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Paper No. 457

KINETICS AND EFFICACY OF FROTH FLOTATION FOR THE RECOVERY OF METAL VALUES FROM PULVERIZED PRINTED CIRCUIT BOARDS

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ABSTRACT

Printed circuit boards (PCBs) constitute a major part of electrical and electronic equipment containing valuable metals such as Cu, Ni, Au, Ag, Pd, Fe, Sn, Pb, etc. The concentration of base and precious metals in PCBs is observed to be several times more than those in their respective ores. Therefore, the recycling of PCBs is necessary to recover the valuable materials. However, the ultrafine particles pose a big challenge. Removal of them is suggested prior to processing by flotation. Froth flotation is observed to be a promising technique for rejecting the plastics from the comminution product. In the present work, enrichment of ground 1.0 mm PCB powder was investigated through flotation route by varying the operating variables such as frother dosage, pulp density, air flow rate and rotational speed of the impeller. The liberation studies indicate that excellent liberation of metal values is achieved from the non-metallic constituents at –1.0 mm size and below. The particulate system is quite rich in metal value with about 23% total metal content. The non-metallic constituents such as plastics are observed to possess strong hydrophobicity while the metal particles in the pulverized mass are hydrophilic in nature. Froth flotation kinetics is studied in depth with a view to facilitate high rejection of plastics and identify optimum operating conditions for the same.

A number of experiments are performed to establish the influence of the operating variables on flotation performance. The conditions for achieving higher yield of the metal-rich fraction with respect to a specified grade are discussed in the light of the experimental results. It is found that the requirement of reagents is negligible which could be a very important factor from the commercial stand point. Single-stage flotation increases the metal content from 23% to over 32% with a mass yield of around 75% and over 90% recovery of metal values. 32% of the materials in the feed could be effectively rejected in the float fraction losing less than 4% metal values. The dependence of kinetics on the process variables is also discussed. It was concluded that a high rotor speed helps in efficiently rejecting the plastics. Frother should be added to help stabilize the froth and enhance the kinetics. A moderate air flow is required while pulp density must be kept low for efficient pre-concentration. It is established that the entire –1.0 mm comminution product could be treated by flotation for generating a pre-concentrate.

Keywords: printed circuit boards, recycling, froth flotation, kinetics, recovery

INTRODUCTION

The issue of electronic waste has been taken into consideration not only by the government but also by the public due to their hazardous substances which are harmful to human health and the environment. The disposal of these requires special treatment to prevent the leakage and dissipation of toxics into the environment (Cui and Zhang, 2008; Niu and Li, 2007; Nnorom *et al,* 2007, Widmer *et al,* 2005, Cui and Forssberg, 2003). The printed circuit board (PCB) is a major constituent of these obsolete and discarded electronic scraps containing valuable metals

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such as Cu, Ni, Au, Ag, Pd, Fe, Sn and Pb etc. Physical (or mechanical) processing is recognized as the most environmentally friendly alternative for resource recovery from end-of-life printed circuit board (Goosey and Kellner, 2002, 2003). It has been noted that froth flotation can be an effective enrichment technique towards recovery of values from –75 μm comminution fines (Ogunnyi and Vermaak, 2007). Assessing this as an applied minerals processing problem, froth flotation has been advanced as a promising beneficiation technique for this fine fraction (Ogunnyi and Vermaak, 2009). Froth flotation has also been applied in processing of municipal solid waste (Shen *et al,* 1999; Dodbida *et al,* 2002; Alter, 2005). PCB fines consist of mixture of particles of metals, alloys, ceramics, and plastics, each with distinct surface properties that should enable selective wetting and make froth flotation separation possible. The fine plastic particles are expected to float under their natural hydrophobicity, thus making it possible to achieve an initial bulk metallic enrichment of the sink before attempting any surface conditioning for further selective floats. This implies a reverse flotation in respect of metallic values.

