7.0 INVESTIGATION OF CHEMICAL CONDITIONING SCHEMES FOR FROTH FLOTATION OF PCB CF

7.1 INTRODUCTION

The investigations into the chemical conditioning schemes are presented and discussed in this chapter. As outlined in Section 4.6, the collectors used were PAX, SMBT and TBAC; the depressants were sodium carboxyl methyl cellulose and Betamin 127A, respectively abbreviated as CMC and B127A hereafter. Investigations with PAX, described separately in Sections 4.6.2 to 4.6.4, are presented together herein for ease of comparison of the treatments.

7.2 MACROMOLECULAR VERSUS GAMMA DEPRESSION

7.2.1 Bulk Depression

As a result of the high response observed under the NHR scheme, application of depressant appears very relevant in PCB CF flotation. Bulk depression was therefore considered first to determine wether the high natural hydrophobic pull could be suppressed, prior to chemical conditioning for selective flotation. Considerations for depressant selection and probable depressants for this type of sample were discussed in Section 3.5.2. As detailed in Section 4.6.1, CMC and B127 were employed for this investigation. With CMC, preliminary dosages from 200 g/ton in steps up to 2 kg/ton did not show any remarkable depression. At these dosages, steady froth built and cumulative mass pull remained high. The high mass pull to be suppressed was blamed. Much higher dosages continued to be used, but frothing and high mass pull continued up to very high dosages used. At 10 mass percent (100 kg/ton) CMC, mass pull of 19.5% was still obtained. At a profuse dosage of 30 mass percent CMC, a 5.7 % mass pull was still obtained. At this dosage, the pulp viscosity had increased noticeably.

A dosage of 500 g/t normally would suffice for effect in normal mineral applications (Bulatovic, 1999). That mass pulls persist at these extreme dosages basically implies that depression of the NHR response with CMC is ineffective. Only physical coating of particles, as in slime coating, appears to be occurring. The froth-phase-bound particles are in a very high proportion, with the bulk of this at −38 µm. It implies that, without definite chemisorbtion, physical coating with hydrophilic molecules will require a very large dosage for a remarkable drop in mass pull to be observed in this system. The idea of total depression, therefore, appears not feasible within practical CMC dosages.

B127A, on the other hand, shows observable suppression of the natural hydrophobic froth, however, frothing entrainment sets in. Before aeration, the pulp surface shows evidence of wetting as faint traces of natural hydrophobic particles that is normally on the pulp surface was totally absent, being wetted and sank. Froth loading visibly dropped with increasing dosage, as the froth changed to a faintly loaded dirty white and eventually to a clearly unloaded white froth. On skimming, the froth released entrained particles to give a high mass pull, as Figure 7.1 shows. Relative standard deviations (δ_R, %) of the duplicate CMP data in Table A2.12 (Appendix II) all show acceptable spread: the higher spread in the first few minutes of flotation can be allude to imprecision in float skimming between repeats due to higher mass pull rate in this time interval.

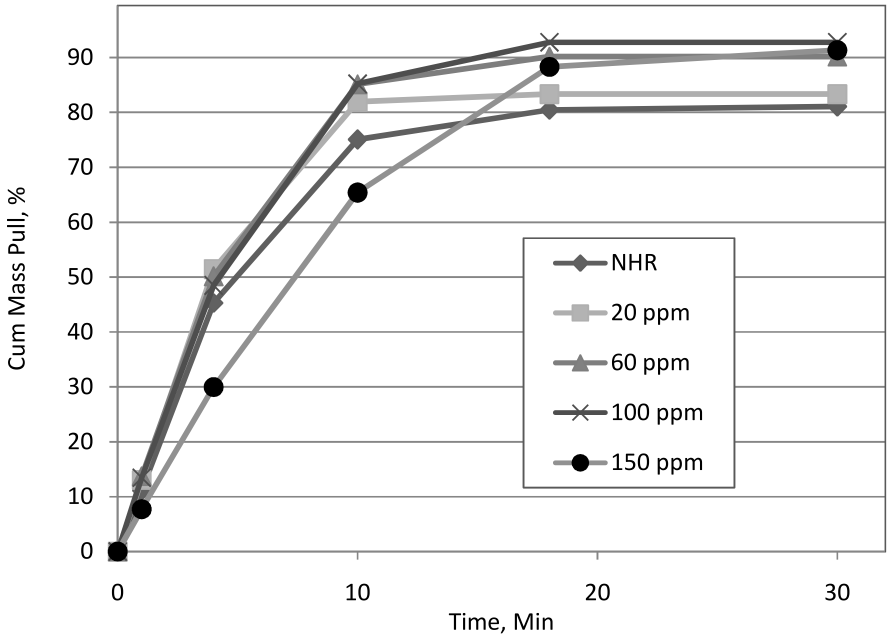

Figure 7.1: Mass pull over time in PBC comminution fine flotation with Betamin 127A as depressant at various dosages.

Generally, the response shows the ease with which the pulp particles entrain readily with water after wetting. The low density and fine size of much of the pulp particles also aid this. As can be observed from Figure 7.1, mass pull increased with dosage, indicating increasing contribution of entrainment. Lower surface tension at higher surfactant concentration (see Equation 3.2) led to easier frothing, smaller bubble sizes, higher froth volume and more froth interstitials (Harris, 1982; Pugh, 2007), all of which promote entrainment. At 150 ppm, the mass pull rate was noticeably slower, indicating that extensive wetting of the particles had occurred; natural hydrophobic response was fully depressed and entrainment was about the only means of particle transport to froth. The run gave a cumulative water recovery of 10.5 %. The plot (Figure 7.1) shows the deviation from classical first order response towards linearity with time until 10 minutes (first four data points for the 150 ppm plot). The entrainment slowed down only after pulp particles neared exhaustion.

Table 7.1: Reverse recovery and sink enrichment ratio for select metallic values at different Betamin 127A depressant dosages (NHR condition implies 0ppm depressant dosage)

	NHR		20 ppm		150 ppm	
Element	Recovery, %	ER, %	Recovery, %	ER, %	Recovery, %	ER, %
Ag	19	1.04	14	0.84	12	1.44
Al	16	0.83	15	0.90	7	0.77
Au	58	3.08	55	3.32	48	5.61
Ca	12	0.66	12	0.73	5	0.59
Cu	38	2.04	31	1.85	18	2.11
Fe	33	1.76	26	1.55	20	2.29
Mg	17	0.90	16	0.95	7	0.86
Ni	50	2.66	39	2.36	22	2.55
Pb	45	2.37	34	2.07	22	2.56
Pd	52	2.74	42	2.54	22	2.51
Si	30	1.57	19	1.16	12	1.42
Sn	40	2.12	30	1.83	21	2.42
Ti	66	3.52	52	3.15	22	2.55
V	25	1.33	21	1.29	12	1.35
Zn	47	2.50	36	2.19	21	2.41

It follows that while trying to subdue one effect of direct mass pull, due mostly to natural hydrophobicity, another major effect of froth entrainment after wetting was setting in. Table 7.1 shows elemental recovery and enrichment ratios at the extreme dosages of B127A used (20 and 150 ppm) and at 0 ppm. The 0 ppm dosage corresponds to the E21C NHR condition. A consistent drop in recovery upon the wetting agent being added can be observed across all the elements. The higher the dosage, the more the values entrained. Wetting increased at the reduced surface tension, depressing natural hydrophobicity; but more froth also formed, with more interstices until entrainment predominated. By 150 ppm, reverse recovery of metallic values compared to that under NHR showed a sharp decrease.

The assays also showed a consistent decrease for some of the elements, such as Pd, Pb, Ti. Only Au appeared to show a remarkable assay increase in compensation for the recovery drop, as shown in Figure 7.2. Cu, also shown in Figure 7.2, shows a minimal assay increase for more than 50% recovery loss compared to recovery at 0 ppm (as in Table 7.1). In general, the observation and analysis show unselective entrainment of otherwise sink phase particles after wetting. Perhaps a lower dosage of B127 would have reduced the frothing and entrainment as the high natural hydrophobic pull to be suppressed demands the high dosages used.

