A RAPID SEPARATION PROCESS OF ULTRAFINE PARTICLES FROM DILUTE AQUEOUS SUSPENSION*

Herman D. Mendoza, Dr. Eng.

Department of Mining and Metallurgical Engineering, College of Engineering,
University of the Philippines, Diliman, Quezon City

ABSTRACT

A potential rapid separation process of ultrafine particles from dilute aqueous suspensions is introduced. This process involves the separation of one or two types of ultrafine particles in aqueous suspension by heterocoagulation phenomena.

The objective of this **study** *was to develop a rapid separation process of hematite* (**a-**Fe_2O_3: 0.1μm) *particles and mixed particles of hematite and silica* (SiO_2: 0.12μm) *from their aqueous suspension using a macroscopic collector (glass beads, 80μm). Hematite particles were rapidly separated at an acidic condition, i.e.,* **-** *pH* ***5.*** *were positively charged hematite particles attached onto the negatively charged glass beads collectors. For a mixed suspension of hematite and silica particles, simultaneous separation of both silica and hematite particles occurred at an acidic condition, where both silica and glass* ***beads*** *were negatively charged, while hematite particles were positively charged. Attachment was possible because hematite particles acted as a bridge between silica particles and glass beads. This rapid solidliquid separation process is referred to as tumbling method.*

The mechanism involved in this process could be applied in the separation of ultrafine silica from geothermal effluent.

1.0 INTRODUCTION

The separation of ultrafine particles from aqueous media is of great necessity either because these particles pose a danger to the aquatic environment and/or because they are materials of great value. Ultrafine particles of iron hydroxides and oxides and other metallic compounds formed from the treatment of mine waste waters (1) and colloid materials from industrial wastes **(2)** are concrete examples of deleterious particles that need to be separated from the aquatic environment. On the other hand, the recovery of ultrafine particles of minerals, ceramic materials, cutting wastes (3), etc., from the bulk of aqueous media is also important. However, since the development of separation treatments is a very sensitive subject because of environmental and economic constraints, a set of criteria must be formulated to serve **as** basis for the development of a separation process for ultrafine particles from the aqueous environment. These criteria should include rapidity of separation, simplicity of operation, non-contamination and low costs.

Generally, separation from aqueous media becomes difficult when particles become so small that Brownian movement rather than gravitational force begins to govern their behavior. Moreover, separation becomes difficult when the concentration of ultrafine particles is very low in relation to its bulk media. Presently, the more common solid/liquid separation treatments for ultrafine particles are ultracentrifugation, ultrafiltration (4), and flocculation ***(5)*** methods. These processes, however, make use of special equipment which require high power and pressure application. Moreover, the use of flocculants usually results in additional contamination of the aqueous environment. This negates the above mentioned criteria.

---

* A portion **of** this report **is** to be published in the Intern. Journal **of** Mineral Processing (1995)

To be able to develop a simple and effective process, focus is placed on the distinct surface characteristics of ultrafine particles in aqueous suspension to achieve solid/liquid separation. Many works have already investigated the application of heterocoagulation as the basis for separation, which includes the attachment of a single type of fine'particle from flowing suspension onto macroscopic solid surfaces (sometimes referred to as collectors). These served as model studies for various sectors like in industries which deal with corrosion(6), filtration(7), paper making(8), ceramics(9), and mineral extraction. From a practical viewpoint, however, these works are not necessarily in conformity with the above mentioned criteria. It is then the aim of this study to introduce a mechanism to serve as a potential alternative to separate ultrafine particles of low concentration in aqueous suspension which incorporates the elements of rapidity, simplicity, non-contamination and low costs. Moreover, investigation was done not only on the separation of one type of fine particle but also on the simultaneous separation of two types of ultrafine particles with different surface characteristics from the bulk of aqueous suspension. The study of separating two types of ultrafine particles from aqueous environment is very important because in most cases ultrafine particles, which are considered pollutants, are usually composed of one or a mixture of various materials.

To understand clearly the mechanism involved in the separation process, a comprehensive step-by-step investigation of the stability of the different materials in aqueous suspension will be presented in the following order: First, the attachment behavior or stability of silica-hematite, hematite-glass beads, and glass beads-silica interactions; and lastly, the stability of glass beads-hematite-silica interaction. The stability of hematite-hematite and silica-silica interactions were already investigated by Chen.(10).

