The processing of eWaste. Part 2. The electrochemical leaching behaviour of a metallic alloy derived from waste printed circuit boards

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Synopsis

Scrap printed circuit boards were selectively smelted at 1 200°C to produce a metallic alloy having three phases. These phases were identified as a lead-rich phase, a low tin content alpha bronze phase, and a high tin delta phase.

Electrochemical leaching studies on this alloy were done in 1 mol/dm³ sulfuric acid or in 2 mol/dm³ hydrochloric acid (adjusted to an ionic strength of 3 mol/dm³). The lead rich phase was more strongly passivated in sulfate media, and in this medium the high tin content delta bronze was more resistant to corrosion than the lower tin alpha bronze phase.

In chloride medium the lead phase and both bronze phases corroded readily, but with current densities about an order of magnitude lower than in sulfate medium (static conditions) for the bronze phases. The high tin delta bronze phase was found to form a passivating layer in sulfate media. A similar layer was not seen in chloride medium.

The leaching studies in sulfate medium also showed the existence of an alpha bronze phase of lower tin content in the centres of the alpha phase grains. This phase was quite resistant to leaching in sulfate medium.

Introduction

In an earlier paper[1] it was shown that a heterogeneous metallic alloy consisting of various phases may be produced by the selective smelting of electronic printed circuit boards. The alloy was characterized using SEM-EDS, and by using a combination of phase diagrams and thermodynamic calculations, it was shown that there is about 56 mass per cent of an alpha bronze phase, about 35 per cent delta bronze phase as well as 9 per cent of a lead-rich phase. Minor elements such as nickel, zinc, gold and silver are distributed between the various bronze phases and the lead phase. An advantage of a selective smelting route is that iron and steel as well as aluminium are rejected, which is advantageous for subsequent hydrometal-lurgical processing.

The alloy produced by selective smelting appears to have sufficient mechanical strength and electrical conductivity to consider it for making impure copper anodes to be used in a standard copper refinery. As copper is a major component of the alloy, viz. 70 mass per cent, it would seem reasonable to use this route for producing saleable metal. Other metals such as lead, tin, gold, etc. would report either to the anode slime or to the copper electrolyte, and could eventually be recovered.

For the alloy to function effectively as an impure anode in copper electrorefining, it was important to establish its electrochemical leaching behaviour. It had to be established whether selective leaching of certain phases would occur, whether passivation was likely, and whether the anode material would retain sufficient mechanical strength.

Although the selective smelting step is useful in reducing an extremely complex and heterogeneous feed to a much simpler intermediate, the intermediate contains several metallic phases with a number of important metallic constituents. In order to deal with this complex feed material, hydrometallurgical methods could be used to obtain the selectivity that is required. Hydrometallurgical extraction could follow one of two broad routes, viz. selective or non-selective leaching, followed by suitable separation and recovery methods. The work reported here studies the critical leaching step for hydrometallurgical processing of the alloy.

Experimental

Rotating disk electrodes were made up from pure metal or waste metal alloy rods. The metal rod was mounted in a suitable Teflon holder using Impset epoxy resin. Electrical contact was made to the rotator shaft using a compressive copper wire contact. A Pine Instruments rotator was used. Electrode preparation was done by grinding the electrode surface, finishing with 2 400 grit. The electrode was then placed in the deoxygenated

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electrolyte, and given a cathodic treatment to reduce surface oxides and obtain a reproducible electrode surface. The potential used was 0.8 V except in the case of copper, where potentials of –0.4 and –0.5 V were used in sulfate and chloride media respectively.

The sulfate and chloride electrolytes were made up to a molar ionic strength of 3 mol/dm³ as 1 mol/dm³ sulfuric acid, or 2 mol/dm³ hydrochloric acid with added sodium chloride. Ionic strength as used here has its normal meaning, except that molarities were used as the concentration unit.

A standard three electrode electrochemical cell was used, with the rotating disk electrode as the working electrode. The cell temperature was controlled to 25°C by using a water jacket. The counter electrode was either a 5 mm graphite rod (in sulfate media) or a platinum wire (in chloride media). The Ag/AgCl reference electrode (-222 mV vs SHE) was placed in a suitable Luggin capillary, such that the tip of the capillary was within 2 mm from the working electrode surface. The capillary tube was filled with either a saturated solution of sodium sulfate or potassium chloride, so that the anion of the bridging solution matched that of the working electrolyte.

