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### ON THE CAUSE OF THE CEMENTING VALUE OF ROCK POWDERS AND THE PLASTICITY OF CLAYS.

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IN the course of the investigation of rocks as road-building material, it early became apparent that in addition to the hardness, resistance to wear, and other physical, mechanical, and economical conditions that required consideration, the binding power, or as it has come to be called, the cementing value, was one of the most important factors in deciding as to the nature and value of the material.

The description of methods of reducing the materials to powders, the formation from these powders of briquettes under constant pressure, and the subsequent impact testing by which the cementing value is obtained, has already been thoroughly described by Mr. L. W. Page,<sup>1</sup> to whom the development of the study of the cementing value of rocks and the methods of impact testing is due. An outline description of the methods employed is all that is necessary here. The stone or other material is ground in a ball mill until it passes a screen with 40 meshes per centimeter

(100 per inch). This sifted powder is then mixed with sufficient water to make a stiff "dough." After standing twenty-four hours, cylindrical briquettes are made of standard size (25 mm.  $\times$  25 mm.) at a standard pressure of 100 kilograms per square centimeter. This is done in a specially designed hydraulic press. The briquettes are then dried in an air-bath at 100° and tested in an impact machine which delivers a standard blow of 1 kilogram, falling 1 cm. The cementing value is measured in this laboratory by the average number of standard blows that a series of briquettes made from a rock powder will stand. The tests on many hundred samples, including clays, gravels and rocks of every description have shown a range of cementing values varying from those which will stand several thousand blows down to those that will barely stand one. A careful scrutiny of recorded tests in connection with the nature and chemical composition of a given material does not reveal the reason for the phenomenon. Rocks which, on chemical analysis, show themselves essentially identical in composition frequently vary widely in cementing value.

We are at once reminded of the great variation in plasticity which has been found in the case of clays. That the plasticity of clays is a phenomenon allied to, if not identical with, the binding power of rock dust there seems to be no doubt. The same property which makes a rock dust bind makes it form a plastic mass when worked up with water. It has never been positively decided whether there is a definite combination constituting the essential basis of all substances to which the name clay is applied.<sup>1</sup> If there is, however, one quality which marks and characterizes a clay and distinguishes it from other finely divided material found in nature, it is plasticity. The classification of materials, according to the size of the particles into silts and clays, is in the opinion of the writer incorrect. Powdered glass in the finest state of subdivision in which it can be obtained by elutriation has no cementing value whatever, and the same thing is true of the powders obtained from the natural glasses and semiglasses represented by some of the igneous and metamorphic rocks.

If we compare a plastic powder with a non-plastic one, nothing is explained when we say that in the former case the particles cohere, while in the latter they do not. The problem still remains to discover, if possible, the reasons for this cohesion. No adequate

<sup>1</sup> Compare Century Dictionary.

explanation of the plasticity of clays has as yet been advanced. So high an authority as Dr. Heinrich Ries<sup>1</sup> has left the subject open by his statement that: "Plasticity, *whatever its cause*, is an important property from a commercial standpoint and interesting from a scientific one." The same authority presents to us the various theories that have from time to time been advanced to account for the phenomenon, and finally decides on a combination of the two theories, of Cook<sup>2</sup> and Olchewsky.<sup>3</sup> "Cook considered plasticity to be due to a plate structure present in the clay, the plates sliding over each other and thus permitting mobility in the mass without cracking. He further found that in the kaolins the plates of kaolinite were frequently collected in little bunches, and that, after these were rubbed in a mortar, in order to tear apart the plates, they showed increased plasticity. Olchewsky was probably the first to suggest that the plasticity and cohesion of a clay are dependent on the interlocking of the clay particles and kaolin plates, and in this connection used the briquette method of testing the plasticity, or rather obtaining a numeric expression of it by testing the tensile strength of the air-dried clay."<sup>4</sup> The above explanation, if explanation it can be called, is far from satisfactory. In fact we are no nearer an understanding of the phenomenon when we say that clay particles "interlock" than when we say that they cohere. Moreover, simple plate-shaped particles do not, *ipso facto*, lead to high cementing value and plasticity, as many substances, such as mica, talc, graphite, etc., do not yield plastic powders. It has been claimed that the explanation is to be sought<sup>5</sup> in the size as well as the shape of the particles, but, though undoubtedly both these elements enter into the problem, it is none the less true, as will be shown later, that at no obtainable degree of fineness does a non-plastic powder begin to show plastic qualities. Orton,<sup>6</sup> commenting on the work of Cook, says: "Clays already naturally plastic show no plates at all, only a homogeneous matrix. These points indicate that the plasticity of a clay depends on the extent to which the tendency to a crystalline structure has been destroyed in the treatment that the clay has received." It is well

<sup>1</sup> Bull. N. Y. State Museum, 35, No. 7, p. 544 (1900).

