WALLACE

The Dissociation of a Shale by Calcium Carbonate through Heat

Ceramic Engineering

B. S.

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THE DISSOCIATION OF A SHALE BY CALCIUM CARBONATE THROUGH HEAT

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

M. Frank M. Wallace

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The Dissociation of a Shale by Calcium Carbonate Through Heat

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF

B. S. in Ceramic Engineering

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THE DISSOCIATION OF A SHALE BY CALCIUM CARBONATE THROUGH HEAT.

The valuation of cement making materials has been most generally based upon the results of chemical gross analysis. Since for cement making process the form of the silica and alumina which unite with lime to form silicates and aluminates is of great importance in respect to the ease of perfecting chemical union, the materials which furnish these constituents, the clays, should be put through tests to determine their mineralogical and physical character.

It is the object of this work to determine
1. The lowest temperature at which the dissociation of a shale by calcium carbonate is most complete.
2. To show the effect of using clay of different sizes.
3. To determine if possible some direct relation between the size of grain and the amount of soluble silica, as found by rational analysis.

The investigators who have devised methods for the determination of the hydraulic value of cements are: Seger\(^1\) with his method of rational analysis, its modifications by Fresenius\(^2\) and Heintzel, Lunge\(^3\) and Schochor and Bleininger\(^5\) in his work for the Ohio State Geological Survey.

\(^{1}\)Seger volume I
\(^{2}\)Fresenius quantitative analysis Vol. II
\(^{3}\)Journal of Applied Chemistry 1894, 7, 481 and Vol. 3 Trans. of American Ceramic Society.
\(^{4}\)Volume 3 Transactions of American Ceramic Society
In brief, Seger makes use of the fact that boiling sulphuric acid dissolves that portion of a clay called clay substance of the theoretical composition \( \text{Al}_2\text{O}_3\text{Si}2\text{O}_5\cdot \text{2H}_2\text{O} \), but does not attach feldspar and quartz, the other two essential constituents of the clays. From the analysis of the residue, the percent. of feldspathic minerals and quartz can be calculated.

This method, though giving valuable data in regard to the mineralogical character of a clay, yet neglects to give expression to the coarseness or fineness of the grains composing the insoluble matter and hence fails to bring out the degree to which a clay unites with lime to form silicates and aluminates of lime. Therefore it would be necessary to make a mechanical analysis of the residue, but this would still fail to tell just which of the various sizes are feldspar and which quartz. Lime can decompose and unite with the constituents of feldspar, the latter being a silicate, with far greater ease than with quartz assuming both being of the same size of grain. Hence we see that the ordinary rational analysis is deficient and does not produce exactly the kind of data desired.

The Fresenius and Heintzel methods are specially intended to show the fitness of calcareous clays for cement purposes. They assume that the solubility of the raw material in acid is a criterion of its value. This opinion, though accepted by a number of chemists, is erroneous, as has been amply shown by Lunge and Schochor.

Lunge and Schochor proceed on entirely different bases
and made use of the fact that silicates are unlocked by being heated in contact with lime, as is clearly shown by the J. Lawrence Smith method of determination of the alkalies. These investigators, though they worked with marls, succeeded in showing that lime attacks most readily the combined silica and the silica present in a fine state of division, but does not render soluble the coarser portion, thus giving a direct expression of the cement making value of the materials.

Their results obtained may be summed up as follows:

The solubility of raw marls in acid is not sufficient for the determination of their hydraulic value, because acids are not suitable reagents to determine the unlockable silica. Also the acid treatment does not discriminate between the coarse and fine silica, between amorphous and the crystalline silica.

Although quartz and amorphous silica when not ground to great fineness and heated with the same quantity of lime show a variation in amount of soluble silica, yet if ground extremely fine, practically all the silica in either form is soluble.

Chemically combined silica is almost completely unlocked. No matter how fine free silica is, it is always attacked less than combined silica, hence the best source of silica for cement purposes is a silicate. Or as has been intimated the higher the percent. of dissolved material after heating with lime and treating with hydrochloric acid and sodium carbonate the greater is the value of the clay for cement purposes.

The above investigators heated their samples in the form of lumps to 1100°C without mixing or pulverizing. The burned material was then treated as given. The value of the respective
marls was expressed inversely by the percent. of the residue.

In order to prove that their work was satisfactory and that their results meant something, they ground the material after calcination to vitrification and proceeded to make cement tests from them. These tests confirmed the accomplishment of their purpose.

Upon studying the results obtained by Lunze and Schochor, Edward Orton Jr. suggested a method for testing clays in regard to their solubility for cement manufacture. The investigators just named had limited their methods to marls. They had three variable factors in their analyses, i. e., the coarse and fine grained material and the content of lime. It was therefore decided to use a constant amount of lime and eliminate one variable.

