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A study of chrome and diaspore mixes

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THESIS

A STUDY OF CHROME AND DIASPORE MIXES.

PRESENTED TO

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The high refractoriness of both chrome and diaspore make them very valuable to the refractory industry. Chrome ore has been experimented with since 1879[1] and used in brick form since 1886. Diaspore on the other hand, has just recently been recognized as a refractory material.[2]

After going through all the available literature on the subject I have been unable to find any mention of any work carried on in which mixtures of chrome and diaspore were used. In "Dana's Manual of Mineralogy," by Ford mention is made of the use of Bauxite in the manufacture of Chrome bricks. This however is in small amounts and is used as a binder.

The high refractory nature and resistance to acid and basic slags are the main valuable properties of Chrome shapes. Their main disadvantages are their sensitiveness to rapid thermal change and their inability to support loads at high temperature. The melting point of Chrome brick as determined by Kanolt is 2050°C.[3]

Footnotes:-

1. Ferd. Gauthier, "On a Neutral Lining for Metallurgical Furnaces," Jour. Iron Steel Inst., 28,151 (1886)
2. D. C. Wysor. "Diaspore clay of Arkansas and Missouri," Jour. Amer. Ceram. Soc., 6,501-509 (1923)
3. G. R. Brown, "Notes on Load Test made on Magnesia, Chrome, and Silica Brick," Trans. Am. Ceram. Soc., 14,391 (1912)

Chrome brick are shiny black in color and the standard 9" brick weighs 10-11 pounds. Their bulk specific gravity is therefore approximately 3.1. Chrome brick have great strength in the cold condition. On flat they run as high as three to five thousand pounds per square inch at room temperature. However when set on end and heated at standard rate in load testing furnace they will fail under 50 pounds per square inch pressure at 1450°C.[1]

The experiments of Bodin indicate that the crushing strength of chrome brick is practically constant from room temperature up to 950°C., falling off rapidly above the point.[2]

Mineralogy:-

Chromite is $FeCr_2O_4$ or $FeO.Cr_2O_3$ and is made up as follows: Chromium sesquioxide 68.0, iron protoxide 32.0. The iron may be replaced by magnesium and the chromium by aluminum and ferric iron. Its structure is commonly massive, granular to compact and is iron-black to brownish black in color. Chromite streak on porcelain body is dark brown.

Occurence:-

Found only sparingly in U.S. in Pennsylvania, Maryland, California, North Carolina, Oregon, Wyoming and Alaska. Rhodesia, New Calcedonia, Turkey, India, Greece, Canada, Cuba, and Brazil, have deposits of one kind or another.

Footnotes:-

1. G.R. Brown, "Notes on Load test made on Magnesia, Chrome and Silica Brick," Trans. Amer. Ceramic Soc., 14,391 (1912)

2. V. Bodin, "Tests on refractory products under load of different temperatures, "Trans. Cer. Soc. (British), 21, (1), 43(1921-22)

The most important producers at the present time are Turkey, New Calcedonia, Rhodesia, Greece and Canada.

Diaspore deposits are limited to Missouri mainly in this country. Its character is taken up in the accompanying abstract by S. M. Phelps in, "A study of the shrinkage of Diaspore clays."

ABSTRACT OF, "A STUDY OF THE SHRINKAGE OF DIASPORE CLAYS." by S. M. PHELPS.

Diaspore- bearing clays such as found in the Missouri district run from 50 to 80% in alumina content. They vary in texture from a fine-grained plastic clay like substance to a coarse, gritty short material. The diaspore is present in this material principally as "oolites." These oolites are small nodules and are imbedded in a matrix of refractory clay.

The big trouble which arises when this highly refractory material is used in making bricks and shapes for refractory use is the high and continued shrinkage in service.

Phelps proves by experimental data: That the shrinkage of the various types of Diaspore Clays under given conditions of time and temperature is inversely in order of alumina content.

The duration of firing is of great importance in the causing of maximum shrinkage to take place.

The state of division is of importance in effecting shrinkage, i.e., fine material has much greater volume shrinkage than coarse for same amount of firing.

The firing properties of the bond or plastic portion and the grain portion are vastly different; i. e., the plastic portion has about one-third porosity and three times volume shrinkage that of grain portion after reheating.