<sup>2</sup> N. J. Geological Survey, (1878); Clays of N. J.

<sup>3</sup> *Töpf. u. Zieg. Ztg.* (1882), p. 29.

<sup>4</sup> Ries: *Loc. cit.*

<sup>5</sup> Compare G. P. Merrill's "Rock, Rock Weathering and Soils."

<sup>6</sup> Orton: *Geol. Surv. of Ohio*, 7, 1.

known that the plasticity of many clays is increased by soaking and kneading with water, and the same thing is noticed in the case of the cementing power of rock dusts, granting that there is a certain plasticity to begin with. Starting with a non-plastic powder no amount of working-up will give it cementing power. Any further discussion of these points will now be deferred until certain results have been presented which bear directly upon the cementing power of rock powders.

#### THE CEMENTING VALUE OF ROCK POWDERS.

It was realized from the beginning of the investigation that the phenomenon of the cementing power of rock dusts was possibly the result of several if not many causes. Among those which might be expected to have more or less influence, may be mentioned:

(1) Solubility, however slight, of the material or of certain ingredients of the material.

(2) Size and shape of the particles.

(3) Chemical reactions set up on moistening the powders, as in the cases of Portland cements, mortar, etc.

(4) Crystalline forces operating under either 1 or 3, as in the cases of plaster-of-Paris, mortar, cements.

(5) Physical nature or condition of the particles and their relations to water: (a) Unbound water; (b) hygroscopic water; (c) water of crystallization; (d) water of constitution, or combination.

After many experiments in this laboratory, some of which are detailed in the following pages, the conclusion was reached that, although the causes put down under the first four headings are to a certain degree operative in many cases, and even perhaps of paramount importance in exceptional ones, it is under the fifth heading that the true cause of cementing power and plasticity must be sought.

If a rock powder is ignited at a temperature at which all the water of combination is expelled, the cementing power is invariably totally destroyed. This is also true as regards the plasticity of all grades and varieties of clays. No better indication could be had that the binding power is a function of the combined water or of some condition of the particles which is invariably accompanied

by the presence of combined water. Early in the investigation the idea had suggested itself that there must be a physical difference in the nature of the particles. Powders which cement well, must be composed of particles which present to one another more or less "sticky" or adherent surfaces. As a matter of fact, a trained eye can at once detect a powder that is likely to give a high cementing value. A plastic powder when poured on a flat surface will form a more or less cone-shaped heap, while a non-plastic powder, to use the language of the clay worker, "squats." Most authorities have rejected the notion<sup>1</sup> that water of combination conditions the plasticity, for the simple reason that many totally non-plastic earthy deposits and minerals have a high water content. The difficulty has probably arisen from a failure to distinguish *different kinds* of water of combination. The whole question of combined water in inorganic materials is a most interesting one and will be more fully discussed later on.

In the earlier experiments, four road-building materials were selected, which, while essentially similar in geological character and chemical composition, had shown a wide variation in cementing value. The number, analysis, cementing value, specific gravity and weight of the dry 25 mm. briquettes are given in the table below.

TABLE I.

	No. 441.	No. 341.	No. 342.	No. 414.
H <sub>2</sub> O.....	5.20	4.73	3.00	0.20
SiO <sub>2</sub> .....	83.22	83.35	88.06	95.90
Al <sub>2</sub> O <sub>3</sub> .....	7.75	9.53	6.00	2.60
Fe <sub>2</sub> O <sub>3</sub> .....	3.10	2.23	2.34	1.05
CaCO <sub>3</sub> .....	0.75	trace	0.00	0.50
MgCO <sub>3</sub> .....	0.00	0.00	0.00	trace
	100.02	99.84	99.40	100.05
Cementing value .....	297.0	101.0	74.0	2.0
Specific gravity of powder ...	2.3	2.6	2.5	2.5
	Grams.	Grams.	Grams.	Grams.
Weight dry briquette.....	22.5	23.6	21.0	18.8

A study of these records shows that the degree of hydration, in so far, at least, as these four samples are concerned, has followed the order of the cementation. In addition to this, it is seen that the respective weights of the 25-mm. briquettes are not in the ratio of the specific gravities. In other words, some rock powders are

<sup>1</sup> Compare Cook : *Loc. cit.*, p. 288.

apparently more compressible than others. In so far as the writer is aware, little or no attention has been given to the subject of the compressibility of rock powders; it is not even known what bearing water of combination has on the volume relations of powders. In order to pursue this subject, it was decided to further investigate the samples, the analyses of which have been given above. Portions of the rock powders were ignited at a red heat until completely dehydrated; a series of briquettes were then prepared by weighing exactly 20 grams of each of the powders, both raw and ignited. These briquettes were then carefully measured, and determinations of the specific gravity of the powders made. The results are contained in the following table.

