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The production of high alumina refractories bonded with Lumnite refractory cement

Joseph Lewis Hoffman

THE PRODUCTION OF HIGH ALUMINA REFRACTORIES BONDED WITH LUMNITE REFRACTORY CEMENT

BY

JOSEPH L. HOFFMAN

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THESIS

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Introduction:

Users of refractories are constantly demanding a better product. There is a demand for a satisfactory neutral or basic refractory with a P.C.E. equavilent of cone 35 or better. A refractory with a very high alumina content would seem to solve this problem, however, the main difficulty has been to bond the unplastic alumina.

From the literature it was learned that Lumnite cement has been satisfactory in the manufacture of a refractory concrete. Therefore this investigation was carried out to determine the adaptability of bonding corundum with Lumnite.

Characteristics of Lumnite Cement:[1]

"Lumnite is a hydrolic cement which hardens or 'sets' when mixed with water. It is used as a binder for refractory, heat resistant and insulating aggregates in the making of these several kinds of concrete.

1. The Atlas Lumnite Cement Co., "Lumnite", (Pamphlet)

Concrete made with Lumnite and suitable aggregates has the property of retaining a considerable part of its cold strength after continued exposure at high temperatures. Lumnite is not in itself a refractory material. It is used in making refractory concrete because its effectiveness as a binder is not destroyed by the service temperatures.

Lumnite is a calcium aluminate cement as distinguished from portland cement in which the principal constituants are calcium silicates. The calcium aluminate cements are the only commercial hydraulic cements which have heat resistant properties required for refractory concrete.

Table I

Chemical Analysis of Lumnite Cement

		Per Cent
SiO_2	------	3.68
Al_2O_3	------	45.14
FeO	------	10.14
Fe_2O_3	------	6.53
CaO	------	33.45
MgO	------	0.50
	Total	99.44

Emperical Formula

$$\left.\begin{matrix} .7945\ CaO \\ .0165\ MgO \\ .1880\ FeO \end{matrix}\right. \quad \left.\begin{matrix} .599\ Al_2O_3 \\ .055\ Fe_2O_3 \end{matrix}\right. \quad .0815\ SiO_2$$

The only literature which is available on the use of Lumnite cement in refractories is some work done by Walker and Stone on the bonding of crushed olivene with Lumnite.[2]

"It was one of the primary purposes of this investigation to develop a cold setting bonding agent that could be used to bond crushed olivene in the production of an unfired refractory designed to meet the following requirements:

(1) The cold crushing strength to be sufficient to withstand service loads.

(2) The product to be sufficiently strong to permit shipping and handling in construction without damage.

(3) a. The bonding agent must not develop an amount of glass in the fired product that would cause slumping under load at high temperatures.

2. A. F. Greaves-Walker and R. L. Stone; "Study of Bonding Agents", North Carolina State College Record, Vol. 38, No. 1, Sept., 1938

(3) b. A fired glass bond of high viscosity.

(4) The bonding agent not to lower the pyrometric cone equivalent of the product below cone 36.

(5) The bonding agent not to fail in use, due to loss of cementing properties before glass is formed."

The test bars were made by dry pressing, and the following was said about drying:

"Lumnite cement generates considerable heat while setting. When used in making small trial pieces, precautions must be taken to prevent evaporation of the water before crystallization is complete.

"Two methods of drying were investigated: (a) Air dried for fourteen days and then dried completely at 110°C in a drying oven; (b) dried under controlled humidity conditions for 48 hours, then in the air for twelve days, and then dried at 110°C in a drying oven.

"The first method dried the surface of the specimens too rapidly.

"The second method gave excellent results when properly controlled. The specimens were hard and sound, with strong edges.

It is important, however, that the relative humidity be kept below the saturation point. If moisture is permitted to condense on the product, the surface will be weak and easily rubbed off with the fingers.

"The compressive strength increased with increases in cement additions. The maximum amount added was 11.3%, which produced a compressive strength of approximately 1900 pounds per square inch. The rate of increase in strength decreased when more than 7.4% of cement was used.

Specimens of these mixes were characterized by sudden failure when the critical load was reached.

