Chrysotile asbestos can be dispersed essentially to the colloidal state when agitated at high speed in water in the presence of colloidal alumina. Presumably the coating of colloidal alumina, evidenced in Fig. 4, provides a strong positive repulsive charge which promotes separation of ultimate fibrils. Such dilute (0.5 to 2%) viscous translucent sols can be dried to semitransparent asbestos sheets in which the alumina plays the additional role of binder.

Kaolin and graphite, when coated with colloidal alumina, are adsorbed from dilute solution onto surfaces such as glass or cellulose and remain as a thin layer which is not easily rinsed off. An excess of colloidal alumina must be avoided in this case; only enough must be added to coat the clay or graphite, since if more is present, the glass or cellulose will be covered preferentially with the free colloidal alumina to the exclusion of the larger alumina-coated particles.

The foregoing phenomena suggest means for depositing very uniform layers of alumina-coated particles of the order of 1μ in thickness on a variety of surfaces. Effects on lubricity, electrical conductivity, light transmission, and other phenomena might be expected, depending on the nature of the deposited material.

Acknowledgment

The writer wishes to acknowledge the cooperation of Vernon Keirstead in preparing the electron micrographs.

Oxidation-Reduction Equilibria in Iron-Containing Glass

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The oxidation-reduction equilibrium between ferrous and ferric iron in $Na_2O \cdot 2SiO_2$ glass melts was studied by equilibrating melts with various oxygen partial pressures. Exceedingly long equilibration times were required to obtain meaningful results. The reaction appears to be diffusion-controlled and may be expressed as $2O^{2-} + 4Fe^{3+} \rightleftharpoons 4Fe^{2+} + O_2$. Data are presented in which the valence of iron varies from predominantly +3 to predominantly +2.

I. Introduction

Very little quantitative work has been done to elucidate *oxidation-reduction* equilibria of variable valence ions in glass melts. The state of knowledge has been reviewed by Tress,[1] who was forced to relate thermodynamic equilibria for pure oxide systems to what was presumed to be an oxidation-reduction sequence in glass obtained from the observation of glass colors. An attempt at a more quantitative study has since been made by Baak and Hornyak,[2] who measured the iron oxidation state in air as a function of temperature in glass melts containing small additions of iron oxide. In their work, the iron was almost completely trivalent. A more extensive investigation of the iron-oxygen equilibria in low-viscosity, high-iron silicate slags of metallurgical interest has been made by Turkdogan and Bills.[3] In their work, the iron valence was varied from predominantly divalent to predominantly trivalent. A general review of the literature dealing with iron-containing glass has been made by Weyl.[4]

In no case has a systematic investigation of the iron oxidation-reduction equilibria been made on a high-viscosity glass melt in which the oxidation state of the iron was varied over a wide range. The purpose of the present work was to determine the conditions for the formation of the various valence states of iron and to permit an oxidation-reduction equation to be written describing this process.

II. Experimental Procedure

Glass melts containing small quantities of dissolved iron oxide were equilibrated in various atmospheres. The oxidation state of iron in the melt was then determined by chemical analysis.

The glass used had the nominal composition $Na_2O \cdot 2SiO_2$ + ~2.5 wt% Fe_2O_3. Several master melts were prepared from reagent-grade Na_2CO_3, SiO_2, and Fe_2O_3 in a platinum crucible.

Small quantities of the master melts (2 or 3 g) were placed in 5- or 10-cm³ Morganite recrystallized alumina crucibles or in some cases, as mentioned later, in platinum crucibles. The crucible was lowered by a platinum or molybdenum wire into the hot zone of a vertical tube furnace under a controlled atmosphere. At the end of the experiment, the crucible was quenched by raising it out of the hot zone. Samples were repeatedly reground and refired for periods of at least 20 hours until a constant chemical analysis indicated that equilibrium had been attained. The furnace tube was constructed of mullite. The temperature of the furnace was controlled to within ±1°C as indicated by a Pt–Pt10Rh thermocouple encased in a mullite sheath suspended inside the furnace tube beside the sample. The temperatures used were 1100°, 1200°, 1270°, 1300°, and 1450°C.