2.0 METHODS

2.1 Materials

Monodispersed spherical silica particles, with a modal diameter of 0.12 µm were prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in a water-ethanol mixture containing ammonia as in the method by Stóber and Fink (11). Monodispersed hematite particles with a modal diameter of 0.10 µm were prepared by hydrothermal aging of an acidic $FeCl_3$ solution as described in the method of Matijevic and Scheiner (12). Glass beads were of commercial grade (Toshin Co.) and were purchased locally. It is generally composed of 71.5 % SiO_2, 14% Na_2O and 13% CaO. Spherical glass beads of commercial grade were passed through 105 µm and retained on 74 µm **JIS** sieves to classify glass beads with a mean diameter of 80 µm.

The size, shape, and distribution of the hematite and silica particles were determined using the Transmission Electron Microscope (Model H-600, Hitachi Corp.). Particle size distribution was also measured using the BI-90 Particle Analyzer (Brookhaven Instruments Corp.). Density measurements were done using a pycnometer with a volume of 1.00 cm^3 and using distilled water/toluene as solvents at 25°C. The densities of silica and hematite were 2.2 and 3.9 gm cm^{-3}, respectively. The density of the glass beads supplied by the manufacturer was 2.5 gm cm^{-3}. The above data were used to calculate the particle number concentrations.

All chemicals were of analytical reagent grade and were used without further purification. Water was doubly distilled first in stainless steel and finally in Pyrex glass boilers.

2.2 Apparatus

The apparatus was composed of two parts: a Pyrex test tube to contain the suspension and a motor drive. The test tube had an inside diameter of 1.6 cm and was 22 cm long with a fitted screw cap. This test tube was clamped to a holder which in turn was connected to the center of a motor with the purpose of rotating the test tube end-over-end. The rotation of the motor can be varied from 1 to 8 rpm.

2.3 Zeta(ζ)- Potential Measurements

Electrophoretic velocities of hematite and glass beads in aqueous solution were measured using a Rank Brothers Mark II micrelectrophoresis apparatus with a flat rectangular quartz cell. Glass beads crushed to a modal diameter of 5 μm were used to determine the ζ- potentials of the glass beads, on the assumption that the potentials measured would be the same as those of the original glass beads. The ζ- potentials were calculated using Henry's equation(13). The ζ - potentials of silica particles were measured using the Electrophoretic Light Scattering Spectrophotometer ELS-800, Otsuka Electronics Co. (14).

2.4 Coagulation/ Dispersion Tests for Silica and Hematite Particles

The dispersion or coagulation of particle suspension was determined by measuring the absorbance of the suspension in the presence of 1×10^{-3} mol dm^{-3} KNO_3 as supporting electrolyte. Particle number concentration of the suspension for heterocoagulation experiments was 1.35×10^{10} particles per cm^3. In the case of the mixed suspension, the particle number concentration ratio of the silica to hematite particles was 1:1. The 30 cm^3 suspensions in test tubes, pH of which was adjusted to the desired value, were treated by ultrasonic irradiation for 10 minutes and then left to stand for around 24 hours at room temperature. Samples with a volume of 4 cm^3 were taken from the top solution and placed into a 4 cm^3 cell for absorbance measurement at a wavelength of 400 nm using the Shimadzu UV 240 Spectrophotometer.

2.5 Separation Stage

Individual suspensions of silica and hematite particles having the same particle number concentration of 1.35×10^{10} particles per cm^3 were prepared. Each suspension was equilibrated separately at the desired pH in the presence of a constant electrolyte concentration (10^{-3} mol dm^{-3} KNO_3). For separation of mixed particles, suspensions of hematite and silica of the same pH were mixed together in equal proportions. The glass beads, which were used as the collector, were also equilibrated at the desired pH and in the presence of the same electrolyte concentration.

The tumbling method was used to effect the attachment of hematite, silica particles, and their mixtures onto glass beads. Five (5) grams of glass beads with an electrolyte solution of desired pH were initially placed into a 30 cm^3 Pyrex glass tube fitted with a screw cap. The supernatant solution formed as a result of the settling of the glass beads at the bottom of the tube was removed by decantation. After this procedure, a suspension pre-treated with ultrasonic irradiation for 10 minutes was then added. The tumbling tube was capped and the contents were immediately mixed by rotating the tube end-over-end at a rate of 8 rpm for 20 minutes at 25°C. After tumbling, the tube was left to stand for around 10 minutes in an upright position until all the glass beads loaded with particles had settled at the bottom of the tumbling tube. The supernatant solution was removed by decantation and placed in clean containers and later the concentration of the remaining unattached particles were then analyzed.

The concentrations of hematite and/or silica particles in the supernatant solution after tumbling procedure were determined simultaneously by chemical analysis using the Inductively Coupled Plasma- Atomic Emission Spectroscopy (ICP-AES).

