

The Ion Effect on Dewaterability of Alumina-Metal EDTA System

Jeung-Bea Kim

Faculty of Environmental Studies, Keimyung University, Daegu 704-701, Korea

(Manuscript received 25 March, 2003; accepted 13 May, 2003)

The specific ion effects are observed in the alumina-metal EDTA(Ethylene Diamine Tetraacetic Acid) system. These effects seem to be associated with the fluidity of the metal ion in the complex. A consideration of the order of adsorption of the complexes on alumina indicates that a specific ion effect also affects the stability of the system. It is clear that EDTA and its heavy metal complexes have a significant effect on the dewaterability of alumina. These effects are not well represented by zeta potential measurements, especially for EDTA alone. With the nonspecciating complexes, though, the maximum permeability is predicted by the pH_{zpc} from zeta potential measurements. At other pH value, the refiltration rate is better predicted by the state of coagulation as measured by $\log W$.

Key words : Dewaterability, Refiltration, Zeta potential, Alumina, EDTA

1. Introduction

Water and wastewater treatment involve solid-liquid separation at some stage in the process. Mining processes must remove solids from liquid phases in ore recovery and in wash water treatment. In paper manufacturing, fibers are separated from aqueous slurries in very specific ways to obtain a given type of product. In all these cases, two processes of solid separation are dominant-flocculation and dewatering. There are many instances in which the removal of a dispersed solid phase from a continuous liquid phase is required. Particles of the solid phase are first aggregated so they will settle through the liquid. To further reduce the amount of solvent, some additional dewatering step such as filtration or centrifugation is utilized. The solid phase is thus effectively separated from the dispersion and the water is clarified. Waste treatment schemes aim to produce clear water, while mining and paper industries are more

interested in the characteristics of the solids. It is therefore apparent that research in the area of solid-liquid separation is of environmental as well as industrial value.

Ultimately, the solid-liquid separation process involves the dewatering of unstable, settled slurries. This aspect of the process at times can be the most difficult. Mining slurries consisting of swelling clays and phosphate are on example in which 80~90% of the slurry may be water in gel form. In order to landfill these wastes, it is necessary to dewater the solids to an extent that they can bear a load¹⁾. Water treatment facilities also create large amounts of chemical sludges from softening and coagulation processes which must be dewatered to reduce transportation and disposal costs.

A number of studies have reported that the dewaterability of a slurry is greatly influenced by the chemical pretreatment²⁻⁵⁾. The chemical conditions in solution mostly affect sludge dewaterability by altering the state of aggregation of the solids. Improved aggregation is usually assumed to cause improved permeability of a sludge cake due to a decrease in the effective surface area over which the fluid must flow^{2,3,6)}. A consideration of the Kozeny-Carman

Corresponding Author : Jeung-Bea Kim, Faculty of Environmental Studies, Keimyung University, Daegu 704-701, Korea
Phone : +82-53-580-5244
E-mail : jbkim@kmu.ac.kr

equation(1) shows that the flow of fluid is inversely related to the square of the surface area⁷⁾.

$$\begin{aligned} \frac{Q}{A} &= \frac{\varepsilon^3}{\kappa S_c (1-\varepsilon)^2} \times \frac{dP}{dz} \times \frac{1}{\mu} \\ &= \frac{1}{\xi} \times \frac{dP}{dz} \times \frac{1}{\mu} \end{aligned} \quad (1)$$

Where ξ is specific resistance(sec²/gm), ε = porosity of cake(void volume), κ = constant (function of pore geometry), S_c = surface area of solids in cake, P = pressure drop across cake, z = cake thickness, μ = fluid viscosity, Q = flowrate of filtrate and A is area of filter cake.

