The Importance of Colloid Science for Highway Construction and Research

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The most basic problems of colloid science in highway research and highway construction are discussed on the basis of the most important phenomena involved. Why a more profound knowledge of the colloid science of clay minerals is necessary for highway research and construction is explained. Also discussed are some of the most important problems a highway engineer faces when using bituminous substances which contain inorganic fillers and when using concrete and mixtures thereof with other inorganic matter. In addition, a few suggestions are offered for making some improvements if more attention is paid to colloid science.

● EVERYONE interested in highway construction and research should know, at least to some extent, what the book "Silicic Science" (*1*) actually implies. We have now reached the state where work pertaining to siliceous matter (and this also includes silicones) must be considered as a science in its own right.

The book is largely based on one of the courses I offer at the Massachusetts Institute of Technology, where I also teach general colloid science. Up to a few years ago these courses and the field in general were known as "colloid chemistry," but the term "chemistry" is misleading since this is not the predominant factor in research pertaining to colloids. It is the surface phenomena of the substance under investigation which must be studied when one is dealing with colloidal matter.

For this reason it seems advisable first to give a condensed review of what the term "colloid" really implies and then try to indicate the real importance of colloid science in highway construction and research. Anyone concerned with highway construction and research should have at least a basic knowledge of colloid science and also of silicic science, since in these fields we are always dealing with colloidal problems.

In 1861 the British scientist Thomas Graham coined the word "colloid," which he derived from the Greek expressions "kolla,"

meaning "glue," and "eidos," meaning "like." He never used the word "chemistry," however, in referring to colloids, but spoke only of the "colloidal state of matter." In one of his papers he stated:

"Bearing in mind that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter, but greatly more developed in some substances than in others, it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions."

Following Graham's discovery, however, very little progress was made in colloidal research, unfortunately. In those days physico-chemistry was just beginning to develop and therefore most chemists devoted their work either to organic chemistry or to physico-chemistry. They simply would not accept the fact that with colloids we deal with matter where only the surface is of predominant importance; and, unfortunately, even today some physico-chemists take the same attitude.

Not until 40 years after Graham's work did one of the strongest opponents of the so-called heterogeneous theory of the colloidal state, Richard Zsigmondy, on the basis of pure logical reasoning, decide to see whether the Faraday-Tyndall phenomenon could be made visible with a microscope; but he expected that no particles would be observed. Thereby he hoped to be able to disprove the hetero-

geneous theory and to prove the so-called solution theory which he so strongly supported. In 1903 he published a paper (2) in which he stated:

"Since these fluids (Zsigmondy refers to colloidal gold solutions) showed, in general, the mutual properties, and could in practice be differentiated from each other only by their greater or lesser turbidity, I assumed that turbidity is not an essential, but an incidental characteristic of colloidal gold solutions, occasioned by the presence of larger particles. . . . The addition of a minute quantity of the very turbid fluid to the perfectly clear one sufficed to endow the latter with the polarized dispersion of the former, as evidenced by means of the light cone; and this made evident how small a quantity of coarse gold particles is necessary to produce in a gold solution assumed to be homogeneous, the diffuse dispersion referred to. . . .
It must be acknowledged, however, that although the facts above referred to were favorable to my view, they gave no evidence of the existence of an optically clear gold solution. I hoped to be able to find out the truth by microscopical examination of the cone of light. . . ."

He then reasoned as follows:

"It seemed to me probable that the larger particles assumed to be present in gold hydrosols, whose previously mentioned property of dispersing transmitted light was known to me by the above experiments, could be made individually perceptible by a microscopic examination of the light cone; for if the small particles reflected enough sunlight, even if their size was below the limit of microscopic resolvability, they would, just as were the narrow rays of light, be individually perceptible under the microscope and act to a certain extent as fragments of such light slits. The microscopical investigation should also allow me to determine if the space between the coarser individual particles was optically clear or filled with smaller gold particles."