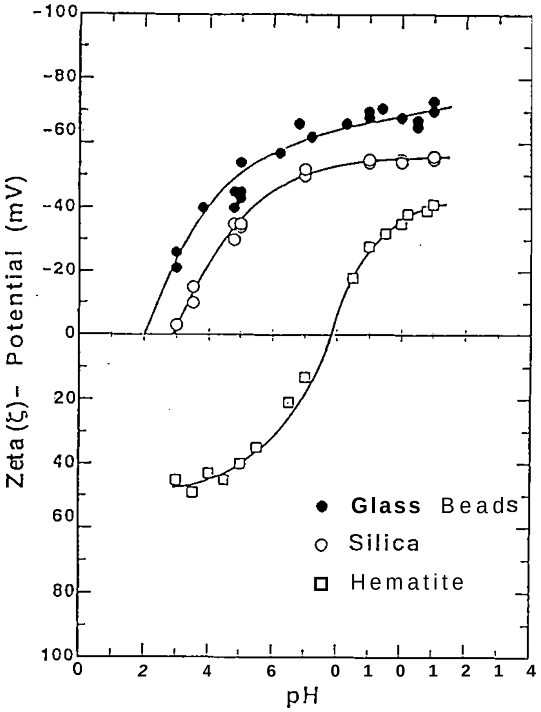

Fig. I. Zeta(ζ)- potential measurements for glass beads, hematite, and silica particles as a function of pH Electrolyte concentration of 1×10^{-3} mol dm^{-3} KNO_3, at 25 °C.

3.0 RESULTS AND DISCUSSION

3.1 Zeta(ζ)-Potential Measurements

The 5-potentials of glass beads, hematite and silica particles as a function of pH are shown in Fig. 1. The iso-electric points of glass beads, silica, and hematite particles are at pH 2, 2.9, and **7.8,** respectively.

3.2 Silica-Hematite Interaction

Maintaining the total particle number concentration of a mixed suspension of silica and hematite with ratio 1:1, the stability of the mixed suspension as a function of pH was determined, as shown in Fig. 2. After 12 hours, the suspension exhibited destabilization generally at acidic conditions, as indicated by the lowering of absorbance. Under the conditions between pH 3 and **8,** significant heterocoagulation of hematite and silica particles was evident with the formation of settled aggregates at the bottom of the test tubes.

3.3 Glass Beads-Silica Interaction

The stability of silica particles and glass beads in aqueous media was also determined. The fraction of silica particles attached to glass beads as a function of pH is shown in Fig. 3 . There was no significant attachment of silica particles onto glass beads observed throughout the pH ranges investigated.

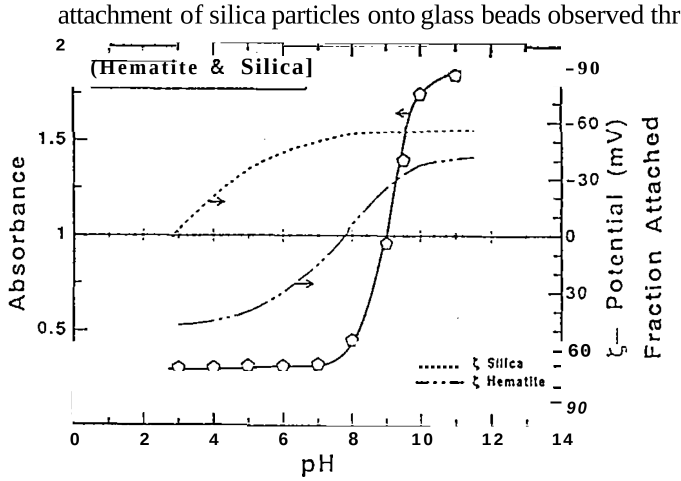

Fig. 2. Absorbance of a mixture of silica and hematite suspension as a function of pH (after 12 hours) and in relation to the <- potentials of hematite and silica particles. Total particle no. concentration of hematite and silica particles with a 1:1 ratio is $\approx 1.35 \times 10^{10}$ particles per cm ^{3} . Volume of suspension is 30 cm ^{3} .

