1.0 INTRODUCTION

In the physical processing stage of material recovery from end-of-life printed circuit boards (eol PCB), metallic and non-metallic values on the boards are separated into different materials fractions through a series of stage-wise comminution-separations. Various separation technologies are employed in processing the diverse mixture of materials that the comminution operations produce at different stages. These include magnetic separation, eddy current separation, electrostatic separation, air tables, gravity air classifiers, air cyclones and shape screens, among others (Goosey and Kellner, 2003; Li *et al.*, 2004; Kang and Schoenung, 2005; Hamos GmbH).

As expected, each separation operation gives optimum efficiencies at specific size ranges. At smaller sizes, below 2mm, electrostatic separation has been mostly applied for copper recovery from the grinding mix (Zhang and Forssberg, 1997; Iuga *et al.*, 1998; Li *et al*, 2004, Hamos GmbH; Kang and Schoenung, 2005). From classical mineral processing, application of electrostatic separation is known to give poor separation efficiencies at −100 µm fine sizes (Wills, 1997). Zhao *et al.* (2004) demonstrated the application of a type of column air separator compared to an electrostatic separator. For the −75 µm fractions, copper recoveries of 27.83 % at a grade of 26.8 % were obtained from the pneumatic separator while separation from the electrostatics at that size was declared poor and not reported. The low recovery implies valuable metal loss at this size range, while such poor grade implies product contamination, thereby complicating the finishing recovery processes. Overall improvement to the physical processing stage, in order to produce cleaner fractions, has been emphasized (Goosey and Kellner, 2003).

In the cited instance (Zhao *et al.*, 2004), more than 20 % of the product of the hammer mill grinding from 30 mm feed top size reported to the -75 µm fraction, assaying almost 2.9 % copper. Less than half copper recovery from this fraction implies that more than 0.29 % of the total grinding product by weight, ~2.9 kg/ton of copper, will be lost. In NEC corporation recycling operation, at -300 + 100 µm (Yokoyama and Iji, 1997; Iji and Yokoyama, 1997), copper rich powder (82%Cu, at >90% recovery) was produced from the electrostatic separation, with the non-conducting fraction containing 64 % glass fibre, 34 % epoxy resin, 2.1 % Cu, and solders. Some end-use applications, such as filler for epoxy resin polymer products, were investigated for the glass fibre-resin fraction. However, at 2.1 % copper content, the fibre glass-resin non-conducting fraction assays higher than many natural porphyry copper deposits that are being mined and economically processed (Wills, 1997). It therefore deserves further beneficiation. Moreover, as precious metals are coated to a few microns in the printed circuit board (PCB) sockets and slots, and on the edge connectors, abrasion in the event of comminution is likely to make this precious metal report to this fine fraction also. With the poor separation efficiencies of electrostatic separation at -100 µm, these precious metal fraction will mostly report to the non-conducting fraction (Kelly and Spottiswood, 1989), representing a major loss to the economic drive of the whole operation. Traces of noble metal anti-etch materials used during the printed copper circuit production (Li *et al*., 2004) should also be present on the copper traces; copper particles not recovered carry such to waste. All these underscore the point that the fine fraction from PCB grinding presents the challenges of low separation efficiency and contamination of product fractions, while contributing a drop to the overall physical processing recovery relative to coarser size fractions.

The inefficiency of electrostatic separation in processing the fine fraction has been tolerated by recycling operations, possibly because of preference for keeping the operations dry. Wet processes are avoided in most recycling operations, to avoid wash water circuit and treatment costs, among other reasons (Kellerwessel, 1993). Given the diverse material make-up of printed circuit boards (PCB), chances of hazardous leaching during wet processing may also be contemplated. However, at this stage of PCB physical processing, the operation need not be restricted to dry. Wet processing, and especially froth flotation, appears very promising. Success in this direction can be a pointer to improved processing approach and overall improvement in PCB physical processing. Density-based applications for wet table and centrifugal separations have been reported (Galbraith and Devereux, 2002; Xuefeng *et al*., 2005). Froth flotation exploits distinct surface property of individual particles and it appears very promising for detailed investigation, more so that there has not been any effort to conduct empirical research into its applicability. Froth flotation is well explored in minerals and, to some extent, in waste processing. Outstanding features of froth flotation are its selectivity, flexibility, throughput and handling of relatively fine sizes. These make it very relevant to this application. Froth flotation has been used for beneficiation of ore bearing native metals and oxides minerals, among others. Flotation of plastics has also been applied in municipal solid waste treatment (Shent *et al*., 1999; Alter, 2005). PCB fines consist of a mixture of metals, alloys, ceramics and plastics with distinct surface properties that should enable selective wetting and make froth flotation separation possible. This is a broad hypothesis upon which froth flotation can be expected to be applicable for the beneficiation of this material mixture. However, if co-occurrence of three minerals such as chalcopyrite, pyrite and galena is recognised as complex in conventional minerals processing (Wills, 1997), then this sample is really complex. It will present an interesting challenge to the versatility of flotation technique.

The general objective of this research is, therefore, to investigate froth flotation for beneficiation of this material mixture, with the aim of being able to conclude on the applicability. In this connection, characterisation relevant to flotation investigation of the sample will first have to be done. From the peculiarities of the sample based on the characterisation, along with general literature survey, and with pointers from trial investigations, logical flotation schemes will be drawn for the investigations. Toward these ends, a general background literature review is first presented. This is followed by a more focused literature-based discourse aimed at drawing the flotation schemes, and at stating more specific objectives, and approaches to, the investigation.

2.0 BACKGROUND – PCB PHYSICAL PROCESSING

2.1 INTRODUCTION

Physical processing is admitted to be the most environmentally-friendly approach among others such as pyrometallurgical and hydrometallurgical processes for materials recovery from end-of-life (eol) printed circuit boards (PCB), and general waste in electrical and electronic equipment (WEEE). Table 2.1 summarises the basics of the different techniques.

Table 2.1: A comparison of general e-waste treatment approaches

Treatment Approach	Operation	Merits	Demerits
Landfilling	Direct dumping of classified wastes in landfills	A means of disposal; at least removes physical junks	Leaching of hazardous constituents; wasteful disposal of otherwise huge material resources.
Hydro-metallurgy	A secondary processing, entailing leaching and winning.	Gives high purity product; can handle small tonnages of feed supply	Preconcentration is important on complexity of the leaching and winning. Treatment of secondary effluent streams
Pyro-metallurgy	Smelting in furnaces, giving three products: noble metals report to molten metal phase, metal with more stable oxides report to slag phase, while metals with high vapor pressure will be collected from the vapor phase. Each product further treated separately.	Little feed preparation: sizing, removal of hazardous components - mercury bearing, capacitors.	Require consistent high grade and quantity of feed; dedicated plant highly capital intensive; feasible where there are existing facilities which accepts e-waste as secondary feed materials; recovers zero value for plastic constituents; off-gas treatment; facilities not available in many parts of the world.
Physical Processing	Applied mineral processing: comminution and separation of constituent materials by exploring variations in physical properties.	Already relevant in feed preparation for hydro or pyro routes; handling of varying feed constituents; amenable for low or high scale operation; least impact on the environment.	Dust handling in aggressive grinding for total liberation; possible precious metal losses; noise; not very clean fractions.

Major demerits of the physical processing option include product fractions that remain largely unsorted to have best end-values as separate material fractions (Lee *et al.*, 2004). This makes pyrometallurgical follow-up processing indispensable and extensive (Lee *et al.*, 2004; Shuey, *et al.*, 2006). This points to the need for cleaner fractions from the physical processing stage.

A background review of PCB physical processing will help to place the various aspects of the operation into perspective. A characterisation to appraise the huge material resource and the diversity in the material stream will be informative. This is followed by a review of the physical processing operations in almost three decade of this endeavor. This will clarify how improvement in the beneficiation of the comminution fines can contribute to improving the operation.

2.2 PCB CHARACTERISATION

2.2.1 Occurrence and Reserve

Printed circuit board (PCBs) mechanically support and electrically connect electronic components by using conductive pathways, or traces, etched from copper sheets laminated onto a non-conductive substrate (Wikipedia). Alternative names are printed wiring board (PWB), etched wiring board (EWB). Populated PCBs have mounted components, while unpopulated ones comprise of only reinforced resin and printed copper wiring laminate. PCBs are found in almost all electronic applications, spanning personal computers, telecommunication equipment, hospital equipment, cellphones and various consumer electronics. Continuing and rapid advances in technological innovations result in a high rate of obsolescence of this equipment, leading to large tonnages of PCB going into the WEEE stream.

In the United States of America (USA), for personal computers (PC) alone, 63 million units was estimated to be obsolete in 2005 (Figure 2.1; Kang and Schoenung, 2005). At about 0.75 kg PCB per PC unit or 2.75 % by weight, and one PC unit with monitor weighing about 27.5kg (Shuey *et al.*, 2006), the huge tonnage of materials this translates to can be appreciated. In the UK, about 50 000 tons of waste PCBs are generated *per annum* (Goosey and Kellner, 2003). Of these, about 40 000 tons are populated PCBs, and 10 000 tons are unpopulated or associated boards manufacturing scrap. The estimate for 2006 is 100500 tons (Shuey *et al.*, 2006). A year 2000 review in Taiwan claims about 300 000 scrap PC units *per annum* (Lee *et al.*, 2000), and this had risen to 700 000 by 2004 (Lee *et al.*, 2004). With generally few statistics for South Africa, more than 500 000 PC units are reported dumped per year. Intel South Africa, an original equipment manufacturer (OEM), has been in business for 35 years and has sold more than one billion CPUs. This implies a lot of PCs out somewhere (Mackay, 2004). Large undocumented accumulation, or scatters, of PCBs occur around the world, much due to shipment of used PC to developing countries. A 2005 British Broadcasting Corporation (BBC) report, focused on Nigeria, claimed that about 400 000 used computers are imported to Nigeria monthly. Almost 75 % of these cannot be used, cannot be repaired economically or resold. The situation is typical of many developing countries (Laurie, 2005).

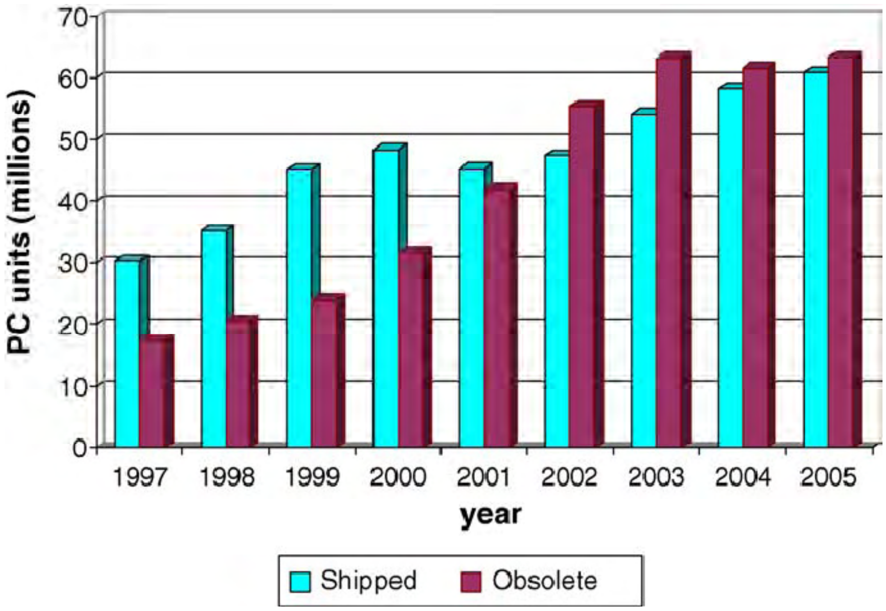

Figure 2.1: Personal computer shipments and obsolescence in the United States (Kang and Schoenung, 2005)

Taking PCBs as a highly valuable polymetallic resource, the foregoing has been an attempt to present its occurrence and 'reserve'. Recognizing the material values it contains (see Section 2.2.3), eol PCB stream can be referred to as a type of ore, rather than a waste stream. Though not containing specific minerals with definite chemical composition, according to the classical definition of an ore, the stream contains many of the metallic elements in the periodic table, in proportions greater than many natural deposits of such metals. It therefore deserves better recognition as a resource stock. PCB processing yields concentrates that feed into metal production, just like run-of-mines. On this basis, PCBs and other end-of-life electronic equipment can regarded as a type ore – industrial ores (Castro *et al.*, 2005). This distinguishes PCBs from natural ore from the mine, because this material stream is from the industry after a service life. In the broad view of cyclic material use, WEEE is essentially a transit title.

2.2.2 PCB Structure

PCB structures have varied with technological advances over time. Earlier boards were single-sided with large components on one side of the board and the soldering for mechanical support on the order side. Etched copper wiring makes electrical connections from the soldering side (see Figure 2.2). All the components had terminals dipping through the board. The top side and the bottom side were therefore referred to as the component side and the solder side, respectively (Holm, 2001). This type of boards was used in very primitive circuits.

