

Simulated model studies on the beneficiation of calcareous phosphate ore

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INTRODUCTION :

The main sources of rock phosphate are located in Rajasthan, Mussoorie (U.P.), Singhbhum (Bihar), Purulia (W.B.) etc. Phosphate rocks generally occur as calcitic, siliceous and ferruginous in nature. Rajasthan and Mussoorie rocks are calcareous (CaO 40–50%). Hence to enrich the phosphate in the rock from average 16–20% to above 30% P_2O_5 , two possible alternatives to beneficiate this ore are :

1. Calcining the ore at 900° to 1000°C followed by hot quenching, attrition, scrubbing and repeated desliming. This method could increase the P_2O_5 content around 28%.

2. Separation of calcite or phosphorite by flotation method.

Both these have been utilised in different laboratories namely Cerphos, Paris; Serrans, Jacupirange, Brazil; Sala International, Sweden; National Metallurgical Laboratory, India and Indian Bureau of Mines, India. Except Sala International, other organisations have followed basically the same method for separating calcite from phosphorite. The results reported from different laboratories are quite divergent.

It seems that the basic characteristics at solid-liquid-gas interfaces of the minerals in a flotation cell have not been thoroughly investigated. Before attempting to separate calcite from phosphorite, an attempt was made to study the surface properties of calcite and phosphorite in presence of conditioner and collectors by measuring the electrokinetic potential of the suspension. So far, a detailed study has been made on calcite and attempt is being made to extend the study to phosphorite. However,

laboratory tests have indicated that calcite can be separated even without the use of phosphoric acid as phosphorite depressant used all over the world.

EXPERIMENTALS :

Material :

Distilled water used throughout the experiment was deionised and then redistilled in a pyrex glass still and had a conductivity of 1×10^{-6} (Ω cm) – 1. Standard samples of HCl and Na_2CO_3 were from B. D. H. Glaxo, India. Hexadecyl Pyridinium Bromide (C. P. B.) and Dodecyl Pyridinium Bromide (D. P. B.) were prepared in laboratory. Sodium dodecyl sulphate (S.D.S.) was from Fluka AG, Switzerland. Other chemicals viz. copper sulphate, thorium nitrate, lanthanum carbonate were either certified or Analar grade reagents. Certified 'A' grade of measuring glass apparatus were used in the study.

Preparation and characterisation of sol and suspension of $CaCO_3$:

A suspension of calcium carbonate bearing negative charge was prepared in the laboratory. The ionic strength in suspension medium was 2mM in terms of sodium carbonate and sodium chloride. The sol was allowed to age for one and half hour and was stable subsequently for three hours. The concentration of the sol was ~ 0.063 gm/litre. The particle size of the sol was found to be $\sim 2 \times 10^{-6}$ cm using electron micrography technique and the crystalline parameters were $a = 1.135A^\circ$, $C = 8.524 A^\circ$, $C/a = 1.1947$, $Z = 6$ where Z equal to no. of formula unit per unit cell. It was identified as μ -calcium carbonate. Identification of the calcium carbonate

powder is under study. Since it is a synthetic sample it may bear the same crystalline parameter as the sol particles. The pH of the sol samples prepared was found to be $8.9 \pm .2$.

Measurement of Zeta potential (ζ) :

The electrophoretic mobilities were measured by Zeta meter, using Type II UVA plexiglass electrophoretic cell and molybdenum cylindrical anode and platinum iridium strip cathode. The mobilities of different samples of sol particles were $1.17 \pm .05 \mu \text{ Sec}^{-1} \text{ Volt}^{-1} \text{ cm}^{-1}$. All measurements on electrokinetic potential were made within the period of three hours after the preparation of sol.

Adsorption Experiment :

Adsorption of the small ions namely Cu^{++} and Co^{++} in the same environment as that of the sol particles were carried on calcium carbonate powder at $30^\circ \pm 0.1^\circ\text{C}$. Since the measurement of electrophoretic mobilities of the sol particles were carried out at $27.5 \pm 2^\circ\text{C}$, the experimental conditions for the adsorption experiment may be taken to be similar as that for sol particles. The concentration range was varied from 10^{-7}M to 10^{-2}M , hence to determine accurately, the amount of Cu^{++} and Co^{++} in the lower concentration region, Atomic Adsorption Spectrophotometer was used. Solutions of higher concentration were diluted to bring them into the working range of the instrument.

Results :

In order to define the structure of the double layer at solid-solution interface, it would have been better to study the interaction of conventional mono, di and trivalent cations i.e. sodium, barium and lanthanum, since the coagulation concentration would effect the measurement of mobilities because of high conducting medium. The variation of zeta potential with these ions except sodium is shown in Fig. 1. It seems that trivalent ions also reverse the charge of the sol particles whereas highly hydrolysable thorium ions do not. A possible explanation for such behaviour is given later.

Consistent with the aim of the present work, hydrolysable metal ions, commonly used in flotation practice were selected, namely Co^{++} , Ni^{++} , Cu^{++} and Zn^{++} . The variation of zeta potential in their presence are shown in Fig. 2. These results show a sensitisation process occurs at very low concentration.

