

## **CAN WE DECREASE THE ECOLOGICAL FOOTPRINT OF BASE METAL PRODUCTION BY RECYCLING?**

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### **1. Introduction**

The South African base metals industry has been one mainly focused on the production of metals or metal compounds from primary ores. This is true for metals such as titanium, vanadium, chrome, manganese, cobalt, nickel, copper, zinc and aluminium. The steel making industry has traditionally used a substantial portion of scrap steel, and could thus be considered to be somewhat of an exception.

Secondary sources have played much less of a role, possibly due to at least some of the following factors. Scrap material is often of unknown composition, and thus it requires additional chemical analysis, and possibly special treatment. Tonnages are relatively small, and the incorporation of secondary materials is possibly seen to carry undue risk and inadequate benefit. South African consumers are still not very conservation and recycling conscious, which limits the amount of scrap made available. This attitude might also be expected to influence decision makers in these industries. Finally, pressure from environmentally motivated activists locally has not been unduly large.

This landscape has been changing, and is continuing to do so. Various municipal authorities such as those of Pretoria, Johannesburg and Cape Town are reporting increasingly limited landscape for waste (Bondolfi, 2007). There are increasing concerns regarding the leaching of hazardous metals such as chromium, mercury and cadmium from landfill waste, especially electronic and electric wastes – the so-called eWastes. In more developed countries such as the United States of America and Western Europe the problem of eWaste has grown to the extent where legislation has been enacted, such as the Waste Electrical and Electronic Equipment (WEEE) legislation of the EU (European Union Directive 2002/96/EC).

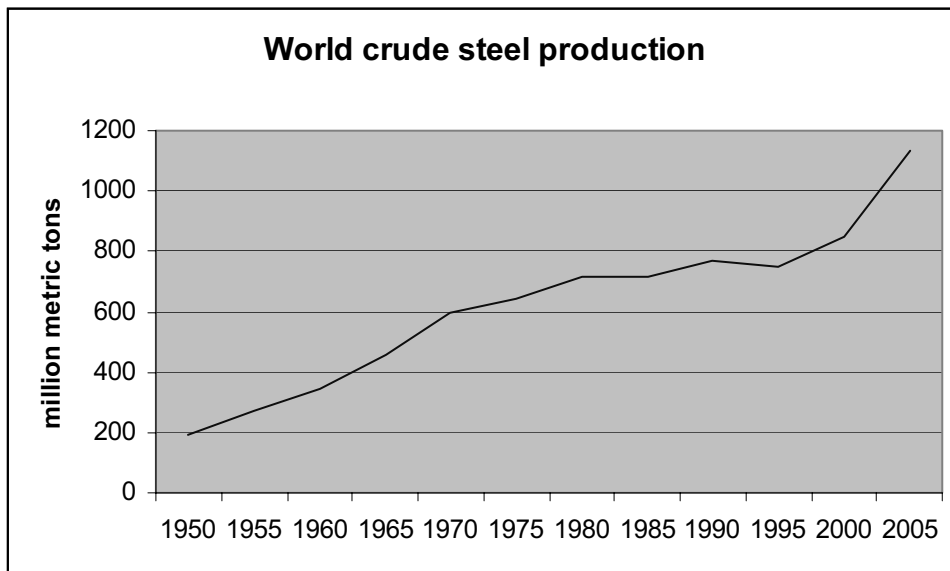
The 19<sup>th</sup> and 20<sup>th</sup> centuries have seen major technological advances. Relevant to this paper is the availability of centrally generated electrical power, telecommunication, entertainment through recorded and transmitted music and images, the growth and pervasive influence of electronics, and the handling of digital data by computers and microprocessors. These developments have placed ever increasing demands on resources for the manufacture of electrical and electronic equipment, as well as on the generation of electrical power. Most of the resources required are non-renewable: copper, steel, aluminium and other metals, various thermoplastic polymers such as PVC (polyvinyl chloride), polyethylene and ABS (acrylonitrile-butadiene-styrene), thermosetting polymers such as epoxies, elastomers such as butyl rubber, glasses and ceramics, and composites such as fibre reinforced plastic (fibreglass). The conservation of non-renewable resources inevitably includes recycling.

To a certain extent, recycling of materials locally is well established. Thus glass, paper, used oil, car batteries, ferrous scrap such as beverage cans and non-ferrous scrap such as

copper and aluminium are often recycled. The materials in especially printed circuit boards (PCBs) present a greater problem however. Often only the gold, which is the major metal of value, is extracted overseas by processes that are suspect from a safety, health and environment perspective. The acids used and the residues might not be disposed of responsibly.

