Lead-Free Solders: Issues of Toxicity, Availability and Impacts of Extraction

Anna Ku[a], Prof. Oladele Ogunseitan[b], Prof. Jean-Daniel Saphores[c],
Dr. Andrew Shapiro[d], and Prof. Julie M. Schoenung[e]

[a] SOMA Environmental Engineering, Inc.
San Ramon, California 94583 USA

[b] Department of Environmental Analysis and Design
University of California, Irvine
Irvine, CA 92697-7070 USA

[c] Department of Urban and Regional Planning
University of California, Irvine
Irvine, CA 92697-7070 USA

[d] Microelectronics Material and Processes
Electronic Packaging and Fabrication Section
Jet Propulsion Laboratory
Pasadena, CA 91109-8099 USA

[e] Presenting & Corresponding Author:
Department of Chemical Engineering and Materials Science
University of California, Davis
Davis, CA 95616-5294 USA
530-752-5840; 530-752-9554 (fax)
jmschoenung@ucdavis.edu

Abstract

Lead-tin solders are used for the interconnecting and packaging of electronic components. Due to increasing concerns regarding the toxicity and environmental impacts of lead, the European Union and Japan are considering the adoption of legislation to reduce and phase out lead usage in the electronics industry. Research and development efforts have been made to discover alternatives to tin-lead solders for electronic applications. This project set out to evaluate the critical issues of toxicity and public health effects, material availability, and the environmental impacts of raw material extraction and metal finishing, with the goal of using environmental impact as a factor in selecting feasible lead-free alloys. Six alternative metals were evaluated using lead as a baseline for the comparison. Qualitative metrics were developed to organize and compare information between lead and the six alternative metals. A toxicity metric focused on the issues that are of most concern to human health. Results of the toxicity metric suggest that lead is the most toxic, followed by silver and antimony. Tin and copper are least toxic among the seven metals compared. A metric to compare availability and supply focused on the abundance, world production, world reserves, and the price of each metal. Results from the availability and supply metric show that copper is most abundant and that silver and indium may not be feasible alternatives to lead due to their high cost and low supply. An environmental impact metric was developed to evaluate the effects of metal extraction on environmental quality. Results from this metric show that silver extraction is the most energy intensive and has the most adverse environmental effects, while copper production consumes the least amount of energy and has the least effects of the seven metals. A summary metric was developed using a non-weighted scoring model approach. The results of this summary metric indicate that, of the metals under consideration, copper has the least overall environmental impact, while silver has the greatest overall environmental impact.

Introduction

For the past several decades, tin-lead alloys have been the solder material of choice for the interconnecting and packaging electronic components. However, due to increased concerns regarding the toxicity and environmental impacts of lead, research and development of alternative, lead-free solders have become a necessity. Although there is no legislation calling for the elimination or reduction of lead usage in electronics, Europe and Japan have taken initiatives to reduce and limit its use. The United States has also taken measures to reduce lead release into the environment. The European Commission adopted proposals for a Directive on Waste Electrical and Electronic Equipment (WEEE) and the Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (ROHS) [1]. The objectives of these proposals are to prevent waste, promote reuse and recycling of electrical and electronic equipment, and to substitute leadand other heavy metals in electrical and electronic equipment by January 1, 2007. Japan has also taken the initiative to control lead releases into the environment. The Japanese Ministry of Trade and Industry

(MITI) proposed a take-back legislation in 1998 that requires manufacturers to recover harmful materials in consumer electronics. MITI has also set a numerical target for the amount of lead used and ordered that it be reduced to half compared to 1996 by the end of 2000 and to one third by the end of 2005 [2]. In the United States, the Environmental Protection Agency encouraged manufacturers to take voluntary approaches to reduce their hazardous waste stream volumes by source reduction.