Phelps points out the need of sufficient heat treatment during the manufacturing process to approximate a permanent volume. Unless this is done, shrinkage will occur in service as result of continued high temperature use and the time element.

Data to accompany abstract of S. M. Phelps' report on "A Study of the Shrinkage of Diaspore Clays." - Part 1.

Analyses of Clays Tested:-

	A	B	C
Fusion Point	Above 36	Above 36	Above 36
Water of Plasticity	26.7%	23.6%	14.50%
Drying Shrinkage	9.20	11.60	3.90
Volume Shrinkage after 5 hours at 1400° C.	24.3	24.4	15.20
Porosity after 5 hours at 1400° C.	27.70	28.00	45.20
Soluable salts	.04	.03	.03
Chamical Analysis:-			
Ignition loss	13.46	14.32	14.20
Silica	28.36	9.40	2.56
Alumina	53.64	72.23	78.71
Iron Oxide	.56	.59	1.58
Titania	2.80	2.92	2.75
Lime	.12	.31	.28
Magnesia	.26	.23	.34
Alkalis	.97	.93	.29
Miscellaneous:-			
Plastic properties	Quite Plastic	Less Plastic "Mealy"	Short and Mealy
Screen analysis			
On 30-mesh	17.5	21.5	11.1
Through 100-mesh	55.35	54.10	58.30

Remainder on intermediate meshes.

PLAN OF WORK.

In making a study of chrome and diaspore I shall first determine the softening point of various mixtures. In this way it will show whether or not an eutectic reaction between diaspore and chrome will lower the melting point of the materials. Should a low melting eutectic be formed it would be of no use to continue experimenting with the idea of producing a super refractory.

The next matter to be taken up will be to determine the workability of the mixtures and thus find out the best way to form ware. This will be done by soft mud, stiff mud and dry press operations.

After the best forming conditions are determined and the cone fusion test run for softening points of mixtures a series of tests will be run to give porosity, shrinkage on firing and reheating. Also a comparative slag action and spalling test will be undertaken.

Laboratory Procedure I.- Softening Point.

The softening points were determined with representative samples of chrome and diaspore in the following mixtures:

A. (50% Chrome
   (50% Diaspore

B. (75% Chrome
   (25% Diaspore

C. (25% Chrome
   (75% Diaspore

D. (66 2/3% Chrome
   (33 1/3% Diaspore

E. (33 1/3% Chrome
   (66 2/3% Diaspore

See Plate I.

The results of this experiment are reported in terms of Orton pyrometric cones. As the idea was to find the lowest melting eutectic I ground the samples to pass 100 mesh rather than 60 mesh as the standard test calls for. Since the particles would be more finely divided it is reasonable to expect reactions at lower temperature if any change at all occurred.

