

A Study of Absorbed Water on Clay by Steady State Nuclear Magnetic Resonance

A. G. PICKETT, Southwest Research Institute, San Antonio

● THE CONCEPT of water film strength, reported by Terzaghi (1) in his earliest works on soil mechanics and developed into a more elaborate theory by such investigators as Winterkorn (2, 3), Forslind (4, 5), and Grim (6, 7) may be summarized as follows:

1. An adsorbed film of strongly oriented water molecules is firmly bound to the clay surface.
2. The water molecule orientation extends for some distance into interparticle water.
3. The oriented water molecules resist deorientation and this resistance to deorientation is a significant part of the shear strength of a wet clay soil.

The source of this bonding and orienting force is the polar nature of the water molecule itself and a similar property of the clay crystal surface. Although an atom is electrically neutral, the formation of an ionic valence bond in which electrons are "borrowed" from one atom to help fill the outer electron shell of another causes a dislocation of electric charge, the donor atom becoming positively charged and the borrower negatively charged. The asymmetric water molecule behaves, therefore, as a body with oppositely charged ends, one of which is attracted and the other repelled by the clay crystal surface which is charged by a similar mechanism. The enormous surface area of clays, estimated by Hendricks, Nelson, and Alexander (8) as being in the neighborhood of 8×10^6 sq cm per g for a montmorillonite, offers this force the opportunity of being a very important parameter of shear strength. Opposing the development of orientation, however, is the Brownian movement, which is also of consequence at this phenomenological level and the estimates of the resultant thickness of strongly oriented layers and their resistance to a shearing stress—based on theoretical analyses by various investigators—vary widely. It has been conclusively demonstrated, however, that the polar bonding forces are of real significance in the resistance of materials to shearing stresses and that they can be measured by appropriate techniques. In particular, Debye delineated their role as "dashpot" elements in viscoelastic materials and demonstrated that a measurement of their relaxation times by any means also described the functions in determining the mechanical properties of a material.

The unique feature of the electrostatic linkage is the immobilization of the hydrogen atom. This immobilization can be measured in terms of resistance to shearing stress (viscosity or shear strength) by steady state nuclear magnetic resonance.

Steady state nuclear magnetic resonance (NMR)(9) measures two relaxation times. T_1 , called the thermal relaxation time, is the time required for the energy absorbed by a nucleus whose equilibrium has been disturbed to be dissipated to the lattice. T_2 , called the spin-spin relaxation time, is a time constant associated with the influence of the magnetic field of one nucleus on another nucleus, which is a measure of the proximity of nuclei. Bloembergen, Purcell, and Pound (10) and Grant (11) showed that T_2 is also a measure of the potential resistance of an assemblage of water molecules to shearing stress.

The great advantage of this technique is that it is nondestructive and measures water film strength directly. The viscosity of intralayer water of montmorillonite is measured as easily as that of the interlayer water, for example.

In order to limit the variables, clays of well-known properties were prepared and tested. These clays were (a) Georgia kaolin, (b) homionic Wyoming bentonites, and

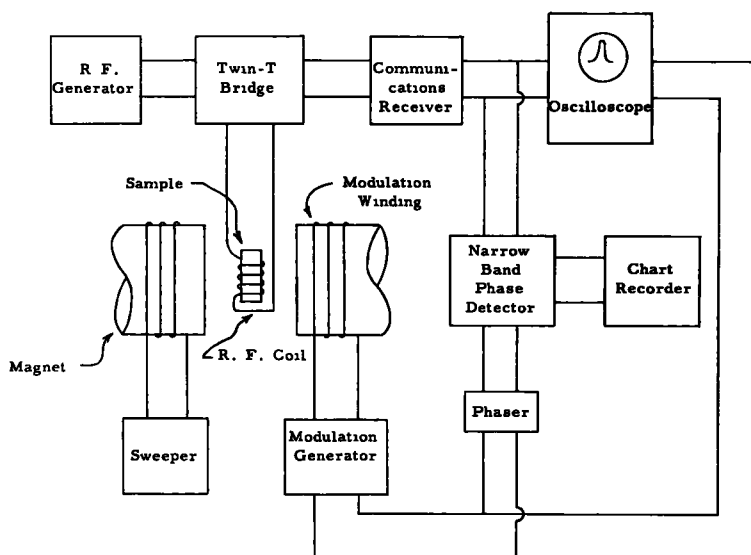


Figure 1. Block diagram of NMR equipment used.