Lead-tin solders are used for metal interconnections due to their desirable soldering properties, such as low melting temperatures, good workability, ductility, and excellent wetting [3] combined with ease of manufacturability and low cost. Lead-bearing solders, especially the eutectic, Sn63Pb37 (63% of tin, 37% of lead by weight), or near-eutectic tin-lead alloys (i.e. Sn60Pb40), has become indispensable for the interconnection and packaging of electronic devices and circuits, and have been used extensively in the assembly of modern electronic circuits [3]. Most of the lead-free solders rely on using tin as the base metal, with the addition of smaller amounts of antimony, bismuth, copper, indium, and silver to enhance its properties so that it will have a reliability similar to current tin-lead solders. The two main requirements for adoption of lead-free solders are low melting temperature and low toxicity. The melting temperature of tin-lead eutectic alloy is 183°C, and typical soldering temperatures are 230°C for reflow and 250°C for wave soldering. Melting temperatures for lead-free solders should be close these values. Other requirements of lead-free solders include electrical conductivity and the reliability of the alloy, which involves factors such as strength, ductility, the ability to withstand thermal and mechanical fatigue, creep, and shock resistance. Reworkability of the soldering alloy is also important. This involves the resistance to formation of undesirable alloys or intermetallic structures upon multiple remelts. Good wetting is another requirement of lead-free solders, because favorable surface energy difference with common bonding metals is necessary to prevent the solder from balling up and falling off. Lastly, low alpha particle emission should also be taken into account for sensitive devices, such as flip chip configuration [4].

The goal of this paper is to evaluate some critical issues of lead-free solders using environmental impacts as a factor in selecting feasible alloys. The critical issues addressed in this study are toxicity and public health effects, material availability, and environmental impacts of raw material extraction and metal refining. Six alternative metals, antimony (Sb), bismuth (Bi), copper (Cu), indium (In), silver (Ag), and tin (Sn) will be compared using lead as a baseline.

Methodology

Allenby [5] developed a qualitative, matrix-based methodology to assess the impact of substituting indium-tin, bismuth-tin, or silver-based conductive epoxy solders for the lead-tin solder from a Design for the Environment perspective. He evaluated whether indium-tin, bismuth-tin, and silver-based conductive epoxy alternatives would be environmentally preferable to lead-tin solders using a Design for Environment Information System (DFEIS). The DFEIS is a matrix system that graphically presents information to develop, organize, and communicate environmental information to product and process designers in a format that integrates environmental considerations into the design process. At the time that the DFEIS was developed, there was no legislation or government initiatives forcing the implementation of lead-free solders. Now, as a result of the legislative directives in the European Union, the industry is considering the need to change alloys more seriously. Thus, there is a need to re-evaluate the environmental impacts of lead-free alternatives.

Using Allenby's method as the basis, metrics are developed in this project to organize and compare information between lead and the six alternative metals. Each metal is ranked and compared in categories. For the toxicity and public health impact metric, the metals are ranked according to whether the metal is bioaccumulable in living organisms, a carcinogen, causes birth defects (teratogenic), the EPA drinking water standard (mg/L), and the Occupational Safety and Health Administration's (OSHA) Permissible Exposure Limited (PEL) (mg/m^3). For the availability and raw material supply metric, the metals are compared and ranked according to their abundance in the Earth's crust (parts per million), world production (metric tons), world reserve (metric tons), and price per pound (U.S. dollars). The production processes of each metal are presented and compared in the environmental impact of extraction metric. Energy consumption is important because the production of energy is a primary source of environmental pollution. Finally, a summary metric compiled from the toxicity, availability, and extraction metrics provide an overall ranking for each metal.

Results and Discussion

Figure 1 presents a toxicity metric developed to rank the toxicity of each metal [6 7, 8, 9, 10 and 11]. The metals are ranked and shown in decreasing toxicity by whether it is bioaccumulable, a carcinogen, causes birth defects (teratogenic), the EPA drinking water standard (mg/L), and OSHA's Permissible Exposure Limit (mg/m^3). Bioaccumulation is considered the most important aspect in this metric due to the metal's persistence in the environment. When metals persist in the environment, they can bioaccumulate in living organisms. Although organisms are able to moderate the concentrations of most substances within their bodies, some substances, such as lead, cannot be regulated and consequently tend to become more concentrated in living tissues as they move through the food chain. Through bioaccumulation, the levels of a pollutant in an animal can be far higher than they are in the water. According to the American Cancer Society [12], there were over 1.26 million new cases of cancer in 2001 in the United States, and 553,400 American were expected to die of cancer. Because cancer is the second leading cause of death in the U.S., whether the metal is carcinogenic was used as the second category to rank the toxicity of the metals. The ability of the metal to cause birth defects is the next category, followed by drinking water standards and OSHA's PEL.

