## T. P. 1198

# Electroflotation—A critical review

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#### ABSTRACT

Flotation of fine particles has been gaining technological importance in recent years. Various attempts are being made for the beneficiation/purification of low grade ores/waste water from different industries Electroflotation is one such method which performs an effective separation of fine slimes that resists the usual methods. In the present paper, problems encountered in the separation of fine particles are described. The peculiar advantages of electroflotation are also outlined. The background of electroflotation technique and its applications in various fields are discussed with a little emphasis on the flotation of fine minerals.

### INTRODUCTION

The use of electrolysis for obtaining gas bubbles in the process of mineral beneficiation was suggested by Elmore in 1904<sup>1</sup>. Electroflotation-"Flotation by electrically generated bubbles as a means of separating solid from liquid phases or one liquid phase from another" has been discussed in earlier papers2". This technique gained the attention of many researchers when it was first adopted in the field of waste water treatment in 1965. Colloidal or finely dispersed particles in sewage systems are removed by introducing very small bubbles (oxygen/hydrogen-by means of electrolysis) which are able to lift even the smallest particles to clarify the solution4. The commercial success of electroflotation is reported to be very effective in the fields of silk and meat industries, leather industries, oil refinery and also in steel plants. However this technique has been confined mostly in USSR and sparcely in Germany, Japan and U.K.

The wide application of electroflotation in the field of mineral processing aroused after the thorough analysis of hydrodynamics in the flotation system. The behaviour of fine particles in a flotation cell involves complicated hydrodynamics. The effect of particle size on the flotation behaviour was first attempted by Gaudin et al<sup>5</sup>. The best recoveries were obtained in the size range 20-50  $\mu$ m. As reviewed by earlier workers<sup>6-9</sup> large specific surface area and the small mass of the particles affects flotation in a number of ways. Because of their small mass and momentum fine particles will be carried into the froth after getting

entrained or mechanically entrapped causing a reduction in the grade. On the other hand small mass of the fine particle will decrease the collision and adhesion probability. Several articles have appeared in recent years predicting certain models on collision and adhesion of fine particles to bubbles<sup>10–12</sup>. Though the detailed examination shows that more phases are involved, according to Derjaguin and Dukhin two phases are more important in the elementary flotation act.

(1) Surface of the particle approaching the bubble and (2) fixing of the particle on the bubble. Changing over from coarse to fine particles the mechanism of flotation process changes qualitatively both in approaching and fixing stages. Sufficiently large particles move under the effect of inertial forces in an almost rectilinear way until it colloides with the bubble surface. The smaller the particle size and the difference between its density and that of the medium, the smaller will be the inertial forces acting on it and the more exactly does the particle trajectory coincide with the liquid flow lines shown in Fig. 1. The bubble distorts the liquid flow lines and thus bends the trajectory of fine particles—that is it affects them hydrodynamically through the liquid velocity field. In the case of coarse particles the inertial forces are considerably greater than the long range hydrodynamic inter-action forces and the particle could overcome these forces by an inertial impact on the bubble surface which will finally lead to three phase wetting contact. In the case of flotation of fine particles the formation of wetting parameter is redundant. The difficulty in fixing the fine particles on the surface of

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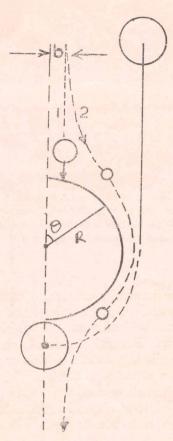


Fig. 1 The influence' of the inertia of the particles on their trajectory in the vicinity of the floating bubble
Line 1—Trajectories of the coarse particle
Line 2—Trajectories of the fine particle
Particles at the same target distance "b"

the bubble due to the necessity of overcoming the energy barrier was explained by Sheludko<sup>13</sup>.

Calculations based on the assumption that a fraction of the bubble surface is available for transporting particles and without regard to how the particles reach the bubble, indicates that the transport is proportional to Qafdp/db

where

Qa=aeration rate f=Fraction of the bubble area covered dp=Particle diameter

and db=Bubble diamer

More sophisticated modelling based on interception theories reveals that the collection efficiencies are depending on the ratio  $(dp/db)^n$  with the exponent usually in the range of 1.5 to 2.0.