Figure 2.2: Single sided boards

Double-sided boards are more recent boards having conductor patterns on both sides of the board with interconnecting electrical 'bridges' called vias. Vias (singular: via) are holes in the PCB that are filled or plated with metal and touch the conductor pattern on both sides. Since the surface available for the conductor pattern is twice as large compared to single-side boards, and wiring can now cross the sides, double-sided PCBs are for more complex circuits than the single-sided ones: the wiring is thinner and much denser, and the components are usually surface-mounted chips without leads (see Figure 2.3).

Figure 2.3: Double-sided PCBs – top (left) and bottom (right) views

Multilayered boards are developments on the double-sided boards and are formed by bonding together separately etched thin boards such that these boards have trace (wiring) layers inside the compact board. Two, four, eight, twelve and sixteen layers boards have been produced (Vinod and Sanjay, 2005; Wikipedia). The conducting traces are connected through vias. Either the holes are electroplated or small rivets are inserted. Such high-density PCBs have blind vias, which are visible only on one surface, or buried vias, connecting the interlayer, and so not visible on either surfaces. In 2005, multilayered boards accounted for about 20 % of total PCB production (Vinod and Sanjay, 2005), and manufacturers are confident this will become the dominant type of board. Rigid flex and flexible printed circuits are other types of boards found in specialised applications like printers and communication equipment.

Sockets and edge connectors are common features on the PCBs. The sockets serve to connect removable components such as memory units to the PCB. Figure 2.4 shows a zero insertion force (ZIF) socket for mounting a processor. Edge connectors, consisting of small uncovered pads of copper located along one side of the PCB (see Figure 2.4), are used to connect the circuit on one board to another board (for example, sound or graphic card to the motherboard). Edge connectors and sockets are usually plated with precious metals to ensure least junction resistance.

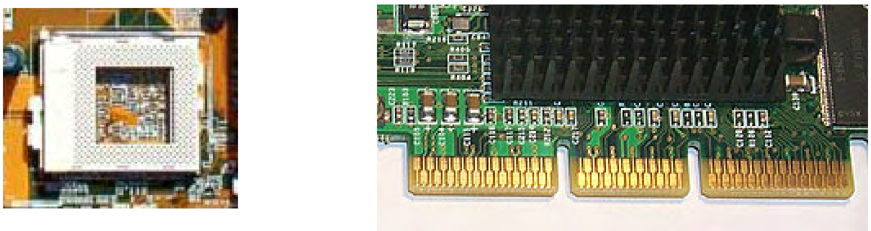

Figure 2.4: ZIF socket (left) and edge connector (right)

2.2.3 PCB Material Make-Up

The materials make-up of PCB is very diverse. Populated PCBs are reported to contain most of the elements in the periodic table (Li *et al.*, 2004). Unpopulated boards consists of conducting copper traces and non-conducting substrate. During production of the printed wiring by etching, thin film of metals such as nickel, silver, tin, tin-lead and gold are used as etch-resistant materials to protect part of the copper layer which will represent the wiring from the etchant. The substrate is a composite material. It originally consisted of woven glass fibre impregnated with an epoxy resin matrix containing bromine additive as flame retardant.

The matrix material called FR4 was the industry standard for many years until environmental concern started protesting against the use of the material because of its hazardous brominated flame retardant (BFR) content (Directive 2002/95/EC; D'Silva, 2004). This led to the development of various halogen-free materials. Phosphorus and antimony additives have been used for flame retardants. Up to five types of halogen free epoxy resins have been tested qualified for use in PCB production. These include epoxy resin cross linked with aminophenyl phosphate (Ehrler, 2002; Mauerer, 2005). There have also been developments toward improving the Tg (glass transition temperature) of the board material using epoxy resin blends and alternative resin materials. From the PCB materials development efforts, quite a number of plastic materials can now be found in waste PCB (Ehrler, 2002). These include:

- The conventional FR-4.
- Higher Tg FR-4, with a higher content of tetra- or multifunctional epoxy resins in the formulation to give greater cross-linking density in the cured material.
- Cyanate ester (CE) resin based, also with a relatively high Tg.
- GETEK^R/MEGTRON resin, a blend of 70/30 high Tg epoxy and thermoplastic polyphenylene oxide (PPO), developed by General Electric.
- Bismaleimide-triazine (BT) based material, developed by Mitsubishi Gas Chemical.
- Hydrocarbon resin filled with fine grained ceramics, designed for high frequency high speed applications by Rogers.
- A-PPE resin, in which polyphenylene oxide has been modified into a thermosetting resin

- Thermount^R reinforced materials: a para-aramyd polymer fibre reinforced material developed by Thermount^R DuPont Advance Fibre Systems.

Alternative reinforcement materials to glass fibres have also been developed. The paper-like para-aramid polymer fibre called Kevlar^R for Thermount^R is an example. Details about the thermomechanical and electrical properties significant for PCB applications, such as the dielectric constants, dissipation factor, through hole reliability, copper peel strength, z-axis expansion, volume resistivity and solder shock laminate, are available in literature (Roesch and Ehrler, 1997; Ehrler, 2002).

Populated boards have components put in place on them. It is expected to find resistors, chips, aluminium heat sinks, batteries, switches, capacitors, inductors, transistors (triodes, diodes and thyristors), fan units, connector terminals/slots, cables, transformers, solders, screws and rivet fittings, among others. The different components have different material compositions. Many metals, alloys, ceramics and plastics are used in these components and fittings. For the solders, more than 100 solder alloys are known (MatWeb). Table 2.2 shows some of these solders and their compositions.

Table 2.2: Representative solders: Composition, melting point and density (MatWeb) (The number in front of the elements is the mass percent in the alloy)

Solders	Composition (mass, %)	Melting Point (^OC)	Specific Gravity
Pb-Sn Eutectic (ASTM B 32 Grade Sn63)	37Pb 60Sn 3(Ag, Al, As, Zn, Sb, Cd, Cu, Fe)	183	8.4
95Sn-5Ag (ASTM B 32 Grade Sn95)	95Sn 4.4-4.8Ag, (Al, As, Zn, Sb, Cd, Cu, Fe)	221 - 245	7.5
95Sn-5Sb, ASTM B 32 Grade S65	95Sn, 4.5Sb, (Al, As, Zn, Sb, Cd, Cu, Fe)	234 - 240	7.25
AIM47 Fusible alloy	22.6Pb, 44.7Bi, 5.3Cd, 19.1In 8.3Sn	47	8.86
WS363 Lead Free	98.65Au 3.15Si	363	15.7
WS305 Lead Free	78Au 22Sn	280 - 305	14.81
WS238A	97Sn 3Sb	232 - 238	9.28
Indalloy^R 281 Bi-Sn	58Bi 42Sn	138	8.56
Indalloy^R 227 Sn-In-Ag	77.2Sn 20In 2.8Ag	175 - 187	7.25

Leaded solders are expected in earlier boards, while more recent boards may use unleaded solders. Base metals such as iron (in screws, transformers, electromagnets and rivets), copper (in inductors, transformers and cables), aluminium (in heat sinks, foils and wrappings) and tin, can be found in fair bulk sizes on PCBs. Rare metals, such as tantalum, are found in high performance capacitors. Noble metals, such as gold, silver and palladium, occur in sockets and edge connector plating and in some high performance components. Gallium and other platinum group elements can also be found. Lead, cadmium, chromium and mercury are usually concentrated in batteries. Mercury is also found in relays and switches, while cadmium is found in some surface-mounted chip resistors, infrared detectors and semiconductors. Ceramics, used in bridges and slots on the boards, include alumina and beryllium oxide. Silica, other alkaline earth oxides, mica and barium titanate are also found. Chip components contain elements such as Ga, In, Ti, Si, Ge, As, Sb, Se and Te, while semiconductors contain Ge, Si, Se, Ga and other elements in small quantities.

Apart from the board resins, other plastics generally found in populated boards are polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS) and polystyrene (PS). Varying amounts of these plastics may be found on the PCB depending on the socket, slots and cable coating materials used. Varieties of plastics that can be found in the populated PCB materials streams, including density and critical surface tension of some of the plastics, are presented in Table 2.3.

In general, there are a number of overall material compositions reported for the PCB. Some of these compositions, as well as one determined in this work, are contained in Table 2.4. The data for each element can be seen to vary across the different compositions. This is expected as PCBs material make-up continues to change with technology over time. This makes quantitative analysis of the stream really difficult, and a ‘typical’ PCB composition may not be presented rigidly. Unfortunately, the OEMs are not of help in this context: more than one manufacturer is responsible for one populated PCB, while components are ordered according to electronic functions and not by materials composition. PCB manufacturers therefore do not have complete information regarding the material composition (Li *et al.*, 2004). The bulk comes back to the materials processor to determine a composition upon which resource recovery analysis can be based. There are other implications of PCB material make-up on its physical processing.

Table 2.3: Plastics obtainable from PCB materials streams

Plastics	Specific Gravity	γ_c, critical surface tension
Polyethylene (PE)		31
Polyethylene terephthalate (PET)	1.33 – 1.37	43
Polyvinylchloride (PVC)	1.16 – 1.38	39
Polytetrafluorethane (PTFE)	2.3 – 2.32	18
Nylon	1.1 – 1.35	
Polypropylene (PP)		
Acrylonitrile butadiene styrene – ABS	1.04	35
Fibre reinforced ABS (Acrylonitrile butadiene styrene)	1.286 - 1.45	
Polystrene (PS)	1.04	33
Cyanate Ester (CE) Resin		
Polyphenylene oxides (PPO)Resin		
Polyphenylene ether (PPE)		
Bismaleimide-Triazine (BT) Resin		
FR-4 Epoxy resin	1.8-2	47
FR-2 Phenolic resin based		
Para-aramid polymer fibre		

2.2.4 Physical Processing Implications

The material make-up of PCB has implication both on the comminution and the separation operations in the physical processing. The PCB structure presented shows that classical mineral processing comminution equipment such as gyratory/jaw crushers and tumbling mills will not apply because brittle cleavage or shatter fracture may not be expected from PCBs. This was demonstrated by trial comminution in a laboratory ball mill with 35 mm steel balls. The fragments were only rubbed and beaten smooth after twenty minutes of operation (Ogunniyi, 2006). Shear shredders, which can be considered as a modification of toothed roll crushers, are used mostly for primary crushing, while hammer mills, which employ impact and shear, are mostly used for the grinding operation (Taylor, 2002; Goosey and Kellner, 2003; Hamos GmbH; Sander *et al.*, 2004, Schubert and Bernotat, 2004). Grinding in impact equipment with cryogenic conditioning to enhance the brittleness of the polymer matrix has also been reported (Kravchencko *et al.*, 1983; Goosey and Kellner, 2002). It should be noted that PCB comminution need not seek to obtain a characteristic breakage function. For instance, single-sided older generation boards with a high proportion of fibre glass and low density of the copper trace will be expected to show more overall brittle tendency compared to recent high density multilayereded boards with poly-aramid reinforcement. Populated boards will present more varied characteristics.

Table 2.4: Material Compositions of PCB (Weight %)

Materials		%[1]	%[2]	%[3]	%[4] *	%[5]	%[6]	%[7]
Metals (Max. 40%)[1]	Cu	20	26.8	10	15.6	22	17.85	23.47
	Al	2	4.7	7	--	--	4.78	1.33
	Pb	2	--	1.2	1.35	1.55	4.19	0.99
	Zn	1	1.5	1.6	0.16	--	2.17	1.51
	Ni	2	0.47	0.85	0.28	0.32	1.63	2.35
	Fe	8	5.3	--	1.4	3.6	2.0	1.22
	Sn	4	1.0	--	3.24	2.6	5.28	1.54
	Sb	0.4	0.06	--	--	--	--	--
	Au/ppm	1000	80	280	420	350	350	570
	Pt/ppm	-	-	-	-	--	4.6	30
	Ag/ppm	2000	3300	110	1240	--	1300	3301
	Pd/ppm	50	-	-	10	--	250	294
Ceramics (Max 30%)[1]	SiO_2	15	15		41.86	30		--
	Al_2O_3	6	--	--	6.97	--		
	Alkaline and Alkaline earth oxides	6	--	--	CaO 9.95 MgO 0.48	--	--	
	Titanates, Mica, etc	3	--	--	--	--	--	--
Plastics (Max 30%)[1]	Polyethylene	9.9	--	--		16	--	--
	Polypropylene	4.8						
	Polyesters	4.8						
	Epoxies	4.8						
	Polyvinyl-chloride	2.4						
	Polytetra-flouroethane	2.4						
	Nylon	0.9						

[1]Shuey *et al.*, 2006 from Sum, 1991; [2]Zhao *et al.*, 2004 from Lehner, 1998; [3]Cui, 2005 from Zhang and Forssberg, 1997; [4]Kim *et al.*, 2004, *Incinerated PCB Product; [5]Iji and Yokoyama, 1997; [6]Patent Application, 2006; [7]ICPOES analysis of cellphone PCBs

Another consequence of the diversity of valued constituents on PCBs is the complexity of beneficiation into clean material fractions. Target metallic values range from percentages to ppm proportions, in various forms of man-made ‘occurrences’ or ‘dissemination’. Among the valuables are hazardous contents. Lead, mercury, cadmium, hexavalent chromium and polychlorinated biphenyl (pcb) are among the six materials declared hazardous in the RoHS (Restriction on Hazardous Substances) directives (Directive 2002/95/EC). Polychlorinated biphenyl is found in some capacitors, while batteries contain cadmium, mercury, lead and chromium. These components must not be ground along with others, but must be removed for separate treatment (see section 2.2.3). This is why physical processing has to be in stages of comminution-separation, decongesting the stream as comminution progresses to finer sizes, and different values are being liberated. In this manner, the materials variety would have been significantly reduced before final grinding to liberate the values within the laminates.

