, and mucous membranes. Ecotoxicity, reproductive effects, and mutagenicity have been observed in laboratory studies; however, toxicological data has not been fully investigated.

Antimony and antimony compounds can cause biological effects such as severe digestive tract irritation with abdominal pain, nausea, vomiting, and diarrhea. Toxicological data has not been fully investigated; however, antimony carries one of the lowest allowable concentration limits in drinking water.

Copper and copper compounds can cause biological effects such as severe digestive tract irritation with abdominal pain, nausea, vomiting, and diarrhea. Ecotoxicity has been observed in laboratory studies; however, toxicological data has not been fully investigated.

Based on the toxicity and environmental impact data that is available for these lead free solder alloys, it appears that the alloys are also harmful to human health and the environment.

Regulatory Impacts

There are regulatory concerns for the lead replacement metals regarding environmental impact and use in the workplace. PCB manufacturers using lead free solder materials would need to evaluate these new materials in the workplace for environmental permitting, management, and industrial hygiene issues.

Various tin/ tin compounds are regulated as an AICGH Hazardous Chemical, OSHA Workplace Air Contaminant, California State Superfund Hazardous Substances, CAL-OSHA Director's List of Hazardous Substances, and California HWCL Hazardous Wastes.

Various silver/ silver compounds are regulated under Superfund, SARA 313, RCRA, Clean Water Act Toxic Pollutant, California State Superfund Hazardous Substances, CAL-OSHA Director's List of Hazardous Substances, and California HWCL Hazardous Wastes.

Various antimony/antimony compounds are regulated under Superfund, SARA 313, Clean Air Act Hazardous Air Pollutant, Clean Water Act Toxic Pollutant, California State Superfund Hazardous Substances, CAL-OSHA Director's List of Hazardous Substances, and California HWCL Hazardous Wastes.

Various copper/ copper compounds are regulated under Superfund, SARA 313, Clean Water Act Toxic Pollutant, California State Superfund Hazardous Substances, CAL-OSHA Director's List of Hazardous Substances, and California HWCL Hazardous Wastes.

Based on the regulatory impacts listed above, lead free replacement solder alloys may not provide the PCB manufacturer any less regulatory burden than that imposed by conventional tin/lead solders.

Experimental Methods

Experiments with five lead free alloys were undertaken to show their toxicity relative to each other and to conventional tin-lead solders. Wire solder, solder solids, and solder dross were the physical forms of solder tested. These physical forms of solder mimic the waste streams from PCB manufacture. The five alloys chosen are:

1) 96.3 Tin, 3.2 Silver, 0.5 Copper
2) 96.5 Tin, 3.5 Silver
3) 98 Tin, 2 Silver
4) 99.3 Tin, 0.7 Copper
5) 95 Tin, 5 Antimony

Alloys of bismuth are excluded because the primary source of bismuth is lead manufacture. Alloys of indium are excluded because of the poor availability of indium. Zinc gives poor wetting action and is not currently used as a surface finish metal in PCB manufacture. Alloys of zinc were thus excluded[5].

Sample Preparation

Each metal was procured in an elemental state, then alloyed under oxygen free conditions. Solder wire was 0.032 inch diameter. Solder solids were bar stock, milled to pieces no larger than 0.375 inch by 0.375 inch. This maximum particle size is mandated by the USEPA leaching methods. Solder dross was produced by heating the alloyed solder solids in an ambient atmosphere while occasionally removing the dross from the surface of the solder melt using a titanium bar. An analysis of the oxide content of the dross produced in this manner showed it contained approximately ninety percent entrapped metal, and ten percent metal oxide.

Leaching Procedures

After preparation of the "waste" samples, each was leached according to USEPA protocols. Blank samples (laboratory samples prepared so as to have none of the metals under analysis), as well as "spiked" samples (laboratory samples prepared to have a known amount of metal under study) were both used to provide quality control over the leaching process and the metals analysis. TCLP samples leached for eighteen hours, while the seven day leach samples leached for seven days.

Metals Analytical

The metals analyses were performed using a Perkin-Elmer P2000 ICP unit. Each sample was analyzed with two readings, which were averaged. Calibration verification was performed after every ten samples, and at the end of the analytical run.

Results

Tables two through six below give the results of the metals analysis.

