

C H A P T E R - I

I N T R O D U C T I O N

Flotation was perhaps known to man as early as the eighteenth century. But the importance of this process could be felt only in the early part of 20th century since this process could handle the mineral fines which were difficult to be processed by gravity separation method. There is a saying that 'flotation is more of an art than a science'. This is perhaps due to a number of variables acting together in a flotation system. K. L. Sutherland and I.W. Wark have listed some thirtytwo variables for sulphide flotation, out of which ten are beyond control. Similarly, oxide minerals also pose problems except for the variables related to surface oxidation as in the case of sulphides. The uncontrollable variables are originated from the inherent nature of the ores and this perhaps forces the mineral engineers to depend on 'hit and trial method' or on experience out of handling the minerals for flotation. The complexity that comes up due to a number of variables acting together, leads to a state of confusion for the experimentalists working in this field. One may expect that the samples of a particular mineral collected from different deposits or from the same deposit should behave almost similarly under identical conditions in a flotation system. But unfortunately one may arrive at some frustrating results. This is due to those variables which are inherently associated with the minerals.

One of such is the defect structure of the mineral. The variation in defect structure of the same mineral may be due to very minor amount of impurities within the solid minerals. The studies on such type of variable in flotation process have started very recently. The pioneering and independent studies on this aspect have been reported by I. N. Plaksin and R. S. Shafeev and by G. Simkovich, only in 1962-63. The effect of defect structure on the interfacial properties of the minerals at solid/water interface needs an extensive study with different systems since the most widely used flotation process is largely dependent on these properties.

Point of zero charge (pzc) is the most important parameter which describes the electrical double layer of a mineral in water. It can be said that pzc represents the pH below which the charge on the solid surface is positive and above which it is negative. Since the sign of charge determines the type of adsorbate to be required for mineral flotation, the location of the pzc is of vital importance. The pzc has been found to vary with change in defect structure and thereby influences the success of mineral flotation. Only a few systems have been studied so far on this aspect. However, considering the type of defect structure, G. A. Parks has put forward a prediction stating that the n-type semiconductors are expected to show a more basic isoelectric point (iep) than predicted for stoichiometric oxide due to stabilization of adsorbed H^+ ions by mobile electrons, and on the other hand, p-type semiconductors are expected to show

a more acid iep than predicted for stoichiometric oxide due to repulsion of H^+ ions or stabilization of adsorbed OH^- ions.

Since in absence of specific adsorption, iep and pzc assume the same value, G. A. Parks has not differentiated between these two terms. However, this prediction has been experimentally verified through the work of F. F. Aplan, G. Simkovich, E. Y. Spearin and K. C. Thompson on NiO system by doping with either Al_2O_3 or Li_2O and also on p-type and n-type PbS. The reportings on $\alpha-Fe_2O_3$ by E. Y. Spearin, G. Simkovich and F. F. Aplan also agree with the prediction of G. A. Parks. But, the work of P. Roy and D. W. Fuerstenau on Al_2O_3 does not agree with this prediction. They have shown just opposite trend in the shift of pzc as predicted by G. A. Parks. Such contradiction in experimental observations demand further study with different systems having various types of defects to yield a more clear idea about dependence of pzc on defect structures of solids.

Besides the shift in pzc with variation of defect structure, it is also reported that the pzc of any system varies as the oxidation state increases. The work of V. Pravdic and S. Sotman on uranium oxide system supports this concept. G. A. Parks has also mentioned that the structural impurities shift the pzc towards the characteristic pzc of the impurity oxide.

All these aspects which have been described above are studied for only very limited systems and therefore, the results

obtained by the different workers are very much insufficient to arrive at a definite relation between the defect structure and point of zero charge. Furthermore, the effect of defect structure on adsorption process is of great importance since the results derived from the adsorption of flotation reagents determine the success of mineral flotation.

The p-typeness or n-typeness of various compounds based on electronic defects alone may not be able to explain the effect of defect structure on pzc for wide variety of systems. Systems such as ionic conductors, where the electronic defects play a minor role, are known to be greatly affected by the presence of impurity atoms. The electronic defects i.e. positive holes or excess electrons are the results of non-stoichiometry in terms of cation vacancies, interstitials, or anion vacancies and it is not clearly established whether for all such situations, pzc is predominantly affected by the electronic defects.