Since the sol is negatively charged, cationic surface active agents namely cetylene pyridinium bromide (C.P.B.) and dodecyl pyridinium bromide (D.P.B.) were selected to study their interaction with sol particles. Fig 3 gives the data. The surface active agents used below CMC are uni-univalent inorganic electrolyte viz. KCl, NaCl etc. This interaction should have shown similar trend as reported by Ottewill and Rastogi(1) on AgI solution interface. A similarity does occur i.e. concentration at which the first charge reversal occurs is about 10^4 lower than the monovalent ion indicating the process of adsorption to be sensitised. It is upto the region of zero zeta potential, the surface may be taken as becoming oleophilic, i.e. carbon like, hence may be amenable to make a definite contact angle with air bubble. Higher concentration than 1×10^{-8} and $1.66 \times 10^{-8}\text{M}$ lead to the formation of second layer and the surface again becomes hydrophilic. Hence in this region any concentration of the collecting ions will be detrimental to flotation studies.

Generally the flotation of calcite is done in acid medium. Sodium dodecyl sulphate (S.D.S.) was also included along with cationic surface active agent. The variation of zeta potential in its presence is shown in Figure-4.

As reported earlier Cu^{++} and Co^{++} were both found to reverse the charge on calcite particles at very low concentration. Three different concentrations viz $8.7 \times 10^{-5}\text{M}$, $7.14 \times 10^{-4}\text{M}$ and $1.428 \times 10^{-4}\text{M}$ corresponding to the region of positive zeta potential were selected in order to have a comparative study of the concentration of Cu^{++} ion on sensitisation. The interaction of the sol particles having fixed

Cu^{++} ion concentration was followed a function of S. D. S. concentration. Results are in Figure 4.

It can be seen from Figure 4 that the Cu^{++} ion at a concentration 8.5×10^{-5} M are very effective but the concentration of S.D.S. required to reduce ζ to zero is more than the other two cases of higher concentration of Cu^{++} ions. In such cases efficiency and the cost involved in the use of collecting ion should form the criteria for selecting the concentration of the activator.

A comparative study of the effectiveness of Cu^{++} and Co^{++} ions was made using the same molar concentration and at the same pH. The results of the interaction with S. D. S. are included in Figure 5. It can be seen from that Cu^{++} is more effective than Co^{++} ions in activating the surface.

To probe this result further a direct adsorption measurement of these ions were carried out on CaCO_3 suspension. Adsorption curves are shown in Figure 6. It further confirms that the Cu^{++} ions adsorbed more strongly than the Co^{++} ions.

Effect of pH :

The pH of the sol prepared remain within the range 8.9 ± 0.2 . An attempt was made to study the effect of pH on surface charge. Since the carbonate is highly soluble in acid, it was difficult to reach below pH=7. Perusal of the Figure 7 indicates that the surface charge is slightly increased and it became constant at pH=10. Hence one can safely work with the sol around pH=10.

Similar studies were made with fixed concentration of Co^{++} ions both in the negative and positive range of zeta potential. The variation of pH was studied in both cases. At concentration 8.5×10^{-6} M, the charge of the sol particles reverses at pH=9.7, while in other case there is a tendency to increase zeta potential but it became constant above pH=10. Charge

reversal in first case may be attributed to increase the concentration of hydrolysis production on the surface.

On the basis of information received from the foregoing experimental data, laboratory tests were performed for the flotation of CaCO_3 and $\text{CO}_3(\text{PO}_4)_2$ under similar condition. These suspension were conditioned at 9 pH. The pH in both cases was changed from 9 to 5. Using S.D.S. as collector, flotation experiments were performed. It was found that carbonate floated very well but under the similar conditions phosphate did not.

Discussion :

The changes in electrokinetic potential of the sol particles can be better interpreted if the structure of the double layer formed is known. The experimental conditions for the preparation of CaCO_3 sol suggest that the structure of the double layer should be as shown in Figure 8 (a).

Since the surface bears a negative charge the balancing charge will be comprised of uni- and di-valent cations present in solution. Much talked zeta potential (ζ) should not be taken to represent either the surface potential ψ_0 or ψ_σ , the Stern potential. It is best defined as the fall of potential between the surface of shear and the bulk when the double layer is subjected either to mechanical or electrical stress.

Since the particles are ($\sim 2 \times 10^{-6}$ cm) small assumed to be spherical and the changes in zeta potential values with and without the electrolyte remain in the range of ± 25 mv, these were calculated using Huckel² equation namely

$$\zeta = \frac{6 \pi \eta \mu}{\epsilon}$$

Where η = co-efficient of viscosity of the medium

μ = Electrophoretic mobility

ϵ = Dielectric constant

and no attempt was made to correct these values for electrophoretic and relaxation effects.