Additionally, it has been shown that not only the extent of, but also the manner of flocculation is important^{4,8)}. Grace found that upon application of compressive stress, a weak floc structure would quickly disperse into primary particles causing the filtration resistance to rapidly increase⁴⁾. Other workers have found that clay slurries are also dependent on the type of flocculation which occurs. A stacking of platelets was shown to be preferable to an edge to face aggregation because the latter was easily broken down and inhibited dewatering at increasing pressure¹⁾. Thus, it seems that the process of dewatering is significantly affected by coagulation properties and a study which would accurately measure the coagulation properties of a particular system, could provide insight into the dewatering process. The dewaterability of aluminum oxide was therefore measured and the following objectives were defined. It is known that aluminum oxide is useful in heavy metal remove metal from water by acting as an adsorbent⁹⁻¹²⁾. Permeability data were to be compared to accurate stability data to assess the inter-relationship between coagulation and dewaterability. Secondly, if heavy metal removal by alumina adsorption is to be a viable process, a dewatering step would be included, thus knowledge of how adsorbed metal-EDTA species affect dewaterability and an identification of the controlling parameters would be essential. Finally, and most importantly, it was believed that chemical effects on the solvent which affect these two processes might be best observed in a concentrated slurry. It has been shown in the literature that ionic effects which were not observed in light scattering measurements of

coagulation, were discernable in filtration rate studies done by capillary suction time measurements.¹⁶⁾ Recall that the hypothesis to be investigated was that solvent effects, caused by the ions at the processes. Therefore, it was anticipated that a study of a concentrated slurry might reveal effects that would not be measurable in a more dilute, coagulation experiment. It was decided that an adaptation of the refiltration technique used by LaMer^{2,3,6)}, would be utilized to measure chemical effects on the dewatering of alumina in the presence of various chemical species.

In the present study, the dewaterability of the flocculated oxide was investigated. Removal of as much water as possible is accomplished in the dewatering step. Improvement here provides economic benefits by reducing the volume of the slurry. This decreases transportation costs if disposal of the slurry is required as it is in waste treatment.

2. Experimental Methods

2.1. Materials and Equipments

The refiltration experiments were run using a 25 mm plastic in-line filter holder with 0.45 μ m filters, connected to a heavy walled glass reservoir. A valve was placed between the reservoir and the filter, so that the refiltered sample could be introduced into the reservoir without reducing the pressure on the deposited cake. Pressurized nitrogen was used to create a pressure drop of 20 psig. Air would not have been useful due to its effect on the pH, this oxide system being very sensitive to pH.

Solutions were made up as in the coagulation experiments, using the same materials. It was necessary to determine an optimum volume of the 300 mg/L suspension which would give a thick enough cake to provide good sensitivity. Sixty milliliters was found to be satisfactory with the 25 mm filters.

2.2. Procedure

The pH of the solution was adjusted and allowed to come to equilibrium. This usually only required one to two minutes, except near the point of zero zeta potential, where perhaps four to five minutes was necessary. Obviously, aggregation was occurring during this time, thus,

to normalize the experiment, a sonic redispersion was done for 1 minute on the adjusted samples. These were then immediately introduced into the reservoir, which was pressurized and the filtrate collected. When all but 2 ml had been collected, the valve was shut and the reservoir depressurized. This left some liquid in the tube above the filter so that the cake was undisturbed. The filtrate pH was measured and readjusted to the original value if necessary, then reintroduced into the reservoir. Pressure was again established and the valve opened. At least five milliliters were allowed to flow through before measurements of volume and time were recorded. This last step allowed any remaining dispersion to be deposited before the refiltration rate was measured. Ten milliliters total were refiltered from which 20 data points of volume and time were taken. One had to always be careful not to allow gas bubbles to reside on the filter as a consistent cake would not be deposited. Results were reported as refiltration rate (ml/min) versus pH for various chemical condition.

3. Results and Discussion

3.1. Results of refiltration rate

The results of refiltration experiments for the 2.5×10^{-2} M NaClO₄ background, 10^{-4} M EDTA, and five metal-EDTA complexes, also at 10^{-4} M,

are displayed in Fig. 1 through 7. For ease of comparison, the data is presented in combination with zeta potential and stability ratio measurements using a common abscissa in pH. All aspects of the stability and dewaterability, as tested in this work, are indicated, providing one with information regarding the interplay of these two processes in solid-liquid separation.