After Zsigmondy had constructed what is known today as the ultramicroscope, he had to admit that the colloidal state is indeed heterogeneous. In discussing his epoch-making discovery he pointed out that large gold particles in a colloidal gold solution float quietly in the fluid and slowly sink to the bottom or else show only an unimportant Brownian movement, and that by considering colloidal solutions as suspensions, one would naturally imagine that the gold particles in these would also be as quiet as those in the real suspensions. He admitted his mistake in the following words:

"How entirely erroneous was this idea! The small gold particles no longer float, they move —and that with astonishing rapidity. A swarm of dancing gnats in a sunbeam will give one an idea of the motion of the gold particles in the hydrosol of gold! . . .
This motion gives an indication of the continuous mixing up of the fluid, and it lasts hours, weeks, months, and if the fluid is stable, even years. . . ."

Any substance may be classed as a colloid if it lies in the range from 1 mμ to 500 mμ, or even up to 1 μ, that is, within the colloidal range of dimensions. Such a substance exhibits properties which just cannot be predicted or explained by simple chemical analysis or by the reasoning of classical chemistry (1, 2). It must also be realized that it is necessary for only one of the three possible dimensions to be present in the colloidal range in order for the material to be classed as colloidal. This is the case with nearly every clay mineral. If we decrease the dimensions further, the ratio of volume to exposed surface will become more pronounced, until we have reached the dimensional range of the individual atoms or ions of which the matter under consideration is composed. When this condition has been reached, differentiation between volume and surface becomes meaningless because we are now dealing with a gas or a dispersion of dissociated ions, namely, a true solution.

In the introduction to his book, "Kolloidik," (3) A. Buzagh, one of the pioneers in modern colloid science, referred to the first book in the field, which was written by Wolfgang Ostwald and first published in 1915 under the title "The World of Neglected Dimensions." Both Buzagh and I agreed a long time ago that we are dealing here with a world of dimensions we just may no longer neglect (2). For this reason I would like to quote a statement taken from Ostwald's book as it appeared in English translation:

"Modern Colloid Chemistry teaches that there are no sharp differences between mechanical suspensions, colloid solutions, and molecular solutions. There is gradual and continuous transition from the first through the second to the third. It is best to regard all three from the same viewpoint and first to emphasize their similarities. After this has been done, their special peculiarities may be taken up." (2, p. 20; 4, p. 14)

Why must so much attention be paid to the surface-to-volume ratio of matter? Let us look

at a silver bromide crystal of colloidal dimensions, for example. The silver ions should be surrounded by six bromide ions. But with a silver ion lying in the surface, only four are visible; they too lie on the surface; the fifth is located within the crystal and, what is even more important, the sixth is missing altogether. The silver ions located in the corners of the crystal even lack three bromide ions which would be necessary for electrical neutrality. This deficiency, so pronounced in crystalline matter when present in a colloidal state of subdivision, makes it clear why these particles exhibit a reactivity and certain properties which cannot be explained on the basis of their chemical composition alone. To achieve neutrality these ions tend to adsorb positive or negative charges, respectively, from the medium or to release them from their structure (6).

It was the German chemist H. von Helmholtz who was the first to offer a purely physical interpretation of what is known as the theory of the electrical double layer. This is schematically demonstrated in Figure 1a. We know today that a colloidal particle present in a sol carries an electrical charge and will therefore migrate to the negative or positive pole in an electric field, depending on the type of charge it carries. In the case of silver bromide the particles carry a positive charge and therefore migrate to the negative pole. When von Helmholtz made his contribution in 1879 (2), he seemingly did not realize that the potential gradient at the interface necessitates the assumption that the layers carrying opposite charges are separated only by a monomolecular distance. This would mean that a colloidal particle would move in absolutely dry condition through the sol whenever an electric field was applied. If Helmholtz's theory is used to explain the properties of colloidal sols, it becomes more than questionable because it would call for the migration of a perfectly dry particle through the surrounding liquid. This stands in direct opposition to observations made when a piece of matter is moved through a liquid; if the particle is then withdrawn it of course will be coated with a layer of the liquid instead of being dry as this theory would require.