A Solartron SI 1287 potentiostat, controlled via a personal computer running the appropriate software, was used. Scan rates were 20 mV/s. Electrolytes were deoxygenated using nitrogen gas, and experiments were conducted in a nitrogen atmosphere.

The solution resistance for the experimental arrangement at the open circuit potential was measured, and was found to approach zero. Thus the reported currents are not corrected for solution resistance. Electrode potentials are reported against the Ag/AgCl reference. Current densities are calculated based on the geometrical area.

Surface characterization of the electrodes was done using either a suitable optical microscope, or a Jeol JSM 6300 scanning electron microscope with Noran EDS (energy dispersive X-ray spectroscopy) facilities. Before surface characterization the electrode was washed thoroughly with distilled water. When analysing samples with the SEM, the samples were dried under high vacuum to remove entrained water. When EDS was used for phase analysis, typical counts were of the order of a few thousand.

Pourbaix (Eh-pH) diagrams were generated using the W32-STABCAL 2000 software[2].

Results and discussion

Dissolution in sulfate media

Due to the complexity of the alloy material, for comparison purposes electrodes were also made of the pure major component metals, viz. copper, tin and lead. The voltam-mogram for the alloy material was then compared to those for the pure metals. The anodic corrosion behaviour of copper is shown on the combined cyclic polarization diagram, Figure 1. Copper may be seen to corrode actively above about –0.05V, which agrees well (when the potential is converted to the SHE scale) with the copper Pourbaix diagram in Figure 2. The stability region for cuprous ions is small, and separate copper dissolution peaks are not expected on the voltammogram.

The oxidation of copper to cupric ions is a two step process that occurs through the cuprous ion[3]. Beyond about 0.3 V passivation of the surface occurs, probably through the formation of solid hydrated cupric sulfate. Similar passivation

is a well known problem in the electrorefining of copper[4], where the passive layer is referred to as 'blue stone'. When convection is introduced, the peak height at about 0.3 V increases, as well as the limiting current density in the plateau region beyond 0.5 V. An increase in sulfuric acid concentration to 2 mol/dm³ shows that passivation occurs about 0.1 V below the potential recorded at 1 mol/dm³. A passivation mechanism involving cupric sulfate is in agreement with these observations.

Tin metal also corrodes at a high rate in 1 mol/dm³ sulfuric acid medium, even under conditions without forced convection. Figure 1 illustrates this.

A very low dissolution rate of lead was expected in sulfate media, since lead readily forms a protective passive film of lead sulfate at the lower potentials, while a lead dioxide surface layer is expected to be present at the higher potentials according to the Pourbaix diagram for lead, Figure 3. The voltammogram for lead, Figure 4, has a well defined peak from -0.55 V to -0.4 V after which passivation occurs. It is expected that a lead sulfate surface layer forms at -0.47 V where the initial peak current density drops off rapidly.
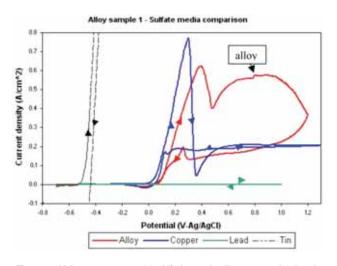

Figure 1—Voltammograms at 20 mV/s for static alloy, copper, lead and tin electrodes in deoxygenated 1 mol/dm³ sulfuric acid
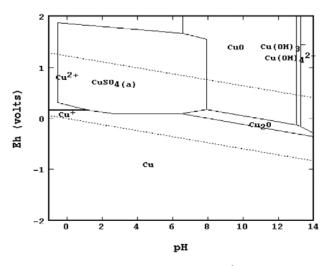

Figure 2—Pourbaix diagram for copper in 1 mol/dm³ sulfuric acid and a copper ion concentration of 1x10⁻⁶ mol/dm³
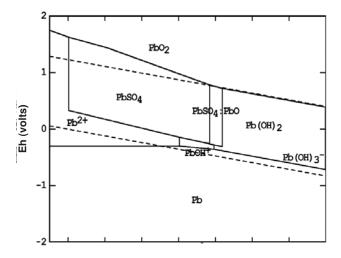
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Figure 3—Pourbaix diagram for lead in 1 mol/dm³ sulfuric acid and a lead ion concentration of 1x10⁻⁶ mol/dm³
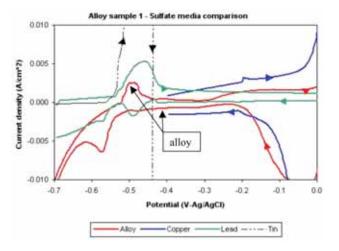

Figure 4—The lower potential region of Figure 1

The voltammogram for alloy dissolution is substantially the same as that of copper, up to about 0.5 V. Passivation occurs at a lower current density and higher potential than for pure copper. The anodic shift of about 0.1 V indicates that the bronze phases are more resistant to corrosion than pure copper.