TABLE II.

No.	Water. Per cent.	sp. gr.	Height of 20- gram briquette.	Cementing value.	Compres- sion.
441.....	5.20	2.3	22.2	297	7
441 ignited ....	0.00	2.5	29.0	2	—
341.....	4.73	2.5	21.2	101	2.8
341 ignited ....	0.00	2.6	25.2	2	—
342.....	3.00	2.5	23.8	74	2.4
342 ignited ....	0.00	2.5	27.0	2	—
414.....	0.20	2.5	26.6	2	—
414 ignited ....	0.00	2.4	28.9	2	0.2

An inspection of the above table shows that the briquettes made from ignited powder are invariably larger than those made from raw powder, and that this difference in height is not entirely accounted for by the slight difference in specific gravity. Assuming that the water of constitution is so included in the particles of the raw powder as not to add materially to their bulk, a correction must be applied for this. For instance, in the case of No. 441, 5.2 per cent. of the 20 grams weighed, or 1.04 grams, consisted of combined water. In No. 441 ignited, this proportion of the weight is substituted by material which certainly adds to the volume. In this table the values in the column headed compression are obtained by applying corrections for the change in specific gravity and loss in water. The following formula gives at once the compression from the data involved:

$$C = B - \left( \frac{Aa}{b} + \frac{yB}{100} \right),$$

where A and B are the respective heights of the raw and ignited

briquettes,  $a$  and  $b$  the corresponding specific gravities, and  $\gamma$  the percentage of water of hydration.

It appears from these results, which have been confirmed by many others not here given that plastic powders molded into briquettes under a given pressure apparently suffer a certain compression which is not shown by the material after the plastic condition has been destroyed by ignition. We have now to inquire if any reason can be found not only for this compression but for the fact that it seems to accompany the plastic condition.

Compressibility may be conditioned by: (1) Porosity and plasticity of the particles which would allow of their being "squeezed" into closer contact and configuration. (2) Shape and size of the particles governing their resistance to close contact and the inclosure of voids.

In this work it was found that the ignited powder always contained a much larger proportion of impalpably fine dust than the raw hydrated powders. This is shown not only by microscopic examinations but proved by dropping the respective powders into water, when it is easily seen that the former contains a greater proportion of fine material which remains longer in suspension.

It is conceivable that a hydrated material may possess a porosity so fine that the magnitude of the interstitial spaces is submicroscopic, perhaps not far removed from that of the water molecules themselves. The heating by ignition of a powder consisting of such hydrated particles would have a bursting or disrupting effect upon the particles which would thus fall down to a more impalpable dust.<sup>1</sup>

In order to investigate the effect of size of particle on the volume of briquettes it was decided to prepare glass powders of different degrees of fineness. A quantity of the best French plate glass was accordingly powdered in the ball mill and sifted through a 0.25-mm. mesh screen. A quantity of the sifted powder was shaken up with a large excess of distilled water and allowed to settle for ten minutes. The portion in suspension was then decanted to another vessel and allowed to settle again for thirty minutes; the decantation was then repeated and the third or finest portion allowed to settle completely. The three portions were thoroughly dried in an air-bath, and the three powders examined under a high-

<sup>1</sup> At the time at which the above was written the author was not familiar with the interesting work of Van Bemmelen on the dehydration of inorganic colloids (the so-called hydrogels), or with the miscellian theory of Nageli.

power microscope fitted with a micrometer eye-piece, with a view to getting some notion of the comparative size of the particles in the respective samples. As the size of the different particles was in no case uniform, the best that could be done was to measure the largest particle that presented itself in each field and then select one that seemed more nearly to represent an average; 20-gram briquettes were then made from each of the three powders, and carefully measured. The cementing value is given in each case to show that it does not increase with the fineness of the particles, if a non-plastic powder is being dealt with. The results are given in the following table:

TABLE III.