Whereas Lunze and Schochor burned their samples in lumps, the Ohio Geological Survey reduced the samples by the use of water but without grinding and accomplished a mixture of clay and lime when the former was in fluid suspension.

1. Determination of the lowest permissible temperature at which dissociation of a shale by calcium carbonate is most complete.

In this work the order of procedure was as follows:

Preparation of clay samples.

A Shale, found in the laboratory of the Ceramics Department of the University of Illinois was selected for the investigation. The sample chosen consisted of slate-like particles. These cakes were broken up in a jaw crusher and put through a twenty mesh sieve. In order to obtain a
uniform sample, the clay was mixed by means of a spatula. Accomplishing this, by the process of quartering, a sample of about five grams was chosen for analysis. The latter was ground to a fineness corresponding to that of a two hundred mesh sieve.

Analyzed by Hillebrand's method, the shale showed the following composition:

- \( \text{SiO}_2 \) 63.20 per cent.
- \( \text{Al}_2\text{O}_3 \) 13.32 per cent.
- \( \text{Fe}_2\text{O}_3 \) 6.12 per cent.
- \( \text{CaO} \) 1.92 per cent.
- \( \text{MgO} \) 2.86 per cent.

 Portions of the same shale were reduced in a porcelain mortar to different mesh sizes, i. e., they passed the coarser but not the finer sieve in the following order:

- 20-40
- 40-60
- 60-80
- 80-100
- 100-120
- 120-200
- 200-

In order to determine the proper burning temperature a sample of the last and finest size was used and mixed with eight times its weight of chemically pure calcium carbonate. This mixture was obtained by placing the two constituents in a dry ball mill containing no pebbles and allowing it to run for a time, after which it was removed to pans where it was mixed with a spatula until uniformity was evident.
Five Battersea fire clay crucibles were lined with a coat of whiting and allowed to stand until dry. A sample of the above two hundred mesh size shale was then introduced into each and burnt.

This took place in the side down draft test kiln of the University of Illinois. A time-temperature curve was followed as closely as possible. The temperature was recorded by a Le Chatelier pyrometer and draws were taken at the following temperatures: 1200, 1250, 1300, 1350, and 1350°C.

Figure I represents this time-temperature curve.
Figure I showing Time-Temperature Relation

Temperature in Degrees Centigrade

Time expressed in Hours
The calcined samples obtained were removed, the lumps reduced in a porcelain mortar, and placed in labeled test tubes for analysis.

According to the method given in the Ohio Geological Survey Bulletin No. 3 each sample was treated with hot dilute hydrochloric (1:2) acid, boiled, filtered and washed. To the residue was added a solution containing 0.2 grams of caustic soda and 3 grams of sodium carbonate. This was heated but not boiled for an hour and filtered. The residue remaining is treated with alkali of half the strength and repeated until no more flocculent silicic acid could be detected in the filtrate. The total filtrate was then made distinctly acid and evaporated to dryness until fumes of hydrochloric were completely expelled. The precipitate was taken up with acid and hot water and filtered. The residue washed free from chlorine was ignited and weighed. Volatilizing the silica by Hydrofluoric acid, the difference in weight gave the amount of soluble silica. The results are:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Burned Samples Show</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200°C</td>
<td>10.20 per cent. SiO₂</td>
</tr>
<tr>
<td>1250°C</td>
<td>10.29 per cent. SiO₂</td>
</tr>
<tr>
<td>1300°C</td>
<td>11.15 per cent. SiO₂</td>
</tr>
<tr>
<td>1350°C</td>
<td>10.84 per cent. SiO₂</td>
</tr>
</tbody>
</table>

1350°C + C burned samples show 9.24 per cent. SiO₂

This data shows 1300°C to be the best temperature for burning the mix, as most silica is rendered soluble when given that degree of heat. In other words the lime when mixed with the clay and burned to 1300°C combines and breaks up the silicate mixture to a greater extent, the fineness of grain of the clay remaining constant.
II Effect of size of grain

The samples representing the other sieve sizes were now mixed with eight parts by weight of calcium carbonate and burned in the same manner. However in this particular burn the voltmeter ceased to give accurate readings and it was necessary to guage the final temperature by cone 9 (1310°C). As a definite temperature had been selected all samples were burned to the one temperature, and hence no draws were taken and the time of burning was shortened considerably. The kiln was allowed to cool during twelve hours and samples were removed.