Discussion

Lead free solders showed several elements leaching at levels above USEPA allowable limits in different leaching media. Most striking is the 95Sn:5Sb alloy. With a 0.006 mg/L allowable drinking water limit for Antimony, the derived leachable levels of several mg/L are approximately 10,000 times the maximum allowable. The 95Tin-5Antimony alloy studied leached above regulatory limits in every physical form and in all leach methods.

Other elements showed excessive leach concentrations, or statistically could leach above the allowable limits. All lead free alloys containing silver and antimony leached above regulatory limits for the TCLP leach. Silver bearing lead free alloys were close to the USEPA limit of 0.1 mg/L in drinking water for all Seven Day leach tests using deionized water. When groundwater was used in this test for silver, the silver levels went above the regulatory limit. Tin did not leach in most of the tests. Salts of tin tend to be insoluble in water at room temperature.

Conclusion

Lead free solders are not a panacea for solving the potentially toxic effects from tin-lead solder alloys. The data from these experiments shows that lead free solders leach at levels that would cause them to be classified as a hazardous waste, failing both silver and antimony levels. If lead free solders containing silver or antimony are improperly disposed and contacted groundwater, the solders could render that groundwater unsafe to drink per USEPA standards. Solder dross from these alloys carries much the same risks, as the dross behaved similarly to the parent alloys in these experiments.

Further Work

These experiments will be continued using other forms of solder alloy such as solder pastes. Other leach methods such as the USEPA Synthetic Precipitation Leaching Procedure will also be studied. The Synthetic Precipitation Leaching Procedure does not take into account co-disposed wastes, only the effects on a waste pile from acid rain.[6]

Acknowledgement

Special thanks to Dr. Smith and the staff at EFEH & Associates laboratories for their assistance with the analytical work. The laboratory may be reached at 281-996-5031.

References

[1] Surface Mount Technology, Volume 12 Number 12 (December 1998), Page 40.

[2] IPC Review, October 1998, Page 1

[3] U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Volumes I and II (SW-846), 3rd Edition, November 1986.

[4] Sources for this and the next section include: Registry of Toxic Effects of Chemical Substances (RTECS) published by National Institutes of Safety and Health (NIOSH); material safety data sheets for the metal elements; 29 and 40 CFR; and Waste Classification Regulation Guidance Manual, California Environmental Protection Agency, August 1994.

[5] Bastecki, Chris; A Benchmark Process for the Lead-Free Assembly of Mixed Technology PCB's.

[6] A full explanation of the TCLP and the SPLP methods for leaching wastes is found under method 1311 (TCLP) and method 1312 (SPLP) in U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Volumes I and II (SW-846), 3rd Edition, November 1986.

[7] Management of Hazardous Waste Leachate; United States Environmental Protection Agency September 1982

[P1] Montgomery, Carla; Environmental Geology, fourth edition; William C. Brown Publishers, Dubuque, Iowa; 1995

Notes for tables two through six:

Alloy 1	96.3 Tin, 3.2 Silver, 0.5 Copper	(96.3Sn/3.2Ag/0.7Cu)
Alloy 2	96.5 Tin, 3.5 Silver	(96.5Sn/3.5Ag)
Alloy 3	98 Tin, 2 Silver	(98Sn/2Ag)
Alloy 4	99.3 Tin, 0.7 Copper	(99.3Sn/0.7Cu)
Alloy 5	95 Tin, 5 Antimony	(95Sn/5Sb)

<u>Average</u> represents the average of any samples that showed the element of interest
<u>Standard Deviation</u> represents the standard deviation of these measurements
<u>3s upper</u> represents the average plus three times the standard deviation, and would be the three sigma upper limit of the concentration of the element of interest, using a normal distribution of the measurements. See figure two below for a graphical representation.

Table 2 - Complete Results of the TCLP Leach - *3/8 inch size solder solids used except where noted*

Alloy	Sn, mg/L	Ag, mg/L	Cu, mg/L	Sb mg/L	Pb, mg/L
1	<0.05	9.32	43.75	NA	NA
2	<0.05	11.56	NA	NA	NA
3	<0.05	8.46	NA	NA	NA
4	<0.05	NA	44.52	NA	NA
5	<0.05	NA	NA	55.50	NA
Sn/Pb paste	11.39	NA	NA	NA	1800
Sn/Pb wire	0.082	NA	NA	NA	1002
average Pb free	<0.05	9.78	44.14	55.50	standard dev.
1.60	0.54	3s upper	14.58	45.77	average SnPb
5.74	1401	standard dev.	8.00	564	3s upper
29.72	3094				

