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UTILIZATION OF MINERAL SLIMES AND INDUSTRIAL WASTE

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INTRODUCTION

Several billion tonnes of mineral fines generated during mining, milling and other metallurgical operations are either ignored or treated empirically by conventional mineral processing techniques. In some cases, fines are deliberately produced to liberate mineral values from the gangue, whereas in some processes too fine a material than desired is produced as part of overall process. In clay industry, 90-95% of Kaoline occurs mostly in submicron size fraction. Other examples of oxide ores that must be beneficiated to fine sizes are iron ores containing alumina, magnesite ores containing silica and phosphate ore with clay. Particularly, the loss of valuable material as slime is considerable during the washing stage. For example, depending on the liberartion size and the nature of gangue, approximately 15-40% of ROM is being discarded as slimes from the washings of coal, iron, tin, phosphate, clay and tungsten ores. The problems arising out of slime generation can be visualised by the huge tailing ponds at Florida where 4.5 billion tonnes of water is locked up with nearly 1.5 billion tonnes of phosphate slimes in the pond. Slimes thus discarded are not only a loss of wealth but also pose serious threat to environment. During the monsoon period, suspended solids from tailing dams may reach nearby water streams and lakes and settle in the form of silt which adversely affects the quality of aquatic life. Acid drainage formed from the coal rejects not only leads to serious water pollution problems but also affects the quality of air. It is known that noxious gases like CO, CO_2, SO_2 and H_2S are released into the atmosphere by burning and smouldering of waste material from coal. With an ever growing scarcity of the available water resources, particularly in mining industry, water reuse has a special significance. Hence there is an increasing need for slimes treatment and water clarification.

The steady depletion of mineral resources and the increasing demand for mineral values, coupled with the general policy on mineral conservation, demands the utilization of such wastes and low grade finely dessiminated ores which are abundant. Some of the metal and mineral constituents generated by the iron and steel companies—so also the fines generated during the mining operations of aluminium, clay, phosphate and copper ores and coal mining have potential economic value and their recovery can augment our primary resource supply base. The conventional mineral processing techniques are normally inadequate to treat such fines. In recent years, a cohesive and sustained research in both phenomenological and technological aspects of fine particles has been initiated and various techniques like, flocculation, column flotation, electroflotation, etc. are developed at NML Madras Centre for the beneficiation of mineral fines.

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PHYSICO-CHEMICAL PROPERTIES OF FINE PARTICLES

As the particles become colloidal in size, the mass of the particle becomes very small and the specific surface area becomes large. The influence of these two properties of fines on flotation and selective flocculation is schematically shown in Fig.1. Small mass of the fine particles will decrease the collision and adhesion probability. Several articles have appeared in recent years predicting certain models on collision and adhesion probability of fine particles to bubbles (Derjaguin *et al.*, 1979; Kappor *et al.*, 1973). As the particles become smaller, the mechanism of flotation process changes qualitatively both at the approaching and fixing stages of the particle and bubble. Sufficiently large partiicles move under rectilinear way until they collide with the bubble surface which takes place if $b < r + a$. Since the inertial forces acting on the fine particle are small, the particle trajectory coincides with the liquid flow lines (Fig. 2) and bends the trajectory of fine particles, i.e. 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 interaction 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.

Calculations based on the assumption that a fraction of bubble surface is available for transporting particles and without regard to how the particles reach the bubble, indicate 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 diameter

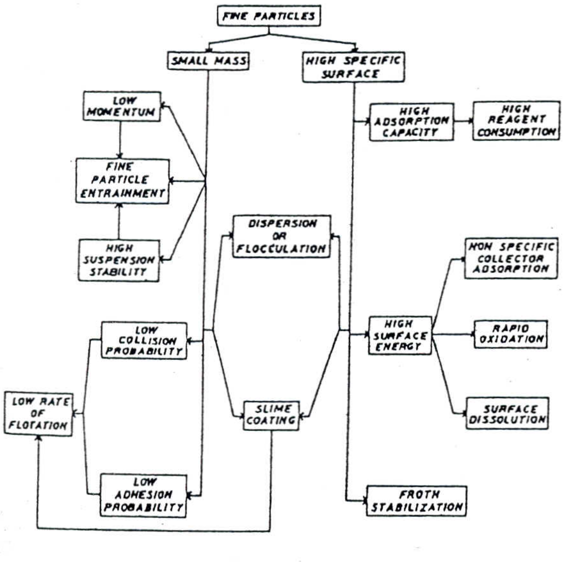

Fig. 1. Schematic Diagram showing the Influence of Small Mass and High Specific Surface on the Properties of Fine Particles with Reference to their Floatability.

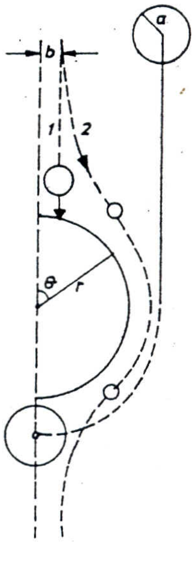

Fig. 2. The Influence of the Particles on their Trajectory in the Vicinity of the Floating Bubble

Line 1 – Trajectories of the coarse particle

Line 2 – Trajectories of the fine particle

Particles at the same target distance "b"

More sophisticated modelling based on interception theories reveals that the collection efficiency depends on the ratio $(dp/db)^n$ with an exponent usually in the range of 1.5-2.0.

