4.0 MATERIALS AND METHODS

4.1 INTRODUCTION

On the basis of the reviews and objectives presented in the previous chapters, the materials and methods for this investigation are presented in this chapter. Other investigations that are relevant, consequent upon or supplementary to the primary investigations are also presented.

4.2 PCB COMMINUTION FINES GENERATION

About 250 kg of assorted of eol populated printed circuit boards from PCs, cellphones, radio equipment and switchboards were obtained. The boards mostly spanned the period 1989 to 2002, PI to PIV and different makes such as Cyrix, Intel Celeron, IBM, Octek, and Socket 3, 7 and 8. Most of the boards are multilayered (with maximum of four layers), with few older single-sided types. Components such as capacitors, liquid crystal displays and batteries which are usually rich in hazardous substances (Cui and Forssberg, 2003; EU, 2003) were first removed from the boards before comminution.

The boards were first cut with a bench guillotine (employing a shearing action as in shear shredders) into roughly 4 cm x 6 cm fragments appropriate for the choke of the swing hammer mill (Eriez magnetics MACSA Pedestal Type, Model 300) used for the fine crushing and grinding. The comminution was basically the result of impact, with shear, compression and abrasion, until a particle get below the screen size in at least two of its dimensions and favourably oriented to pass through. The size reduction was done in stages, starting from 20 mm closed fine crushing. Product from this stage was screened into size classes. The −13200 µm + 1180 µm fraction was removed from the stream as it consisted of sufficiently liberated metallic and plastic pieces that are amenable to eddy current separation, gravity air classifier and magnetic separation.

The +13200 µm fraction, containing almost bare board fragments go through closed comminution again at 8 mm, 5 mm and 2 mm screens to liberate the copper traces, solders still locked in the board vias, pin insertions, board fibres and resins. The −1180 µm fraction from the first stage was mixed with the final product from the 2 mm grinding, and the −75 µm fraction was screened from the final −2 mm fraction. Hazards associated with this operation were well appreciated, and adequate personal protective equipment was used. A documentary of the sample generation is shown in Appendix 1.

The total sample obtained was split with vibratory rotary splitters to 12 subsamples of average mass 5.6 kg (relative standard deviation = 4 %). These batches were split further down as required for each investigation.

4.3 SAMPLE CHARACTERISATION

4.3.1 Particle Size Distribution and Density

With a set of sieves of 105 µm, 75 µm, 53 µm and 38 µm aperture diameters, about 200g true split samples were shaken using Electrolab Electromagnetic sieve shaker, Model EMS-8, at the maximum power setting of 20. After every ten minutes of shaking, the sieve set was dissembled to confirm when all the sample has passed through the 105 µm. In this manner a period of 120 minutes was concluded as the proper screening period for this sample at that power setting. Repeat batch sieving was therefore done over this period to obtain a good representation of the particle size distribution (PSD) of the sample generated. This also gave fractions with narrower PSDs of −75+53 µm, −75 µm +38 µm, −53+38 µm, and −38 µm, for other investigations.

A column of PCB CF was observed to compact on vibration. The apparent volume therefore depends on how packed the volume is. Densities of the generated sample were therefore determined as true density, also as ‘loose bulk density’ and ‘tapped bulk density’ after the procedure for solids that compact, such as powdered milk (Svarosky, 1987; Niro A/S, 2009). Loose bulk density is based on a given volume loosely and gently filled with the sample and weighed, while tapped bulk density is based on volume compacted by gentle impacts on hard surface until height in a beaker remains constant. Tapped density is also quoted as ‘1000 tapped density', although for the PCB CF, the height of the column stabilise well before tapping 100 times.

A milliliter-graduated 100 ml cylinder was gently filled with sample to the 100 ml mark. The volume mark of this sample was obtained after tapping 200 times, and the weight of the sample finally obtained. For the true density, the true volume of a known mass of sample was obtained as displaced liquid volume. Samples of 20 g and 10 g were made into suspensions in a milliliter-graduated (100 ml) narrow cylinder, using water from a known volume in graduated cylinder. The density determinations were done in triplicates.

4.3.2 Liberation Assessment and Particle Shape Characterization

Qualitative liberation assessment of the fines was done by examining polished sections of the sample in two size ranges of −75+38 µm and −38 µm. Complementary observations were done with a Nikon Eclipse ME600 light microscope and a Jeol JSM 6300 scanning electron microscope. The electron microscope was operated at 30 keV to generate all useful lines under energy dispersive X-ray spectroscopy mode. To improve contrast between organic particles in the sample and the mounting medium in secondary and back-scattered electron modes, iodoform was embedded in the mounting resin. This increases the electron density of the mounting medium compared to the plastic particles.

The iodoform, 10 % by weight of resin plus hardener (Gomez *et al.*, 1984), was first dissolved in the resin before adding the hardener. The resin and hardener used – Eli-CAST FRF 676 – are cold setting combination products of Elite chemicals. This resin system was selected as it uses a slow hardener to prevent vigorous exothermic reaction with iodoform that was observed when faster hardener systems were first used. Another polished section was obtained from a sample mounted in clear setting resin to enhance natural colour contrast under light optical microscope. A micrograph from the clear mounting medium was used for circularity shape factor analysis of the particles, using ImageJ (version 1.42q). ImageJ is a public domain Java-based image processing program developed at the US National Institutes of Health (NIH, 2009).

4.3.3 Comparative Wet Spectroscopic Analysis

The total fines sample generated was split down in stages with rotary vibratory splitters. Approximately 50 g true split sample was taken, from which, after thorough mixing, samples for all the investigations were finally taken. This was done to eliminate sampling error as much as possible. A combination of reagent and environment to achieve total digestion was first sought. Hot aqua regia, and two other aggressive combinations were considered: HNO_3 + HF + microwave radiation and sodium peroxide fusion followed by HCl dissolution. The three conditions were designated as AR, HHM and SPF respectively.

1g sample was taken for AR and HHM digestion. The recipe for SPF is 0.5 g sample with 3.0 g sodium peroxide plus 1.5 g sodium carbonate. The mixture was heated over a gas flame in a zirconium crucible. This gives a vigorous exothermic reaction, charring red with a momentary flame, before it fuses into a liquid. The whole crucible was then immersed in concentrated HCl solution (25 ml of 32 % analytical grade HCl added to 100 ml deionised H_2O) to digest the fused sample totally.

For aqua regia digestion, 50 ml acid was added and the sample heated until the brown nitrous fume ceased and the fume became faint white (steam). The content was evaporated down slightly. About a total of another 30 ml acid was added and the heating cycle repeated. Heating to incipient fusion, as in recommended procedures (Babara, 2003; Henryk, 2003) was not done, because this produces fused particles that will not disperse on further addition of acid.

Digestion for each condition was done in duplicate. When necessary, undigested residue was filtered to obtain the analysis liquor. Inductively-coupled plasma-optical emission spectroscopy readings were done for each solution in triplicate and averaged. Inductively-coupled plasma-mass spectroscopy was used to analyse for Au, Ag, Pt and Pd separately with solutions from AR and HHM only. Averages of triplicate readings over duplicate samples were calculated. The SPF solution was not analysed for the precious metals, reasons expanded in Chapter 5. All the analyses were done with UIS Analytical Services, South Africa.

4.3.4 Thermogravimetric Analyses for Organic Constituents

Thermogravimetry (TG), along with other thermal techniques such as differential thermal analysis (DTA), has being reported as applicable to PCB composition analysis (Li *et al.*, 2004). The extent of applicability may be debated because of the diversity of the constituents. Many reactions can occur simultaneously and obtaining precise inflexions to enable useful characterisation of constituents may be difficult. However, being well established techniques, an exploration may be worthwhile. This investigation will thus serve a first purpose of clarifying the applicability of TG for PCB comminution fines characterisation, upon which it can be adopted in characterisation of any of the constituents in this sample. A contrary conclusion will still be useful, so that PCB characterisation efforts will be aware of the techniques that are not applicable even if such have been well established for other types of samples.

The thermogravimetric analysis was performed both in air and nitrogen, from room temperature to 800 ^{o}C, in steps of 10 ^{o}C/min. The plots were presented together with the derivative plots. The analysis was done using a Mettler Toledo thermal analyzer with the STARe software, and sample size of 20 mg.

4.4 PRELIMINARY MICROFLOTATION INVESTIGATION

A 6 g sample from a small true-split sample was used for microflotation. This is larger than about 2 g often used in conventional mineral microflotation experiments (Bradshaw and O'Connor, 1996) to ensure representative sampling of a sample with such wide variety of material particles. Pulping was meticulously done in a small volume, as the sample tends to form globules (see section 5.2 and 6.3.1), before transferring the sample into the microflotation cell. Natural pulp pH was measured over time in a separate pulp every 5 minutes until 60 minutes, and then at 120, 240 and 360 minutes.