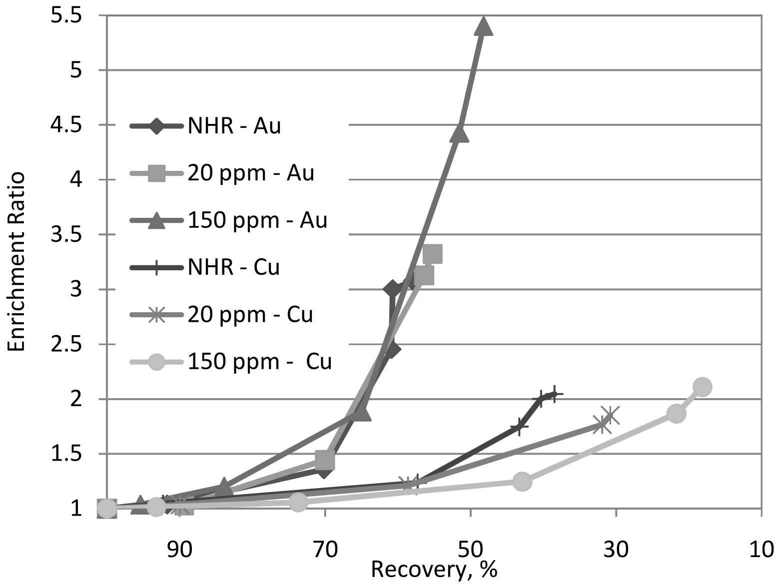

Figure 7.2: Enrichment ratio versus recovery for Au and Cu at varying Betamin 127A dosages

From these observations, attempting to suppress the natural hydrophobic response to allow for direct chemical conditioning of the sample is not advisable. Given the bulk proportion that wants to report to the froth on natural hydrophobicity, it is rational to allow and exhaust this natural response before conditioning. Perhaps a moderate dosage of the depressants will then be effective to subdue any little residual natural hydrophobic particles.

7.2.2 Depression of Residual NHR

After allowing NHR for 30 minutes, a moderate depressant dosage was investigated to suppress any residual natural response. The idea was to ensure a clean undiluted response after chemical conditioning. After conditioning with the depressants, 30 ppm B127A and 3.3% CMC (Section 4.6.1), the responses obtained further reinforced observation made from the depression of the bulk sample. With CMC conditioning after 30 minutes of NHR, froth still formed as when NHR is subsiding. It was lightly loaded, with the particle stabilised froth building up slowly over time. The total sample recovered over the 18 minutes of aeration was 3.8 g, which is 4.7 % of the sink mass before the conditioning (i.e. after the NHR pull).

The B127A conditioning, on the other hand, gave unloaded white froth with small froth bubble sizes, also building slowly up over time. On skimming, the unloaded froth collapsed to release entrained particles giving, a total of 4.5 g mass pull. This is 5.7 % of the sink mass before the conditioning. Under XNHR, in this time interval, the F3 fraction pulled 10.9 wt. % of the residual sink (see Section 6.3.5). Table 7.2 shows the assays of select elements from these fractions with averaged assays of the XNHR F3 (30 to 48 minutes) fraction for comparison. The assays tend to show that when CMC is compared to NHR, it will slightly lower value pull from the residual NHR pulp, in the 30 – 48 minutes of flotation. Given that Ag and Al follow trends opposite to other metallic values in NHR, B127A generally tends to entrain a little more value into the froth. As explained above, the increased wetting in the bulk causes easy entrainment, carrying target metallic values along. This same wetting and entrainment effect was still observed at the 30 ppm dosage in the residual NHR pulp.

Based on the mass pull, some depression of the NHR response can be inferred, but a definite recommendation needs careful consideration. It is notable that CMC dosage was 3.3 % (33kg/ton). A depressant requiring this dosage level is obviously ineffective and cannot be recommended for application. B127A, on the other hand, suppresses particle bubble attachment, giving clearly unloaded froth. In any case, the overall mass pull difference, with or without these depressants, after pulling the bulk NHR particles, may not amount to too much contamination of a float fraction after collector conditioning. The final decision to use a depressant along with a collector, therefore, depends on how the system responds to conditioning with the collector alone.

Table 7.2: Elemental assays (ppm) of fractions after NHR and depressant treatments

Elements	B127A	CMC	XNHR - F3
Ag	504	431	513
Al	24 250	20 688	23 000
Au	68	61	81
Ca	76 375	63 000	74 250
Cr	117	115	137
Cu	16 263	15 013	18 900
Fe	17 700	13 463	15 900
Mg	2 103	1 764	2 340
Ni	890	713	1 065
Pb	11 925	10 063	13 175
Pd	60	40	67
Sn	18 713	16 500	20 550
Ti	818	570	845
V	28	23	28
Zn	2 160	1 745	2 525

7.3 PAX CONDITIONING SCHEMES

PAX conditioning of NHR sink was considered probable for achieving a bulk metallic float fraction (see Section 3.5.2). The treatments include consideration for activation with NaHS, as well as depression with B127A. For ease of reference, Table 7.3 provides the description and designation of treatments employing PAX (see Sections 4.6.2 to 4.6.5). After conditioning, mass pull showed a slight increase above that from XNHR in the 30 – 48 minutes. The pulp generally gave a moderate froth, compared to ordinary NHR in this time interval.

Figure 7.3 shows the mass pulls (%) obtained under the different PAX treatments. Understanding that the figures are mass percentages pulled from residual NHR sinks, it shows that the actual masses pulled were not large. The small masses were obtained with relatively high water to mass recovery ratios. These factors may be responsible for the large spread in these data compared to the NHR mass pulls such as in Figure (6.14). Increased mass pull with PAX dosage can be seen with the 100 and 400 g/ton dosages. Sulfidation also showed an increase in mass pull at the PAX dosage of 400 g/ton. Judging from the visual observation of the float fraction during flotation and after drying, the response did not appear to be strictly selective of metallic particles only. Fibre particles were obvious in the fractions. The elemental assay analysis gave a recovery and enrichment ratio from the treatments as shown in Table 7.4. Recovery here is with respect to the float and not the sink fraction, as for the NHR reverse flotation analysis. The enrichment ratio was calculated as elemental assay of the float fraction divided by respective elemental assay of the sink before conditioning (see Section 4.6).

Table 7.3: Designation and description of treatments involving PAX conditioning (Section 4.6.2).

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

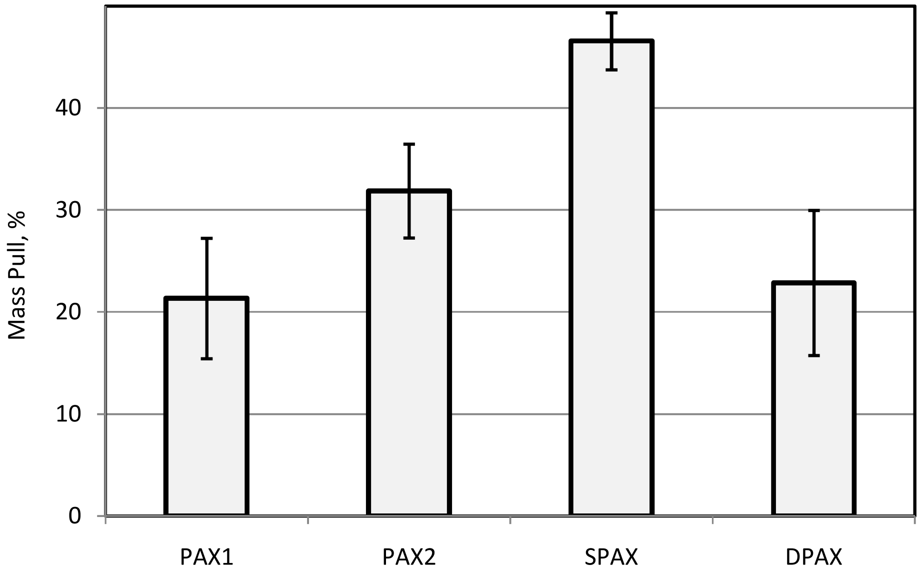

Figure 7.3: Mass pull under different PAX treatments.