Considerable interest has been shown on the production of small bubbles where surface area is more and can accommodate more solid particles. Though it is not impossible, it is comparatively expensive to disperse the gas by conventional methods. 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 turbulance in the frothing zone which is quite undesirable. According to Sutherland (1948), better collision probability between particles and bubbles can be achieved if the size of the particles and bubbles is maintained in the same order. Based on the above analysis vacuum flotation and electroflotation are 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.

The high specific surface of fines leads to high reagent/flocculant consumption and non-specific adsorption of reagent due to high surface energy which will affect the recovery and grade of the concentrate. Further, the high specific surface energy of fine particles influences the flotation in a number of ways: (i) increased dissolution causes unintentional activation of gangue minerals or depression of desired material, (ii) increases the tendency of collectors to adsorb non-specifically, i.e. adsorption may occur irrespective of electrical double layer and thus lead to flotation of undesired minerals.

As the particle becomes colloidal in size, long range inter- molecular forces and electrical double layer forces dominate and control the interaction of a particle with other particles or bubbles in suspension. If the double layer is thick and the potentials are large, the particles will remain dispersed whereas if the double layer is thin or absent, attractive forces dominate and the particles will coagulate/flocculate. The processs of slime coating, which refers to the attachment of fine particles to the larger particles, is also controlled by long range inter-molecular forces similar to those that determine interactions between a bubble and a particle. The research done on these aspects has been reviewed by Fuerstenau (1980), Chander (1978) and Trahar *et al.* (1976).

Electroflotation and selective flocculation or the combination of both seems to be most effective and highly promising techniques compared to other methods.

ELECTROFLOTATION

The use of electrolysis for obtaining gas bubbles in the process of mineral beneficiation was suggested by Elmore (1904). Electroflotation can be defined as flotation by electrically generated bubbles as a means of separating solid particles from liquid phase or one liquid from another. Bubbles are formed through an electrochemical process as represented below :

$40H^- \text{ ---> } 2H_2O + O_2\,(g) + 4c$ Anodic reaction

$4H^+ + 4e \text{ ---> } 2H_2\,(g)$ Cathodic reaction

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 which can lift even the smallest particles to clarify the solution. The commerical success of electroflotation is reported to be very effective in silk, meat, leather, oil, and steel industries.

The nacent hydrogen and oxygen liberated during the electrolysis induce significant changes in the surface conditions of the minerals. Some of the minerals can be beneficiated without the collector by taking advantage of the oxidation-reduction transformation of the mineral surface.

ELECTROFLOTATION CELLS

Various electroflotation cells are designed depending on the application and the material to be processed.

Schematic diagrams of electroflotation cells are shown in Figs. 3-6. A simple electroflotation cell consists of two electrodes arranged horizontally one over the other with a minimum gap to avoid short circuiting. The leads of the two electrodes are connected to a rectifier to draw current.

This can be used only for batch type experiments and it involves huge quantities of electrolyte. A micro electro flotation cell was designed to make use of particular gas bubbles of either hydrogen or oxygen as shown in Fig. 4. In this cell. electrodes are separated by a current conducting membrane (diaphragm) to separate the gases. The current conducting membrane serves the dual purpose of confining the pulp in the upper compartment and prevents the gas of the lower electrode from entering the flotation zone.

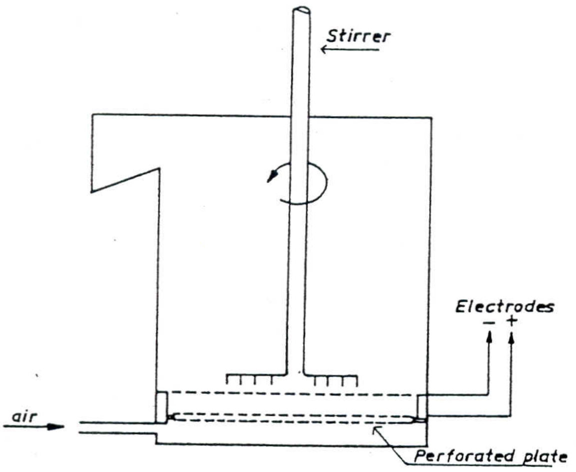

Fig. 3. Schematic Diagram of Simple Electroflotation Cell

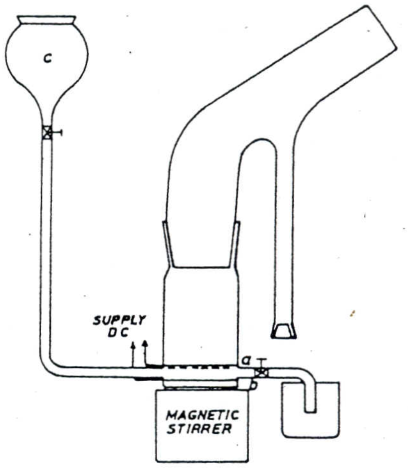

Fig. 4. Hallimond Tube Micro Electroflotation Cell : (a) and (b) Anode and Cathode, (c) Electrolyte Reservoir

In a semi continuous electroflotation machine shown in Fig. 5 (Glembotskei *et al.*, 1975) the pump of the thermostatic bath supplies the electrolyte at a constant temperature to a constant level tank from where it passes at constant pressure through a valve to the intra-electrode space. The excess electrolyte is allowed to return into the thermostatic bath through an overflow funnel. The electrolyte can be reused after adjusting the pH. A slightly better version of the same is shown in Fig. 6 where the electrolyte solution is circulated in the outer zone of the cell. Accumulation of gas bubbles generated from the bottom electrode can be fully avoided in this cell. Better performance is noted by using vibrating electrodes.