## 2.      **The need for recycling**

As mentioned above, there are ongoing trends toward greater mechanisation, more use of electrical and electronic equipment, and increasing use of mechanised transport. These trends are resulting in increased use of energy and material resources. As an example, the growth in global steel production is shown (International Iron and Steel Institute, 2006) in Figure 1.



**Figure 1.** World crude steel production figures from 1950 to 2005.

To consider the effect of the use of any equipment on the environment, it is useful to employ the “ecological footprint” metaphor. The term was originated in 1992 by the Canadian ecologist, professor William Rees of the University of British Columbia (Cited by Global Footprint Network). It is used to indicate how much biologically productive water and land is hypothetically required by a human population in order to sustain itself and absorb its wastes, while using present technologies. Thus the use of food, water, energy, and materials is added up and converted into an area measure that represents a typical area required for providing these resources and absorbing the waste materials. The calculated area is normally expressed in global hectares (gha) per person.

The ecological footprint is thus a useful way of expressing the environmental impact of resource use and consumption, but excludes material resource use. Clearly, there are simplifying assumptions made in the calculations, as well as some crude assumptions which lead to criticism as regards the accuracy of the numbers. However, the concept does seem to provide a useful method of summing many relevant factors into an easily understood impact number. Unfortunately, the ecological footprint is difficult to

calculate due to the many factors that are involved. A simpler calculation for the carbon footprint estimates the amount of carbon dioxide emitted due to the burning of fossil fuel for energy generation. In the case of materials it refers to the embodied energy required to produce that material. The carbon footprint is often a large part of the ecological footprint (Global Footprint Network).

To quantify the environmental impact of non-renewable resource use, a material footprint may be defined. The term has been used in various ways in literature, and seems to refer mainly to the quantity (mass) of material used for an application, such as the total mass of concrete and brick in a house.

It is suggested that for metals a different approach could be useful. Figures are available for minerals, e.g. as supplied by the US Geological Survey, indicating the global reserve base of a number of commercially important minerals. These can be converted to a metal reserve base using the published average grade.

An important factor to take into consideration is that the global reserve base numbers are estimates made using present mining- and production practice, and measured plus indicated ore deposits. They include currently economic reserves, marginal- and currently sub economic reserves.

By calculating the ratio of the amount of metal used to the global reserve base value, the result could be understood as an impact factor, or a material footprint. Thus for the use of a given material in a specific application:

$$\text{Material Footprint} = \text{mass of material used} / \text{mass of global reserve base},$$

where the same units of mass are used.

As the global reserve base numbers are rather large, a multiplication factor of  $1 \times 10^{13}$  may be used to obtain manageable numbers. Thus:

$$\text{Material Footprint (MF)} = \text{mass of material used} * 10^{13} / \text{global reserve base}.$$

It should be noted that the calculation is only applicable to situations where virgin material is used, i.e. material directly produced from primary ores. In a recycling scenario where there is partial (or complete) recovery of the material, it should be remembered that these footprint calculations would be an overestimation of the material footprint. In that situation the ratio could be modified as follows:

$$\text{MF}_{\text{rec}} = (\text{mass used} - \text{mass recovered}) * 10^{13} / \text{global reserve base}$$

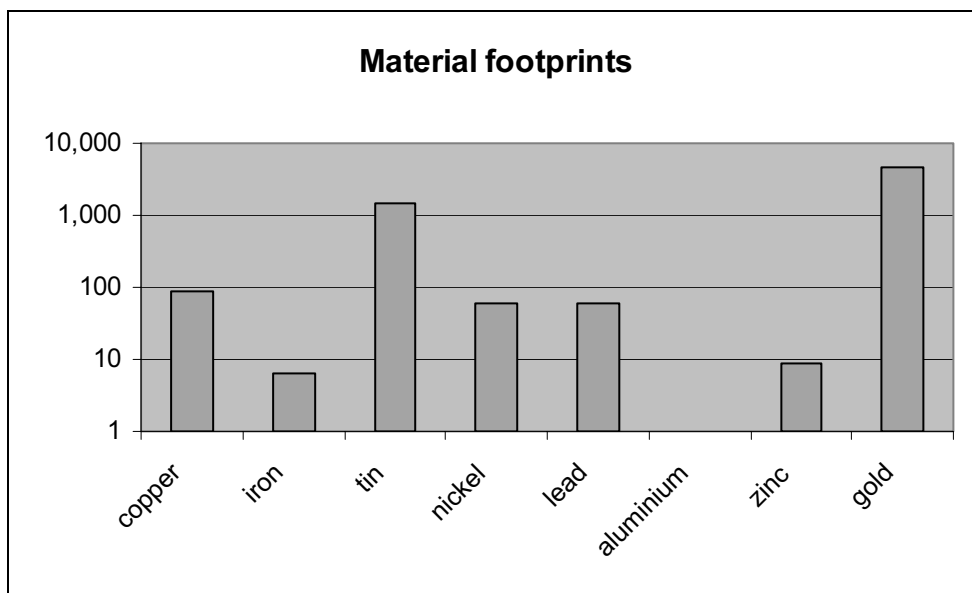
A total material footprint for a given item could be calculated by summing the individual materials footprints to arrive at a total material impact figure.