Sample.	Approximate size of powders. mm.	Amount of water used in making briquettes. cc.	Height of briquette. mm.	Cementing value.
Coarse.....	{ maximum 0.2 average 0.025	4	29	I
Medium .....	{ maximum 0.050 average 0.017	4	34	I
Fine .....	{ maximum 0.012 average 0.004	4	36	I

It may be questioned whether the difference in the observed volume of the briquettes could be occasioned by a difference in the specific gravity of the various powders. The extreme compression observed between the minimum and maximum volume in these glass briquettes is 9.5 mm.; this corresponds to a calculated difference of 0.7 of a unit in the specific gravity. That is to say, if the powder had a specific gravity equal to 2.5, the finest would have to have a specific gravity equal to 1.8 in order to account for the variations. It is impossible to believe that such a homogeneous material as plate glass could be separated into portions of such widely differing gravities, and, moreover, in spite of the difficulties attending the determination of the specific gravity of very fine powders, such wide differences could not escape experimental detection. As a matter of fact, determinations carefully carried out showed little or no deviations in specific gravity.

The question then is, how are we to explain these results? As far as the writer is aware there is little information available in the literature on the volume relations of fine powders under given pressures, although much has been said on the subject when it is a question of a far larger order of magnitude, *i. e.*, in relation to



the size and shape of broken stone and pebble in concrete mixtures. It is possible, of course, that the finer powders enclose voids that resist compression more than do the coarser and more angular particles. Again it may be considered that in the form of a solid cylinder, glass is occupying the smallest volume it can occupy. If the glass is crushed to fragments these fragments can be compressed to a certain degree by a given pressure; if we break these fragments still smaller, the resulting fragments, however tiny, are made up of particles arranged in more compact order and in less space than they could be arranged again if once set free. From purely theoretical consideration, therefore, we may say that in reducing the fineness of a powder we are approaching an ideal condition of unit particles which can not be forced by any ordinary pressures into the same space they occupied as part of fused masses. Whatever the proper explanation of these results may be, it is certain that an increase in the amount of impalpable dust of the smallest possible magnitudes apparently decreases the compressibility of the material by a given pressure. Turning again to the results on rock powders we are led to the conclusion that the driving off of water of combination breaks up the particles to a finer dust, also that this destruction of the particles leads to loss of plasticity.

As there were on hand in this laboratory a large number of thoroughly air-dried samples of rock powders and clays, of which the cementing value was known, it was decided to determine the water content of these, with a view to seeing if indeed any relation could be traced between cementing value and water of combination. The determinations were made by igniting the powders in a platinum boat contained in a hard glass tube and absorbing the water set free in a weighed sulphuric acid bulb-tube. The results are contained in the following tables:

TABLE IV.  
*Dolomites and Limestones.*

No.	Cementing value.	Water. Per cent.	Name.
451.....	9	0.40	Dolomite.
665.....	10	0.30	Dolomite.
537.....	10	0.50	Dolomite.
663.....	12	0.35	Limestone.
489.....	13	0.14	Calcite.
470.....	16	0.48	Dolomite.
487.....	26	0.38	Limestone.

No.	Cementing value.	Water. Per cent.	Name.
343.....	32	0.40	Dolomite.
515.....	38	0.40	Limestone.
664.....	41	0.40	Limestone.
503.....	54	0.58	Limestone.
666.....	58	0.66	Limestone.
347.....	95	0.34	Limestone.
424.....	99	0.64	Limestone.
336.....	158	1.00	Limestone.
361.....	158	2.26	Clay limestone.
462.....	161	1.20	Dolomite.
377.....	195	1.20	Limestone.
557.....	595	6.10	Clay limestone.

*Miscellaneous Rocks.*

No.	Cementing value.	Water. Per cent.	Name.
468.....	2	0.00	Gneiss.
580.....	2	0.43	Gravel.
414.....	2	0.20	Metamorphic silicious rock.
499.....	4	0.02	Quartzite.
652.....	8	3.2	Gravel.
451.....	9	0.40	Gravel.
465.....	14	0.81	Gravel.
651.....	17	1.30	Gravel.
372.....	25	0.56	Gneiss.
592.....	41	1.50	Gravel.
342.....	74	3.00	Silicious chert.
536.....	77	0.68	Gravel.
341.....	101	4.73	Gravel.
335.....	110	1.90	Trap rock.
361.....	158	2.26	Calcareous clay.
441.....	297	5.20	Gravel conglomerate.
396.....	327	2.00	Felsite.
534.....	475	5.00	Red clay.
398.....	577	2.50	Rhyolite.