APPLICATIONS

A. *Waste Water from Leather Industry.* Waste water from leather industry usually consists of chromium, fat, surface active agents, BOD and COD and a high amount of suspended solids. Surface active agents and chromium can be recovered and the amount of BOD, COD and suspended solids can be removed by using electroflotation technique (Mamakov *et al.*, 1973). Cr^{3+} is recovered in the

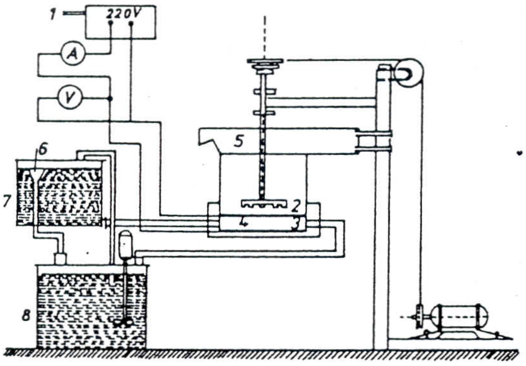

Fig. 5. Circuit Diagram of Electroflotation Machine. 1. Power supply, 2 and 3. Electrodes, 4. Current conducting membrane (diaphragm), 5. Flotation chamber, 6. Overflow funnel, 7. Constant level tank, 8. Thermostatic bath

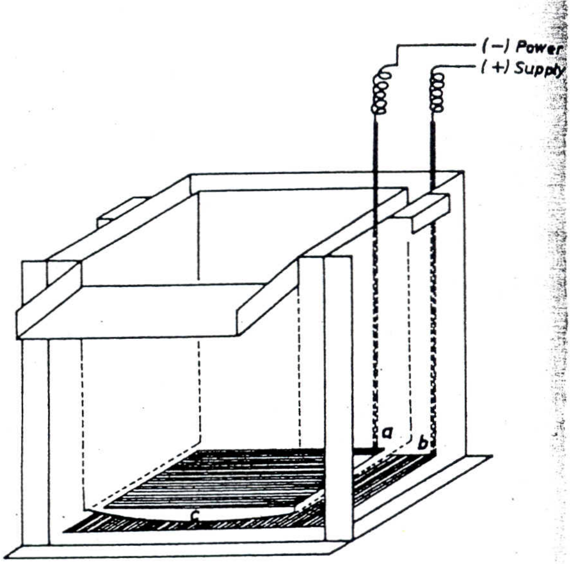

Fig. 6. Improved Version of Electroflotation Cell : (a) and (b) Electrodes, (c) Diaphragm

form of $Cr_2(SO_4)_3$ with $Ca(OH)_2$ as coagulant. The fourth product is treated at 300 dec. C and the residue is dissolved in dil. H_2SO_4 to separate chromium. The degree of purification is found to be 99.7% compared to that of 92.8% from coagulation.

B. *Waste Water from Textile Industry*. Electroflotation method is found to be effective for the removal of suspended solids from the effluent of silk production plant (Batov, 1966). Even trace quantities of Fe and Zn used as catalyst can be either eliminated or extracted from the waste waters of rayon manufacturing plants (Krainzman, 1973) by electroflotation.

C. *Electroflotation in the Field of Metallurgical Industries*. Removal of cations like Co, Zn, Cu, Ni, Fe, etc. from the waste waters of metallurgical industries by electroflotation method is cited in the literature. Gol'man *et al.* (1971) suggested the removal of non-ferrous metals like Cu and Zn from brass rolling mill waste water by precipitating with Na_2CO_3/NaOH or $Ca(OH)_2$ and separation of these precipitates by electroflotation. A more efficient and less expensive precipitation recovery operation for Cr^{6+} from coolling tower blow down water is suggested by electroflotations (Demonbrun *et al.* 1977). Flotation is carried out employing hydrogen bubbles and by using dodecyl sodium sulphate as reagent and quaternary ammonium salt as a promotor.

Waste water from cadmium plating industry is clarified by electroflotation using Al as anode (Nenyro *et al.*, 1974). $Al(OH)_3$ formed from the dissolved anode was found to aid adsorption and precipitation than conventional $AlCl_3$ or alum. Thus the minute quantities of metal values can be easily recovered by electroflotation.

D. *Electroflotation in the Field of Mineral Beneficiation*. In 1970, Mamakov *et al.* (1969) tried electroflotation for the beneficiation of cassiterite. The electrodes are separated by a diaphragm to separate the gases. C7-C9 aliphatic acids are used as collectors. The separation is found to be effective by using hydrogen bubbles. The corresponding surface reactions are represented as under :

$$\begin{aligned} SnO_2 + H &= SnO_2H \\ SnO_2H + HA &= SnOA + H_2O \end{aligned}$$

The removal of diaphragm has drastically reduced the efficieny of the process. It is attributed to the inactivation of cassiterite surface by oxygen. Separation of cassiterite by electroflotation technique is 20% more efficient than the conventional flotation techniques.

Electroflotation tests on manganese minerals like pyrolusite and psilomelane are compared with the column flotation technique (Romanov *et al.*, 1973). The extraction of manganese with hydrogen bubbles, generated electrolytically is 92-95%, which is found to be 10 times more effective than column flotation. Electroflotation of uranium by using aluminium, iron and magnesium as supporting electrodes is attempted by Turovtseva (1978). Hydroxides of aluminium and iron will act as carriers of uranium hydroxides bringing the purification level to 98% and 92% respectively.