The Orion 3-Star Plus benchtop pH meter of Thermo Scientific was used for the pH measurement. The cell volume was 250 cm^3 and distilled water was used. The peristaltic pump setting was started at 130 rpm, (Bradshaw and O'Connor, 1996), but the particle turbulence observed was too high. The pumping setting was reduced to 100 rpm (Martinovic *et al.*, 2004). It was further reduced in stages to between 8 rpm and 40 rmp, equivalent to a pulp circulation rate of 190 ml/min to 1350 ml/min respectively, according to the pumping rate calibration of the pump settings. Figure A.2 in Appendix I shows a picture of the microflotation cell employed. Air was used as the flotation gas at a rotameter setting of 4.5, which is 10 cm^3/min (Martinovic *et al.*, 2004), according to the flow rate calibration of the rotameter settings. Preliminary sodium isobutyl xanthate (SIBX) flotation at 50, 100 and 200 g/ton was performed. This was followed by collectorless flotation and another conditioning step using SIBX with 0.1 g detergent (sodium sulphonate active constituent) as wetting agent. Froth was collected at 90, 300 and 720 seconds of aeration. Inferences for detailed investigations were made based on visual and cumulative mass pull data.

4.5 APPLICABLE KINETIC REGIME AND THE NATURAL HYDROPHOBIC RESPONSE (NHR) FLOTATION SCHEME

With the backgrounds presented in Sections 3.5.1, 3.6 and 3.7, investigation of favourable kinetics in the prospect of froth flotation beneficiation of PCB comminution fines was pursued along with that of the feasibility of the natural hydrophobic response (NHR) scheme. The kinetic parameters of interest were narrowed to air flow rate, impeller speed and pulp density. The interaction of these factors influences other factors such as bubble sizes, pulp viscosity and turbulent dissipation energy, so that all the parameters need not be individually investigated to establish useful regimes.

A 3.5 *l* Leeds cell (supplied by University of Cape Town) was used for experimental reproducibility. The picture of the cell is shown in Figure A.3 (in the Appendix I). From the density characterisation result, a 600 g batch sample was chosen, but the response observed necessitated smaller sample size of 300 g (Section 6.3.2). Each true split batch sample from the total sample generated (see Section 4.2) was split down to subsamples of about 500 g and 50 g, followed by splits and combinations, so that each batch flotation sample were true split as much as possible. Reconstituted assays with regard to the target constituent elements of the flotation fractions from the investigations (Section 6.3.4, Table 6.2) give good indication of the representativeness of the batch samples obtained from the splitting.

Using distilled water, flotation pulps containing 300 g and 600 g sample were prepared per batch. This gave pulp solid concentrations of 9 and 18 wt. % respectively. The pulping was done by first forming a paste of the sample, introducing the paste into the cell, before filling up with water. This procedure was adopted because the sample floats if it is poured on water, while water simply displaces it if water is poured over it. This observation is linked to and the rationales explained in Sections 5.2 (density) and 6.3.1 (surface property). No collector was used.

It also turned out that no frother was needed (see Section 6.3.2). Air flow rates were varied over 500 and 1000 ml/min and impeller speeds over 300, 400 and 500 rpm for the 300 g. Only one condition was experimented for the 600 g pulp due to experimental observations (Section 6.3.2). Designations of the combinations of the experimental conditions are summarized in Table 4.1. Compared to natural mineral investigations with values such as 1200 rpm impeller speed and 1.8 to 5.4 *l*/min and higher aeration (Lins and Adamian, 1993; Forrest *et al.*, 2001; Miller *et al.*, 2006), the low regimes chosen for these parameters is based on initial microflotation (Section 6.2) and Leeds cell trials.

Table 4.1: Designations of experimental conditions for kinetic and natural hydrophobic response investigation.

Designation	Solid concentration (wt %)	Aeration (ml/min)	Agitation Speed (rpm)
E11A	18	500	300
E21A	9	500	300
E21B	9	500	400
E21C	9	500	500
E22A	9	1000	300
E22B	9	1000	400
E22C	9	1000	500

Above the range of 500 rpm agitation and 1000 ml/min aeration, the turbulence was too high. The quiescent zone was destroyed and the pulp surface swirled. The natural pulp pH was measured in the pulps, for record. Each experimental condition was run in duplicate and mass pulls were collected at one, four, 10, 18 and 30 minutes. Scraping was done every 30 seconds for the first four minutes, every minute from the fourth to the eighteenth minute, and every two minutes from the eighteenth to the thirtieth minute.

Filtration of the recovered fractions was not done to avoid loss of trace values to porous filter medium. Instead, floats were collected in stainless steel bowls while sinks were flushed into buckets, allowed to settle down (usually overnight), decanted and the sink fraction recovered. Float and sink fractions were oven dried, and the weight of fractions obtained thereafter. All the mass pulls were confirmed to repeat within 5 – 10 %. Repeats that fell outside this range, due to procedural imprecision, were rerun to ensure all the data conformed to this level of repeatability. The concentrate mass percent (the fraction of the feed remaining in the sink) was calculated as an inverse indication of the ratio of concentration for the reverse flotation. For a first check of the conformity of the response to flotation behaviour, the cumulative mass fraction recovered to float for all conditions was fitted to the classical first-order kinetics model in the form (Kelly and Spottiswood, 1989; Polat and Chander, 2000):

$$ln\left(\frac{R_m}{R_m-R}\right) = kt \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad 4.1$$

where R_m (%) is the maximum cumulative recovery, k (min^{-1}) is the rate constant, and R is recovery at time, t, in minutes.

Samples of the fractions were digested in hot aqua regia among other possible digestion routes (based on the comparative digestion analysis, Section 5.4). After thorough mixing, for the digestion, a 2 g sample was taken for every 50 g float fraction weight, or parts thereof. 1 g analysis sample was used for fractions that are well below 10 g in mass. The variation in quantity of sample taken for digestion is to account for variations in the total quantity, so as to ensure representative sampling of each float fraction. Undigested residue was filtered and weighed, while the final digestion liquor was made up to 250 ml with deionized water and about 5ml aqua regia. A quick assessment of the enrichment of metallic values into the sink was first done using the fractions of each sink sample digested as an indication of total metallic assay. Indication of recoveries was also computed based on this. Assays of selected elements were analyzed from the leach liquor with ICP-OES for a better indication of the deportments (concentrations) of the elements in each float fraction. The ppm assay of the leach liquor was converted to actual assay in percentages of the individual float fraction by using a divisor factor of 40, 80, 160 and 240 for every 1 g, 2 g, 4 g and 6 g digested sample, respectively. The factors derive from the constant 250 ml final volume after digestion (see Appendix 1.3).

Specifically Ag, Al, Au, Ca, Cu, Fe, Mg, Ni, Pb, Pd, Pt, Si, Sn, Ti and Zn were assayed. The analysis was done on Perkin Elmer instruments with UIS Analytical Services, Centurion, South Africa. Elemental assays, enrichment ratios (ratio of the reverse flotation concentrate assay to feed assay) and recoveries over time into sink were computed from these data. Although batch feeds were obtained as true split samples, to eliminate error that may be due to any sample assay variation, the computations were based on reconstituted feed assays of each run.

4.5.1 Possibility of Formation of NHR Froth by Inherent Surfactant in the Sample

Based on the result from the NHR scheme, it was expedient to investigate the possibility of inherent presence of surfactant in the sample. Comparison of the dynamic froth stability of the pulp itself and that of filtrate from the pulp will indicate any frothing effect due to surfactant presence in the pulp liquid. Pulp filtrate surface tension measurement was also considered a necessary complement.

The dynamic froth stability tests were done using a Betachem modified Bikerman test rig (Bikerman, 1973; Betachem (Pty) Ltd., South Africa). The test unit uses a Watson Marlow peristaltic pump with about 30 mm (external diameter) pipe pumping capacity. The froth column is marked at a 5 *l* level for reference pulp or solution height before aeration. A picture of the test rig is shown in Appendix 1, Figure A1.6. A pulp containing 425 g sample in total volume of 5000 ml (the same solid concentration as investigated for the NHR 300 g scheme) and a clear filtrate from a pulp of the same solid concentration were used for the test. The aeration rate and the peristaltic pump setting were kept constant when measuring the frothing of the pulp and the filtrate. The dynamic froth height measurements were done at the constant rotameter setting of 20 (equivalent to about 4 *l*/min, as calibrated) and peristaltic pump setting of 30 on the test rig. The tests and measurements were repeated three times using different pulp filtrates.

The surface tension of the pulp filtrate was measured using the pendant drop technique in an automated contact angle goniometer with RHI 2001 imaging software (Rame-Hart Inc., 1999). Figure A1.7 (Appendix I) shows the goniometer stand. Instances of pendant drop of the filtrate almost detaching from the accessory needle were created in front of the camera. The live image display around reference lines helped to ensure the needle was exactly vertical. At hydrostatic and interfacial equilibrium, the imaging software determines the profile of the pendant drop and, with the liquid type information provided, generates the surface energy value. The procedure, being straight forward, was repeated 10 times. Results from these approaches suffice for necessary concrete inferences. Higher precision surface tension analysis, such as capillary rise method, was therefore unnecessary.