Alloys are often more resistant to corrosion than the least resistant pure metal component in the alloy, as seen in the Cu-Co-Fe system[5–7], the Cu-Ni brass system[8], and the Cu-Sn bronze system[9].

The dissolution of alloy materials can be selective or non-selective, depending on the redox potential at which dissolution occurs, as well as on the composition of the alloy. Non-selective dissolution occurs with single phase alloys (solid solutions), if the difference in standard potentials of the component metals is small, or at large overvoltages. Their behaviour depends on the difference in standard potentials, and on the alloy compositions[10]. Alloys with their more noble component exceeding 50 per cent (which is the present case) have a dissolution potential higher than that of the less noble component[11].

When selective dissolution of a binary alloy occurs, the polarization diagram would have two regions due to the difference in standard potentials of the components being large. The first region occurs when the potential range is close to the dissolution potential of the less noble component. Selective dissolution of the less noble component generally occurs in this potential region[9]. The region is characterized by a low limiting current density that is associated with the rate determining dissolution of the less noble constituent. When the potential increases to the dissolution potential of the more noble component, a high rate of dissolution of either the less noble component only, or the dissolution of both components is seen. The second region has higher current densities, with a potential increase corresponding to the dissolution potential of the more noble component. This increase occurs after the critical potential has been reached. Selective dissolution occurs frequently when the more noble content of the alloy constitutes a small portion[10]. In the electrorefining of copper anodes, anode slimes containing noble metals are thus released from the matrix due to selective dissolution of the copper matrix.

The voltammograms obtained for alloy dissolution were examined in the lower potential region. An example is shown in Figure 4.

It appears that at low potentials, around –0.5 V, tin is leached at a low rate from the bronze phases. This is suggested by the small anodic peak at –0.5 V, and the corresponding reduction peak at –0.57 V, and corresponds to the first potential region mentioned above. Selective dissolution of tin has been shown to occur in this potential region on alpha phase bronze[9].

Above 0 V the more noble bronze phases can corrode, as may be seen from Figure 1. When this occurs, a copper reduction peak is seen at –0.02 V. The reduction peak height increases as the maximum electrode potential increases, up to 0.5 V. Selective copper dissolution has been found to occur from the alpha bronze phase in sulfate media at potentials in the second region[9]. This is unexpected, but appears to be due to the formation of a tin oxide passive layer. This layer is not very protective, allowing a substantial copper dissolution rate. Archaeological bronzes show similar patinas enriched in tin.

In the transpassive region, above 0.5 V in Figure 1, the alloy behaviour is markedly different from that of copper. Passivation of the electrode is appreciably less than that of copper. When the electrode is polarized to these potentials the copper reduction peak height decreases, but a shoulder is formed at –0.1 V, and the tin reduction peak also increases in height. The reduction process at –0.1 V is probably due to the reduction of copper(I) species. It seems that the passivation layer is enriched in tin, but that copper(I) species are also formed. Copper(I) oxide species have been found in the passive layer formed during bronze corrosion[12]. Although the Pourbaix diagram shows cuprous oxide to be stable only at pH values higher than about 4 at low dissolved copper concentrations, its stability at lower pH values increases markedly as the dissolved copper ion concentration increases. High copper ion concentrations at the electrode solution interface would be expected at sufficiently high electrode potentials in the absence of convection.

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It was found that a thin black layer is seen on the delta bronze when the electrode is polarized to 0.2 V or higher. EDS analysis of this layer shows appreciable enrichment in tin, lead, gold and silver, while still having a high copper content. The passive layer formed on the alloy thus appears to be quite complex in composition.