Generally, excellent agreement between the various parameters exist. The refiltration rate rises in conjunction with the decrease of stability and peaks near the point of zero zeta potential. In all cases except 10^{-4} M EDTA, the refiltration rate maximum predicts the pH_{zpc} surprisingly well, within 0.25 pH units. EDTA, Fig. 2, instead shows a maximum in permeability at pH 7 where the zeta potential curve displays a minimum. At this point, a significant amount of the trivalent species exists and although the adsorption density is decreasing, the zeta potential begins to increase due to the increase in valence, thus causing the minimum. Note also that the maximum never reaches the same magnitude as it does in the presence of the other complexes. At pH 9, the pH_{zpc} , the rate has in fact decreased slightly from the maximum, which is not expected due to the small amount adsorbed. Above pH 9 the refiltration rate continues to be lower than the background even though there is less than 1% of the EDTA adsorbed in our preliminary experiments. Evidently, not much

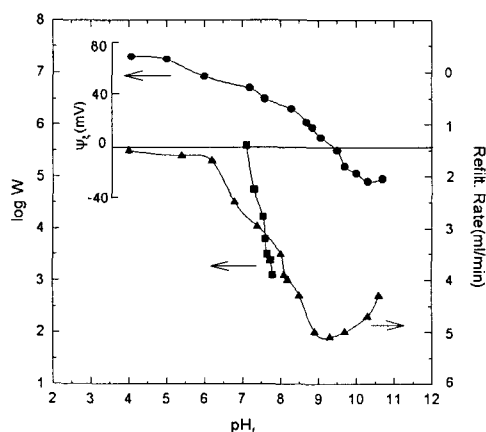


Fig. 1. Interrelationship of zeta potential, Ψ_{ζ} (●), stability ratio, W (■), and refiltration rate (▲), for 0.3g/L γ -Al₂O₃ and 0.025 M NaClO₄.

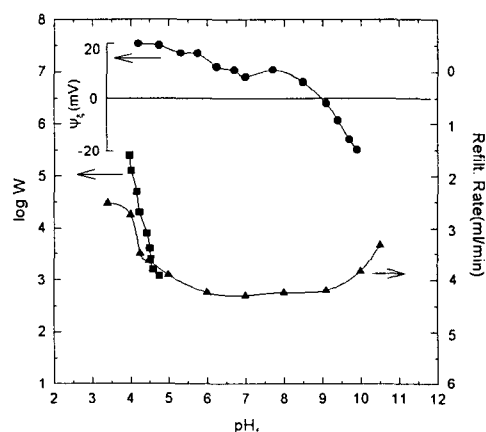


Fig. 2. Interrelationship of zeta potential, Ψ_{ζ} (●), stability ratio, W (■), and refiltration rate (▲), for 0.3g/L γ -Al₂O₃, 0.025 M NaClO₄ and 10^{-4} M Na-EDTA initial concentration.

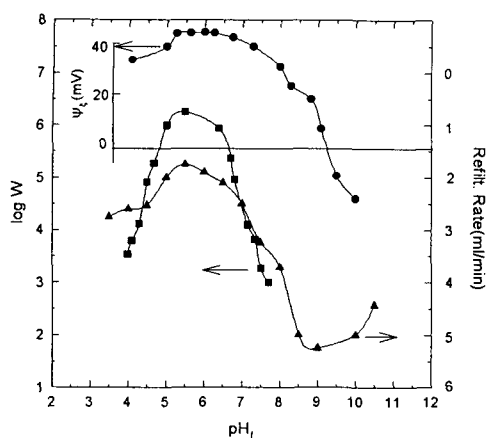


Fig. 3. Interrelationship of zeta potential, Ψ_{ζ} (●), stability ratio, W (■), and refiltration rate (▲), for 0.3g/L γ - Al_2O_3 , 0.025 M NaClO_4 and 10^{-4} M Pb-EDTA initial concentration.