Atmospheres used included oxygen, air, oxygen-free CO_2, CO-CO_2 mixtures, CO in equilibrium with carbon (the crucible in this case), and H_2 saturated with H_2O at 0°C. The CO-CO_2 mixtures were metered using constant-head-type capillary

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[1] H. J. Tress, "Thermodynamic Approach to Redox Equilibria in Glasses," *Phys. Chem. Glasses*, 1 [6] 196–97 (1960); *Ceram. Abstr.*, 1961, October, p. 238*i*.

[2] T. Baak and E. J. Hornyak, Jr., "Iron-Oxygen Equilibrium in Glass: Effect of Platinum on Fe^{3+}/Fe^{2+} Equilibrium," *J. Am. Ceram. Soc.*, 44 [11] 541–44 (1961).

[3] E. T. Turkdogan and P. M. Bills, "Thermodynamic Study of FeO–Fe_2O_3–SiO_2, FeO–Fe_2O_3–P_2O_5, and FeO–Fe_2O_3–SiO_2–P_2O_5 Molten Systems," *J. Iron Steel Inst. (London)*, 186, 329–39 (1957).

[4] W. A. Weyl, Coloured Glasses. Dawsons of Pall Mall, London, 1959. 541 pp.

Measurements of these charges have been made by raising the temperature and permitting the charge to flow out of the n. This is an indirect approach and the nature of the and its distribution is difficult to deduce. A direct technique or optical technique would be desirable. harges can also arise due to artificial carriers injected ed by ordinary light as discussed by Rohatgi[8] and by [9] Again direct measurements of charge densities ot been attempted.

rets represent another form of charge distribution e in insulators. Electrets made of various organic organic compounds have been studied extensively but s not often included.[10] The work of Gubkin and i[49] indicates that a space charge can be frozen in as Pyrex-brand glass is cooled under a field. They state that the charge observed 30 minutes later at 50°C is opposite to the polarity of the electrode used to induce the charge.

Acknowledgments

The writer's thanks are due to various staff support groups at the Philco Research Laboratories for assistance in the preparation of this series.

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Adsorption of Colloidal Silica on Alumina and of Colloidal Alumina on Silica

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The mutual adsorption of colloidal silica on alumina and of colloidal alumina on silica and silicate materials occurs in aqueous suspension at about pH 4. It is shown that the adsorption of colloidal particles on the surface of opposite charge is limited to essentially a monoparticle layer. An adsorbed layer of fibrils of colloidal alumina on the surfaces of silica, asbestos, graphite, and finely divided clay is shown in electron micrographs. The effect of the adsorbed colloid on dispersibility of the substrate materials is discussed.

I. Introduction

It is the purpose of this paper to present examples of the adsorption of colloidal alumina and of colloidal silica from aqueous sols onto the surface of particles of some typical ceramic raw materials and related substances and to discuss the effects of such interaction.

It is well known that when two sols of opposite sign are mixed, mutual coagulation may occur.[1] Thus when sols of colloidal silica and colloidal alumina are mixed, there is a marked increase in viscosity owing to mutual flocculation. When, however, either one type of particle or the other is present in large excess, coagulation does not occur because the particles in the minority become covered with the particles that are in excess. For example, particles of colloidal gold are stabilized or protected by the adsorption of protein.[2] Thus there is a reversal of charge when one colloid is mixed with another protective colloid.[3] However, the protective colloids usually have been organic in nature, e.g., proteins or gums. The coating of one type of inorganic particle by another inorganic colloid is less well known, although the reversal of charge of clay particles by adsorption of colloidal alumina has been reported by Bugosh.[4]

In the present paper it is shown that when a suspension of alumina is stirred into an excess of colloidal silica, each particle of alumina becomes coated with an adsorbed layer of particles of colloidal silica. The alumina particles which were previously positively charged take on a negative charge owing to the layer of adsorbed silica. Since the coated alumina particle now has the same charge as the surrounding silica particles present in excess, there is no flocculation. Similarly, when silica particles in a ball-milled silica slip are mixed with an excess of colloidal alumina, the surface of the silica becomes coated with a layer of alumina particles. This adsorption is demonstrated by chemical analysis and by changes in specific surface area.