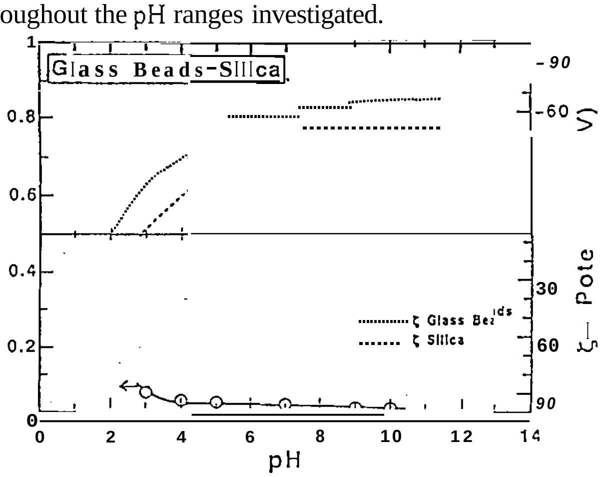

Fig. 3. Fraction of silica particles attached to glass beads after tumbling, as a function of pH and in relation to the ſ- potentials of glass beads and silica particles. Tumbling time is 20 minutes and speed of 8 rpm. Particle no. concentration of silica particles is $\approx 1.35 \times 10^{10}$ particles per cm ^{3} . Vol. of suspension is 30 cm ^{3} . Weight of glass beads is five (5) grams.

3.4 Glass Beads-Hematite Interaction

Similarly, Fig. 4 shows the attachment behavior of hematite onto glass beads, which is in terms of the fraction of hematite particles attached to glass beads as a function of pH. There was almost complete deposition of hematite particles on glass beads at conditions between pH 3 and **8** after 10 minutes of tumbling. This was because of the strong attraction existing between hematite particles and the glass beads collector due to their opposite surface potentials.

3.5 Glass Beads-Hematite-Silica Interaction

The attachment of silica and hematite particles in their mixed dispersion formed with glass beads is shown as a function of pH in Fig. **5.** At conditions between pH 3 and pH **7,** there was almost a complete recovery of silica and hematite particles by glass beads. The simultaneous deposition of hematite and silica particles onto the glass beads can be explained by the fact that hematite particles act as a bridge between glass beads and silica particles. This is clearly shown in a scanning electron micrograph in Fig. ***6.*** This was possible because at these conditions silica particles and glass beads carry negative surface potentials while hematite particles carry positive surface potentials. At pH **8-11**, all the materials carry negative surface potentials thus

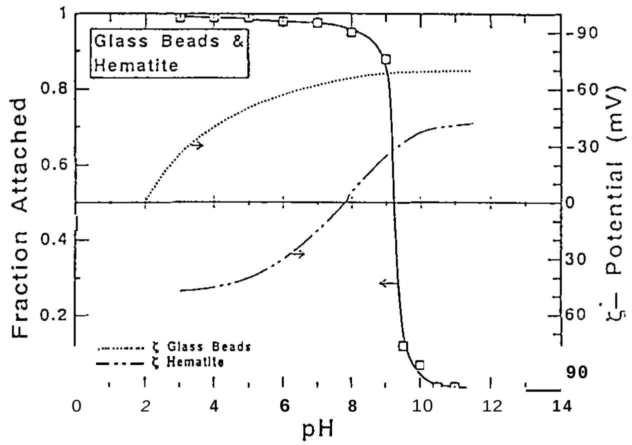

Fig. *4*. Fraction of hematite particles attached to glass beads after tumbling, as a function of pH and in relation to the ζ-potentials of glass beads and hematite particles. Tumbling time is **20** minutes and speed of **8** rpm. Particle no. concentration of hematite particles is $\approx$**1 .35**x 10 '"particles per cm^3 Volume of suspension is **30** cm^3 . Weight of glass beads is five grams.

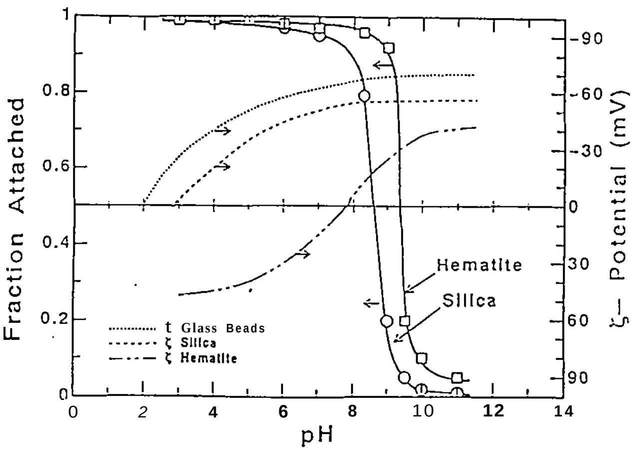

Fig. **5.** Fraction of silica and hematite particles attached to glass beads after tumbling a mixture of hematite and silica particles with glass beads. as a function of pH and in relation to the ζ- potentials of glass beads, hematite, and silica particles, Tumbling time is **20** minutes and speed of **8** rpm. Particle no. concentration of silica and hematite particles with a ratio of I: I **is –1.35** x 10^{10} particles per cm^3. Vol. of suspension is 30 cm^3. Weight of glass beads is five grams.

repulsion becomes the prevailing force among the materials and attachment becomes less pronounced. Above pH 10, minimum attachment was observed.