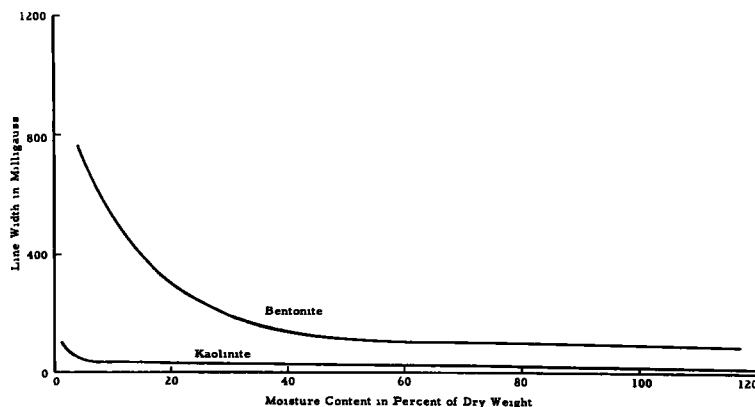


Figure 2. Moisture content, natural bentonite and natural kaolinite.

treated homionic montmorillonites. These clays were prepared at various moisture contents, and the line width of the recorder derivative signal (equal to $1/\sqrt{3}\pi T_2$) was measured and plotted as a function of moisture content. Stored at constant moisture content (in sealed bottles), the samples exhibited no change in line width despite noticeable changes in strength properties (caused by thixotropic behavior and remodeling) that resulted from aging and agitation. The only measurements made by NMR were of line width. The moisture content was measured by standard oven-drying technique. Figures 1 through 5 show the equipment used, typical NMR signals, and the final results. The magnitude of this bonding force, compared with ice 1, is low—indicating that the contribution to shear strength is relatively small. For example, ice at -2 C (Bloemrogen, Purcell, and Pound (10)) has a line width of 4,000 milligauss and sodium montmorillonite has line widths of 1,600 milligauss at 0.48 percent moisture content by dry weight and 950 milligauss at 3.46 percent. It is interesting to note that comparable line widths were measured in dry, aged portland cement concrete, and that some organic thixotropic gels exhibited no increase in line width on setting up. From experiments on

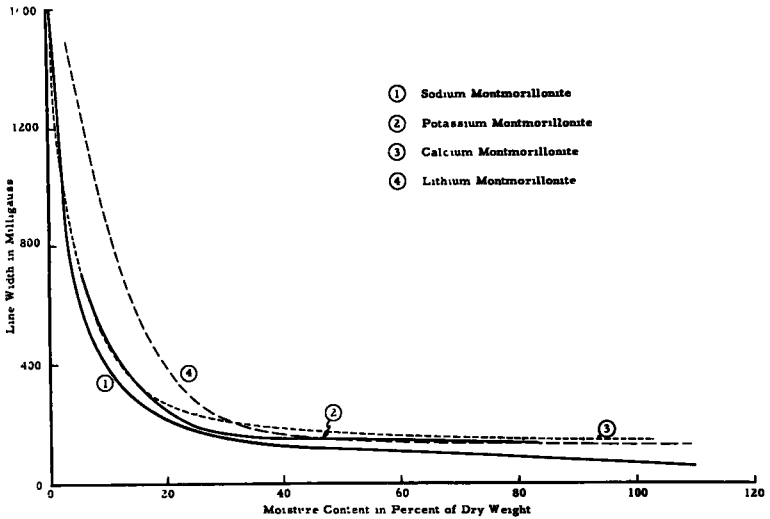


Figure 3. Moisture content, homoionic clays.