II. Experimental

(1) Materials

Ball-milled powders of dense, fused alumina and of fused silica glass were kindly furnished by J. D. Walton of the Georgia Institute of Technology.

Amorphous silica I (not acid washed): This powder had been wet ball-milled, dried, and then dry-milled; specific surface area (nitrogen adsorption), 7.2 m^2 per g; alumina, 0.57% by weight.

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[1] H. B. Weiser, Colloid Chemistry, 2d ed., Chapter 17. John Wiley & Sons, Inc., New York, 1949. 440 pp.

[2] J. Th. G. Overbeek, "Specific Effects of Flocculating Ions" pp. 310–18 in Colloid Science: Vol. I, Irreversible Systems Edited by H. R. Kruyt. Elsevier Publishing Co., Inc., Houston 1952. 389 pp.; *Ceram. Abstr.*, 1953, September, p. 169*i*.

[3] H. G. Bungenberg de Jong, "Reversal of Charge Phenomena in Mixtures of Colloids"; pp. 321–34 in Colloid Science: Vol. II Reversible Systems. Edited by H. R. Kruyt. Elsevier Publishing Co., Inc., New York, 1949. 753 pp.; *Ceram. Abstr.*, 1951 May, p. 95*i*.

[4] John Bugosh, " 'Baymal' Colloidal Alumina," *Am. Ink Make* 40 [5] 54–55, 57–58, 130–31 (1962).

Table I. Adsorption of Colloidal Alumina on Silica

Fraction →	Silica I with colloidal alumina			Silica II with colloidal alumina	Silica II, untreated		
	Coarse	Fine	Colloidal	Coarse	Coarse	Fine	Colloidal
Solids recovered (%)	75	5.3	11.3	84	71.5	8.7	6.0
Specific surface area (m^2/g)	4.0	23	42	4.3	2.6	15	20
Composition (%)							
Silica	97.7	92.2		97.40	98.2	97.4	
Alumina	1.2	4.82	8.31	0.85	0.52	0.9	0.71

Amorphous silica II (acid washed): The foregoing powder was slurried in concentrated nitric acid for 24 hours, washed with distilled water by decantation until the pH of the suspension was 4.0, and kept as a suspension; specific surface area, 6.9 m^2 per g; alumina content, 0.50% on a solids basis (see also Table I).

Alpha alumina: The powder as received was treated with concentrated nitric acid and washed as above; specific surface area, 2.3 m^2 per g; silica content, 1.37% on a solids basis.

Colloidal silica:* Aqueous sol containing 30.0% SiO_2; pH, 9.8; ratio SiO_2/Na_2O, 95; specific surface area, 200 m^2 per g of silica; approximate particle diameter, 15 mμ.

Colloidal alumina†: Dispersible powder; AlOOH, 83.1%; acetic acid, 9.8%; sulfate ion, 1.7%; moisture, 5.0%; particles fibrillar, approximately 5 mμ in diameter; specific surface area, 275 m^2 per g; pH of 4% sol in water, about 4.

(2) Procedure

The colloidal alumina powder was agitated in distilled water at a concentration of from 1 to 5% in a high-speed blendor for a few minutes and the dispersion was left to stand overnight. The colloidal silica was diluted with distilled water just before use and acidified to pH 3 or 4 with acetic acid.

The general procedure was to pour a dilute, weakly acidic suspension of the coarser particles into an excess of colloidal solution of the smaller particles of opposite charge at the same pH while the mixture was intensively stirred. The coarser particles were then recovered by settling or centrifugation, resuspended in acidified water, and centrifuged to wash out excess colloid.