The French chemist, G. Gouy, formulated an amended theory in 1910 on a purely theoretical basis, and somewhat later the German colloid scientist, H. Freundlich, offered the first experimental contribution to this theory (2), which is today known as the Gouy-Freundlich diffuse double-layer theory. This is schematically demonstrated in Figure 1b. It can be seen that the particle as such carries in a lyosphere attached to it an insufficient number of negative ions to cause complete coagulation, which actually would have to occur on the basis of the Helmholtz theory. Helmholtz postulated that every positive ion is covered with a negative ion so that the colloidal particles now carry no charge; this would result in coagulation. The so-called diffuse double layer, on the other hand, is composed of the ions either belonging to or firmly adsorbed on the surface of the particle and of the counterions which surround it at a distance which depends on the strength of the electrostatic attraction and solvation of the ions. The firmly attached layer remains motionless, i. e., it acts as if it were an integral part of the solid wall of the dispersed particle. The particle plus its diffuse double layer is known today as the colloidal micelle.

Until quite recently the chemist and physicist who relied only on the results of chemical analysis and physical research were baffled because they really had no means of offering a simple explanation for the electrical forces connected with what we now term the colloidal micelle, namely, the particle and the liquid layer (often called the hydrosphere) firmly attached to it.

A kaolinite particle, for example, is a mono-
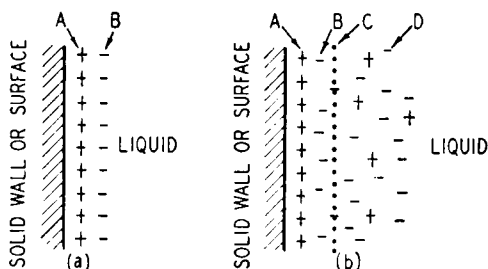
Figure 1. Double layers. (a) Helmholtz double layer. (b) Gouy-Freundlich diffuse double layer. A, charges firmly attached to the particle; Ba, charges of liquid layer; Bb, ions located in liquid layer which are attached to the particle; C, thickness of attached diffuse double layer depending on mean offstand distance of ions from solid wall; D, diffuse ions present in movable part of liquid. The particle plus the complete diffuse double layer is called a colloidal micelle.
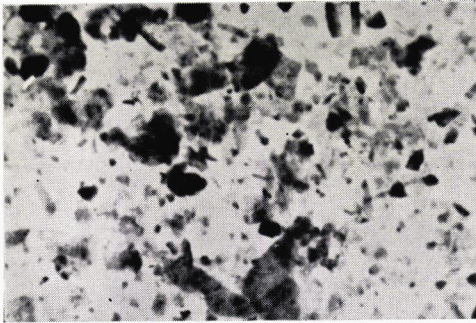
clinic system which displays good cleavage (Figure 2). Since broken bonds are found with most kaolinite and other clay crystals, we must bear in mind that they serve as the basis for the preferential adsorption of hydroxyl ions. It must also be realized that these hydroxyl ions are held by dipolar bonds to the oxygen ions of the basal silica sheet and that they carry with them water molecules which constitute part of the water hull surrounding the colloidal particle. However, if only a small trace of electrolyte is either added to the system or is already present, then profound changes in the forces connected with the micelle occur as a result of the preferential ion adsorption on the particle and of the rearrangement of the counterion charges, as schematically shown in Figure 3.

Figure 3a is a schematic drawing of a sodium-bentonite crystal. If we now add to the crystal, when it is in suspension, a polyvalent water-soluble cation, as is found for example in calcium chloride, we will cause a base-exchange reaction of the sodium ions with the calcium cations, as shown schematically in Figure 3b. Since the calcium ion is divalent and is much less hydratable than the sodium ion, a far smaller amount of calcium ions is needed for electric neutralization of the clay particle; but besides this, the hydratability of the calcium ion is also far less pronounced than that of the sodium ion and for this reason the particles are much less reactive and do not swell. It is this concept of the colloidal micelle and of the electric forces connected with it which have finally made it possible to offer a simple explanation for the most important properties of clay minerals.

The colloid science of clay minerals also involves ultra- and electron-microscopy, X-ray diffraction analysis, infrared spectroscopy, as well as a careful study of base-exchange capacity, to mention only the most important items.