The breakage characteristics of metals and the non-metals in the PCBs are drastically different. Good liberation requires size reduction in a fine range. In the process, significant amount of ultrafines are generated although these are not desirable. The fraction less than 75 micron poses a big challenge in the recovery of metal values. However, the removal of the ultrafines in a large scale operation could be another challenging task considering the low density of the plastics. In view of this, the present study was undertaken to investigate the possibility of using flotation as a pre-concentration step for the entire –1.0 mm material. The influences of the process variables such as frother dosage, pulp density, air flow rate and rotational speed of the impeller on the effectiveness of plastic rejection were studied. The dependence of the overall flotation rate on the operating variables was also investigated.

MATERIALS AND CHARACTERIZATION METHODS

Raw material preparation

100 kg of waste PCB is procured from different sources. These boards are cut into small pieces using mechanical shearing machine and then down to a size of about 3–5 mm by a shredding machine. These small pieces were then subjected to dry grinding in a ball mill to a top size of 1.0 mm. The ball mill was intermittently stopped, and the fines taken out by screening in order to prevent the generation of ultra fines. The grinding process was terminated when all the material was less than 1.0 mm in size. The pulverized PCB powder was used as the feed material for further characterization and flotation studies.

Size distribution

Pulverized PCB was subjected to size analysis by wet sieving, and the results are shown in Table 1. It is observed that a significant amount of fines (–35 micron) is generated during pulverization. A substantial amount remained in the 1000 × 500 micron fraction. Nearly half of the material was in the size range of 500 × 35 micron.

Liberation studies

Liberation analysis was also performed to know the degree of interlocking in each size class using stereo zoom microscope. Four hundred frames were counted for each size. In each frame, the numbers of free metals, free plastic and interlocked metal-plastic pieces were counted. The number percentages of each type were computed from the overall counts which exhibited the liberation pattern of the starting material. The liberation data of the ground powder is also shown in Table 1. From this Table, it is seen that the coarsest (1000 × 500 micron) size class contains only about 5% (by number) interlocking of metallic and non-metallic constituents. Interlocking is not observed below 150 micron size and the metal values are adequately liberated in the pulverized mass. Hence, it was decided that the grind size for adequate liberation should be 1.0 mm.

Table 1. Size analysis and microscopic liberation data for the powdered PCB scrap

Size (microns)	Weight (%)	Liberation Analysis (Number %)		
		Free Metal	Interlocked	Free Gangue
1000	26.64	18.3	5.3	76.4
500	15.07	17.4	3.2	79.4
300	10.79	15.6	1.3	83.1
150	6.89	13.4	0	86.6
100	4.42	11.2	0	88.8
75	7.40	9.3	0	90.7
50	2.86	-	-	-
35	25.93	-	-	-

Chemical analysis

Chemical analysis of the head sample of the powder as well as that of each size fraction, was carried out, and the analysis data are shown in Table 2. It may be seen from Table 2 that the total metal in the powdered sample is around 23%. This powder mainly contains 6.3% Cu, 2.7% Pb, 2.7% Sn, 3.0% Al and about 0.1% Ni. It is evident that the metal content decreased significantly in the finer size fractions. Al is mainly obtained from the capacitors where it is in the form of thin foil. During grinding the size reduction for these are mainly due to shear which is reflected in relatively uniform distribution of Al over the size classes. For other metals attrition is the primary mode of size reduction which is reflected in decreasing concentration of them in lower size classes. Ni concentration is too low to have any practical significance from recycling standpoint.

Table 2. Chemical analysis of the powdered PCB scrap

Size (microns)	Cu (%)	Pb (%)	Sn (%)	Fe (%)	Al (%)	Ni (%)	Total Metal (%)
Head Sample (analyzed)	6.3	2.73	2.67	3.08	7.93	0.113	22.94
1000	8.89	3.96	3.54	4.22	7.92	0.112	28.78
500	8.04	3.02	3.04	3.94	7.41	0.122	25.67
300	7.26	2.75	2.64	3.14	7.18	0.134	23.24
150	6.28	2.27	2.04	3.01	7.6	0.126	21.44
100	5.29	1.87	1.81	2.89	7.55	0.131	19.64
75	4.22	1.49	2.17	2.83	7.51	0.156	18.44
50	3.78	1.29	2.03	2.56	7.78	0.103	17.65
35	2.67	1.23	1.63	1.83	7.02	0.093	14.59
Head (Calculated)	6.14	2.51	2.55	3.15	7.46	0.116	22.04