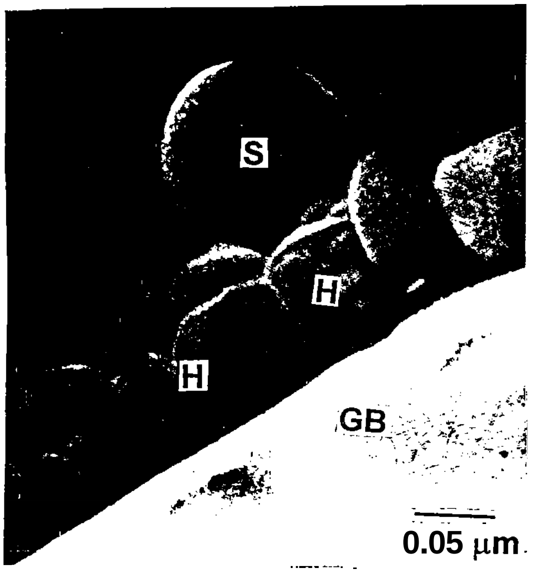

Fig 6. Scanning electron micrograph **(SEM)** of the resulting configuration formed after the attachment of hematite (H) and Silica (S) particles onto glass beads (GB) after tumbling at pH **5**.

3.6 Separation Rates

The attached fraction of the hematite particles at pH 5 by the tumbling method is shown as a function of time in Fig. 7. Obviously, all hematite particles were collected within 10 min which is significantly faster than that of the conventional separation processes such as homocoagulation performed near the iso-electric point. With such conventional separation method it took around 24 hours for hematite particles to be separated from the bulk of aqueous suspension.

Fig. 8 shows the behavior of the attached fraction of hematite and silica particles from their mixed suspension to glass beads as a function of time at pH 5. The time for complete solid/liquid separation is also rather short. It is interesting to note, however, that the separation behavior of hematite is identical when it was without silica and that the separation rate is fairly higher than that of silica particles. These facts suggest that hematite particles adhered first to the glass beads and then silica particles were attached to the hematite particles already on the surface of the glass beads. Moreover, by using the conventional heterocoagulation method of separation it took about 12 hours for silica and hematite particles to heterocoagulate in the absence of glass beads as collector, as shown in Fig. 2.

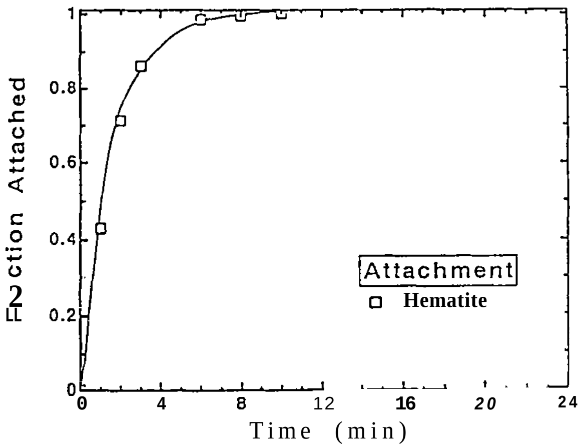

Fig. 7. Fraction of hematite particles attached to glass beads as a function of time. Tumbling time is 20 minutes and speed of 8 rpm. Particle no. concentration of hematite particles is 1.35 x 10 "'particles per cm^3. Volume of suspension is 30 cm^3. Weight of glass beads is five grams.

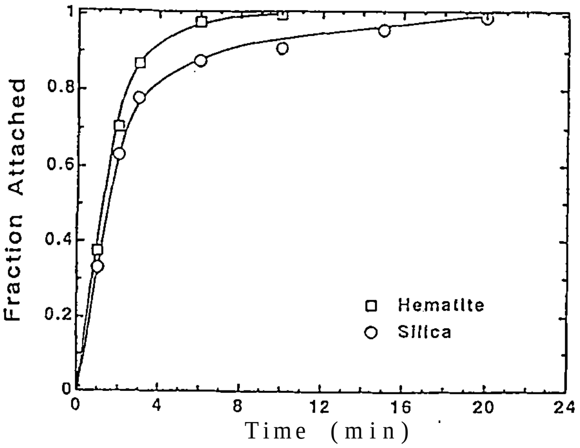

Fig. 8. Fraction of hematite and silica particles (mixed form) attached to glass beads as a function of tumbling time. Tumbling speed is 8 rpm. Particle no. concentration of silica and hematite particles with a ratio of 1:1 is ≈1.35 x 10^{10} particles per cm^3. Volume of suspension is 30 cm^3. Weight of glass beads is five grams.