TABLE V.—DIABASE TRAP ROCK.

No.	Cementing value.	Water. Per cent.	Average.		
415.....	2	0.81	Low group	{	Cementing value, 6.00
420.....	6	0.81			
354.....	10	0.84			
405.....	19	1.14	Middle group	{	Cementing value, 25.00
350.....	19	1.46			
566.....	38	1.45			
357.....	72	1.80	High group	{	Cementing value, 87.00
517.....	76	1.67			
467.....	91	2.81			
335.....	110	1.90			
					Water content, 2.04

An inspection of these results shows at a glance that high cementing values show a decided tendency to accompany a high water content. At the same time we see that there are several exceptions revealed, and it is probable, that an even greater number of results would show other discrepancies, as it is well known that many minerals with high water content do not yield plastic powders. On the other hand, if a certain kind of water of combination invariably accompanies the plastic condition, this active water would be added to the inactive and an explanation furnished, not only for the general tendency, as shown above, but also for the exceptions to it.

We have to inquire what is meant by water of combination. Probably no term in chemistry has been more loosely used than this. Ordinarily speaking, it refers to the water which is contained in a substance in such a way that no amount of drying at 100 C. is able to dislodge it. In this way it is differentiated from unbound water and probably from hygroscopic moisture. Such a definition, however, would include as a general thing water of crystallization, which is not usually meant when we speak of water of combination. It might be subdivided into chemically bound or hydroxyl water, and physically bound or included water, but as a matter of fact, so little is known about the relation of water to structure, that classification is at present impossible.

The question of opalline or zeolytic water has been much discussed<sup>1</sup> but recent work seems to indicate that the combined water in these cases exists in a physically rather than in a chemically bound condition. Even the water in the metallic hydroxides to which we assign arbitrary formulas has fallen under grave suspicion.<sup>2</sup>

In 1893 Van Bemmelen began the publication of a series of researches<sup>3</sup> on the inorganic colloids or "Hydrogels". Nearly all metallic oxides and many salts have the power of entering into that peculiar hydrated, non-crystalline condition which Graham<sup>4</sup> in 1861 denominated colloid or glue-like. The special hydrogel

<sup>1</sup> See Friedel: *Bull. Soc. Min.*, 19, 14, 94 (1896); also *Compt. Rend.*, 122, 1006.

<sup>2</sup> "Die Frage scheint erlaubt, wann endlich in den Handbüchern und in den Abhandlungen von Hydraten mit chemischen Formeln zu sprechen aufhören wird, bei Substanzen, die nur eingetrocknete Hydrogels sind. So begegnet man, z. B., überall dem Eisen-oxydhydrat mit der falschen Formel  $\text{Fe}_2(\text{OH})_6$ . Diese kristalloidale Verbindung wurde noch nie bereitet." V. Bemmelen und Klobbie: *J. prakt. Chem.*, 46, 497-529 (1892).

<sup>3</sup> *Ztschr. anorg. Chem.*, 5, 466; *Ibid.*, 13, 233; *Ibid.*, 18, 14; *Ibid.*, 20, 185; *Ibid.*, 22, 313.

<sup>4</sup> *Phil. Trans.* (1861), p. 183.

which Van Bemmelen studied most minutely was that of silicic acid, although his researches include the oxides of copper, tin, iron, alumina, etc., etc. As a result of these extensive investigations the author cited adopts the suggestion of Nageli of the micellian structure of colloids, that is to say, that these curious substances consist of heterogeneous molecular complexes which possess a submicroscopical, web-like, porous formation, one of the distinguishing characteristics of which is the peculiar relation to and dependency upon water which they exhibit. The water content of these hydrogels varies continually with the temperature and the vapor-pressure of the atmosphere in which they find themselves. Dried at high temperatures up to a certain critical point, they will loose nearly all their water, only to take it back again eagerly when allowed to cool in free air or in moist atmospheres. This dehydration and rehydration can be repeated indefinitely unless the temperature of drying is carried too high, when the faculty is gradually lost and finally destroyed. We have here to do with a certain kind of water of combination which, following Van Bemmelen, we shall denominate micellian water. It is just as much a characteristic of the plastic or colloid condition as water of crystallization is a characteristic of many crystals, although just as we may have in certain cases crystal water replaced by alcohol or ether, etc., of crystallization, we can have the water in these colloids replaced by organic liquids, yielding alkogels, sulphogels, glycerogels, acetogels, etc. Further than this, all the recent work that has been done on the occlusion of solids by colloids points to the fact that water can be replaced by numbers of other substances. Even solids seem to be absorbed into the micellian structure, but this leads up to the question of solid solutions, a subject too large for discussion in the present paper.

