

SILICIC CHEMISTRY IN HIGHWAY RESEARCH

ERNST A. HAUSER

Massachusetts Institute of Technology

SYNOPSIS

Modern colloid chemistry is important in any problem in which natural soils are involved. With the exception of oxygen, the element silicon is by far the most widely distributed one on this planet, and eighty years before Thomas Graham coined the term "colloid" it was known that alkali silicates do not obey the laws of classical chemistry. Since then it has been proved that they also cannot be harnessed into the rigid equations of physical chemistry.

The highway must be designed so that it will not be subjected to the strains a soil substratum will set up as a result of the effect changes in temperature, moisture, etc., will have on its colloidal components.

The colloid chemistry of silicon, or "silicic chemistry," is the chemistry of siliceous matter characterized by a preponderance of surface over total volume. This results in structures characterized by an unbalanced distribution of electric charges, which explains their reactivity as compared to that exhibited by the same chemical compound if present in a coarser state of subdivision than that which has been termed the colloidal range of dimensions. The application of our knowledge of the colloid chemistry of siliceous matter is important in modern highway construction and soil stabilization.

Application of the colloid chemistry of subsoils, for example, will help to make them more or less permeable to water without losing any of their coherence. It will permit us to treat gravel or the like in such a way that, when mixed with asphalt or cement, it becomes an inherent part of the layer after it has set, and not only an inert filler. That such a composition will have far greater mechanical strength and be less affected by changes in weather is self-evident.

Colloid chemistry is not limited to inorganic matter but is equally applicable to organic colloids. It has already been possible to produce moldable thermosetting plastics from siliceous matter by using less than one percent of polymerizable organic compounds as binder, firmly combined with the inorganic constituent. There is no reason why the same principle could not be applied to highway construction using concrete or asphalt surfaces.

It seems appropriate first to offer a brief explanation of the term "silicic chemistry," before discussing the importance of this new branch of colloid chemistry for highway research.

Very few people realize that long before the term "colloid" had been coined it was well known to scientists that siliceous compounds exhibit properties now considered especially characteristic for this state of matter (1, 2).¹ Still fewer people, however, realize even today that a fundamental knowledge of the colloid chemistry of siliceous matter is essential to any improvements in such fields as soil solidification, flood control, agriculture, and highway construction.

It must be admitted that a great deal has

¹ Italicized figures in parentheses refer to list of references at the end of the paper.

been accomplished by means of X-ray diffraction studies and infrared spectroscopy (2) in our attempt to explain the basic differences between carbonaceous and siliceous compounds. A truly satisfactory and comprehensive explanation is, however, impossible as long as the colloidal state of siliceous matter is not taken more seriously into consideration. Up to quite recently, the case was exactly the same with most organic colloids. To make this point clearer, let us take one example from the organic kingdom of matter. If natural rubber is subjected to chemical analysis, one finds that it is a polymer of the liquid called isoprene (C_5H_8). The same, however, is also true for gutta percha, although the properties of these two organic compounds differ quite appreciably. X-ray diffraction has offered some explanation for

these differences by proving that rubber is composed of polyisoprene in *cis*-, gutta percha in *trans*-configuration. With this information as a basis, the theory was advanced that the difference in elasticity of these chemically identical hydrocarbon polymers is only the result of the hindrance to molecular oscillation caused by the *trans*-configuration. What has been completely overlooked, however, is the fact that rubber, if subjected to fractionation,

generally far more reactive than one could assume by taking only their chemical composition into consideration.

All these points which have been discussed in regard to the organic kingdom apply equally to siliceous matter, and this is the reason why the term "silicic chemistry" has been coined, and the same terminology introduced into this branch of colloid chemistry (4). The silicon

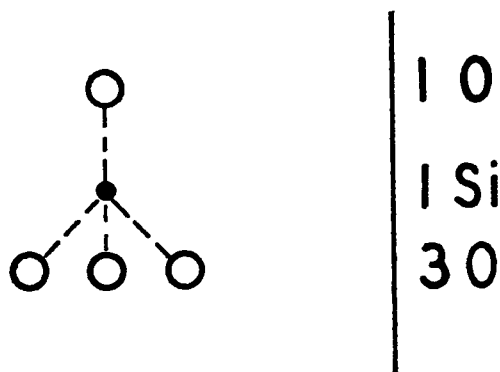


Figure 1. Silicon Tetrahedron (Monomer)