The following were the conclusions on the work on bonding agents done by Greaves-Walker and Stone:

"(1) The following bonding agents were selected as those showing most promise in the manufacture of an unfired forsterite refractory:

a. Lumnite cement (not over 9.1%)

b. Sodium silicates ("O Brand" preferable, not over 2.9%).

(2) The investigation has shown conclusively that the following materials cannot be added to mixes containing either of the above bonding agents without being detrimental to cold-set properties:

a. water soluble magnesium salts.

b. Dead burned magnesite (to sodium silicate only.)

c. Lime.

d. Colloidal Slurry.

e. Organic binders.

(3) The investigation has also shown that:

a. Lumnite cement and sodium silicate cannot be combined as bonding agents without destroying the cold-set properties possessed by either when used alone.

b. For best results, the mixes containing Lumnite cement must be kept cool under high humidity conditions for at least 48 hours after forming."

<u>Procedure and Data:</u>

The materials used were Lumnite Cement, 8 mesh corundum and 200 mesh corundum from the Aluminum Ore Company, East St. Louis, Illinois.

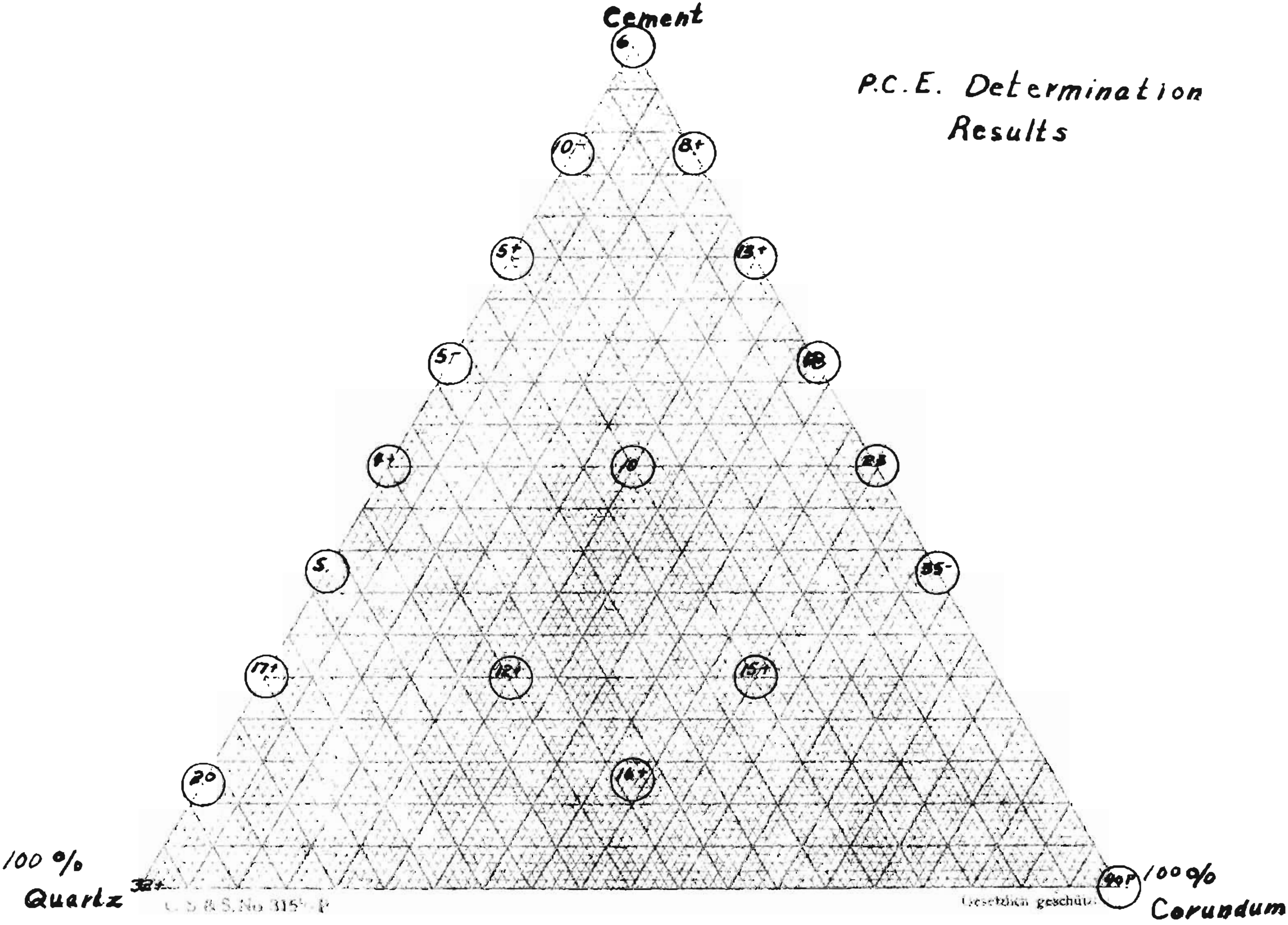
P.C.E. determinations were made first. Various mixtures of cement, corundum, and quartz were run. The results of this determination showed that any mixture of cement and corundum containing 64.5% or more of corundum has a P.C.E. value of cone 35 or better. Any addition of quartz lowers the P.C.E. value, therefore the investigation was limited to mixtures of corundum and Lumnite, which contained between 62.5% and 100% corundum.