Considerable interest has been shown to the production of bubbles of the most effective size with desired characteristics. A given volume of air will have more surface area if finely dispersed and can accommodate more solid particles on its surface. Though not it is impossible, it is comparatively expensive to disperse the gas. The buoyancy of the large bubble is so high that it rushes to the surface with less opportunities for particle-bubble encounters. It also creates turbulence in the frothing zone which is quite undesirable. Considering these types of problems Sutherland<sup>14</sup> proposed that to achieve better collision, the particle should have the bubble of the same radius. Based on the above analysis vacuum flotation and electroflotation were developed to have smaller bubbles approximately equal to the dia of particles. Vacuum flotation technique has its own limitations in the plant scale and also in the investment cost, whereas electroflotation technique is fully advantageous.

### Some peculiar advantages of electroflotation

The process of electroflotation leads to the formation of extremely finely dispersed gas bubbles. The average size of the gas bubble in conventional flotation is of the order of 0.9 to 2.0 mm whereas the electroflotation ensures the generation of large quantities of finely dispersed gas bubbles ranging from 8 to 15 microns. Apart from this, bubbles produced by electrolysis are homogeneous in size. The size of the desired bubble generation can be thoroughly controlled by chosing various metal electrodes with various surface geometries. A predetermined size of the bubble can be produced with a wire mesh of a particular gauze. Desired distribution curve of a bubble can be achieved by varying the parameters like current density, temperature, concentration and the pH of the electrolyte. The results of the investigation regarding the dependence of the size of the bubble on the pH value and the electrode material are shown in Fig. 2.

The size variation of the bubbles tends to follow a trend opposite to that of the excess ion, i. e. the hydrogen bubbles are larger in an acid medium than they are in a neutral or alkaline medium. The minimum bubble dimensions occur in a neutral medium (no matter what cathode material is used) and in an alkaline medium. In the acid medium the effect of the cathode material on the size of the bubbles is extremely pronounced. The value of the mean bubble

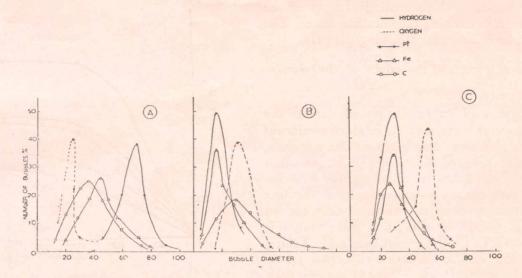


Fig. 2 Effect of electrode material and pH of the medium on the bubble dimensions. Current density: 25 mA/cm<sup>2</sup>, Electrode diameter: 0.4 mm, Temperature: 20°C. A. pH; 2.0, B. pH; 7.0, C. pH: 12 0.

diameter being found to vary in the range between 20 and 70 microns. The different cathodic metals affect the bubble size according to their position in the electromotive series. The effect of the cathode material on the dimension of the hydrogen bubbles becomes less marked in an alkaline medium, the mean diameter of the bubble varying between 15 and 30 microns. In the neutral medium the size of the hydrogen bubbles is practically independent of the cathode material, mean diameter of the bubble being found to be limited to the range between 15 and 20 microns.

The bubbles of oxygen formed on a platinum electrode attained a minimum size 25 microns in an acid medium and the diameter then increased as the medium become first neutral and then alkaline (30 to 55 microns respectively). When the pH is about 6.0 the distribution curves of the two gases come very close to each other. Thus the so called absolute control of the bubble size can be easily achieved by varying the pH value of the medium and the electrode materials.

The electrode material should be chosen in such a manner as to be practically insoluble in liquid phase of the pulp. Platinum, copper, tin and silver wires as well as stainless steel wire, graphite rod with a diameter of 0.2 to 1.0 mm can be used as electrodes. Platinum, graphite, nickel coated stainless steel can be used as anodes. The circuit diagram of electroflota-

tion machine is shown in Fig. 3. The current is supplied through a rectifier and the parameters of the electrode unit are measured by an ammeter and a voltmeter. The pump of the thermostatic bath supplies the electrolyte at a constant temperature to the constant level tank, from where it passes at constant pressure through a valve into the intraelectrode space. The excess electrolyte is allowed to return into the thermostatic bath through an overflow funnel. The current conducting membrane (diaphragm) serves the dual purpose of confining the pulp

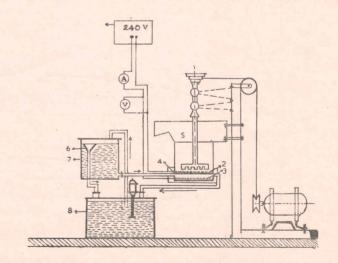


Fig. 3 Circuit diagram of electroflotation machine
1. Power supply, 2 & 3 Electrodes, 4. Current conducting membrane (diaphragm), 5. Flotation chamber, 6. Overflow funnel, 7. Constant level tank, 8. Thermostatic bath.

in the upper region and preventing the gas of the lower electrode from entering the flotation zone. The electrolyte can be reused after adjusting the pH.