2.3 PCB PHYSICAL PROCESSING OPERATIONS

In the 1970s the predominant method of recovery of metals from electronic scrap was via the blast furnace in conjunction with secondary copper/lead smelter (Sum, 1991). Details about physical processing effort were rare until the early 1980s. Figure 2.5 is a typical flowchart of earlier physical processing of scrap from multi-component REE – radio-electronics equipment (Kravchenko *et al.*, 1983). Scrap REE has now taken on the WEEE nomenclature. Features of this processing included differentiated disassembly (more recently referred to as selective disassembly), cryogenic cooling and crushing, airflow classification, stages of magnetic separations and, finally, magneto-hydrostatic separation (MHS). The magneto-hydrostatic separation density was first set to 2000 kg/m^3 (2 g/cm^3), then to 3000 kg/m^3. This will cause non-metallic stuff to be floated first, followed by aluminum in the second stage, while copper, lead and tin were in the sink product.

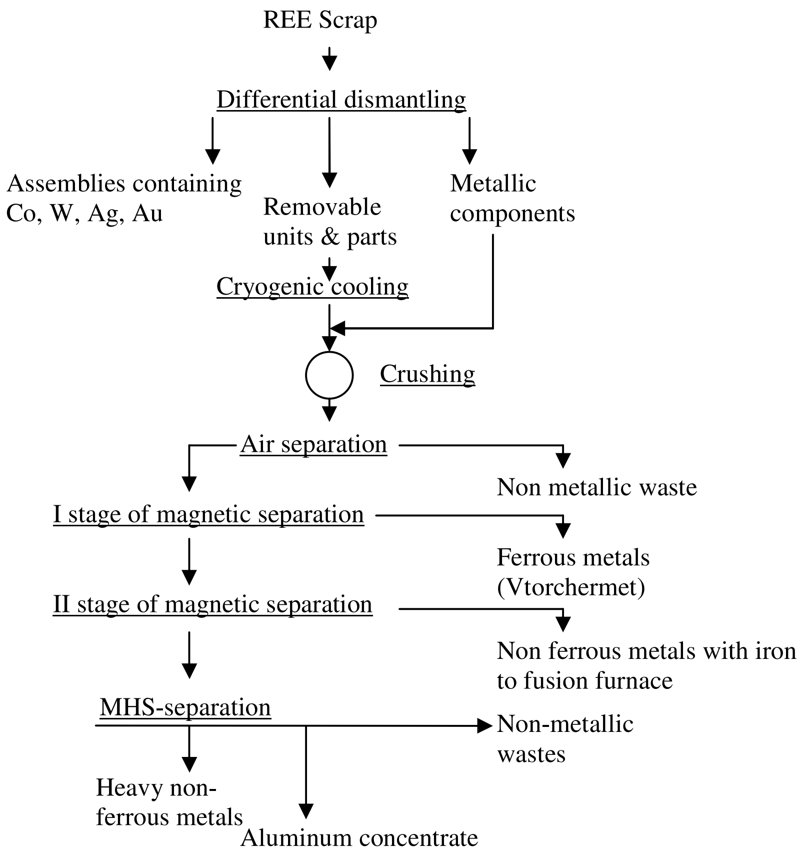

Figure 2.5: Flowsheet for reprocessing of multicomponent REE scrap (Kravchencko *et al.*, 1983 - Redrawn)

Magneto-hydrostatic separation, also called ferro-hydrostatic separation (FHS), is a technology that uses colloidally stable and magnetizable fluids. It dates back a few decades, with reported application for municipal solid waste processing (Khalafalla, 1973, 1976; Zhan and Shenton, 1980; Vesilind and Rimer, 1981). More recently, Debeers group reported efforts to apply it to mineral processing (Svoboda, 2000). A suspension of nanosized magnetic particles (often in kerosene) forms the ferrofluid whose apparent density can be varied by its surrounding magnetic field; the apparent density increases with increasing field strength. Under the influence of the field, the nanoparticles tend to align in space inside the ferrofluid and become stationary. This tends to make the fluid rigid so that particles sink through it with greater resistance, making the density appear higher. In application, the apparent density can be varied up to a specific gravity above 20 in fine steps, making it possible to achieve sink float separation of a mix to tenths of specific gravity.

In later operations, electrostatic separation was broadly used in place of the FHS for treating the fine fractions. Low throughput, high electricity costs for the field electromagnets in scale-up and optimal feed size, identified as limitations of the FHS (Kruger, 2006), could have been some of the reasons for this trend. By the 1990s, emphases were on the disassembly stage before crushing. The recovered component would be tested, refurbished and then resold in some second user specialist marketplace. Design for easy disassembly became an issue for the original equipment manufacturers (OEMs), and many works were towards automated disassembly, for components recycling (Feldmann and Sheller, 1995; Stennett and Whalley, 1999).

Figure 2.6 shows the flowchart of the recycling operation of NEC Corporation, Japan (Yokoyama and Iji, 1997). The operation entails first stage components and solders removal by heating, impacting and shearing (Yokoyama and Iji, 1997). The evacuated board then goes through pulverising and separation stages. The pulverising stage is considered critical to liberating copper in multi layered boards. Two types of equipment are used for crushing and fine pulverising. The first employs a cutting and shearing force for size reduction to 10 mm. The second employs a pulverizing roller on a table to apply compressive and shearing forces. The operation has a notable feature of liberating the copper more coarse than the glass fibre and the resin, due to differences in brittleness, see Figure 2.7 (Higashiyama and Asano, 1998). A gravimetric separator, based on density, is used on the product to produce a 23 wt % copper-rich residue. This is followed by a rotor-type electrostatic separator, producing recovery and grade of more than 90 % and 60 %, respectively, on the 100 – 300 µm size fraction.

Prior manual disassembly of precious metal bearing parts on the PCB was employed at Noell Abfall, Germany, and Energietechnik in their 21000 tonnes *per annum* plant in 1996 (Goosey and Kellner 2002). The plant was specifically intended for redundant telecomunication scrap and eol PCBs were also treated. The overall methodology deploys a three-stage liberation and sequential separation route with ferromagnetic removal via overhead permanent magnets and eddy current techniques, because of the effectiveness of the eddy current separation force on the fractions in the 5 mm to 200 mm particle size range. Air table techniques were used to separate particulate fractions in the 5 mm to 10 mm, 2 mm to 5 mm and less than 2 mm ranges respectively.

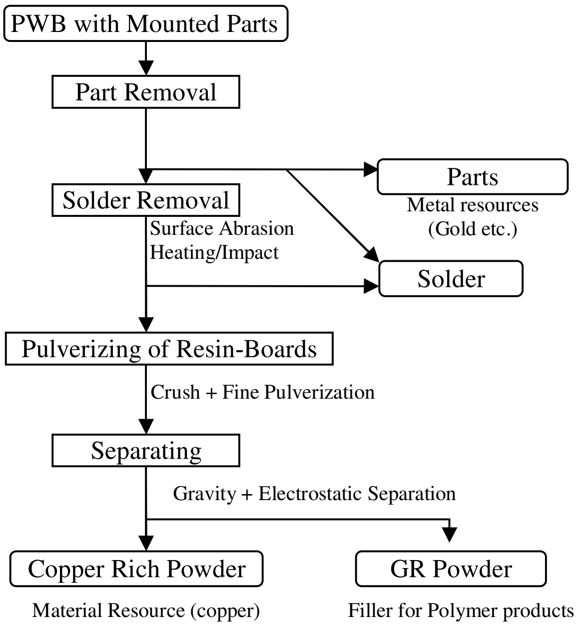

Figure 2.6: Flowchart of the NEC's recycling process (Yokoyama and Iji, 1997)

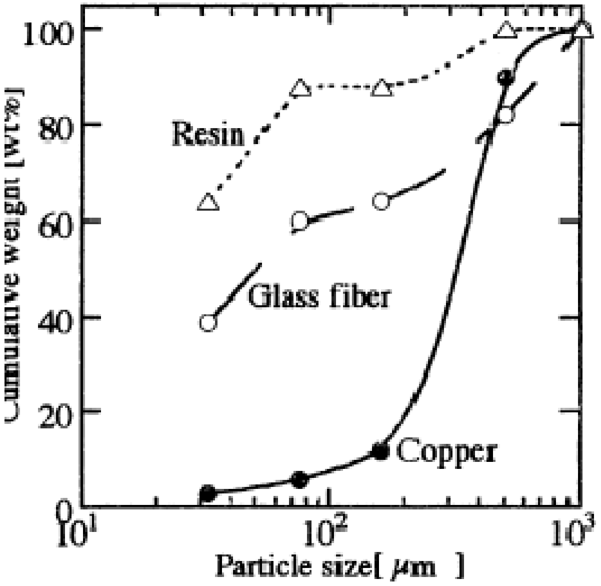

Figure 2.7: Size distribution of the NEC Corp comminution product (Higashiyama and Asano, 1998)

Cost effective automated disassembly, either by ‘look and pick’ or ‘evacuate and sort’, is a specialised technology on its own. It requires a data-intensive object-image recognition information system for sorting after evacuation; special numerically controlled jaw grippers for through-hole-device disassembly; vacuum grippers for surface-mounted devices; chemical or electrochemical dissolution of solders with specialised etchants, among other features (Feldmann and Scheller, 1995; Stennett and Whalley, 1999; Jianzhi *et al.*, 2004).

Although robotic technology operating on a cost effective component identification and disassembly was reported in the USA (Goosey and Kellner, 2002), this automation suffered setbacks in case of old ‘orphan’ boards with no existing database. Another strong factor against component recycling is the rapid advancement in production and materials technology. This makes components obsolete too quickly, not reusable, and new ones much cheaper. More recently, emphases for selective disassembly reduced greatly (Taylor, 2002). Total feed comminution in shredders, followed by separation, now substitutes disassembly devices in many operations. Although some extent of manual dismantling, to single out hazardous component, can be judged as indispensable because of the complex nature of the stream (www.desco.co.za), efforts to further disassembly expertise still continue (Elif and Surendra, 2006).

In Taiwan, all capacitors on the boards (possibly containing polychlorinated biphenyl) that have diameters greater than one centimetre and a height larger than two centimeters are usually removed manually from the board before comminution (Lee *et al.*, 2004). Products from integrated circuit (IC) boards in computer recycling plants are generally classified into three groups: ferrous, non-ferrous and non-metals – and each fraction sells at minimum of US$ 57, US$ 743, and US$ 43 per ton respectively. The Huei-Chia-Dien Company (Taiwan) has a dedicated flowsheet for physical processing of scrap IC boards, Figure 2.8 (Lee *et al.*, 2004). Iron, plastics, fibre glass and resin, aluminium and copper fractions are obtained. Except for the ferrous fraction, the other metallic fractions is usually a mixture of metals and are sold to smelters.

VOGT Electronic FUBA, Germany, runs a recycle centre for unmounted PCBs and material scrap, with 5000 tons per year capacity, adjacent to its PCB manufacturing plant (Goosey and Kellner, 2002; Gold and Dietz, 2003). The operation is fully mechanical and dry (see Figure 2.9).

Hammer mills convert the scrap feed into fairly liberated small pieces of particles or fragments for separation, while material separation uses the different specific gravities and electrical conductivities of the metal, glass and resin. The products obtained consist of copper metal and two plastic products – fibrous and powdery. The recovered copper is returned to metal smelters. The glass fibre and resin fraction finds most successful use in production of pallets for underground mining and storage. This product takes advantage of the flame retardant property of the resin fraction (Goosey and Kellner, 2002). A block diagram of the operation is shown in Figure 2.9.