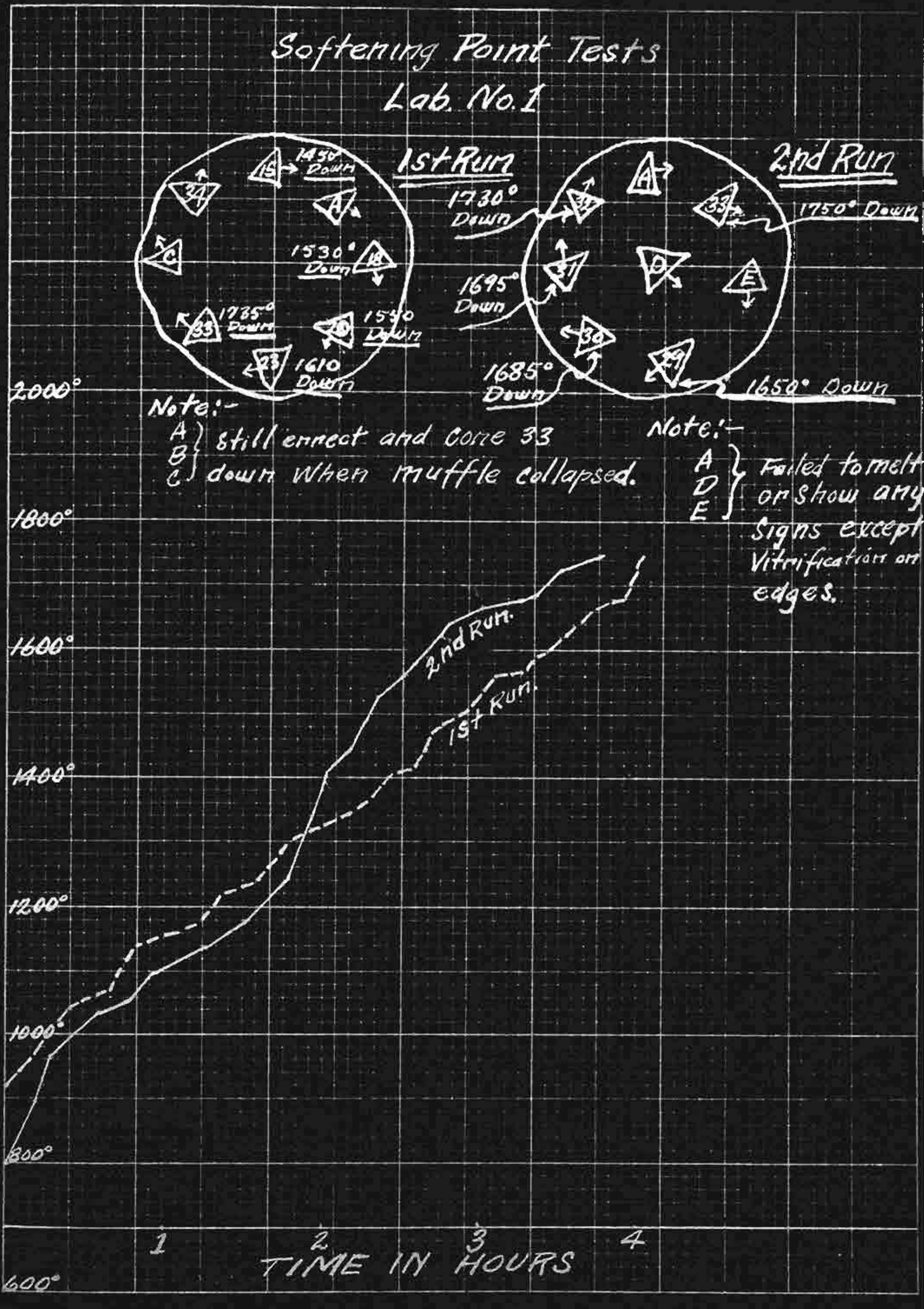
The test mixtures were thoroughly mixed, dextrine solution added and moulded to conform to standard test procedure.

The results given by these two runs were highly satisfactory inasmuch as none of the mixtures melted down at the temperature attained. Cone 33 was completely melted so it is safe to say that cone 34 would also be down. As it was not considered safe to use the furnace at a higher temperature than cone 34 the actual determination of the cone fusion points had to be abandoned.

That the mixes would stand cone 33-34 without any signs of failing puts them in the class of super-refractories.

The temperature was taken at five minute intervals throughout the run with a Leeds and Northrup Optical Pyrometer. The highest temperature taken was 1750°Centigrade which is a fair check on the melting temperature of cone 33 which is 1790°Centigrade.

Plate 1


Softening Point Tests
Lab. No.1
1st Run
2nd Run
1450° Down
1530° Down
1785° Down
1550° Down
1610 Down
1730° Down
1695° Down
1685° Down
1750° Down
1650° Down
Note:-
A } still errect and Cone 33
B } down when muffle collapsed.
C }
Note:-
A } Failed to melt
D } or show any
E } signs except
Vitrification on
edges.
2nd Run.
1st Run.
TEMPERATURE IN DEGREES CENTIGRADE.
2000°
1800°
1600°
1400°
1200°
1000°
800°
600°
1
2
3
4
TIME IN HOURS

Laboratory Proceedure No. 2.

A study of the forming conditions and determination of Modulus of Rupture.

I made up bars of chrome and diaspore mixtures by soft mud and dry press methods. It was impossible to make any by the stiff mud process due to the extremely low plasticity of the material.

The bars made by soft mud method, i. e., tamping wet mix in bar mould, were hard to make and as results show are very weak in green state.

No trouble was experienced in the dry press method however and the bars show high enough strength in green state to be made as a commercial proposition.

The bars were fired in a frit furnace under very unfavorable conditions. The temperature could not be kept constantly increasing due to small area of combustion chamber and type of burners used.

Cone 16 was brought down at the end of a six hour fire and a temperature near 1400°C was maintained for the last hour of the burn.