A general overview of the recovery data shows that the target metallic values did not preferentially report to the float after the PAX conditioning and the bulk values remained in the sink. The understanding is that the initial 30 minutes of natural hydrophobic pull at the XNHR condition is towards maximizing reverse recovery, so that some natural hydrophobic particles are still left in the sink. The NHR scheme (see Section 6.3.2) showed mass pulls up to 80 % compared to about 52 % obtained at the XNHR condition for 30 minutes (see Table 6.3). Increasing the impeller speed, for instance, would have increased particle bubble collision efficiency and caused further pull. By keeping the kinetics constant after the 30 minutes and conditioning the system with xanthate, only metallic particles are expected to start floating, since natural hydrophobic response had already subsided at the prevailing kinetics. The float is, therefore expected to contain more of the targeted conditioned metallic values.

Table 7.4: Recovery and Enrichment Ratio for fractions from the different PAX treatments (described in Table 7.3)

Elements	Recovery, %				Enrichment Ratio			
	PAX1	PAX2	SPAX	DPAX	PAX1	PAX2	SPAX	DPAX
Ag	30	41	34	38	1.41	1.30	0.74	1.68
Al	22	38	45	31	1.05	1.18	0.96	1.36
Au	7	12	21	7	0.31	0.37	0.45	0.29
Ca	25	40	47	34	1.15	1.25	1.02	1.49
Cr	20	30	42	21	0.92	0.95	0.90	0.91
Cu	12	22	50	18	0.56	0.70	1.07	0.78
Fe	16	25	35	16	0.75	0.79	0.74	0.71
Mg	23	37	44	30	1.08	1.15	0.94	1.32
Ni	9	16	32	11	0.41	0.49	0.68	0.50
Pb	11	19	29	12	0.53	0.61	0.62	0.54
Pt	7	16	29	12	0.34	0.51	0.61	0.53
Pd	9	17	30	12	0.41	0.55	0.64	0.54
Sn	12	20	28	13	0.57	0.64	0.60	0.57
Ti	6	11	16	10	0.27	0.35	0.35	0.44
V	19	30	35	24	0.89	0.95	0.75	1.04
Zn	9	17	36	15	0.44	0.53	0.76	0.64

The recoveries analysis however did not show this. The enrichment ratios obtained were also below 1 (except for Ag, Al, and Ca, Mg which always tend to show reverse trends to other metals from the NHR scheme). This shows that the float is even poorer in the metallic values when compared to the pulp at the beginning of conditioning, i.e.: the resulting sinks have actually been enriched after the treatment. This implies that although the mass pull increased with an increasing dosage of PAX, as well as on sulfidation, the conditioning appeared to influence other pulp particles even more than the metallic particles. This increased the floatability of otherwise natural hydrophobic particles at supposedly unfavorable prevailing kinetics.

However, studying the recovery and assay data closely shows assays and recovery increase together with increasing dosage of PAX, i.e. the response does not show assay-recovery compromise. Sulfidation also gave higher recoveries and assays, except for Ag, Ca, Al, Mg (noted for opposite responses). This shows that PAX was actually interacting with the metallic particles as projected, and that sulfidation was also achieving activation of the surface to xanthates. Increase in enrichment and recovery as dosage increases shows that these reagents target these particles somehow. The problem therefore appears to be that other particles were activated along with, and even ahead of, the target metallic particles, giving the overall low recovery and enrichment. Since the other particles are in higher proportion in the float, it shows that certain mechanism favours flotation of such particles over the target metal particles.

Xanthate conditioning is well studied and understood at least for metals that occur in native forms (Lins and Adamian, 1993; Woods, 1996; Forrest *et al.*, 2001). Formation of metal xanthates, chemisorption, and/or dixanthogen adsorption on such metallic particles and activation, as a result, were therefore expected (see Section 3.3). But for the plastics and glass fibres, study of adsorption of xanthates on these surfaces is very scarce. Nevertheless, given the low reactivity of plastics, or the negative surface charges of quartz at this pH, xanthate activation would not be expected for these materials.

A probable explanation for the competing activation of other particles could be modification of the frothing behavior of the pulp by the xanthate, which assists in stabilizing the froth of the natural hydrophobic particles when fine particle stabilization has subsided at the prevailing kinetics. Residual natural hydrophobic particles in the pulp would still float if the kinetics changed favourably. For instance, increased bubble surface areas available at higher impeller speeds and/or aeration rate would maintain particle bubble collision efficiency for effective transport to the froth phase. At the prevailing kinetics, the surfactant addition could amount to an alteration of the physical chemistry of the pulp and compensate for the slower kinetics. Xanthates, though dedicated collectors (see Table 3.1), are heteropolar and in essence will have air-water interface activity, no matter how little relative to dedicated frothers. This could be particularly true of PAX, with the long chain amyl hydrocarbon: the higher the hydrocarbon length, the more the surfactant effect. Any such little surfactant activity could be effective here, given that the competing particles are naturally hydrophobic in the first place, needing only the stabilisation of bubble-particle agglomerates.

Another possible explanation for the response is traceable to the noticeably high proportion of calcium in the PCB CF sample, and in the NHR float fractions. Lime addition for pH increase is known to have a depressant effect in normal mineral flotation, resulting from Ca^{2+} adsorption or calcium precipitation products (see Section 3.3.1). $CaSO_4$ or $CaCO_3$ can precipitate on particle surfaces (Wills, 1997). In pyrite flotation, when lime is used for pH regulation instead of KOH or K_2CO_3, electrostatic adsorption of calcium ion (on negatively charged pyrite at pH > 7) is known for pyrite depression (Fuerstenau, 1982). If the metallic particles in the PCB CF pulp are oxidised, as increased recovery due to sulfidation tends to show, the oxide could have negative surface charges at the natural pulp pH on which Ca^{2+} could physisorb, preventing collector interaction.

This explanation appears plausible, given that gold surface in aqueous solutions shows negative surface potentials down to an isoelectric point at pH 2 (Thompson and Collins, 1992). Judging from dependence of electrophoretic mobility of the gold particles on pH, coupled with other reactive inferences, the charge development was attributed to surface oxidation and not simple (chemically less stable) adsorption of OH^-/H+ species. Other less noble metals would therefore be expected to oxidize (even if only up to a few monolayers) and carry negative surface potentials by the same surface oxide charging mechanism at the prevailing natural alkaline pH of the PCB CF pulp.

The idea of using a starvation dosage of B127A, just sufficient for depression of residual NHR, stemmed from this observation, with a target to subdue any competing natural hydrophobic response to ensure that only conditioned metallic surfaces were pulled to the froth. After the 30 minutes pull before conditioning with xanthates, 10 ppm B127A was found to suffice to subdue residual natural hydrophobic loading of bubbles (see Section 4.6.4). At this dosage, stable froth was not forming. The dosage barely sufficed to achieve the depression without causing too much reduction in the pulp surface tension, which would lead to stable frothing, and hindering of bubble-particle attachment in the pulp. MIBC was added as frother to assist in stabilising any pull after conditioning. having observed that MIBC does not depress the natural hydrophobic response and does not promote two phase frothing significantly. Trials without MIBC in this depressant plus collector scheme did not actually form stable froth. No froth loading was also shown at 30 ppm dosage of B127A.

After conditioning, the froth loading was light and the froth built up slowly over time. The froth still did not appear metal selective, and glass fibres could still be seen in the fraction after drying. The resulting mass pull (see Figure 7.3), showed a drop compared to the PAX2 condition, with the same 400 g/ton PAX dosage. This was expected as the projection was to have a smaller, cleaner froth. The recovery and enrichment data, provided in Table 7.4, however, indicate the response did not show targeted selectivity. The recovery dropped below that obtained under PAX2 for all the elements. So also is the enrichment for some of the elements. Other particles, apart from the targeted metallic values, still reported to the small mass pull. It generally appears, as earlier explained, that the natural hydrophobic particles and some other particles that entrain more readily will always compete to report to any froth phase that will be formed in this pulp. Perhaps sulfidising the depressed pulp could achieve some improvement in the response of the metallic values; but judging from the data range from these treatments, the response will still be a far cry from a remarkable improvement.

7.4 SMBT CONDITIONING

After aeration, faintly loaded watery froth was collected. The total mass pull was 9 %. This is a total average of 6.3 g mass pulled out of a residual NHR sink of 69.7 g before conditioning. The mass pull was accompanied with 85 g of water (2.4% water recovery) in this interval; i.e. more than 12 g of water per gram mass pull.