To coat the fine amorphous silica powder with colloidal alumina, a 20 to 30% slurry of the silica in water adjusted to pH 4 with acetic acid was run into a dilute sol of colloidal alumina at the same pH, with violent agitation in a blendor, for 1 or 2 minutes. At least 5 g of colloidal alumina solids per 100 g of silica were present to ensure an excess of alumina over that required to coat the silica. The mixture was permitted to stand while the coarser and finally the finer fractions of silica powder had settled out and had been removed. The colloidal alumina remaining in the supernatant fluid was discarded. The silica fractions were repeatedly suspended in water at pH 4 and recovered by centrifuging until the wash water was free from colloidal alumina. A sample of silica II was similarly suspended in water and separated into fractions as a control.

The fine alumina powder was coated with colloidal silica by slowly adding the alumina suspension (pH of about 3) to a 5% sol of colloidal silica previously acidified with acetic acid. In this case 15 g of silica solids per 100 g of alumina powder were present.

A variety of powders were coated with colloidal alumina by suspending them in water at about pH 4, adjusting with acetic acid, adding the suspension to an excess of a sol of colloidal alumina at about the same pH, and separating the coated material from excess colloidal alumina and washing, as previously described. When the material to be coated contained substantial amounts of exchangeable cations, a preliminary washing with dilute acetic acid was necessary to obtain a suspension that would remain at pH 4.

III. Results

(1) Silica Coated with Colloidal Alumina

Analyses of the recovered fractions of silica powders are given in Table I. It should be pointed out that fractionated silica powder, derived from a fused-silica glass, contained, on the average, about 0.7% Al_2O_3. In the coated samples, the adsorbed colloidal alumina is thus indicated by the amount of alumina in excess of the original amount.

The most striking observation is that colloidal alumina was adsorbed on silica I but not on silica II which had been treated with concentrated nitric acid. Such treatment undoubtedly removed metal ions such as aluminum from the surface. Chemical analysis showed that some alumina was still present, but this no doubt was in the interior of the particles. It was also observed that the silica II powder was not peptized by the colloidal alumina but remained flocculated and settled rapidly so that there was no separation into finer and coarser fractions. On the other hand, silica I, which adsorbed colloidal alumina, was peptized.

The lower adsorption of colloidal alumina on pure silica than on an aluminosilicate has been previously noted in this laboratory. For example, P. C. Yates has observed that colloidal alumina is strongly adsorbed at pH 4 on commercial heat-cleaned glass fibers, which contain some alumina, but to a much less degree on acid-treated silica fibers.

It is postulated that for the colloidal alumina to be adsorbed, the silica surface must bear a negative charge. As has been previously discussed by the writer,[‡] the presence of aluminosilicate ions on the surface of silica maintains a negative charge on the surface even at a pH as low as 4, whereas on pure silica there is little adsorption of hydroxyl ions or development of a surface charge at this pH. However, except after being treated with strong acid, most siliceous surfaces are contaminated with traces of iron or aluminum which provide surface sites that remain negatively charged down to pH 3 or 4.

The thickness of the adsorbed layer of colloidal alumina on the surface of different fractions of silica I can be calculated from the percentage of adsorbed alumina and the surface area of the coated material. Since the writer has previously shown that the specific surface area, as determined by nitrogen adsorption, is not appreciably changed when a colloidal alumina sol is dried to a powder, it is also likely that the surface area of the fibrils is unchanged when the fibrils are adsorbed randomly on the surface of a silica particle. Considering the fine fractions of coated and uncoated silica I, the increase in colloidal alumina content of the coated fraction is 4.82% − 0.9%, or a gain of 3.92% Al_2O_3. This corresponds

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* "Ludox" HS; registered trademark for Du Pont colloidal silica.

† "Baymal"; registered trademark for Du Pont colloidal alumina.

‡ R. K. Iler, Colloidal Chemistry of Silica and Silicates, Chapter VIII. Cornell University Press, Ithaca, New York, 1955. 324 pp.; *Ceram. Abstr.*, 1956, May, p. 107g.

Fig. 1. Alpha alumina particles coated with colloidal silica.