Table II

% Cement	%Corundum	P.C.E.
100		6
88	12	8 +
75	25	13+
62½	37½	18
50	50	23
37½	62½	35

The following diagram gives a complete picture of the P.C.E. tests made.

P.C.E. Determination Results



Variations were made in percentage composition, and the grain size of the corundum. Five different grain sizes were used, viz:

Table III

A -	100% thru 200 mesh		
B -	75% thru 200 mesh	---	25% thru 8 mesh
C -	50% thru 200 mesh	---	50% thru 8 mesh
D -	25% thru 200 mesh	---	75% thru 8 mesh
E -	100% thru 8 mesh		

Six different batches were made for each grain size group with the following compositions:

Table IV

1.	62½% corundum	------	37½% cement
2.	75% corundum	------	25 % cement
3.	85 % corundum	------	15% cement
4.	87½% corundum	------	12½% cement
5.	92½% corundum	------	7½% cement
6.	95 % corundum	------	5 % cement

Hereafter in this report each grain size group will be referred to with the capital letter A, B, C, D, or E, while each batch will be referred to as 1, 2, 3, 4, 5, or 6 as represented in the two preceding tables. For example; test piece A1 will be a piece containing 62½% corundum through 200 mesh and 37½% cement.

Six 1" x 1" x 6" test pieces were made for each batch of each group. These test pieces were made by adding from 12% to 15% water to the dry cement-alumina mixture.

The test pieces were not removed from the brass moulds for 24 hours and during this time they were covered by damp cloths in order to allow the cement to "set" and to keep it from drying too fast on the surface and cracking.

After the test bars were removed from the moulds they were dried in the air for 72 hours, and then dried at 110°C. for eight hours.

The test pieces were then fired to cone 15 in the oil fired kiln.

The pieces were tested for cross breaking strength, from which the modulus of rupture was calculated; absorption; and shrinkage.

Data and Results:

Green Modulus of Rupture

Group (Grain Size)	Batch	Ave. Modulus
A	1	1294
	2	677
	3	694
	4	1142
	5	468
	6	187
B	1	1465
	2	1813
	3	1212
	4	1013
	5	900
	6	543
C	1	1672
	2	1330
	3	900
	4	937
	5	785
	6	813

Green Modulus (Con't)

