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Missouri super duty refractories and their probable application for blast furnace linings

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MISSOURI SUPER DUTY REFRACTORIES AND THEIR PROBABLE APPLICATION FOR BLAST FURNACE LININGS

BY

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Introduction:

The use of Missouri Super Duty Refractories in steel plant service is not new, although their use in blast furnace service has been limited chiefly to stove installations. They have, however, been used in a sufficient number of places where severe operating conditions exist, so that they are a definitely known quantity and they have consistently shown much longer service under conditions of high temperatures and contact with slag and molten iron.

One outstanding comparison of the service which these brick give over ordinary first quality brick is in the bottom of a malleable iron furnace. No first quality refractory has successfully been used for this service, and until A. P. Green Fire Brick Company pioneered this service for their super duty brick it was necessary for the malleable operator to use a sand bottom and rebuild the bottom at the end of each week. No first quality refractories had lasted over thirty to thirty-five heats under these conditions, but super duty brick consistently give from one hundred to one hundred and fifty heats, making it much more economical to use these brick for this service. It must be remembered that in malleable bottoms the brick are subjected to the direct erosion of molten metal and slag at 3000°F., which is extremely severe service.

Data and Discussion:

In the evaluation of any brick for a particular service it is the usual practice to compare the physical properties of the brick under consideration with those of brick which are actually used in the service. Before recommending super duty refractories for blast furnace service, complete physical tests were run on several brands of standard blast furnace refractories and comparisons were made with the known physical

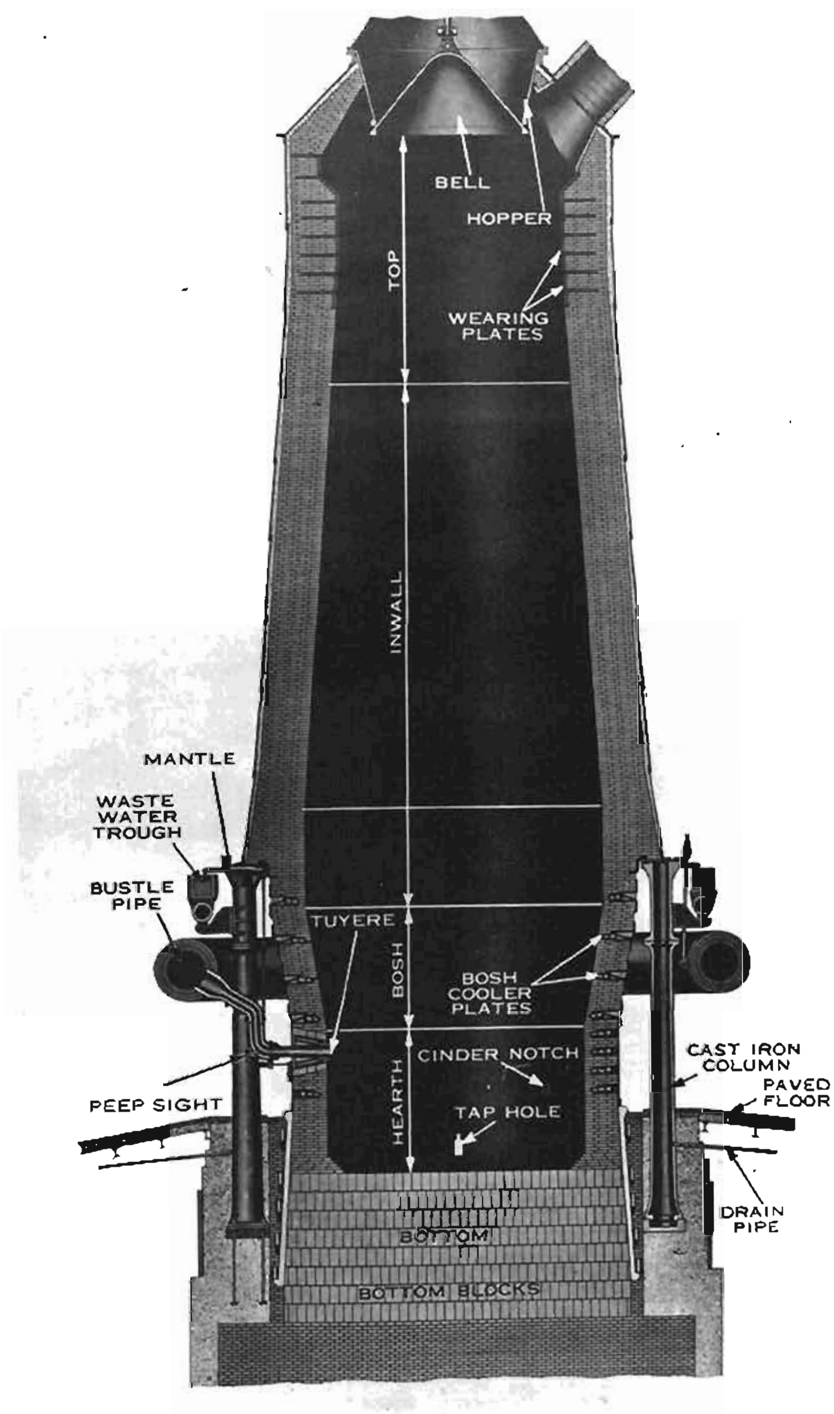

Fig. 1. Diagramatic layout of blast furnace.

properties of Missouri fire clay refractories. The comparisons revealed that in every respect super duty brick were better. Test data is given later in this paper.

It also is understood that in recommending a fire brick for a given service the investigator must have a comprehensive knowledge of all the service conditions which exist in the contemplated furnace. The writer has made a study of these conditions from the existing data on the subject as well as from examinations of linings at the end of campaigns of a number of furnaces.

The existing data indicates that the refractories used in a modern blast furnace are subjected to several different conditions. Based on this knowledge, the furnace may be and usually is considered as being divided into several different zones or areas. A separation of the refractories has long been made into Top Quality, Inwall Quality, and Hearth and Bosh Quality. This, of course, recognizes the three main sections of the blast furnace and its division into the top inwall, the middle inwall and the lower inwall, which latter is also extended to include the bosh, the hearth area and the bottom (See Figure 1).

In the top inwall section the refractories are subjected to rather low temperatures, of course, but in the area around the stock line the refractories are subjected to an appreciable amount of abrasion and wear from the introduction of the charge as it drops from the bell and is distributed around the periphery of the furnace. The charge of limestone and coke as well as the ore often times hits the linings with considerable force. This jarring and bumping, as well as scraping of the charge against the sidewall in its subsequent travel through the furnace, loosens, abrades, and finally knocks out some of the refractory lining. This action at the stock line has been lessened to some extent by the use of wearing plates in the stock line area but often it will be noted that the lining is appreciably gouged out just below the area which is protected by wearing plates.

Below this gouged out area of the lining and extending down an indefinite distance the middle inwall section is often found to be not as badly worn. This, of course, is not a definite area and its extent may vary greatly in different furnaces and may also vary between campaigns in the same furnace, depending upon variations in stock distribution and channeling which may take place in the furnace. In this area the temperatures are not high, as far as the normal resistance to heat, or good quality refractories, is concerned. But there are other factors which develop during the campaign of a furnace which affect the refractories in this area. It is usually considered that good, first quality refractories will satisfactorily withstand the service in this area, but in the minds of some operators there is a strong question as to whether the present refractories are all that can be desired in this area.