Metal	Bio accumulative	Carcinogen	Birth Defects	EPA Drinking Water Standard (mg/L)	OSHA PEL (mg/m^3)
Lead	Yes	Yes	Yes	0.015	0.05
Silver	Yes	No	No	0.05	0.01
Antimony	No	Yes (Cal EPA)	No	0.006	0.5
Indium	No	No	Yes (lab animals)	None	0.1
Bismuth	No	No	No	0.05	None
Copper	No	No	No	1	0.1
Tin	No	No	No	None	2

Figure 1. Toxicity metric. Metals ranked by descending toxicity according to the categories of bioaccumulativity, carcinogenicity, teratogenicity, EPA drinking water standard limits, and OSHA's Permissible Exposure Limit.

Using this metric, lead is ranked as the most toxic of the seven metals. Lead is bioaccumulative, a carcinogen, causes birth defects, and has one of the lowest concentration limits in drinking water by the U.S. EPA. Silver is ranked second most toxic due to its moderate bioaccumulativity in aquatic organisms. Antimony follows silver as third in the toxicity ranking because it is listed by the California EPA as a human carcinogen. Indium, bismuth, copper, and tin seem relatively innocuous compared to lead, silver, and antimony. However, the amount of bismuth and indium released into the environment is magnitudes less than lead. Since abundance of bismuth and indium in the earth's crust is approximately 0.1 ppm each, there is no information on the impact of bismuth and indium if the release was as great as lead.

Figure 2 shows a metric that compares the availability and supply of each metal. Using information from the Mineral Yearbook published by the United States Geologic Survey [13, 14, 15, 16, 17, 18, 19, 20]. The seven metals are ranked according to their abundance in the Earth's crust (ppm), world production (metric tons), world reserve (metric tons), and price per pound (U.S. dollars). World reserves are defined as the quantities of a metal which can be economically extracted using currently existing technology at current market price. The most important category to rank the availability and supply of the metals is their abundance in the Earth's crust. The abundance is critical in determining the production amount of each metal, subsequently affecting the price. From this metric, copper has the highest abundance and world production. This suggests that supply for tin-copper alloys will not be a problem. However, lead has a larger world reserve and costs significantly less than copper. Indium, being the most expensive and least available, with world production of only 240 metric tons in 1998 and no reserves at all, will probably not be feasible as a lead-free alternative. Lead-free solders composed of indium and silver will cost much more than those composed of antimony, tin and copper. Supply of indium, silver and bismuth will be a problem if demand for these metals increases as lead-free solder technology develops.

Metal	Abundance in Earth's Crust (ppm)	World Production (metric tons)	World Reserves (metric tons)	Price per Pound ($)
Copper	60-70	37.9 million	>340 million	$0.70
Lead	12	8.9 million	1.4 billion	$0.05
Tin	2	431,500	10,700	$3.10
Antimony	0.2-0.5	140,000	2.1 million	$0.72
Silver	0.1	16,400	4,372*	$80.79
Bismuth	0.1	7,800	0	$3.60
Indium	0.1	240	0	$136.35

**U.S. Reserves*

Figure 2. Availability and supply metric. Metals are listed in descending order of abundance and world production.

The environmental impact of metal extraction and energy consumption metric is shown in Figure 3. The information in this metric is compiled from results presented in [19, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30]. The metals are ranked and shown in descending order of environmental impact according to energy requirements, hazardous material releases, and air pollutant releases of extraction.