In Figure 4 an electron micrograph which was taken with an original magnification of $15,000\times$ shows a sample of sodium-bentonite. In comparing this with Figure 5, a sample of calcium-bentonite taken at the same magnification, we see immediately that the first preparation is noticeably less aggregated than the second. In addition, the calcium-bentonite particles are not so thin as those of the sodium-bentonite.

Figure 2. Electron micrograph of a single kaolin crystal, using shadow technique. Original magnification approximately $10,000\times$ (API).

o - MONOVALENT COUNTER ION
$\bullet$ - POLYVALENT COUNTER ION
— - MONOVALENT ANION

Figure 3. Changes which occur in the dispersion of a clay micelle upon the addition of polyvalent counter ions or acids.

X-ray analysis of sodium-bentonite, carried out with a Norelco Geiger-Mueller X-ray Spectrometer (1), reveals a spectrograph as shown in Figure 6. The clay mineral illite, which shows substantially no expanding lattice characteristics and differs from sodium-bentonite primarily by a replacement of sodium with potassium, reveals an X-ray spectrograph as shown in Figure 7. To anyone

Figure 4. Electron micrograph of sodium-bentonite (orginal magnification approximately 15,000×).

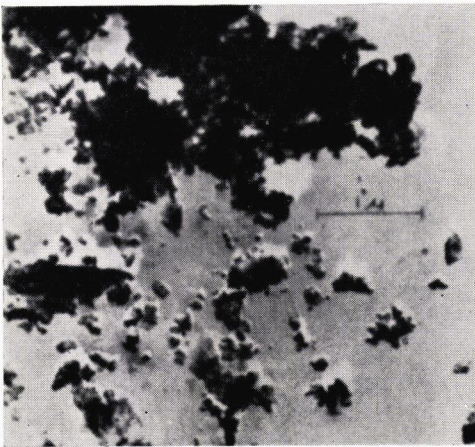Figure 7. X-ray diffraction analysis of the clay mineral illite.

Figure 5. Electron micrograph of calcium-bentonite (original magnification approximately 15,000×)

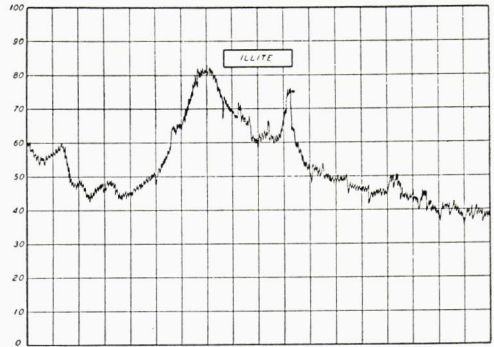Figure 6. X-ray diffraction analysis of sodium-bentonite (Wyoming).

familiar with X-ray spectrography, the lack of lattice expansion is evident.

As can be seen in Figure 8, the infrared absorption spectra of sodium-bentonite show distinct absorption bands at a reciprocal wave length of 3700 cm.$^{-1}$ due to free hydroxyl groups and also between 3600 and 3200 cm.$^{-1}$ due to associated hydroxyl groups or adsorbed water. If the drying temperature of the film is increased, the second absorption band is pronouncedly reduced, whereas the first one remains almost unchanged. In contrast, in the spectra for calcium-bentonite (Figure 9) the first absorption band increases noticeably with increasing temperature, which indicates that more free hydroxyl groups are adsorbed on this preparation with increasing temperature (1).