As the global reserve base numbers include currently economic reserves, marginal- and currently sub economic reserves, these reserve base numbers are thus somewhat optimistic. That means that calculated material footprints are smaller than what is presently realistic. A further disadvantage is that what is considered sub-economic

today is likely to be considered economic in future. Thus, importantly, the material footprints are technology- and commodity price related. As a result, the calculated material footprint numbers are unfortunately not time invariant.

The material footprint defined above was related to metals only. A similar calculation could probably be done for polymeric and elastomeric materials. However, much of global crude oil reserves are used for energy rather than material production. A material footprint calculation could be done for some components of specialised or technical glasses and ceramic materials. For example, the lead used to produce lead glass as used in CRT (cathode ray tube) computer and television screens. For standard soda- or borate glasses the carbon footprint is probably the only relevant impact, as the silica, lime etc. component materials are rather common.

For the metals relevant to computers material footprint numbers calculated from US Geological Survey data (US Geological Survey Mineral Commodity Summaries) were represented graphically using a logarithmic scale, as in Figure 2 (recycling not considered). Metal contents were as listed in Table 2 for eWaste (below), and a total mass of 41 kg for the combined computer, printer and CRT screen.



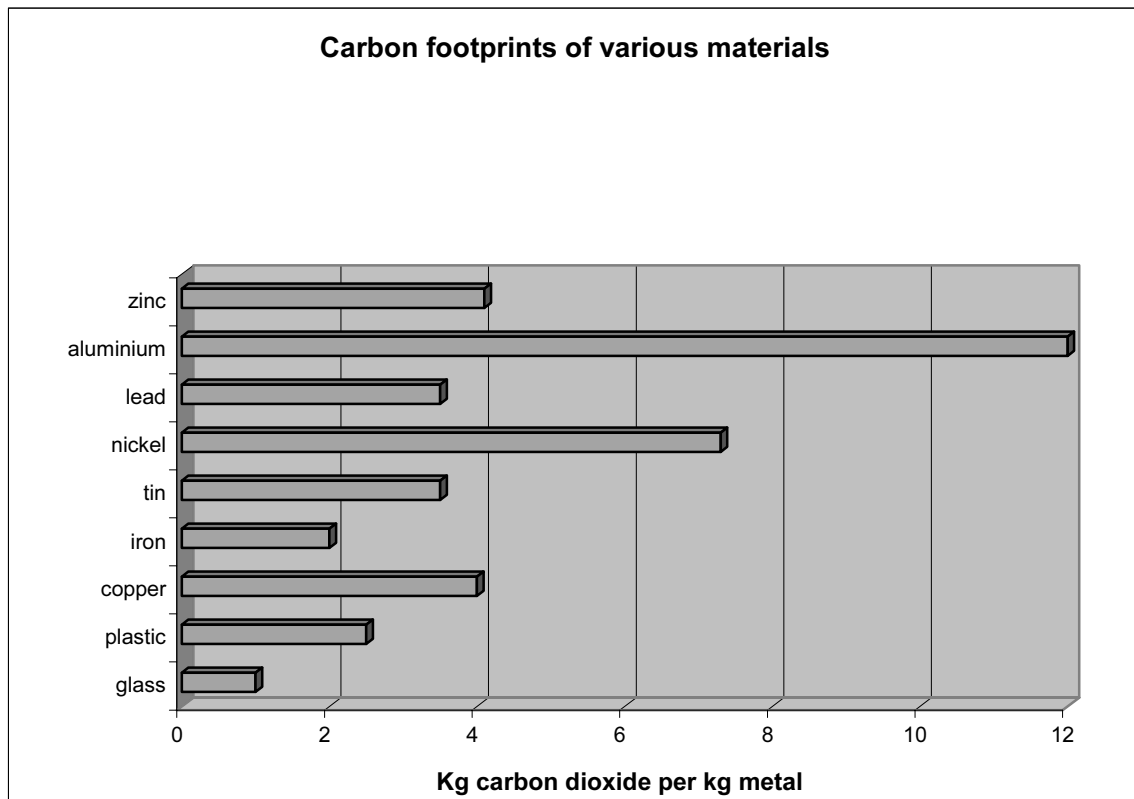
**Figure 2.** Calculated material footprints for a several metals as present in a typical personal computer, printer and CRT screen.