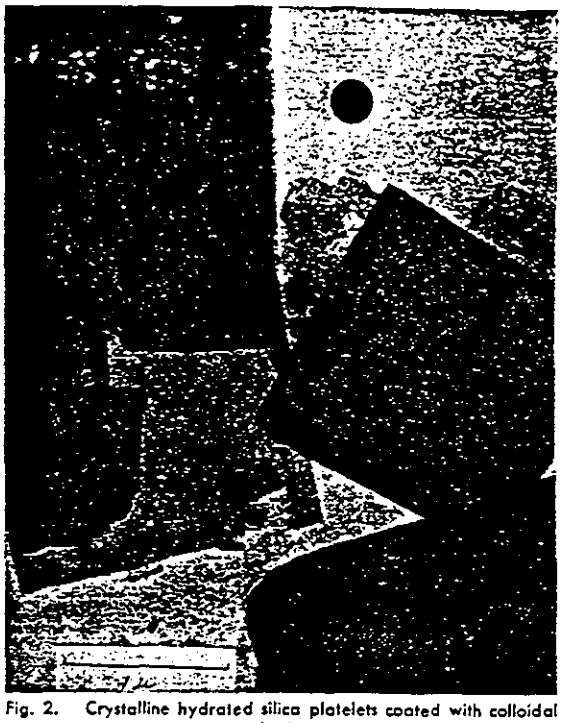

Fig. 2. Crystalline hydrated silica platelets coated with colloidal alumina.

to 5.5% by weight of colloidal alumina which has a specific surface area of 275 m^2 per g. Thus the colloidal alumina contributes an area of 15.2 m^2 per g to the coated powder, which has a measured specific area of 23 m^2 per g. The difference, 7.8 m^2, is due to the area of the silica itself which constitutes 92.2% of the sample. The specific surface area of the silica is thus 8.2 m^2 per g.

The colloidal alumina is known to dry to a porous film having a density of about 1.0 g per cm^3. Assuming that the alumina is spread evenly over the silica surface, the thickness of the alumina coating is calculated to be about 5 mμ. This is about the thickness of a colloidal alumina fibrillar particle; thus the silica surface is covered by about a monolayer of alumina particles lying flat on the surface.

Similar calculations for the coarse fraction of coated silica I indicate that it has a specific surface area of 1.5 m^2 per g and that the alumina coating is 4.3 mμ thick. The colloidal fraction contains a higher proportion of alumina, indicating the greater difficulty of separating the extremely fine coated silica from the excess of colloidal alumina particles; the calculated coating thickness is about 10 mμ.

(2) Alumina Coated with Colloidal Silica

The alpha alumina coated with colloidal silica was recovered in an 84% yield; the finer material was lost in washing. The recovered silica-coated alumina had a specific surface area of 4.1 m^2 per g and contained 2.78% silica and 96.5% Al_2O_3.

By a calculation like that used for the foregoing silica powder, the thickness of the adsorbed silica layer is estimated, based on the fact that the colloidal silica has a specific surface area of 200 m^2 per g and dries to a porous solid having a density of 1.0 g per cm^3. By difference the specific surface area of the recovered alumina is 1.3 m^2 per g, corresponding approximately to 1μ particles.

The calculated thickness of the adsorbed layer of colloidal silica is 10 mμ. Since the average particle size of the colloidal silica is 15 mμ, the thickness of the coating thus corresponds approximately to a single layer of silica particles.

This is borne out by the electron micrograph in Fig. 1.

(3) Colloidal Alumina Adsorbed on Other Materials

It has been observed that colloidal alumina is not strongly adsorbed on surfaces if the sol is too strongly acidified, e.g., below pH 2. Under these circumstances, it is believed that some alumina passes into solution as basic aluminum ions and that these are adsorbed on the negative surfaces and compete with or displace the colloidal alumina particles. On the other hand, adsorption is also difficult to demonstrate if the pH is higher than 5 or 6, because the colloidal alumina is flocculated and it is difficult to distinguish adsorbed alumina particles from mechanically trapped and flocculated aggregates. For this reason, adsorptions are carried out in the pH range 3.5 to 4.5.

