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T H E S E S .

DETERMINATION

of the

HYDRAULICITY

of

LOCAL LIME-STONE

C. D. Grove

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M^a SCHOOL OF MINES,

CLASS-94.

Hydraulic Cement

I took as the subject of my Thesis
The hydraulic Properties of the Fine Stone
of this vicinity and compared my researches
to two of the larger Fine Stone Quarries about
one mile South west of Falls

The fine Stone of this region is very
variable as to texture, as well as Chemical
constitution and even in the same local-
ities some parts are compact and firmly ce-
mented while other portions are loose
and cherty, capable of being easily dis-
integrated. This is especially noticeable
in surface Stone, and for the reason
of appearance such Stone is unfit for
building except in the case of foundations.

as the surface would soon become uneven
no matter how carefully dressed

This Stone not only contains many
little facets of lime and alumine from
which the CO_2 has been expelled, but in
many cases small pieces of chert, flint
compact silicious sand, and often even
granular sand that can easily be
removed by the finger nail. Such
Stone as this would be unfit for good
lime, & it would be very desirable to
have some method of utilizing these large
deposits by some profitable means.

The Stones vary also largely in the
amount of Magnesia present, from a mere
trace in some of the Oriskany regions to

limit. The silica is also a variable quantity, but its varying disposition depends more on the minute individual deposits in the fine stone, than when combined chemically or intimately mixed.

All the specimens I have seen contain some Ferric Oxide and Alumina, these constituents seem to vary less than any other parts of the stone, but are small.

The Calcium Carbonate of course varies with the Magnesium Carbonate as the lime is singly displaced by Magnesia.

The Carbon Dioxide varies inversely with the sum of the impurities, I.e. Alumina and Ferric Oxide.

For the method of my work I have

drawn from the following authors:

Heath on Lime and Cement.

Feid on Portland Cement.

De Fers on Masonry.

Chemical Review.

Thorp's Dictionary of Chemistry.

Watts

Transactions Am. Engrs. Assoc.

and Missouri Geological Survey.

I have taken as standards to work from
the Portland and Rosendale Cements.

The authors all agree approximately on
the chemical composition necessary to make
good cement and De Fers goes so far as
to question whether Hydraulic Cement may
not be made from any lime stone

It probably could if the proper con-
ditions were added to make the
Chemical formulae agree to that needed.
But my work was with local products, and
was to be cheap, so that it could be of a
practical advantage. Moreover I question
if it were ever possible to make good
Cement from any kind of stone as I think
The hydraulicity of lime stones does not
depend entirely on its chemical compo-
sition, at least on such composition as
we are capable of preparing. It may be
due to some extent to great pressure or
great lengths of time, at any rate there
are records of many failures to make
good Hydraulic Cement by careful

with iron and good machinery.

It is supposed by some that Magnesia is inert in Cement, thus say it is unimportant when not exceeding 2 or 3 % but in large quantities causes the Cement to expand after some time thus injuring the masonry by cracking and loosening the joints.

Terre Brûlée is thought by some to be advantageous, by others of no consequence, but all agree that it should not exceed 1 or 2 %.

The Alkalies are generally considered as beneficial as they assist in forming Sulphate and Soda Silicate when heated, which aids in cementing the particles firmly together on the addition of water.

They are never in such quantity as to be considered detrimental.

The lime is the essential ingredient assisted by the silica, this forms silicates of lime on fusing that give the product the cementing power.

Alumina acts as basic, acidic or neutral combining with silica forming silicates of alumina or with lime, forming aluminates of lime. When in excess it appears to be neutral and would then only be an adulterant. The same is would be the case if sifted in after the cement is made.

The amount of alumina needed will vary depends on the excess of silica over

8
Kind of Magnesia, or the Concretion

The essentials to a good Hydraulic Cement as has been determined by experiment, is fine and close, all others being subordinate.

Hydraulic fine stone is generally of a dark grey color, or dark blue or black.

It is of compact texture, massive with some or channeled fracture, and a clayey smell and taste.

The following are analyses of fine stone and clay, which very well represent Portland and Rosendale Cement.