The part of the stack which usually receives the most wear extends from the bottom of this rather indefinite area to the top of the bosh section or to the mantel. It is usually this area of the stack which is first to show signs of serious wear. If the refractories in the stack cause the campaign of the furnace to be ended it is usually found that the hot spot develops in this area. Current blast furnace refractories manufacturers, recognizing the need for good refractories in this area have "sweetened" the mix used in their Hearth and Bosh Quality until it is more refractory than ordinary first quality brick. This may be partly responsible for some of the longer campaigns which have been attained in the last decade or so. There are, of course, other reasons for this longer campaign life and it is difficult, if not impossible, to say that any one factor is the reason for it.

The increased refractoriness of the Hearth and Bosh quality refractory is continued on down through the bosh and the hearth into the bottom where experience has taught that the best refractories available are none too good. In many cases the reason for the ending of a blast furnace campaign will be found in a failure of the bottom refractories - either because of the quality of the refractories used or because of faulty installation. Because of the severe temperature and slag erosion in this area of the furnace, and the lack of adequate cooling facilities, the refractory manufacturer watches the quality of the bottom blocks with great care and the operator insists upon uniformity of sizes to assure tight joints.

Since we have seen that the blast furnace refractories are divided into three general types of brick, an examination of the physical properties of each of these has been made to ascertain just how well suited they are to withstand the service which they encounter. Tests have been run upon a number of samples of the different manufacturers' brick. Most of the tests conducted on the various refractories are standard tests and, therefore, will not be described. However, the carbon monoxide disintegration test and the cold abrasion test are unusual and will be described.

In order to study the effect of the gases which are generated on the inside of a blast furnace, upon the refractories which are used in it's lining, a number of different forms of laboratory equipment have been evolved. Regardless of the form of the equipment, the apparatus consists essentially of a carbon monoxide generator, and a gas tight chamber where the gas is brought into contact with the refractories, under definitely controlled temperature conditions.

One such apparatus is shown in Figure 2. Others of equal success have been developed, having various capacities and having different types of equipment.

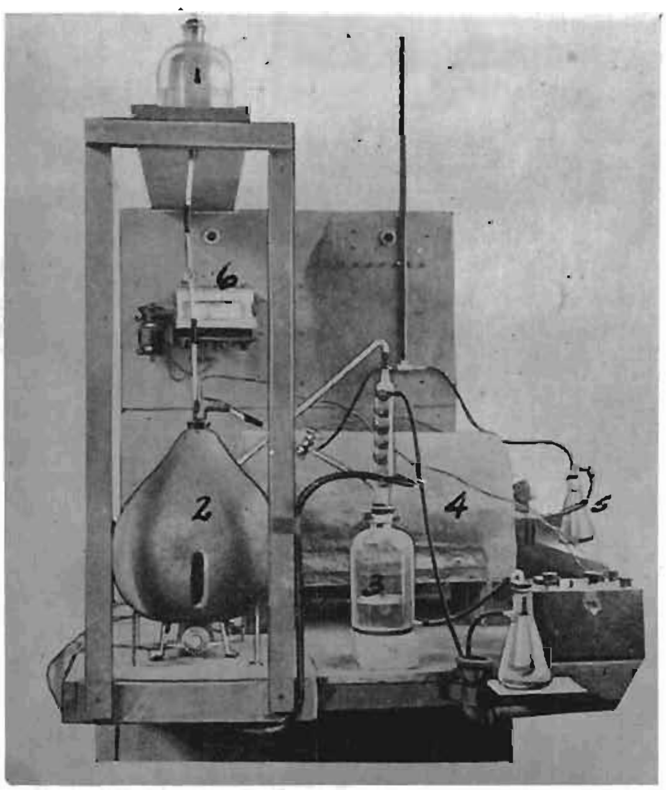

Fig. 2. - CO generator

In the illustration formic acid which is contained in bottle (1) is siphoned out so that it will drop into the bottle or still (2). The speed at which the formic acid drops into the bottle (2), which is partly filled with phosphoric acid, is controlled by a stop-cock in the line leading to the bottle. The bottle of phosphoric acid rests upon, and is heated by, an electric hot plate. The generation of carbon monoxide gas is based upon the reaction of formic acid upon phosphoric acid according to the reaction

$$H_2CO_2 \; + \; 2H_3PO_4 \; = 4H_2O + \; CO \; + P_2O_5$$

Since considerable water is generated in the reaction, it is necessary to eliminate it from the still which is accomplished by the use of the hot plate. The temperature of bottle (2) or the still is controlled at 275° F. The carbon monoxide and the water vapor leave the generator and enter the condenser and water bottle (3) where the water vapor is condensed leaving the carbon monoxide free to enter the reaction chamber (4).

In this particular investigation, the rate of application of the formic acid was controlled so that approximately four cubic feet of carbon monoxide was generated per hour.

The reaction chamber (4) consists of a monel tube, approximately six inches in diameter and twenty four inches long, flanged on each end for the application of a cap and gasket to make it air tight. The cap on each end is tapped and a short nipple inserted to enable the carbon monoxide gas to enter the chamber, react with the test specimen and exhaust to the atmosphere through a bubbling bottle (5). The bubbling bottle eliminates any possible counter flow of gas and makes the flow of gas through the system visible at all times.

Two hot plates are placed under the reaction chamber and separated from direct contact by asbestos, and the entire chamber is insulated. A thermocouple is placed in the chamber attached to the thermostat (6) in order that the temperature of the furnace might be accurately and continuously controlled. In the case of this investigation, the temperature was held at 850° F. throughout the entire run of the furnace on the test.

Various investigators have used varying lengths of time for the test of resistance to disintegration caused by the carbon monoxide. Some investigators have used fifty hours, others one hundred hours, while one or two have extended the test for one thousand hours. In the test data referred to in this paper, the length of the test runs was two hundred hours.

Each time the test was run, in order to assure that the conditions which occurred in the reaction chamber were such as to promote disintegration, it was necessary to include a "standard". The standard consisted of a test specimen size of a refractory which was known to have low resistance to the disintegrating effect of the gas. When, at the end of a run of the furnace the "standard" showed signs of serious disintegration, it was known that the atmosphere was conductive to disintegration even though the test samples might not show any.

The test specimen consisted of cubes two inches on a side and were cut from larger pieces of the refractory which was under investigation. The cutting of the cubes was done with a silicon carbide saw and it was always endeavored to cut the specimen in such a manner that three or more of the faces were the original face of the refractory brick.

ABRASION RESISTANCE TEST

The abrasion test is one developed in the laboratory of the A. P. Green Fire Brick Company. It is one that was develpped specifically in connection with this investigation and is therefore not a standard test as recognized by the American Society for Testing Materials.

The test was developed and conducted on the machine shown in Figure 3. The equipment consisted of an old Universal Tool Grinder which was altered in such a manner that it adequately differentiated between the relative hardness of the various test specimen, and produced a numerical value as a designation of the hardness.

The movable table on which the test specimen were clamped was adjustible and was capable of being moved in three planes mutually at right angles to each other. A coarse grained grinding wheel, propelled by a $\frac{1}{2}$ h.p. motor, was mounted in a stationary position above the movable table. The speed of the motor was 3450 r.p.m. while that of the driven abrasion wheel was 3775 r.p.m. The stone was 9 inches in diameter and 3/8 inch wide, being manufactured by the Abrasive Company, Tacony and Fraley Streets, Philadelphia, Pa., and is identified as Abrasive, E 209-PB-61.