The bars were well cintered and as the results tabulated show were strong enough for commercial use as a super-refractory. The bars were fired at a rapid rate and then cooled in a period of 8 hours yet no cracks or checks appeared. This makes it appear that they would be fool proof in any manufacturing process.

Results of Lab. Procedure No. 2.

Mixture % Diaspore	% Chrome	Modulus of Rupture average of four bars	Process	Condition
50	50	12.4#/sq.in.	Soft mud	green
75	25	12.2 " "	" "	"
25	75	unable to mould	" "	"
50	50	81.9#/sq.in	dry press	"
75	25	117.1 " "	" "	"
25	75	55.0 " "	" "	"
50	50	1549#/sq.in.	Soft mud	fired to cone 16-17
75	25	1197 " "	" "	"
25	75	Not made	" "	"
50	50	1848#/sq.in.	dry press	fired to cone 16-17
75	25	2047 " "	" "	"
25	75	1729 " "	" "	"

Laboratory Proceedure No. 3. From laboratory work under proceedure No. I. it was found that the combinations would be super-refractory. From proceedure No. 2 it was found that it was most practical to make ware by the dry press method. The modulus of rupture of specimens made was sufficiently high to warrant their use in the commercial field.

A series of mixtures of chrome and diaspore were made up in order that a study could be made of their absorption, shrinkage, spalling, and slag action characteristics.

The chrome and diaspore were ground to pass 20 mesh, proportioned as desired, thoroughly mixed and dry pressed into bars 1" X 1" X 8". The press used was a hand operated screw type made by the Patterson Clay Working Machinery Company. Three thousand pounds per square inch pressure could be applied with the use of this press.

The bars were fired in a direct fired furnace using oil burners. The bars were fired in a slightly oxidized atmosphere and taken up at a gradual rate. (See firing schedule on Page 16.)

The bars were marked for shrinkage and absorption was taken after the initial fire and again after a reheat run of 1400°C for five hours. The results of this can be found on pages 14 and 15.

The bars made in this firing were free from cracks, well cintered and perfect shaped.

The absorption is highest at a mix of 75% diaspore and lowest on solid chrome bar.

There is however no great change throughout the mixtures. The lower absorption of 90% diaspore and 10% of 100 mesh chrome is low, as to be expected because of the finer ground chrome addition.

The percent linear shrinkage curves (see page 14) are exceedingly interesting. The greater the proportion of diaspore the greater the shrinkage as would be expected. However the change is much more rapid on the diaspore end of the curve. This means that to cut down excessive shrinkage of diaspore products in service chrome ore can be used about 50% of each would give maximum effect. A more thorough study would give a definite mix which would undoubtedly be nearer the diaspore end of the line diagram.

Plate 2.

% Linear Shrinkage Curves.