Metal	Energy Required for Metal Extraction (MJ/kg)	Hazardous Material or Strong Acid in Waste	Criteria Pollutants
Silver	3024	Arsenic, cadmium, lead, mercury, sulfuric acid, possibly cyanide	Carbon monoxide, lead, nitrogen oxides, particulates, sulfur dioxide
Tin	240	Strong acid	Carbon monoxide, nitrogen oxides, particulates, sulfur dioxide
Indium*	>73.7*	Arsenic, cadmium, lead, mercury, sulfuric acid, hydrochloric acid	Carbon monoxide, lead, nitrogen oxides, particulates sulfur dioxide
Antimony*	>73.7*	Arsenic, cadmium, lead, mercury, sulfuric acid	Carbon monoxide, lead, nitrogen oxides, particulates sulfur dioxide
Bismuth*	>73.7*	Arsenic, cadmium, lead, mercury, sulfuric acid	Carbon monoxide, lead, nitrogen oxides, particulates sulfur dioxide
Lead	73.7	Arsenic, cadmium, lead, mercury, sulfuric acid	Carbon monoxide, lead, nitrogen oxides, particulates sulfur dioxide
Copper	69	Strong acid	Carbon monoxide, nitrogen oxides, particulates, sulfur dioxide

**Antimony, bismuth, and indium refining is a by-product of lead production, values for these metals are estimated.*

Figure 3. Environmental impact of metal extraction metric. Metals are ranked by descending quantity of energy required for extraction, hazardous material or strong acids released into the environment, and criteria pollutants established by the Clean Air Act of 1970.

To rank the metal in terms of adverse environmental impact, energy consumption is the most important factor because the production of energy is a primary source of environmental pollution. Fossil fuels, such as coal, oil, and natural gas, provide approximately 95 percent of all the commercial energy in the world. The primary metals industry consumes over 25 percent of that energy [31]. The combustion of fossil fuels to generate electricity releases air pollutants (sulfur dioxide, hydrocarbons, particulates, metals, etc.) and carbon dioxide into the atmosphere. These releases contribute to the visual degradation of the environment, acid rain, smog, and global warming.

The environmental impact of metal extraction metric shows the estimated energy of raw material extraction (MJ/kg) for lead, copper, silver, and tin. The values for antimony, bismuth, and indium are not available. However, since the extraction of these metals is a by-product of lead smelting, it is safe to assume that their energy consumption is more intensive than that of lead. The energy requirement of antimony, bismuth, and indium extraction is thereby assumed to be greater than 73.7 MJ/kg. Silver extraction consumes the most energy, followed by tin production. Copper production has the least energy intensive processes. This metric suggests that the energy needed to extract silver, antimony, bismuth, and indium will be considerably more than that of lead.

The next category used to rank each metal is the presence of hazardous materials or strong acids in the waste stream. The waste from lead production contains hazardous substances, such as arsenic, cadmium, lead, mercury, and sulfuric acid. Wastes from the production of antimony, bismuth, indium, and silver also contain these hazardous materials, as well as other strong acids used in leaching or electrolytic processes. Arsenic is regarded as a hazardous substance by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The EPA classified arsenic as a confirmed human carcinogen and established a drinking water limit of 0.05 mg/L. The OSHA PEL for arsenic was established at 0.01 mg/m^3. Cadmium is listed as a hazardous waste under the Resource Conservation and Recovery Act, which is designed to protect human health and the environment, to reduce or eliminate the generation of hazardous wastes, and to conserve energy and natural resources. Cadmium is classified by the EPA as a probable human carcinogen with a drinking water standard limit of 0.005 mg/L. The OSHA PEL for cadmium is 0.0005 mg/m^3. The EPA regulates mercury as a hazardous air pollutant under the Clean Air Act, and a priority pollutant under the Clean Water Act. It is a probable human carcinogen and has an allowable limit of 0.002 mg/L in drinking water. Strong acids, such as sulfuric and hydrochloric acids, are also listed as hazardous substances. Although the EPA does not have a drinking water standard limit for these acids, they are corrosive and carcinogenic [6]. The metric suggests that silver is the most environmentally toxic. In addition to the hazardous material from lead smelting, the waste from silver production may also contain cyanide if the cyanide extraction method was used. The waste from copper production was found to contain only strong acids and does not contain any other hazardous material.