Figure II shows the time-temperature relations of the burn.
Figure II

Showing

Time-Temperature Relation

Temperature
in Degrees Centigrade

Time expressed in Hours

200° 400° 600° 800° 1000° 1200° 1300°
The calcined samples were removed, the lumps reduced and analyzed as those in the earlier part of the work. The percentages of silica obtained were percentages in terms of the clay plus the lime and therefore must be expressed in terms of the actual amount of clay contained in the one gram sample. It is seen that when eight grams of calcium carbonate burn to calcium oxide we have 4.48 grams. Now to this was added one gram of clay which gave a total weight of 5.48 grams. From this the percent. of soluble silica was found to be as follows:

- 20-40 mesh 40.5 percent. $\text{SiO}_2$
- 40-60 mesh 42.7 percent. $\text{SiO}_2$
- 60-80 mesh 48.7 percent. $\text{SiO}_2$
- 80-100 mesh 61.2 percent. $\text{SiO}_2$
- 100-120 mesh 62.4 percent. $\text{SiO}_2$

From this data it can be seen that coarse grained clay would be almost useless for cement purposes. Economy alone would inhibit its use, while with machinery such that the clay could be ground to pass through at least a hundred mesh sieve, the same shale would be used to advantage. Hence we see that the size of grain is very important. Again it is useless to grind too fine since the wear and tear on machinery exceeds the value obtained from the clay. Therefore such data is necessary for cement purposes.

III To determine the relation between soluble silica and size of grain.

In order to make a graph showing the relation between the amount of soluble silica and size of grain it is necessary to have the average diameters of the grains passed through
the different mesh sieves.

A microscopic examination shows on the average of fifty grams of each the following diameters:

<table>
<thead>
<tr>
<th>Mesh Size</th>
<th>Av. Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-40 mesh</td>
<td>.0226 inches</td>
</tr>
<tr>
<td>40-60 mesh</td>
<td>.0185 inches</td>
</tr>
<tr>
<td>60-80 mesh</td>
<td>.0087 inches</td>
</tr>
<tr>
<td>80-100 mesh</td>
<td>.0067 inches</td>
</tr>
<tr>
<td>100-120 mesh</td>
<td>.0063 inches</td>
</tr>
</tbody>
</table>

The influence of fineness of grinding on the properties of Potter's material cannot be doubted and it is therefore of importance to be able to compare these ground materials in that respect. The usual method of passing powders in suspension in water, or dry, through various sizes of lawns is not sufficient. Such a method gives information as to how coarse the material is not but does not say how fine it is. Therefore the method of comparison used "surface factor" enables a judgment to be immediately formed by simple inspection. It depends on the fact that the finer a material is divided the greater is the total surface of its particles per unit mass, and if shapes of the particles are taken to be approximate, the surface varies inversely as the mean diameter of the particles.

Since it has been shown that different sized clay acts differently and that the greater the area or surface exposed the less is the action or combination when burned with lime, it follows that it is necessary to compare the $SiO_2$ rendered soluble with the reciprocal of the diameter or the surface factor of the clay.
The surface factors of the above given screened materials are:

<table>
<thead>
<tr>
<th>Av. Diameter</th>
<th>Surface Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0226</td>
<td>44.2</td>
</tr>
<tr>
<td>.0185</td>
<td>53.0</td>
</tr>
<tr>
<td>.0087</td>
<td>115.0</td>
</tr>
<tr>
<td>.0067</td>
<td>149.0</td>
</tr>
<tr>
<td>.0063</td>
<td>158.8</td>
</tr>
</tbody>
</table>

Figure III shows the relation between the soluble SiO₂ and the surface factor.
Summarizing and drawing up the permissible conclusions of the test we have:

The best temperature to burn a mixture of clay or any other silicate and lime was found to be 1300°C since most of the silica in the clay became soluble after burning at this temperature.

As has been stated the greater the amount of soluble silica the greater is the hydraulic value of the mix for cement making purposes. The greater the amount of soluble matter extracted from a clay by this treatment the greater must be its value for the above purpose. This method therefore affords a criterion either of the mechanical value of a raw clay or a raw cement mix. This value thus makes it possible to fix the fineness to which a cement mix must be ground, thus preventing either too coarse as well as too fine grinding. The latter evidently is unnecessary as it means waste of power. It is recommended that the surface factor be used in expressing fineness of cement mixtures in agreement with Rittinger's proportion that the work of grinding is proportional to the surface factor.

"The work actually performed in comminution is proportional to the product obtained by multiplying the amount of material ground in unit time by the difference in the surface factors of the materials before and after grinding."

In the case of shale it is suffice to grind it so that it passes the 100 mesh sieve which agrees with practice. Roughly speaking it might be said that the soluble matter of clays increases with the surface factor, though this is far from being shown with any degree of definiteness.