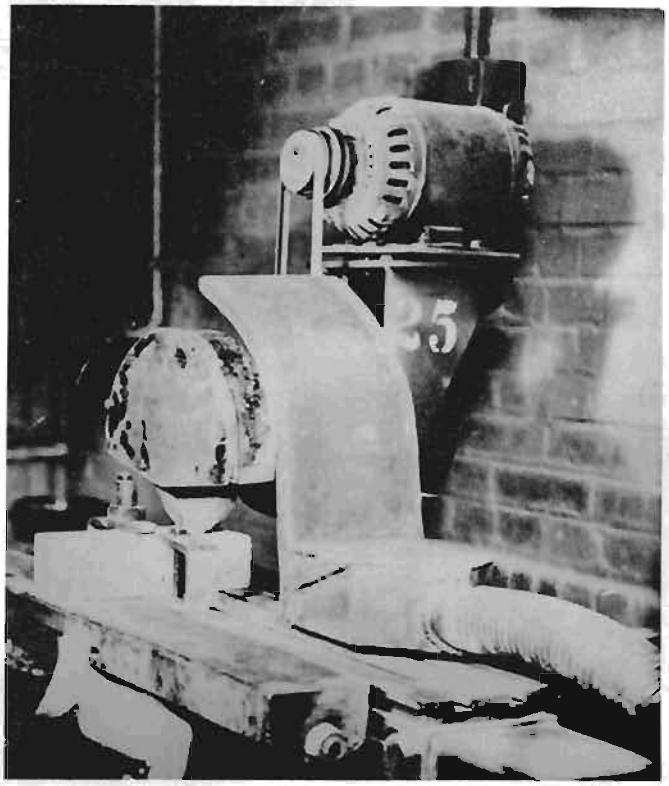

Fig. 3. - Cold abrasion tester.

The test brick were clamped rigidly to the table with the longitudinal axis of the specimen parallel to the axis passing through the center of the grinding wheel disc. The position was such that the grinding wheel would cut a 3/8 inch groove across the four and one half inch dimension of the 4-1/2" x 9" face of the brick. The face upon which the test was conducted, was always the one opposite the branded face.

A very light cut was taken across the face of the test specimen first in order to smooth up any irregularities that might have occurred in the surface. The table was then raised an amount which judgement and experience dictated to be about right, and then by trial, or several trials, a determination was made of the maximum depth of groove which could be cut in the test specimen, while feeding the brick into the wheel at the rate of one inch per second approximately, without stalling the wheel. After the correct depth was determined, several checks were made to assure the accuracy of the determination.

The comparitive degree of vitrification, or the relative hardness of the brick is then in inverse ratio to the depth of the cut which it was possible to make in the brick.

The data given in Tables I, II, III and IV, are not necessarily the results obtained on any particular sample but are representative of a number of different samples tested.

TABLE I

BLAST FURNACE TOP QUALITY FIRE BRICK

	Missouri Hard Burned, Super Duty+	1st Quality Missouri	Kentucky Blast Furnace Refractories	
			"A"	"B"
P.C.E.	33-34	32-33	32-32½	31-32
Porosity	12.4%	16%	11.5%	15.4%
Cold Abrasion	.125	.200	.100	.250
Resistance to CO*	Fig. 21	Fig. 24	Fig. 18	

* Standard Missouri Super Duty Refractories are burned commercially at approximately cone 14.

\+ Hard Burned Super Duty Missouri Refractories are burned commercially at cone 20 or higher

TABLE II

BLAST FURNACE INWALL QUALITY FIRE BRICK

	Missouri Hard Burn. Super-Duty	Missouri Super Duty	1st Qual. Missouri	Kentucky Blast Furnace Refractories "A"	Kentucky Blast Furnace Refractories "B"
Volume Change in 2912°F., 5 Hr. Reheat	Cont. 3.0%	Exp. 1.7%	Exp. 3.6%	Exp. 23.5%	Exp. 11.1%
App. Porosity Before 2912°F. Reheat	12.4%	15.7%	14.9%	11.8%	16.8%
True Porosity Before 2912°F. Reheat	16.95%	17.45%	17.8%	14.22%	18.65%
App. Porosity After 2912°F. Reheat	8.8%	8.8%	2.6%	8.7%	10.4%
True Porosity After 2912°F. Reheat	13.63%	18.19%	14.23%	30.30%	27.30%
P.C.E.	33-34	33-34	32-33	32-33	32½-33
Cold Abrasion	.175	.300	.200	.100	.125
Polished Section Before Reheat	Fig. 27	Fig. 26	Fig. 34	Fig. 30	Fig. 33
Polished Section After Reheat	Fig. 36	Fig. 35	Fig. 43	Fig. 39	Fig. 42
Resistance to CO	Fig. 21	Fig. 25	Fig. 24	Fig. 17	Fig. 19

TABLE III

BLAST FURNACE HEARTH & BOSH QUALITY FIRE BRICK

	Missouri Hard Burned Super Duty	Missouri Super Duty	Kentucky Blast Furnace Refractories "A"	Kentucky Blast Furnace Refractories "B"
Volume change in 2912°F. Reheat 5 Hrs.	Cont. 3.0%	Exp. 1.7%	Exp. 7.4%	Exp. 22.5%
App. Porosity Before 2912°F. Reheat	12.4%	15.7%	14.7%	13.8%
True Porosity Before 2912°F Reheat	16.95%	17.45%	16.05%	18.65%
App. Porosity After 2912°F. Reheat	8.8%	8.8%	14.0%	13.6%
True Porosity After 2912°F. Reheat	13.63%	18.19%	36.0%	32.0%
P.C.E.	33-34	33-34	32-33	32½-33
Cold Abrasion	.175	.300	.080	.150
Polished Section Before Reheat	Fig. 27	Fig. 26	Fig. 31	Fig. 32
Polished Section After Reheat	Fig. 36	Fig. 35	Fig. 40	Fig. 41
Resistance to CO	Fig. 21	Fig. 25	Fig. 23	Fig. 20

TABLE IV

BLAST FURNACE $4\frac{1}{2}$" x 9" x 18" BOTTOM BLOCKS

	Missouri Hard Burned Super Duty	Missouri Super Duty	Kentucky Blast Furnace Refractories		
			"B"	"C"	"A"
Volume Change in 2912°F. Reheat 5 Hrs.	Cont. 2.4%	Exp. 1.4%	Cont. 5.4%	Cont. 3.0%	Exp. 3.0%
App. Porosity Before 2912°F. Reheat	13.6%	16.1%	16.6%	21.5%	16.2%
True Porosity Before 2912°F. Reheat	17.2%	16.5%	-	-	-
App. Porosity After 2912°F. Reheat	5.5%	9.6%	.7%	10.9%	1.5%
True Porosity After 2912°F. Reheat	11.85%	16.4%	-	-	-
2642°F. Hot Load Test	Cont. 3.2%	Cont. 6.0%			
P.C.E.	33-34	33-34	$32\frac{1}{2}$-33	32-33	33
Cold Abrasion	.125"	.800"	.300"	.500"	.175"
Polished Section Before Reheat	Fig. 29	Fig. 28	Fig. 45	Fig. 46	Fig. 44
Polished Section After Reheat	Fig. 38	Fig. 37	Fig. 48	Fig. 49	Fig. 47
Resistance to CO	Fig. 22	Fig. 25	Fig. 19	Fig. 20	Fig. 16

While the physical properties which a brick possesses give a very good indication of what might be expected from it in actual service, there are also other properties that might well be investigated. In dealing with brick of the nature of Missouri super duty, it soon becomes apparent that the difference in P.C.E. value between them and first quality brick does not tell the whole story. That is, while the difference in P.C.E. value is only about one to one and a half cones, the difference in service, where the temperatures are high, often is in the neighborhood of 200 to 300 per cent better in the case of the super duty brick. The probable reason for this paradox lies in the chemical and pyrochemical properties of the two types of brick. Let us develop this point further.