Table 7.5 shows the recovery and enrichment ratio for the select elements from the analysis of the float fraction resulting from this conditioning scheme. The result shows overall poor recovery and enrichment. Even the primary target elements here (Cu and Pb) were poorly recovered.

SMBT is a recognized selective collector of tarnished or oxidized lead and copper minerals (Wills, 1997). The response observed here may be explained by reactivity difference between a natural mineral and end use alloy particles. The natural pulp pH or potential might not favor the interaction with the alloyed surface. The calcium depression mentioned above also remains a possibility here. Since sulfidation appeared to show improvement, which tends to indicate oxidation / tarnishing of the metallic values, SMBT conditioning would be expected to give improved recovery. That this was not observed shows a major depressant presence may have limited the response. The high dosages of PAX and NaHS used are an indication that a constraint needed to be overcome for the projected response to be observed.

Table 7.5: Recovery and Enrichment Ratio of select elements after SMBT conditioning.

Elements	Recovery (%)	Enrichment Ratio
Ag	8.2	1.04
Al	7.2	1.01
Au	1.7	0.24
Ca	7.8	1.09
Cr	6.0	0.82
Cu	4.2	0.58
Fe	4.4	0.59
Mg	7.2	1.01
Ni	2.7	0.36
Pb	3.4	0.48
Pt	2.9	0.42
Pd	2.8	0.40
Sn	3.6	0.51
Ti	1.7	0.23
V	5.8	0.84
Zn	3.0	0.42

7.5 TBAC CONDITIONING

The first observation to be noted here is about regulating the pulp pH. Three pH levels were to be used (see Section 4.6.5). The basic pH of 10 was easy to achieve and it remained stable; but reducing to pH 4 was difficult. The pulp showed a strong buffering against lowering the pH. On addition of acid, while maintaining agitation, the pulp pH dropped and rose again, unlike the steady natural pH the pulp showed over time (see Figure 6.1). Buffering over more than one pH unit easily occurred within a minute or two, pushing the pH back to higher values. Since the pH was easy to increase to 10, the pulp was not acting strictly as a buffer system, containing an acid-base conjugate pair (Kotz and Treichel, 1999). Rather, it represents a system with a high weak base reserve, so that a shift in the pH downwards drives the activity of the base. Acid solution had to be added well in excess of the normal dilution ratio to drag the pH down to 4. During aeration, it still rose close to 5. Continuous compensation for the pH was not done, as no mass pull was being observed at this acidic pH range.

Figure 7.4 shows the mass pull at the various pH levels. At the natural pH, a mass pull of about 16 % was observed, which was a bit lower when compared to that under PAX1, despite the fact that MIBC was used to assist frothing here. XNHR gave an increase of about 5 % in cumulative mass pull in this time interval (see Table 6.3), which is equivalent to about 12% of the residual NHR sink. At the more basic pH 10, increase in this pull was observed. Tetra butyl ammonium ions were expected to physisorb on negatively charged particles, and the higher the negative surface potential, the higher the adsorption expected.

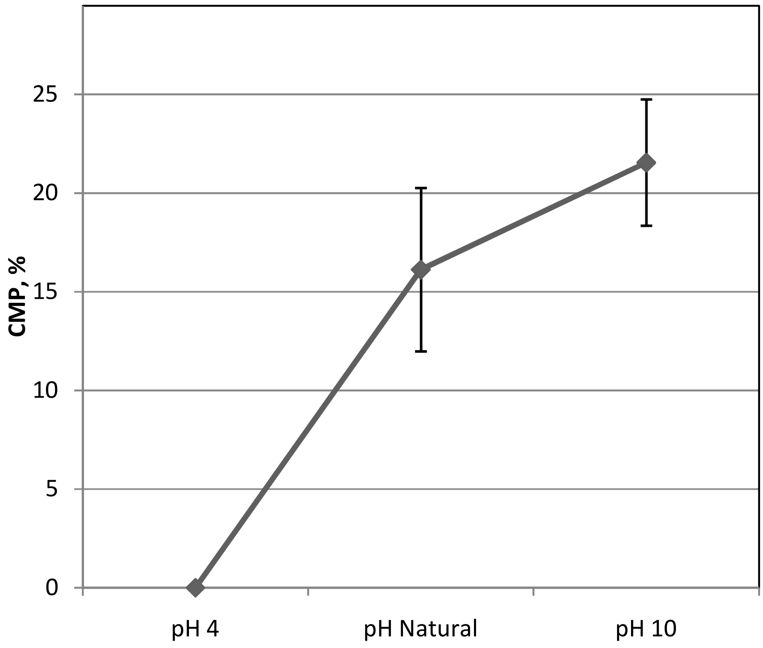

Figure 7.4: Cumulative mass pull under TBAC conditioning with varying pH

Particles with negative surface potentials were expected to be in higher proportion in this pulp and the overall mass pull level was expected to be higher. Surface hydration, hydroxylation and/or oxidation with development of general negative charges by the particles were expected at the higher pH level. Silica (glass fibre) particles were in high proportion and these would be at negative surface potential over this pH range (Fuerstenau and Fuerstenau, 1982). Many other oxides were also expected to be present. Metallic particles would be expected to show some surface hydroxylation/oxidation and acquire negative surface potentials at higher pH values.

Based on these projections, the chance of this scheme achieving good selectivity was considered to be better towards acidic pH. The projection at the acidic or natural pulp pH was that a very high mass pull of the silica particles for instance would be obtained, leaving a richer, more metallic sink. At the basic pH, a higher but less selective pull was expected. It turned out that the basic pH showed little pull, which increased from the natural pulp pH 8 to the pH 10 condition, while low (acidic) pH 4 achieved no pull.

Considering this low response to TBAC, the presence of calcium in the sample is still probable, coupled with the fact that calcium has been showing high recovery to the NHR float. Calcium ion activation of quartz surface for soap (anionic) collector is an effective scheme in heamatite-quartz flotation; heamatite in the scheme being depressed by chemisorbtion of starch (Fuerstenau and Fuerstenau, 1982). The silica particles in the PCB comminution fine pulp could, therefore, have been conditioned by calcium ions, giving them a positive surface potential, which hindered adsorption of the butyl ammonium ions. This reasoning is the basis for the investigations into calcium dissemination in the sample and its presence in the process water, detailed in Section 4.7.2. The results are discussed separately in Section 7.6.

Analysis of the float fractions from the natural pH and the pH 10 treatments gave recoveries and enrichment ratios shown in Table 7.6. The data shows that the recovery of metallic value to the froth after the conditioning was generally low; lower at neutral pH, with a little increase at pH 10, which obviously derives from the higher mass pull. The enrichment ratios also show broadly low levels. These indicate that the metallic values were selectively rejected to the sink. The slight increase in recovery from the natural pH to pH 10 was accompanied by some increase in enrichment (see Table 7.6). As explained, at the higher pH levels, development of negative surface charges by the particles was expected. A higher proportion of OH^-, which is a potential determining ion for oxides, would promote this. It follows that the metallic values developed more negative surface charges and hence the increase in their relative response at the higher pH.

Table 7.6: Recovery and enrichment ratio of elements under the TBAC condition scheme

Elements	Recovery (%)		Enrichment Ratio	
	Natural pH	pH 10	Natural pH	pH 10
Ag	28.0	23.3	1.69	0.96
Al	24.8	26.8	1.50	1.11
Au	3.1	4.8	0.19	0.20
Ca	27.8	32.9	1.68	1.36
Cr	14.3	20.1	0.87	0.83
Cu	7.5	10.1	0.45	0.42
Fe	10.8	16.1	0.65	0.66
Mg	24.3	27.9	1.47	1.15
Ni	5.9	10.5	0.35	0.43
Pb	6.0	10.8	0.36	0.45
Pt	4.4	7.4	0.27	0.31
Pd	5.0	8.5	0.30	0.35
Sn	6.1	12.0	0.37	0.50
Ti	4.4	5.2	0.27	0.22
V	16.4	22.9	0.99	0.94
Zn	6.4	9.2	0.38	0.38

Assessing the performance of the TBAC conditioning from the viewpoint of enriching the NHR sink further with metallic values, the natural pH condition achieved about 16% mass pull, that is, 16% mass reduction of the NHR sink (see Figure 7.4), with about 3% compromise of gold content in sink, Pd 5 %, Pt 4 % and Cu 4 %. The pH 10 condition showed a higher loss to the float at 21% reduction of the sink mass. The natural or lower pH therefore appear better for selective rejection of the metallic values to the sink, except that higher mass pull would still be desired, given the relative proportion of particles desired to be adsorbed and floated by TBAC. Yet, higher pH will promote loss of metallic values to the float.