The third category used to rank the environmental impact of metal extraction is criteria pollutant emission. Adverse environmental effects caused by air pollutants released during the extraction processes can contribute to acid rain and the formation of photochemical smog. The Clean Air Act of 1970 designated seven pollutants that pose a serious threat to public and environmental health. These criteria pollutants include carbon monoxide (CO), hydrocarbons, lead, nitrogen oxides (NO and NO_2), particulates, photochemical oxidants, and sulfur dioxide (SO_2) [31]. Five of the seven criteria pollutants are emitted during the extraction of lead, antimony, bismuth, indium, and silver, as shown in Figure 3. Copper and tin production processes emit four of the seven criteria pollutants.

Carbon monoxide is a colorless, odorless, non-irritating poison that can cause death at low concentrations by reducing the blood's capacity to carry oxygen to bodily tissues. Industrial processes such as metal extraction can contribute up to 6% of CO in the atmosphere. Mixtures of nitrogen oxides (NO_x) are critical components in the reactions to form photochemical smog:

$$N_2 + O_2 \rightarrow 2NO$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + \text{ultraviolet radiation} + \text{hydrocarbons} + O_2 \rightarrow NO + O_3 + \text{PAN} + \text{aldehydes}$$

Peroxyacetyl nitrate (PAN) is a severe eye irritant and a strong oxidant that can damage materials. Aldehydes, such as formaldehyde, acetaldehyde, and benzaldehyde, produced from these reactions are poisonous and sometimes carcinogenic. Nitrogen oxides in the atmosphere can also react with water vapor in the presence of oxidizing agents, such as ozone, hydrogen peroxide, and hydroxyl ions, to form nitric acid, a source of acid rain. Particulates are small pieces of solid or liquid materials, from 0.005 to 100 microns in diameter, dispersed in the atmosphere. Particulates released from the extraction processes can reduce visibility, cause respiratory problems, and can possibly be carcinogenic. Sulfur dioxide is a colorless, poisonous, corrosive gas that can cause respiratory irritation. The major concern with SO_2 is that it can react in the atmosphere with other materials to form sulfuric acid. Sulfuric and nitric acids in the atmosphere causes of acid rain.

All the metal extraction processes release CO, NO_x, particulates, and SO_2 into the atmosphere. The antimony, bismuth, indium, lead, and silver processes also release lead particles. Figure 3 suggests that silver may have the most adverse effect on environmental quality based on energy consumption and hazardous materials released during extraction. There is not enough information to evaluate antimony, bismuth, and indium, but it is assumed that their environmental impact may be greater than lead because their extraction processes require lead smelting as a first step. The results of the toxicity metric was used to rank antimony and bismuth since their values for each of the three categories are the same. Based on the environmental impact of extraction metric, it seems that copper extraction has the least adverse effect on environmental quality.

A summary metric is developed based on the results from the toxicity metric, the availability and supply metric, and the environmental impact of extraction metric. The results from the previous metrics were weighted equally and summarized in Figure 4 to produce an overall rank for each metal. A ranking of one being least desirable or feasible for evaluating the critical issues of lead-free alternatives, while seven is the most desirable rank. The final ranking shows that silver is the least desirable alternative to lead, mostly due to its low availability and high energy consumption. Indium, antimony, and bismuth metals have ranks of two, three, and four, respectively. This metric also shows that copper is the most desirable substitute for lead in lead-free alloys in terms of availability, public health effects, and environmental impacts.

Metal	Toxicity Metric Ranking	Availability and Supply Metric Ranking	Environmental Impact of Extraction Metric Ranking	Sum of the Metric Rankings	Final Rank of Metal
Lead	1	6	6	13	5
Antimony	3	4	4	11	3
Bismuth	5	2	5	12	4
Copper	6	7	7	20	7
Indium	4	1	3	8	2
Silver	2	3	1	6	1
Tin	7	5	2	14	6

Ranking: 1 = Least Desirable; 7 = Most Desirable

Figure 4. Summary metric. The final ranking of each metal based on the results of the toxicity metric, the availability and supply metric, and the environmental impact of extraction metric.