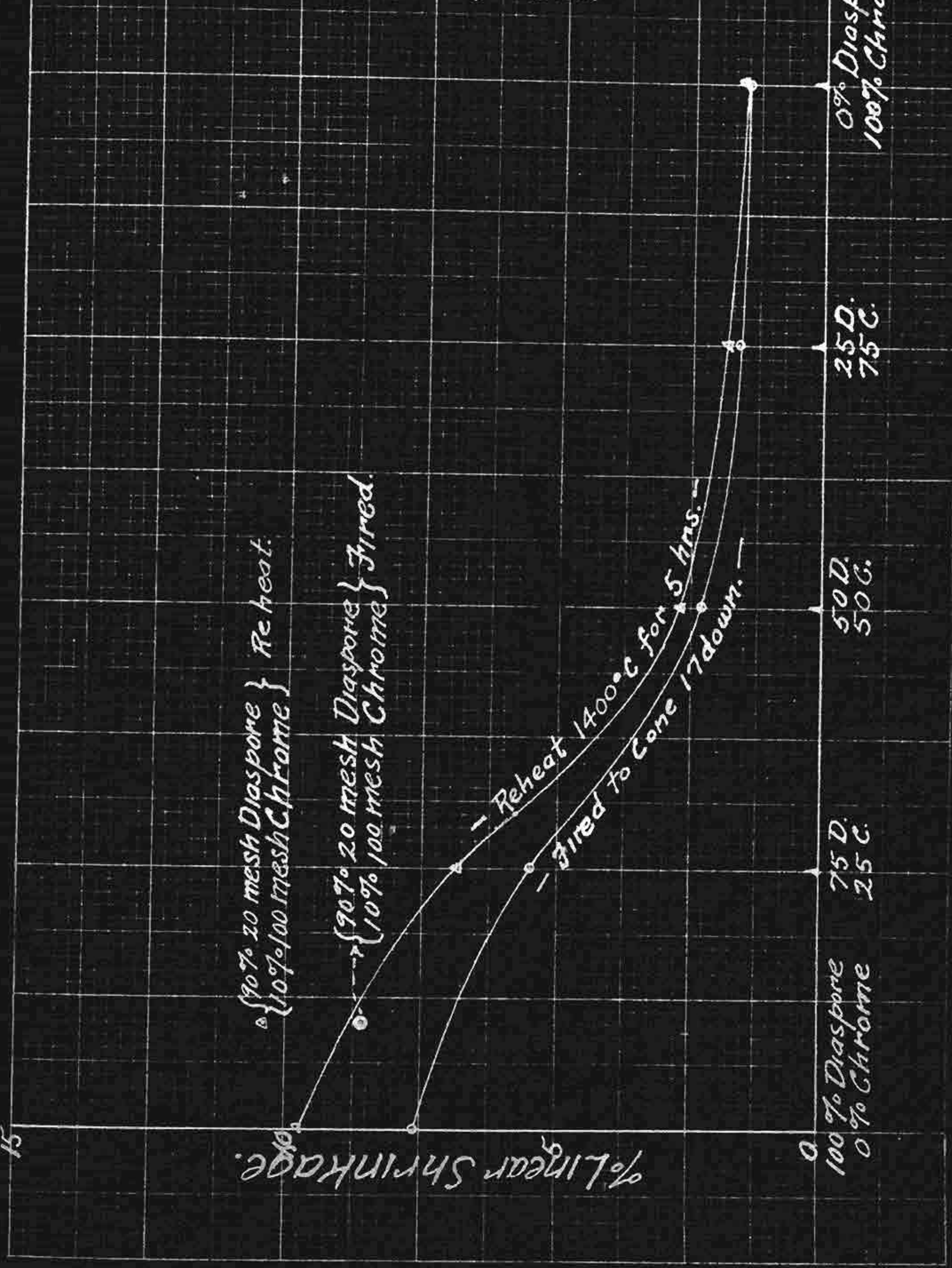
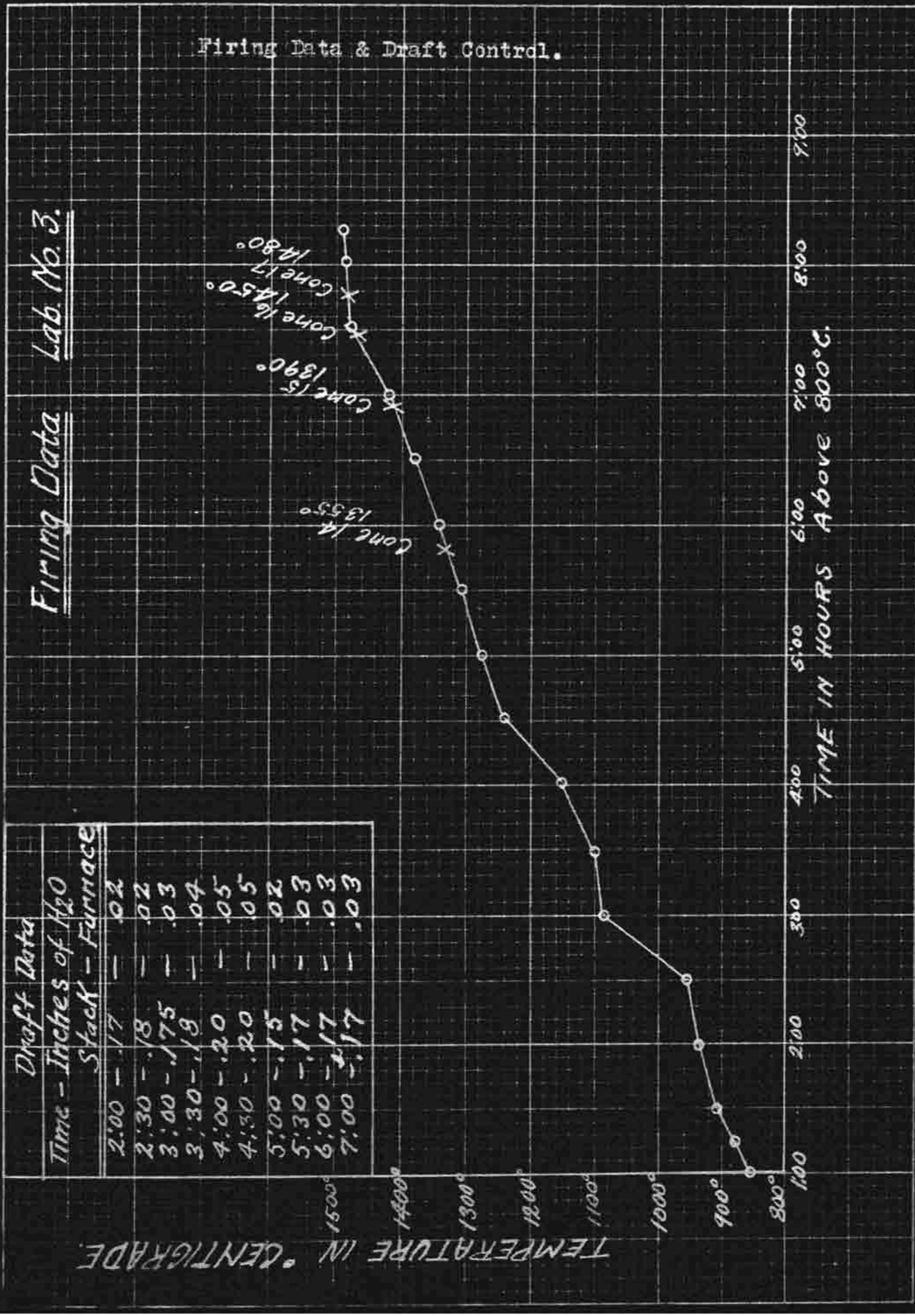