Glembotskii *et al.* (1975) have successfully implemented the technique of electroflotation for the beneficiation of pyrite, manganese slimes and fine diamonds. The grade of manganese slimes –10 microns) is found to reach 60% from the initial value of 9.5% by electroflotation. Attempts on the recovery of diamonds by conventional flotation methods are found to be quite unsatisfactory whereas complete recovery of diamonds can be achieved by electroflotation method. Thus utilization of raw materials that cannot be beneficiated by other conventional methods is possible by means of electroflotation.

98% of pyrite is recovered by using electrolytic oxygen bubbles alone. Electrolflotation 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% (Fig. 7) respectively with oxygen and hydrogen without reagent (Bhaskar Raju *et al.*, 1984). Thus the role of the size of the bubble is quite apparent. Significant effect is observed by electrolytic oxygen on the flotation of sulfide minerals. Electro chemical investigations on the flotation of sulfide minerals in the presence of oxygen is thoroughly established by the earlier workers (Gardner *et al.*, 1979; Heyes *et al.*, 1977). Controlled oxidation eventually leads to the formation of elemental sulfur on the surface of the mineral giving sufficient hydrophobicity for the bubble contact, e.g. $CuFeS_2 + O_2 = CuS + Fe^{2+} + S + 2e$

Thus lowering or complete elimination of collector consumption is possible by electroflotation.

Electroflotation tests on cassiterite showed that the process of electroflotation is 10 times costlier than the ordinary flotation (Hogan *et al.*, 1979). But these calculations are based on the use of mixed bubbles instead of exploiting the surface changes by hydrogen bubbles alone.

E. *Miscellaneous Fields.* Waste water solution containing 50% used drilling oil emulsions and detergent wash water is treated both by electroflotation and conventional flotation techniques. Air introduced through porous plate at the bottom is able to settle the sludge only after 24 hours, whereas by electroflotation, clear water can be obtained within 15 minutes (Hans, 1965). The general data regarding the effectiveness of the electroflotation is shown in Table 1. It is clear from the table that the process of electroflotation is less expensive and highly effective.

Purification and disinfection of highly polluted waste water from food industry is also possible by electroflotation using Al and Fe as electrodes. In this process BOD, COD are reduced to 60-80%, the Coli index from 2×10^9 to 2×10^3, the pathogenic enterobacteria by 99.9% and the helminth cells by 98.9% (Surgeev *et al.*, 1977).

Waste water from slaughter house has been treated using corrodible metals like aluminium as electrode. The scum collected at the top can be burnt off at the expense of electrolytic gases.

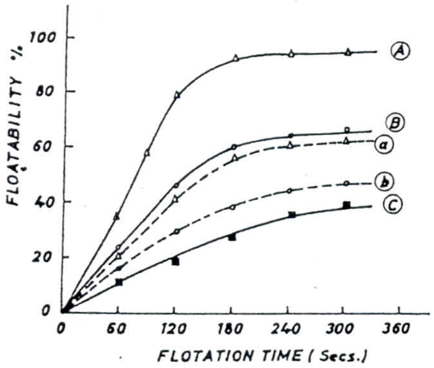

Fig. 7a Flotability of Chalcopyrite
A. Floation with electrolytic oxygen. Collector K.Et.X : 140 mg/lit. current density : 11 mA/cm^2
B. Flotation with electrolytic hydrogen. Collector K.Et.X : 140 mg/lit. current density : 196 mA/cm^2
C. Flotation with cylinder oxygen flow rate 0.5 lit/min. Collector K.Et.X : 140 mg/lit.
a, b (dotted lines) represent without collector

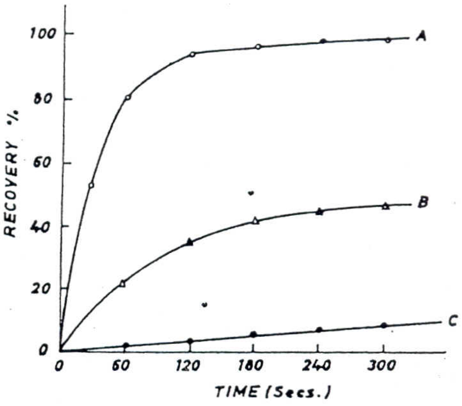

Fig. 7b Pyrite Recovery as a Function of Flotation Time
A. . Flotation of pyrite without reagent with oxygen bubbles
B. Flotation of pyrite with hydrogen bubbles in the presence of collector amylxanthate
C. Flotation with air in the presence of collector
(Collector consumption 150 g/t)

Recovery of magnesium from sea water is attempted by electroflotation using hydrogen bubbles. It was found that the freshly precipated Mg $(OH)_2$ poses a significant capacity of undergoing flotation with hydrogen bubbles (Lewandowski *et al.*, 1975).

Purification of waste water from beat sugar industry was also attempted by preliminary coagulation with 0.01 % $FeCl_3$. Efficiency of the process was further improved to 99% using foaming agents like saponins (Sand Bank *et al.*, 1974).

Waste water from petroleum refinery was experimented with electroflotation technique for the removal of oils, present at the rate of more than 3000 mg/lit (Fedotkin *et al.*, 1974) normally.