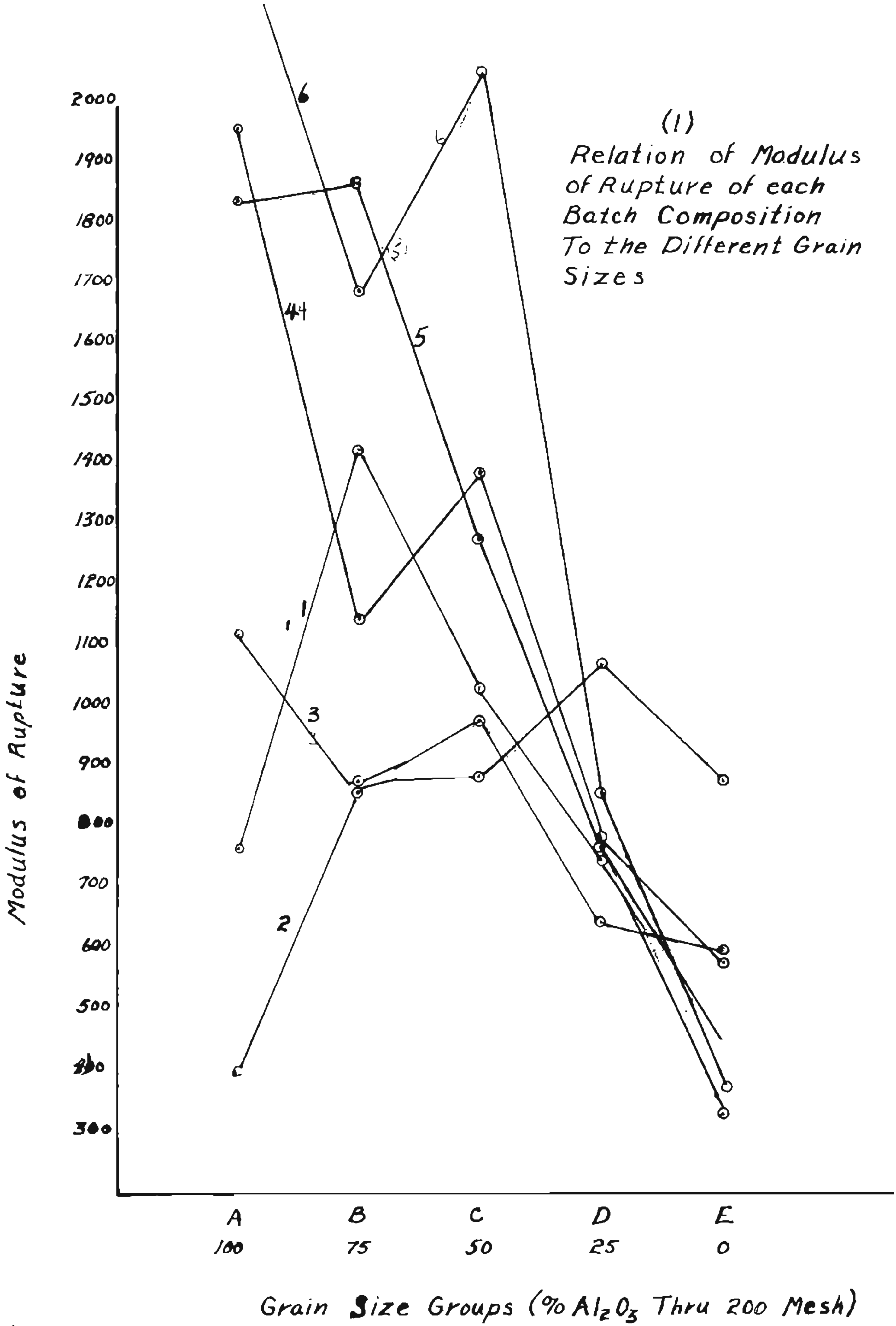
Grain Size Group	Batch	Average Modulus
D	1	1725
	2	1565
	3	1500
	4	1725
	5	907
	6	702
E	1	1697
	2	1610
	3	1135
	4	900
	5	600
	6	330