As seen from the tin voltammogram, this metal in pure form does not seem to passivate under the conditions of this study. Partial anodic passivation has been reported to occur only at sulfuric acid concentrations above 3 mol/dm3, with an electrode potential >0.35 V. The passive layer is mainly a thin (ca. 100 nm), amorphous SnO layer[13]. During the corrosion of bronze in neutral solutions a tin oxide layer has also been found to form. This layer still allows dissolution of underlying copper[9]. It is concluded that in the present case the passive layer is also a tin oxide that additionally contains the typical anode slime components formed during copper electrorefining[4].

Eventually, from a peak potential of 0.8 V the current density on the negative scan is similar to that of the passivated copper electrode. It is likely that a hydrated copper sulfate product is thus also formed on the alloy.

Selective alloy dissolution will result in surface pitting or even the formation of a porous structure. When under mass transport control conditions, the electrochemical dissolution kinetics of such a system would be expected to change with time, due to a change in the surface areas of the alloy phases, as well as due to changes in the mass transport of reactants and products.

Microscopic examination of the electrode surface in this study confirmed that the alpha bronze (lower tin) phase corroded preferentially compared to the delta bronze phase. This is in agreement with the findings of Mabille[9], who found preferential dissolution on sites characterized by a low tin content.

Figure 5 shows an optical micrograph of an electrode subjected to a potential scan from –0.3 V to 1.2 V.

The porosity due to selective dissolution of the alpha bronze phase is seen, as well as an inert phase (lower left corner) with its polishing scratches.

In composition this inert phase was rather similar to the alpha bronze phase, with slightly higher copper and iron levels, but somewhat lower in tin. It was seen in the centres of the alpha phase grains, and is thus copper rich material formed during cooling. Under the optical microscope the inert phase could be differentiated from the others.

The alloy behaviour was further studied under constant potential conditions. A potential of 0.2 V was used for 600 s. This potential is well within the region of activation control for both copper and alloy dissolution. The current density was found to decrease with time. Selective dissolution of bismuth occurred from the lead rich phase. Again preferential dissolution of the alpha bronze was seen, as well as the thin, black layer on the delta bronze phase. The layer could be scratched off easily.

From the constant potential corrosion studies and the voltammetric work it was possible to determine which alloy phases corroded in a particular potential range. The findings are summarized in Table I. The alpha (low tin content) bronze phase was found to leach more rapidly than the delta phase.

Corrosion in chloride media

Chloride media are generally more aggressive than sulfate media in terms of leaching, due to the ability of chloride to effectively stabilize many metal cations in aqueous solution. Less selective dissolution reactions are thus expected.

Copper was found to dissolve effectively in chloride medium, as may be seen from Figure 6. Dissolution occurs at lower potentials than in sulfate media, from -0.2 V, due to stabilization of the copper cations. The maximum current density reached before passivation takes place (at about –0.05 V) is lower in chloride medium than in sulfate.

The electrodissolution of copper in chloride media has been reviewed by Kear[14]. At low overpotentials $CuCl_2^-$ is formed under conditions of mixed charge transfer and product mass transport control. In the next potential region,
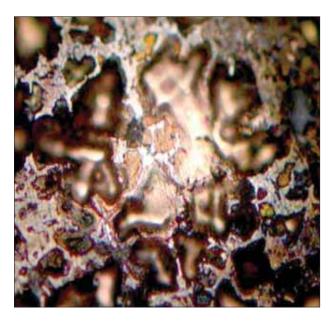

Figure 5—Optical micrograph of a leached alloy electrode surface

Table I

The rate of leaching observed for various alloy phases in 1 mol/dm3 H_2SO_4

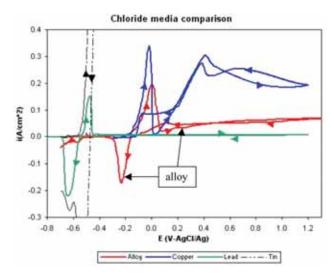| Element	Alloy composition			
	Lead phase mass %	Bronze, low tin mass %	Bronze, high tin mass %	Inert phase mass %
Ag	0.8	0	0.5	0.2
Al	0.2	0.5	0.1	0.3
Au	0	0.8	0	0.2
Bi	3.5	0.9	0	0.1
Cl	0	0.2	0	0.2
Cu	6.2	74.6	62.8	79.3
Fe	0.3	0.5	0.2	1.0
Ni	0.1	1.1	1.6	1.2
Pb	87.9	0.6	0	0.5
Sn	0.4	13.0	32.0	9.5
Zn	0.6	7.8	2.8	7.5
1 mol/dm3 H_2SO_4 Potential range (V)	Rate of leaching			
-0.7 to –0.3	Very slow	None	None	None
-0.3 to 0.1	None	None	None	None
0.1 to 1.2	None	High	Slow	None