Summing up, particles expected to have a negative surface charge (at the natural pulp pH for instance) were probably neutral, or depressed by Ca^{2+} adsorption. This impeded TBAC adsorption and the pull was therefore not as high as expected. The lower pH possibly conditioned all pulp particles to positive surface charges or generated more Ca^{2+} and this further depressed particles with negative surface charges. The calcium proportion in this sample was much higher than that of all the target elements (Table 6.1) to the extent that any effect due to calcium in the response to treatments can be overwhelming. The increase in pull at the more basic pH 10 shows the system responded to the basic projection of the TBAC conditioning scheme (higher negative surface potential with increasing pH), albeit very low. As observed, activity of Ca^{2+} remains a major suspect for the response being observed in this system. Being in such a high proportion, the conditioning could not subdue its effect. The overall performance indicates the peculiarities of a complex flotation system that this sample represents.

7.6 CALCIUM DESEMINATION IN THE PCB COMMINUTION FINES AND PRESENCE IN PROCESS WATER

As pointed out earlier, calcium ions appear culpable of the observed response of PCB CF to chemical conditioning. Hence, dissemination of calcium in the samples and its presence in the process water were investigated, as laid out in Section 4.7. Figure 7.5 shows a backscattered electron micrograph of dispersed unpolished particles of the sample, showing various particles contrasted based on the atomic number grayscales. The long cylindrical shapes of the glass fibres also serve as distinct contrast. The SEM-EDS spectra of some of the phases, as marked in Figure 7.5, are shown in Figure 7.6. The spectra confirmed calcium presence inside the glass fibres particles (P8). In addition, Ca was found in other particles, such as the titanium bearing particle P1. With calcium being constituent of the glass fibres and the high relative abundance of glass fibres in the sample, the high proportion of calcium in the sample chemical composition (see Table 5.4 and 6.1) can be understood.

For the process water analysis, only 25 of the 68 elements scanned were found in the process water (see Table A4.1 in Appendix IV). Of these, only the six indicated were in Table 7.7 were above 1 ppm concentration level. Although distilled water was always used for the experiments, a sample of the laboratory mains water supply was also analysed, as can be seen in the table. The result shows the presence of calcium in the process water. Other metals, such as sodium and potassium, also found in the water form soluble salts and would therefore not depress the way calcium would do. Given the high content of calcium in the sample, its equilibrium concentration in solution will be easily maintained. Any reaction using up calcium from the solution would therefore be sustained remarkably. If calcium ion in the aqueous phase is forming an insoluble compound and causing depression in this system, such activity will be sustained by the large

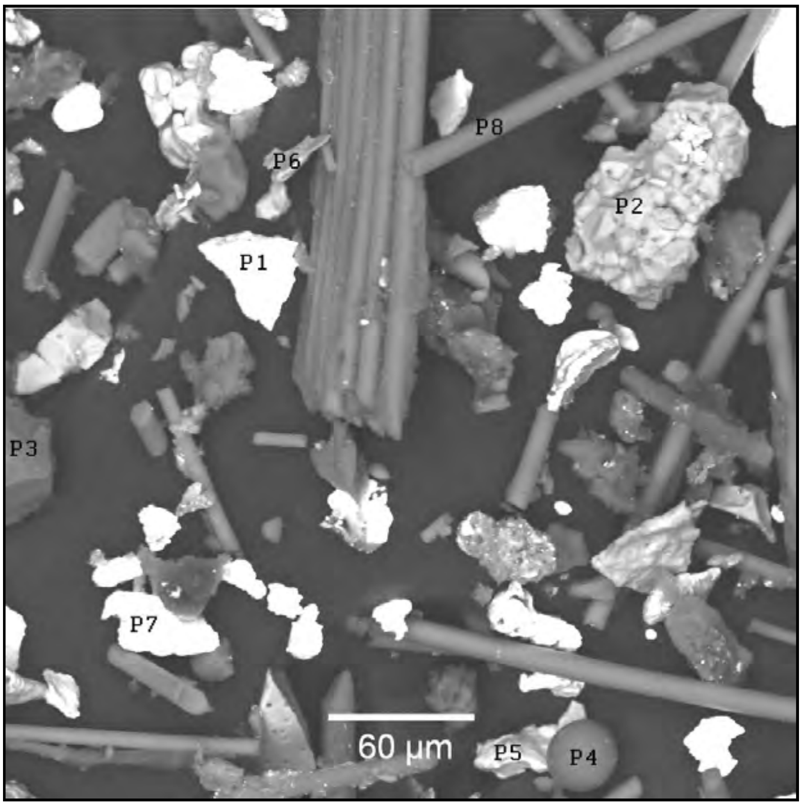

Figure 7.5: Backscattered electron SEM micrograph of dispersed particles of PCB CF
P1 – P8 correspond to particles whose EDS spectra are shown in Figure 7.6

Table 7.7: ICP-MS scan results for elements above 1 ppm concentration in PCB CF pulp filtrate

	Background	Lab Water (ppm)	PCB CF Filtrate (ppm)
Ca	<0.01	1.47	7.07
K	<0.01	0.78	6.84
Mg	<0.01	0.38	3.09
Na	<0.01	3.24	14.04
Si	<0.01	0.39	2.76
Zn	<0.01	0.01	1.28