4.5.2 Improving the Performance of the NHR Scheme

Based on observed recoveries and enrichment ratios from the NHR scheme, the possibility of improving on the performance was investigated. The material bulk density being low, the projection is to reduce turbulence in the pulp by variation or modification of some kinetic parameters. This is expected to reduce entrainment and entrapment of sink particles thereby improving recovery without compromising enrichment.

On this basis, effect of pulp solid concentration on mass pull was studied by varying pulp solid concentration of 300 g down to 50 g at the same aeration rate and impeller speed as under E21C condition (see Table 4.1). From this, a 150 g sample size was chosen, as there was indication that lower solid content minimises turbulence, but to another extreme lowers overall mass pull unacceptably. The impeller speed was kept at the low speed of 300 rpm, and aeration rate at 0.5 *l*pm. As this setting, the bubble sizes resulting from this impeller speed were large, with short residence time, visually bursting through the froth zone.

The aeration pipe of the impeller system was therefore modified as shown in Figure 4.1 to achieve bubble size reduction at the same aeration rate and impeller speed. The pipe diameter at the air outlet was reduced from 8 mm in the single aeration pipe to about 4 mm in four smaller outlet pipes, keeping total outlet area and in turn the exit air velocity effectively the same at constant aeration rate. Using the two aeration pipes, frozen frames of the resulting bubbles as they rise through clean water were taken for a visual indication of the effect of the modification on bubble sizes. The frames were taken using Sony digital camera DSC W55 at ISO 1000.

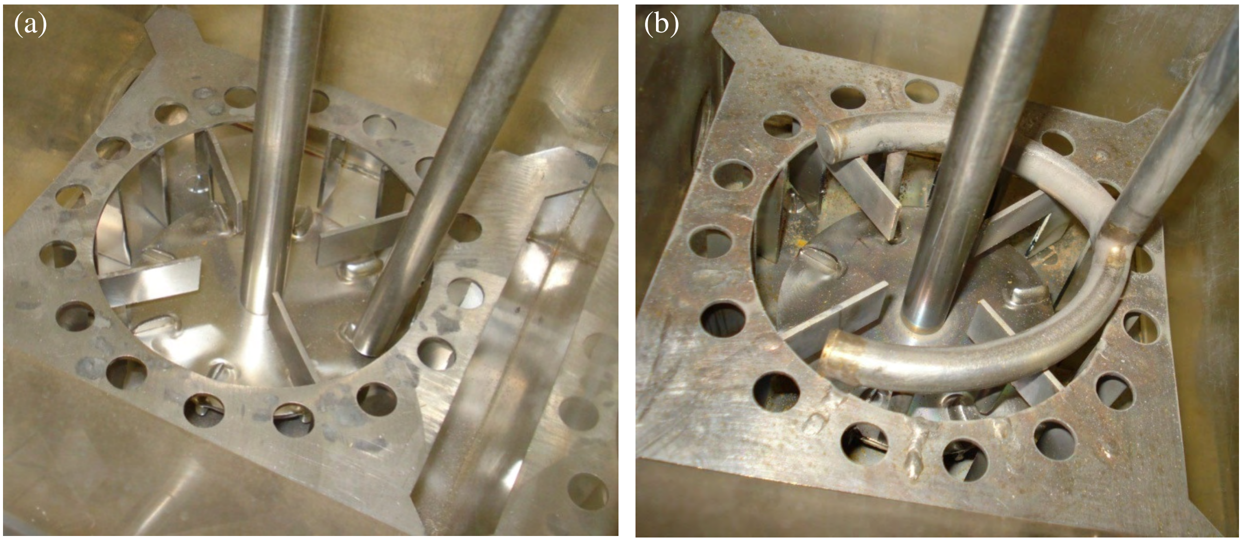

Figure 4.1: Impeller system of the Leeds cell used before (a) and after modification (b).

As trial runs indicated, the resulting kinetics with the modified impeller system achieved moderate turbulence but resulted in low mass pull rates. Further investigations were therefore carried out for a flotation period of 48 minutes, collecting float fractions F1, F2 and F3 at 18, 30 and 48 minutes respectively. The impeller speed was increased to 350 rpm after 18 minutes of flotation to improve efficiency of collision after a significant fraction has been pulled and mass pull became very slow with time.

This NHR improvement investigation and procedure is designated XNHR for ease of reference. At this kinetics (impeller speed and aeration rate), natural hydrophobic flotation over narrower PSDs of −38 µm, +38−75 µm and +75−106 µm were done. The necessary data for computing water recovery for each fraction were obtained following a careful procedure (see Appendix 1.3). This investigation was used to compare water recovery at varying particle sizes and to conclude on contribution of particle entrainment in water to the flotation response observed. The investigation also shows the size fraction most favoured by this kinetics. It also explores the possibility of applying froth flotation to larger size fraction (−106 + 75 µm) of PCB comminution product.

4.6 CHEMICAL CONDITIONING SCHEMES

The rationales for some of the specifics of the chemical conditioning investigations described below follow from the results and observations from previous investigations, which are discussed in Chapter 5 and 6. The following procedure applies to all the chemical conditioning schemes, except for Section 4.6.1, or when otherwise stated.

A sample mass of 150 g, and aeration rate of 0.5 *l*pm was used. 30 minutes of natural hydrophobic flotation was first performed before chemical conditioning of the residual sink. During the natural hydrophobic flotation, the impeller speed was 300 rpm for the first 18 minutes, and 350 rpm for the period 18 to 30 minutes. This is the condition used for the XNHR investigations. It is to maximize reverse recovery of the metallic particles before reagent conditioning. Conditioning time after each collector addition was five minutes, and when frother is added, another two minutes of conditioning was allowed to elapsed before aeration (Forrest *et al.*, 2001; Bravo *et al.*, 2004; Martinovic *et al.*, 2004), to ensure that the response was not impeded due to short conditioning time.

After conditioning, the impeller speed of 350 rpm was maintained and flotation continued for another 18 minutes. Skimming was done every one minute or every two minutes as mass pull rate changes; one minute for the first 8 minutes, and two minutes for the last 10 minutes of the scheme. Data to compute water recovery for each fraction were obtained as before. The floats from conditioned sinks were collected in one fraction as only the bulk recovery and the assay were of interest.

Trial runs were performed extensively to observe the response to each reagent added. Dosage levels that did not show distinct effects as projected were discarded. The experiments were run mostly in triplicate. Fractions recovered were oven dried and masses of fractions obtained, as under the NHR scheme. Mass pull was computed based on the mass of float obtained after conditioning and the final sink fraction. These reconstitute the mass just before conditioning.

Aqua regia digestion for chemical composition analysis, as described, was also done for the float and sink fractions. The target analytes were Ag, Al, Au, Ca, Cr, Cu, Fe, Mg, Ni, Pb, Pd, Pt, Sn, Ti, V and Zn. For this purpose, inductively-coupled plasma optical emission spectroscopy

(ICPOES), and supplementary mass spectroscopy (MS) were used for the elements in relative trace proportions, particularly to have more accurate information on the Pt response. Based on the assay and mass of the fractions, assay of the residual sink after the NHR stage were computed to obtain enrichment ratio and recovery of metallic values to the float fractions obtained from sinks conditioned with reagents.

4.6.1 Macromolecular versus Gamma Depression

Two reagents were investigated for the selective depression of the sample: sodium carboxyl methyl cellulose, NaCMC (obtained from Cellulose Derivatives Property Ltd., SA) as a macromolecular depressant, and Betamin 127A (see Section 3.4) supplied by Betachem (Pty) Ltd., South Africa, for the gamma depression concept (see Section 3.5.2.4).

The depressants were studied against the natural hydrophobic response at the kinetic conditions of E21C (500 rpm impeller speed at 0.5 *l*pm aeration). Starting at 200 g/ton and increasing to 2 kg/t and above, increasing dosages of NaCMC were used to observe achievable depressions of the NHR in the bulk sample. Dosages of 10 and 30 wt. % were eventually used for reported experiments (see Section 7.2.1). For gamma depression, 0, 20, 60, 100 and 150 ppm dosages of B127A were first used on the bulk sample.

A second set of treatments was intended to establish an effective depressant for residual natural hydrophobic particles after 30 minutes of NHR flotation – as can be done before collector conditioning. A NaCMC dosage of 3.3 wt. % was used with a conditioning time of five minutes before aerating for 18 minutes.

For Betamin 127A, a 30 ppm dosage was used with one minute conditioning before aeration for 18 minutes. Inductively-coupled plasma optical emission spectroscopy and inductively-coupled plasma mass spectroscopy were combined for assaying of selected elements in the resulting fractions. The assays were compared and discussed.

4.6.2 Bulk Metallic Flotation (BMF)

The NHR residual sink was conditioned with PAX (potassium amly xanthate) using two dosages of 100 g/t and 400 g/ton. The choice of PAX is intended to achieve maximum bulk collection

(Section 3.5.2). Other trial dosages were used but these two will suffice in reporting the effects observed.