The total potential energy ,V, ,of interaction between dissimilar spherical particles, which can be applied to hematite and silica interaction, is given as (15)

$$V_t = \{+[\varepsilon\, a_1 a_2/4\,(a_1 + a_2)]\,[(\psi_1 + \psi_2)^2 \ln(1 + e^{-\kappa H_o}) + [(\psi_1 - \psi_2)^2 \ln(1 - e^{-\kappa H_o})]\}$$

$$- [A_{132}\, a_1 a_2 / 6\, H_o\, (a_1 + a_2)] \qquad [1]$$

where a,, a, and ψ_1, ψ_2 are radii and surface potentials of the respective dissimilar particles, ε is the dielectric constant of the medium, A_{132} is the Hamaker constant between particles 1 and 2 in the medium 3, κ is the Debye parameter, and H, is the surface to surface separation. The values of ψ_1 and ψ_2 were assumed to be equal to the electrokinetic or ζ -potentials. A_{132} is given as

$$A_{132} = (A_{131} A_{232})^{1/2} \qquad [2]$$

where A_{131} and A_{232} refer to the Hamaker constants between identical particles in water, i.e., glass beads-water-glass beads, silica-water-silica, and hematite-water-hematite.

The Hamaker constants for the individual materials were determined experimentally by measuring first the critical coagulation concentration (c.c.c.) of an electrolyte in the suspension under examination and the ζ-potential of the particles at c.c.c.. The derived Hamaker constants for glass beads and silica particles in water agree with the constants compiled by Visser (16). Watillon and Gerard (17) proposed a Hamaker constant of amorphous silica in water of 2 - 3 x 10^{-21} Joules. While the derived Hamaker constant for hematite particles in water is close to the value of 4.5 x 10^{-20} joules as given by Fowkes (18). Using the above equation, Hamaker constants, A_{132}, for glass beads-hematite and silica-hematite interactions in aqueous media were computed to be 1.87 x 10^{-20} and 1.12 x 10^{-20} joules, respectively.

For the plane-sphere interaction, which is a simulation of the interaction between a glass bead and a particle of either hematite or silica, the total potential energy, V_t, is given by equating the radius of one to infinity (19-22) and expressed as,

$$V_t = \{+(\varepsilon a/4)\,[(\psi_1 + \psi_2)^2 \ln(1 + e^{-\kappa H_o}) + [(\psi_1 - \psi_2)^2 \ln(1 - e^{-\kappa H_o})]\} - (A_{132}\, a/ 6\, H_o) \qquad [3]$$

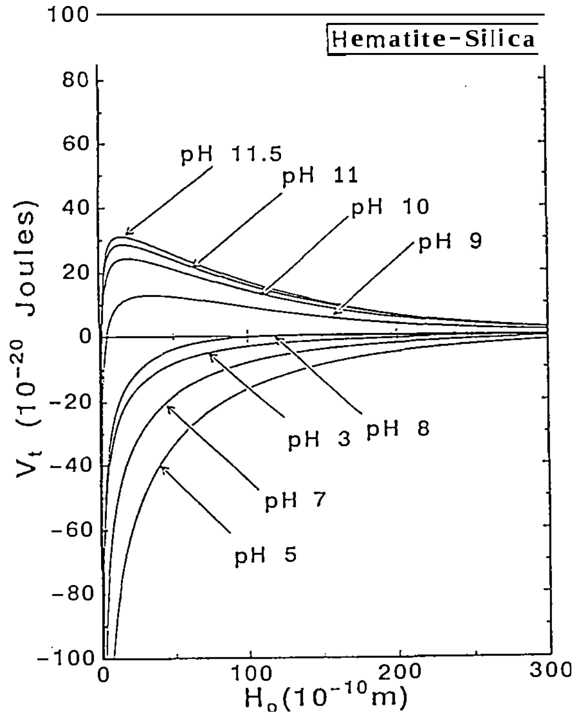

Fig. 9. Total potential energy curves for hematite- silica interaction at different pH conditions as a function of separation distance. H_0. A_{132} = 1.12x 10^{-20} joules.