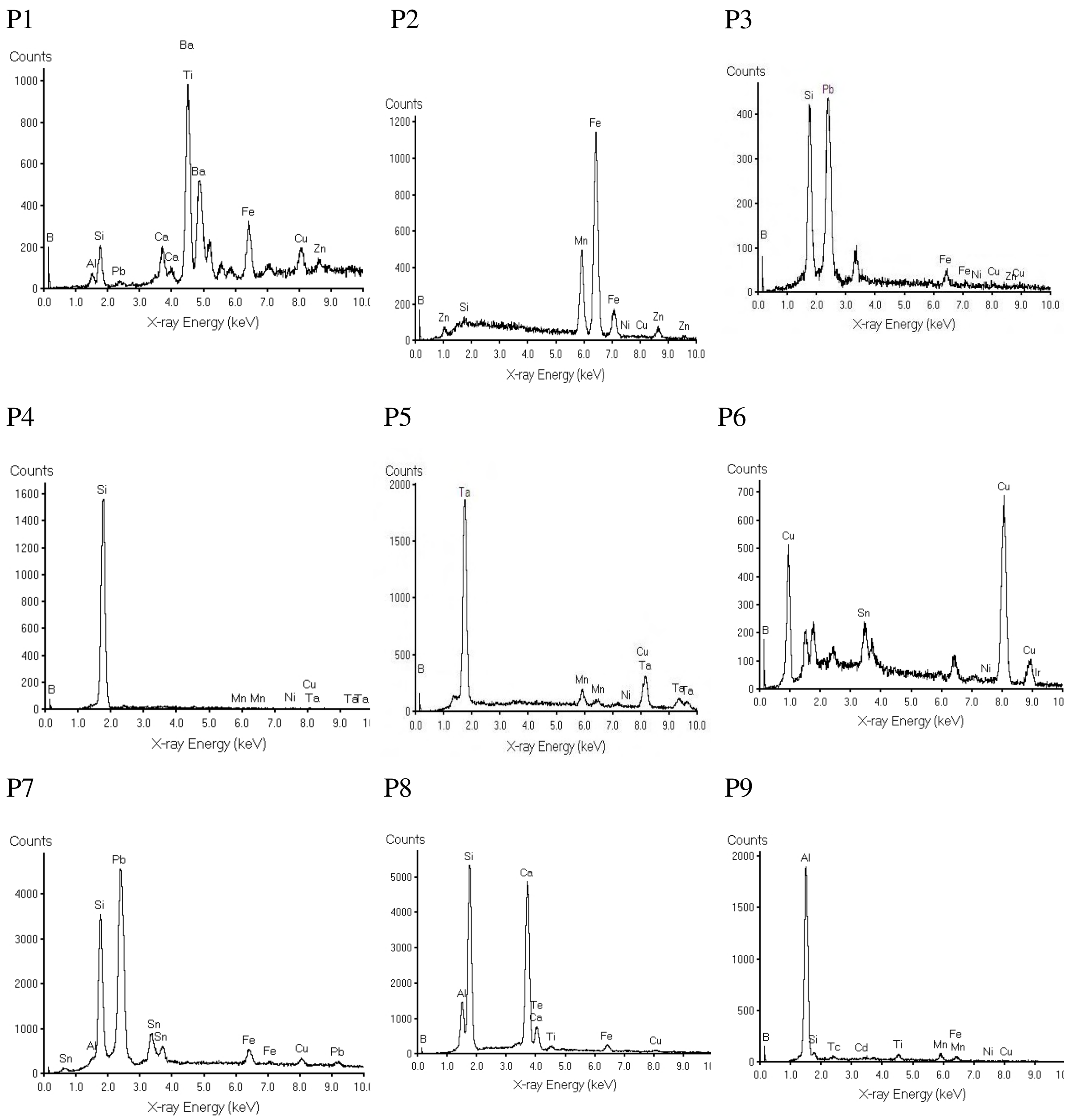

Figure 7.6: Sample EDS spectra of particles in the PCB CF.
(The label on each spectra corresponds to that of the respective particles it identifies in Figure 6.6, except for spectra P9 which is for an aluminum bearing particle from another micrograph which is not shown.)

calcium reserve in the sample. The depression will, therefore, be overwhelming. Since this reaction would have taken place well before a collector is introduced, it would be difficult for the collector to displace the surface compound already formed. This most possibly explains the poor response to collector observed in this system.

7.7 SEM AND AES INVESTIGATION OF PARTICLE SURFACES

Another possibility mentioned for the observed level of response to chemical conditioning by PCB CF in the froth flotation investigations is the surface condition of the metallic particles themselves. Surface investigations were therefore carried out as detailed in Section 4.7.3. Observation of the copper traces in the FE SEM gave the micrograph shown in Figure 7.7. The 'log' in the figure is a micrograph of a bare copper trace particle about 25 µm in diameter. The micrograph gave an indication of a surface that is not purely metallic, indicated by the bright electron charging effect in the micrograph. This effect was observed at a voltage of 1 kV. Total blur was observed on some fibres at higher voltages. A normal metallic surface would be conducting and would therefore not accumulate charges at the positive polarity of the sample stage inside the microscope. This presupposes the presence of a non conducting layer. This can be an organic coating residue or an oxide layer.

Also looking at the micrograph, the narrow gully found across the length may indicate a soft-left over of the PCB resins on the trace copper particle. This would also hinder collector interaction. It was mentioned that such left-over resin, depending on the extent of surface coverage, could be responsible for such a particle reporting to float under the NHR scheme (see Section 6.2). However, the auger electron spectroscopy investigation was more informative regarding the actual make-up of this surface and other sample surfaces of the particles in the sample.

Figure 7.8 shows a secondary electron image (at 1 kV landing voltage of primary beam) of the particles on carbon tape, as presented for the Auger spectroscopy investigation (see the details in Section 4.7.3). Figures 7.9 to 7.12 shows the depth composition profiles on the surfaces of particle P1, P2 and F2, as well as stacks of kinetic energy spectrum at various depths from the surface on F5. More detailed data from the Auger electron spectroscopic investigation of the surfaces of various particles, as laid out in Section 4.7.3, are presented in Appendix 4.

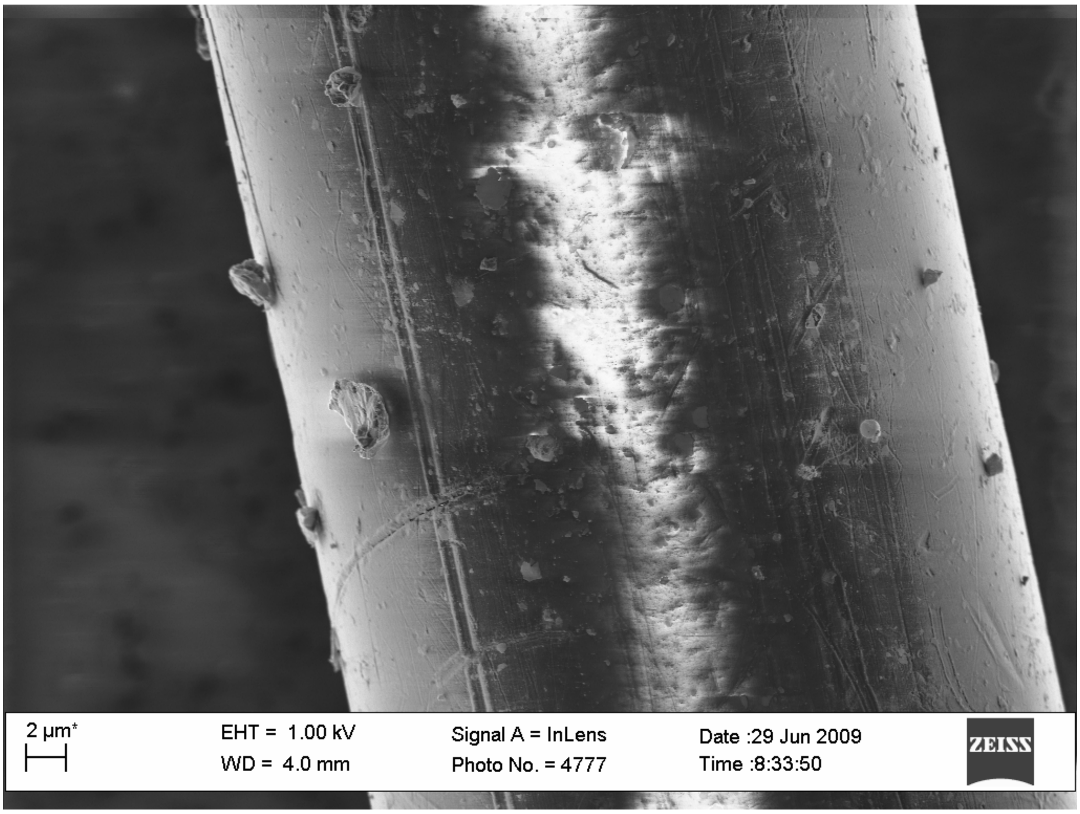

Figure 7.7: Field emission SEM micrograph of the surface of a PCB copper trace particle.

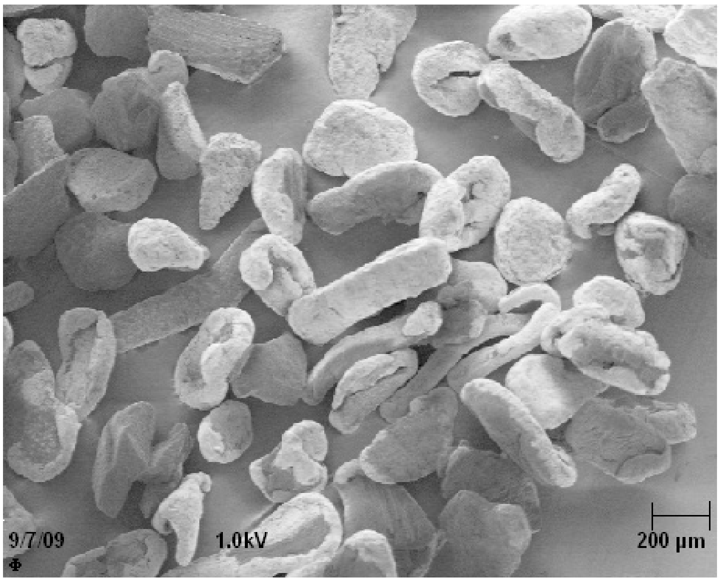

Figure 7.8: Secondary electron image of assorted metallic particles on carbon tape as presented for the auger electron spectroscopic investigation.