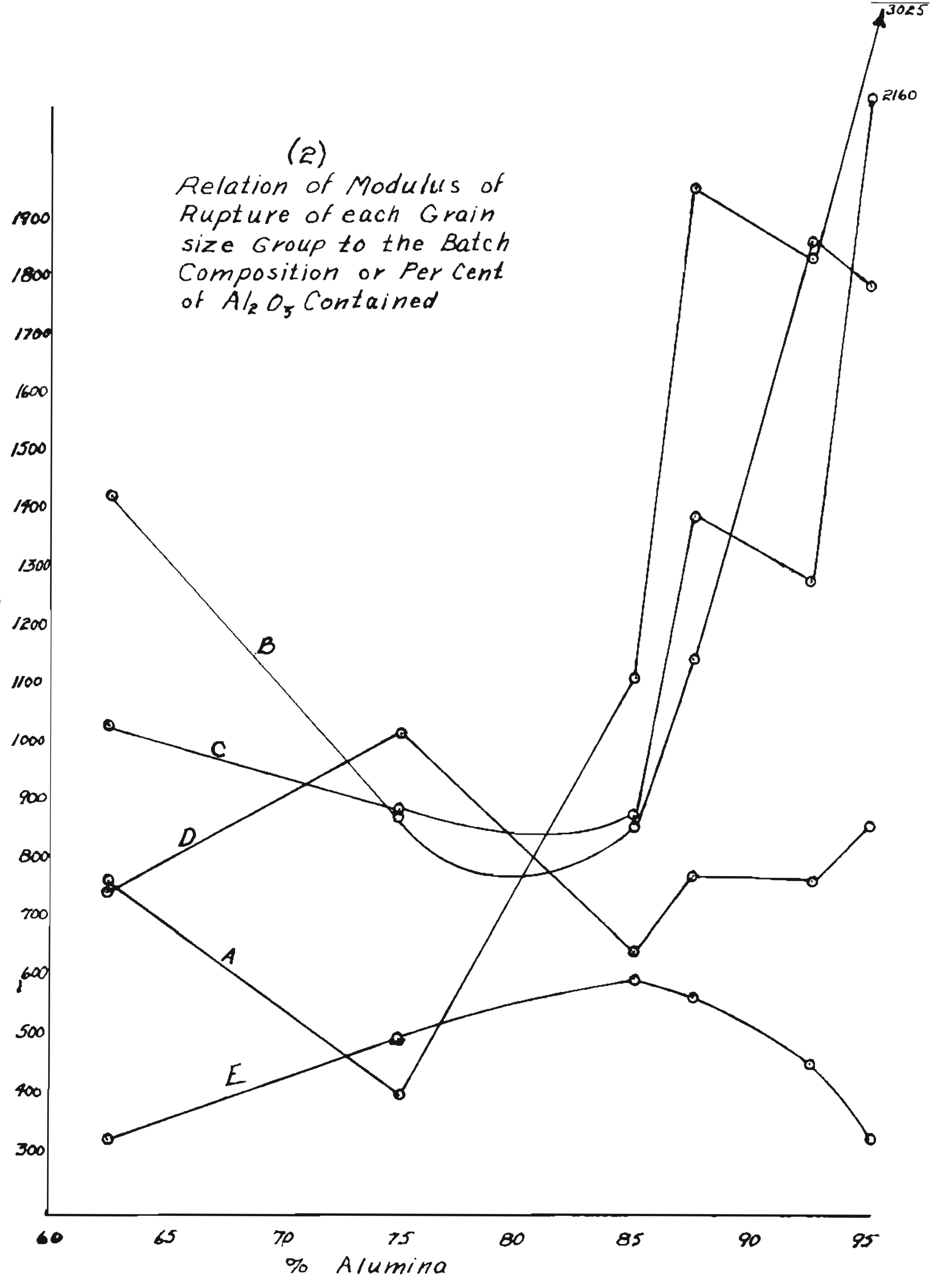
Data on Fired Bars
(Modulus, Shrinkage, Absorption)