It is found that the tin used mainly in standard solders has a large footprint – almost 2 000 times that of aluminium. Although only small amounts of gold are used, the relative footprint is disproportionately large at nearly 5 000 times that of aluminium. This is probably true for other precious metals such as platinum and palladium, which have not been considered. The total material footprint for the metals considered above amounts to 6 300. This compares to 2 900 for a small car, 95 for a washing machine and 42 for a microwave oven.

The numbers calculated for the material footprints also give a useful indication for where recycling efforts should be focused, when considered from a sustainability point

of view. In order to decrease the materials footprint, the recycling attention should focus firstly on gold and tin, and thereafter on nickel, copper and lead.

Apart from the problem of the loss of the material resources, another aspect of disposal is the loss of the embodied energy in these materials. The embodied energy as the number of kilograms CO<sub>2</sub> produced per kilogram of metal, for various metals, general plastic and glass (Data converted from Hayes, 1993 and from CES, 2006) is shown in Figure 3. Aluminium has the highest embodied energy. Other metals that have high values are nickel and copper.



**Figure 3.** Carbon footprints as a measure of embodied energy for various materials relevant to electrical and electronic equipment.

The embodied energy in plastics is easily recovered through combustion, as these are carbonaceous materials. However, the embodied energy in metals is generally not recovered. If the metals are recycled for use, much of the embodied energy is at least not lost. Table 1 illustrates the substantial energy savings that can be made through reuse of metals, based on the values for the energy requirement for metal production, as reported 30 years ago by Kellogg (1977). It is important to note that the energy requirements for primary metal production were reported as "process fuel equivalents" (PFEs), the sum of the amount of fuel used directly, and the fuel equivalent of electricity and reagents, with credits for waste-heat recovery included. In the case of electrical energy, the total energy requirement per kWh of energy (as used in the process) was taken to be 11.07 GJ/kWh, which implies an overall efficiency (of electricity generation and transmission) of some 32.5%. Note also that the values in Table 1 are for production of metal from concentrates, and do not include the energy requirements of mining and minerals processing. For reprocessing of scrap, the energy

requirement listed is only the energy for electrical furnace melting of the metal (except for Zn, where the value is for vaporisation), so no energy required for collection and separation of scrap, nor for melting of impurities, is included in the value. Required energy increments for heating and melting (or vaporisation) of the metal were taken from FactSage (Bale et al., 2002), using the same value of 11.07 GJ/kWh, and assuming an energy efficiency of 30% within the melting furnace. Given the many assumptions behind the values in Table 1, and the large differences between plants and ores, the values are indicative only.

**Table 1.** Comparison of estimated energy requirement (in "process fuel equivalent", or PFE) for primary production of metals from concentrates (Kellogg, 1977), with the energy required to re-melt scrap (re-vaporise in the case of Zn) (values from FactSage; Bale et al., 2002). See text for details of assumptions.

Metal	Primary production			Reprocessing		$\frac{PFE_{reproc}}{PFE_{prim}}$
	Product	Steps	$PFE_{prim}$ (GJ/t)	$PFE_{reproc}$ (GJ/t)	$T_{product}$ (°C)	
Al	Ingot	Bayer leach, Hall electrolysis	280	11	700	0.04
Cu	Cathode	Flash smelt, convert, electrorefine	23	8	1200	0.33
Zn	Special high-grade Zn	Roast, leach, electrowin	51	24	1000 (vapour)	0.46
Steel	Ingot	Blast furnace, oxygen steelmaking	22	14	1600	0.63
Pb	Refined Pb	Blast furnace, dross, fire-refine	21	1	400	0.04

Recovery by recycling of metal values is advantageous from an energy (carbon footprint) point of view, but is clearly also beneficial as regards the material footprint. The total material footprint calculated for a computer with printer and CRT monitor is about 6 300 considering only the metals mentioned in the table above. If 80% of these metals may be recovered by recycling, the total material footprint drops to about 1 300.

By way of comparison, the material footprints (metals) for a typical small car, washing machine and a microwave are 2 900, 95 and 42 respectively. The metals footprint for a computer are so much higher largely due to the contributions from gold, tin and copper. Thus the disposal of one computer with its ancillary equipment, without recycling, could be considered equivalent to the material footprint loss of 2.3 cars, or 70 washing machines, or 160 microwave ovens. Several scarce metals are used in quantities that considerably affect the total material footprint for metals of computing equipment. Recycling of these metals is thus vital from a conservation point of view.