(*A*) *Crystalline Hydrated Silica:* The crystalline sodium polysilicate described by McCulloch[5] was prepared and extracted with acetic acid to remove the sodium and then coated with colloidal alumina. In Fig. 2 there are two extremely thin rectangular sheets of this silica that are transparent to the electron beam, so that the adsorbed layer of colloidal alumina fibrils can be clearly seen. It is evident that there is orientation of the alumina fibrils, many of which lie parallel to the edges of the silica sheets, suggesting that the negative ionic charges are regularly arranged on the surface of the crystal lattice of the silica.

(*B*) *Kaolin:* Four hundred grams of clay* were suspended in 3320 g of water acidified with 30 g of acetic acid. When 280 g of a 7% colloidal alumina sol was added with intensive mixing and the mixture was diluted tenfold and again adjusted to pH 4, the clay was so well dispersed that the resulting sol could be passed through E and D No. 615 filter paper under suction. It was only with difficulty that the coated clay could be separated from the excess colloidal alumina by centrifuging.

As shown in Fig. 3, the kaolin is still not quite free of unadsorbed alumina. It is clear, however, that the surfaces of the clay platelets are covered with a crisscrossed layer of fibrils of colloidal alumina. It was found that on some samples of kaolin, adsorption of colloidal alumina was quite poor. Possibly in these clays the surface was already partly covered with positively charged basic aluminum ions from the original natural environment.

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[5] Leon McCulloch, "New Highly Siliceous Soda-Silica Compound," *J. Am. Chem. Soc.*, 74 [10] 2453–56 (1952); *Ceram. Abstr.*, 1953, July, p. 119*b*.

* "Hydrite"-UF, Georgia Kaolin Company, Elizabeth, N. J.

Fig. 3. Kaolin platelets coated with colloidal alumina.

Fig. 4. Uncoated chrysotile asbestos fibers *(left)* and fibers coated with colloidal alumina *(right)*.

(*C*) *Chrysotile Asbestos:* This mineral was first washed with 2% nitric acid to remove magnesium ions from the surface so that a suspension could be prepared in water with a pH of 4. After treatment with colloidal alumina, a small amount of the coated fibers was repeatedly washed by dispersing about 0.1% in water at pH 4 and centrifuging.

Coated and uncoated asbestos fibers are shown in the electron micrographs of Fig. 4; the fine tangled layer of adhering colloidal alumina can be seen on the coated sample.

(*D*) *Graphite:* In Fig. 5, some thin graphite platelets* permit the adsorbed fibrils of alumina to be observed. It is likely that the surface of graphite contains sufficient carboxylic acid groups from oxidation to provide the negatively charged sites necessary for adsorption of colloidal alumina.

IV. Discussion

The surfaces of most siliceous substrates, including fused silica, glass, and silicate minerals, bear a negative ionic charge in water at pH 4 and will adsorb a layer of colloidal alumina particles. This surface layer then bears a positive charge and the original charge of the substrate is thus reversed. The positive charge on metal oxide particles such as alumina can be similarly reversed by the adsorption of colloidal silica.

To achieve charge reversal, however, the colloid being adsorbed must be present in excess and the particles to be coated must be added to the sol with violent agitation at the point of mixing. The colloidal particles otherwise will merely form bridges between the larger particles and flocculation will occur. It is probably for this reason that the adsorption of a single layer of colloidal particles on the surfaces of larger particles of opposite charge has been difficult to observe.

Specific applications for this phenomenon will become apparent from the changes observed in the behavior of the coated materials.

Coating alumina particles with colloidal silica provides a negatively charged alumina slip which then is not thickened or flocculated when mixed with other negatively charged ceramic components such as clays. A silica slip ordinarily will thicken or flocculate when mixed with an acidic alumina slip, but pretreatment of the silica with colloidal alumina will prevent this. Possibilities are thus suggested for the use of colloids in varying the degree of dispersion and thixotropic behavior of ceramic slips and plastic masses.

Fig. 5. Graphite flakes with adsorbed colloidal alumina.

* "Air-Spun" graphite, Joseph Dixon Crucible Company, Jersey City, N. J.