These dosages were chosen as the response tends to be negligible at the usual lower dosages. Collector consumption in excess of 200 g/ton is known in operating plants, specifically those that treat tarnished sulphides (Bulatovic, 2003). The PAX was obtained from Betachem (Pty) Ltd., South Africa. It was always freshly purified before use by dissolving it in chemically pure acetone (minimum 98 %, from Merck), followed by filtration and extraction from the filtrate by adding petroleum ether (AR, from Merck, University of Pretoria) as a desolvent, to precipitate the xanthate as fine faint yellow solid (Rao, 1971).

4.6.3 Sulfidation Activation

Analytical grade sodium hydrogen sulfide (NaSH), supplied by Sigma Aldrich (Cat. #: 161527) was used for the sulfidation scheme. Given the natural pulp pH of the system, which is alkaline (see Section 6.2), equations 3.6 b and 3.6 c will tend to favour generation of the depressant ions (see Section 3.3). A minimal dose is appropriate to avoid the depression effect. Hence, a dosage of 500 g/t was used. This is moderate compared to the 1575 g/ton used in controlled potential sulfidation by Lee *et al.* (2009). The pulp was conditioned for three minutes before adding PAX at 400 g/t. The pulp was conditioned again for another five minutes before aeration. No frother was used.

4.6.4 Depression followed by PAX Activation

In an attempt to take advantage of observations from various treatments, a scheme intended to achieve a clean metallic fraction was conceived.

A prolong NHR flotation of 48 minutes was run to exhaust the natural hydrophobic response as much as possible. Impeller speed was maintained at 350 rpm for the extended 30 – 48 minutes. Betamin 127A was then added to the pulp in 2 ppm increments, with trial aeration in between to observe bubble loading. In this manner, 10 ppm dosage was obtained after which the bubbles were no longer loaded, the bulk of the NH particle being pulled already.

Hence, 10 ppm Betamin 127A was added after 48 minutes of NHR. This was followed by 400 g/t of PAX, five minutes conditioning, 50 ppm methyl isobutyl carbinol (MIBC) as frother, a further two minutes of conditioning and aeration for 18 minutes. Designations and a summary of all the treatments using PAX are presented in Table 4.2.

Table 4.2: Designation and description for treatments involving PAX

Designation	*Description*
PAX1	Bulk metallic flotation scheme with 100 g/ton PAX
PAX2	Bulk metallic flotation scheme with 400 g/ton PAX
SPAX	Bulk metallic flotation with sulphidation; 400 g/ton PAX+500 g/ton NaHS
DPAX	Depressant followed by PAX conditioning, then frother: 10 ppm B127A, 400 g/ton PAX, 50 ppm MIBC

4.6.5 Cationic conditioning

Cationic conditioning, as explained in Section 3.5.2, was investigated using tetrabutyl ammominum chloride. The quaternary amine was chosen to ensure that pH variation, which is considered to be a deciding variable in exploring particle surface potential, does not affect the collector activity (dissociation). The butyl hydrocarbon was used to ensure impartation of higher hydrophobicity compare to shorter alkyl groups. Three pH levels – natural pulp pH (about 8), pH 4 and pH 10 – were used for the preliminary runs.

Approximately 0.02 M (1.8385×10^{-2} M) acid solution, used to lower the pulp pH, was made by adding 1 cm^3 of 98 % concentrated sulphuric acid (oil of aerosol, SG 1.98, 18.385 M) supplied by Merck (University of Pretoria) to 1 *l* of distilled water. After addition of appropriate volumetric proportions, and monitoring with Orion pH meter, the pulp showed a gradual rise in pH. More acid solution was needed to drag the pH down to desired value.

Anhydrous sodium hydroxide pellet (supplied by Merck, University of Pretoria) was used for preparing the basic solution to regulate the pulp pH to 10. Tetrabutylammonium chloride (AR), obtained from Merck, SA, was used at 100 g/t dosage. Judging from the preliminary trials (see Section 7.5), the pH 4 condition was dropped from further investigation and frother addition was considered necessary for this scheme. Thus, 50 ppm MIBC was added and the pulp conditioned for two minutes before aeration.

4.6.6 Selective Metallic Flotation

As noted in Section 3.5.2, sodium mercaptobenzothiazole (SMBT), supplied by Betachem (Pty) Ltd., SA, was used for the selective metal flotation investigation. SMBT is a selective collector of tarnished or oxidised lead and copper minerals (Fuerstenau and Raghavan, 1986). The copper and lead particles in this sample can be conceived as tarnished. This is because the particles are from end-use alloys that have been exposed to the atmosphere all their service lives. Outcropped native metals in mineral deposits tarnish simply by being exposed to the atmosphere.

A dosage of 200 g/t SMBT was used for the reported flotation. A very selective flotation was expected. The natural hydrophobic flotation was therefore carried out for 48 minutes before the conditioning. The impeller speed was set at 300 rpm for the first 18 minutes, then at 350 rpm for the last 30 minutes of the NHR flotation. After conditioning, it was maintained at 350 rpm for the 18 minutes of aeration. Skimming was done every two minutes after the conditioning. Fractions were recovered and analyses done for selected elements as described above.

4.7 FOLLOW UP INVESTIGATION FROM THE CHEMICAL CONDITITONING SCHEME

The following investigations were carried out in attempt to substantiate the probable causatives advanced (in Section 7.6) for explaining the responses observed from the various chemical conditioning schemes.

4.7.1 Calcium Dissemination in PCB CF

Direct observation of particles of the sample was done in JOEL JSM 3600 scanning electron microscope in the Industrial Minerals and Materials Research Institute (IMMRI) in the Materials Science and Metallurgical Engineering department, University of Pretoria. A dispersed layer of the sample was made on carbon tape and the layer was coated by carbon deposition. The particles were observed in both backscattered electron and secondary electron modes to enhance composition contrasts and achievable resolution of surface features. Clearly defined phases and morphologies were focused by the electron beam. The energy dispersive X-ray spectra of the phases were observed to identify-calcium bearing particles. Representative spectra of the particles in the sample were also taken.

4.7.2 Calcium Presence in Process Water

For the process water composition study, filtrates of the flotation pulp were obtained and trace element ICP-MS scan of the filtrate was done to establish the elements that leach into the filtrate. The scan was for a total of 68 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Ru, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr. This investigation can also serve to assess hazardous contamination with elements such as Pb, Cr, Hg and Cd during PCB CF wet processing.

4.7.3 Investigation of Particle Surfaces

High resolution observation of the surface of copper trace particles, picked from the fine sample and mounted on carbon tape, at 1 kV electron energy was done. The Carl Zeiss Field Emission Scanning Electron Microscope (FESEM) at the Electron Microscopy facilities of the University of Pretoria, was used for this investigation. Auger electron spectroscopic investigation for information about the surface make up of metal particles in the sample was also done.

For this investigation, a survey of auger kinetic energies on each surface was first taken, then profiled for 40 minutes. Surveys were taking every five minutes of profiling. The primary electron beam was kept at a landing voltage of 5 kV and a 10 nA beam current. The argon ion gun was operated at 2 kV, 2 µA, giving about 85 Å sputter depth per minute (as characterised for SiO_2)**.** The auger electron kinetic energy surveys for all the surfaces spanned 0 – 2400 eV, to be a comprehensive search for all possible elements. The PHI 700 Scanning Auger Nanoprobe of the Department of Physics, University of Free State, Bloemfontein, South Africa, was used for this study.

A total of eight particle surfaces were studied. Three were from assorted particles in the conducting fraction from corona electrostatic separation of +212 – 300 µm size fraction of PCB comminution product. This conducting fraction is very rich in copper particles so that a copper surface can be easily picked up from the fraction when inside the microscope. Most of the particles in the actual −75 µm fine fraction were not metallic particles of interest for the surface investigation. Searching out the actual metallic particles for observation from such a sample will involve time-consuming surveys. Moreover, the bulk in the fine fraction is non-conducting and the majority of the particles will be charging profusely. This is why grains of the actual −75 µm fraction were not used for this purpose. The metallic particles surfaces in the +212 – 300 µm fraction can be taken to represent that of metallic particles in the –75 µm fraction, since they are screened from product of the same comminution stage. The particles from the coarser fraction were therefore used. The five other particles were elongated (fibre) particles. These were easily distinguishable in and selected from the –75µm fraction.

A portion of the assorted particles (electrostatic conducting fraction) was taken and rinsed in distilled water, drained and allowed to dry in the open laboratory room temperature for four hours. Another portion was rinsed in the PCB CF pulp filtrate and a third portion was untreated. The fibres were also given similar treatments. Table 4.3 summarised the designation and description of the surfaces.

A few grains from each portion of the assorted particles were carefully placed on separate carbon tape with a clean spatula. The tape was then blown by pure nitrogen gas to remove particles lying on top of others and not directly adhering to the tape. This gave a dispersed almost monolayer of the particles on the tape. The fibres were also carefully placed on the carbon tape, ensuring that the particles do not roll on the tape in the process.