Sink-float analysis

In order to have an understanding of metal content in the powder, it was subjected sink-float analysis in heavy liquid. A mixture of bromoform and benzene with a specific gravity of 2.0 was used as the heavy liquid. The specific gravity of the plastics was lower than 2.0 while all metals were having a specific gravity more than 2.0. Hence, liberated metals sank in the liquid while liberated plastic particles floated. However, depending upon the proportion of plastics in the interlocked particles they sank or floated. The data are given in Table 3. It is evident from Table 3 that the finer fractions contain lower quantity of metals. In the larger size classes, the metals embedded in plastic also reported in the sink.

Table 3. Sink-float analysis of the powdered PCB scrap

Sample ->	Head	-1000 +500	-500 +300	-300 +150	-150 +100	-100 +75	-75 +50	-50 +35	-35
Sink (%)	31.4	40.0	36.6	32.2	29.7	26.1	23.5	19.7	12.2
Float (%)	68.6	60.0	53.4	67.8	70.3	73.9	76.5	80.3	87.8

EXPERIMENTAL

The non-metallic particles possessed a high degree of hydrophobicity while the metallic particles were strongly hydrophilic in nature. It is also known that flotation performance is better if the feed size range is relatively narrower. The difference in the degree of hydrophobicity between non-metals and metals is exploited using froth flotation. In this operation, the hydrophobic plastic particles are separated from the hydrophilic metal particles by reverse flotation using only a froth stabilizer. The hydrophobic plastic particles are made to attach with the air bubbles and float to the top while the metal particles remained in the pulp. Metallic particles will have high surface energy, be hydrophilic (Gupta and Yan, 2006) and therefore, prefer the sink. Density advantage is also expected here to enhance the separability between denser hydrophilic metallic particles and lighter hydrophobic particles. The froth stabilizer is used to ensure that the bubble-particle aggregate is stable, and there is no detachment of the bubble-particle assembly.

Bench scale flotation tests were performed with 500g of −1.0 mm PCB powder for each experiment in a WEMCO laboratory cell of the Fagergren type with a cell volume of 2.7 litres. The pulp was conditioned for about 15 minutes. Plastic particles possess natural hydrophobicity and are expected to float while metal particles, being hydrophilic, should remain in the pulp. This is essentially a case of reverse flotation with respect to the metal values in which the undesirable materials float and the valuables remain in the pulp. Considering the fact that the plastic particles which are to be floated, are of low density it was decided that a relatively larger size of the feed may be used. It was envisaged that the fine plastic particles may lack the necessary momentum to rupture the bubble film for effective attachment, the probability of these particles floating are likely to be less. However, it would be extremely difficult to remove such low density ultra fines from the feed in an industrial scale. Therefore, it was decided to investigate the flotation of the whole −1.0 mm feed in this study.

Several flotation experiments were performed to establish the influence of four operating variables on the separation performance. The four operating variables studied were stirrer speed, frother dosage, pulp density and air flow rate. The conditions for these experiments and the concentration response in the form of yield and grade are shown in the Table 4. The product samples were collected, dried, weighed and analyzed for total metal content (grade). The flotation response is quantified in the form of yield of the metal-rich tailings and the total metal content (grade) in it. The recovery of the valuables was also estimated. It is seen from this table that the yield varies from 67% to 80% and while the grade obtained varies from 26.8% to 32.3% total metal. Over 90% recovery was achieved under all circumstances.

In order to have an idea of the flotation rate, kinetic studies were undertaken. For each experiment, float samples were collected at 0.5, 1.0 and 2.0 minutes. The float fractions were dried, weighed and analyzed for total metal. In order to understand the kinetics these data were processed assuming a first order rate equation. The rate equation can be written as follows:

$$kt = \ln [1/1-R] \qquad (1)$$

Where R is the recovery of metals at time t (min) and k is the rate constant

A plot of the right hand side of the above equation against time gives a straight line with a slope ‘k’, the rate constant. The rate constants were estimated from the plots for all experiments. Table 4 also lists the of rate constants obtained under various operating conditions.