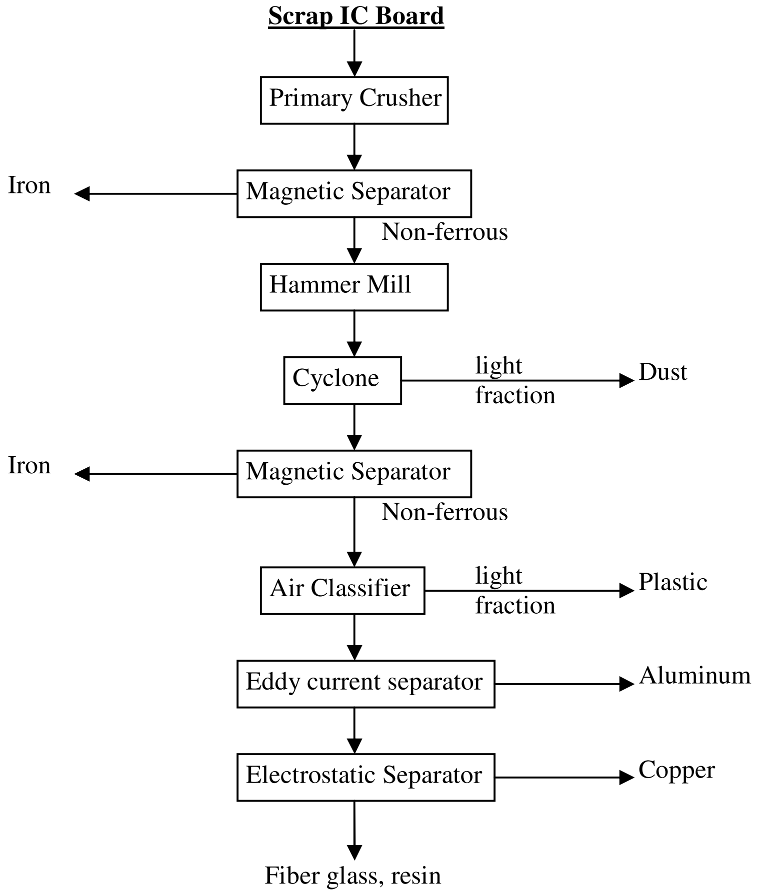

Figure 2.8: Huei-Chia-Dien Company's physical separation flowsheet for recycling of scrap IC boards (Lee *et al.*, 2004).

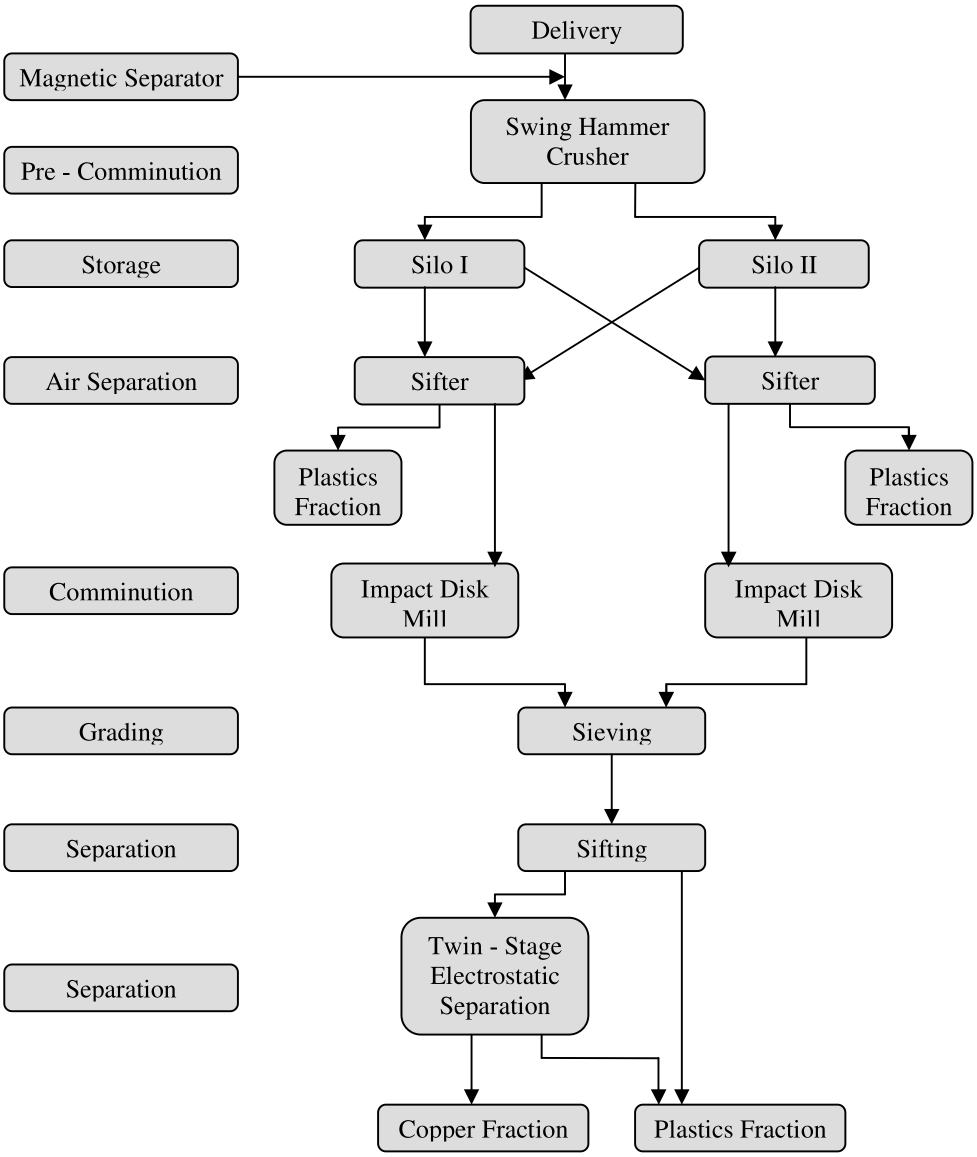

Figure 2.9: Block diagram of PCB recycling operation at FUBA, GmbH (Goosey and Kellner, 2002)

A commercial turnkey electronic recycling plant (ERP) for a wide range of electronic scraps, including populated PCBs, was developed by Hamos recycling and separation technologies, Germany (Hamos GmbH, Germany). It is an automated and integrated mechanical system, Figure 2.10, producing three products: a ferrous metal fraction, a mixture of non-ferrous metals and a mixed fraction of plastics and ceramics. The major stages of the operations involve pre-comminution for a coarse liberation; magnetic and eddy-current separation of coarse ferrous and non-ferrous metals; liberation of non-ferrous metals; classification for improved separation; electrostatic separation of the metal fraction; subsequent comminution of unliberated materials; dust extraction; and optional gravity or eddy-current separation of coarse metal fractions (Hamos GmbH, Germany).

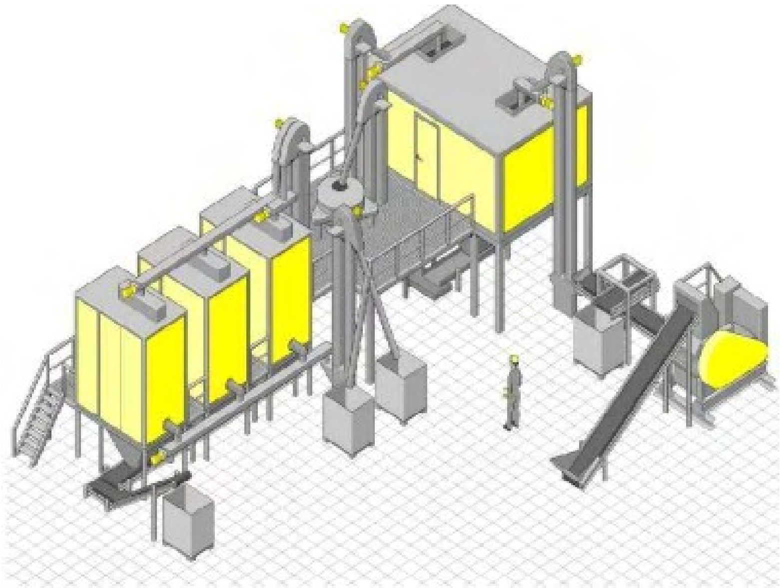

Figure 2.10: Hamos GmbH ERP – electronic recycling plant

Noranda Recycling Inc. operates in USA, Canada and Asia. The firm has established smelting operations and uses mechanical processing to upgrade general electronic wastes for smelting the feed (Shuey, 2006). Hazardous components are first removed manually before introducing the handpicked waste into a series of shredders that reduces the junk to five centimetre-sized pieces. Separation technologies, such as magnetic and eddy current, are used. In this way, the electronic scrap is separated into various commodity streams which are sent to different Noranda operations. Fractions rich in copper and precious metals, copper-plastic mixed fraction and circuit boards are sent to the copper smelting operations to recover copper, silver, gold, platinum, palladium, selenium, tellurium, cadmium and nickel. The steel output from the mechanical processing goes directly to the steel foundry, while the aluminium fraction goes to an aluminium smelter. As Noranda's products are dedicated to established smelters, the mechanical processing does not try to achieve the best clean material fractions possible.

In the USA, physical processing is generally applied to electronics waste at MRFs (material recovery facilities) to produce three fractions of ferrous metals, non-ferrous metals and plastics. The unit operations, Figure 2.11, usually involve physical sorting, comminution, screening, and magnetic, eddy current and density separations (Kang and Schoenung, 2005). The fractions are then forwarded to appropriate material processing plants.

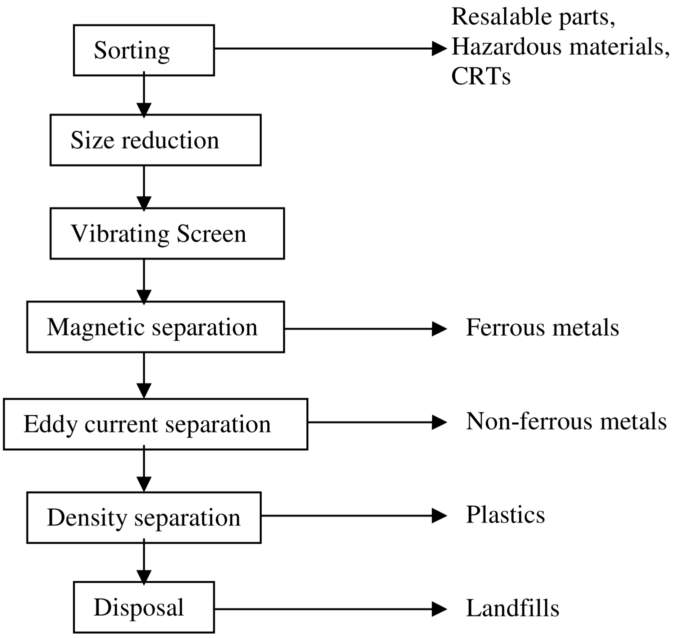

Figure 2.11: Simplified flowsheet at a materials recovery facility, MRF (Kang and Schoenung, 2005)

Researchers at Daimler Benz in Germany developed a process comprising initial size reduction to ~2 cm x 2 cm and magnetic separation. Then cryogenic grinding was done by passing $-196\ ^{o}C$ liquid nitrogen through a hammer mill. This imparts brittleness to the feed, effects process cooling, and provides inert atmosphere which prevents oxidation by-products such as dioxins and furans. Sieving and electrostatic separation is applied for material separation of the milled product (Goosey and Kellner, 2002).

In South Africa, two major recyclers – Desco Electronic Recyclers and Universal Recycling Company – are known in the e-waste recycling industry. Of these, only Desco Electronic Recyclers is reported to have dedicated PCB processing operation (eWaste Guide, 2006; Finlay, 2005). Another establishment, Reclaim, is considered to be the largest recycling organisation in South Africa. It also accepts e-waste, but passes it onto Universal Recycling (Finlay, 2005). Other minor players basically serve as collectors and pass on the general e-waste to any of the two major establishments. African Sky, who also accepts e-waste, carries out very minimal processing or value addition before exporting the stock virtually as-received to Citiraya waste recycling company in Singapore (Finlay, 2005). Citiraya, which now operates as Centillion Environment and Recycling UK Limited (www.centillion-er.com; www.researchandmarkets.com), is considered to be one of the world biggest processor of corporate e-waste and deals with multinationals such as Nokia and HP (Finlay, 2005; eWaste Guide, 2006).

Desco Electronic Recyclers is reported to process about 400 tons of PCBs along with about 2000 tons of other electronic waste annually (eWaste Guide, 2006). Desco strips the feed manually, disassembles and sorts it into separate specific components and material types. Materials for recycling are not thrown into the shredder as whole units. This prevents a mixture of plastics, ferrous and non-ferrous materials being shredded together (www.desco.co.za). Plastics are separated from the PCBs, producing a relatively clean plastic fraction for the final plastic recycler clients. The boards are then shredded, followed by pulverisation, and separation stages. The machinery used is designed and built by Desco, and the details are proprietary.

The operation at Universal Recycling is fully mechanised, without any hand sorting. The stock is conveyed via belts between different operations. These include shredding, heavy media separation, eddy current separation, sorting, milling, granulation and rotary magnetic separation (www.urc.co.za). The heavy media separates the comminution products, based on densities in stages, giving product fractions of plastics, glasses and metals. The water for the heavy media separation is fully recycled (Finlay, 2005). The operation, however, handles the feed as a mixed load with no specific provision for e-waste or PCBs. Electronics are simply considered along with non-ferrous materials. Components such as nickel-cadmium batteries, bearing hazardous constituents all go through the shredder, but somehow along the line, they are separated (Finlay, 2005). The final products from these operations are sold mostly to Rand refineries, South Africa, as non-ferrous fraction from waste recycling.