The results obtained from differential thermal analyses at temperatures from 0 to 1000°C. for sodium-bentonite are shown in Figure 10 and for calcium-bentonite in Figure 11. The sodium-bentonite shows a pronounced minimum at about 175°C. The calcium-bentonite also reveals a minimum, at a somewhat higher temperature, but it is not so strong by far. The curves for both clays are nearly constant between 300 and 600°C. At about 725°C. the sodium-bentonite shows an endothermic peak; this peak is even more pronounced in the calcium-bentonite. Both clays show more or less pronounced exothermic peaks between 900 and 950°C.; these are in all probability associated with the formation of the mineral spinel. The initial endothermic peak must be attributed to adsorbed water located on the surface of the material. The
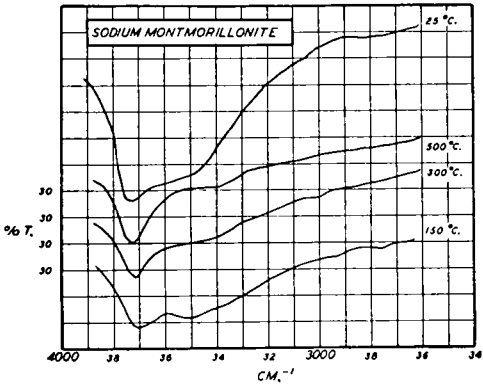
Figure 8. Infrared absorption spectra of sodium-montmorillonite determined at different temperatures.
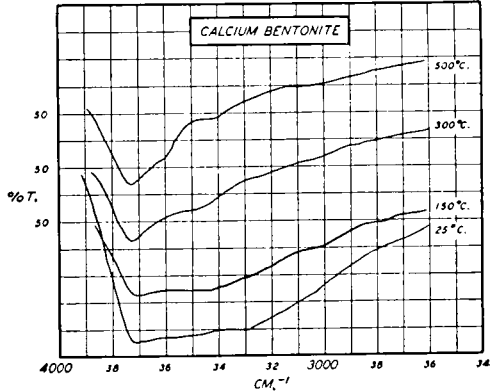

Figure 9. Infrared absorption spectra of calcium-bentonite determined at different temperatures.

most pronounced endothermic peaks refer to the loss of lattice water, and the last endothermic peaks correspond to a breakdown of the lattice itself (1).

As far as the base-exchange capacities are concerned, a pronounced difference is again found between sodium-bentonite (Wyoming bentonite) and calcium-bentonite. The method by which the base exchange capacity is determined must always be considered in order to obtain comparable results.

Phenomena like plasticity, thixotropy, dilatancy, and rheopexy must also be borne in mind when dealing with subsoils composed of clay minerals because they quite definitely will cause troubles if not dealt with before the new surface is placed on the soil. My good friend, Dr. Hans F. Winterkorn of Princeton University, has already made many basic contributions to highway research which are more or less based on colloid science, and for this he unquestionably deserves special credit. What seemingly is still not sufficiently realized, however, is that highway construction is based on surface phenomena and that the chemical composition of the subsoil and the material with which it is coated are actually of secondary importance. In closing, I therefore plan to give a few examples pertaining to bituminous paving mixtures and also to the use of portland cement in highway construction.

In Bulletin 105 of the Highway Research Board, "Bituminous Paving Mixtures," Lloyd F. Rader, Chairman of the Committee on Design of Bituminous Paving Mixtures, stated that in order to select suitable bituminous ma-
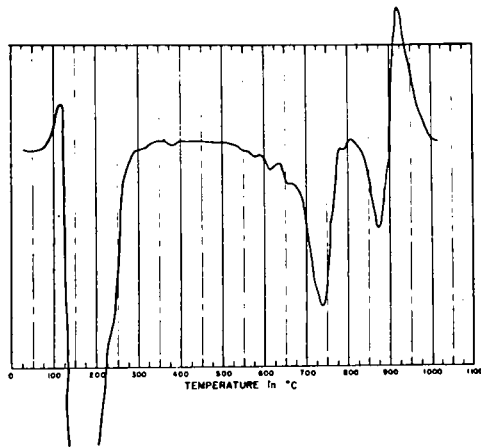

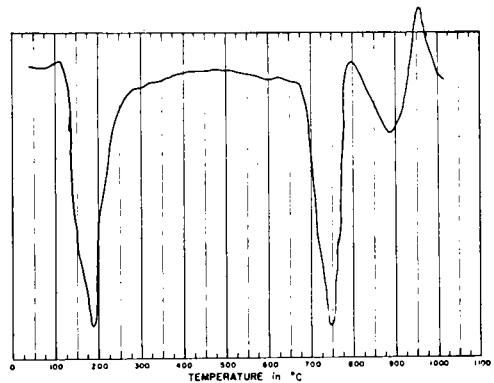Figure 10. Differential thermal analysis of sodium-bentonite (Wyoming).