# Physico-chemical aspects of the effect of the electrolytic gases on the surface of the mineral

The hydrogen and oxygen liberated during the process of electrolysis are apt to produce significant changes in the surface conditions of the minerals, owing to the absorption of these gases. The gases that liberate from the electrodes are in very active state i.e. in the form of their atomic states. In spite of the fact that these forms remain in existance only for an extremely brief period of time, and this duration is sufficient to interact with the mineral surface. Taking advantage of the surface oxidation-reduction transformations of the mineral surface some of the minerals can be beneficiated without the collector additions. Glembotskii et al<sup>15</sup> in their investigation on the flotation of pyrite with oxygen bubbles were able to have the recovery upto 98% without the need of reagent. It is apparent from the Fig. 4 that electrolytic oxygen makes the surface of the pyrite strongly hydrophobic that there is no need to use a flotation reagent at all. Similar results were obtained on the flotation of chalcopyrite fines<sup>16</sup> as shown in Fig. 5.

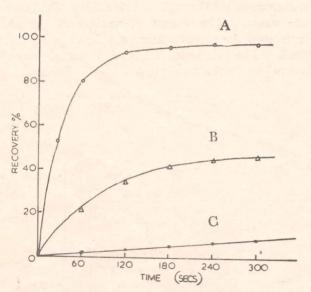


Fig. 4 Pyrite recovery as a function of flotation time

- A. Flotation of pyrite without reagent with oxygen bubbles.
- B. Flotation of pyrite with hydrogen bubbles in the presence of collector amylxanthate
- C. Flotation with air in the presence of collector (Collector consumption 150 g/t)

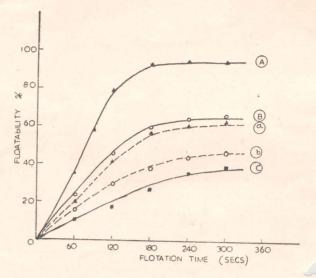


Fig. 5 Floatability of chalcopyrite

- A. Flotation with electrolytic oxygen Collector K. Et. X: 140 mg/lit Current density: 111 mA/cm²
- B. Flotation with electrolytic hydrogen Collector K. Et. X: 140 mg/lit Current density: 196 mA/cm²
- C. Flotation with cylinder oxygen flow rate 0.5 lit/minute Collector K. Et. X: 140 mg/lit.
- a,b (dotted lines) represent without collector

Mamakov et al<sup>17</sup> beneficiated cassiterite by activating the surface with hydrogen bubbles. Thus electroflotation can be effectively utilised in the separation of minerals particularly the sulfides which are very sensitive to oxidation reduction changes.

In certain cases the anodic and cathodic potentials suitable to the maximum flotation can be provided by adjusting the current density.

The disadvantage of the technique is the control of the pH of the system. Since OH-/H+ ions are continuously released into the system the changes in the pH during the process is difficult to control. Higher the current density, higher the changes in the pH of the pulp. This doesn't have much effect where the selectivity vary in wide range of pH. The nascent gases liberating from the electrodes will affect the unabsorbed reagent and also the surface compound. The collectors that are sensitive to oxidation-reduction changes will be distructed due to these gases. Thus the recirculation of the unabsorbed collectors is not possible. So the selection of the collectors should be in such a way that they are least affected by the gases. Collectors like xanthates are more useful, because

even the oxidation product dixanthogen is also a good collector for sulfide minerals.

# Electroflotation in the field of mineral beneficiation

In 1970 Mamakov et al<sup>17</sup> introduced the electroflotation for the beneficiation of cassiterite. The electrodes were separated by a diaphragm to separate the gases. C7-C9 aliphatic acids were used as collectors. The separation was improved by using hydrogen bubbles generated from the cathode. Hydrogen reacts with the surface according to the equations.

$$SnO_2+H\rightarrow SnO_2H$$
 ... 1  
 $SnO_2H+HA\rightarrow SnOA+H_2O$  ... 2

The removal of diaphragm reduced the efficiency. It may be due to the cassiterite surface was inactivated by oxygen. Compared to the conventional flotation, separation of the cassiterite was exceeded by 20%.