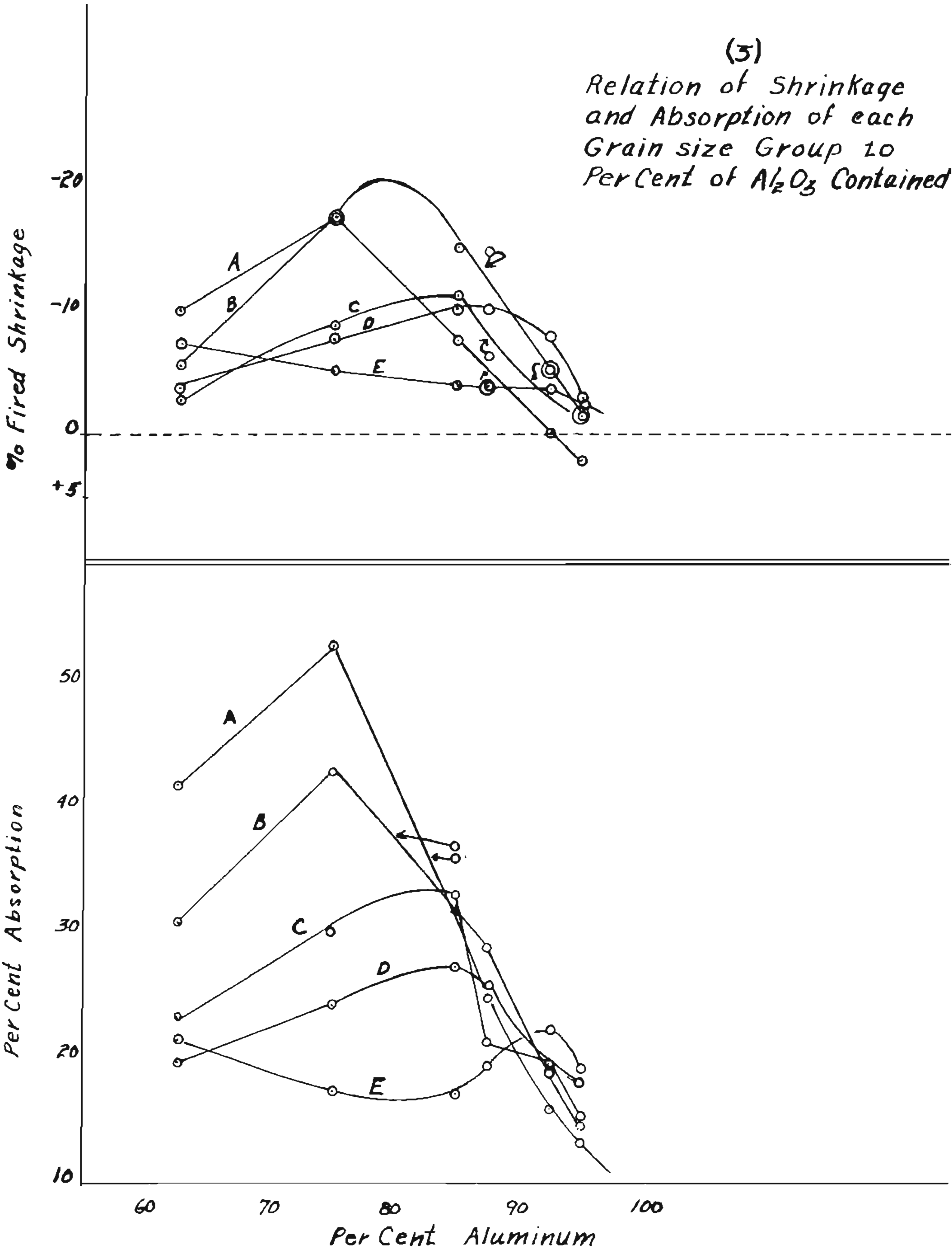
Grain Size Group	Batch	Average Modulus	Shrinkage %	Absorption %
A	1	770	-10.0	41.8
	2	403	-17.65	53.0
	3	1120	- 5.0	36.8
	4	1960	- 3.8	25.0
	5	1840	0.0	15.6
	6	3025	+ 4.3	13.2
B	1	1425	- 7.6	30.9
	2	880	-17.65	42.7
	3	867	-15.0	36.0
	4	1049	-15.0	28.8
	5	1865	- 5.0	18.8
	6	1690	- 1.2	14.5
C	1	1031	- 2.6	23.2
	2	893	- 8.8	30.0
	3	979	-11.1	33.2
	4	1391	- 6.2	22.2
	5	1280	-5.0	19.3
	6	2160	- 1.2	15.3

Data on Fired Bars(Con't)