4.8 STATISCAL ANALYSES AND ERRORS

Although detailed data for some repeat runs are presented as appendix data, some are reported directly as averages. For an indication of the scatter of the actual values for the averaged data, when considered necessary, relative standard deviations of the mean (δ_r,%) were computed as:

$$\delta_r, \% = 100.\delta/\bar{x} = 100\sqrt{\frac{(x-\bar{x})^2}{n}}\ /\ \bar{x} \quad . \quad . \quad . \quad . \quad . \quad . \qquad 4.2$$

where δ is the standard deviation of the averaged data, n is the number of runs averaged, $(x - \bar{x})$ is the difference between each data value and the averaged value. This is tabulated with such averaged data. The associated errors with the averages were computed as the standard error of mean (ε) for such data points as:

$$\varepsilon = {}^{\delta}/_{\sqrt{n}} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad 4.3$$

The standard errors are indicated as negative and positive error bars when plots are made from averaged data.

Table 4.3: Designation and description of particles surfaces studied by Auger Electron Spectroscopy

Designation	Description and Surface condition
P1	From assorted particles as taken.
P2	From assorted particles soaked in process water (PCB pulp filtrate) and dried in open laboratory air.
P3	From assorted particles soaked in distilled water and dried in open laboratory air.
F1	Copper trace fibre particle soaked in process water and dried in open laboratory air.
F2	Copper trace fibre particle soaked in distilled water and dried in open laboratory air.
F3	Copper trace fibre particle as taken from the PCB CF sample.
F4	A more brownish (possibly copper) fibre particle as taken from the PCB CF sample.
F5	A whitish fibre particle as taken from the PCB CF sample.

5.0 CHARACTERIZATION OF PCB COMMINUTION FINES FOR FROTH FLOTATION INVESTIGATION

5.1 INTRODUCTION

The total printed circuit board comminution fines (PCB CF) sample generated weighed about 70 kg (see Appendix 1). Results and discussion of the relevant characterization investigations on the sample towards the flotation investigations are presented in this chapter. It covers particle size distribution, sample density, liberation and comparative chemical composition analysis.

5.2 DENSITY AND PARTICLE SIZE DISTRIBUTION

Table 5.1 (detailed data is given in Appendix 2) shows the density figures obtained for the PCB CF sample. The small deviations are from systemic errors resulting from imprecision in repeatedly filling the fixed volume with exactly the same mass of sample. The values show that the fines sample is not very dense, as the loose and tapped bulk density values indicate in particular. An implication of this property value on flotation is that the sample will pour unto water and not into water during pulping. That is, the bulk sample can float on water. Water can as well simply displace the sample when poured over it in a cell. This, in fact, was the experience during the preliminary microflotation trials (see Section 4.4), after which the density determination was carried out. Sample pulping hence has to be done by first forming a paste of the sample with a small quantity of water. The paste is then dispersed under water. This is what was done when determining the true density.

Table 5.1: Density values for the PCB CF sample

Description	Value (g/cm^3)	Relative Std. Dev, % (triplicate test)
Loose bulk density	0.54	1.4
Tapped bulk density	0.90	0.7
True density	2.9	2.3

The true density value of 2.9 g/cm^3 shows that the actual particles are generally much denser than what the bulk density (0.9 g/cm^3) indicates. This shows that packing even after 200 tappings is not perfect, and porosity in the column accounts for the bulk volume. Poor packing is indicative of very diverse particle morphology (shape) and is clearly confirmed in the liberation study below.

Figure 5.1 shows the particles size distribution obtained from the –75 to +38 µm sieving analysis (data for the figure is shown in Appendix 2). This plot is only an indication of the size distribution, as sub-sieve analyses were not done because of the particle morphology and material diversity constraints. These are addressed below (see Section 5.3).

However, the data generally indicate that a large proportion (66.7 %) passed 38 µm. It follows that certain PCB components break selectively into very fine particle sizes. Metallic particles are ductile and cannot be expected to crumble into fines. Instead, grinding into powder can be expected with brittle comminution of glassy particles, ceramics glazing on certain resistors, semiconductor diode valves, chips, insulating ceramics (such as mica) and components with brittle thermosets (see Section 2.3).

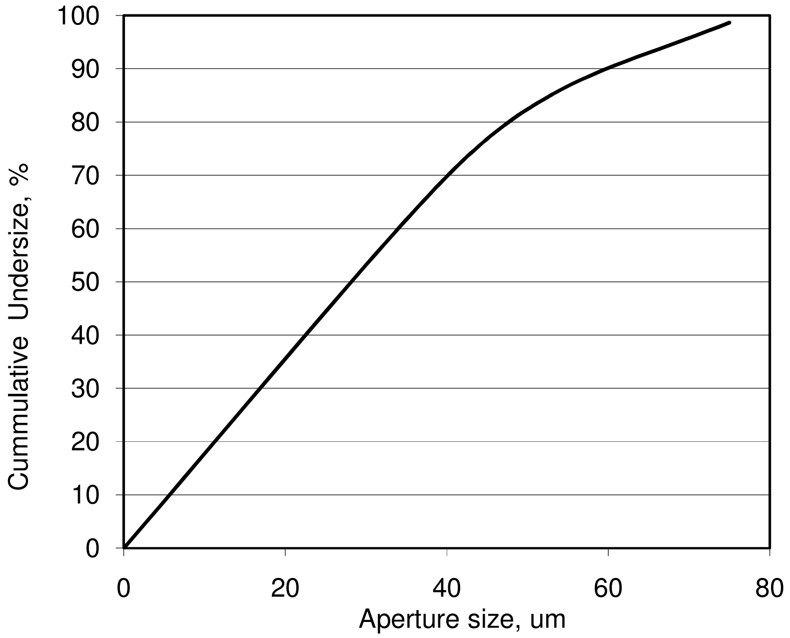

Figure 5.1: Particle size distribution of PCB CF

Given the peculiarities of fines in flotation behavior (Pease *et al*., 2005), a major influence of fine particles on the flotation response can be expected (see Section 6.3.1). Sub-sieve analysis also appears necessary, but the liberation assessment gave important constraints discussed below.

5.3 MORPHOLOGY AND LIBERATION ASSESSMENT

Figure 5.2 (a – d) shows the optical micrographs of polished sections of the printed circuit boards comminution fines. Dark field, compared to bright field, illumination was used for these images to enhance colour and relief contrasts in the sample (Murphy, 2001). On a conservative analysis, the white particles are the more reflective metallic particles, the black patches include organic particles, and glass fibres remain distinctly fibrous. Judging from the reflectivity, the metallic particles are in much smaller proportion, while the fibrous particles are the most common. The general morphology shows that the particles are present in very random shapes – fibrous, angular, subangular, partially rounded, and almost cubical.

Leaving the distinctly fibrous glass particles out, the circularity shape factors of the other particle were obtained from the binarised image shown in Figure 5.3. This image is from an optical micrograph of a polished section (in clear, non-iodised, resin) shown in Figure A2.1, while Table A2.3 (both in Appendix A) shows the shape analysis data for a total particle count of 116. Small pixel-sized specks of particles up to 50 pixel square in area (approximately 16 μm^2 from pixel size to scale bar ratio of image) were left out to avoid erroneous circularity of 1, which will be caused by poor boundary and aspect ratio definitions in small particles.

The average circularity was found to be 0.63, while average solidity was 0.85. These conform to the visible diverse particle morphology in the sections. It is indicative of material diversity, as well as various shear, tensile, impact and complex forces under which the comminution of the particles was achieved. The glass fibres, on the other hand, produce particles with length well above the sieve aperture diameter (d_A) of 75 µm, as easily seen in the sections.