Figure 11. Differential thermal analysis of calcium-bentonite (Princeton, British Columbia).

terials and aggregates and to design properly the proportions of bitumen and aggregates for a paving project involving given conditions of traffic and climate, the engineer should have an understanding of the fundamentals governing their design.

If we bear in mind the fact that such mixtures are based on surface phenomena, we realize that truly satisfactory results can be obtained only if more attention is paid to the interfacial problems involved. From a strictly colloidal point of view this means that the inorganic substances which are mixed into the asphalt or bitumen remain only fillers which have no affinity for the continuous phase. Therefore cracking and the like are bound to occur, particularly with drastic changes in temperature. Before the inorganic matter, like clay, is mixed with the bituminous substance, it should first be reacted with an appropriate reagent so that it now carries a surface which will react or combine with the bitumen. Already today there are quite a few substances of this type available, but basic research might offer us a chance to develop entirely new products which would serve their purpose at such low cost that they would be of general interest and value.

Talking from a strictly colloidal point of view, we need a protective colloid which also must have the property of combining with the inorganic material as well as with the bituminous one, so that we wind up with a bitumen in which the inorganic substances are not just present as standard fillers. If this is accomplished, then some of the most serious problems of highway construction which uses bitumen as a basis will be solved.

Another thing which also may not be overlooked is the type of surface layer of the soil, since this layer is actually the basis for all our pavements; therefore the proper combination of that surface soil layer and the applied bituminous layer will react in an entirely different way than the middle or top layer of the bitumen. It might even be advisable first to treat the soil top layer with a special mixture of bitumen before applying the bituminous top layer. This type of work should be classified as basic research in highway construction.

When dealing with portland cement the problem is somewhat simpler because in this case we are not dealing with any organic mat-

ter. Nevertheless, even here we must bear in mind that special precautions are necessary to permit a true combination of the filler with the portland cement.

In his book, "Soluble Silicates" (5), James E. Vail mentions that a review of the literature from 1871 to 1930 emphasizes to the modern reader the importance of defining objectives before passing judgment on the results. For example, what is the importance of such factors as setting time, wearing quality, permeability, or the possibility of the appearance of efflorescence, and what is the importance of cost in a given case? To this I would only like to add the importance of colloid science. Without it we will never obtain really satisfactory results.

A method which has been approved in the construction of concrete highways is curing. After the surface of the road has begun to set under moist burlap, a solution of sodium silicate is poured onto the surface, and this results in improved strength at all stages of maturity. However, since concrete invariably contains free lime when it becomes a firm solid, it is impossible, according to Vail, to realize its full possibilities of improved physical properties under these conditions. We must also bear in mind that the maintenance of a wet surface during the curing of the concrete or its slabs in arid countries is always very expensive. However, if during mixing we introduce some type of colloidal silica or even a silicate solution into the solution, we end with a product which exhibits superior properties.

In 1947 one of the biggest German companies filed a patent using salts of humic acid with soluble silicates to produce a liquefying effect on cement-water mixtures. This means that a far lower concentration of water would be needed in making a usable portland cement mixture for highway construction, and that is just what we need. Humic acid is known to be a very effective dispersing agent for colloidal matter, and we must admit that for many years prior to World War II the Germans were the leaders in modern colloid science. For this reason we must pay more attention to colloid science and its importance in highway construction.

I have purposely picked only these few examples to prove my point because I am not engaged specifically in highway research problems, but if I have been able to offer some

explanation why a basic knowledge of colloid science is essential for this field, then I have accomplished what I planned to do.

SUMMARY

An explanation of the most basic problems of colloid science involved in highway research and construction is given and their implications discussed. Particular attention is drawn to the most important problems which the engineer faces when using bituminous substances containing inorganic fillers and when using concrete and mixtures thereof for the production of highways.

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