Table 4. The flotation experimental conditions

Expt. No.	Stirrer speed (rpm)	Frother dosage (kg/t)	Pulp density (%)	Air flow rate (lpm)	Yield (%)	Grade (%)	Recovery (%)	Rate Constant K (/min)
1	1000	2	6	20	70.1	31.0	94.7	0.3332
2	1200	4	9	20	67.5	32.3	95.0	0.3944
3	1000	2	9	35	75.2	27.3	89.5	0.2835
4	1100	2	12	5	76.8	27.7	92.7	0.2828
5	1100	0	12	20	76.6	28.1	93.8	0.2585
6	1200	2	9	35	75.5	27.7	91.2	0.2680
7	1200	2	12	20	68.3	32.3	96.2	0.3979
8	1100	4	9	35	72.4	29.5	93.1	0.3086
9	1100	2	6	5	79.9	26.8	93.3	0.2264
10	1000	0	9	20	75.5	28.4	93.5	0.2712

RESULTS AND DISCUSSION

Beneficiation by froth flotation

The loss of metal values in the float fraction was of primary concern in this study. A few exploratory tests indicated that a purer grade may be achieved at a much lower yield of the valuable stream along with significant metal loss in the froth. Therefore, in this study a better recovery was aimed at rather than a purer grade. This may serve as a pre-concentration step.

From the characterization data, it was noted that 77% of the feed is plastic which is being targeted for flotation. Since, the density of the plastic particles is low in terms of percentage of plastic particles by number, it would be much higher. Therefore, it was envisaged that a low pulp density and a high aeration rate need to be used. Higher impeller speeds produces finer bubbles and also increases turbulence. These will increase particle-bubble collision frequency (Duan *et al,* 2003; Pyke *et al,* 2003), which is a precursor to attachment. Smaller bubbles also improve fines recovery to float (Pease *et al,* 2005). However, higher turbulence can also increase entrainment and lead to metal losses.

The grades of the valuables stream are indeed low. Evidently, not a great deal of enrichment has taken place. However, it should be noted that nearly 20–30% of the material is rejected in the float fraction with very little loss of metal values in the float fraction. Above 90% recovery under all circumstances corroborates this.

The mass yield in the sink is highest in Expt. No. 9. However, the grade is poor as the air flow rate is low. Low rejection of plastics is attributed to inadequate air availability. The best grade of the sink is obtained in Expts. 2 and 7. In both these cases, the impeller speed was high. This ensured larger number of bubbles and good turbulence which enhanced the bubble-particle collision frequency. Expts. 5 and 10 reflect the effect of adding no frother. The low grades of the sink under these conditions indicate that the stability of the froth is seriously compromised which led to drop back of the plastic particles in the pulp. The effect of a high aeration rate can be seen from the results of Expts. 3, 6 and 8. The recovery of valuables in the sink is low under these conditions signifying greater entrainment of valuables. The large number of air bubbles available under these conditions lead to the high entrainment. The level of air flow is probably excessive which leads to a highly turbulent pulp. Consequently, detachment of bubble-particle assembly increases and the grade of the sink decreases. In the range considered, the effect of pulp density is not much. However, the pulp density needs to be kept low in view of the large concentration of plastic particles in this reverse flotation.

Kinetic response

The values of the rate constant indicate that the flotation rates are only moderate. The extents of fit of the kinetic responses to Eq (1) can be seen in Figure 1 which depicts a high, intermediate and low flotation rate as obtained in this study. All the conditions resulted in good correlation indicating that the observed response conforms to first order flotation kinetics. The reasons for the attainment of such rates in these tests are discussed along with other experiments below.