Electroflotation has its extended routes in the treatment of rubber latex wastes, waste water of wood processing industry and also in dairy and fish processing industries. Thus the effectiveness of electroflotation in the extraction of finely dispersed solids from the waste waters of hydrometallurgical plants, industrial effluents and in other fields was found to be economically viable. 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.

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 changees in the pH during the process is difficult to control. Higher the current density, higher will be the changs in the pH of the pulp. This does not have much effect where the selectivity varies in wide range of pH. The nascent gases liberating from the electrodes will affect the unadsorbed reagent and also the surface compound. The collectors that are sensitive to oxidation-reduction changes will be destroyed due to these gases (Bhaskar Raju and Khangaonkar, 1984). Thus the recirculation of the unabsorbed collectors is not possible. Hence the selection of the collectors should be in such a way that they are least affected by the gases.

TABLE 1 : DETAILS ON THE TREATMENT OF SOME INDUSTRIAL EFFLUENTS BY ELECTROFLOTATION

Source	*Constituents and Conc. of Effluents*			*Degree of Water Purification*	*Energy Consumption* (Kwh/m^3)
	Constituents	*Concentration* (mg/lit.)			
		Feed	*After electroflotation*		
Tannery	Suspended solids	860	97	99.7 % (92.8% by flocculation)	0.4
	Chromium	24.6	97		
	Fat content	86.0	90		
	Surface active agents	14.6	71		
	BOD	1500	36		
	COD	3200	35		
Textile industry	Zn	120	1.0	96-98 % at the waste water flow rates of 135 m^3/h	0.2-0.4
	Suspended solids	200	1.0		
	Fe	8	0.05		
	CS_2	20	NIL		
	H_2S	10	NIL		
	COD	300	30		
Slaughter house	BOD	268	63	98 % Bacteria content was reduced by 50% due to nacent Cl liberated during electrolysis	
	COD	800	64		
	Suspended solids	25000	–		
	Coli index	2×10^9	2×10^3		
Refinery	Oil content	1500	30-35	100%	0.43-1.04
Sugar industry	–	–	–	99%	0.3-0.5
Syn. fats	–	–	–	95 % Mechanical purification 80% and UV illumination using high pressure quartz-Hg lamps 96%	0.4

COST COMPARISION FOR ELECTROCOAGULATION AND OTHER OIL REMOVAL TECHNIQUES

	Capital cost $	*Operating cost* $/1000 gal.
Chemical coagulation	75,000	0.85
Ultra filtration	1,75,000	–
Electrocoagulation	60,000	0.68

Based on treatment plant capacity of 45,000 gpd influent oil of 1000 mg/lit.

Collectors like xanthates are more useful, because even the oxidation product dixanthogen is a good collector for sulfide minerals. Usually the percentage of solids in flotation operations is as high as 20-30%. Under these conditions electroflotation alone is not effective to achieve better metallurgical results. It is found that better results can be achieved by introducing air bubbles alongwith electrolytic bubbles (Bhasker Raju *et al.*, 1982a; Bhaskar Raju *et al.*, 1982b and Bhaskar Raju *et al.* 1987)

FLOCCULATION

Beneficiation of low grade non-precious metals by flotation is not economically viable mostly due to high reagent consumption and selectivity. A process that appears promising is selective flocculation followed by a separation technique such as flotation or elutriation. Inorganic electrolytes, natural polymers and synthetic high molecular weight polymers have been used as coagulants or flocculants for clarification of effluents. The flocculation process in mineral processing systems is rather complex. A major problem in devising efficient selective flocculation schemes is the lack of specificity in the adsorption of polymers on mineral surfaces due to the absence of suitable active groups in the polymeric chains. Specificity can, however, be achieved by incorporating chelating groups into the polymer chain. Certain amount of specificity can also be achieved by controlling the dissolved ions content of the suspending medium in order to obtain favourable interfacial charge conditions near the particles.

Fine particles constituting a mineral mixture usually have a tendency to coat each other. This problem of slimes coating and heterocoagulation is usually overcome by use of dispersants (Read *et al.*, 1976). Selective adsorption of polymer molecules on particles can also be achieved (Derjaguin *et al.*, 1979) by adjusting the chemical composition of the suspending medium in order to exploit the dependence of adsorption of ionic polymers on surface charge (Kapoor *et al.*, 1973) introducing into the polymer active functional groups that will form complexes or salts with the metal atoms on the surface of the desired mineral and (Sutherland, 1948) using depressants such as sodium silicate which would adsorb on the undesired mineral surface, thereby preventing adsorption of the polymer. The success of selective flocculation rests on the appropriate application of surface chemical principles for the control of variables in the mixed pulp. Details of the theory and perspectives of selective flocculation were reviewed by several investigators (Read *et al.*, 1976; Attia *et al.*, 1975; Eigeles *et al.*, 1975; Pugh *et al.*, 1972; Yarar *et al.*, 1970; Sresty *et al.*, 1980 and Yarar, 1979).

In a mixture of minerals, flocculation of a particular mineral can be controlled by using modifiers (activator and depressant). For example, separation of hematite-quartz mixture by selective flocculation using anionic polyacrylamide has been reported to be effective after the addition of calgon and sodium fluoride (Read, 1972). Attia and Kitchner (1975) have reported the possibility of depressing flocculation of heavy minerals by xanthates using depressants such as sodium sulphide, polyphosphates and polyacrylates.