Table 3 - Complete Results of the Seven Day Leach using Deionized Water - *3/8 inch size solder solids used*

Alloy	Sn, mg/L	Ag, mg/L	Cu, mg/L	Sb mg/L	Pb, mg/L
1	12.006	0.045	0.113	NA	NA
2	2.109	0.087	NA	NA	NA
3	5.38	0.042	NA	NA	NA
4	0.574	NA	0.199	NA	NA
5	0.612	NA	NA	32.123	NA
average	4.14	0.06	0.16	32.12	standard dev.
4.81	0.03	0.06	3s upper	18.58	0.13
0.34					

Table 4 - Complete Results of the Seven Day Leach using Groundwater - *3/8 inch size solder solids*

used	Alloy	Sn, mg/L	Ag, mg/L	Cu, mg/L	Sb mg/L
Pb, mg/L	1	17.335	0.313	0.152	NA
NA	2	20.459	0.365	NA	NA
NA	3	0.187	0.015	NA	NA
NA	4	2.238	NA	0.078	NA
NA	5	2.003	NA	NA	68.445
NA	average	8.44	0.23	0.12	68.45
standard dev.	9.64	0.20	0.05	3s upper	37.36
0.80	0.27				

Table 5 - Complete Results of the Seven Day Leach using Deionized Water - *3/8 inch size solder dross used*

Alloy	Sn, mg/L	Ag, mg/L	Cu, mg/L	Sb mg/L	Pb, mg/L
1	5.44	0.085	0.089	NA	NA
2	5.31	0.066	NA	NA	NA
3	4.38	0.093	NA	NA	NA
4	0.853	NA	0.146	NA	NA
5	0.399	NA	NA	27.71	NA
average	3.28	0.081	0.118	27.71	standard dev.
2.46	0.014	0.040	3s upper	10.66	0.123
0.239					

Table 6 - Complete Results of the Seven Day Leach using Groundwater - *3/8 inch size solder dross used*

Alloy	Sn, mg/L	Ag, mg/L	Cu, mg/L	Sb mg/L	Pb, mg/L
1	9.220	0.259	0.181	NA	NA
2	9.803	0.303	NA	NA	NA
3	2.502	0.370	NA	NA	NA
4	1.158	NA	0.064	NA	NA
5	1.912	NA	NA	53.47	NA
average	4.919	0.311	0.123	53.47	standard dev.
4.224	0.056	0.083	3s upper	17.59	0.479
0.371					

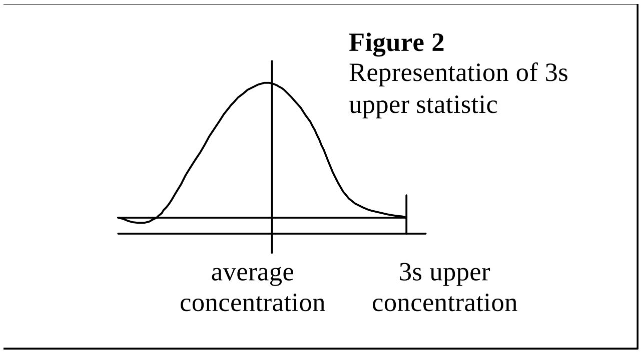

Figure 2 – Representation of 3s Upper Statistic

Table 7 - Regulatory Limits and Sources

Element	Media	Limit, mg/L	Source
Tin	All	None found	Silver
Drinking Water	0.10	USEPA 40 CFR 141	Silver
TCLP Leachate	5.0	USEPA 40 CFR 261	Antimony
Drinking Water	0.006	USEPA 40 CFR 141	Antimony
TCLP Leachate	1.0	TNRCC 30 TAC 335[a]	Copper
Drinking Water	1.0	USEPA 40 CFR 141	Copper
TCLP Leachate	500	Various State Regulations	Lead
Drinking Water	0.015	USEPA 40 CFR 141	Lead
TCLP Leachate	5.0	USEPA 40 CFR 261[b]	

[a] TNRCC 30 TAC 335 refers to State of Texas statutes

[b] some jurisdictions observe a 1.5 mg/L limit, based on a multiple of the 0.015 mg/L drinking water limit