The only stable form of alumina and silica at high temperatures is the mineral mullite ($3Al_2O_3\ 2SiO_2$). Therefore, if any fire clay refractory is subjected to sufficiently high heat for long enough time, a mineralization process sets up within the brick so that the alumina combines with the silica in the mullite ratio, that is three to two. This usually leaves an excess of silica which cannot combine with alumina. It is, therefore, free to combine with any chemical constituents for which it has an affinity. Some of the available elements for this combination are sodium, potassium, iron, magnesium, and calcium. Silica in itself is, of course, very refractory, but when combined with basic materials as mentioned above, the refractoriness greatly diminishes. The larger the amounts of these bases available, the lower will be the melting point of the subsequent glass which is formed; and the lower the melting point the greater will be the chemical reactivity of this glass with slags which come in contact with it in service. Since in the case of super duty refractories, the basic impurity content is low, the quality of glass which is formed is very high, and it is not as likely to be chemically attacked as much as the regular first quality brick at equal temperatures. Thus, Missouri super duty refractories should stand up better than ordinary first quality refractories in the hottest parts of blast furnaces.

The amount of potential mullite which can be formed can be closely figured from the chemical analysis of the refractory but the type of mullite formed and the type and amount of glass which is formed can best be ascertained by the use of the petrographic microscope.

Below, is a series of thin section photomicrographs which clearly demonstrate the difference which exists between first quality and super duty refractories. In each case the refractories have been reheated for five hours at 3000° F. entirely surrounded by heat and the thin section made from the brick heated in this way.

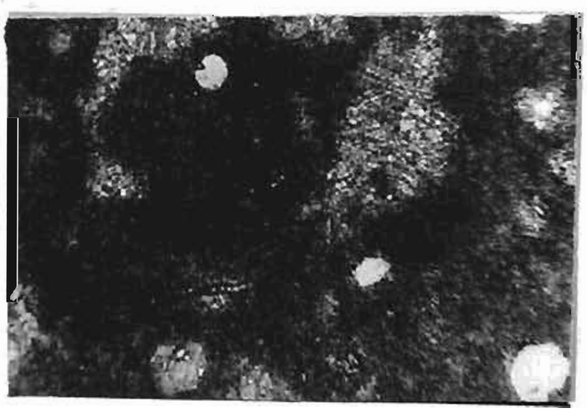

Fig. 4 - Thin Section of first quality Missouri fire brick (140 X)

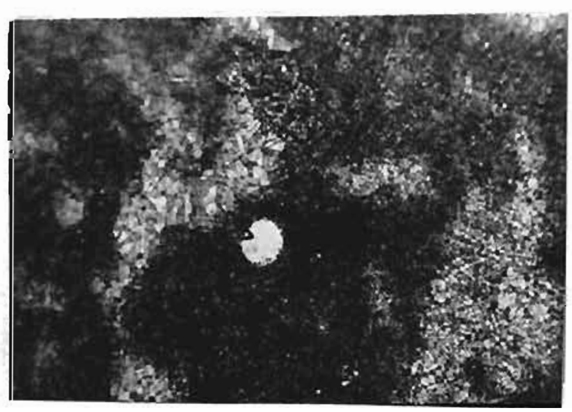

Fig. 5 - Thin section of first quality Missouri fire brick (220 X)

Note: the very clear spots are holes in the thin section which were torn out during grinding.

In figures 4 and 5 it can readily be seen that the mullite crystals (the long needle-like crystals) are rather large, well defined ones, imbedded and interlaced in the clearer areas. The clearer areas are the glass which has been formed and it can be seen that it is present in rather large amounts.

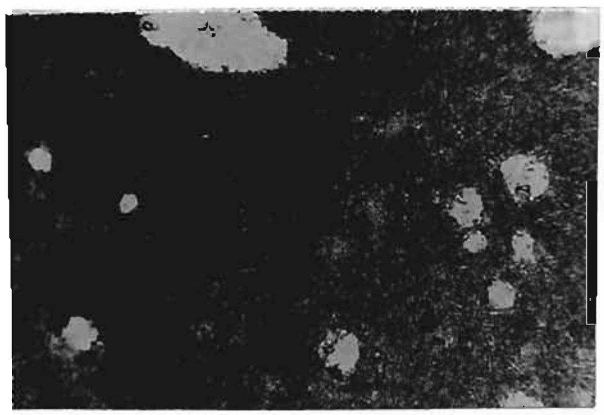

Fig. 6 - Thin section of
Blast Furnace Brick "A"
Hearth & Bosh Qual. (140 X)

Fig. 7 - Thin section of
Blast Furnace Brick "A"
Hearth & Bosh Qual. (220 X)

See note on Figures 4 and 5.

Figure 6 and figure 7 show a commercial blast furnace refractory of hearth and bosh quality. This indicates a somewhat lower glass content evenly distributed over the area. The refractory was relatively fine grained, evenly mixed, and gave a slightly better pattern of small mullite crystals imbedded in a smaller amount of glass than was evidenced in the case of the first quality brick. This shows an improvement over first quality.

Fig. 8 - Thin section of Super Duty Missouri fire brick (140 X)

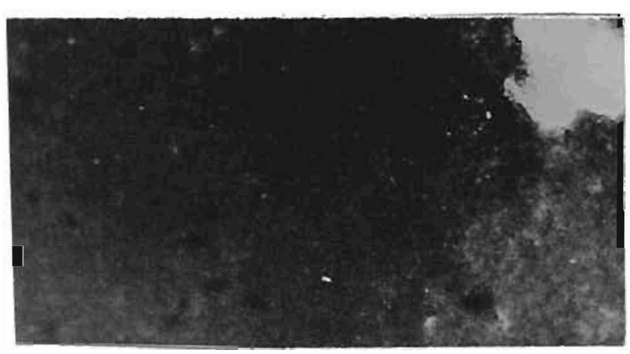

Fig. 9 - Thin section of Super Duty Missouri fire brick (220 X)

See note on figures 4 and 5.

Figures 8 and 9 show a section through one of the high grade flint grains with a small section of the plastic bond clay adjacent to it. It shows plainly the small amount of glass formed in the flint grains and the typical, rather opaque structure of the flint clay grain. It shows also the tight knitting together of the high grade plastic clay which has formed an excellent bond with the flint grain.