FLOCCULATION OF MINERAL FINES

Reported work on selective flocculation deals mostly with synthetic binary mineral systems (Attia *et al.*, 1975 and Collins *et al.*, 1971). Commercial exploitation of the process on the beneficiation of multicomponent natural ores was achieved by Frommer (1975) and Carta *et al.*, (1975). Summary of some of the investigations regarding the flocculation and selective flocculation of fines is given in Table 2.

Iron Ores. Recently commercial scale trials were conducted on non-magnetic teconite fines by selective flocculation by U.S. Bereau of Mines-Cleveland and Cliffs Iron Company at Tilden Mine. The process involves selective flocculation of oxidized taconite (85% -150 mesh) with starch after dispersing the ore with sodium silicate and tripoly phosphate (Frommer *et al.*, 1966). Reverse flotation of the selectively deslimed ore is carried out with an amine collector and dextrin as a depressant for haematite. The prinicipal reagents' cost in selective flocculation is due to the dispersants rather than the flocculants. It is suggested that savings can be made by treating the overflow products and recycling the water. Typical results are given in Table 3. These results indicate that the elutriation separater is capable of producing an excellent separation of the flocs away from the dispersed material.

TABLE 2 : SUMMARY OF THE EARLIER WORK ON FLOCCULATION AND RELATED STUDIES ON SOME MINERAL FINES

Mineral-flocculant system	*Result*
Haematite-quartz-corundum-starch	In a ternary artificial mixture of haematite, quartz and corundum, the alumina/silica ratio is reduced from 1.5 to 0.9 through selective flocculation.
Iron Oxide Kaoline-anionic polyacrylamide	High molecular weight polyacrylamides containing upto 8.3% hydroxamate functional groups are used as polymers. Starting with a feed grade of 35% Fe, 92% recovery with an acceptable grade of 60% Fe has been achieved using the modified polyacrylamide.
Iron ore corn starch	The mechanism of dispersion using sodium silicate in the presence of calcium ions and magnesium hydroxide precipitates is examined by settling tests, abstraction tests, selective flocculation tests, and electron microscopy. A model is proposed to explain pulp dispersion in the presence of these species.
Haematite high molecular weight polymers-surfactants	The selectivity of flocculation for haematite can be enhanced by use of high molecular weight ploymers in combination with proper surfactants. The optimum results are obtained using hydrolytic polyacrylamides in combination with sodium oleate. The grade of feed (mixture of haematite-quartz) is increased from 34.6% to 62.3% Fe with a recovery of 97% in the presence of 2 ppm of HPAM and 5×10^{-4}M soduim oleate. Flocculation and settling operations are repeated minimum three times.
Chalcopyrite covellite sepiolite – Magnafloc and Bistrin	All the three flocculants viz., non-ionic magnafloc - 351, anionic magnafloc - 155, and Bistrin A3 have shown rapid and complete flocculation of chalcopyrite fines. In the case of sepiolite, magnafloc - 351 has proved superior compared to other two flocculants.
Limestone-Zetac series and Anionic Magnafloc 155	Cationic polymers like Zetag 51, 63, 92 and 94 and Anionic Magnafloc - 155 are used in the flocculation of lime stone sludges obtained from flotation of phosphate ores. Magnafloc - 155 is found to be efficient.
Sphalerite fines with 8.5% Fe-Magnafloc 351	Commercial Magnafloc - 351 is found to be a viable floculant in separating sphalerite from a leached slurry containing 8.5% of Fe.
Chalcopyrite quartz-hydroxypropyl cellulose and xanthate. Haematite-quartz-ploystyrene sulphonate	The time of maximum flocculation for various minerals differ from each other, so that it could be considered as a potential factor for achieving selectivity. Also, cleaning of the selectively flocculated product by simple redispersion in water improves the separation.
Malachite, fluorapatite and coal - PAMG-2	Several sample preparation methods to examine the floc structure are investigated using transmission and scanning electron microscope. The study indicated that the bridging mechanism involves polymer-polymer linkages in addition to polymer-particle attachments.
Apatites-Polyacrylamide	Nephelometric and U.V. Spectrophotometric techniques are used to determine the residual concentration of the polyacrylamide in the solution after adsorption studies. Adsorption appears to result mainly through hydrogen bonding between –OH groups on the apatite surface and –CONH groups of polyacrylamide molecules. The specific free energy of adsorption is estimated to be –24.1 KJ/mole of monomer.
Cassiterite $\frac{1}{2}$cm different dispersants	At neutral pH aminophosphonates and polyphosphates are found to be effective dispersants for cassiterite. The stability of carboxylates as dispersants depends on the number of functional groups and the presence or absence of hydroxyl groups. However, non-ionic reagents containing only alcoholic- –OH groups, are found to be ineffective.
Quartz, calcite, galena-polyacrylamide	Selective flocculation of galena from a mixture of galena-calcite-quartz is studied alongwith zeta-potential measurements.

TABLE 3: COMPARATIVE FLOTATION RESULTS WITH AND WITHOUT SELECTIVE FLOCCULATION

Product	*Wt. distribution %*	*Analysis %*		*Fe distribution*
		Fe	SiO_2	
Without				
Concentrate	42.9	63.9	6.6	75.0
Tailings	53.5	14.7	–	21.5
Slime	3.6	35.4	–	3.5
Composite feed	100.0	36.5	–	100.0
With				
	46.5	65.1	4.8	83.7
	43.0	9.9	–	11.8
	10.5	15.4	–	4.5
	100.0	36.2	–	100.0

Clays. Generally clay particles are predominantly finer than 1 micron. The established methods of beneficiating clays mainly involve the removal of coarser contaminants. Recently, removal of ultrafine contaminants by flocculation was developed with the following objectives:-

1. removal of colured impurities to improve brightness;
2. removal of fine quartz in order to reduce abrasiveness of the product;
3. removal of swelling clays in order to reduce slip viscosity; and
4. separation from boehmite in treatment of low grade bauxite.