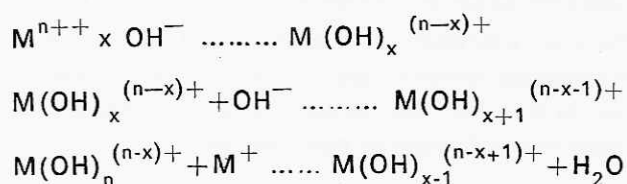
In this study the changes in zeta potential have been measured in the presence of both long chain ions and small metal ions. The charge reversal occurs even in the presence of small ions. The changes in double layer structure are shown in Figure 8(b) and 8(c).

Charge reversal may be assigned to adsorption of one or more of the species formed in processes enumerated below (3, 4, 5, 6) :

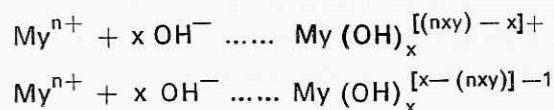
- (a) the free aquo cations or first hydrolysis product
- (b) polynuclear complex of discrete composition
- (c) a surface polymer or precipitate of metal hydroxide at a certain concentration depending on pH.

Collector to be used in these studies must have a well defined chemical composition and structure and of known purity. In this case charge reversal may be assigned to factor (a) because these act as a uni univalent electrolyte below C M C.

The charge reversal in the case of hydrolysable metal cation may be either due to factor (b) or (c). The scheme of charging in the surface according to mechanism (c) is given below :



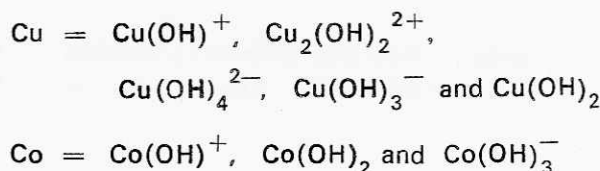
and for (b) the scheme is :



where n = no. of charge
 x = no. of hydroxyl ions
 y = no. of metal ions

Since Cu⁺⁺ and Co⁺⁺ ions were used extensively in this study, the probable hydrolysis

products and polynuclear complexes of these ions are given below :



At the interfacial region the situation is completely different from bulk. The interface is a region where the electric field is large and is of the order of 10⁶ vcm⁻¹ or more (7,8). The primary consequence of this field is to lower the dielectric constant of the interfacial medium. In aqueous media it is around 6.

Therefore, the reaction occurring in the interface should be regarded different than occurring in the bulk. As such the surface precipitation (6) may occur at lower concentration than required for bulk and may be regarded as a separate phase.

In the present study, the charge reversal on CaCO₃ particles may be due to the precipitation of hydrolysed species of hydrolysable metal ions namely Co⁺⁺, Ni⁺⁺, Cu⁺⁺ and Zn⁺⁺. As concentration of the above divalent ions are increased, the hydrolysed species of the ions increase and adsorbed at the Stern layer at calcite-water interface. When the concentration of these ions reached to a critical value (see Figure 3) they are precipitated and reverse the charge of the sol particles.

In the case of aluminium, first charge reversal is due to the precipitation of hydrolysed metal ions, but when their concentration is increased further the second reversal of charge occurs. This may be due to the dissolution of the surface precipitate. The third charge reversal may be ascribed due to the formation of polynuclear complex formed at higher concentration of Al³⁺ ions and also at higher pH. In the case of lanthanum ions, possibility of polynuclear complex are remote, hence after second charge reversal the particles remain negatively charged.