Conclusions

This project sets out to evaluate some critical environmental impact issues in selecting feasible lead-free solders. Six alternative metals were evaluated using a series of comparison metrics. The issues addressed are the toxicity and public health effects, availability and supply of raw materials, and the environmental effects of the production processes of lead and the six alternative metals

The toxicity metric (Figure 1) focuses on the issues that are of most concern to human health. The metals are evaluated by whether they can bioaccumulate in organisms and move up the food chain; whether exposure to each metal can cause cancer or birth defects; and the government regulations of the allowable limits in drinking water and in the work place. Results of this metric suggest that lead is the most toxic, followed by silver and antimony. Tin and copper are found to be least toxic among the seven metals compared.

The availability and supply metric (Figure 2) focuses on the abundance, world production, world reserves, and the price of each metal. The results from this metric show that copper is the most abundant, which is three magnitudes greater than antimony, silver, bismuth, and indium. The availability and supply metric also show that silver and indium may not be feasible alternatives to lead due to their high cost.

This metric further shows that there will be supply problems for antimony, silver, bismuth, and indium should they be chosen as a substitute for lead.

An environmental impact metric was developed to evaluate the effects of metal extraction on environmental quality. Estimated energy consumption, hazardous waste, and criteria pollutants of each extraction process were used to determine the environmental effects. Figure 3 shows that silver extraction is the most energy intensive and has the most adverse environmental effects, while copper production consumes the least amount of energy and has the least effects. Tin production was estimated to consume more energy than the antimony, bismuth, indium, and lead processes. In order to consider silver, indium, antimony, and bismuth to substitute lead in the soldering technologies, alternative methods of extraction must be developed to reduce the environment impact of the production processes.

Results from this project suggest that most of the alternatives are safer than lead in terms of toxicity and environmental impact. However, there is no evidence to fully support this suggestion because the abundance and current environmental loading of the alternative metals are less than that of lead. It is not known that if similar amounts of the alternative metals are released into the environment, whether it will have the same toxicity effects as lead. Further research is necessary to fully assess the toxicity and environmental impact of the alternative metals.

Acknowledgments

Place acknowledgments here, if needed.