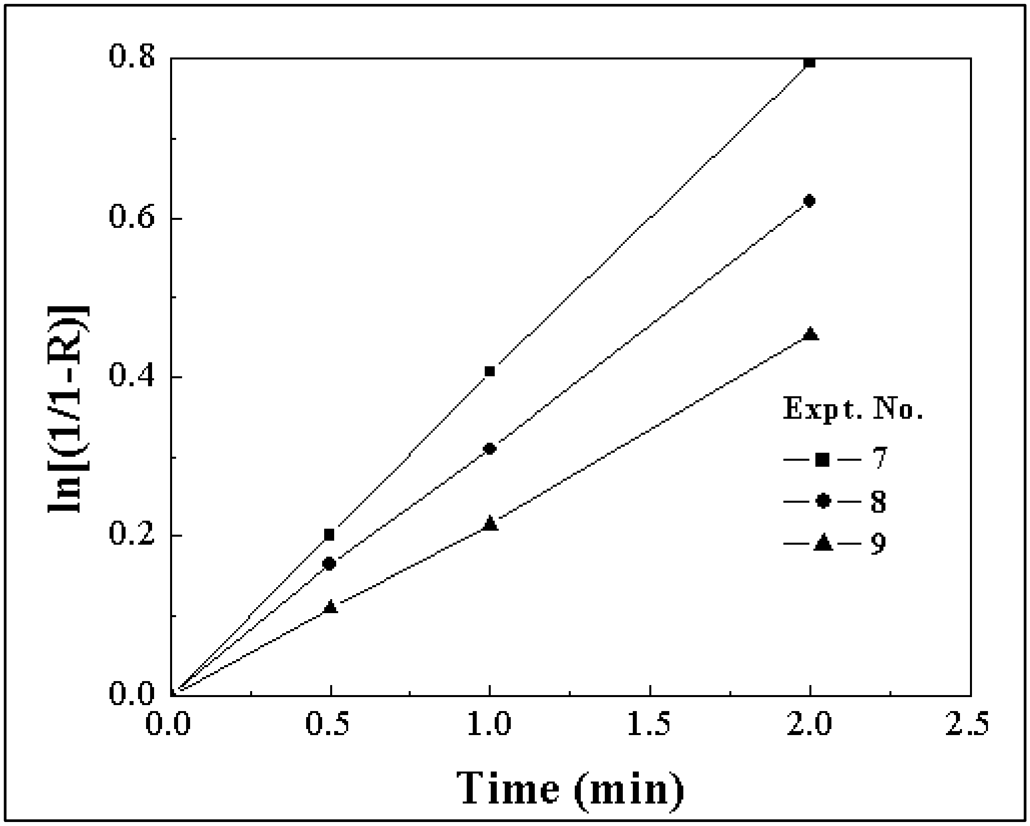

Figure 1. First order fitting of flotation responses under various process conditions

As seen from Table 4, highest k values are obtained in Expts. 2 and 7. The air flow rate was moderate in both cases indicating appropriate concentration of air bubbles and degree of turbulence. A high pulp density in Expt. 7 enhanced collision frequency and a high frother dosage in Expt. 2 ensured proper stability of the froth. Another important feature in these cases is the high rotor speed. It helped in having a high concentration of bubble and a good degree of turbulence. Light plastic particles acquired adequate momentum to partially rupture the bubble film which enhanced the probability of attachment. These features led to favorable conditions for flotation due to which higher flotation rates were obtained. Inadequate air flow resulted in a poor flotation rate for expt. No 9. Also, when no frother was added the rate of flotation was observed to be poor due to low froth stability (expt. No. 5 and 10). At very high air flow rate, the rate of flotation was again poor due to detachment (expts. 3 and 6). However, other favorable conditions improve the flotation rate in expt. 8 to some extent in spite of a high air flow rate. Under all other conditions, moderate flotation rates were observed.