All these operations are basically preparatory to finishing recovery via smelting. Consequently, clean fractions are not paramount. Except for ferrous fractions which can be achieved at fairly high grade and recovery, optimum reports for copper, for instance, include 60 % copper grade and 90 % recovery in 100 – 300 μm fraction (Yokoyama and Iji, 1997). FUBA operation reports 92 % copper grade from unpopulated boards, which is a less complex feed. Product grades from many operations are rare in reports. Zhang and other workers conducted various investigations on PCB and WEEE physical processing (Zhang *et al.*, 1997; Zhang and Forssberg, 1997). Using air table separation, optimum result reported 72 % grade and 76 % recovery for copper in the 1 mm to 0.6 mm mill fraction (Zhang and Forssberg, 1997).

Compared to typical assay figures in conventional minerals processing, the copper assays in the product fractions appear satisfactory. Chalcopyrite ($CuFeS_2$), for instance, is the main ore mineral of copper, and the best copper assay from its processing is 34.7 %. Such chalcopyrite concentrate is amenable to straightforward matte smelting chemistry, oxidizing iron sulphide to the slag phase and sulphur to the gas phase, leaving metallic (blister) copper (Rosenqvist, 1988). In contrast, for PCB non-ferrous copper rich separation products, at much higher assays, the smelting and refining processes are much more extensive. This is because for a fraction assaying, say, 90 % copper, the 10% complementary matter will not be from a single mineral element (such as sulphur alone with copper in chalcocite) or a few definite co-occurring elements, but a lot of contaminants. This is to say that, while poor separation efficiencies are obtained at non-optimal size fractions, even the products with best grades still need improving.

From what commonly obtains at present: (i) returns to the independent physical processing plant are not maximized (some prices are cited for Taiwan); (ii) overall recycling ratio is low (as secondary use of unsorted fraction is limited); and (iii) secondary smelting for metallic value recovery requires extensive facilities. Such a smelting facility, Pb-Cu smelter, is cost intensive and not available in many parts of the world where PCB and general electronics waste recycling has to be done. In fact the more complex Pb-Cu-Zn smelters with facilities for recovery of metals such as zinc from volatiles are the most appropriate. Constructing such a capital-intensive metallurgical plant specifically for e-waste processing will require a more integrated collection and shipping infrastructure of the waste stream. Although the pyrometallurgical follow-up route may not be avoided outright, the downstream processing chemistry can be simplified considerably by cleaner fractions from the physical processing.

Improving eol PCBs beneficiation demands that the material complexity involved is recognised and an effective beneficiation operation is developed to match. While ores containing three target minerals are considered complex in classical minerals processing, with extensive beneficiation operation, common eol PCBs beneficiation flowsheet, are generally too brief for the task.

2.4 IMPROVING PCB PHYSICAL PROCESSING: FINES BENEFICIATION

It can be seen from the review of PCB physical processing presented that, for the −2 mm comminution products, electrostatic separation is the technology been employed. In conventional mineral processing, it is known that separation efficiency of corona or high tension electrostatics separator drops rapidly below 75 µm feed sizes (Wills, 1997; Kelly and Spottiswood, 1989).

Zhao *et al*. (2004) compared a type of column air separator to electrostatic separator for recovery of metal values from PCB hammer mill grinding products (Tables 2.5 and 2.6). More than 20 % of the product of the hammer mill grinding from 30 mm feed size reported to the −75 µm fraction, assaying almost 2.9 % copper. Copper recoveries of 27.83 % at a grade of 26.8 wt. % were obtained from the pneumatic separator. Separation from the electrostatics at that size was not reported, probably because it was too poor. The work concluded that below 75 µm, electrostatic separation efficiency is poor for PCB grinding fines.

In the NEC's operation (Yokoyama and Iji, 1997; Iji and Yokoyama, 1997), at −300 + 100 µm, copper-rich powder (82 % Cu, at less than 90 % recovery) was produced. The non-conducting fraction from the electrostatics separation contained 64 % glass fibre, 34 % epoxy resin, 2.1 % copper and solders. Some end-use applications, such as filler for epoxy resin polymer product, were investigated for the glass fibre-resin fraction. But at 2.1 % copper content, the fibre glass-resin fraction assays higher than many natural deposits being mined and processed economically. It therefore deserves further beneficiation.

Table 2.5: PCB Grinding Size Distribution (Zhao *et al.*, 2004)

Size Range (mm)	Weight (%)	
	Open Circuit Hammer Mill Grinding	*1mm Closed Circuit Hammer Mill Grinding*
+1	15.86	0
−1 + 0.5	35.26	40.87
−0.5 + 0.25	10.10	11.73
−0.25 + 0.125	12.86	15.23
−0.125 + 0.075	4.70	5.54
−0.075	21.22	26.73

Table 2.6: Copper recovery and grade versus size range and separation technology (Zhao *et al.*, 2004)

Size Range	Pneumatic Separation (Air Classifier)		Electrostatic (Corona)	
	Recovery	*Grade*	*Recovery*	*Grade*
−1.0 + 0.5 mm	70.11	49.08	97.65	53.75
−500 + 250µm	66.42	54.66	97.88	71.61
−250 + 125µm	90.76	49.54	43.78	90.62
−125 + 75µm	80.35	29.98	37.57	90.90
−75µm	27.83	26.81	--	--

Precious metals are usually coated in a couple of microns in the PCB sockets and slots, and on the edge connectors. Abrasion in the event of comminution is therefore likely to make them report to the −75 µm fraction. With electrostatics separation, these fine metallic particle will be poor recovered (Kelly and Spottiswood, 1989), representing a major loss to the economic drive of the whole operation. Traces of noble metals used as anti-etch materials during the printed copper circuit production (Li *et al.*, 2004) can also be present on the copper particles. Unrecovered copper therefore carries such to waste.

The inefficiency of electrostatics separation with PCB grinding fines could have been tolerated because (i) the relatively higher assays and better recoveries from the coarser fractions (Yokoyama and Iji, 1997; Zhao *et al.*, 2004) pay for the operation profitably well; (ii) the metallic products of PCB physical separation are generally being destined to pyrometallurgical operations (Shuey *et al.*, 2006; Lee *et al.*, 2004), and (iii) dry operations are preferred for handling the PCBs.

Only the last point can make the tolerance understandable. Wet processes are avoided in most recycling operations to avoid wash water circuit and treatment costs, among other reasons (Kellerwessel, 1993). In particular, because PCBs contains such a wide diversity of materials, leaching and oxidation behaviours cannot be absolutely predicted in a wet process. Also, at the coarse fractions of the comminution-separation operation (with particles of all sorts of shapes) particle flow will not be good. But at finer sizes, slurry flow is much better. The issue of hazardous leaching or material oxidation still remains. It could, however, be much reduced at the fine sizes, as many materials from many components, particularly components bearing hazardous substances, have being removed. Materials expected will be mostly chippings from metallic particles, copper from the traces, solder remains, ceramics used in small resistors and chips, resin materials like epoxy, remains of plastics used in slots and reinforcement material such as glass fibre.

At this stage of PCB physical processing, the operation need not be restricted to dry. Froth flotation is a specific wet processing technique that appears very promising for beneficiation of the fine fraction. Froth flotation, exploits distinct surface properties of individual particles; it is particularly effective in the −75 µm range; and it can be executed via different schemes toward enhancing selectivity. The prospect therefore deserves detailed investigations. An overview of how froth flotation can be applied to this material stream will be presented in the next chapter in order to set out a detailed methodology for the investigation.

2.5 CONCLUSION

Physical processing of PCB dates to about three decades now - not totally a new area of endeavor, yet not fully developed. Essentially, it remains a stage-wise comminution-separation operation. Given the peculiar material composition of the printed circuit boards, shear shredders can be taken as the industry standard comminution equipment used. Separation technologies employed in the industry include magnetic, eddy-current, electrostatic, dense-medium and air-classification. Product material fractions are ferrous, non-ferrous, plastics and ceramics, with different degrees of cross contamination depending on particle liberation and the size at which the material fraction was obtained. The non-ferrous fraction mostly serves as secondary feed at established smelters having requisite extensive facilities. Hydrometallurgical follow-up route to the physical processing has relative advantages over the pyrometallurgical routes, but it requires much cleaner material fractions to simplify process chemistry. The −75 μm fine fraction in the comminution products has been observed to contribute a drop to the overall recovery and separation efficiencies. Loss of precious metals to the fine fraction is also possible, representing a major economic loss to the operation. Froth flotation appears very promising for investigation into its applicability for beneficiation of the metallic values deported to this fine size fraction.

3.0 FROTH FLOTATION FOR THE BENEFICIATION OF PCB FINES

3.1 INTRODUCTION

As presented in Chapter 2, the material constituents of the comminution fines will be quite diverse. This will include copper from the traces; solder remains; precious metals – gold, palladium, platinum – relatively in trace proportions; chipped or torn particles of various alloys; synthetic or natural ceramics used in certain resistors, semiconductors, glazed components and chips; resin materials like epoxy; particles of plastics used in slots; and board reinforcement material such as glass fiber. It follows that flotation of native metals, plastics, and ceramics (oxides, conventional minerals) are all of relevance towards evolving logical flotation schemes for the sample. These and other relevant concepts are reviewed in this chapter. The concepts are used to advance probable schemes, and to make more specific objective statements for the investigation. As this application will traverse a broad spectrum of surfactants, a brief on surfactants are presented first.

3.2 SURFACE ACTIVE AGENTS

Surface active agents (surfactants) are organic compounds with a heteropolar molecular structure. The non-polar hydrocarbon chain group of the molecule prefers to attach to air, while the polar functional groups prefer aqueous phase. The surface activity derives from this property. They can therefore adsorb (accumulate) at air-water, air-mineral and/or water-mineral interfaces. The specific application of a surfactant is determined by the properties of the polar functional group, which can be ionic – cationic or anionic, or non-ionic. Ionic surfactants are electrolytes. They can adsorb at mineral-water interfaces, electrostatically and/or chemically. This makes them useful as collectors. Non ionic surfactants are non-electrolytes, and they adsorb majorly at air-water interface. Table 3.1 shows some common surfactants compounds. The adsorption at air-water interface lowers the surface tension of the solution. This makes thin films of the solution metastable and therefore supports frothing. It also creates wetting effects, lowering overall surface energy and tension.

Table 3.1: Some common surfactant and applications

Classification		Example	Major Application
Ionic	Salts of organic acid	Carboxylate salts	Soap
		Sodium alkly sulphonate	Wetting and Detergency
		Alkyl phosphate salt	Wetting and Detergency
	Amine Salts	Primary Amine	Collectors
	Sulphydryl	Dithiocarbonates	
		Trithiocarbonates	
		Dithiophosphates	
Non-ionic	Alcohols	Methyl IsoButyl Carbinol	Neutral Frothers
		Pine Oil	
	Hydroxylated polyglycol ethers	Polypropylene glycol methyl ether	
		Tripolypropylene glycol methyl ether	
		Nonylphenol polyglycol ether.	
	Alkoxy substituted Parafins (R`OH)$_x$H	Multi ethoxylated butane (1,1,3 Tri ethoxy butane)	

The reduction in the surface tension of the aqueous solution is towards that of the surfactant in proportion to the concentration of the surfactant molecules adsorbed at the interface. This can be described by the Gibb's adsorption equation in the form:

$$d\gamma = -S_S dT - \sum_i \Gamma_i d\mu_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{3.1}$$

where $d\gamma$, S_S, T, Γ_i and μ_i are the changes in surface tension, surface entropy, temperature of the system, adsorption density of specie *i* and the chemical potential of specie *i*, respectively, at constant pressure (Fuerstenau, 1982). Defining i = 1 for the solvent specie, then $\Gamma_1 = 0$ as the solvent does not adsorb in itself. Since, $d\mu_i = RTd \ln a_i$, at constant temperature, as in flotation process, it follows that:

$$d\gamma = -RT\sum_{i=2}\Gamma_i^1 d\ln a_i \cong -RT\sum_{i=2}\Gamma_i^1 d\ln C_i \quad . \quad . \quad . \quad . \tag{3.2}$$

where Γ_i^1 refers to the surface excess (adsorption density) of specie i relative to the solvent at the interface, and a_i is the activity of i, which approximates the concentration of i, C_i, in very dilute solutions.

However, Eq. 3.2 is not a continuous function. The surface tension decreases towards a limiting value which is that of the surfactant, and C_i is defined within the solubility range of the surfactant, beyond which micelle or droplet formation (phase separation) commences. With further increase in concentration such droplet will act as antifoamer in frothing application (Pugh, 2007). The selective wetting achievable by surface tension control is the basis for gamma flotation separation of plastics (see Section 3.4).