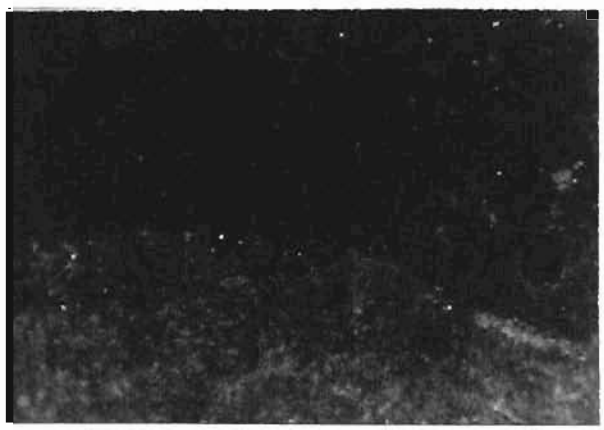

Fig. 10 - Thin section of Hard Burned, Super Duty Missouri fire brick (140 X)

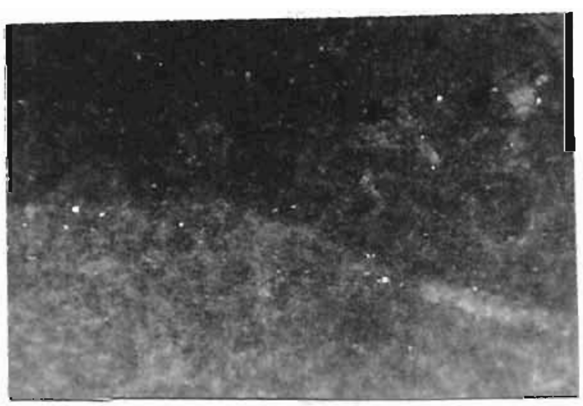

Fig. 11 - Thin section of Hard Burned, Super Duty Missouri fire brick (220 X)

Figures 10 and 11 show the same characteristic opaque, fine-grained, mullite development in super duty refractories which gives the maximum resistance to heat and chemical reaction.

Petrographic analysis of the scab interface between the slag of the blast furnace and the refractories, shows that the flint grains are always the last to go into solution with the slag of the furnace. These grains, therefore, are more resistant to blast furnace slags than the less refractory bond clay. The well developed sections of figure 10 and figure 11 show why this is so.

It is a commonly known fact that when any fire clay refractory is overfired it develops a vesicular or bleb structure which has been attributed to the release of certain gases within the refractory itself, which in expanding are able to form these blebs or blow holes in the then soft, sticky refractory. This is a common condition in fire clay refractories which have been heated beyond their ultimate temperature resistance. These blebs or blow holes would appear on a thin section as holes in the section and, therefore, the number of blow holes may be used to indicate roughly the difference in quality between two or more refractories which have received the same heat treatment. This can be seen by a comparison of Figure 12, Figure 13, and Figure 14. Figure 12 is that of a standard first quality, fire clay refractory and shows an abundance of blow holes.

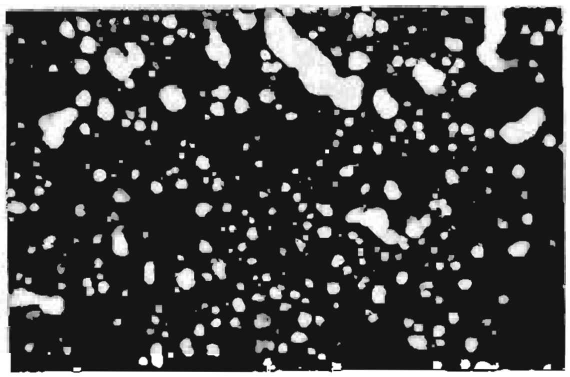

Fig. 12 - First Quality
Missouri fire brick
(60 X)

Figure 13 is that of a standard Hearth and Bosh quality blast furnace refractory which shows that less bleb structure has been developed and it can be interpreted that less over-firing has taken place.

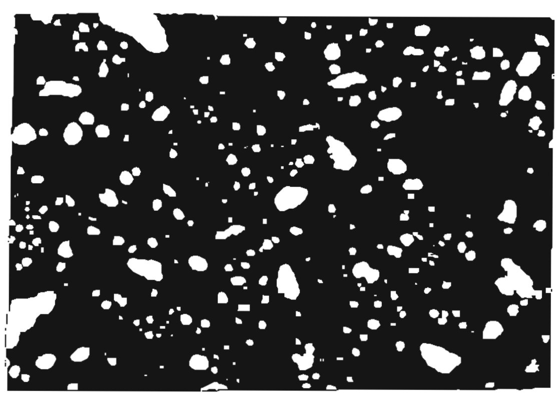

Fig. 13 - Blast Furnace Brick "A"
Hearth & Bosh Quality
(60 X)

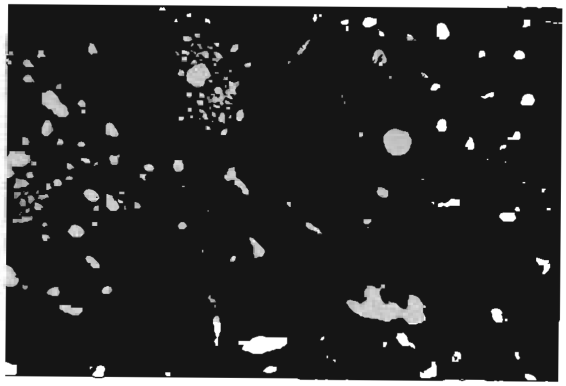

Fig. 14 - Super Duty Missouri
fire brick
(60 X)

Figure 14 shows the development of even fewer holes in the super duty refractory, which indicates that it is more refractory and less susceptible to overfiring at the same temperature.

From the investigation of the physical properties and from observation and study of some of the pyro-chemical properties of the brick that are being used to line blast furnaces today, as well as super-duty brick, it is readily apparent that the super-duty brick have properties which are superior to first quality brick but which for some reason or another may not be adaptable to lining blast furnaces.

In order to truly evaluate Missouri Super Duty refractories for blast furnace service it is necessary to discuss the parts played by the different individual physical properties when the brick are in service in the furnace. In order to do this it is necessary to consider some of the things which take place in the furnace and their relation to the refractories used to line it.

It is well known and frequently observed after the campaign of a furnace has been completed that the lines of the furnace vary and

and that it is worn at some places more than others. In many furnaces the brickwork right under the wearing plates in the stock line area is worn back so that the lining is thinner at this point. The lines come back again below this gouged-out area and are not as a rule worn back as badly to some point from fifteen to twenty feet above the mantel. From this point to the mantel the lining is again worn back to a greater extent than the lining above it. The lines of this worn area come back rapidly at the mantel, due to cooling, to the lines of the refractory at the bosh. Due to the relatively thin lining and the extreme water cooling of the bosh and hearth area the wear is rather uniform. In the bottom, however, again evidence of great refractory wear may be seen in the large salamanders that form in many blast furnaces.

There are, of course, reasons and different ones for the uneven wearing of the furnace lines. In one part it is heat accompanied by slag action; in others it is disintegration of the refractory lining caused by the action of carbon monoxide, in others it may be a combination of these coupled with the wearing or scorifying action of the abrasive charge, and in others it may be spalling of the refractories due to the hot refractories coming in contact with cold, wet material after the original structure of the brick has been altered by heat. This, of course, is the reason for the different types of brick being used in different sections of the furnace.

3 sp.

TOP INWALL

It seems feasible to examine the possible conditions which may occur, beginning at the top and continuing down through the furnace.

Sweetser[1] states "It is the author's opinion that no one knows just what takes place inside the iron blast furnace, we know what goes in at the top and at the bottom and what comes out at the top and at the bottom, and vaguely what radiates into the air and what goes off with the cooling water between the top and the bottom of the blast furnace. But we know positively that the temperature of the iron and the slag flowing from the furnace is never constant, neither is the temperature of the top gases the same for long, and the slag is never constant; we must strike averages of all these changing conditions". Around the stock line area the brick wear might be attributed to a combination of abrasion, disintegration, and spalling. In this area of the lining a rather inconstant condition exists. Speaking of a particular furnace, Sweetser[2] quotes Kinney as saying, "High gas velocity at the inwall is directly responsible for excessive wear and ultimate deterioration of the stock line section of the furnace shaft."