Van Bemmelen has shown that this inhibited or micellian water differs from hygroscopic water in the ordinary sense of that word. Micellian water is absorbed into the structure of the particles of a powder of an inorganic hydrogel without changing the physical appearance, even under the microscope. Hygroscopic water is usually adsorbed on the particles, producing a distinct appearance of wetness. Heating does not usually destroy the hygroscopic qualities of a substance; it invariably destroys the absorptive power of the micellian structure, if pushed far enough.

It is not the purpose of this paper to review the work that has been done on colloids. A good bibliography of the whole subject has been given, up to 1901 by Whitney and Ober.<sup>1</sup> The immediate object is to call attention to certain significant qualities which are shared in common by such inorganic hydrogels as silicic acid, and ferric hydroxide on the one hand, and plastic clays and rock powders on the other. Both contain combined water; both lose water on heating, and take it up again on cooling in moist atmospheres (see curves in Fig. 1). Both gradually lose this

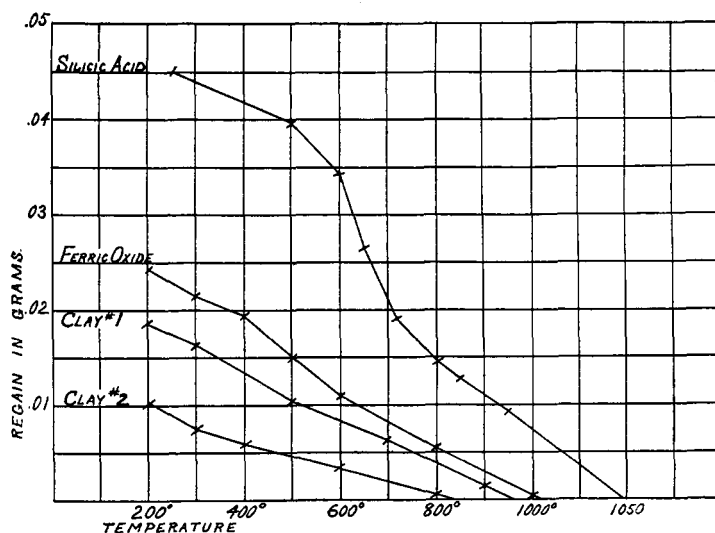


Fig. 1.

power on continued heating at high temperatures, and finally lose it entirely, together with plasticity, if the heating is pushed far enough. Very highly plastic clays and rock powders, after working up with water, usually shrink and deform on drying out; this quality is also universally noted in the case of the hydrogels. Silicic acid which has been air-dried can have water pressed out of it by subjecting it to very high pressures; the same phenomenon is known in the case of clays in the manufacture of hydraulic pressed brick. It has been frequently claimed that the cause of plasticity is to be sought in the aluminum silicate (kaolin) which forms the essential ingredient in all clays. The following is

<sup>1</sup> *Loc. cit.*

quoted from a late writer on the subject.<sup>1</sup> "Based on the work of various chemists, on that of investigators, using the microscope, with high powers, and on the physical experiments of Le Chatelier, it may now be said to have been established, that there are various hydrous silicates of aluminum, which differ in the proportion in which the elements are combined, and in form and structure, *some being colloid or amorphous* and others crystalline."

G. H. Cook,<sup>2</sup> a high authority on clays, writing in 1878 and describing his microscopical examinations, says: "Some clays appear to consist of well-defined crystalline forms; others show a few of these in a mass of fragmentary shapes; others still seem to be wholly made up of irregular forms and exceedingly fine particles of matter." Cook then calls attention to the fact that highly plastic clays are in the latter class and finally includes this very suggestive sentence; "We know that in some of the metals a tendency to crystallization reduces their tensile strength—most notably in the case of iron; and it may be that the crystalline structure of clay is somewhat analogous to the metals. Thus far there seems to be a close correspondence between this [non-crystalline] state or condition and the property of plasticity, and it appears to be a reasonable explanation consistent with most if not all the facts."

If indeed plasticity is a question of a colloid condition of the particles, it seemed that plastic clays and rock powders ought to show the same peculiar relation to water as is shown by the hydrogels, and in a diminishing degree as the plasticity diminishes.