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Figure 6—Cyclovoltammograms at 20 mV/s for static alloy, copper, lead and tin electrodes in deoxygenated 2 mol/dm³ hydrochloric acid (adjusted to an ionic strength of 3 mol/dm³)

(above about –0.1 V in 4.0 mol/dm³ NaCl) CuCl film formation occurs in acidic solutions. The extent of film formation is dependent on the chloride concentration and on convection. At still higher potentials both the dichloro copper (I) complex and cupric ion species are formed.

In the case of tin the behaviour in chloride medium is similar to that in sulfate medium, but even higher current densities were seen. There was no indication of passivation, which might be expected to occur through the formation of , for instance, SnO_2 species. The Pourbaix diagram in Figure 7 shows that at high acidity and chloride levels passivating solids such as SnO_2 are not necessarily formed.

Lead dissolves at a higher rate in chloride media than in sulfate, as may be seen from Figure 6, especially when compared to Figure 1. Lead chloride is appreciably more soluble than lead sulfate. Lead can form[15] the sparingly soluble lead chloride in solutions with relatively low concentrations of chloride, and increasing amounts of $PbCl_4^{-2}$ when the concentration of chloride increases beyond 0.1 mol/dm³. Passivation by lead chloride starts at –0.5 V. Reduction of this layer takes place on the reverse scan, starting from –0.55 V. If the rotation rate of the electrode is increased, the reduction peak decreases, due to improved mass transport of chloride ions that dissolve the lead chloride passive layer.

From the studies on the pure metals it may be concluded that tin and lead will dissolve more readily in chloride medium than in sulfate, but for copper it is the converse. This is seen in the voltammograms illustrated in Figure 6.

Again the alloy behaviour is substantially similar to that of copper, but with lower currents in the region above 0 V. The corrosion layer on Cu-13Sn alloy has been found to be thicker and more stable than those on the pure metals[12]. The stability of this layer has been attributed to the presence or formation of tin-containing species[16]. According to these authors the electrochemical behaviour of the alloy at potentials above about 0 V is complex, involving both copper and tin species, the diffusion of chloride and complex metal product species, as well as porous layer formation.

Increasing rotation rate increased the currents in the potential region above –0.2 V. Improved mass transport of chloride would be expected to lead to smaller amounts of CuCl in the corrosion layer, and thus less passivation. The reduction peak seen during the cathodic scan at –0.2 V disappears when rotation is introduced. This peak is due to the reduction of CuCl, which occurs at –0.2 V in 1 mol/dm³ HCl solution[17]. With increased mass transport the CuCl layer will react chemically with chloride to form soluble complex species.

When the anodic scan limit for a static alloy electrode was increased stepwise from 0.3 V to 1.3 V, the currents in the transpassive region remained unchanged, but the height of the reduction peak increased with an increasing anodic scan limit, due to the electrode being in the high potential region for longer times, forming more of the cuprous species in the corrosion layer.

A comparison of alloy leaching in the two media is shown in Figure 8. The stabilization of copper species and the greater extent of passivation in chloride media is clearly seen.

Constant potential anodic dissolution experiments were done at –0.05 V and 0.3 V, in the activation control and transpassive dissolution regions in the chloride media. This
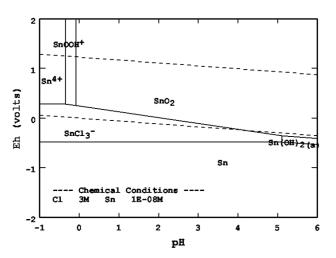

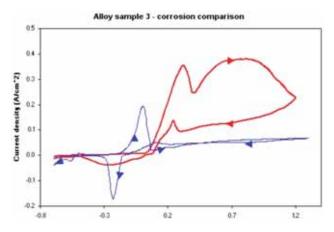**Figure 7—Pourbaix diagram for tin in a chloride medium**

Figure 8—Voltammograms at 20 mV/s for an alloy electrode in deoxygenated 1 mol/dm³ sulfuric acid or 2 mol/dm³ hydrochloric acid adjusted to an ionic strength of 3 mol/dm³

helped to identify the phases that leached in the various electrode potential regions. Table II summarizes the results obtained from these experiments and the voltammetric work.