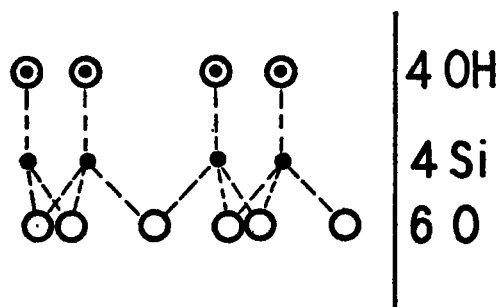


Figure 2. Hydrated Silica Chain (Polymer)

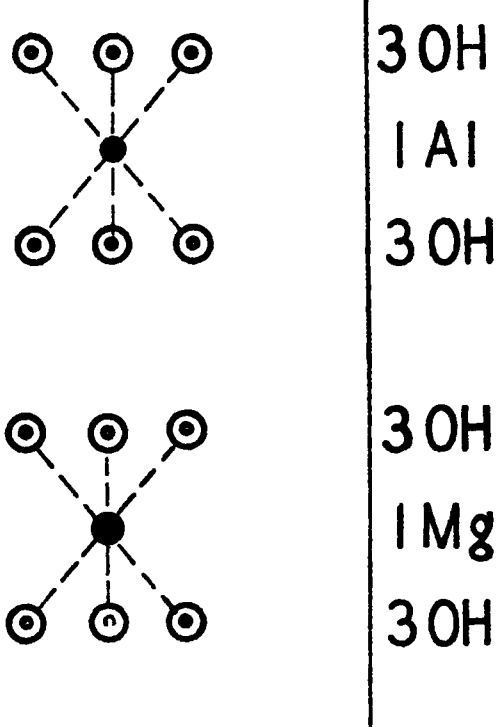


Figure 3. Aluminum and Magnesium Octahedra (Monomers)

can be separated into a very viscous low molecular weight fraction and a hard and brittle high molecular weight fraction. It is the combination of various molecular weight fractions which accounts for elasticity (3). The swelling of rubber in organic solvents is another phenomenon which cannot be explained by organic chemistry alone. The high molecular weight fractions are far more difficult to solvate than the low ones, because the latter offer more surface to the solvent. In the colloidal state the surface is preponderant, and this explains why colloids are

tetrahedron is the monomer (Figure 1). A fibrillar structure like that of hydrated silica, or a platey or cubical one resulting from condensation or electron sharing of its oxygen atoms, would then constitute the polymer (Figure 2). Similar structures are formed between aluminum or magnesium and oxygen, the only difference being that these build up to octahedra as monomers (Figure 3). The minerals gibbsite (Figure 4) and brucite (Figure 5) are the corresponding polymers. All clay minerals are combinations of the pure silicates and Al- or Mg hydroxide layers.

They are inorganic copolymers (Figures 6-8), just as Buna S (GR-S in the United States during the war) is a copolymer of butadiene

science which it has deserved for so long. Nothing can prove better than the development of the silicone resins, that the colloidal state of siliceous matter is the natural bridge between the organic and inorganic kingdoms. R. R. McGregor gives such an excellent explanation of these resins that I take the liberty of quoting him verbatim (5):

"Carbon chemistry not only appears to be exclusive, but in some ways seems to think of

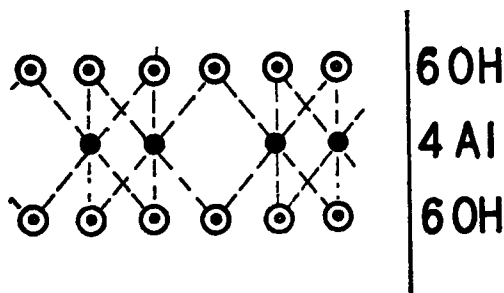


Figure 4. Gibbsite (Aluminum Octahedra Polymer)

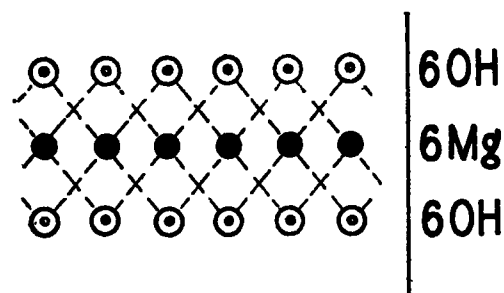


Figure 5. Brucite (Magnesium Octahedra Polymer)