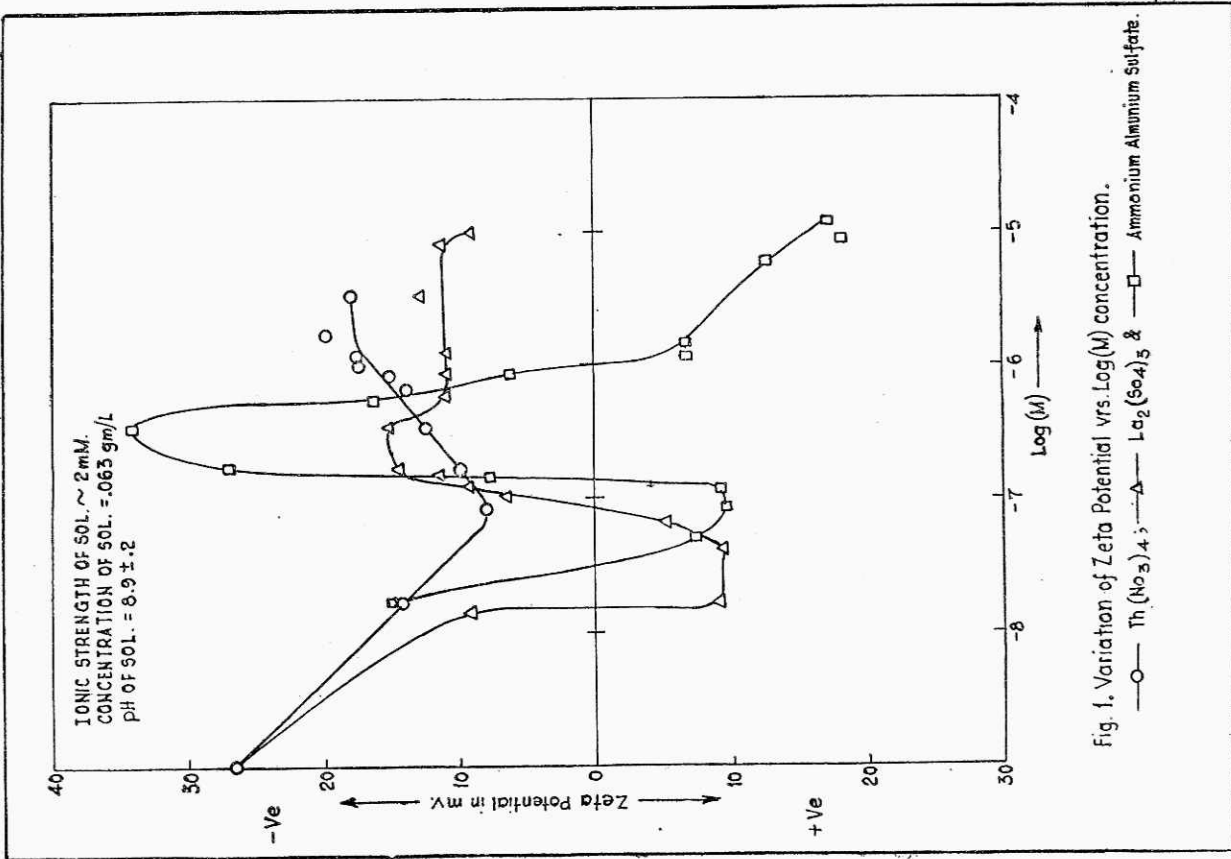


Fig. 1. Variation of Zeta Potential vs. Log(M) concentration.