While the conditions undoubtedly are continually changing, enough observations have been made to know probably what are the average conditions prevailing. A strong atmosphere of carbon monoxide is present under considerable pressure which forces the gas well into the lining, completely penetrating the refractories. The action of carbon monoxide upon refractories has been well if not completely explored by a number of independent investigators. Due to these investigations it

1. Sweetser, R. H., Blast furnace practise. N.Y., McGraw-Hill, 1938, p. 176.
2. Sweetser, op. cit. p. 197.

is a well known fact that the iron in the refractories in the uncombined state causes carbon from the CO gas at certain temperatures to be deposited around the iron. This deposition of carbon under ideal conditions of temperature exerts sufficient pressure within the brick during its deposition to, at times, completely disrupt and disintegrate the brick to small, crumbly pieces which will readily be worn away by the descending charge. The ideal temperature for the formation of the carbon deposition, according to the work of Nesbit and Bell[3], is between the temperature of 788° F. and 878° F. Assuming that these temperatures may be in error somewhat and that the effect of the decomposition of the carbon monoxide gas takes place also at temperatures a little above this, it is reasonable to believe from the work of Kinney[4], Royster[4], Johnson[5] and others that the temperatures which occur near the face of the refractories in the stock line area are in the range of the carbon deposition action, therefore, if the fire brick are susceptible to the deposition of the carbon, there is bound to be considerable breaking of the refractories in this area of the furnace.

The lining is also subjected to considerable abrasion in this area because part of the charge as it drops from the bell rolls over against the lining if the column happens to be low. Then, as the column moves down through the shaft there is a strong abrasive action of the ore and the limestone of the charge. The limestone has not been heated

[3] Nesbit, C. E., and Bell, M. L. Fire-brick disintegration. Brick and Clay Record. v. 62, p. 1042-3 (1923).
[4] Kinney, S. P., Royster, P. H., and Joseph, T. L., Iron blast-furnace reactions. U. S. Bur. Mines. Tech. Paper No. 391, p. 56 (1927).
[5] Johnson, J. E. The physical action of the blast furnace. Trans. Am. Inst. Min. and Met. Eng. v. 36, p. 472 (1906).

sufficiently at this time to drive off the CO_2 and it still retains the original hardness and abrasive properties which it had when charged. This, therefore, calls for a refractory which is hard and tough to give maximum resistance to the abrasion.

The remaining condition in this area which might be a contributory cause for failure is that of spalling. Refractories for this area should be burned hard to convert the iron present to some form of iron silicate if possible, and this means that considerable vitrification will have been produced in the refractory and considerable glass formed, especially if lower grade clays are used. The refractories would, therefore, be sensitive to rapid thermal changes. At times during cold, wet weather the ore and limestone charged may be high in moisture content and when this portion of the charge comes in contact with the refractories of the hot lining, severe spalling conditions will be encountered which would cause the refractories to crack and break off before the ultimate wear had been received from the lining. There are, then, in this area two opposing conditions which demand opposite physical properties from the refractories: to withstand spalling they must not be vitrified and glassy; to resist carbon deposition they must have been burned sufficiently hard to convert the iron to iron silicate. With first quality refractories it is impossible to satisfy both of these requirements, because of lower grade clay which forms a thermally sensitive glass before the conversion of iron to iron silicate occurs.

From an inspection of the physical properties of hard burned, super duty brick, however, it is evident that this brick is unusually well suited to withstand the service in this area. They are first of all made of carefully selected flint clays which are usually low in iron and other impurities. Since they are low in iron, they are inherently resistant to the deposition of carbon. The hard burning which they receive is an additional step which increases the resistance and greatly fortifies them to withstand the service encountered in this area. Proof of this unusual resistance to disintegration may be found in Figure 21, which shows a sample of this material subjected to a highly concentrated atmosphere of CO for 200 hours at 865° F. This is not the result of only one test but many have been run on different samples of this type of brick and in every case its resistance to disintegration has been remarkable.

The hard firing which hard burned, super duty brick receive gives them very great resistance to abrasion so that they can well resist the wearing action of the descending burden as well as the impact of the charge as it drops from the bell.

It is difficult to give numerical figures on spalling resistance from a relatively small number of tests. Also, it is difficult to use standard A.S.T.M. Tests for spalling to evaluate the brick to be used in the top section of a blast furnace. Standard A.S.T.M.[7] designation C122-40 prescribes a high degree of preheat for the refractories to be tested before the samples are actually spalled in the procedure. The high degree of vitrification developed by the preheat is not developed in the refractories in service in the top inwall area and, therefore, the standard test can be misleading.

7 American Society for Testing Materials Standards. 1940 Supplement. Part II, p. 71.

In order to get the inherent resistance to spalling of super duty refractories in comparison to standard "Top Quality" refractories, a special spalling test was adopted in which the standard spalling procedure was used, eliminating the preheat. More than one series of spallings was required to produce an appreciable loss in either type of refractories. Twelve cycles of spalling are used in the standard A.S.T.M. Test while Figure 15 shows the appearance of both types of brick after being subjected to fifty-nine cycles.

Fig. 15 Column of Standard Top Quality Blast Furnace Refractory at the left shows a 9% loss after being subjected to spalling test. The Hard Burned Super Duty material at the right subjected to the same spalling test shows a loss of only three tenths of one per cent.

Hard burned super duty fireclay brick, as shown, displays outstanding resistance to spalling. During the hard firing which the brick undergoes in manufacture, it becomes exceedingly well bonded by the action of the heat, but due to its chemical purity, the glass phase which is developed and which produces the bond is of a high type that has great resistance to reversible thermal changes, imparting high spalling resisting properties to the brick. Therefore, less cracking and breaking of super duty refractories may be expected than is usually found in brick used to line this portion of the furnace.

The distance below the stock line to which this brick can be economically used is, of course, a variable depending upon the average conditions which exist in any given blast furnace. Some furnaces give more trouble in this area than others and in making definite recommendations as to the extent of this area it should best be worked out with the operators with regard to the severity of the service in the particular furnace under consideration.

MIDDLE INWALL

In the middle inwall section of the furnace a somewhat different set of conditions probably exist. In this area the temperatures on the face of the refractory may vary between 2400° F. in the lower part of the section to 1600° F. in the upper part. These temperatures are not excessive and it is usually noticed that the lining is not quite as badly worn in this area as it is above and below it, although this is by no means found to be the case in every lining. Even though the temperatures may not be considered excessive there is ample evidence that considerable reaction has taken place between the slag and the refractories at the interface. The brick usually used in this section are not quite as refractory as those used farther down in the stack and, therefore, could be expected to become soft and chemically reactive at somewhat lower temperatures. It is quite conceivable at times, because of uneven stock distribution, that channeling of the hot gases takes place, and parts of the lining in this area may temporarily become quite hot. This would accelerate the chemical reaction between the slag and the refractories. During this action, the slag may stick to the refractory lining and during subsequent operation this portion of the lining may cool down, thus, freezing the slag in place on the refractories. If the bonding of the slag to the refractories is strong enough this scab may remain in place, actually protecting the lining until some time when conditions again are such that the temperatures are great enough to melt off the scab, thus, again subjecting the lining to the slag and wearing conditions of the furnace. Both conditions of slag action and abrasion probably exist in this zone of the furnace and each do their share of destruction to the lining, gradually wearing it away.