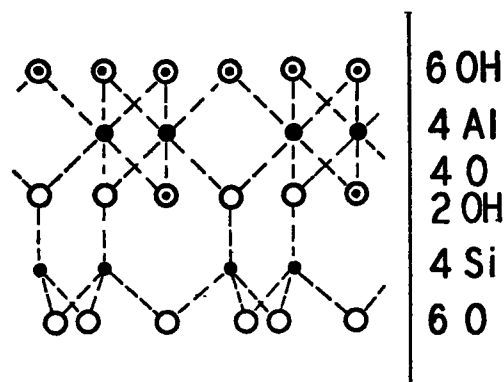


Figure 6. Kaolinite (Condensation Copolymer of Gibbsite and Hydrated Silica)

and styrene, or Butyl rubber is a copolymer of isobutylene and isoprene or butadiene.

The day has finally come when the chemistry of siliceous matter has found the place in

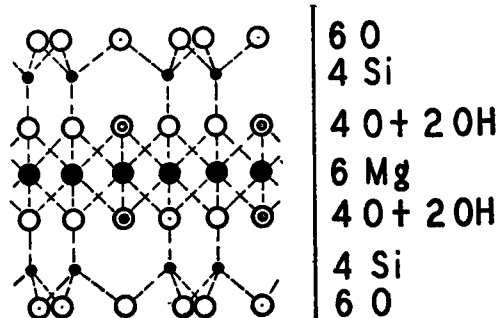


Figure 7. Talc (Condensation Copolymer of Brucite and Two Hydrated Silica Layers)

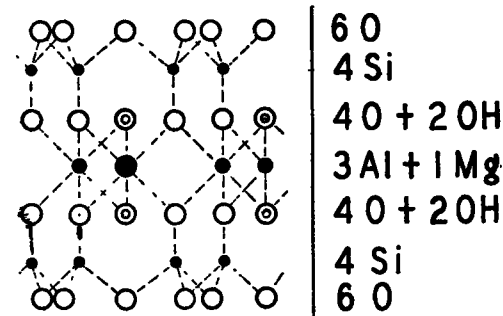
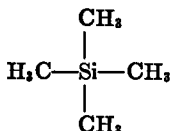


Figure 8. Montmorillonite (Condensation Copolymer of an Aluminum and Magnesium Octahedra Copolymer with Two Hydrated Silica Layers)

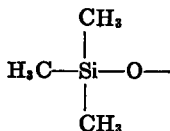
itself as the aristocrat of the elements. It has been systematized, organized and advertized. The chemistry of silicon has not had the notoriety of carbon, and this element may be considered a modest and unassuming member of the proletariat. It is a product of the soil, found in sand, bricks and mortar—a very humble member of society. In human relations intermarriage between different ethnologic groups is generally frowned upon, for you never know what will come of it. This

may be the reason that the families of carbon and silicon were kept apart for so long. But the union finally took place, and as a result we find a very unusual and happy progeny."

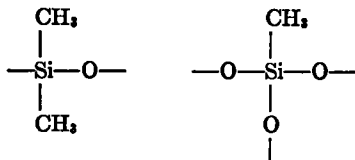
If one replaces the oxygens of the silicon tetrahedron (Figure 1) with methyl groups, tetramethyl silane results (6):



This compound has a functionality of zero and therefore cannot be used to build a polymer. If one replaces one methyl group with an oxygen atom, one has a trimethylsiloxy group. This is now monofunctional. It can block chain growth, but cannot propagate:



A dimethylsiloxy group is difunctional and, like the monomethylsiloxane unit, which is trifunctional, is capable of chain or network polymerization.



All this is only one way of building the bridge, however. The substituted montmorillonites carry a net negative charge and in nature have sodium preferentially adsorbed to balance it. This, however, can be replaced by base exchange reaction with complex ions, as for example lead acrylate, thus giving the clay an organic surface which permits bonding of so-treated clay particles by polymerization (7).

The colloid chemistry of siliceous matter, and particularly of clays (1), also has other important contributions to offer in many problems with which highway research is faced. Since highway construction and soil conservation and solidification are dependent in one way or another upon siliceous compounds, it is high time that more cognizance of this fact

be taken into consideration if we finally want to reap the harvest of the seeds which have been sown many years ago.

Highway research is clearly dependent on silicic chemistry, and must take more cognizance of its developments so that the highway engineer can apply this information as he feels will be most promising to the problems with which he is faced.