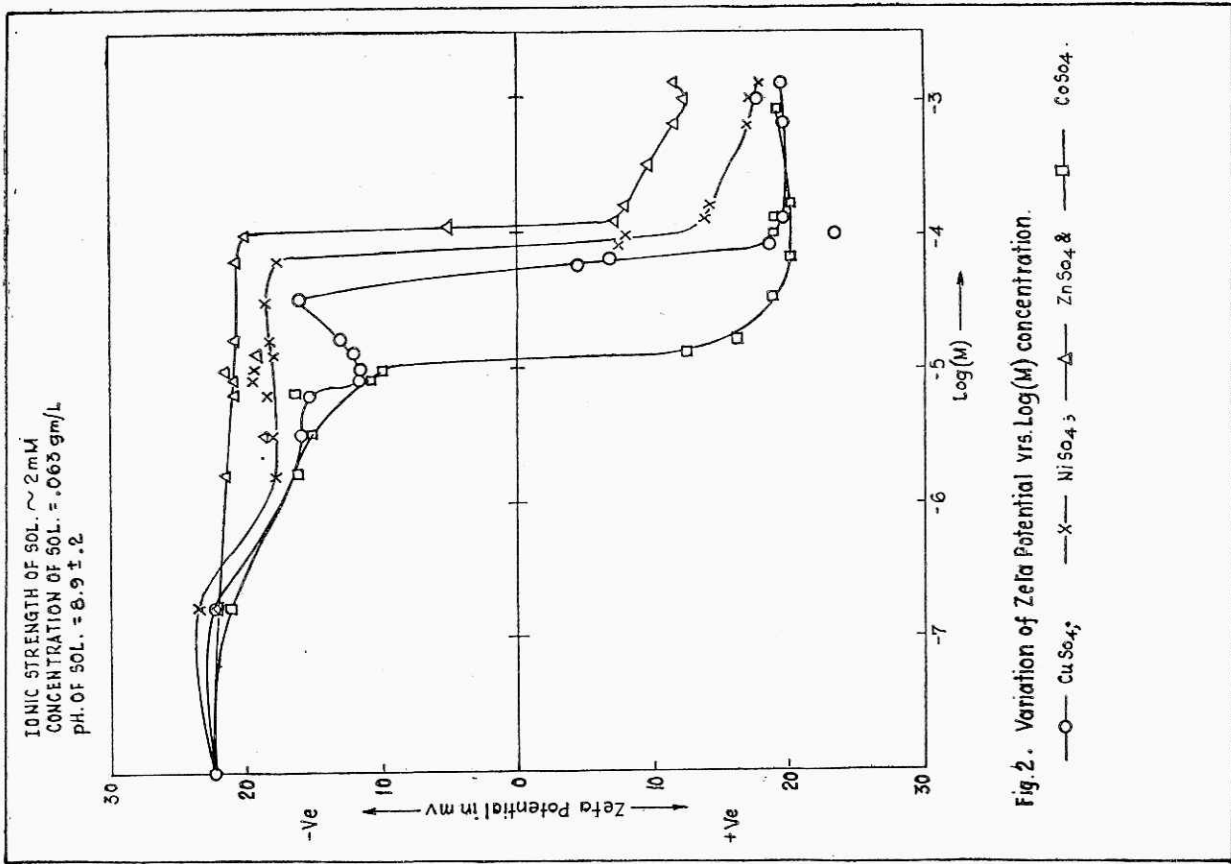
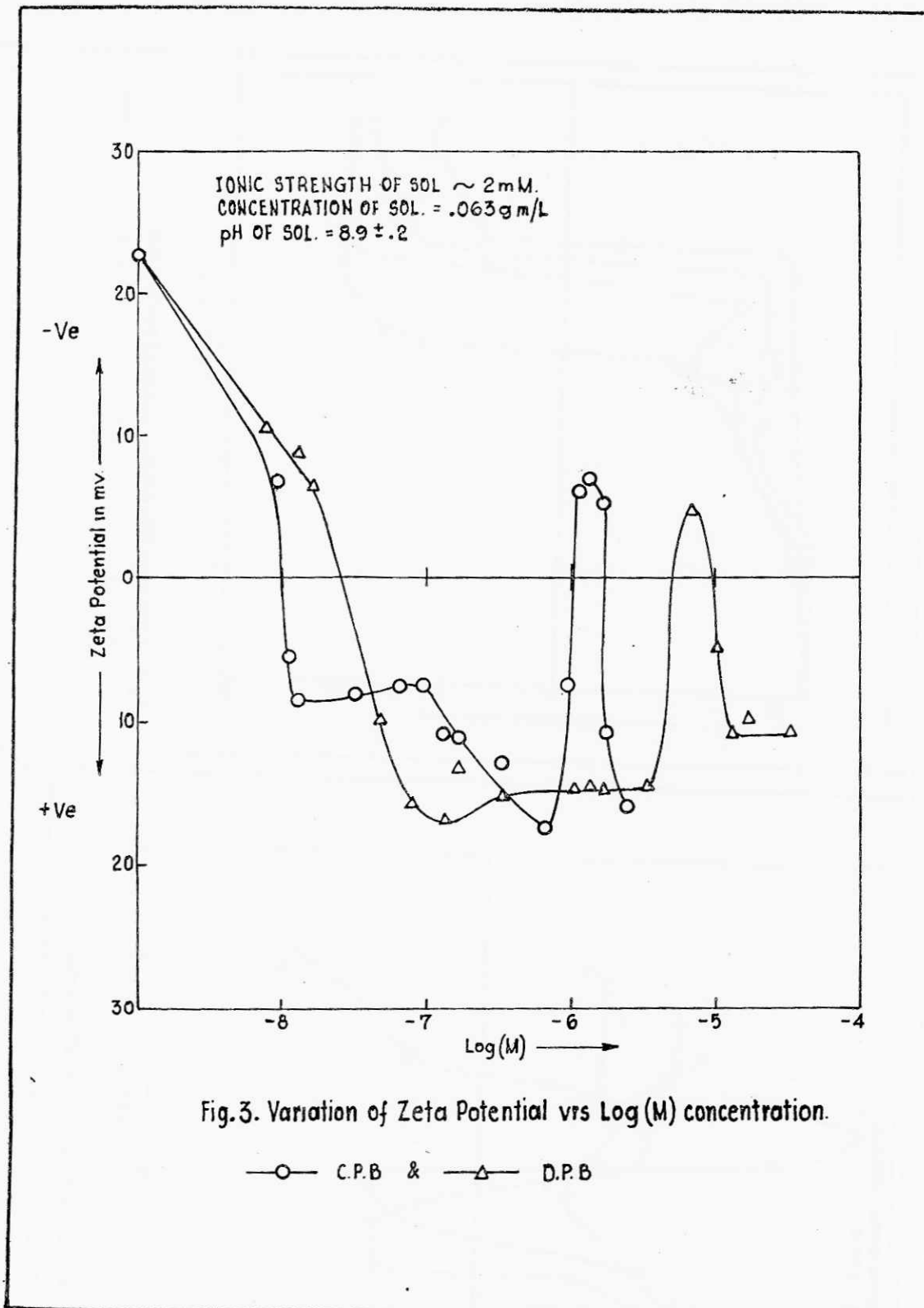