Keeping all the above points in view, the following oxide systems have been chosen in the present study :

- (1) Cuprous oxide, a metal deficient p-type semiconductor that shows the presence of cation vacancies in the oxide lattice and equivalent number of electron holes in the valence band. Cuprous oxide has been doped with Cr_2O_3 to increase the concentration of cation vacancies and reduce the concentration of positive holes. Cuprous oxide has also been doped with Li_2O to examine whether vacancy plugging brings in any change in pzc.

- (2) Cupric oxide which is also a p-type semiconductor has been obtained by oxidizing the cuprous oxide and its doped varieties in order to examine the effects of higher oxidation state both for pure and doped varieties.
- (3) Zinc oxide, a metal excess n-type semiconductor having excess zinc ions in interstitial positions and equivalent number of excess electrons in the conduction band, is doped with Cr_2O_3 and Li_2O to reduce and increase the concentration of zinc interstitial ions respectively and also to increase or decrease the concentration of corresponding electron defects.
- (4) Magnesium oxide, an ionic compound at room temperature shows both magnesium and oxygen vacancies and is reported to exhibit predominance of Schottky defects. This is doped with Li_2O to see the effects of increased cation vacancy concentration. Magnesium oxide has been heated along with Al_2O_3 at a temperature which is not sufficient for doping, so that Al_2O_3 remains on the surface of MgO as dispersed impurity.

The points of zero charge of all these oxides have been determined by the method as suggested by A. L. Mular and R. B. Roberts.

The shift in pzc for p-type oxides like Cu_2O and CuO is in agreement with the prediction of G. A. Parks. Doping of Cu_2O by Li_2O has shifted the pzc towards acid side. Results on zinc oxide system does not agree with the above prediction as in the case of Al_2O_3 , reported by P. Roy and D. W. Fuerstenau. The results have been discussed in the light of the role of interstitial zinc ions. MgO on doping with Li_2O has shifted the pzc to the acid side. The dispersed Al_2O_3 on MgO brings down the pzc towards the pzc of pure Al_2O_3 .

To study the adsorption behaviour of these oxides, dyes like tartrazine yellow (anionic) and methylene blue (cationic) have been used. The isotherms for adsorption of these dyes on all the oxide systems have been found out. The characteristics of these isotherms have been explained in the light of the classification given by C. H. Giles, T. H. MacEwan, S. N. Nakhaw and D. Smith. The linearity of these isotherms has been tested with Freundlich and Langmuir relations.

Effect of pH on adsorption of the anionic and cationic dyes has been studied and found that pzc decidedly exerts its effect leading to minimum adsorption near the pH corresponding to pzc even for the complex dye molecules. Certain exceptions have also been observed and discussed.

Effect of temperature on adsorption of dyes indicate that most of the adsorption process is exothermic in nature.

Similar studies have been conducted for the following sulphide systems :

- (1) Silver sulphide- an n-type semiconductor and CdS-doped silver sulphide with increased excess electrons in the conduction band.
- (2) Lead sulphide- that has shown p-type nature.
- (3) Zinc sulphide - an n-type semiconductor.

The dyes used for adsorption studies are :

- (a) Tartrazine yellow (anionic)
and
- (b) Safranine-T (cationic).

The adsorption isotherms obtained have been explained in the light of the classification as suggested by C. H. Giles, T. H. MacEwan, S. N. Nakhaw and D. Smith. The isotherms have been tested with the Freundlich and Langmuir relations.

The effect of pH on adsorption of these dyes has helped in determining the probable pzc values for PbS and ZnS systems.

An overview analysis of the present work on the defect structure and pzc, taking all other systems as studied by others into consideration, points out that besides the electronic defects, the nature of the point defects at times, predominantly influences the pzc. Systems with interstitial ions are in general slightly abnormal in their behaviour.

The effect of pH on adsorption process in general point to importance of coulombic forces during the adsorption process which always reach a minimum value near pzc except for a few systems. Near pzc for some systems, the amount of dye adsorbed approaches almost zero but for some other cases this is not found to be so. At present, it is difficult to provide an explanation for such behaviour. Since in the presence of any specific adsorption of dyes, the pzc is not equal to iep i.e., iep might have shifted slightly or perhaps some other type of adsorption might have taken place at pzc which gives a small value of adsorption. The complexity of adsorption process as evident from the isotherms can only be qualitatively explained in terms of the models suggested by others. Charges of the dyes have been found to play an important role for both oxide and sulphide systems suggesting the importance of electrostatic force of attraction.