System response

The system response is shown in Figure 2 in the form of variation of yield and recovery with the grade of the valuable fraction. The figure indicates that the yield of the valuable fraction drops sharply as a better grade of it is targeted. However, the recovery values remain almost similar under the conditions tested. There is a small increase in the recovery at high target grades under specific conditions. Of course, these should be the preferred conditions for the pre-concentration targeted in this study. It indicates that Expt. 7 gives the best conditions. Under these conditions, less than 4% metals are lost in the float fraction. A low yield of the sink indicates very effective rejection of plastics in to the froth. Nearly one third of the feed is reporting to the float fraction with very little metal value in it. As discussed above, effective rejection of plastics under these conditions is attributed to good stability of the froth, high concentration of air bubbles, appropriate turbulence level, high collision frequency and adequate momentum of plastic particles.

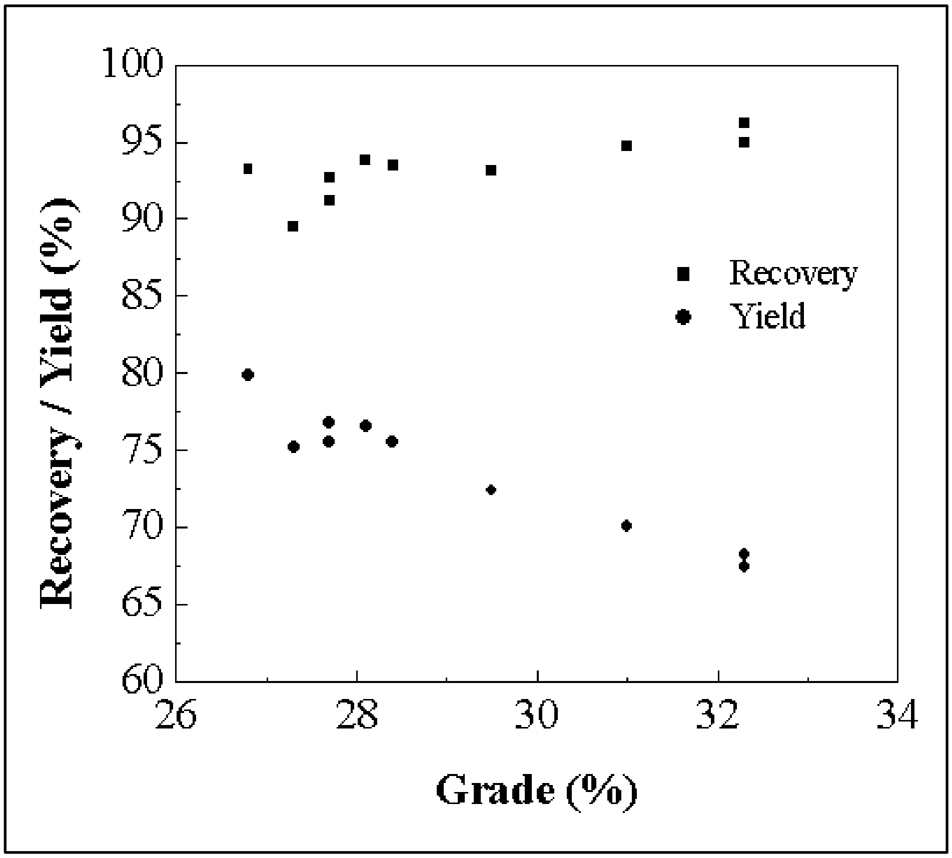

Figure 2. Grade vs. recovery / yield curve for all the experimental conditions

CONCLUSIONS

The –1.0 mm comminution product of e-waste can be treated using flotation. However, if the ultra fines are not removed from the feed effective enhancement of the grade cannot be achieved. It can be used only as a pre-concentration. However, effective rejection of plastics could be obtained under specific conditions. A high rotor speed is essential for efficient rejection of plastics. A moderate air flow is also essential. Too high or too low aeration rate affect flotation performance adversely. Pulp density should be kept low. Addition of frother helps significantly in stabilizing the froth leading to good flotation performance. Since, removal of light ultra fines pose a major problem in fine PCB processing, collector less flotation may serve the purpose of effective pre-concentration.

ACKNOWLEDGEMENT

The financial support from the Ministry of Environment and Forests, Govt. of India for carrying out the research is gratefully acknowledged.

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