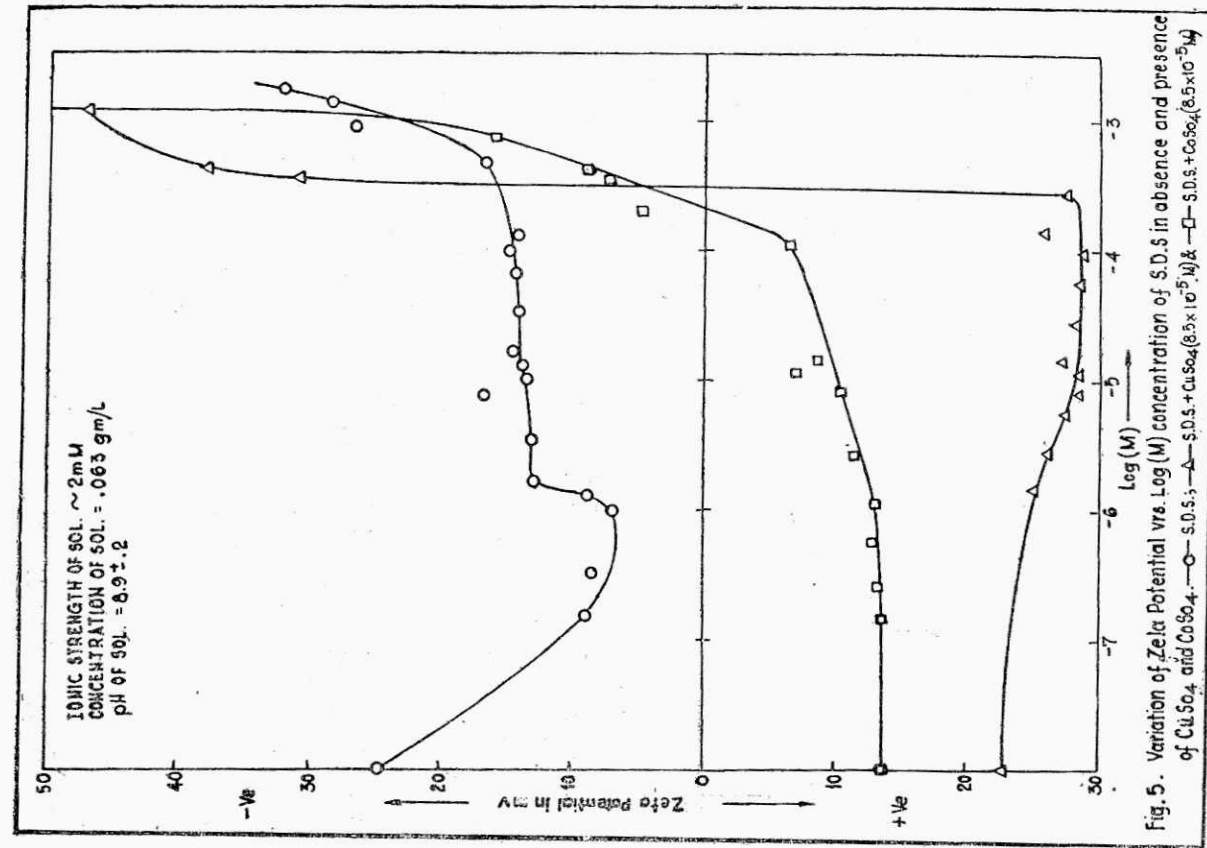
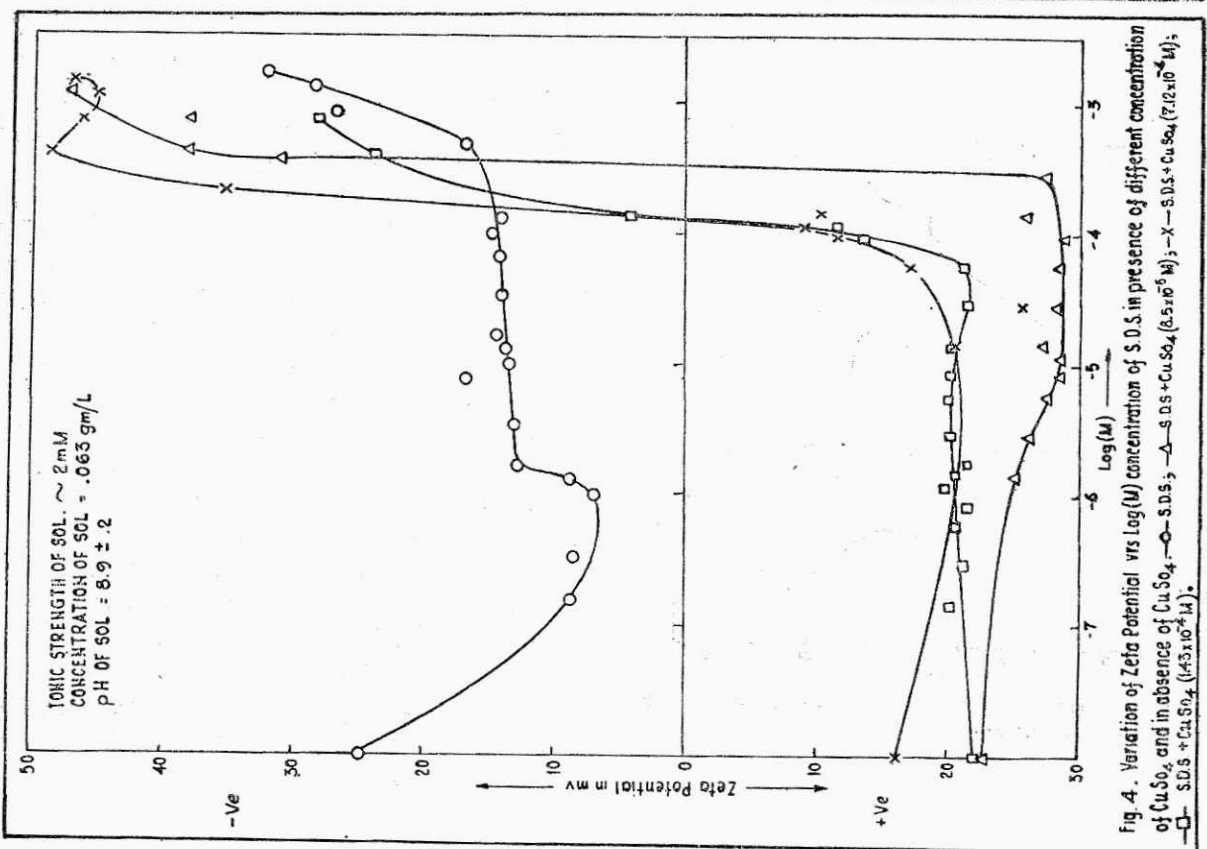