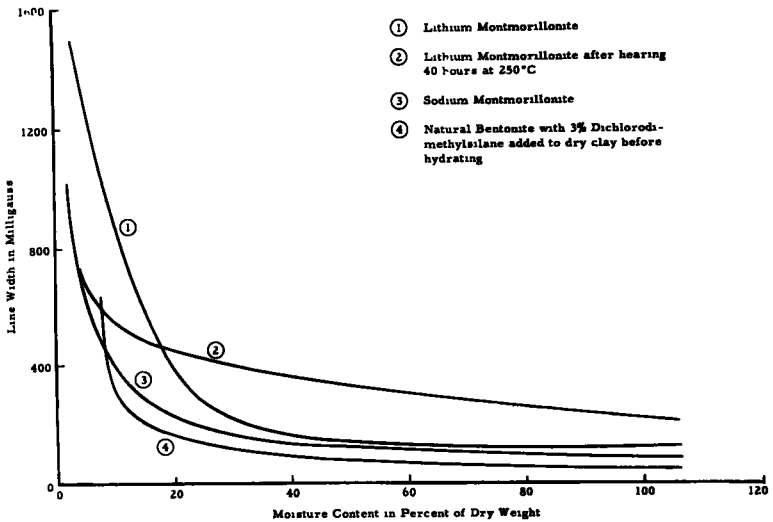


Figure 4. Moisture content, modified clays.

clays, it was concluded that the major bonding forces in clays were other than water film strength.

The modified clays were prepared to investigate the difference in the condition of water on the different surfaces of montmorillonite crystal stacks. The lithium montmorillonite, after heating, has no intralayer water. The silaned clay has intralayer water, but has no exterior water film. However, no difference was observed in mode or energy of bonding between the two systems.

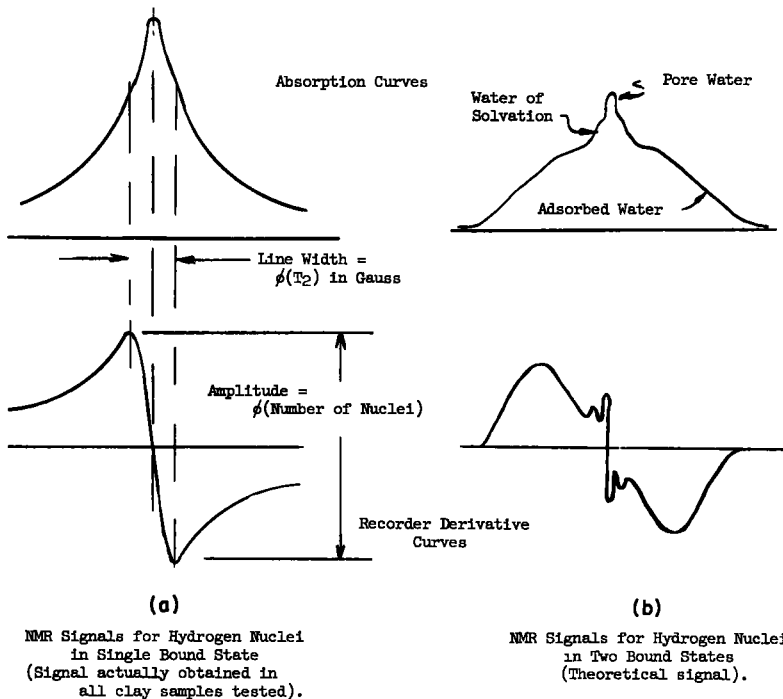


Figure 5. Measured and theoretical NMR signals, with frequency constant and field strength varied.

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SELECTED BIBLIOGRAPHY ON NUCLEAR MAGNETIC RESONANCE

Prepared by the Physics Department, Southwest Research Institute, San Antonio, Texas.—The following bibliography was assembled in late 1954 to provide an introduction to the literature on nuclear magnetic resonance for technical persons contemplating the use of NMR techniques for measuring moisture in hygroscopic solids. Inasmuch as over 400 articles on NMR had been published by January 1954 alone, no attempt has been made to cover the field completely. A sufficient number of references has been included to provide a general background, and those interested in pursuing the subject further are referred to the extensive bibliographies contained in the review articles listed in Part II.