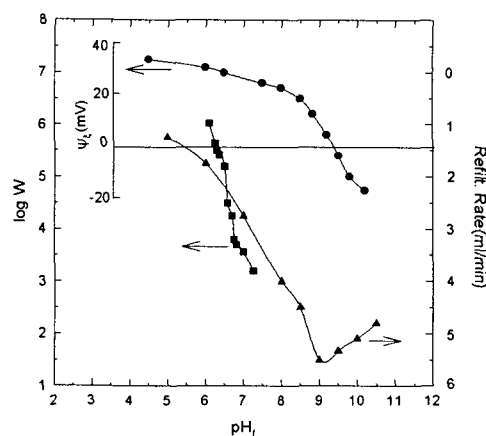


Fig. 4. Interrelationship of zeta potential, Ψ_{ζ} (●), stability ratio, W (■), and refiltration rate (▲), for 0.3g/L γ - Al_2O_3 , 0.025 M NaClO_4 and 10^{-4} M Cd-EDTA initial concentration.

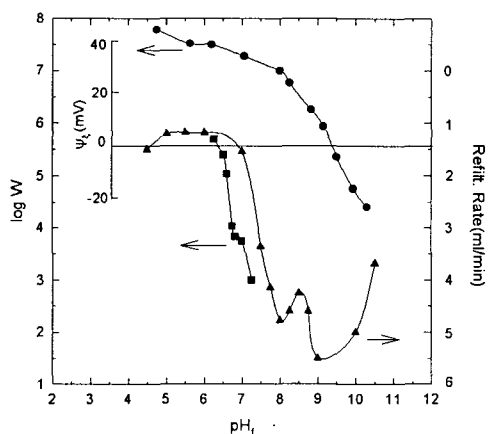


Fig. 5. Interrelationship of zeta potential, Ψ_{ζ} (●), stability ratio, W (■), and refiltration rate (▲), for 0.3g/L γ - Al_2O_3 , 0.025 M NaClO_4 and 10^{-4} M Zn-EDTA initial concentration.

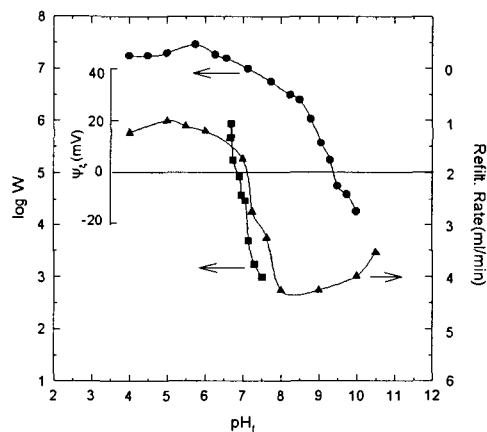


Fig. 6. Interrelationship of zeta potential, Ψ_{ζ} (●), stability ratio, W (■), and refiltration rate (▲), for 0.3g/L γ - Al_2O_3 , 0.025 M NaClO_4 and 10^{-4} M Ni-EDTA initial concentration.

adsorption of the trivalent species is necessary to affect the permeability. That some adsorption is indeed occurring, however, is shown by the fact that the zeta potential between pH 9 and 11 is lower than it is for the background as shown in Fig. 1.

It is concluded that the adsorbed EDTA is hindering the refiltration rate from reaching its maximum due to either a difference in the manner of coagulation which is altering the cake properties, or due to changes in interstitial

solvent viscosity. At the refiltration peak, the state of the system, as measured by the stability ratio, is completely destabilized, however, one can see that changes are occurring in the refiltration rate. In the region where log W is not measurable, it is impossible to distinguish between the two effects mentioned above. This discrimination can only be done in the region where log W values can be measured. Therefore, filtration rates can be compared at equal log W values which keeps cake properties constant and