Electroflotation tests of manganese minerals like pyrolusite and psilomelane were compared with the column flotation technique<sup>18</sup>. The extraction of manganese with hydrogen bubbles generated electrolytically was 92-95%, which is 10 times greater than column flotation. Electroflotation of uranium by using Al, Fe and Mg as supporting electrodes was attempted by Turovtseva<sup>19</sup>. Hydroxides of Al and Fe will act as carriers of uranium hydroxides bringing the purification level to 98% and 92% respectively.

Glembotskii et al<sup>15</sup> adopted electroflotation for the beneficiation of pyrite, manganese slimes and the recovery of fine diamonds. The recovery of manganese slimes (-10 µm) by electroflotation reached 60% from the feed value of 9.5%. Attempts on the recovery of diamonds by conventional flotation methods are quite unsatisfactory whereas by electroflotation technique, complete recovery of diamonds was demonstrated. Thus utilization of raw materials that cannot be beneficiated by any other existing process is possible by means of electroflotation.

98% of pyrite was recovered by using electrolytic oxygen bubbles alone. Electroflotation experiments on the recovery of chalcopyrite followed the same pattern. Conventional Hallimond tube experiments with cylinder oxygen hardly gave 35% recovery whereas electroflotation resulted in 62% and 47% respectively with oxygen and hydrogen without reagent. Thus the role of the size of the bubble is quite apparent. Significant effect was observed by electrolytic

oxygen on the flotation of sulfide minerals. Electrochemical investigations on the flotation of sulfide minerals in the presence of oxygen was thoroughly established by the earlier workers<sup>20–21</sup>. Controlled oxidation by the oxygen will form an elemental sulfur on the surface of the mineral giving sufficient hydrophobicity for the bubble contact.

### Example

$$CuFeS_2+O_2\rightarrow CuS+Fe^{2+}+S+2e$$

Thus lowering or complete elimination of collector consumption is possible. From the Figs. 3 and 4 it is apparent that the rate of flotation was highly improved.

Electroflotation of mixture of electrolytic gases provides high recoveries of ferrocyanides, oxy-quinolates and hydroxides of Cu, Ni, Co, Ti, Zn and Mo<sup>22</sup>.

However electroflotation tests on cassiterite<sup>23</sup> showed that the process of electroflotation was 10 times costlier than the ordinary flotation. But these calculations were based on use of mixed bubbles instead of exploiting the surface changes by hydrogen bubbles alone. Whatsoever, this technique is unique where the problems were not solved by conventional flotation technique.

#### Electroflotation in the field of metallurgical industries

Recovery of Co, Zn, Cu, Ni, Fe etc from the waste waters of metallurgical industries were effectively done by electroflotation method. Golman<sup>23</sup> suggested the removal of non-ferrous metals Cu and Zn from brass rolling mill waste water by precipitation with Na<sub>2</sub>CO<sub>3</sub> or NaOH or Ca (OH)<sub>2</sub> and separation of these precipitates by electroflotation. A more efficient and less expensive precipitation recovery operation for Cr<sup>6+</sup> from cooling tower blow down water was established<sup>24</sup>. Flotation was carried out with hydrogen bubbles with the reagent dodecyl sodium sulphate or quantarnary ammonium salt as a promotor.

Waste water from cadmium plating industry was clarified by electrolysis by using Al as anode<sup>25</sup>. A strong flocculant Al (OH)<sub>3</sub> from anode is found to be more effective than conventional AlCl<sub>3</sub> or alum. The presence of cadmium even at low PPM (10) was removed/recovered by 75-80% with the collector solution of sodium dimethyldithiocarbamate which is somewhat impracticable<sup>26</sup>. Thus the removal of minute quantities of metal values can be easily recovered by electroflotation.

## Waste water from leather industry

Waste water from leather industry will normally carry chromium, fat, surface active agents, BOD and COD and a high amount of suspended solids. Surface active agents and chromium were recovered and amount of BOD, COD and suspended solids were removed by using electroflotation technique<sup>27</sup>. Cr3<sup>+</sup> was removed in the forms of Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> with Ca (OH)<sub>2</sub> to adjust the pH and as coagulant. The froth product was treated to 300°C and the residue dissolved in dil. H<sub>2</sub>SO<sub>4</sub> to separate the chromium. Better procedure was suggested by Revenko and Mamakov<sup>28</sup> without the addition of coagulant. Waste water was electrolysed between Al electrodes and then subjected to electroflotation. The degree of purification was 99.7% to that of 92.8% from coagulation.