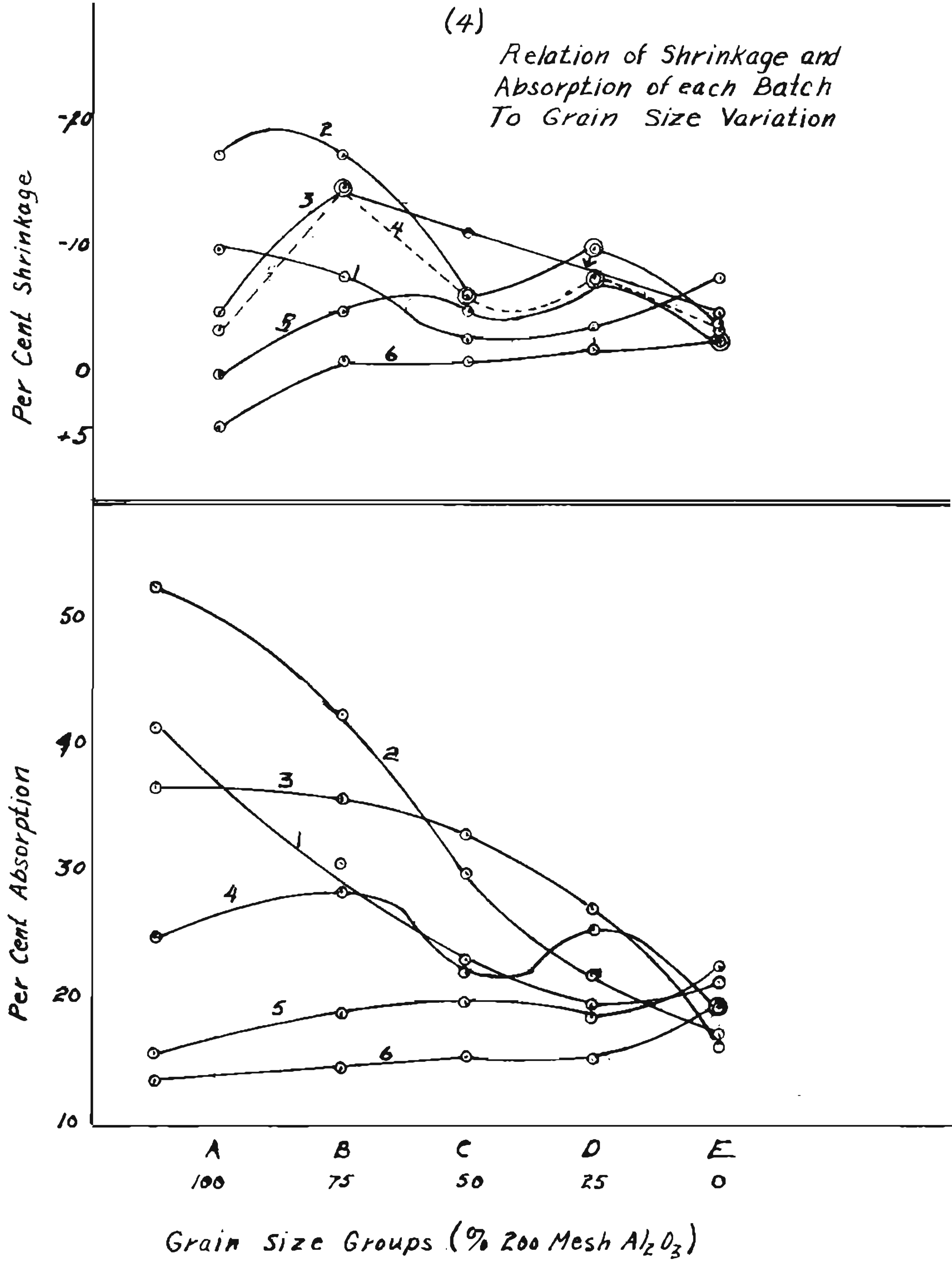
Grain Size Group	Batch	Average Modulus	Shrinkage %	Absorption %
D	1	750	- 3.8	19.6
	2	1017	- 7.6	24.2
	3	647	-10.0	27.2
	4	782	-10.0	25.7
	5	776	- 7.6	18.7
	6	867	- 2.6	15.1
E	1	330	- 7.6	21.3
	2	495	- 5.0	17.4
	3	605	- 3.8	17.1
	4	577	- 3.8	19.4
	5	454	- 3.8	22.4
	6	330	-2.7	19.0


(1)
Relation of Modulus of Rupture of each Batch Composition To the Different Grain Sizes
Modulus of Rupture
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
6
5
4
1
3
2
A
B
C
D
E
100
75
50
25
0
Grain Size Groups (% Al_2O_3 Thru 200 Mesh)


(2)
Relation of Modulus of Rupture of each Grain size Group to the Batch Composition or Per Cent of Al_2O_3 Contained
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
3025
2160
A
B
C
D
E
60
65
70
75
80
85
90
95
% Alumina