3.3 FLOTATION OF METALS AND ALLOYS FOR PCB FINES APPLICATION

Many studies have shown that metallic particles can be rendered hydrophobic and floated. With higher surface energies (than plastics), metallic particles can react with collector molecules (chemisorption) forming hydrophobic surfaces. Woods (1996) included the adsorption of xanthates on gold, platinum, silver and copper in a detailed review of chemisorption of thiols on metals and metal sulphides. For platinum and gold, voltamogramms of their electrodes in ethyl xanthate indicate anodic peaks at the region of the reversible potentials of the ethyl xanthate/dixanthogen couple:

$$2C_2H_5OCS_2^- \rightleftharpoons (C_2H_5OCS_2)_2 + 2é \quad . \quad . \quad . \quad . \quad . \quad . \quad 3.4$$

Peaks corresponding to the cathodic reduction of the anodic oxidation product can also be observed on the reverse potential scan. It was inferred that anodic oxidation of ethyl xanthate to dixanthogen and adsorption of the latter occurs on the metals. Tafel slope for the anodic oxidation, however, indicate that the oxidation to the dimer can proceed via an initial chemisorption step:

$$2C_2H_5OCS_2^- \rightleftharpoons 2(C_2H_5OCS_2)ads + 2é = (C_2H_5OCS_2)_2 + 2é \quad . \quad . \quad 3.5$$

Lins and Adamian (1993) used amyl xanthate as a collector to study the effects of some physical variables on gold flotation. Good recoveries were obtained for gold from a synthetic mixture of silica and gold particles over 0.16 mm – 0.71 mm size ranges. About 90 % recovery and 5 kg/ton gold grade in the float was achieved from a 167 g/ton feed with 0.16 mm d_A sample at 18% pulp density (Figure 3.1). The work of Lins and Adamian is notable considering the good flotation of 0.71 mm gold particles that was claimed.

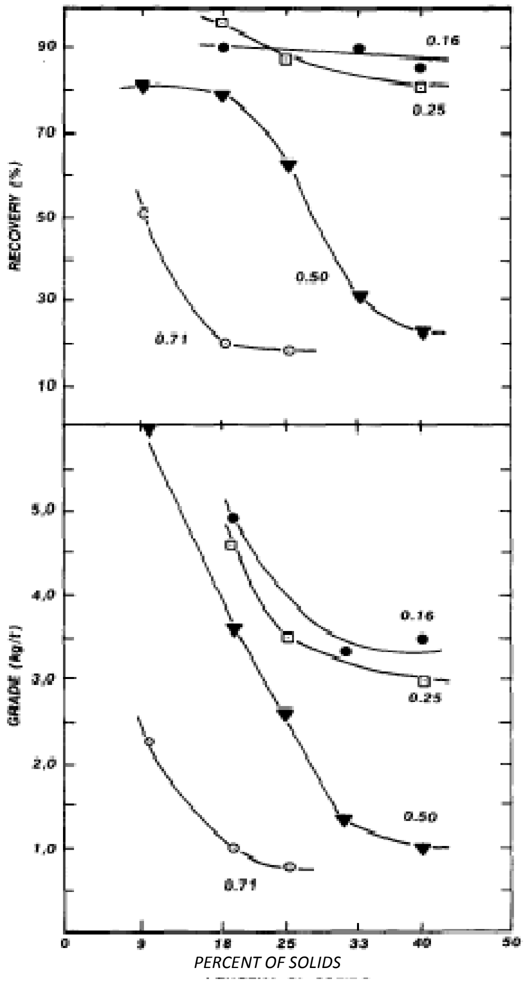

Figure 3.1: Recovery and grade of gold in concentrate as a function of solids present and gold size (mm): 3.6 lpm of air, 1200rpm, 167g Au/t feed (Lins and Adamian, 1993).

Dicresyl monothiophosphate (DCMTP) was used to achieve recovery of native gold against sulphides at a pH above 7 in some specific ores (Nagaraj *et al.*, 1991). Basilio *et al.* (1992)

suggested that DCMTP does not have effect on the floatability of pure gold as such, and infra red spectroscopic measurement confirming this. The improved gold recovery was linked to silver-DCMTP interaction in further studies (Nagaraj *et al*., 1992). It was shown by X-ray photoelectron spectroscopy (XPS) that more DCMTP was adsorbed, and higher recovery observed, when the percentage of silver alloyed with the native gold was higher. Hence, only silver-bearing native gold will respond to DCMTP. The interesting context here is that adsorption on the alloy surface is synergistic. It can therefore be projected that alloys in the PCB mixture will respond to a collector as much as one of its constituent elements interacts with that collector.

Forrest *et al*. (2001) using a range of collectors (Table 3.2) at varying pH on a free-gold bearing copper-pyrite ore, obtained free gold recovery from the sulphides at d_{90} of 106 µm. While chalcopyrite recovery was almost independent of pH in the range 8 – 13, and pyrite recovery drop with increasing pH over the range (see Figure 3.2), gold grade shot up above pH 11.5 (Figure 3.3) for aeroflot 7249 and aeroflot 208. Selectivity for free gold by these collectors was concluded for the gold grade increase at pH above 11.5, since pyrite was depressed and chalcopyrite recovery remained almost the same over the pH range.

Table 3.2: Collector reagents in Forrest *et al*. (2001)

Reagents	Chemical Family
S-5688	Dicresyl monothiophosphate
Aero 7249	Di-isobutyldithiophosphate/ di-isobutylmonothiophospahte blend
Aerofloat 208	Dithiophosphate
Aero 6697	Di-isobutylmonothiophosphate
PAX	Potassium amly xanthate

Although reports on flotation of metals have concentrated more on those that occur in native forms which are the real situations in flotation operations, many metals and alloys in the PCB fines that do not naturally occur in native forms can also be expected to respond to collectors. Auger electron spectroscopy (AES) and XPS studies of the chemisorbed xanthate monolayer on chalcocite and galena showed the same chemical environment for the metal atoms in the substrate and the monolayer xanthate (Buckley and Woods, 1990, 1991; Shchukarev *et al*., 1994). This indicates direct interaction with the metal atoms in a substrate, and implies that under adequate conditions, the metals will interact with collectors and float. However, the potentials at which a collector compound will form on a pure metal and on its mineral compound are expectedly different (Woods, 1996).

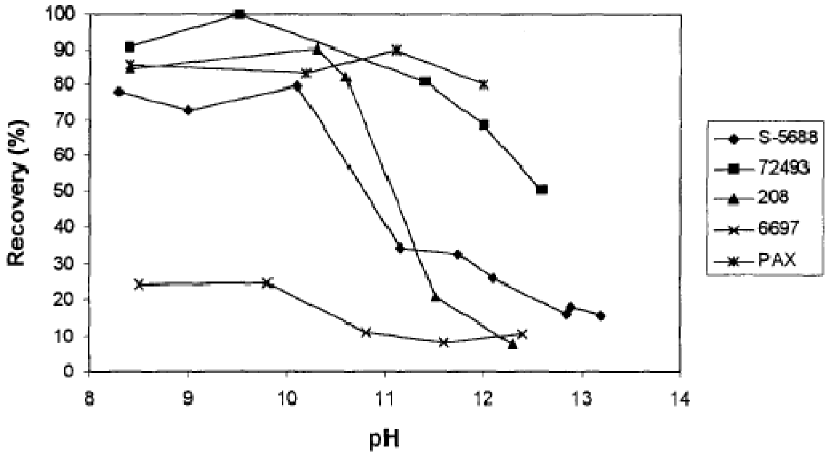

Figure 3.2: Effect of pH on pyrite recovery (Forrest *et al.*, 2001)

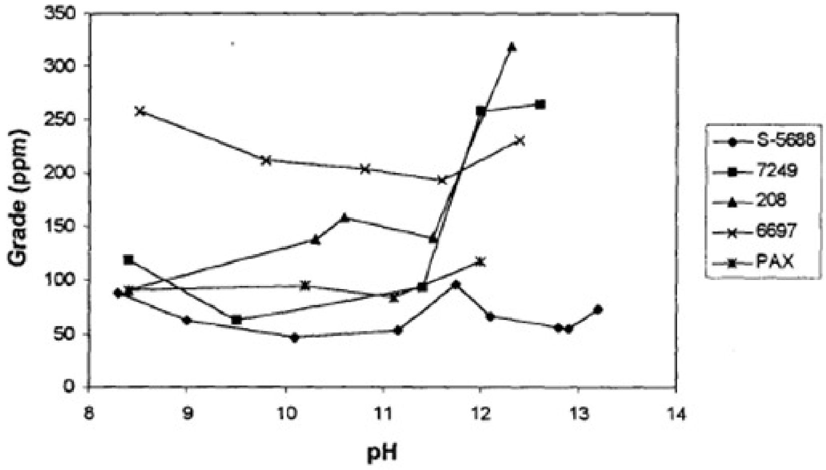

Figure 3.3: Effect of pH on gold concentrate grade (Forrest *et al.*, 2001)

As in conventional mineral processing, activation with $CuSO_4$ should also apply for particles (such as of zinc) whose collector-metal compounds have fairly high K_{eq} (dissociation constant) which makes their surface product fairly soluble and unstable. Possibility of unselective activation can be very important in a pulp with such diverse constituent. Mercaptans, such as sodium mercaptobenzothiazole (SMBT), are a selective collector of native copper (Wills, 1997) and it can be expected that this can be applied in obtaining a selective metal fraction.

In the event of certain alloy particles having tarnished or oxidised surface layer, sulphidation activation should be applicable as with conventional minerals to make such particle interact better with sulphydryl collectors. By addition of sodium sulphide (Na_2S), hydrolysis to sodium hydroxide and hydrogen sulphide occur (Wills, 1997). The hydrogen sulphide dissociates giving hydrosulphide ions (HS^-). These adsorb and dissociate at the surface of the particle, causing sulphur ions to pass into the crystal lattices:

$$Na_2S + 2H_2O \rightleftharpoons 2NaOH + H_2S \quad . \quad . \quad . \quad . \quad . \qquad 3.6a$$

$$H_2S \rightleftharpoons H^+ + HS^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad 3.6b$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad 3.6c$$

This gives a pseudo insoluble sulphide surface, allowing interaction with sulphydryl collectors. Careful dosage of this sulphidisers is very important because excess HS^- ion at a surface gives the particle a high negative surface charge. This prevents adsorption of anionic collectors, causing depression, while too little dosage will not maximize the conditioning effect desired (Wills, 1997; Lee *et al.*, 1998). The dosage required for a system will depend on the pulp pH. At high pH values, equation 3.6b and 3.6c proceed farther to the right, generating the depressant ions. Because of the possibility of altering (increasing) pulp alkanility due to NaOH dissociation from Equation 3.6a, sodium hydrogen sulphide (NaHS) is preferred to sodium sulphide for sulphidation.

In the event of comminution, it is possible that the particle surfaces will be tarnished or oxidised. In this regard, SMBT has been found effective collector for oxidized copper and tarnished ores (Wills, 1997). Also, from general flotation of oxide and silicate minerals, collectors that mainly physisorbs (interacts electrostatically), such as amines and sulphonates can be used.

Flotation of glass fiber can also be conceived, considering the flotation of quartz from heamatite. A reverse flotation of heamatite employs amine at pH 6-7. The amine adsorb on the negatively charged quartz particle to float, leaving the heamatite particles that are relatively neutral at that pH range (Fuerstanau and Healy, 1972).

Another approach floats quartz activated with calcium ion at pH 11-12 with a soap collector, while using starch to depress heamatite. Soap application which can also have the effect of gamma depression (see Section 3.5.2.4) is notable here, but isolating the activity or interactions may not be easy in this very diverse material mixture: depression is already involved, and influences on other particles exist. Interwoven and complicated reagent effects are not unexpected in a sample of this type.

As addressed above, different collectors used with native metal and alloys, and tarnished ores, in conventional minerals processing and in various investigations, can be expected to interact with the metals and alloys in the PCB mixture – xanthates, amines, SMBT are all candidate collectors. However, appropriate pH is critical to reagent-surface interaction.

3.3.1 Selectivity by pH Control

Pure water has a dissociation constant of 10^{-14} in which $-\log [OH^-] = -\log [H^+] = 7$, the pH of neutral water. The concentrations of OH^- and H^+ vary in proportion to maintain the equilibrium constant at other pH values. In aqueous medium, OH^- and H^+ are potential determining ions for particles of oxide minerals and those with bases in their dissociation products, such as carbonates (Kelly and Spottiswood, 1989). The pH of the medium therefore determines the surface charges or neutrality (point of zero charge, or PZC) of the suspended particles. Response to ionic collectors is a function of surface charge condition, and hence a function of pH. This is a basis of selectivity by pH control.

Hydration of the surface and the stable surface species similarly depends on the pH. With iron, for example, the Eh-pH diagram for Fe-O-H system indicates $Fe(OH)_3$ as the stable specie for most of the positive potentials at alkaline pH (see Figure 3.4). This frustrates formation of the less stable metal-collector compound with xanthate collectors at high pH values. Pyrite, for example, will therefore float under xanthate only at pH around 4 or below (Wills, 1997). With lead, the lead-xanthate compound prevails till about pH 8, above which the stable lead-H_2O specie predominates and lead or the lead compound, say galena, get depressed.