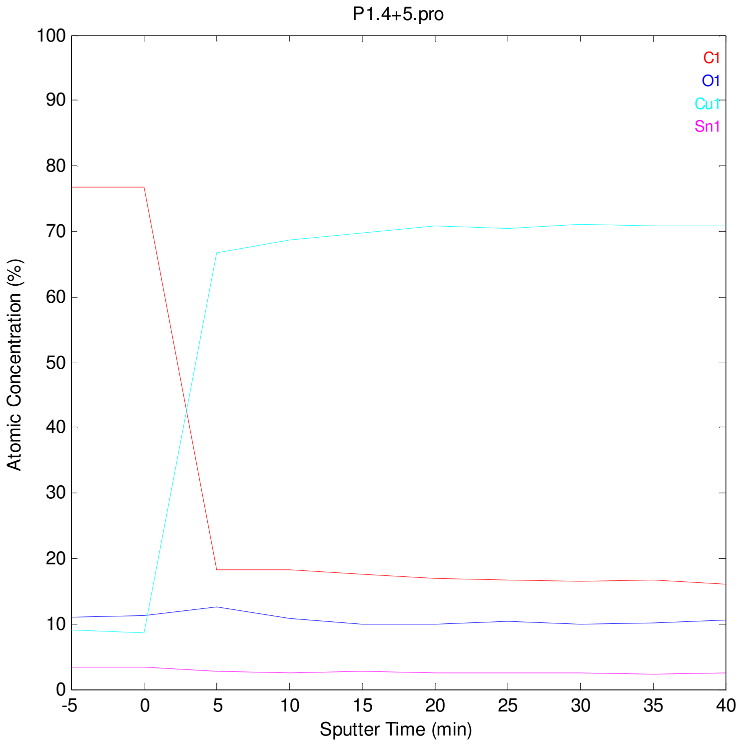

Figure 7.9: Depth concentration profile from AES surveys on the surface of particle P1 at various sputtering times indicative of depths from the surface.

In Figure 7.9, for P1, a high proportion of carbon (76.5 %) and oxygen (about 11.5 %) can be seen on the surface. After five minutes of sputtering, to a depth of about 42 nm (at about 85 Å /minute sputtering), the profile shows that the carbon proportion has reduced remarkably to around 18 %. This continued with a little drop down to about 340 nm (40 minutes of sputtering). Oxygen did not show much drop over this depth. A little representation of tin (about 3%) continued across the profile, while copper fraction increased from below 10% on the surface to above 70 % over this depth.

Interpreting this profile, the bulk particle is copper and the surface tin could be from solder vapor. The high carbon on the surface can be attributed to a huge contribution from the atmosphere, while the smaller fraction down the depth would represent a more tangible layer of organic material on the surface, which could even be up to a micron thick, when comparing depth impressions on Figure 7.7 for instance. The oxygen profile, at the surface, could be taken as a contribution from atmospheric adsorption and oxidation of the fraction of the metal on the surface. Into the surface, the metal concentration increases and so would be the fraction of oxygen from metal oxidation. The slight increase in oxygen concentration when metallic fraction shot up at the fifth minute survey somehow shows this. Away from the surface, the oxidation shows a slight decrease, but the layer down to the end of the profile generally remains oxidized.

From this profile on P1, some explanation can already be presented for flotation responses obtained from copper in this sample. Since the surfaces can be coated by a fairly thick layer of organic matter, which can be hydrophobic, the more coated a particle is, the more the chances are that it can float under NHR, and the less the chances are that it will respond to chemical conditioning – with a range of middling behaviours in between. This can explain why copper recovery in the NHR reverse flotation concentrate is relatively low. The surface oxidation down to a depth above 300 nm would explain the poor response to the xanthate collector, which was slightly improved by sulfidation. That the response on sulfidation was not drastic may then be traced back to the process water ions, such as calcium, as previously discussed.

The profile of P2 is shown in Figure 7.10. This is similar to that of P1, except for some trace elements such as sulfur and chlorine found on the surface. As P2 was soaked in process water, these elements indicate that some process water ions interacted with the surface. It shows, as mentioned, that species from the sample in the pulp really interacted with the surfaces, and will bias the behavior of the surfaces. The fact that trace elements can be detected down to the depths profiled shows a possible ingress through porous surface matter such as organics.

The profile for P3 is shown in Figure 7.11. Particle P3 was soaked in distilled water and the profile does not show such elements from process water ions as found on P2. This profile can be compared to that of P1.The relatively higher tin may not be taken as P3 is a Cu-Sn alloy because Sn commenced continuous decay after five minutes of sputtering. Rather, the profile shows possibly how close this particle surface was to a soldered junction or via. In any case, the profile does show how the flotation response of a supposedly copper particle can be expected to vary due to deposition of another metal on the surface in the production process.

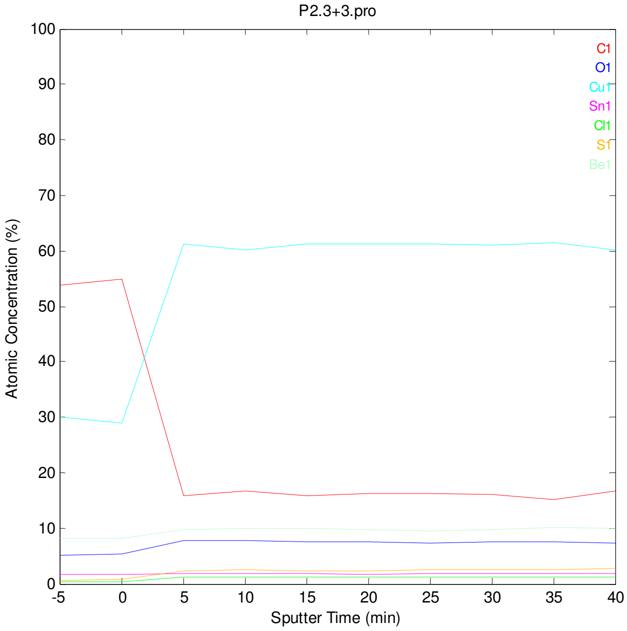

Figure 7.10: Depth concentration profile from AES surveys on the surface of particle P2 at various sputtering times indicative of depths from the surface.

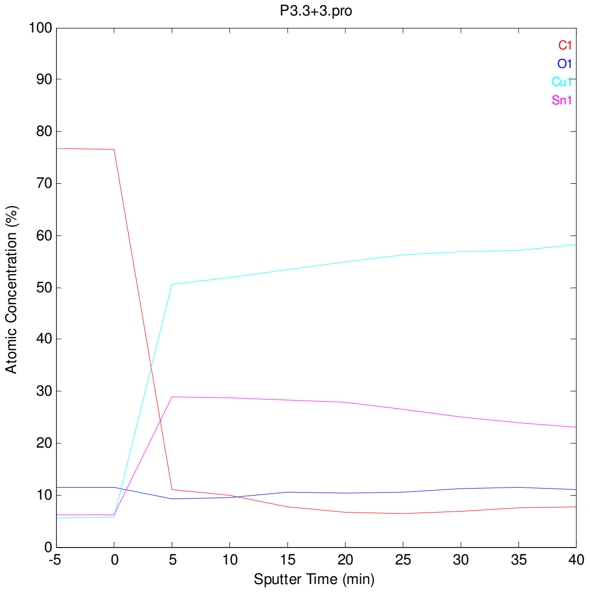

Figure 7.11: Depth concentration profile from AES surveys on the surface of particle P3 at various sputtering times indicative of depths from the surface.

Profiles on the surfaces of the fibre particles F1, F2, F3 and F4, are effectively alike (see Appendix 4) and the one for F3 is shown in Figure 7.12. The surfaces show carbon above 90%, oxygen and nitrogen, down through the depth profiled. The particles are from the actual copper trace wiring of the board which was right inside board resins. The presence of that much layer of organic on the surface is therefore understandable. Such a full organic surface coating would make such particles essentially hydrophobic. This explains the presence of such particles in the NHR float. The relative weight of the fibres, often being quite elongated, can also sever the attachment in the course of upward transport, such that such particles are also found in the NHR sink. The response of these trace particles could be expected to depend totally on these mechanisms – adsorption and detachment and to be totally isolated from reagent conditioning, as the surface compositions did not show any metallic fraction.