After 600 s polarization at –0.05 V the alloy surface was porous, and similar to that obtained in sulphuric acid. However, less of the lead phase was seen. Polarization at 0.3 V resulted in constant currents after about 100 s, indicating a constant rate of diffusion. This was due to a more even corrosion of the alloy surface, with little porosity developed. The lead phase did corrode more slowly than the bronze phases, and areas of lead stood proud of the surface. The inert phase was again not visibly leached.

Conclusions

The leaching behaviour in sulfate and chloride media of an alloy formed by the high temperature smelting of scrap printed circuit board materials was compared to that of the pure metals, copper, tin and lead. Several metallic phases were formed and identified in the alloy: a lead rich phase, and two bronze phases with differing tin contents.

Electrochemical leaching studies showed that the corrosion behaviour of the alloy differed in the two media studied. As expected, the lead rich phase was more strongly passivated in sulfate media, and in this medium the high tin content delta bronze was markedly more resistant to corrosion than the lower tin alpha bronze phase. In chloride medium both bronze phases corroded readily, but with current densities about an order of magnitude lower than in sulfate medium (static conditions). The high tin delta bronze phase was found to form a passivating layer in sulfate media. A similar layer was not seen in chloride medium.

After leaching in sulfate medium the alloy surface showed evidence of a fourth phase which was more inert than the delta bronze phase. This material was seen in the centres of alpha phase grains, and appears to be somewhat enriched in copper. Its composition is about 79 mass per cent

copper and 9.5 per cent tin, while the alpha bronze contained 75 per cent copper and 13 per cent tin. This inert phase is still an alpha tin bronze, as alpha bronze can have a tin content varying between 0 and 15.8 weight per cent. A higher cooling rate might prevent its formation.

The alloy that was formed through direct smelting does not seem to be suitable for making anodes for copper electrorefining. In sulphuric acid the predominant low tin (13 per cent Sn - 75 per cent Cu) alpha bronze phase leaches preferentially to the other phases, and a small variation in composition (to 10 per cent Sn—79 per cent Cu) made the phase inert to leaching under the conditions of these studies. The mechanical integrity of an electrode in copper electrorefining is thus likely to be a problem, while substantial amounts of material seem rather resistant to dissolution.

Additional work would have to be done to determine whether a mixed sulfate/chloride electrolyte would have benefits in minimising preferential dissolution of some phases. It would also be important to establish whether the passive layer would be sufficient non-adherent to form a normal anode slime. Finally, mechanical tests should be carried out on the alloy after partial leaching to ensure that sufficient mechanical strength is retained.

As an alternative route it would seem beneficial to add pure copper to the PCB melt, so that the tin content falls below 10 mass per cent. This would ensure the formation of a single alpha phase bronze, avoiding the formation of the inert phase. The benefits would be improved corrosion rates, the avoidance of the formation of a strongly passive layer in sulfate media, and improved mechanical integrity as the corrosion process proceeds. The lead phase would not be avoided, however, so that in a sulfate electrolyte preferential dissolution of the bronze phase would still occur.

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Table II

The rate of leaching observed for various alloy phases in 2 mol/dm^3 HCl (adjusted to an ionic strength of 3 mol/dm^3)

Element	Alloy composition			
	Lead phase mass %	Bronze, low tin mass %	Bronze, high tin mass %	Inert phase mass %
Ag	0.8	0	0.5	0.2
Al	0.2	0.5	0.1	0.3
Au	0	0.8	0	0.2
Bi	3.5	0.9	0	0.1
Cl	0	0.2	0	0.2
Cu	6.2	74.6	62.8	79.3
Fe	0.3	0.5	0.2	1.0
Ni	0.1	1.1	1.6	1.2
Pb	87.9	0.6	0	0.5
Sn	0.4	13.0	32.0	9.5
Zn	0.6	7.8	2.8	7.5
2 mol/dm^3 HCl Potential range (V)	Rate of leaching			
-0.7 to -0.3	Slow	None	None	None
-0.3 to 0.1	Slow	High	None	None
0.1 to 1.2	Slow	High	High	None

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