### **3.        Recycling of waste materials**

Secondary resources such as scrap may be classified as prompt scrap that arises during manufacturing processes, and obsolete scrap from scrapped items. Prompt scrap is generally immediately recycled. Obsolete scrap is often more complex, requiring disassembly and identification of component materials. For instance, as copper is an undesirable element in steel, wiring harnesses and small electric motors need to be stripped from scrapped cars before the steel can be smelted. Alternatively, scrapped items can be shredded complete, or after partial disassembly to provide adequate liberation of various materials. However, to conserve energy and to enable sorting by, for instance, eddy current separation the final pieces of material should not be too small.

The exact approach taken to process scrap materials depends greatly on the source items and type of material. Hence, the focus here will be the processing of PCB material. These can often be removed fairly intact after a simple disassembly process.

A typical PCB consists of a glass reinforced thermosetting epoxy resin base, or a sheet of phenolic resin impregnated paper material. These are normally impregnated with bromine based fire retardants. The board will have one or more layers of thin copper material defining the conductive interconnects between electronic components. If several layers of copper conductors are used, there are usually through plated holes connecting various layers. Components of various types are connected to the copper tracks by soldered connections. The solders have generally been 60-40 tin-lead types. Due to environmental considerations, there is a movement to replace the lead based solders by lead-free solders which are various binary, ternary or quaternary alloys of copper, silver, zinc, bismuth, or indium with tin. For instance, **CASTIN®** is a combination of copper, antimony, silver and tin. The nominal composition is 96.2% tin, 2.5% silver, 0.8% copper and 0.5% antimony. All of these solders have higher tin contents than the older lead-tin alloys, which will further increase the material footprint, and thus the need for recycling.

The components themselves generally are complex. Integrated circuits often consist of a complex chip of single crystal silicon containing low levels of dopant elements such as arsenic and indium. Electrical connections to outside components are usually made through metallic pins or pads of tinned copper. Fine gold wires connect these pins to connector pads on the silicon chip. All of this is encapsulated in a glass filled epoxy resin or ceramic material. Similarly, resistors, capacitors and inductors make use of a variety of materials such as copper, aluminium, carbon, ferrites etc. Boards may have contact fingers or other connectors that have gold plating to ensure reliable, corrosion-free electrical contacts. Other precious metals such as silver, platinum and palladium may be used for special electrical contacts. A number of other materials and components are generally present such as a variety of thermoplastic polymers, steel fasteners, batteries, CPU fans etc. (The above information may be found in Wikipedia).

Interestingly, the scarce metals, the target metals for recycling, are mainly found in the printed circuit board assemblies. Unfortunately for recycling efforts this constitutes a complex and heterogeneous feed material for metal recovery. The materials are also not found in the sulfide or oxide form that primary metal producers normally deal with.

Other problem components of eWaste are CRT screens as the glass of the CRT contains appreciable amounts of lead, and batteries which often contain nickel and cadmium.

The PCBs are very complex, heterogeneous assemblies containing many materials, including precious metals. However, the levels at which even the precious metals are present are high compared to normal ores. Table 2 illustrates analyses for PCBs (Goosey and Kellner, 2002), a personal computer (eWaste Guide) and for electronic scrap (Sodhi and Reimer, 2001). Boards vary considerably in their metal contents, depending on the application and the technology used.

Material	Approx. material composition, %		
	PCB	Computer	eWaste
Non-metallic	70		
Refractory oxides		25	30
Plastics		23	30
Copper	16	7	20
Solder	4		
Lead		7	2
Tin		1	4
Iron, ferrite	3	20	8
Nickel	2	1	2
Aluminium		14	2
Zinc		2	1
Silver	0.05	0.02	0.2
Gold	0.03	0.002	0.1
Palladium	0.01	0.0003	0.005
Other (Bi, Sb, Ta etc.)	<.0.01		

**Table 2.** Approximate material compositions of typical printed circuit boards, a typical personal computer, and typical electronic waste.

#### **4. Metal recovery from printed circuit boards**

In many respects metal recovery from scrap PCBs parallels normal ore processing techniques. Firstly comminution is required to obtain suitable liberation. Physical separation methods could be used to obtain one or more metallic concentrates. Steel components could be removed through magnetic separation, for instance. The metallic concentrates may go to pyrometallurgical methods of extraction such as smelting or sweating. Alternatively, or in conjunction with the pyrometallurgical methods, hydrometallurgical methods could be used. The latter seem particularly appropriate due to the selectivity that is required to deal with the complex feed. Hydrometallurgical extraction could follow one of two broad routes, *viz.* selective or non-selective leaching, followed by suitable separation and recovery methods.

One of the objectives of scrap treatment is the minimisation of the carbon and material footprints. However, another is to ensure that potentially hazardous materials are not



allowed to enter the ground, air or water in an uncontrolled manner. Thus the recovery of metal values needs to be done in an environmentally responsible fashion. Often standard extractive processes generate gaseous, liquid or solid wastes. Whereas it is important in standard processes to minimise these wastes and their impact on the environment, it becomes vital for the processing of scrap materials. These issues are dealt with in more detail below.