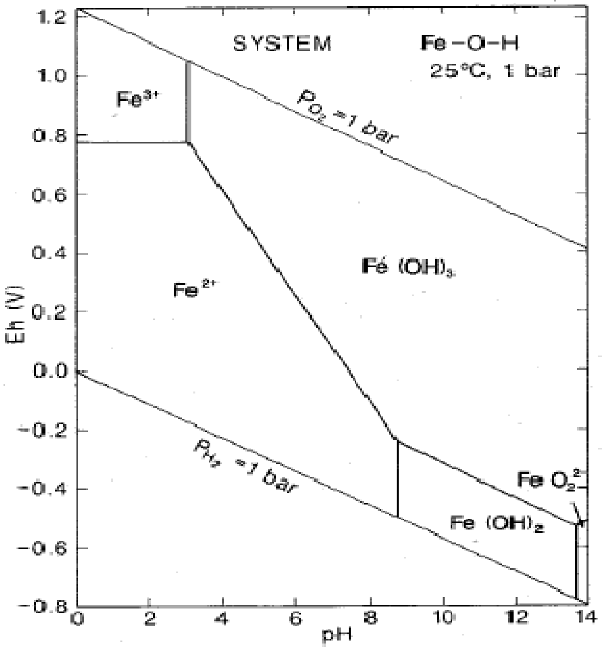

Figure 3.4: Fe-O-H potential-pH diagram (Douglas, 1988)

Parallel bases for selectivity by pH variation can be expected for the corresponding metallic alloys in the PCB mixture. Surface specie as a function of pH of metallic elements should be as in the various Eh-pH diagrams. Differences in the systems are, however, notable. The actual Eh-pH-species diagram that will apply in this multicomponent system will not be the ones for the single metal-water system. Diagrams or data for a ten-element or more system as the PCB mixture analysis will require are scarce in literature. This will be a major challenge to the easy prediction of surface species. However, the window of stability of certain species in the general aqueous system at natural potentials and room temperature is fairly wide to allow some projection. The presence of heavy metals, which can activate particles that should not float at certain pH, remains another source of possible complication in making projections based on pH.

Pulp pH can be varied by the adding acids, bases or salts. Acids are neutral molecules, such as HCl, H_2SO_4, H_2S, CH_3COOH, which dissociate in aqueous solutions giving H^+ cations. Bases are crystalline solids such as NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$, whose anion is OH^-, or neutral molecules such as NH_3, and CH_3NH_2 that forms proton acceptors and causes increase in the OH^- proportion, when dissolved in water. Salts are generally electrolytes whose ions are neither H^+ nor OH^-, but there are acid or basic salts whose aqueous solution is not neutral because they cause proton concentration increase or decrease, respectively, on dissolution. NH_4Cl, for example, is an acid salt, with NH_4^+ cation, which is a proton donor in water:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad 3.7$$

Also Na_2CO_3 in aqueous solution gives CO_3^{2-} which is a weak base – a reluctant proton acceptor in water:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad . \quad . \quad . \quad . \quad . \quad . \qquad 3.8$$

In flotation practice, sulphuric acid [H_2SO_4] and lime [$Ca(OH)_2$] are cheap and effective reagents used to increase acidity and alkalinity, respectively, in pulps. When the depressant effect of lime at high pH can be consequential, Na_2CO_3 is also used instead. Collector stability, as a function of pH is also of importance in pH control and pH may not be varied unilaterally. In regulating pH of PCB fines pulp with acids or bases, it is necessary to first establish the natural pulp pH and to observe its stability with time. Varying pH with time, or buffering when trying to regulate the fines pulp pH from the natural pH, is not impossible in such a complex mixture.

3.4 SELECTIVE WETTING OF PLASTICS FOR PCB FINES FLOTATION APPLICATION: GAMMA FLOTATION

Plastics are naturally hydrophobic. Selective wetting to effect separation of plastics by flotation has been demonstrated under four methods (Shent *et al.*, 1999):

(i) physical conditioning, in which hydrophilic functionalities such as =O, –OH and –COOH, are grafted into polymer chains at the surface usually by plasma treatment;

(ii) selective adsorption of wetting agents or chemical conditioning;

(iii) selective hydrophobic modification, also a chemical conditioning, in which a surface conditioning agent is selectively solubilised in the plastics so that it penetrate to a shallow depth on the surface of some plastics; and

(iv) gamma flotation.

Gamma flotation is the most applied of the four methods and still best understood. It is based on the critical surface tension of wetting of the solids (Buchan and Yarar, 1995), similar to the original Zisman's critical surface tension concept (Zisman, 1964) described by Alter (2005). The critical surface tension of wetting for a solid (γ_C) is the minimum surface tension of a liquid that will not wet the solid. That is, pure liquids or liquid solutions with surface tensions below this value will wet the solid. Hence, by reducing the surface tension of a liquid (γ_{LV}), such as water, to a value between the critical surface tension values of two plastic particles in a mix, say, γ_{C1} and γ_{C2}, so that:

$$\gamma_{C1} < \gamma_{LV} < \gamma_{C2}, \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad 3.9$$

the particles of the plastic with $\gamma_C = \gamma_{C2}$ become wetted, while the particles of the other plastic, with $\gamma_C = \gamma_{C1}$, remain hydrophobic and float with air bubbles. Buchan and Yarar (1995), using 190 ppm methyl isobutyl carbinol (MIBC) as frother, 20 % methanol and 80 % H_2O, achieved an aqueous solution with surface tension of 40.8 dynes/cm, to effect the flotation separation of PVC (γ_C = 39 dynes/cm) from PET (γ_C = 43 dyne/cm) which was wetted and sank. At the pulp density of 1.0 % and pH 11, PET recovery to float was 0 %, while the recovery of PVC reached 92 %.

Shen *et al*. (2002) demonstrated the adsorption mechanism. Methyl cellulose was used for selective chemical conditioning of the surface of seven plastics. Separation into three groups of plastics was achieved. Van der Walls attraction-based physisorption between the numerous polar groups in methyl cellulose and some of the plastics was used to explain the selective adsorption and wetting, as the polar groups in some of the plastics were oriented towards the aqueous phase. Surface tension effect was ruled out as methyl cellulose cannot reduce the surface tension of water to the critical surface tension of wetting, γ_C, of the plastics wetted (see Figure 3.5). The conclusions of the explanation may be debated given that a surface conditioning depressant having hydrophobic non-polar group can as well impart flotation (Alter, 2005).

The work by Fraunholcz *et al.* (1997a, 1997b) is an extensive fundamental research on plastics flotation involving five classes of reagents, as shown in Table 3.3. The work concluded that the effect of non-ionic surfactant on plastic wettability appears to be governed mainly by gamma flotation. It stated further that the inorganic reagents did not affect plastic flotation, while the low molecular weight complex compounds also do not adsorb sufficiently to effect depression. Cations (including Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+} and H^+) were said to have significant effect on the adsorption of the non-ionic weak acid and the anionic macromolecular depressants. Due to the low reactivity of plastics, the influence of pH over the range of 5-12 on plastic flotation was reported to be insignificant (Shibata *et al*., 1996).

For the plastics in PCB grinding mixture, non-ionic surfactants based gamma flotation appears more straightforward and clearer to apply. The surface tension of the pulp is simply reduced below the critical surface tension of wetting for some of the plastic constituents (see Table 2.3). The non-ionic surfactants can also contribute to frothing. As it is necessary to be able to delineate the effect of reagents addition in a sample, the other physical and chemical conditioning methods are not straightforward for a complex mix of this sort. As mentioned, the effects of ionic and weak acid macromolecular depressants depend on many cationic species in the pulp. These effects will be difficult to isolate in a complex pulp such as the pulp of PCB comminution fines, and can even impair flotation of the metallic values afterward.

Equations 3.2 and 3.3 indicate that selective wetting of the plastic particles requires careful choice and dosage of the non-ionic surfactants. Some surfactant can depress surface tension so much that the bulk becomes difficult to float. Also, the surfactant type should be such that desired wetting is achieved with moderate dosage. In the work of Buchan and Yara (1995), 20 % methanol in water was used to reduce the surface tension to 40.8 dyne/cm. This will represent a significant reagent load and consumption. Moreover, the pulp density of 1.0 % used is too dilute and reagent dosage may still shoot up at real industrial pulp densities. With methyl isobutyl carbinol, MIBC, about 200 ppm reduces surface tension to 50 dynes/cm (Buchan and Yara, 1995). Figure 3.5 shows Tergitol 15-S-7 to be more effective in reducing the surface tension below 35 dynes/cm at 20 ppm. Such can, therefore, be a better candidate reagent.

Table 3.3: Reagent investigated by Fraunholcz *et al.* (1997)

Class	Names	**Abbreviation**
1. Non-ionic surfactants (frothers)	Diacetone alcohol	DAL
	Methyl isobutyl carbinol	MIBC
	Tripolypropylene glycol methyl ether	PPG3
	Iso-octanol	IOL
	Pine oil (a-Terpineol)	POIL
	Polyethylene glycol dodecyl	$C_{11}EO_8$
	Nonylphenol polyglycol ether.10EO	$C_{9+6}EO_{10}$
2. Electrolytes	Na_2CO_3	
	NaCl	
	$NaNO_3$	
	$MgCl_2$	
	$CaCl_2$	
	$FeCl_2$	
	$FeCl_3$	
	HCl	
3. Inorganic depressants	Sodium disulphite	NaDS
	Sodium hexa meta phosphate	NaPh
	Sodium silicate	NaSi
4. Low-molecular-weight complex compounds	Malic acid	MAC
	Tartaric acid	TAC
	Citric acid	CAC
	1,2,3-trihydroxy benzene	THB
	2,4,6-trihydroxy benzoic acid	THBA
5. Macromolecular wetting agents	Arabicum gum, composition: m:n:p:q_1:1:3:3	ARG
	Na-carboxymethyl cellulose	NaCMC
	Na-lignin sulfonate	NaLS
	Potato starch	PST
	Quebracho	QUE
	Tannic acid	TNA
	Polyvinyl alcohol	PVA
	Na-polyacrylic acid	NaPAA
	Polyacrylamide	PAM
	Polyethylene oxide	PEO

Different surfactants have been marketed under the trade name Tergitol by Union Carbide Corporation and Dow^R. Dow^R produces nonylphenol ethoxylates (NPEs) and secondary alcohol ethoxylates (SAEs) as Tergitol NP and Tergitol 15-S series, respectively, and ethylene oxide/propylene oxide (EO/PO) copolymers as Tergitol L, XD, XJ and XH series (Dow^R Surfactants). Union Carbide Corporation has other codes and series for similar products, such as TERGITOL® X-series for the EO/PO (TERGITOL® XDLW). In case of availability and cost constraints, these products are generically nonionic surfactants. Other products of these generic constituents, such as Betamin 127A and Betamin 65 of Betachem (Pty) Ltd., South Africa, are good candidate materials for investigation. From Betachem material safety and data sheet (Betachem MSDS, 2007), Betamin 127A is ethoxy nonyl phenol, while Betamin 65 is triethoxy tetradecane (a multiethoxylated alcohol, i.e. an alkoxy substituted paraffin). Common soaps (carboxylate salts) and detergents (alkyl phosphates, etc) will also achieve wetting, with cost advantages, but this are ionic surfactants, and physisorption effect can compound the response.

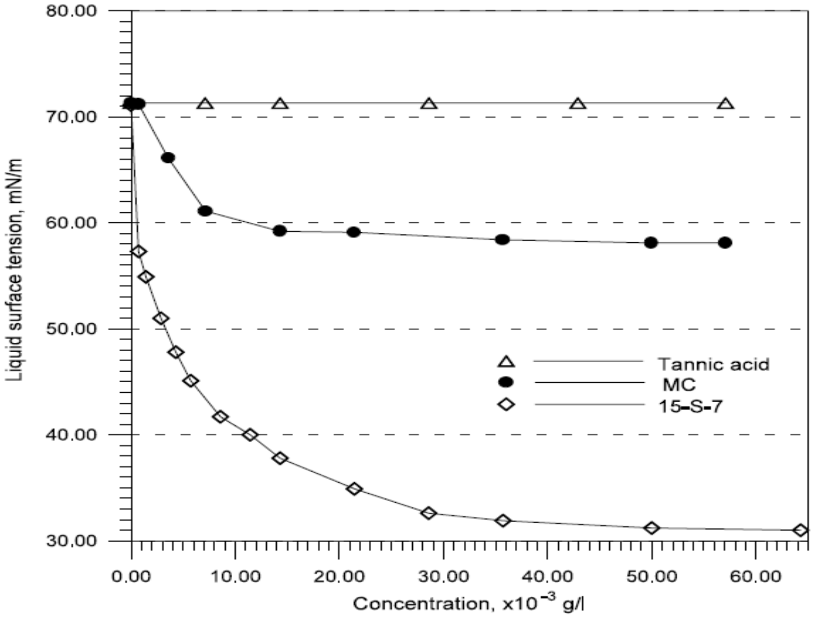

Figure 3.5: Surface tension versus concentration of three reagent solutions: Tannic acid, MC – Methyl Cellulose, Tergitol-15-S-7; 29.4 mg/l MIBC; pH 9.2; 25°C (Shen *et al.*, 2002)

3.5 PROBABLE FLOTATION SCHEMES

From the foregoing previews, probable flotation schemes in this application can be divided into two: natural hydrophobic response and chemical conditioning schemes. These are described as follows.