A ten fold reduction in the level of a titanium dioxide-coloured impurity is achieved by using high molecular weight anionic polyacrylamide (Maynard *et al.*, 1969). The impure clay is first dispersed with a combination of sodium hexa meta phosphate and sodium silicate so as to achieve minimum viscosity. Sodium chloride is added, presumably to promote partial destabilisation. Then, the suspension is allowed to stand and the polymer is added to remove the titanium dioxide (coloured impurity) content. The titanium dioxide level in the dispersed kaolin is reduced in one treatment from 2% to 0.18% at around 50% recovery. Addition of calcium promoted the selective flocculation of kaoline by an anionic polyacrylamide. Cationic activation was also employed to selectively flocculate kaolin from quartz. However, in this case lead ions were used to achieve the activation at a pH of around 11 (Attia *et al.*, 1975).

Phosphates. Approximtely 5 million tonnes of phosphate (P_2O_5) is thrown away each year as fines mostly in the size range of 0.2 to 3 microns from the Florida Phosphate Plant (Colombo, 1975). This constitutes around 30% of the mineral value. These values are not amenable to recovery by conventional flotation. The flotation flowsheets for phosphate beneficiation invariably involve desliming of the pulp at various levels. A considerable part of the phosphate values is thus lost in the slimes. A number of attempts have been made to produce saleable grade concentrates using selective flocculation and other selective aggregation techniques (Colombo, 1975). All the selective flocculation tests involve dispersion of clay gangue with sodium hydroxide at pH 9.0 and flocculation of the phosphate by an anionic starch.

The montmorillonite clay gangue is found to swell during wet processing. As a result, the volume of the tailings exceeds that of the original ore. Selective leaching methods are being considered for phosphate recovery to overcome these problems (Kirby *et al.*, 1975). Beneficiation of some Indian phosphate ores is conducted using various synthetic flocculants like Magnafloc-A155, C-592 and N-351 as anionic, cationic and non-ionic flocculants respectively (Pradip *et al.*, 1983). The results indicate that only partial recovery of phosphate values is possible using polyacrylamide flocculants.

SUMMARY

Electroflotation and selective flocculation or the combination of both appear to be potential techniques for the beneficiation of low grade mineral slimes and fines generated during mining, milling and other metallurgical operations.

Considering the hydrodynamics of flotation process, electroflotation was proved to be an effective and viable technique to separate organic suspending particulate matter generated from leather, textile, metallurgical, oil refinery and food processing plants. Electroflotation is advantageous to process sulphide minerals and minerals that undergo surface changes when exposed to electrolytic oxygen and hydrogen. Adsorption of oxygen, liberated from the anode leads to the formation of elemental sulphur on the surface of the particles. Elemental sulphur thus formed under controlled oxidation enhances the hydrophobicity.

Continuous liberation of H^+ and OH^- leads to drastic changes in the pH of the pulp. Hence, the technique is more disadvantageous where pH is a critical parameter. Also part of the collector will be either destroyed or dissociated under the influence of pH, electrolytic bubbles and oxidation-reduction environment changes.

Selective flocculation of minerals using polymers followed by any one of the separation techniques such as, flotation, elutriation, filtration, etc. offers considerable promise for processing non-precious oxide minerals. Natural and synthetic high molecular weight polymers have been successfully used as flocculants. Lack of desired specificity is the major set back in this process. However, specificity can be introduced by incorporating active groups in the polymers. Though there is enough literature on selective flocculation of synthetic mineral mixtures, reports on the flocculation of multi-component natural ores are scant. Further, it is generally observed that the prediction of selective flocculation on the basis of results obtained from single mineral tests fairly agrees with synthetic mineral mixtures but rarely on natural systems.

Effect of flocculants on subsequent operations of flotation, elutriation and filtration is yet to be understood thoroughly. Information in this regard at present is mostly speculative and only future research has to provide the answers. Also, it is necessary to understand the mechanism of adsorption of such large polymer molecules (flocculants) on the small particles. Role of configuration of the adsorbed polymer, exact mechanism of dispersion and flocculation is to be studied to make the process more viable and effective.