Plate 3.

Absorption Curves.

Plate 4.


Firing Data & Draft Control.
Firing Data Lab. No. 3.
Cone 14 1355°
Cone 15 1390°
Cone 16 1450°
Cone 17 1480°
Draft Data
Time - Inches of H_2O
Stack - Furnace
2:00 - .17 — .02
2:30 - .18 — .02
3:00 - .175 — .03
3:30 - .18 — .04
4:00 - .20 — .05
4:30 - .20 — .05
5:00 - .15 — .02
5:30 - .17 — .03
6:00 - .17 — .03
7:00 - .17 — .03
1:00 2:00 3:00 4:00 5:00 6:00 7:00 8:00 9:00
TIME IN HOURS Above 800°C.
800° 900° 1000° 1100° 1200° 1300° 1400° 1500°
TEMPERATURE IN °CENTIGRADE

Procedure No. 4. Slag Action Test.

It was desired to make a study of Slag Action on the series as named under proocedure No. 3. Bars were made up 1" X 1" X 8" on the dry press as before except that three semi-cylindrical lugs of wood were placed on the surface along the eight inch dimension. Cavities were thus formed 1 1/2" long, 1/2" wide and 3/8" deep. These bars were fired to cone 17 down, along with bars for linear shrinkage and absorption tests. Three types of slags were used: namely, Blast furnace, acid open hearth, and basic open hearth. The slag was crushed to pass 20 mesh and placed in the cavities made by the wood lugs. The bars were fired to 1400°C and held at that temperature for nearly two hours. By inspection the slag could be seen and when it was sufficiently melted the furnace was shut down.

The Blast furnace slag which was furnished by St. Louis Gas & Coke Co., Granite City, Ill. was the first to melt. It melted at about 1340°C. The furnace was cooled down after having been held at 1400°C for two hours.

All of the bars containing over 25% chrome had absorbed the entire sample. There was no apparent effect on these pieces except to make them denser near the slag exposed surface.

The test pieces containing 90% 20 mesh diaspore and 10% 100 mesh chrome had less penetration with about one-half of the slag still on the surface. However a fluxing action had broken down a small amount of the body.

The 100% diaspore trial had the least penetration but as in the case of the 90% diaspore - 10% chrome piece a fluxing action had taken place.