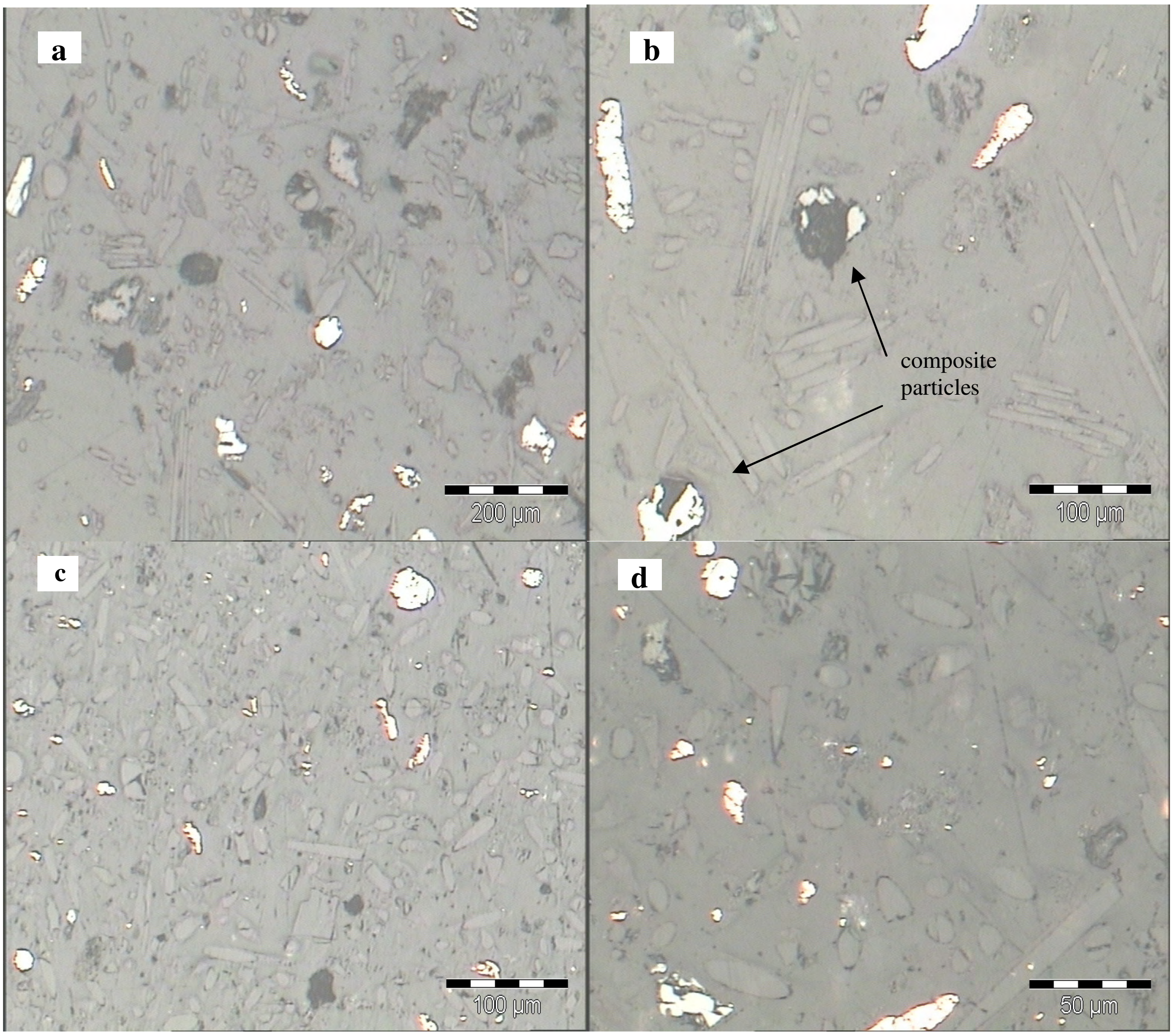

Figure 5.2: Optical micrographs of PCB comminution fines polished sections:
a. −75+38 µm, 50 x magnification; b. −75+38 µm, 100 x magnification; c. -38 µm, 100 x magnification; d. −38 µm, 200 x magnification. *Micrograph clearly shows diverse particle shapes.*

This diverse particle morphology explains why screening time was so prolonged (see Section 4.3.1), despite the maximum amplitude (vibration energy) used. Some particles have to tumble a number of times before assuming favorable orientation to pass through the screen. Another implication of this morphology is its limitation on the effectiveness or applicability of some common techniques for sub-sieve analysis. Although the classification can still easily go a step further down with finer cloth screen in 25 µm sieve, the challenge is to do a detailed analysis down to a micron. For example, the result of analysis from the volume-based laser diffraction technique using the Malvern’s Mastersizer (Rawle, Malvern Instruments) may not be precisely interpreted. A glass fibre particle in the −38 µm fraction from a mesh sieve analysis certainly has two dimensions below the d_A of 38 µm. If a fibre particle is about 35 µm in diameter, and about 150 µm long (as is common in Figures 5.2b and A2.1), its equivalent sphere diameter (d_S) on the Mastersizer will be returned as 65 µm. This follows from equating the volume of a cylindrical particle to that of its volume equivalent sphere as:

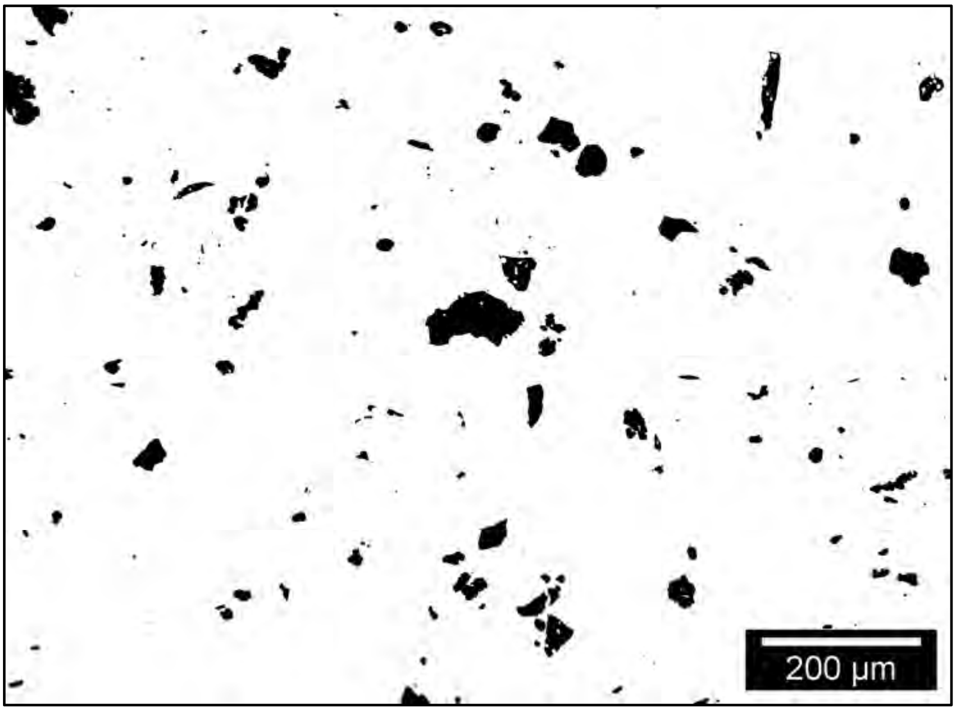

Figure 5.3: Binarised image for circularity shape factor analysis of the metal particles.

$$\frac{1}{4}\pi {d_A}^2 h = \frac{1}{6}\pi {d_s}^3 \qquad . \qquad . \qquad . \qquad . \qquad 5.1$$

where h is the length and d_A is the aperture diameter of a cylindrical particle, while d_S is the diameter of the sphere of the same volume. Then,

$$d_s = \sqrt[3]{\frac{3}{2}\left({d_A}^2 h\right)} \qquad . \qquad . \qquad . \qquad . \qquad 5.2$$

d_A and h are then substituted as 35 µm and 150 µm respectively. With such diverse particle morphology, a PSD based on d_S may therefore not make much sense.

The cyclosizer is another good subsieve device. It separates base on mass effect under centrifugal force. For a sample containing particles of the same material (density), variation in particle mass is also variation in particle size, and the mass-based separation therefore gives size classification. With assorted materials, particles of the same size can have very different masses, and therefore separate to different size classes or generally give poor partition. The assorted material constituents and the diverse particle morphology observed in the PCB CF therefore present major constraints for its sub-sieve size classification.

As an indication of the composition of the fines sample, it can be observed that the bright metallic particles have a low proportion compared to the less reflective phases. It was mentioned that metals are ductile and will not preferentially report to the fines. A low metallic assay of the fines may therefore be expected.

With regard to liberation, Figure 5.2a shows almost total liberation of all the particles in the −75+38 µm range. However, the close-up in Figure 5.2b (at 100x magnification) shows that some composite particles can still be found. For -38 µm size particles, such composite particles could not be found on (four) polished sections at 100 and 200 times magnification (Figure 5.2 c and d).

The scanning electron microscope (SEM) observation provided a more qualitative assessment of the sections. Although almost all the metallic particles in the sections as observed with the SEM are unlocked, unliberated particles could still be found (Figure 5.4a). A close up on such composite particle is shown in Figure 5.4b. Table 5.2, shows the energy dispersive X-ray analysis data of the two distinct phases of this particle. From the image and the composition data, this particle appears to be a copper trace unliberated from solder.

Averaged point counts of such composites relative to totally liberated particles on a number of sections gives a ratio of 1 to 194, implying a degree of liberation above 99 %. As the polished section may not be considered as being accurately representative of the particles' relative abundance in the sample, this value may be taken as an instance only. The primary purpose here is to establish whether or not unliberated particles still exist at −75 µm.