After the lining has been in operation for a time and has been worn back to some extent, there is evidence that other actions have been taking place which affect the ultimate life of the refractories in this zone.

There is a zone in the refractory lining back some twelve to fourteen inches from the face where, due to the temperature gradient through the brick, the temperature drops to between 700° F. and 900° F., which was seen above to be the temperature where disintegration due to carbon monoxide takes place. Over a period of time the refractories in this area crack and break up due to this carbon deposition. Eventually the lining wears back to the point where this disintegration first took place. As it wears back further disintegration takes place back toward the shell of the furnace, so that from this time on the wearing surface consists of a broken and cracked lining which may in places be easily eroded away, and the failure of the lining greatly accelerated. The best means of overcoming this action is by the use of refractories which have better than average resistance to disintegration. This means refractories low in iron, and burned hard enough to make them immune to carbon monoxide.

Another action which has been receiving attention recently and which has been commented upon by several investigators[8,9], is the increase in alkali content of the refractories found in the lining at the end of a campaign. Analysis of these refractories disclose that they contain as much as 10% to 13% alkalies which, of course, are serious fluxes to refractories. This perhaps may not always occur in such large amounts but that there is evidence of this action can hardly be denied. These alkalies may be introduced into the furnace through the ore and the coke and subsequently be released and volatilized in the furnace so that they are forced into the lining, where they cool below their sublimation temperature and solidify in the brick.

[8] Kraner, H. M. Refractories service conditions in the blast furnace. J. Amer. Ceram. Soc., v. 25, p. 311-320 (1942).
[9] Hurst, T. L. Slag action of alkalies on refractories. Amer. Ref. Inst. Tech. Bull. No. 75 (July 1940).

As the lining wears back the refractory portion of the lining which has become saturated with alkalies becomes exposed to the direct action of the heat. The melting point of the refractories is considerably reduced due to the impregnation of the alkali salts, and the brick surface is no longer able to withstand as high temperatures as it would when originally installed in the furnace. It can, therefore, be seen that, at the temperatures which have prevailed in this zone, more reaction means an acceleration of lining wear.

In this zone it would, therefore, seem logical that the application of a higher quality refractory would offer promise of longer life. Missouri Super Duty Refractories have the physical properties which seem to be desirable. They are low in iron, which indicates high resistance to disintegration. This is borne out by Figure 25 which shows the disintegration test on this type brick. While not as good as hard burned, super duty, it still has excellent resistance to this action (Compare Figure 21).

Super Duty Brick are burned sufficiently hard to withstand the abrasive action of this zone of the furnace and compare very favorably with brick which are regularly used for furnaces in this respect. A comparison of this resistance may be obtained from the numerical resistance-to-abrasion figure (see Table II).

In the matter of alkali penetration which reduces the P.C.E. value of the brick, it appears quite evident that the application of brick such as this is a step in the right direction. This can readily be seen by comparing the true porosity after 2912° F. reheat as given in Table II for the various inwall quality fire brick. The brick are dense because of the proper grain sizing, deairing and extreme pressure applied during the forming operation. Therefore, there are less voids in the brick to be saturated with the volatile alkalies and, the P.C.E. value would not be reduced as much as would be the case in more porous brick. There is also an added benefit in the fact that the P.C.E. value of super duty brick is higher to begin with than brick ordinarily used in this zone of the furnace. Since the P.C.E. value is higher, it can suffer the action of the fluxing alkalies and still be a more refractory brick than is the case under the same conditions when present blast furnace brick are used. If it is less affected by the alkalies, longer life of this zone of the furnace could be expected by their use.

LOWER INWALL

The lower inwall often, but not always, shows the greatest signs of wear in the stack. No one has as yet definitely plotted all the various conditions which exist in this zone of the furnace. Any attempt to enumerate the reactions which take place in this zone and to determine the extent to which they take place will unquestionably meet with much contradiction. It is not our intention to talk in specific terms concerning it. There is sufficient evidence available to indicate that considerable chemical reaction takes place between the various slags produced and the refractories used to line the furnace. The temperatures in this zone are very high which, of course, is a condition which accelerates the chemical attack of the fire brick, through the increase in liquid phase of the refractory. Observation of refractories taken a short distance from the exposed face or slag face of linings in this area have shown the presence of nephelite or albite, along with appreciable amounts of anorthite and, in some cases, gehlenite formed in the interstitial areas around well developed mullite "islands". This, of course, is an indication of the reactivity of the glassy portion of the brick matrix with the blast furnace slags, which at the temperatures encountered in this area form a very soft, fluid slag. This mixture of slag and glassy phase of the brick reacts and being soft and fluid washes away the more refractory flint grains on the face of the refractory which had not before been completely dissolved. The flint grains which have been largely altered to extremely fine grained mullite crystals are more resistant to the chemical reaction of the slags, and if the whole brick produced a mineral pattern the same as the flint grains the brick should have considerably more lasting qualities in this area.

It is necessary here to refer back to the photo micrographs of the thin sections of the refractories which had been heated in the laboratory to very high temperatures in the absence of any contaminating slags or minerals. It was noted that the less refractory brick showed a greater proportion of rather clear glass, while the hard burned, super duty brick through the flint grains showed a rather continuous opaque section and indicated a very low glass content which, if it softened at all, would be very viscous and extremely unlikely to be as reactive chemically as the more fluid glass which would occur in less refractory brick. There is almost undisputable evidence that it is the glassy portion of the brick which is the least desirable under these conditions, indicating that brick of higher flint content would naturally be more resistant to the action of the slags in this area.

Hugill, Ainsworth, and Green[10] remark that, "The depth of corrosion increase as the alumina contents of the products (Brick) decrease. In this connection it is interesting to note that recent work by J. R. Raib and R. Hay on the viscosity of lime-silica-alumina melts shows that for $CaO:SiO_2$ ratios varying over a wide range the viscosity increases as the alumina content increases". From their tests it can be seen that there is less corrosion from synthetic blast furnace slags on brick of higher alumina content. It also brings out the fact that slags in general will be more viscous as the alumina content increases, and a slag which has greater viscosity will be less corrosive than one of nearly the same composition with less viscosity.

While this is a more or less acedemic approach to an analysis of what conditions exist and what reactions take place in this area, it is also worth while to look at the question from a more practical point of view. It is probably impossible, as Sweetser[11] indicates, to make laboratory tests that mean anything definite in connection with blast furnace operation. The final answer is found only by trying it in the furnace. But there are other indications that throw some light on it, such as the service of super duty brick in the bottom of a malleable iron furnace. In respect to the corrosive action of slags and the

[10] Hugill, W., Ainsworth, R. L., & Green, A. T. The action of slags on refractory materials. Iron & Steel Institute (British) Spec. Report No. 26, p. 356 (1939).
[11] Sweetser, op. cit, p. 162.

resistance of refractories to it, super duty brick have established a very excellent record in checkers and in the port linings of glass tanks. In this service very corrosive, low melting glasses are deposited upon the brick and, as is the usual case, attack the bond clay first, floating out the more refractory flint clays. It was for this service that the hard burned, super duty refractory was originally developed and the many successful installations of them is material evidence of their satisfactory economical service. If hard burned, super duty brick are so outstanding in this service it should also have good resistance to blast furnace slags which may be considered the city cousins of this glass tank slag.