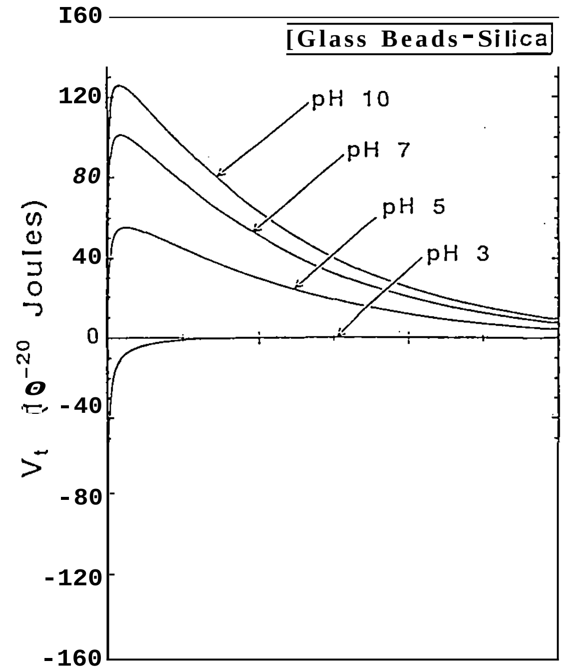

Fig. 10. Total potential energy curves for glass beads- silica interaction at different pH conditions as a function of separation distance, H_0. A_{132} = 4.65 x 10^{-21} joules.

The total potential curves for hematite-silica interaction were calculated as shown in Fig. **9**. Obviously, pH range between **3** and **8** is favored for their heterocoagulation, while above pH 10 V_t is nearly equal to or higher than 25 kT. This is in accord with the criterion of energy barrier for prevention of coagulation(23). These explains the results on the stability of the mixed suspension system in Fig. **4**.

Figs. 10 and 11 show the total potential profiles of glass beads-silica and glass beads-hematite interactions, respectively. The glass beads-silica energy curves are characterized by the presence of high V_{max}, thus repulsion is the dominant force between glass beads and silica particles. This is the reason why there were practically no silica particles attached onto the glass beads. The glass beads-hematite energy curves behave in a manner similar to that of the hematite-silica interaction, as shown in Fig. **9**. Thus, the pH-dependent stability in Fig. **4** can basically be explained in the same way as hematite-silica systems. But at pH 5 for instance, the tangential slope, or attractive force, between glass bead and hematite in Fig. 11 is considerably greater than that between silica and hematite in Fig. **9**. This might be one of the reasons for the rapid adhesion of hematite particles to glass beads as compared to the

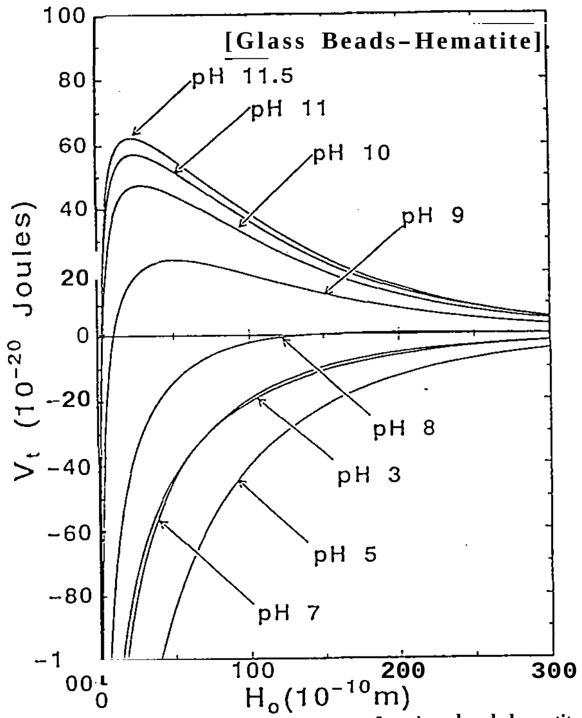

Fig. 11. Total potential energy curves for glass beads-hematite interaction at different pH conditions as a function of separation distance, H_0 A_{132} = 1.87x 10^{-20} joules.

heterocoagulation between hematite and silica particles. However, the attachment of silica particles to the hematite particles on glass beads is also much faster than the heterocoagulation between hematite and silica particles, which cannot be explained in terms of the difference in attractive force. Another reason, perhaps the main one, for the rapid attachment of the particles to the macroscopic collector seems to be attributed to the movement of each glass bead covering much longer distance than the Brownian motion of the fine particles in a given time. The V_{max} values (energy barriers) for each governing interaction at different pH conditions are summarized in Table 1.