Silicic chemistry will be of equal value for any treatment the subsoil should receive to offer the most stable basis for the surface of the highway and for the most appropriate composition of its top layer. The first step will therefore have to be a detailed analysis of the subsoil to ascertain its mineralogical composition and to determine whether there is any organic matter present. To this must be added an equally detailed survey of the colloidal properties of the soil, like base exchange capacity, swelling, effect of leached-out salts, and the like. With this information at hand, the colloid chemist is now in a position to suggest treatments which will cause practically any change in the subsoil structure which may be considered necessary. By incorporating multivalent cations, for example, the constituents of the clay will aggregate, increasing permeability. By introducing complexions carrying polymerizable radicals, the soil can be solidified. If the soil is too porous, one can improve it by incorporating appropriate deflocculating agents, or, by introducing monovalent ions, permeability can be brought to a complete stop, if so desired (1).

In regard to the surface layer of highways silicic chemistry can also offer interesting suggestions which might, if systematically worked out, revolutionize our entire concept of highway construction. Just to give an example, it might be stated that it has recently been possible to produce a highly abrasion resistant and skidproof surface layer composed of 98 percent sea sand and 2 percent of a polymerizable, strongly adsorbed organic binder. Similar results have been obtained by incorporating organophilic, polymerizable clays into native soil.

SUMMARY

The term "silicic chemistry" is explained. The similarities between the colloid chemistry of silicon and of carbon are pointed out. The importance of silicic chemistry for highway

research is explained on the basis of its applicability to subsoil stabilization and surfacing problems.

REFERENCES

1. Hauser, E. A. "Colloid Chemistry of Clays." *Chemical Reviews*, Vol. 37, No. 2, pp. 287-321, Oct., 1945.
2. Hauser, E. A. "Silicic Chemistry" *Journal of Physical and Colloid Chemistry*, Vol. 52, in preparation, 1948.
3. Hauser, E. A. and LeBeau, D. S. "Elasticity Explained." *Scientific American*, Vol. 177, No. 5, pp. 204-206, Nov., 1947.
4. Hauser, E. A. and LeBeau, D. S. "Silicic Chemistry." Van Nostrand, New York. (in preparation)
5. McGregor, R. R. "Silicones: Food for Imagination". *Chemistry*, Vol. 20, No. 4, pp. 5-11, April, 1946.
6. Rochow, E. G. "Siloxane Linkage." *Chemistry*, Vol. 20, No. 4, pp. 12-13, April, 1946.
7. Hauser, E. A. and Dannenberg, E. M. "Molding Composition Molded Product and Method of Making." U. S. Patent 2,401,348, June 4, 1946.

SENSITIVITY OF CLAY TO REMOLDING AND ITS POSSIBLE CAUSES

HANS F. WINTERKORN AND GREGORY P. TSCHBOTARIOFF, *Princeton University*

SYNOPSIS

The sensitivity of clays to remolding is correlated with the general problem of soil structure. The soil-physical facts and theories of structure are presented in a simplified manner. Fragmental and granular soil structures are revealed to be consequences of the law of minimal areas with modification as a result of chemical and (or) mineralogical inhomogeneity of soil composition. The importance of physico-chemical and (or) chemical cementation as a factor in water resistant massive or granular soil structure is emphasized. Experiments performed on five soil samples (two from Mississippi, and three varved clays from Albany, N. Y.) indicate that the great susceptibility of the varved clays to remolding derives from their cementation.

Tests on undisturbed cohesive soils at moisture contents within the plastic range have shown that remolding may result in:

1. Decrease of unconfined compressive strength (3, 8)¹
2. No effect on compressive strength, or
3. Increase of compressive strength (4, 8, 2).

The response of a soil to remolding is of great importance in foundation engineering. Direct determination of this response by unconfined compression test is at least as simple as any other test which can be performed on a soil. Consequently there appears to exist little practical reason for ascertaining the possible cause of the sensitivity of clay to remolding.

As a matter of fact, the effect of disturbance of a cohesive soil on its strength properties is of importance not only for individual foundation

designs but also, and to a much greater extent, because of its bearing on the central problem of stability and strength properties of cohesive soils. It is for this reason that the present study was undertaken.

Most common building materials owe their specific strength properties not only to their composition but also to their structure. A good example of this importance of structure is furnished by the carbon steels in which the chemical composition indicates potential strength properties while the actual properties are determined by the structural arrangement established through heat and mechanical treatment.

Similarly, as in the case in steel, the actual mechanical properties of soils are dependent not only upon their composition but also on the structural arrangement of the component particles, and the forces which hold these particles together.

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