## Waste water from textile industry

Suspended particles in a waste water from silk production plant was removed by electroflotation method<sup>29</sup>. A good elimination/extraction of Zn, Fe, used as catalysts was obtained in a purification process of waste water from rayon manufacturing plant<sup>30</sup>. A lengthy but a simple procedure in the treatment of waste water from dying and finishing textiles was suggested31. In the first stage waste water is mixed with NaCl and electrofloated. Separated froth is condensed and passed through an electrolyser with soluble electrodes, a sedimentation tank and finally to electrolyser with insoluble electrodes. The removal of minute amounts of polystyrene from waste water was suggested by Zhurkov et al32. Thus electroflotation technique was more applicable and effective where the water shortage problems are involved.

## Miscellaneous fields

In fact this technique was first applied in the field of waste water treatment. Colloidal or finely dispersed particles in sewage systems are removed by introducing very small bubbles by means of electrolysis. In USSR so many plants were established for this purpose. A waste water solution containing 50% used drilling oil emulsions and detergent wash water was treated with this method. Air introduced through porous plate at the bottom, able to settle the sludge only after 24 hours whereas electroflotation within 15 minutes<sup>4</sup>.

Electroflotation cell was improved further for the purification of waste water by producing extremely

fine bubbles<sup>32</sup>. This was achieved by giving a vibratory motion to one or both the electrodes. Another model was developed by Janusch and Joven<sup>34</sup>. After screening and settling the waste water was pumped continuously through a battery of upright parallel electrolysis cells provided with nozzles in the base to admit air to promote upward movement. Each of the upright parallel cells has an anode and cathode to provide an approximate current flow. The scum collected at the top can be burnt off at the expense of gases generated electrolytically.

Purification and disinfection of waste water is also possible. They used Al and Fe as electrodes. During this process BOD, COD were reduced by 60-80%. the Coli index from  $2 \times 10^9$  to  $2 \times 10^3$ , the pathogenic enterobacteria by 99.9% and the helminth cells by 98.9%. The odour and clarity of the water were so improved due to (1) the production of Al and Fe flocs with a high sorption activity (2) the sterlizing action of the Nascent chlorine from NaCl and the flotation effect of H and O formed electrolytically<sup>35</sup>.

Highly polluted waste waters from the food industry<sup>36,37</sup> were clarified followed by coagulation and electroflotation CaO and FeCl<sub>3</sub>·6H<sub>2</sub>O were used as flocculants.

Waste water from slaughter house was treated using corrodible metals like aluminium as electrodes, current alternating in direction for every 30-3600 seconds<sup>38</sup>. This process was able to reduce the COD from 2500 to 700 ppm. Emulsions and suspended solids were removed by passing the waste water through horizontal electrodes prepared from perforated material<sup>39-41</sup>.

Recovery of Mg from sea water was attempted by electroflotation using hydrogen bubbles. Mg(OH)<sub>2</sub> freshly precipitated in an alkaline circuits posses a significant capacity of undergoing flotation with hydrozen bubbles<sup>42</sup>.

Algae pond effluents were treated with a patented modification of an electroflotation cell<sup>43</sup>, Power requirements were minimised and effectiveness of this process was compared with other methods of treatment.

Purification of waste water from beat sugar industry was also attempted by priliminary coagulation with 0.01% FeCl<sub>3</sub><sup>44</sup>. Efficiency of the process was further improved to 99% using foaming agents like saponins.

Waste water from petroleum refinery was also experimented with electroflotation technique for the removal of oils, present more than 3000 mg/lit<sup>45</sup>,

Method for the rapid removal of ink<sup>47</sup> from the news print with a high pulp recovery efficiency was developed.

Waste waters from fish processing tank containing lipids and extractives were treated by electroflotation method with high protein removal/extraction at isoelectric point<sup>48–49</sup>.

It has its extended route in the treatment of rubber latex wastes<sup>50</sup>, waste water of wood processing<sup>51</sup> and also in dairy industry.

Thus the effectiveness of electroflotation in the extraction of finely disposed solids from the waste waters of hydrometallurgical plants, industrial effluents and in other fields is economically favourable.

Electroflotation makes possible a full and effective recovery of particles that are so finely dispersed as to put them beyond the possibilities of conventional flotation processes.

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