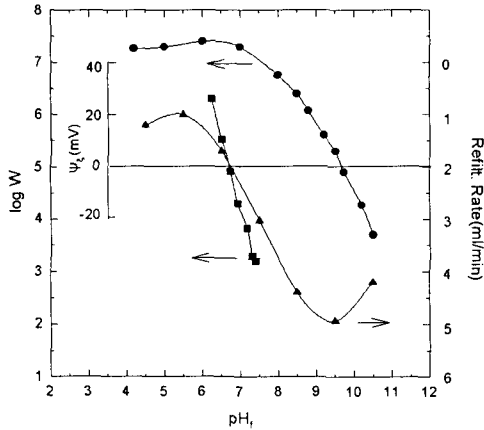


Fig. 7. Interrelationship of zeta potential, Ψ_z (●), stability ratio, W(■), and refiltration rate (▲), for 0.3g/L γ -Al₂O₃, 0.025 M NaClO₄ and 10⁻⁴ M Cu-EDTA initial concentration.

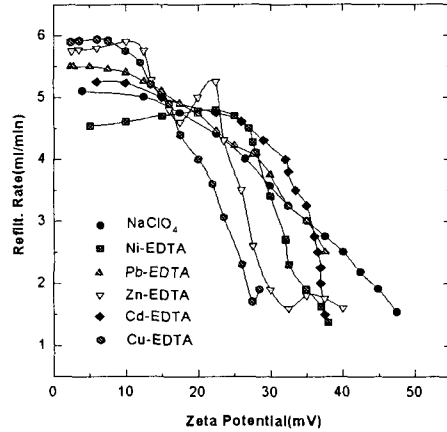


Fig. 9. Refiltration rate of 0.3g/L γ -Al₂O₃ as a function of zeta potential for various adsorbates at 10⁻⁴ M initial concentration and 0.025 M NaClO₄(NaClO₄ curve is a blank with no adsorbate).

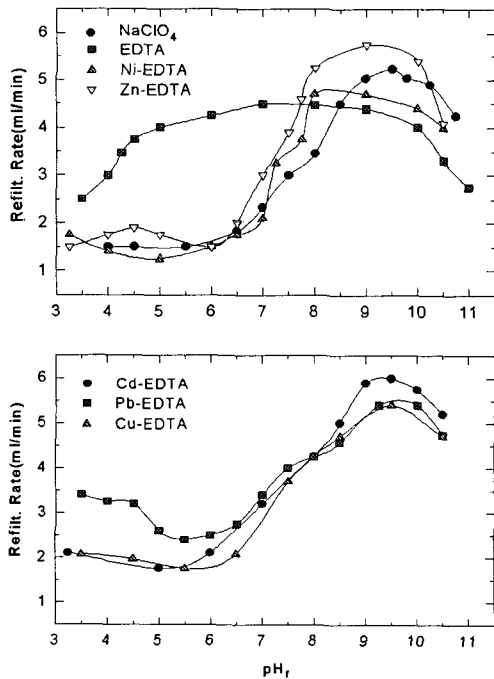


Fig. 8. Refiltration rate of 0.3g/L γ -Al₂O₃ as a function of pH for various adsorbates at 10⁻⁴ M initial concentration and 0.025 M NaClO₄(NaClO₄ curve is a blank with no adsorbate).

any variations in permeability can be attributed to viscosity changes.

3.2. Results of Stability ratio

The stability data (log W vs pH in Fig. 1 through 7) is also in good agreement with the refiltration data. Differences do exist, however, between the various chemical treatments. It is observed that the decrease in refiltration rate with pH is almost parallel to the log W versus pH curve for EDTA, Zn-EDTA and Ni-EDTA which is not the case with the background salt and the other metal-EDTA complexes. As a final general observation, the Zn-EDTA refiltration curve displays a curious maximum at pH 8.5 which does not manifest itself in either the zeta potential or in the stability data. This data was repeated by another worker with the same result, and it is taken to be accurate. Notice that the rate at the maximum corresponds to the lower limit for which stability data could be measured - that at pH 7.3, rate = 3.5 ml/min. Hence, a change in stability could have occurred which would not have been measurable by the stability ratio experiments. Still, it is noteworthy that this effect is independent of the zeta potential and as such must be chemical, not electrical in nature.