REFERENCES

Attia, Y. A. and Kitchner, J. A. (1975). *11th I. M. P. C., Caglairi,* Paper 46.
Batov, B. M. (1966). *Akad. Kauk. Mold SSR*, **3**: 80-82.
Bhaskar Raju, G. and Khangaonkar, P. R. (1982a). *Int. J. Min. Proc.*, **9**: 133-143.
Bhaskar Raju, G. and Khangaonkar, P. R. (1982b). *National Seminar on Fine Particle Processing, Dhanbad* (1982), pp. 98-104.
Bhaskar Raju, G. and Khangaonkar, P. R. (1984). *Int. J. Min. Proc.*, **13**: 211-221.
Bhaskar Raju, G., Prabhakar, S. and Khangaonkar, P. R. (1987). *Bull. Electrochem.*, **3** (1): 37-40.
Carta, M., Alfano, G. B., Delfa, C., Ghiani, M., Massacci, P. and Satta, F. (1975). *11th I. M. P. C., Cagliari*, Paper 41.
Chander, S. (1978). *Trans. I. I. M.*, **31**: 12-18.
Collins, D. N. and Read, A. D. (1971). *Miner. Sci. Engg.*, **3**: 19- 39.
Colombo, A. F. (1975). *11th I. M. P. C., Cagliari*, Paper 17.
Demonbrun, James, R., Schnitt Charles, R. and William Everetti, H. (1977). C. A. 86, 23607.
Derjaguin, B. V. and Dukhin, S. S. (1979). *In*: J. Laskowaski (ed.), *13th I. M. P. C., Warsaw,* pp. 21- 62.
Eigeles, M. A., Kuznetsov, V. P., Volova, M. L., Sokolov, Yu. F., Lyubimova, E. I. and Grebnev, A. N. (1975). *11th I. M. P. C., Caglairi,* pp. 1213-1232.
Elmore, F. (1904). British Patent No. 13578.
Fedotkin, I. M., Arkhipovich, N. A. and Lagoda, V. A. (1974). *Sakh. Prom. St.*, **9**: 27-30.
Frommer, D. W. (1975). *11th I. M. P. C., Cagliari,* Paper D-9.
Frommer, D. W. and Colombo, A. F. (1966). *U. S. Patent*, **3** : 292,780.
Fuerstenau, D. W. (1980). *In*: Somasundaran (ed.). *Proc. of Fine Particles Processing Symposium*, Vol II., *SME/AIME*, Chapter 35, pp.669-705.
Gardner, J. R. and Woods, R. (1979). *Int. J. Min. Proc.*, **6**:1-16.
Glembotskii, V. A., Mamakov, A. A., Ramanov, A. M. and Nenno, V. E. (1973). *IXth Int. Min. Proc. Cong. Caglairi,* 562-581.

Gol'man, A. M., Mekler, L. I., Gonodetskii, M. I. and Egzarav, A. A. (1971). *Tsvet. Met.*, **44** (4): 81-82.

Hans, J. Zimmer (1965). *Verfabreutechnik Ger.* **1** : 203, 702. C. A. 64, 1966, 9422.

Heyes, G. H. and Trahar, W. J. (1977). *Int. J. Min. Proc.*, **4**: 317-344.

Hogan, P., Kuhn, A. T. and Turer, J. F. (1979). *Trans. Inst. Min. and Met.*, **88**: C83-87.

Kapoor, P. C. and Mehrotra, S. P. (1973). *Trans. I. I. M.*, **82**: C 229-234.

Kirby, R. C. and Barclay, J. A. (1975). *Mining Engg.*, **27** (6): 42-47.

Krainzman, M. A., Eiter, I. Z. and Shimko, I. G. (1973). *Khim. Volokua*, **15** (4): 16-19.

Lewandwski, Raymond, Bonet, Jacquer and Fery, Patrik (1975). *Belg.*, 829,007 (C1.CO2 CBO3D). C. A. 85, 1976, 1,30123.

Mamakov, A. A., Fainshtein, L. B., Kubristskaya, J. O. and Kozlova, T. V. (1973). *SER Fiz. - Tech. Mat. Nauk*, **17**: 87-89.

Mamakov, A. A., Sarokina, V. N. and Awakumov M. I. (1969). *Electron Obrab. Mater.*, **4**: 44-49 (Russ.). C. A. 72 1970, 4631507.

Maynard, R. N., Millman, N. and Ianniclli, J. (1969). *Clay Minerals*, **17**: 59-62.

Nenyro, Oyobi Nensho and Ichi, Minoru (1973) 40(8): 739-746. C. A. 80, 1974, 74001.

Pradip, Rambabu, Ch. and Rao, G. U. V. (1983). *Proc. Symp. on Powder Tech.*, I. I. T., Madras.

Pugh, R. J. and Kitchner, J. A. (1972). *J. Colloid Interface Sci.*, **38**: 656-657.

Read, A. D. (1972). *British Poly. J.*, **4**: 253-264.

Read, A. D. and Hollick, C. T. (1976). *Miner. Sci. Engg.*, **8**: 202-213.

Romanov, A. M., Nenno, E. S., Nenno, V. E. and Mamakǒv, A. A. (1973). *Electron Obrab. Mater.*, **1** : 54-56. C. A. 79, 1973, 1068434.

Sand Bank, E., Shelef, G. and Wachs, A. M. (1974). *Water Res.*, **8** (9): 587-592.

Sresty, G. C. and Somasundaran, P. (1980). *Tnt. J. Min. Proc.*, **6**: 303-320.

Surgeev, A. L., Tsaturova, G. A., Golvina, S. V. and Buts, F. I. (1977). *Elektron Obrab. Mater.*, **6**: 66-68 Russ. C. A. 89, 1978, 79704.

Sutherland, K. L. (1948). *J. Phy. Colloid. Chem.*, **52**: 394-425.

Trahar, W. J. and Warren, L. J. (1976). *Int. J. Min. Proc.*, **3**: 103-131.

Turovtseva, S. F. (1978). *Geol. Ruzved*, **21**(6): 104. C. A. 89, 1978, 78198.

Yarar, B. (1979). *2nd World Filtration Cong.*, 317-330.

Yarar, B. and Kitchener, J. A. (1970). *Trans. I. M. M.*, **79**: C23-33.