## **5.        The role of comminution and physical separation methods**

Scrapped electronic equipment is generally first disassembled, and useful components might be recovered at this stage. The scrap PCBs are sorted, graded and shredded. The grading classes generally follow the precious metal content of the boards. Comminution to sub 5 mm particles is required to effect material liberation levels as high as 96% (Goosey and Kellner, 2002). The shredded material is often upgraded in terms of metal content. Generally magnetic and eddy current separation is used to generate ferrous and aluminium fractions. In eddy current separation the shape of conducting particles, in addition to their particle sizes, conductivities and densities have a significant effect on the repulsive forces that are generated, and thus on the separation efficiencies (Goosey and Kellner, 2002). Typically particle sizes between 4 and 100 mm are required for eddy current separation (Williams, 2006). Comminution must be thus be carefully controlled to obtain adequate liberation, and yet remain within a suitable size range for eddy current separation. Electrostatic separation can be used to separate the metallic from the non-conductive materials. Density differences between various metals and non-metallic constituents may also be used to effect separation. Narrow size ranges are typically required, however. Flotation methods are typically not used (Williams, 2006), presumably due to the metals not being present as sulfides and oxides.

The environmental impact of comminution is relatively small, provided that dust and noise control is in place. The shredders are specialized hammer mills operating at high power inputs, as high as 5 MW to shred 250 tph (Monaghan, 1990). Noise levels can be 99 dB and higher (Warczok *et al.*, 1990). Comminution of the glass reinforced board material is likely to generate glass dusts. It appears that these dusts are generally not of respirable size (Boatman *et al.*, 1998), but can cause fibreglass dermatitis (Hsieh *et al.*, 2001).

Several separation processes can be done wet or dry, which will affect their environmental impact. Wet mechanical separation processes have a lower precious metal content loss of typically 10%, compared to the up to 35% levels of dry processes. However, the wet processing methods are likely to generate contaminated fluids that have to be dealt with. Dry processes could have associated dust problems, similar to the comminution step.

## **6.        Metal recovery using pyrometallurgical methods**

Recycling of base metals by pyrometallurgical means is an obvious option; it is an obvious option because of the tendency of the major base metals (copper and nickel) to form sulphides, which can be recovered to a matte phase. Indeed, such recycling is

already practised in pyrometallurgical plants, through the recycling of converter slag to concentrate smelting furnaces, or to slag-cleaning furnaces. The major factors which determine the efficiency of metal recovery are the availability of a sulphide phase as collector, and control of the reduction conditions. These requirements are met in concentrate melting furnaces (where the concentrate is a source of sulphides as collector phase, and also ensures fairly reducing conditions), and are readily met in slag-cleaning furnaces through the addition of concentrate and of carbonaceous reductant.

Given that the existing smelters already practise internal recycling, it appears feasible to recover copper and nickel from secondary sources (such as electronic scrap), by adding these secondary sources to the feed mixtures of the existing smelters. However, in addition to possible capacity limitations (the existing platinum smelters operate at or close to their capacity) the detail of the behaviour of the individual elements needs to be considered.

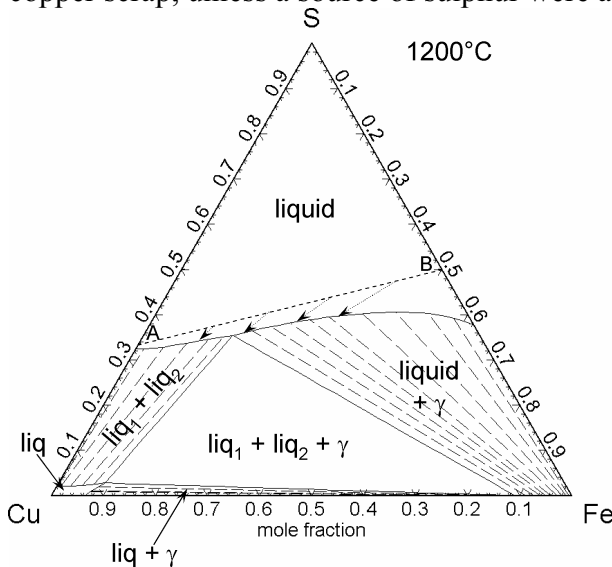
A general indication of the behaviour of the individual elements is given by the review of Broadhurst et al. (2007). This indicates that lead is expected to partition mainly to the vapour phase during smelting; zinc is expected to partition between the vapour and slag phases; tin is expected to report mainly to the slag phase. Of course, noble metals (platinum-group metals, gold and silver) would be recovered quite efficiently by the matte phase. The noble metals would be recovered later in the process – in the anode slimes (in the case of copper plants) or in the precious-metal refinery (in the case of platinum smelters).