Fig. 2. Variation of Zeta Potential vs. Log(M) concentration.





Thorium ions present a different case. As reported earlier, excess of sodium carbonate was present in the bulk to stabilise the calcium carbonate sol. Th^{4+} ions being highly charged, are ineffective in producing the charge reversal on the sol particles. It may be due to the solubility of the thorium hydroxide in excess of carbonate ions (9). This result further confirms the mechanism of charge reversal on sol particles discussed above.

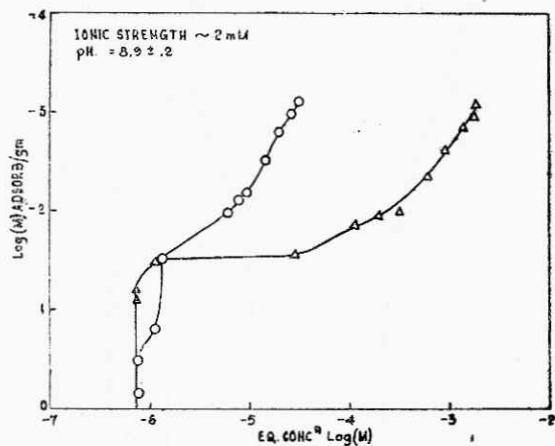


Fig. 6 Adsorption of Cu^{++} and Co^{++} on CaCO_3 powder. —○— CuSO_4 ; —△— CoSO_4

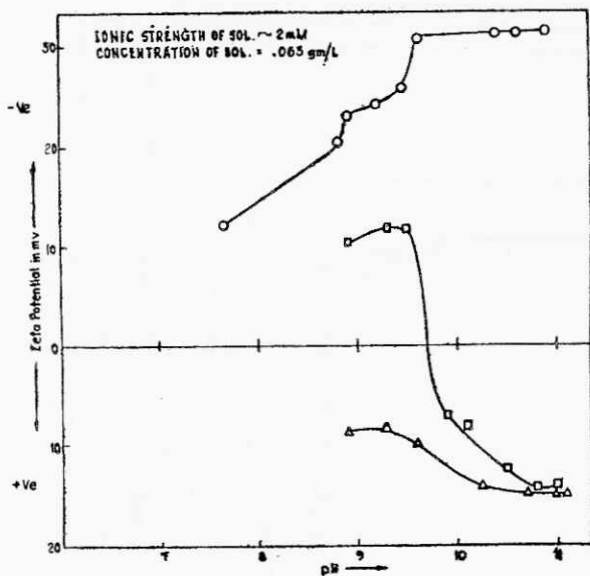


Fig. 7 Variation of Zeta Potential vs pH —○— Sol; —□— Sol + CoSO_4 (0.57×10^{-5}); —△— Sol + CoSO_4 (1.428×10^{-5} M).

Interaction of S. D. S. with calcite suspension in presence of hydrolysable metal ions :

The changes in the structure of the double layer in presence Cu^{++} and Co^{++} ions are shown in Figure 8 (b) and 8 (c), the later gives the change in double layer structure when the charge on the particle is reversed i.e. surface charge becomes positive. The action of these metal ions has been ascribed to activate the surface of calcite suspension. Fig. 8(d) gives the changes in the double layer with varying concentration of S. D. S. in presence of fixed concentration of activating ions. Figure (4) & (5) show a second charge reversal occurs at a certain concentration of S. D. S. depending on concentration of Cu^{++} and Co^{++} ions. This interaction immediately suggest that the surface become again hydrophobic because negative polar group point towards the surface and the tail in the solution. Effective concentration of S.D.S. for the coverage of the surface is 3.57×10^{-4} . Hence S.D.S. and other commercially available anionic surface active agents can be used as collecting ions.

Important work on flotation of calcareous phosphate ore is already mentioned earlier (10, 11). With the exception of work done at Sala International, sodium oleate or oleic acid as collector, sulphuric acid and phosphoric acid as pH regulator and phosphorite depressant respectively has been used. The reported consumption of phosphoric acid is nearly 7 kg/ton. After removing calcite from the calcareous phosphatic ore, sodium silicate was used to depress calcite while Serrana, Jacupiranga, Brazil used Serrana starch. The collector used by Sala International was developed by an associate of the company. However these processes involved costly item for beneficiation of calcareous phosphate ore. The beauty of this work lies in the fact that conventional Cu^{++} or Co^{++} act as activator for calcite and a common anionic surface active agent can be used as collector. The laboratory tests have shown that calcite can be floated at pH 5 after conditioning, while phosphorite does not.