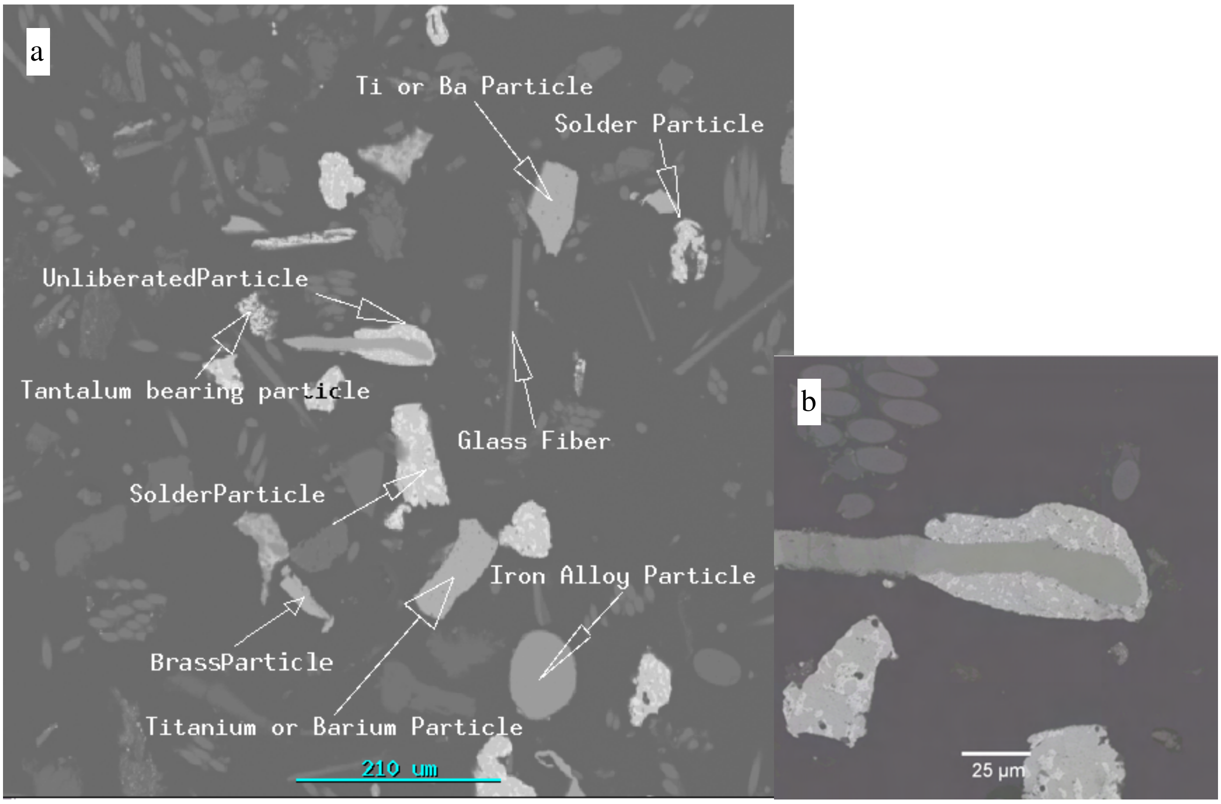

Figure 5.4: SEM back scattered electron images of −75+38 µm printed circuit boards comminution fines section (a), and a close-up of an unliberated particle (b).

On another note, although this degree of liberation can be taken as almost total (as it will be readily taken in conventional mineral processing), in a sample where compositions of the various constituents range from percentages to ppm (see Section 5.4), the small balance can be critical. In clearer perspective, a balance of 0.5 % in the degree of liberation (as the actual computation will roughly give) is equivalent to about 5000 composites per million particles. Assuming a constituent with total assay of 200 ppm is concentrated in the 5000 composite particles, the response of such constituents will grossly deviate from normal expectations in a flotation scheme.

Table 5.2: Energy Dispersive X-ray composition analysis of phases in -75+38 µm printed circuit boards comminution fines polished section.

Phases	Elemental Lines	Atom %	Element wt %
Composite particle outer (Figure 5.2b)	Al-K	1.2	0.3
	Sn-L	82.1	77.0
	Ca-K	0.9	0.3
	Cu-K	1.9	1.0
	Zn-K	1.3	0.7
	Pb-L	12.7	20.8
Composite particle inner (Figure 5.2b)	Sn – L	0.5	1.0
	Ca – K	0.2	0.1
	Cu – K	64.2	63.3
	Zn – K	35.1	35.6
Ti - Barium particle (Figure 5.2a)	Co-L	2.2	1.4
	Al-K	0.7	0.2
	Si-K	0.7	0.2
	Ca-K	2.3	1.0
	Ba-L	43.6	67.3
	Ti-K	44.5	24.0
	Zn-K	1.2	0.9
	Zr-K	4.8	4.9
Fe-alloy particle (Figure 5.2a)	Al-K	0.3	0.2
	Si-K	23.2	13.2
	Mn-K	0.7	0.8
	Fe-K	75.8	85.8
Brass particle (Figure 5.2a)	Sn-L	48.2	63.6
	Fe-K	0.8	0.5
	Cu-K	50.5	35.6
	Zn-K	0.4	0.3

Apart from the existence of composite particles, the EDS analysis of individual particles also showed the liberated particles are made up of alloys. The material make up of liberated particles certainly will have important implications for beneficiation planning. Table 5.2 shows the chemical compositions of some of the particles annotated in Figure 5.4. This implies that beneficiating this sample will, at best, produce fractions that are not cleaner than the alloys. For example, in a solder particle, lead would be inseparable from either zinc or tin. A realistic objective in flotation will be to recover as much as possible of the metallic values into a bulk product fraction. This is the motivation for the bulk metallic flotation proposal (see Sections 3.5.2 and 4.6.2). It was also noted that collector adsorption on alloy surface is synergistic: a collector will interact with an alloy as much as one of its constituent elements interacts with that collector (see Section 3.3). This should assist the response of the alloys to bulk collectors.

5.4 COMPARATIVE WET SPECTROSCOPIC ANALYSIS

Of the three digestion systems employed, only SPF (sodium peroxide (Na_2O_2) fusion followed by HCl dissolution), achieved total digestion of the sample. Aqua regia (AR) and HHM (HF + HNO_3 plus microwave radiation) gave only partial digestions. Various elements dissolve to different extents under the partial digestions as the assays indicate. Table 5.3 shows the assay values for 42 elements from the three digestion conditions. Elements not detected under a digestion condition are entered as ND. These assays are averages for duplicate digestions. The repeatability was within 95% for most elements, but 90% was also noted for some. Notably Pd was observed to give best repeats, about 1.5 % relative standard deviation, while silicon and silver gave about 10 %. This is considered acceptable recognizing that a perfect replicate sample from such highly heterogeneous stock may be unrealistic.

Detailed analysis of sampling variance, element by element, over reasonably large population of samples, while using a single digestion technique, can be informative in this connection. However, this is outside the present scope. Bearing the possibility of sampling variance in mind, only assay differences above 10% are considered significant when comparing the effectiveness of the digestion techniques in recovering a particular element into analysis liquor.

Table 5.3: Assay values from ICP OES and ICP MS analyses of printed circuit boards comminution fines from different digestion conditions (mg/Kg)

Element	AR: Aqua regia	HHM: HNO_3 + HF + Microwave	SPF: Na_2O_2 Fusion + HCl dissolution
Ag	849	18.9	--
Al	32900	32890	32922
As	32.5	N.D.*	--
Au	220	124	--
B	10800	9170	--
Ba	7590	8120	8140
Bi	319	237	--
Ca	63400	64500	75400
Cd	17	11.2	--
Ce	72	48	--
Co	92.2	90.6	--
Cr	160.0	323	416
Cu	42700	43200	42800
Fe	26800	32300	33630
Hf	10.4	N.D.*	--
K	717	737	--
La	91.5	19.9	--
Li	40.3	39.7	--
Mg	2180	2130	2150
Mn	1200	1230	1457
Mo	53.7	40.1	138
Na	2120	2050	--
Ni	1900	2110	2512
P	1120	1110	--
Pb	23100	22300	23530
Pd	158	137	--
Pt	1.7	5.3	--
S	555	2750	--
Sb	2620	3180	--
Se	N.D.*	N.D.*	--
Si	4070	11600	139300
Sn	29100	29800	--
Sr	785	686	780
Te	N.D.*	N.D.*	--
Th	6.0	2.4	--
Ti	3340	4070	4168
Tl	N.D.	N.D.*	--
U	1.9	1.9	--
V	26.3	30.0	30
Y	9.65	5.80	--
Zn	4890	5510	6212
Zr	245	297	--

It should be noted that the assays in Table 5.3 are for printed circuit boards comminution fines and do not represent a complete board analysis as in Table 2.4. In general, metallic value deportment to the finer fractions in the comminution operation is lower than that to the coarser fractions, because metallic materials are generally ductile and do not shatter into fines during comminution. It will also be noted that many elements (including Au, Ag, Pd, Sb, Sn, and Zr) were not read from the total digestion solution from SPF treatment. This is because of possible pronounced matrix effect on these elements under the optical emission spectroscopy (Willard *et al.*, 1988). Hence, only solutions from AR and HHM digestions were analysed for all the 42 elements.

From the data, Si gave values that were more than 10 times higher with SPF digestion compared to AR and HHM digestions. These result from the digestion of glass fibres. It is expected that SPF, which gave total digestion, should give the highest assays, and this is true for almost all of the elements. Some exceptions are for Cu and Mg, which returned highest values from HHM and AR respectively. However, the values are significantly close for all the three conditions that it may not be said that the recovery of Cu and Mg are lesser under SPF digestion. Au, Ag, Pd gave higher assays with AR than with HHM. Ag, in particular, is sparingly digesting under HHM digestion with only 18.9 ppm dissolved, compared to 849 ppm in AR. For Pt, HHM digestion appears to give a better digestion recovery (higher assay), compared to AR digestion. For other elements, the assays from AR and HHM treatments are comparably close and within the range of sampling variations.