Figure 7.13 shows the profile of the whitish fibre particle F5. The profile shows this particle to be essentially a nickel-copper alloy with surface oxidation, as oxygen dropped from about 17% on the surface to around 6% at the final depth profiled. The high presence of calcium and silicon suggest the possible presence of glass fibre partially fused on this particle at this spot during comminution. Trace tin present is possibly from soldering. Some trace sulphur and nitrogen can also be seen, presenting the reality of a typical surface in an end use alloy. This type of particle will most likely report to the sink in NHR flotation, while its response to chemical conditioning can be difficult to predict.

This surface analysis has shed some light on the reality of the surfaces of metallic particles in the PCB CF. In pulp, the atmospheric carbon can be considered washed off, the remaining surfaces ranging from totally organic to totally oxide, with a series of middling coverage possible in between. The observed response chemical conditioning in most of the particles could be as being explained mostly due to relative inertness due to the surface being covered by an organic layer. Fractional oxide representation of the surface still makes some activation possible, as with sulfidation to xanthate, but this is not remarkable due to the high fraction of the surface that is inert. Ionic species in pulp can also be found to interact with the surface, leaving ions that can interfere with reagent activity.

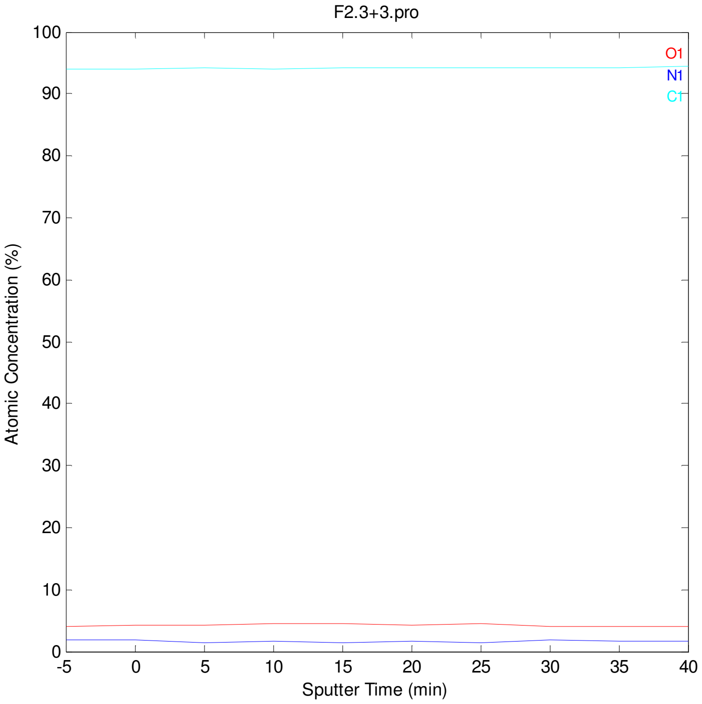

Figure 7.12: Depth concentration profile from AES surveys on the surface of particle F2 at various sputtering times, indicative of depths from the surface.

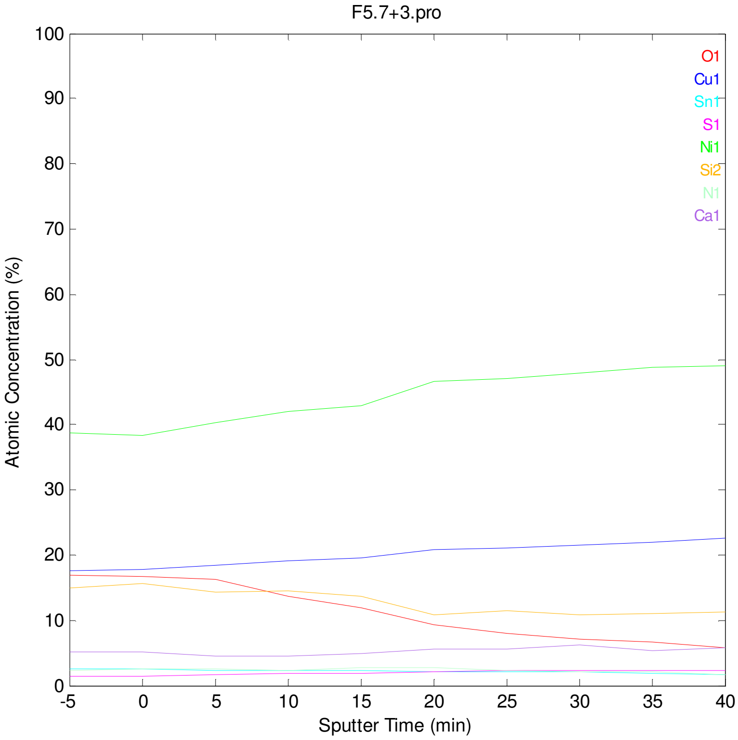

Figure 7.13: Depth concentration profile from AES surveys on the surface of particle F5 at various sputtering times indicative of depths from the surface.

7.8 CONCLUSION

Logical chemical conditioning schemes based on theoretical projections were investigated towards application of froth flotation for PCB comminution fines beneficiation. The results obtained will serve the purpose of providing insight into the response of PCB CF in flotation. Anionic and cationic collector schemes were used, as well as activation. Conditioning with PAX for a bulk collection of metallic particles, in line with native metal collection of xanthates, did not show a strong response. Dosages of up to about 400 g/ton were used to observe some recovery and enrichment in the float, with little further increase on sulfidation.

SMBT is a very selective collector for tarnished copper and lead minerals. It did not show such behavior with the PCB pulp particles. Performance of TBAC in this pulp toward further selective pull of non-metallic values after NHR pull has subsided appears promising. In consideration for depressant application, it is clear that CMC is not an effective depressant in this system, while gamma depression is more effective. Betamin 127A as a reagent for gamma depression can easily depress everything, except at dosages below 10 ppm.

Generally, the overall response obtained from the chemical condition is poor and a number of reasons can be advanced. A higher reagent (xanthate) dosage, for instance, shows the projected response exists, but the alloy surfaces may be relatively inert. Reactivity of minerals compared to end use alloy surfaces could be expected to differ. Engineering alloys have gone through definite finishing alloying treatment processes to make them stable materials that end-use applications demand. This would make the surface inert except to harsh environment which a flotation system may not represent. Oxidation of the metallic surface is another factor that could be responsible for the observed response. Oxides are generally expected on the surface of metallic particles, and the little improved response observed on sulfidation supports this.

Another strong reason that could be presented is the high calcium content of the sample. At about 7% content, far above all other target elements in this sample, any effect due to calcium in the response to the treatments would be overwhelming. Depression due to calcium is known in lime application for alkalinity regulation. It would be difficult to condition the system to respond in a manner opposite to the effect of this bulk constituent.

Follow up investigations on these probable causatives were informative. An ICP-MS trace element scan of the process water showed a calcium concentration in the process water of up to 7 ppm. This is equilibrium level in pulp. If any activity depletes it, it can be restored from the 7 wt. % reserve in the sample. SEM investigation of the particles showed calcium present in the glass fibres, which constitutes the bulk of the sample. Hence, if calcium is depressing anything, there would be sufficient supply to do this effectively.

Surface investigations, starting from FE-SEM showed surface of metallic particles to be charging under an electron beam, indicative of a non-conducting surface coating. This could be an inert organic layer, the presence of which would hinder reagent activity. Auger depth composition profiles on many particles of PCB comminution products further confirm this. The surface layers range from fully organic to metal oxides. None of the surface is pure alloy. Process water also leaves species that could interfere with reagent activity on the surfaces. This provides evidence for explaining the observed responses.

In summary, the prospect of chemical conditioning in PCB CF flotation has been investigated across logical froth flotation schemes. However, the flotation system that PCB CF presents is an interesting challenge to the versatility of froth flotation. The results gave indications of what may or may not work in this prospect. This provides a good basis for further investigation. Such investigation may first be for pure characteristics or phenomenological quest and not necessarily for functional scheme. A whole investigation can focus one specific reagent, thereby generating broader understanding of how the system behaves and its peculiarities. Upon such further understanding, more functional schemes may then be sought.