3.5.1 Natural Hydrophobic Response (NHR) Schemes

The particles in the PCB fines sample being so diverse, it can be expected that some should exhibit natural hydrophobicity while some will be naturally hydrophilic. This is the hypothesis upon which a collectorless flotation can be proposed as a starting scheme for the flotation of this sample. Relative to water's surface tension, plastics have lower energy surfaces and it can be projected that the plastics along with other relatively low free surface energy (LFSE) particles will be hydrophobic and should report to the float, while metals with other high free surface energy (HFSE) particles will be wetted (Gupta and Yan, 2006), and report to the sink. The scheme will therefore represent a reverse flotation in respect of the metallic values. It will essentially separate the HFSE from the LFSE particles. Table 3.4 shows representative surface tension values of some materials.

Table 3.4: Approximate surface tension of some materials at room temperature (Adamson, 1990)

Material	γ (N/m)*
Paraffin	0.025
Graphite	0.110
Halite (NaCl)	0.230
Flourite	0.450
Magnesia (MgO)	1.000
Gold	1.800
Alumina	1.900
Diamond	5.600
Water	0.072

*1000 N/m = dynes/cm.

3.5.2 Chemical Conditioning Schemes

3.5.2.1 Bulk metallic flotation (BMF)

Based on the recognized interaction of xanthates with metal surface, the projection here is to condition the pulp with bulk collector, such as butyl or amyl xanthate, to achieve a float of all the metallic particles into a float fraction. Depending on the extent of recovery observed from the natural hydrophobic response, this scheme can be applied directly on the bulk sample or after the NHR scheme.

3.5.2.2 Sulphidation activation

There is the possibility that metallic particles surfaces can be tarnished or oxidised in the event of comminution. The extent of metallic response obtained from the bulk metallic flotation can be indicative of this. In this case, sulfidation is a conceivable approach to activate such particles to xanthates. Sulfidation is discussed in Section 3.3 and NaHS can be considered as the reagent of choice.

3.5.2.3 Selective metallic flotation (SMF)

Depending on clarity of the response to reagent, some selective metallic flotation can be projected based on reagents known to be selective of certain metallic values. Mercaptobenzothiazole (MBT) is recognized as a selective collector in flotation of tarnished or oxidized lead and copper minerals (Fuerstenau and Raghavan, 1986; Numata *et al.*, 1998). The copper and lead particles in the PCB comminution fines can also be conceived as tarnished (a basis for sulfidation as explained above). The proportions of copper and lead in the PCB comminution fines sample are relatively high. These are good rationales upon which to try selective flotation with MBT. However, the selectivity will depend on the extent of the natural hydrophobic response. This will determine the order of implementing the selective schemes. The selective conditioning may have to be carried out on the sink of the NHR or on the float of the bulk metallic flotation. Careful choice and use of depressant may also be needed to enhance the selectivity. NHR particles, or residuals thereof, may need to be depressed to prevent contamination of intended metallic fraction. Choice of depressant in this type of system will also demand some careful experimentation.

3.5.2.4 Macromolecular and gamma depression

Achieving selectivity often demands selective depression. Generally, depressants selection takes note of the particles in the system versus collector suite. In classical mineral processing, chemical depressants such as cyanide and dichromate solubilise collector-particle surface compound and frustrate air attachment (Wills, 1997). This will not regulate particles floating under their natural hydrophobicity. Besides, the pulp here is complex enough and reagent addition must be carefully regulated so that more active reagents are not added to the system if it can be avoided.

Organic macromolecular depressants, such as starch, tannin and quebracho are non-ionic and can be regarded as less chemically reactive as they tend to smear and cover particles physically, as in slime coating, to insulate them from reagent activation (Wills, 1997). Along this line, the impression will be that these reagents will be bulk depressants. However, selective chemisorption has been observed, such as in starch depression of heamatite from quartz activated to soap collector by calcium ions at pH 11 – 12 (Fuerstenau and Fuerstenau, 1982). Without the starch, heamatite would also float under this condition.

The work of Shent *et al.* (1999) mentioned in Section 3.4, showed the selective adsorption of methyl cellulose (anionic) on some plastics. The explanation was based on physisorption by Vander der wall attraction between the numerous polar groups in methyl cellulose and some of the plastics. Broad acid-base interaction is becoming more convincing in explaining polysaccharides adsorption (Laskowski *et al.*, 2007). In depression of floatable carbonate and silicate gangues in sulphide flotation, anionic organics, such as carboxymethyl cellulose (CMC) are mostly used. Non-ionic ones are also used but high dosage levels are required, thereby depressing the sulphide (Bulatovic, 1999). For possibility of effectiveness at moderate dosage, without causing bulk depression, CMC can be considered as a probable macromolecular depressant in this investigation.

From the idea of gamma flotation in plastics (Section 3.4), reduction in surface tension can be used to achieve depression in the PCB comminution fines pulp. This surface tension (γ) based depression concept can be succinctly described as gamma depression. By lowering the surface tension of the pulp with appropriate surfactants, wetting becomes more favorable; the higher the dosage, the lower the surface tension (Equation 3.2), and the higher the overall depression. This will easily regulate natural hydrophobic flotation. For this purpose, non ionic surfactants (Table 3.2) can be used. This will give the advantage of no further addition of ions into the pulp. Depression alternatives for the PCB comminution fine pulp may therefore be within these two options – macromolecular and gamma depression.

Before this proposition is closed, gamma depression appears to oppose particle-bubble attachment in the same pulp. Gamma depression requires reduction of surface tension of the aqueous medium to effect wetting of some of the particles, whereas bubble attachment is also desired to effect flotation of some particles. The condition for wetting is:

$$\gamma_{LG} + \gamma_{SL} < \gamma_{SG} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad 3.10$$

The opposite is the condition for bubble attachment:

$$\gamma_{LG} + \gamma_{SL} > \gamma_{SG} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad 3.11$$

where, γ_{LG}, γ_{SL} and γ_{SG} are the liquid-gas, solid-liquid and solid-gas interfacial tensions.

It appears that lowering of the medium's surface tension γ_{LG} to achieve wetting is to forfeit bubble attachment, as it becomes difficult for the sum of γ_{LG} and γ_{SL} to exceed γ_{SG} again. Some clarification is required to sustain the prospect of the projected process.

Plastics generally have low γ_{SG}, lower than that of water. This easily satisfies Equation 3.11, so that they hardly wet. However, the magnitudes of γ_{SG} and γ_{SL} for plastics are such that Equation 3.11 can be easily reversed by halving the γ_{LG} for water with surfactants. This will satisfy the conditions of Equation 3.10.

For metallic particles and minerals, with much stronger interatomic bonds than plastics, the γ_{SG} is orders of magnitude greater than γ_{LG} of water. Compare gold to water in Table 3.4 which shows figures of surface tensions of some materials. Equation 3.10 is therefore easily satisfied and they normally wet. The value of γ_{LG} for water is relatively insignificant in this case, regulating it by the absence or presence of surfactant will not reverse Equation 3.10 to make such particles hydrophobic. This is why hydrophobicity is imparted on high energy surfaces by directly modifying such surfaces rather than the surface tension of the medium. This is what the collectors do. By chemically reacting with the high energy surface, or electrostatically attaching to it, a pseudo hydrocarbon surface is formed with γ_{SG} below that of the medium. This prevents wetting.

The application to gamma depression is that bubble attachment will still occur as long as the surfactant dosage does not lower γ_{LG} of the medium so much that it is impossible for the hydrophobic species adsorbed on the particles to meet the condition of equation 3.11. A useful but scarce data to regulate the dosage will be surface tension values (γ_{SG}) of the surface-collector species to allow a projection of the minimum γ_{LG} of the medium for a specific collector. However, the non-polar hydrocarbon chains are hydrophobic. Hence, moderate reduction of γ_{LG} of the pulp will still accommodate flotation of particles on which such surfactants are adsorbed, or particles that are of sufficiently low surface tension values (γ_{SG}). Surfactants (collectors, frothers) have always caused some reduction in medium surface tension, anyway. Yet, particle bubble attachment still occurs in flotation pulps.

3.5.2.5 Cationic conditioning

At a given pH, particles in a pulp develop positive or negative charges or remain neutral (at their point of zero charge). Cationic collectors can therefore be expected to achieve a bulk collection based on surface charges, adsorbing on the negatively charged particles to float. This scheme can be conceived in further beneficiation of the NHR sink. Generally physisorption-based conditioning is considered not to be as selective as those based on chemisorption.

However, given the diversity of particles in this sample, any logical scheme is worth a trial. An obvious variable here is the system pH, which can help improve selectivity. Amines are the popular collector of choice, but with pH considered as a variable, the choice can be restricted to quaternary amines. The fact is that the ionization of primary, secondary and tertiary amines varies with pH so that the same dosage of this class of amines will show varying activity as pH varies, thereby complicating the basis for comparing the response based on pH variation. Quaternary amines, on the other hand, ionize completely at all pH values. Since the hydrophobicity imparted by these heteropolar organic compounds increases with increasing hydrocarbon chain length, the choice can be narrowed down to tetrabutlyammonium chloride, with the long chain butyl groups.

3.6 APPLICABLE RANGE OF KINETIC PARAMETERS AND SAMPLE CHARACTERISATION

The variety of the schemes presented underscores the unconventional flotation system this sample will present. Flotation variables are many – kinetics, reagent types and dosages. In conventional mineral flotation investigations, there are known favorable operating regimes. This helps to narrow down the variables. However, this usual range may not be invoked for this application. Success of any of the schemes therefore depends on appropriate kinetics being established first.

In flotation kinetics, the determinants of rate of particle removal by bubbles in a flotation cell include gas flow rate, bubble diameter, cell volume, turbulence dissipation energy, fluid and particle densities, kinematic viscosity, efficiency of collection (which consists of efficiency of collision, attachment, and stability subprocesses), and of course the quantity of the particles to be removed that are present at a time (Pyke *et al*., 2003).

Fortunately, these variables are not all mutually exclusive, so that not all these need to be investigated. For a broad characterisation or description of the kinetic regime that will be appropriate for this system and the projected schemes, it will suffice to use three basic independent variables of air flow rate, impeller speed and pulp density. Other variables such as bubble size, pulp viscosity, and turbulent dissipation energy are functions of these basic variables. Other specific (material) characterisation that will be necessary here is in respect of liberation and chemical composition analysis of the sample.

Particle liberation in PCB CF reported in literature can be summarized as very good; 100 % below 600 μm, 500 μm, and 250 μm, as reported by various workers (Zhang and Forssberg, 1997; Wen *et al.*, 2005; Zhao *et al.*, 2004). The easy conclusion then is that -75 μm fraction will consist of sole material particles. This arouses suspicion about the figures quoted in literature, moreso that various authors differ. A basic liberation investigation of the fines will easily confirm if liberation is total or not in the fines, and provides a working evidence in this application. On the other hand, chemical composition characterisation is necessary to justify a method of choice for assay analysis in this work.

Background fact here is that analytical procedure for this sample are lacking in standard references (ASTM; ASTM, 2007; ISO). Studies and reviews have recommended and applied various analytical techniques, such as XRF, XRD, FTIR, Raman spectroscopy, thermogravimetry, wet assaying and fire assaying (Li et al 2004). While all of these techniques may not be applicable to this sample, wet spectroscopic techniques appear to be quite relevant for the quantitative work that beneficiation recovery analyses demand. Assays from wet techniques are known to depend on the extent of the recovery of the target constituent to the leach liquor. Given the constitution of PCB fines, 100 % recovery of analytes may be difficult. When little experience is available with respect to the digestion of a matrix, comparison of a number of digestion techniques is recommended (Henryk, 2003). An investigation of comparative digestion techniques can be informative for the assaying requirements in this investigation.

3.7 INVESTIGATION OBJECTIVES

From the foregoing discourse, specific objectives towards this investigation are to:

i. Carry out qualitative liberation analysis of the −75 μm PCB comminution fines to establish if the constituent particles are sole material particles or if composite particles still persist at this size range of PCB comminution product.

ii. Carry out comparative wet digestion analysis to establish the effect of relevant digestion techniques on the wet assay values of PCB comminution fines.

iii. Carry out trial and full experiments to establish favourable range of flotation kinetic parameters applicable in the prospect of PCB comminution fines flotation.

iv. Investigate applicability of flotation for the beneficiation of PCB comminution fines by employing logically probable flotation schemes that are based on expected differences in natural hydrophobicity of particles in the fines sample and on responses to certain chemical conditioning.

Essentially, the third objective must be pursued simultaneously with the fourth as the kinetics must be observed under a scheme. This is the rationale for the preliminary trials, which will have to set out from uncertain kinetic regime under unproven scheme. Some ancillary investigations that may ensue in the course of these investigations, towards understanding the behaviour of the system better, will be attended to, while not deviating too much from the set objectives.

In summary, the investigation will offer material and kinetic characterisation insights relevant to PCB CF flotation prospects. It will establish how the sample responds to the reasonable flotation schemes based on general froth flotation understanding. It will surely provide a basis for pursing further interests in this direction. Detailed work approach towards realising these objectives, as well as secondary investigation objectives that ensued, are presented in the following chapter.