In order to study the subject, a special form of furnace was devised that could be heated by a blast-lamp to any desired temperature up to 1100° C. The temperatures were measured by means of a Le Chatelier platinum-rhodium pyrometer. No difficulty was experienced in maintaining the temperatures constant to within a few degrees. The mode of procedure was as follows: Exact, 2 gram samples of the various substances were heated in the furnace for exactly one hour, cooled in a desiccator over concentrated sulphuric acid for one hour, weighed as quickly as possible and finally exposed under a large bell-jar over dilute sulphuric acid (24 per cent.) which had a vapor-pressure of about 18 mm. at 24° C.<sup>3</sup> At this vapor-pressure, water does not adsorb on the surface of

<sup>1</sup> Ladd: *Clay Record*, 18, 10.

<sup>2</sup> *Loc. cit.*, pp. 287, 288.

<sup>3</sup> Landolt and Börnstein: "Tabellen," Ed. 1894, p. 65.

glass or the particles of a powder so that all gains in weight are a true measure of affinity for water. As nearly as possible, the bell-jar was kept at a constant temperature during the experiments, but when any considerable variation occurred, corrections were made to the results. The silicic acid hydrogel was prepared by neutralizing sodium silicate with dilute hydrochloric acid, and washing the jelly by dialysis until the salt was entirely removed. The pure jelly was dried to a certain point on the steam-bath and finally allowed to air-dry. The resulting white powder, which had every physical appearance of being dry, was found to contain about 20 per cent. of water. The hydrogels of iron, alumina and magnesia were precipitated by dilute solutions of sodium hydroxide,

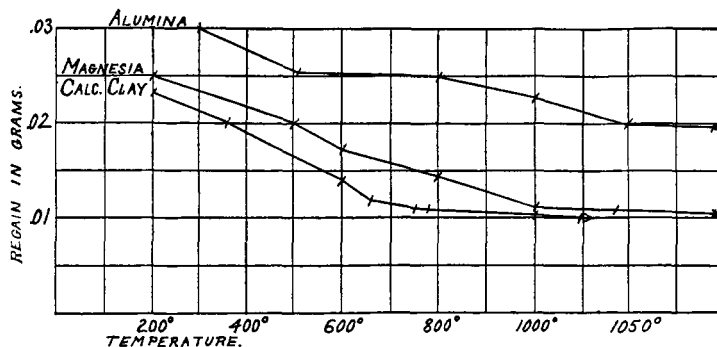


Fig. 2.

thoroughly washed by decantation and finally air-dried. Finally three samples of clay were selected for comparison. Clay No. 1 was highly plastic, clay No. 2 less so, and clay No. 3 contained an unusual amount of calcium carbonate. The results of the experiments are graphically shown in Figs. 1 and 2. On the horizontal axes, the temperatures of the heats in the furnace are shown, and on the vertical axes, the regain weights after one hour's exposure in the bell-jar. The curves of Fig. 1 indicate that identically the same peculiar power of absorbing water, which is gradually destroyed by heating, is possessed by clays and colloids. The difference is merely in degree. In Fig. 2 we have the curves for alumina and magnesia compared with that obtained from a calcareous clay of low fusing-point which contained 30.75 per cent. of calcium carbonate. These curves never descend to the zero-point. No amount of heating will destroy the power of lime, magnesia

and alumina to take up water again. Whatever theory we may hold as to the relation of water to these substances in the process of "slaking" it is quite certain that it is an altogether different phenomenon from the process which goes on when water is absorbed into the peculiar structure of a colloid. Table VI presents a series of observations made on a number of different samples in which the temperature of the heats was constant and the cementing values and the percentage of regain are the variables.

TABLE VI.

Sample No.	Name.	Cementing value.	Loss per cent. at 300.	Regain per cent. in air at 18 mm.	
				V. t.	
534	Clay	595	2.31	2.09	
557	Clay	475	1.00	0.75	
361	Clay limestone	158	0.40	0.40	
335	Diabase	110	0.30	0.18	
517	Diabase	76	0.43	0.43	
566	Diabase	38	0.17	0.13	
499	Quartzite	4	0.07	0.03	
570	Gravel	2	0.08	0.04	
468	Gneiss	1	0.04	0.00	