These observations confirm that (i) printed circuit boards comminution fines wet assaying will depend very much on the digestion condition, and (ii) a single digestion condition cannot give best assays for all the elements combined. While SPF treatments resulted in complete digestion, many elements could not be analysed from the resulting solution. Readings from AR and HHM treatments also did not clearly give one condition as better than the other for all the elements. This reflects the heterogeneity of the sample, as different chemical elements exhibit different activities at the chemical potential of a digestion system.

In this context, the digestion condition that gives the maximum assay value for a particular element can be considered as ideal for that element, and the assay obtained from that condition can be taken as most indicative of the absolute assay for that element in the fines sample. Assays from other digestion conditions will only be fractions of this absolute value. For elements such as Au, Ag, Pd and Ti, the AR condition – hot aqua regia digestion – gives the absolute assay, while for Ni, Fe, Sb and Pt, for instance, the absolute assay is from the HHM treatment.

An implication of these observations for a standard approach to eol printed circuit board composition analysis is that absolute or actual assays of the constituent metallic elements will have to be combined from more than one digestion condition. It may be mentioned that the routine of obtaining the absolute assay may be unnecessary except in analyses for hazardous constituents as in environmental concerns. It may be noted here that no standard procedure yet exist for PCB chemical composition analysis (ASTM; ASTM, 2007; ISO).

In beneficiation investigations, valid inferences can be made based on relative assays of product fractions obtained from one digestion condition, whether absolute assays were obtained for all target values or not. It follows that, the final choice for a particular PCB comminution fines analysis depends on the target elements and the analytical objective, whether for comparative or absolute assaying. This implies that printed circuit boards wet analysis reports need to specify the digestion condition used. This will help data interpretation and inferences.

In any case, when the data from the three digestion conditions are compared, hot aqua regia digestion appears to be the best for general purpose analysis. It is able to give analysis liquor for all the elements. The procedure is also less hazardous compared to using HF in the HHM treatment. Hence, for analysis of flotation performances for the present investigation, hot aqua regia digestion will be used. It gives good assays for major target values such as Au, Pd and Cu.

5.5 THERMOGRAVIMETRIC ANALYSIS FOR ORGANIC CONSTITUENTS

Figure 5.5 shows the result of the thermogravimetric analysis. The top plots show the percentage change in mass with temperature for the air and the nitrogen environment (distinguished by colour). The lower plots show the derivatives (rate of change of mass with temperature) in an attempt to accentuate the inflection points.

The result shows final mass in air as 75.62 %. The analytical question is to determine what constituent fraction the 24.38 % mass loss represent. Certainly there are organics that will be expected to burn off and contribute to the mass loss. However, the drop in mass was continuous over the whole temperature range, indicating continuous reactions that cannot be attributed to a specific organic constituent in the composition. To make the distinction less obvious, the sample contains solder particles that could have developed relatively high vapour pressure as temperatures rose, with consequent volatilisation loss. This is further complicated by the possibility of metallic particles oxidising with weight gain. The overall mass loss may, therefore, not be taken as total but only as net from loss and gain. The mass drop in the air environment may therefore not quantify any particular constituent in the sample.

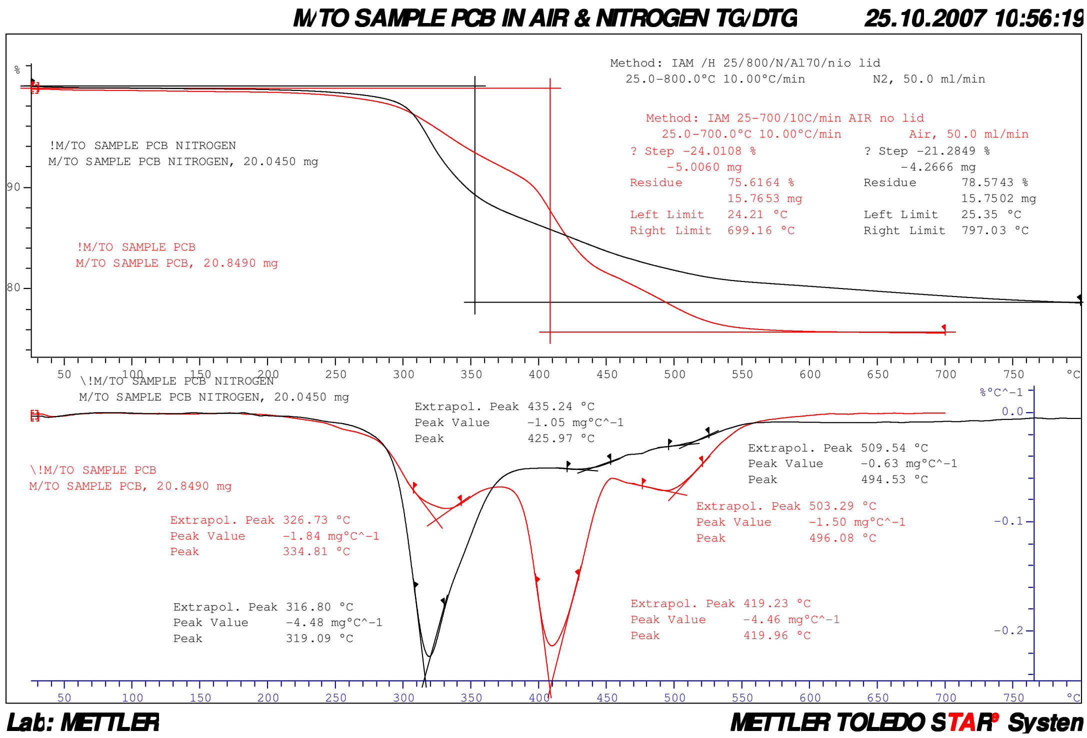

Figure 5.5: Plots of thermogravimetric analysis and the derivatives for PCB CF sample under air and nitrogen.

The nitrogen atmosphere is considered relatively more inert, and some reactions will be expected to be absent so that some distinctions in the trend can be expected. The residue in the nitrogen environment is 78.57 %, implying that combustion loss was lesser than it was in air. The nitrogen plot lying below that of air between 300 °C and 420 °C actually confirms that some weight gain was compensating for the weight loss in air. The weight loss sloped faster under nitrogen, when oxidation weight gain was absent. After this interval, as temperature rose, combustion losses appear higher under air and the mass dropped quickly to stabilise around 600 °C. This was not happening under nitrogen and, as the negative slope reduced, the rate of mass loss became very low. This continued slowly and did not stabilise even at 800 °C.

The comparison shows that combustion loss under air was pronounced in the sample and can be taken as responsible for much of the higher weight loss under air. However, the nitrogen atmosphere either did not characterise any specific constituent in the sample. Early into the heating program, from about 50 °C, mass loss commenced, and continued with a slope all through. Again, no position over the whole temperature range gave zero derivative of mass with temperature (dM/dT = 0), to characterise a constituent distinctly.

This results show that thermogravimetry may not be recommended for PCB composition analysis. No concrete qualitative or quantitative information may be extracted for characterising a given constituent. It appears that more than one reaction or event was occurring simultaneously over the whole temperature range. This can be attributed to the very diverse material constituent of the sample.

5.6 CONCLUSION

Characteristics of PCB CF observed under the characterisation investigation were interesting and peculiar. Without the basic understanding of these material characteristics – the density, PSD, liberation and the chemical composition – and the implications all of these will have on flotation, investigating the prospects of flotation application may not be possible.

It was found that the PCB CF loose bulk density is lighter than the density of water. This, coupled with other peculiar surface properties of the bulk sample, necessitates the careful pulping procedure that had to be adopted in the flotation investigations (see Sections 6.2 and 6.3.1).

The wet assaying of the sample was found to be very dependent on the digestion condition. From the result it was inferred that determining the absolute assays of all constituent elements will require comparing data from more than one digestion condition. However, if the analytical objective is a comparative assaying of samples from beneficiation treatments, aqua regia digestion can be recommended for most of the constituents. The procedure is less hazardous compared to HF, microwave and HNO_3 treatment. It also gives analysis liquor from which all the elements can be analysed, compared to that obtained from the Na_2O_2 fusion + HCl total digestion. Ironically, total digestion has a demerit here due to the complexity of the sample. The sample complexity also posed a limitation when applying the thermal analyses technique. The thermogravimetry analysis gave no distinct inflexion point to characterise any constituent.

Particle liberation in the sample was found to be very high. It may almost be taken as fully liberated, as reported in the literature, except that micrographic evidence obtained to the contrary is too vivid to be ignored. The unliberated fraction can be put at about 5000 particles per million. The particle morphology was observed to be very diverse and this, coupled with the material diversity, is a major constraint to sub-sieve PSD analysis.

Based on the mesh sieve analysis, 67 % of the sample generated was found to be below 38 µm. Pronounced effect of fines on the flotation response of the sample should therefore be expected. The liberated particles themselves contain more than one chemical elements, being alloys. Beneficiation operations therefore cannot attempt to separate these particles into constituent elements: realistic schemes can aim only at achieving some bulk collection of metallic values into a concentrate.