Table 1. Tabulation ofthe V_{max} (energy barrier: kT) for the different prevailing interactions at different pH conditions

Interaction	pH							
	3	5	7	8	9	10	11	11.5
Sil-Sil	0.03	54.2	107.0	120.0	125.0	130.0	131.0	132.0
Hem-Hem	49.5	36.9	17.0	-*	10.0	28.0	37.0	39.0
Hem-Sil	-	-	-	1.2	32.0	60.0	70.0	77.0
GB-Sil	1.80	134.0	247.0	282.0	295.0	306.0	309.0	314.0
GB-Hem	-	-	-	1.8	58.0	115.0	139.0	152.0

- * no energy barrier

4.0 CONCLUSIONS

1) The separation of hematite particles from aqueous suspension is possible when hematite particles and glass beads collector carry opposite surface potentials.
2) In the mixed suspension of hematite and silica, the main process of the adhesion of these particles to glass beads as a collector consists of two basic steps: first, the attachment of hematite particles to the collector beads; and second, the subsequent attachment of silica onto the hematite on the collector. Particles carrying the same charge as the macroscopic collector can then be separated from aqueous suspension by the aid of a bridging particles of opposite charge, as in the glass beads-hematite- silica system.
3) The efficient uptake of suspended particles by a macroscopic collector was explained by the long distance of the effective movement of the collector beads and their strong attractive forces.
4) The tumbling method has been proven to be a potential technique for the separation of ultrafine particles from their dilute aqueous suspension.
5) This mechanism of solid/liquid separation in this study can be used as an alternative separation process of amorphous silica from geothermal waste effluent.

REFERENCES

1. Kelly, M., "Mining and the Freshwater Environment", Elsevier Applied Science, London and New York, 1988. p. 33-44.
2. Mendoza, H.D.. Sasaki, H.. Matsuoka, I., and Sugimoto, T.. Colloid and Surfaces. (submitted).
3. Iwasaki, I., Private Communication (Mitsubishi Materials Corp.), 1993.
4. Svarovsky, L., " Solid-Liquid Separation", (3rd Ed.), Butterworth & Co., Ltd., 1990.
5. Matijević, E. (Ed.), " Surface and Colloid Science". Vol. 12 (Chap. 4), Plenum Press, New York, 1082, p. 104.
6. Matijević, E., " Colloid and Surface Phenomena in the Corrosion of Metals", Atmospheric Corrosion(Ed. by W.H. Ailor), Wiley, New York, 1982, p. 123.
7. Ruchenstein, E. and Prieve, D.C.. J. Chem. Soc. Faraday Trans.II, 69, 1522. 1973.
8. 'Boluk, M.Y. and Van de Ven, T.G.M., Colloid and Surfaces. 46, 157. 1990.
9. Aksy, I.A.,' Fundamental of Powder Consolidation in Colloidal System", in Ceramic: Today and Tomorrow. (Ed. by Naka, S. Soga, N., and Kume, S.), The Ceramic Soc. Japan, 1986, p. 71.
10. Chen,.Z., Cationic Flotation of Fine Quartz and Fine Hematite Particles Using DTAB", Ph.D. Thesis, Tohoku University, 1990.
11. Stöber, W. and Fink, F., J. Colloid Interface Sci., 26, 62, 1968.
12. Matijević, E. and Scheiner, P.J.. J. Colloid Interface Sci., 63, 509, 1978.
13. Henry, D.C., Proc. Royal Soc., A133, 106, 1931.
14. Oka, K.. Otani, W., Kameyama. K.. Kidai, M., and Takagi. T.. Applied and Theoretical Electrophoresis, 1, 273. 1990.
15. Hogg, H., Healy. T.W., and Fuerstenau. D. W.. Trans. Faraday Soc., 62, 1638. 1966.
16. Visser. J.. Adv. in Colloid and Interface Sci., 3, 331, 1972.
17. Watillon, A. and Gerard, P.H., Proc. Intern. Congr. Surface Active Substances. 4th Brussels, 2, 1261. 1964.
18. Fowkes. F. M., Ind. Eng. Chem., 6.40, 1964.
19. Kolakowski. J.E. and Matijevid. E., J. Chem. Soc. Faraday. Trans. I, 75, 65, 1979.
20. Kuo, R. J. and Matijević, E.. J. Chem. Soc. Faraday, Trans. I, 75, 2014, 1979.
21. Kallay. R.J. and Matijević, E.. Corrosion, 39, 15. 1983.
22. Kallay, N., Biskup, B.. Tomic, M., Kunjasic, B., and Matijevid. E.. Colloid and Surfaces, 28, 185.1985.
23. Vervey, E.J.W. and Overbeek, J. Th. G., " Theory of the Stability of Lyophobic Colloids". Elsevier, Amsterdam, 1948.