(3)
Relation of Shrinkage and Absorption of each Grain size Group to Per Cent of Al_2O_3 Contained
% Fired Shrinkage
-20
-10
0
+5
A
B
C
D
E
Per Cent Absorption
50
40
30
20
10
60
70
80
90
100
Per Cent Aluminum


(4)
Relation of Shrinkage and Absorption of each Batch To Grain Size Variation
Per Cent Shrinkage
-20
-10
0
+5
Per Cent Absorption
50
40
30
20
10
1
2
3
4
5
6
A
B
C
D
E
100
75
50
25
0
Grain Size Groups (% 200 Mesh Al_2O_3)

Discussion of Data:

The preceding graphs were plotted in an attempt to correlate the data. At first glance there seems to be little or no relation of the separate curves. However after studying them closely the following conclusions were drawn:

Graph (1)--Here the modulus of rupture of each batch composition was plotted against the different grain size groups. Curves for batch 3, 4, 5, and 6 are similar and in general the strength decreases as the grain size increases. In other words the small grain sizes in batches 3, 4, 5, and 6 have the greatest strength. In batch 1 and 2 the strength increases as the grain size increases to approximately 50% large grain size or group C. Then the strengths drop off as the grain size increases, batch 1 falling most.

Graph (2)--Here the Modulus of rupture of each grain size group was plotted against the per cent of corundum. It can be said in general that the strongest bars contain the least cement.

From curves (1) and (2) the following general conclusion can be drawn: As the cement content decreases the strength increases as the grain size decreases. So, as far as strength is concerned, the best body is A6.

However A6 is rather brittle and the edges chip off easily. This was true mainly on the top of the block, so it may be due to forming. Both A4 and A5 give excellent samples, have plenty of strength and are not as dense as A6. However they have a greater absorption.

From the shrinkage tests it was found that all batches expanded on bloated except A5 and A6. A6 shrunk 4.5% and A5 had no noticable change. These results were somewhat surprising as it was expected that there would be very little linear change. From the curves it can be seen that this change depended both on grain size and per cent cement in the bodies. In general the bars with the greatest amounts of small grain size alumina had the least bloating. This was probably due to the fact that the small grained corundum is low fired, and therefore should give some shrinkage.

In general the absorption curves were directly proportional to the expansion. The absorption was very high in all cases. The least absorption was 13% which was recorded for A6. A5 had 15.6% absorption.

From the tests made, the high absorption was the main detriment found against the use of such a refractory.

The color ranged from a tan in the bars containing large amounts of cement, to white in the bars containing 95% corundum.

Conclusions:

Lumnite cement used as a bonding agent for pure corundum gives excellent working properties in all proportions. No difficulties were incurred in drying if drying was done under conrtolled humidity for at least 48 hours; otherwise there was a weak shell and cracks. The green bars had good strength and sharp edges.

The fired bars range from a soft light mass to a brittle dense mass.

For general refractory use it seems that bodies A4, A5, B5, B6, and C6 are the most satisfactory. As was mentioned before the main detriment is the high absorption. Another point against a body of this type is the high cost of materials used. The corundum costs approximately 2¢ per pound for 200 mesh material and 5¢ for 8 mesh material, and the cement costs approximately 2¢ per pound.

A high alumina refractory of this type would have a high heat conductivity which would make it desirable in saggers. It would also be resistant to slag action.

Lumnite bonded corundum could be used to a great advantage in replacing damaged special shapes. The shape could be cast and installed without pre-firing. This would save a great deal of time and loss due to the damage caused by completely shutting down a furnace.

Further work on grain sizes may give a body which would be more dense.

The dry press method of forming too may give a far superior body in this respect.

Acknowledgment:

The writer wishes to express his thanks to Dr. Paul G. Herold of the Ceramic Department of the Missouri School of Mines for his cooperation and his helpful suggestions in carrying out this research.

Appreciation is also extended to the Atlas Cement Company, Chicago, Illinois for the sample of Lumnite cement.

Bibliography:

1. The Atlas Lumnite Cement Co., "Lumnite", (Pamphlet)

2. A. F. Greaves-Walker and R. L. Stone; "Study of Bonding Agents", North Carolina State College Record, Vol. 38, No. 1, 1938

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