The results are shown graphically in Fig. 3, the cementing

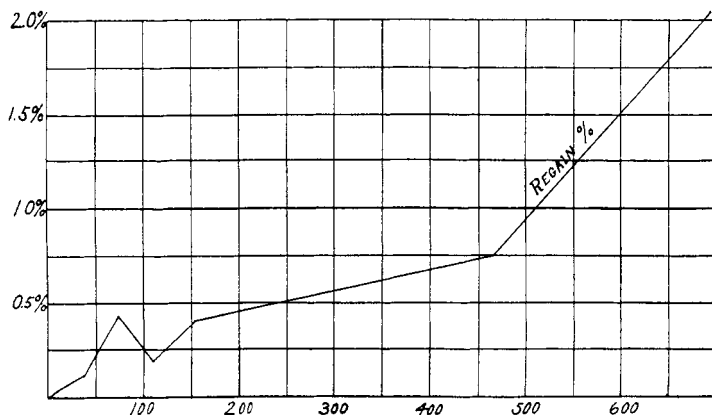


Fig. 3.

values being plotted on the horizontal, and the regain percentages on the vertical axis. The tendency of low regains to accompany low plasticity in these cases is undoubted, although the curve is by no means regular. Good reasons for irregularities are not hard to find; in the first place, impact testing, though it may be the



best, is not a perfect measure of cementing value and is subject to considerable error. In the second place, it is freely admitted that other influences such as shape and size of particles, solubility of ingredients, the ratio of plastic to non-plastic material present, etc., may come into play.

A question that naturally arises is how are we to account for the well-known high-binding powers of many homogeneous crystalline rocks such as limestones and dolomites. Reference to Table IV shows a wide range in cementing value for this class of material. As a matter of fact, pure calcium carbonate has no cementing value whatsoever; this quality is provided by certain hydrated impurities such as silica, ferric oxide or even clay. The amount of these impurities need not necessarily be very large, but the distribution throughout the mass is probably of a very intimate nature. It has long been known to practical road builders that the binding power of many rocks increases as time goes on, under the combined influence of the action of traffic and water. Every potter knows that the plasticity of clay increases under the action of kneading and working with water. In some industries, clay mixtures are stored away for considerable periods under wet blankets. This process is called "sweating" and is believed to be very beneficial. It has lately been suggested that bacterial fermentations are responsible for the improvement in the quality of clays under such treatment. The writer has no data on this subject but it is well known that many of the nitrifying bacteria flourish in media composed of inorganic colloids, which suggests that the presence of bacteria may be a concomitant rather than the cause of improvement. Experiments in the laboratory have shown that the cementing value of briquettes is increased, if the dough made from a rock dust is allowed to stand for some time before being molded, and it is still more increased, if the dough is kneaded. This is plainly shown by the results of a sample of dolomite that had an analysis as follows:  $\text{CaCO}_3$ , 54.30;  $\text{MgCO}_3$ , 36.20; combined water, 0.48; silica, 3.00; iron and alumina, etc., 7.00. This dolomite is a celebrated road-building material in the locality in which it is found and its most marked characteristic is the way that its binding power increases after it has been upon the road for some time. In the following table, the rock dust was mixed with water and briquettes made at separate intervals; finally a new lot

of dust was made to a dough and well kneaded by hand for one hour.

TABLE VII.

Time.		Cementing value.
At once .....		16
Dough 4 hours old .....		50
" 24 " " .....		81
" 72 " " .....		79
" 96 " " .....		77
" 120 " " .....		79
" 144 " " .....		83
" 8 days.....		81
" kneaded 1 hour.....		190

In summarizing the results as presented in this paper it may be said that it has been pointed out: (1) That the cementing power of rock powders is a property similar to the plasticity of clays. (2) That all rock powders that have cementing power show the same peculiar relation to water that is shown by substances that possess an amorphous colloid structure, *i. e.*, they can be dehydrated and rehydrated, until, by prolonged high heating, the structure is destroyed.

It is not the intention of the writer to maintain that the gelatinous mass in which silicic acid separates from a dilute solution is in any way comparable to a plastic clay mass. The question is purely one of the condition of the particles which go to make up the mass of plastic rock-powder or clay. In the opinion of the writer, particles which are entirely crystalline in their nature have nothing to do with plasticity except to act as a diluent. It is the amorphous particles which, by reason of their characteristic structure, are able to absorb water and assume the condition which causes them to exhibit that coherence which in the mass we denominate plasticity.

A series of clays which is at present being studied in this laboratory according to the methods already described for obtaining the curves of Fig. 1, has given results which go to show that the more plastic a clay the more it exhibits the peculiar absorptive power. Before publishing the results, it will be necessary, however, to collect evidence from a great number of different kinds of clays. To that end the writer will be grateful to any one who will send samples to this laboratory for comparison and study.