The commercial diaspore sample, made up of 40% raw diaspore, 10% plastic fire clay and 50% calcined diaspore, had the most vigorous fluxing action and would indicate that any of the other mixtures would be superior in the resistance to slag action of the blast furnace type.

The Basic Open Hearth Slag from Scullin Steel Co., St. Louis, Mo., finely ground when it arrived and so was placed in slag holes in a much finer state than the other slags used. This slag penetrated into the bars in varying degrees, greatest in the 100% chrome bar and least in the 100% diaspore.

The more diaspore in the specimen, the less was the penetration, but greater was the decomposition of the specimen itself. The alumina of the diaspore evidently went into the slag which caused it to become more viscuous thus lowering penetration.

The trial made up of 90% 20 mesh diaspore and 10% 100 mesh chrome showed least penetration of any of the regular mixtures. This was no doubt partly due to the denser nature of the specimen.

As in the case with the Blast furnace slag, the same is true of the basic open hearth in regard to the commercial diaspore mix. That is, the fluxing action of the slag is more pro nounced than on the straight 100 % diaspore. This can be accounted for by two things; first, by the addition of 100% plastic fire clay which may be more easily fluxed, and second, by the more porous nature of the body due to the 50% of calcined diaspore which acts much the same as a grog in ordinary fire brick.

The acid open hearth slag furnished by American Steel Foundry Co., Indiana Harbor, Indiana, was of a higher melting nature and consequently did not melt thoroughly at the temperature of 1400° C. which was reached in the firing of the trials. If the temperature had been taken up any higher the other two slags would have been completely absorbed. The slag appears to have attacked the 100% diaspore bars much more vigorously than the 100% chrome, yet there was no breaking down of any of the intermediate series.

The most useful point brought out in the slag test run was that a small percent addition of finely ground chrome ore to diaspore cut down the slag action considerably. In no place, however, was the slag action apparently detrimental to the chrome samples nor the samples containing as little as 25% chrome. They seemed to adsorb the slag into the surface which would undoubtedly form a practically impenetrable surface upon exposure to further slag action.

Proceedure No. 5 - Spalling Action.

Due to the lack of raw materials and facilities for making 9" shapes on a dry press it was necessary to use bars 1" X 1" X 4". Bars of this shape did not require three minutes to cool down in running water therefore the dipping time was reduced to two minutes. The steaming interval was also lessened from five minutes to three.

The bars were heated on one end up to 850° Centigrade by placing one end in the door of a Hoskins Electric Muffle type furnace. As spalling action caused by thermal shock is most effective below red heat the tentative test standard of 850° Centigrade was used.

The results of the spalling test gave a very definite curve varying from eleven dips for 100% chrome to twenty-three dips for the 100% diaspore bars.

The addition of diaspore to the chrome in every case increased the resistance to spalling action.

A point of interest is brought out in the special mix of 90% - 20 mesh diaspore and 10% - 100 mesh chrome. This group of four bars averaged 31 dips which is 8 more than the average for the straight 100% raw diaspore bars. This indicates that a small addition of chrome ore does not decrease the spalling resistance of the diaspore.