The majority of NMR papers published in the United States are found in Physical Review and Journal of Chemical Physics. More recently, papers on applications of NMR to chemical problems have begun to appear in the chemical journals. The major source of republication information on new advances in the field are the several meetings of the American Physical Society, held at major cities during the year. Advance announcements and abstracts of the papers to be presented are contained in the Bulletin of the American Physical Society. For more detailed information on equipment and experimental techniques than is usually presented in the published papers, one can take advantage of the many doctoral theses on NMR usually obtainable on microfilm at small cost from the university concerned.

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Part III: Equipment

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Part V: Commercial Manufacturers of NMR Equipment

Varian Associates, 611 Hansen Way, Palo Alto, Calif. Useful technical data and various bulletins can be obtained from Emery H. Rogers, Special Products Sales Manager.

Laboratory for Electronics, 75 Pitts St., Boston 14, Mass. Technical data may be obtained from A. Carl Westbom.

DISCUSSION

Question: With respect to the differences in line width at 100 percent moisture in the case of the homoionic clays, do these widths signify that you have differences in the orientation of the water molecules at moisture contents of 100 percent?

Pickett: The observed differences were so small that I do not know whether to attribute them to experimental error, the inhomogeneity of the magnetic field, or the rather large samples used. The samples were 1.5 in. in diameter and the inhomogeneity in the sample, the way it was placed, was of the order of about 50 milligauss. The differences at 100 percent moisture were in the order of about 30 to 40 milligauss. Therefore, I really cannot give a definite answer on this point.

Question: When you compared the viscosity of the absorbed water to the viscosity in ice or free water, is not what you measured an average viscosity of the entire water in this clay piece?

Pickett: Yes, that is right. These graphs give the average viscosity of all of the water. It would take a bit of mathematics to go from layer to layer as you build up layer after layer to reduce the data down to the viscosity of specific layers.

Question: Could this not be done by using different degrees of saturation of the mineral?

Pickett: Well, you see we ran these samples from about 0.5 percent moisture to something over 100 percent in rather small increments.

Question: But your data could be evaluated.

Pickett: They could be, but we have never done it.

Winterkorn: In such an evaluation, it should be kept in mind that the viscosity of a particular water layer depends not only on its distance from the mineral surface but also on the distance to an existing air-water interface.

Question: Has anybody attempted to start with a fairly well-characterized clay hydrate and first analyzed it by X-ray diffraction; then after determining that he was dealing with, perhaps, a monolayer hydrate, run it in a nuclear magnetic resonance (NMR) machine to see what he got in the way of water configuration? He could have gone back and prepared a two-layer hydrate and tested this in the NMR machine, and forth. I should think that if he started out with fairly well-purified clay mineral and hydrates which he had characterized by some standard means, such as X-ray diffraction, this would greatly simplify the interpretation of the results from the NMR machine.

Pickett: I do not know of any study on clays that has been that complete. Our laboratory has done some work that has been that complete on silica gels, but not on clays. Does anyone here know of anybody who has had that much money?

Answer: I do not know of anyone, but the fact that you went through water contents with mono- and dual-layers usually form and got no discontinuities in your curves suggests that the continuous change in the NMR line width represents the viscosity.

Pickett: Thank you. I felt that way, but I cannot prove it.

Winterkorn: I feel that the fog is lifting and that we are getting right at the crux of the problem. Certainly, the NMR method will have an important role to play in its ultimate solution. Mr. Pickett mentioned the money angle involved in this kind of work.

Money is indeed a very important factor. Several years ago, I applied to the National Science Foundation and to other agencies for funds to do this kind of work in the manner suggested. I did not get it and the same thing probably happened to others that were on the same scent. This is why I was so happy when I read Mr. Pickett's work on this subject and why I asked him to speak to us today. Universities are no longer rich enough to provide funds for this kind of work and it seems that we have to hope that the large government and industry laboratories will do it and produce data which we can use.

Dr. Blaine and Mr. Pickett have introduced us to the NMR method and have shown us why and how it can be used for our purpose. Now Dr. Seligmann of the Portland Cement Association Research Laboratories will tell us more about the "why" and also about the advantages and limitations of this method.