From these considerations, it appears quite feasible to recover the valuable metals from secondary material, by simply blending this material into the feed of existing furnaces. As far as the non-metallic content of the material is concerned, the glass-fibre reinforcement in printed circuit boards would give only a minor increase in the slag volume, and polymers in the secondary material would serve as reductant; this would not pose serious difficulties, given that (for example) slag cleaning furnaces already use a carbonaceous reductant as additive.

There are limits on the amount of copper-rich scrap which can be included in the feed of sulphide smelters; these limits are imposed by phase stability: if too much metallic material were to be added, without addition of a source of sulphur, a metal phase would precipitate out of the matte. This is illustrated by Figure 4, which shows the 1200°C isothermal section of the Cu-Fe-S system. (This diagram was calculated with FactSage [Bale et al., 2002], and agrees well with the 1200°C section shown by Raghavan [2004].) The matte compositions in copper smelters typically lie along or close to the Cu<sub>2</sub>S-FeS join, which is indicated by line A-B in the figure. Addition of copper (from electronic scrap, for example) would cause the melt composition to move towards the Cu corner, as shown by the arrows in the diagram. When the amount of added Cu exceeds a critical amount, the melt composition meets a phase boundary, beyond which austenite ( $\gamma$  in the diagram) or liquid copper precipitates out as a separate phase. The formation of such metal phases would be undesirable, since such phases are denser than the matte, and would hence collect on the bottom of the furnace.

The length of the arrows (relative to the distance between the matte composition and the Cu corner) gives the proportion of Cu which could be added without forming a metal

phase. Evidently, the feed to a copper smelter could only contain a minor proportion of copper scrap, unless a source of sulphur were also added to the feed.



**Figure 4.** 1200°C isothermal section of the Cu-Fe-S system. Typical smelter matte compositions lie along line A-B, which joins the compositions of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ . The arrows indicate the direction in which the matte composition would change if Cu were to be added to mattes which initially lay on line A-B.

The presence of brominated flame retardants (BFRs) in printed circuit boards can lead to serious environmental issues, depending on the detail of the conditions in the furnaces and the way in which the material is fed into the furnace. BFRs can lead to the formation of dioxins and furans, under conditions of incomplete combustion (D'Silva et al., 2004). The toxicity of chlorinated dioxins and furans is well-known, and similar effects have been reported for brominated dioxins and furans (D'Silva et al., 2004). The BFRs act as precursors for the formation of bromine-containing furans: Polybrominated dibenzofurans (PDBF) form by thermolysis (low-temperature heating, without combustion) from polybrominated diphenylethers (PBDE), with data reported for temperatures ranging from 400°C to 600°C (Weber and Kuch, 2003). In contrast, Vehlow et al. (2000) demonstrated that co-combustion of PBDE-containing waste and municipal solid waste in a test incinerator (around 900°C) gave low concentrations of bromine-containing dioxins and furans in the gas. For these incineration conditions, the bromine largely reported to the off-gas, as  $\text{HBr}$ . When electronic waste is added to the concentrate stream in a smelter, conditions favourable to thermolysis (slow heating without combustion) are expected in the concentrate layer; hence formation of bromine-containing furans is likely. These furans would report to the off-gas, necessitating extra off-gas treatment if the secondary material is a significant part of the furnace feed. The presence of BFRs in secondary material, and their behaviour during smelting, are hence the major concerns which would limit the blending of secondary material into the feed streams of existing furnaces.

In electrical furnaces (such as those used to melt down platinum-bearing concentrates), the concentrate is fed onto a slag layer, with electrical resistance heating in the slag layer itself. The concentrate layer is "black", or cold. Under such conditions, production of hazardous products by thermolysis of the BFRs (within the concentrate layer) is likely. In contrast, heating in reverberatory furnaces is from above, by

radiation and convection from the furnace roof and gas freeboard. The hot, oxidising freeboard would be favourable to destruction of the dioxins and furans. A reverberatory furnace would hence be more appropriate for melting of BFR-containing scrap.

Pyrometallurgical processing can also be used as a way to pretreat material before further treatment. As indicated above, incineration of PCBs destroys the brominated flame retardants, yielding a product which can be treated by hydrometallurgy or pyrometallurgy. Pyrometallurgical options for such pretreated material include blending it into the feed of existing base-metal smelters (as indicated above); another option would be to treat the material at the integrated smelter-refinery complex of Rand Refinery, which can handle feed material of 150g/t (and higher) gold grade (Rand Refinery, 2007). The original purpose of Rand Refinery, which remains its main activity, is to refine newly mined gold. However, it can treat other metal-containing materials: Plastic-free electronic metallics are recognised as Class 4 of the feed material of the electric arc furnace – converter combination of the Rand Refinery smelter (*ibid.*). In the electrical arc furnace, two collector phases are used: molten lead (collecting mainly gold and silver), and matte (collecting the base metals, and likely most of the platinum-group metals).