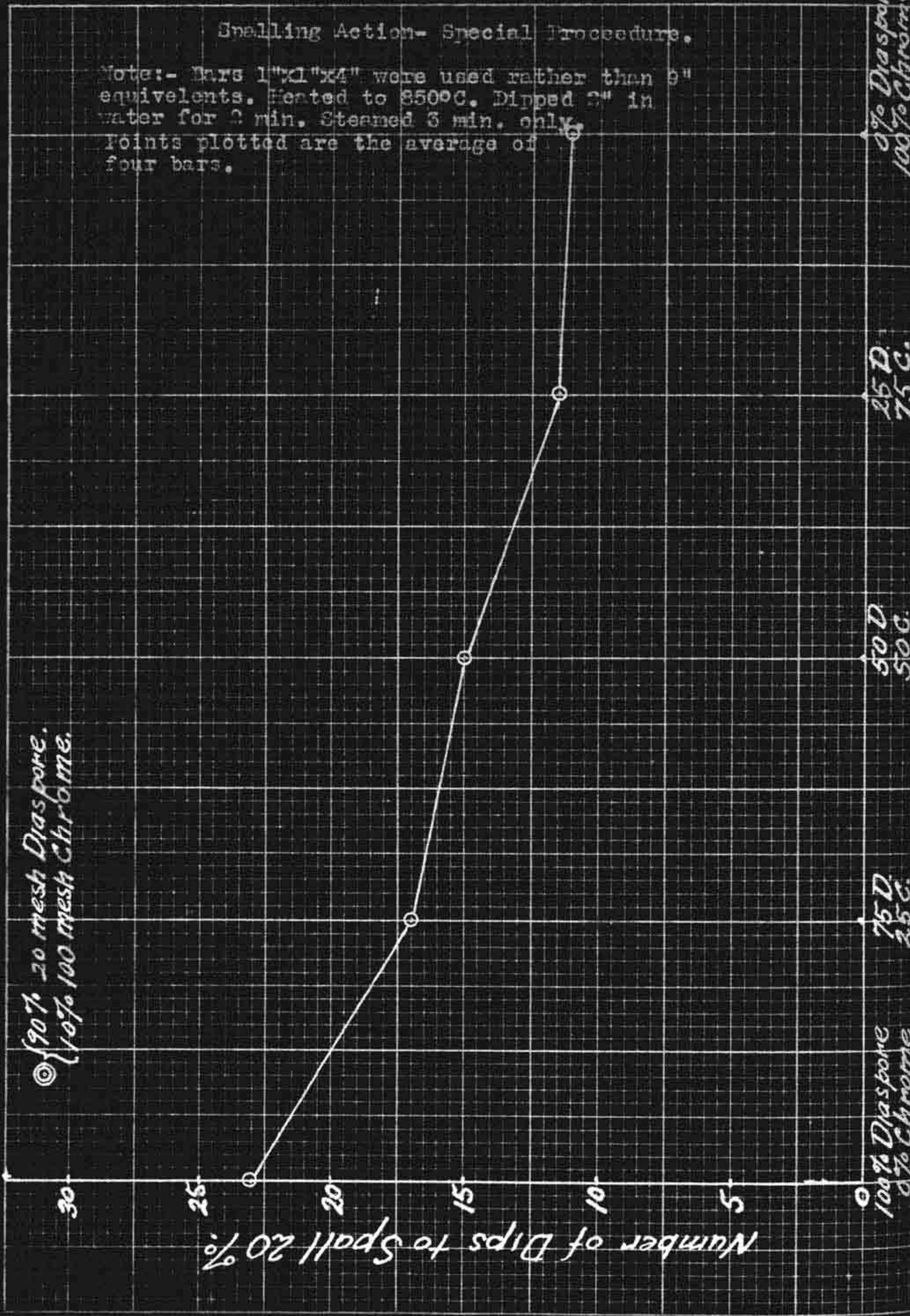
The diaspore used in the above mentioned tests was raw diaspore as it came from the mine. The commercial mix bars that were run in conjunction with this test did not in any case spall over 10% in thirty-five dips.

It was not thought worthwhile to continue the run for this particular set since all of the members of the series had already failed. The reason for the commercial mix being more resistant is due to its make up of 50% calcined diaspore, 40% raw diaspore and 10% plastic fire clay. The calcined diaspore acts much the same as a grog in a fire clay brick and in this instance increased the porosity of the specimens approximately 6 percent.

Plate 5.

Spalling Action- Special Proceadure.

Note:- Bars 1"X1"X4" were used rather than 9" equivelents. Heated to 850°C. Dipped 2" in water for 2 min. Steamed 3 min. only. Points plotted are the average of four bars.



OUTSTANDING RESULTS

1. No combinations of diaspore and chrome could be found which have a cone fusion point below cone 34. It may be several cones above this.

2. The dry press method of forming ware made from mixtures of chrome and diaspore is apparently the best.

3. The use of 50% chrome ore cuts down the shrinkage to about one third that of 100% raw diaspore.

4. Chrome and diaspore have very nearly the same absorption and when mixed this figure does not change materially.

5. The addition of a small amount of finely ground chrome cuts down the action of slag on diaspore.

6. The addition of diaspore to chrome increases its resistance to spalling action also the addition of finely ground chrome to diaspore increases its resistance to spalling action.

ACKNOWLEDGMENTS

I am indebted to the various manufacturing companies for their cooperation in supplying the slags used in the slag action study; and particularly to Dr. M. E. Holmes for his many helpful suggestions and advice during the course of the research.