Further interpretation of these results is more usefully accomplished by plotting all the refiltration data as a function of pH and zeta potential. Figs. 8 through 9 are these plots. Recalling the Kozeny-Carman equation(1), the refiltration rate should be a function of cake properties porosity,

effective surface area, the capillary structure and the viscosity of the interstitial fluid, the pressure drop being constant. These cake properties are, in turn, dependent on the state of aggregation of the solids. As discussed, pH affects the adsorption density and the electrical potential on the solid particles, both of which determine the state of aggregation of the particles. It has often been hoped that the zeta potential would provide an easy parameter to indicate the state of aggregation.

4. Conclusions

It is concluded that specific ion effects are observed in the alumina-metal EDTA system. These effects seem to be associated with the fluidity of the metal ion in the complex. Refiltration data at equal log W values shows that refiltration rate is dependent on the type of complex. A consideration of the order of adsorption of the complexes on alumina indicates that a specific ion effect also affects the stability of the system. It is not expected, that the order or the pH dependence of adsorption will be altered at lower solids concentration. Considering the more practical aspects of the work, it is clear that EDTA and its heavy metal complexes have a significant effect on the dewaterability of alumina. These effects are not well represented by zeta potential measurements, especially for EDTA alone. With the nonspeciating complexes, though, the maximum permeability is predicted by the pH_{zpc} from zeta potential measurements. At other pH value, the refiltration rate is better predicted by the state of coagulation as measured by log W.

References

- 1) Wright, H. J. L. and J. A. Kitchener, 1976, The Problem of Dewatering Clay Slurries : Factors Controlling Filterability, *J. Colloid Interface Sci.*, 56(1), 57-63.
- 2) Smellie, R. H. and V. K. LaMer, 1958, Flocculation, Subsidence and Filtration of Phosphate Slimes, *J. Coll. Sci.*, 23, 589-599.
- 3) Healy, T. W. and V. K. LaMer, 1962, The Adsorption-Flocculation Reactions of a Polymer with an Aqueous Colloidal Dispersion, *J. Phys. Chem.*, 66, 1835-1838.
- 4) Grace, H. P., 1953, Resistance and Compressibility of Filter Cakes, *Chemical Engineering Progress*, 49(6), 303-318.
- 5) Cleasby, J. L., 1981, Filtration-Back to the Basics, *Proceed. AWWA Seminar on Coagulation and Filtration*, AWWA Assoc., Denver, Co, 59-84pp.
- 6) Kane, J. C., V. K. LaMer and H. B. Linford, 1964, The Effect of Solid Content on the Adsorption and Flocculation Behavior of Silica Suspension, *J. Phys. Chem.*, 63, 3539-3544.
- 7) Leclerc, D., 1973, Permeability of Filter Media, *Nato. Advd. Study Insts. Ser. 2, The Scientific Basis of Filtration*, Noordhoff Internatl. Publishing, The Netherlands, 167-182pp.
- 8) Lips A. and E. Willis, 1973, Low Angle Light Scattering Technique for Study of Coagulation, *J. Chem. Soc. Faraday Trans. I*, 69, 1226-1236.
- 9) Huang, C. P. and W. Stumm, 1973, Specific Adsorption of Cations on Hydrous γ -Al₂O₃, *J. Colloid Interface Sci.*, 43(2), 409-420.
- 10) Grahame, D. C., 1947, The Electrical Double Layer and Theory of Electrocapillarity, *Chem. Rev.*, 41, 441-501.
- 11) Levine, S. and A. L. Smith, 1971, Theory of the Differential Capacity of the Oxide/Aqueous Electrolyte Interface, *Faraday Discuss. Chem. Soc.*, 52, 290-301.
- 12) Levine, S., J. Mingins and G. M. Bell, 1967, The Discrete-Ion Effect in Ionic Double-Layer Theory, *J. Electroanal. Chem.*, 13, 280-329.