## **7. Metal recovery using hydrometallurgical methods**

Generally hydrometallurgical methods are used in extractive metallurgy where high selectivity is required to deal with complex feed materials; where concentration upgrading is required due to lean feeds, and where smaller volumes of feed are dealt with (compared to blast furnaces). The disadvantages typically lie with relatively slow kinetics of the leaching and recovery reactions, and the size of processing equipment required due to dilute solutions.

The advantages and disadvantages listed indicate that hydrometallurgical approaches in secondary material treatment may be expected to find application especially where physical separation methods are unable to produce clean fractions suitable for pyrometallurgical methods. Hydrometallurgical methods would also be required for precious metal separation. Contamination of nominally clean metal fractions by hazardous materials such as mercury, arsenic etc. could be removed using a suitable pre-leaching method (Piret and Castle, 1990), (Kurose *et al.*, 2006).

Due to slow leaching kinetics, adequate comminution is required to increase the exposed surface area of the particles to be leached. The leaching stage can be carried out as either a selective series of leaching steps, or a non-selective leaching approach which aims to attain complete dissolution of all desirable metals, which is then followed by suitable separation stages. Selective leaching may use chemistries based on cupric chloride or ammonium sulfate to remove copper, followed by nitric acid or fluoboric acid based solutions to remove solders, followed by aqua regia, cyanide or thiourea to leach the precious metals. Non-selective leaching could use aqua regia or chlorine based reagents. In some cases the gold plating is recovered as metal flake after selective dissolution of the base metal pin or contact substrates (Goosey and Kellner, 2002).

Separation methods after leaching would comprise solvent extraction, ion exchange and other selective sorption methods. Extraction methods could be one or more of the typical electrowinning, cementation, precipitation or crystallisation techniques.

Hydrometallurgical operations have many potential impacts on the environment. Leaching and separation processes may use large amounts of toxic, highly acidic or alkaline materials or flammable materials. Leaching might require the use of pressure reactors which adds a further dimension regarding safety. Waste solids due to the precipitation of contaminants, or waste solutions that contain low concentrations of metals, anions etc. are often generated.

On the other hand, solvent extraction and ion exchange methods can be used to clean waste solutions to ensure that effluent streams meet environmental regulations, and may also be used to recover useful reagents or materials. Some examples are the recovery of HF and HNO<sub>3</sub> from stainless steel pickling baths or Cr(VI) from surface finishing wastewater (Cox and Reinhardt, 2004). Systems involving leaching-solvent extraction-electrowinning may often be designed as closed circuit systems. Solid wastes may be retreated to extract toxic materials (Piret and Castle, 1990).

## **8. Conclusion**

From a materials and energy conservation point of view, the recycling of secondary materials such as waste electrical and electronic equipment is advantageous. Further benefits include minimising the volume of landfill, and minimising the pollution of groundwater and air through mobilisation of hazardous materials.

Treatment of secondary materials can be complex, and is often purpose designed. However, in general it seems that in preference physical separation methods should be used to their fullest extent, as their environmental impact is generally low. Clean metallic fractions could be suitable feeds to pyrometallurgical or hydrometallurgical processing. Mixed materials are probably best treated by hydrometallurgical techniques.

For local processors the cost of establishing refineries to treat secondary materials only is probably prohibitive. With an extensive local industry dealing with primary feed materials, it would seem advantageous to process suitably cleaned secondary materials together with the primary feeds. For instance, a fairly clean copper fraction could probably be accommodated in the anode casting step at Palabora Mining Co. Clean zinc material could possibly be used by Zincor Ltd instead of calcine as neutralising material. For precious metal fractions there should not be a problem to accommodate them at the Rand Refinery Ltd. and the PGM refineries. Platinum and palladium fractions might, with suitable alloy adjustment, be suitable for catalytic converters.

Several recyclers have been operating locally for many years. The problem of eWaste has over the last number of years been receiving greater attention, and several recyclers are dealing with this material. Volumes are still small, and the cleaned metal fractions are generally exported for refining (Bondolfi, 2007). Possibly more attention should be given locally to these secondary feed materials. If present primary producers could accommodate cleaned metallic fractions, environmentally certified processors could

probably import eWaste to increase volumes. This should be beneficial in terms of capital utilisation, work creation, and to the economy.

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