Analysis of Fine Stone for Portland Cement

Calcium Carbonate - $CaCO_3$	57.35 to 96.52%
Silica - SiO_2	1.67 to 6.54
Alumina - Al_2O_3	114 to 93
Magnesium Carbonate - $MgCO_3$	10 to 50
Ferric Oxide - Fe_2O_3	55 to 46
Potash and Soda - K_2O, Na_2O	42 to 419

Analysis of Clay for Portland Cement

Silica - SiO_2	55 to 70%
Alumina - Al_2O_3	16 to 24
Iron - Fe_2O_3	4 to 5
Magnesia - MgO	1 to 2
Iron Oxide - Fe_2O_3	3 to 15
Potash & Soda - K_2O, Na_2O	3 to 6
Carbon Dioxide - CO_2	4 to 5

Analysis of Fine Stone for Portland Cement

Calcium Carbonate - $CaCO_3$	68. to 80.70
Silica - SiO_2	20. to 10.70
Magnesia - MgO about	1.5 - 1.5
Alumina - Al_2O_3	3. to 4.

I have given for comparison two analyses of mine of the fine stone of this vicinity.

They are as follows:

Silica - SiO_2	28.67%	28.60%
Magnesia - MgO	9.47	11.20
Stone - SiO_2	9.28	10.20
Carbon Dioxide - CO_2	43.62	39.60
Alumina & Ferric Oxide - Al_2O_3, Fe_2O_3	3.64	.50
Alkalies - K_2O & Na_2O	5.62	not det.
Water, H_2O	<u>1.22</u>	<u>1.50</u>
	99.52	99.70

My Experiments

I first attempted to burn the quinoline in bars as in burning lime and also Cement sometimes, but soon found that this was impracticable by the method I had in hand. I then ground the stone so that all would pass a 2500 mesh sieve and burned it at a high heat, (about 1200°C). It failed to give any hydraulic properties by this means so I concluded to grind it finer so as to offer more chances of its being exposed entirely to the heat.

The rest of my work was on stone ground so that it would all pass a 6400 mesh screen. I fused the pulp in a Wind Furnace, stirred to expell all moisture

and Carbonic Acid, One lot I heated to about Cherry redness and left it at that heat for three hours. (In none of my fusings were there more than $1\frac{1}{2}\%$ CO_2 remaining.) It failed to develop any marked degree of hydraulicity, so I next tried it at a heat as high as the furnace would give and nearly to vitrification. It was heated so high that some of the pulp - the bottom of the crucible was vitrified. The vitrified mass I rejected and tested the other which gave changes of properties of hydraulicity than any before, but not adhering sufficiently to permit of being moulded.

Finally was efforts futile to make good Hydraulic Cement from the fine stone above.

I next tried fusing it with Clay, consisting chiefly of alumina but containing some silica and iron oxide.

I mixed the fine stone pulp intimately with the fine Clay (made to pass 6400 mesh) in the proportions of 5 = 10 - 20 - 25 and 50 % Clay.

These fusions failed to produce hydraulicity so I next tried the fine stone pulp with ground Silicious sand (6400 mesh screen) in the same proportions as the clay:

5 = 10 - 20 - 25 = 50 % Sand. This increased the hydraulicity some but could be easily broken by the fingers even after three weeks setting.

I next tried the fine stone pulp with both Clay and silica together and the

difference of the hydraulicity with that of
The Clay alone was inappreciable.

I next tried (For the sake of experiment only)
5% of Ferric Oxide with the same stone
I could however detect no difference in its
setting capacity. I then considered my work
at a close as I could conceive of no better
way to perform the experiments and of
no other rational mixtures where local
material could be used. This was plentiful
and cheap.

I allowed all these cements to stand under
water for weeks and some of them down weeks
as they had not set. Then it was pretty good
evidence they never would and even if
they should after such a long time, they

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would be unfit for work for time is always a consideration.

As I have tried in every way I can conceive of to make a cement from local materials that can be obtained cheaply and plentifully and failed in each case to get a Hydraulic Cement that would answer the specifications of any good piece of masonry, in fact not as strong as common lime cement I have concluded that from a practical stand point, Hydraulic Cement cannot be made of the same class of the Territory.

Respectfully Submitted

C. J. Grove

June 14 - 94.