References

1. Commission of the European Communities. (2000). Proposal for a Directive of the European Parliament and of the Council on Waste Electrical and Electronic Equipment and on the restriction of the use of certain hazardous substances in electrical and electronic equipment. COM 2000.
2. Le Fèvre, P.J. (2002). "Environmental issues in power electronics (Lead free). APEC 2002.
3. Suganuma, K. (2001). "Advances in lead-free electronics soldering." *Current Opinion in Solid State and Material Science.* 5:55-64.
4. Shapiro, A. (2002). "Assembly techniques and alloy alternatives." Industrial Ecology Lecture Notes. Retrieved May 23, 2002 from the University of Californina, Irvine web site: http://eee.uci.edu/02s/51749/Lectures/Shapiro/outline_shapiro.html.
5. Allenby, B.R. (1992). Dissertation. Design for Environment: Implementing Industrial Ecology. 379pp.
6. Agency for Toxic Substances and Disease Registry (ATSDR). (2001, June 22). Public Health Statements. Retrieved March 5, 2002, from http://www.atsdr.cdc.gov/phshome.html.
7. Comino Ltd. (2000a). Material Safety Data Sheet for Bismuth Metal.
8. Comino Ltd. (2000b). Material Safety Data Sheet for Indium Metal.
9. Comino Ltd. (2000c). Material Safety Data Sheet for Lead Metal.
10. Fowler, B., Yamauchi, H., Conner, E., and M. Akkerman. (1993). "Cancer risks for humans from exposure to the semiconductor metals." *Scandinavian Journal of Work Environment and Health.* 19 suppl.: 101-103.
11. National Institute for Occupational Safety and Health. (1978). Criteria for a recommended standard, occupational exposure to antimony. Publication No. 78-216.
12. American Cancer Society. (2002). Cancer Facts and Figures 2001. Retrieved May 23, 2002, from http://www.cancer.org/downloads/SST/F&F2001.pdf.
13. Brown, R.D. Jr. (1998a). "Bismuth." *U.S. Geological Survey, Minerals Yearbook, Metals and Minerals*, 1:12.1-12.6.
14. Brown, R.D. Jr. (1998b). "Indium." *U.S. Geological Survey, Minerals Yearbook, Metals and Minerals*, 1:37.1-37.3.
15. Carlin, J.F. Jr. (1998a). "Antimony." *U.S. Geological Survey, Minerals Yearbook, Metals and Minerals*, 1:6.1-6.7.
16. Carlin, J.F. Jr. (1998b). "Tin." *U.S. Geological Survey, Minerals Yearbook, Metals and Minerals*, 1:78.1-78.13.
17. Edelstein, D.L. (1998.) "Copper." *U.S. Geological Survey, Minerals Yearbook, Metals and Minerals*, 1:22.1-22.28.
18. Hilliard, H.E. (1998). "Silver." *U.S. Geological Survey, Minerals Yearbook, Metals and Minerals*, 1:69.1-69.10.
19. Li, T., Archer, G., and S. Carapella. (1992). Antimony and antimony alloys. . In *Encyclopedia of Chemical Technology*, 4th ed. (Kroschwitz, J. and M. Howe-Grant, eds). John Wiley & Sons, New York, NY, vol. 3, pp. 367-381.
20. Smith, G.R. (1998). "Lead." *U.S. Geological Survey, Minerals Yearbook, Metals and Minerals*, 1:44.1-44.24.
21. Chagnon, M. (1992). Bismuth and bismuth alloys. In *Encyclopedia of Chemical Technology*, 4th ed. (Kroschwitz, J. and M. Howe-Grant, eds). John Wiley & Sons, New York, NY, vol. 4, pp. 237-245.
22. Etris, S.F. (1992). Silver and silver alloys. In *Encyclopedia of Chemical Technology*, 4th ed. (Kroschwitz, J. and M. Howe-Grant, eds). John Wiley & Sons, New York, NY, vol. 22, pp. 163-178.
23. George, D.B. Copper. (1992). In *Encyclopedia of Chemical Technology*, 4th ed. (Kroschwitz, J. and M. Howe-Grant, eds). John Wiley & Sons, New York, NY, vol. 7, pp. 381-428.
24. Graver, C.C. (1992). Tin and tin alloys. In *Encyclopedia of Chemical Technology*, 4th ed. (Kroschwitz, J. and M. Howe-Grant, eds). John Wiley & Sons, New York, NY, vol. 24, pp.105-122.
25. King, M. and V. Ramachandran. (1992). Lead. In *Encyclopedia of Chemical Technology*, 4th ed. (Kroschwitz, J. and M. Howe-Grant, eds). John Wiley & Sons, New York, NY, vol 15, pp. 69-113.

26. Moyes, A.J. (2002). The Intec Copper Process, superior and sustainable copper production. Retrieved April 3, 2002, from http://www.hgeng.com/pdf/Intec.pdf.
27. Nedians Engineering Fundamentals. (2002). General metallurgy: The process of extraction of metals from their ores and refining them. Retrieved May 23, 2002 from http://www.nedians.8m.com/Physical.html.
28. Paiva, A.P. (2001). "Recovery of indium from aqueous solutions by solvent extraction." *Separation Science and Technology*. 36:1395-1419.
29. Slattery, J.A. (1992). Indium and indium compounds. In *Encyclopedia of Chemical Technology*, 4th ed. (Kroschwitz, J. and M. Howe-Grant, eds). John Wiley & Sons, New York, NY, vol. 14, pp. 155-160.
30. World Bank Group. (1998). Pollution prevention and abatement handbook: toward cleaner production. The World Bank Group in collaboration with the United Nations Environment Programme and the United Nations Industrial Development Organization Washington, D.C.
31. Bishop, P.L. (2000). *Pollution Prevention Fundamentals and Practice*. Boston: McGraw-Hill.