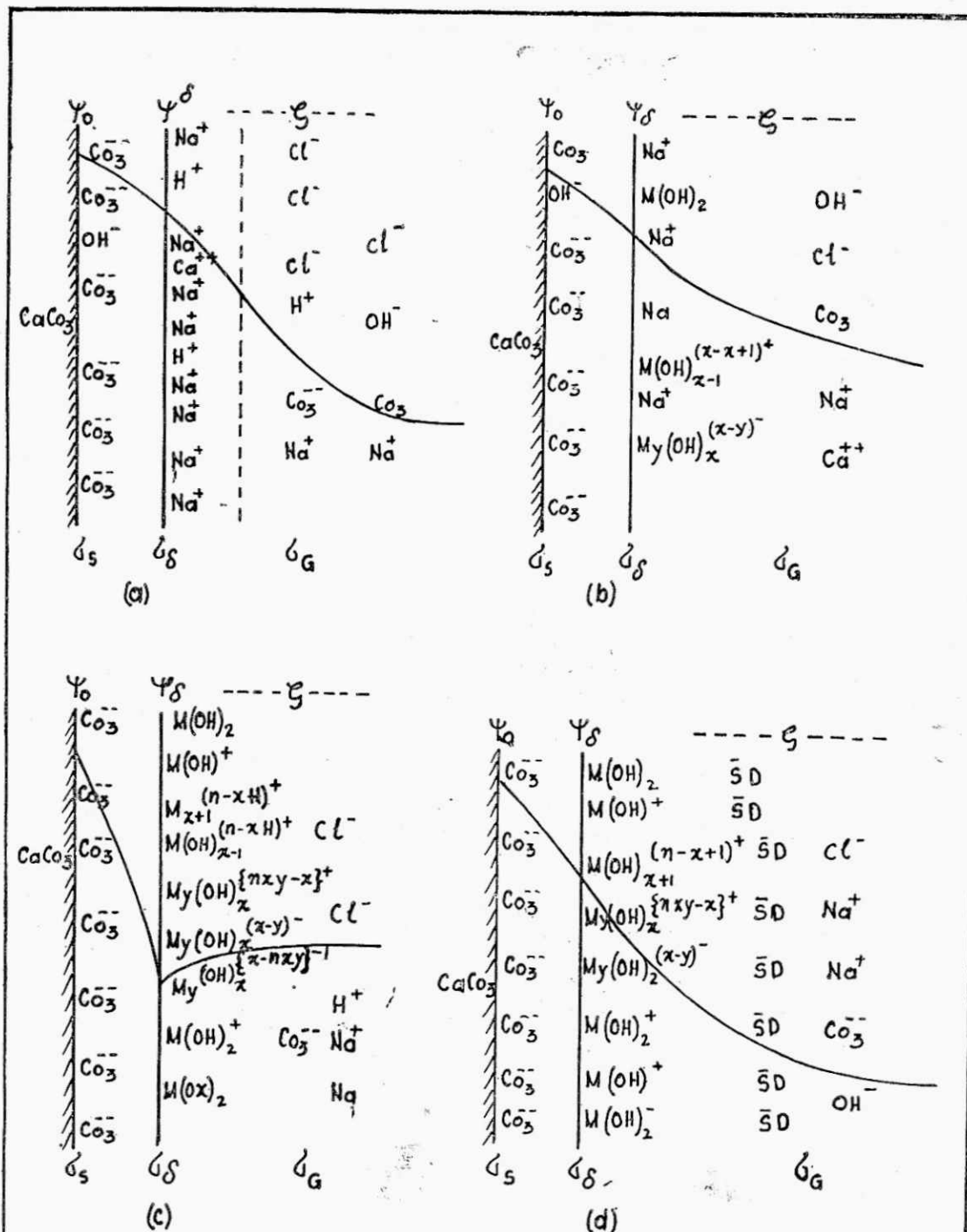


Fig. 8. Structure of double layer; (a) CaCO_3 (negative) sol; (b) In presence of hydrolysable metal ions with a negative charge; (c) In presence of hydrolysable ions with charge reversal and (d) in presence of hydrolysable metal ions and S.D.S.

Acknowledgement :

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DISCUSSION :

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Question : State of Bihar has a sedimentary deposit of calcareous phosphate containing on an average of 2% P_2O_5 , 20% $CaCO_3$, 25% Silica and micro constituents like Cu, Zn, The in traces. Can this material be beneficiated for commercial utilisation?

One of us (B.K.L. Das) is thankful to the Ministry of Education and Culture, Government of India for the award of J. R. F. and also to Principal, R. I. T., Jamshedpur for the award of Institute Junior Research Fellowship.

Author : I think the ore can be upgraded provided fundamental studies on nature of gangue minerals etc. are performed. Since calcite and silica both are activated under a particular condition by transition metal ions, the ore may be beneficiated with suitable collectors after determining the prerequisite conditions.