Because, then, of the additional refractoriness of super duty brick over regular hearth and bosh quality, because of the density of hard burned, super duty brick which will resist the penetration of slags and permeating vapors, as well as the high mineral development of mullite which it possesses, we feel that its use is particularly well adapted to the lower portion of the stack and believe it will justify its use in additional service.

BOSH

The same conditions of service exist in the bosh area as are found in the lower inwall up fifteen to twenty feet from the mantel. The action upon the brick in all probability is the same as that in the zone above but in all probability this action is greatly retarded by the very high rate of cooling which is derived from the cooling plates used in this zone. At the end of a furnace campaign the bosh section is usually pretty well worn and requires a complete replacement, but it is seldom that a furnace is blown out because of a failure of the refractories here.

Since the heat treatment which the refractories receive is severe in the bosh it is believed that the use of super-duty brick is justified, but regular fired, super duty brick should be satisfactory to withstand this service as the extreme heat should form a highly developed mineral pattern in service. The regular burn, super duty quality brick is more refractory than that of standard Hearth and Bosh Quality and, therefore, should offer a greater factor of safety and make the bosh area last longer, to equal the longer campaigns which should be derived from the use of higher quality brick throughout the lining.

HEARTH

The refractories in the hearth of the furnace have some of the service conditions which exist higher in the furnace, although the temperature may not be as great as in the section above the tuyeres. The slag action on the refractories in the hearth may be somewhat more concentrated at this point where the slag accumulates and floats on top of the iron batch but there perhaps has not been sufficient data accumulated to differentiate accurately between the slag action at this point and at points higher in the stack. There is unquestionably some difference in service because the temperatures are somewhat lower and there is a certain amount of water cooling of the refractories, and because the slag has been somewhat more "satisfied" by an increased content of alumina which it has acquired by coming in contact with refractories as it descended through the stack. During part of the period between casts the refractories are somewhat protected from the radiated heat in the tuyere section above by being covered by the iron and the slag which is floating on top of the iron. This protection from radiated heat is more than might ordinarily be expected unless definite experience has been had with the effect of radiated heat.

Because of the relatively thin lining and the water cooling of the hearth jacket it is our opinion that the use of regular burn, super duty refractories in this area to be both desirable and economical, and will tend to balance the increased service from the higher quality refractories used higher in the furnace.

BOTTOM

The service conditions of the bottom are probably different from any other part of the furnace as far as the refractories are concerned. It is considered by some operators that the bottom refractories are more important than any other part of the furnace because in their particular furnaces trouble more often takes place here than other zones. This, of course, is not universal and many operators never experience any difficulty with bottom refractories at all, and seldom if ever experience break outs in this zone.

It is significant, however, that refractories used in this section of the furnace are equal to the most refractory used in blast furnace linings. Little information seems to be available about the actual conditions which are encountered in this section of the furnace. We have no record of information as to the rate of wear of the refractories in the bottom as we have in the case of the stack and our knowledge has largely only come from observation of the refractories which were left in the bottom at the end of a campaign. There have been many expressions as to what probably happens to the bottom during the campaign of a furnace but little information is definitely in the record. There have been many discussions as to just what percentage of the bottom is worn out and what percentage, if any, floats out but very little of positive evidence is available. Some will contend heatedly that many of the blocks in the bottom become loose because of one reason or another and are forced out of position and then float to the surface of the iron where they are eventually dissolved by the slag and leave the furnace through the slag notch in solution. Whether it is actually true or not, it is true that there are potential conditions in the furnace which could easily cause it to happen. With the trend towards larger furnaces which has developed within the last twenty-five years the furnace bottoms have, of course, become proportionately larger.

This means that there is less opportunity for the refractories in the center of the hearth to cool themselves by conduction of the heat to the surrounding ground and the cooling castings to be dissipated. As a result, there is a gradual build-up of heat in the bottom which has an important, if not serious, effect upon the refractories. It may be serious enough that if the blocks do not possess to a high degree the most desirable physical properties, they may be the direct cause for a failure of the bottom. The physical properties which are important with respect to bottom service are permanency of volume, refractoriness and density to say nothing of uniformity of size and symetry.

The fact that the bottom is not able to dissipate the heat to which it is subjected as is the case in the bosh area is, of course, the reason for the large amount of refractories which is used in the bottom. The heat treatment which these refractories receive is tremendous as is evidenced by the appearance of what is left at the end of a campaign. When the blocks are put into the furnace, they have a porosity of from 16 to 20 per cent and at the end of the campaign the brick twelve inches back from the working face, and farther, have absolutely zero porosity. This means that one of two things or both has taken place. Either the voids have been filled with iron or other vaporous elements which have soldified in the voids of the clay mass, or the block which has softened, has been so compressed due to the pressure which exists on them that the voids are completely eliminated. If the latter were entirely true it would mean that the volume of the block would have been reduced approximately one-fifty which would be considerable shrinkage from the original volume. If the actual facts were known it probably would be found that some of both actions take place. It is known that the refractories in the bottom are subjected to very high pressures and when it is considered that the refractories are plastic some distance back of the working face, it can easily be conceived that the brick could be compressed to zero porosity. It is also known that there is some deposition of free quartz in the bottom blocks which probably come from quartz which has been vaporized in the furnace conditions and entered the brick as vapor and solidified. Alkalis act in the same way and, therefore, the closer a block approaches zero porosity when installed the less will be the shrinkage or compression of the bottom blocks in service.

Super Duty Refractories are very dense and would permit less penetration of vaporous alkalies and also would have less volume shrinkage in the attaining of zero porosity. Computation has shown that there is actually 24% less potential volume shrinkage in super duty refractories than in many refractories now used in bottoms. This volume reduction of the brick is often referred to as shrinkage but in reality it is actually compression and, therefore, it is well to have a refractory which is resistant to compression under load and super duty refractories are better than ordinary refractories in this respect, especially under strong reducing conditions which exist in the blast furnace.

Another physical property which has some bearing on the permanency of volume as well as upon the rate of wear of the bottom is refractoriness. A brick which is more refractory will be less plastic and, therefore, will be less inclined to be compressed to zero porosity and will have a tendency to retain its original volume for a longer period of time. Super Duty Refractories are more refractory than other blast furnace refractories and, therefore, should more nearly meet the requirements of brick for this service.

The rate of wear of the bottom depends upon some of the same factors brought out above in consideration of the refractories for the lower stack such as the development of the glassy phase of the brick and its subsequent chemical reaction with slag. In the bottom of the furnace the evidence indicates that there is a constant movement of the iron in the salamander. This may be caused by convection currents set up in the iron. If this is so, then, it seems probable that this convection movement carries part of the slag down with it where it reacts with the refractories to form low melting complex alumina silicates, ($WNa_2O.XCaO.YAl_2O_3.ZSiO_2$). Samples taken from the bottoms of furnaces indicate this to be true. Large, well developed anorthite crystals have been identified at the reaction face between the salamander and refractories in very deep formed salamanders which indicates that calcium of the slag on the surface of the iron has been carried down to the bottom of the salamander and reacted with the proper constituents of the brick to form anorthite ($CaO.Al_2O_3.2SiO_2$). Anorthite can be readily formed by reaction of calcium with fire clay because in a high grade fire clay, irrespective of some free quartz and some alkali impurities which may be present, the clay substance is already largely combined in the proper proportion of alumina and silica (Al_2O_3 $2SiO_2$). It is, therefore, necessary to have a hard burn of the refractories to form as great an amount of mullite ($3Al_2O_3$ $2SiO_2$) grains as possible to cut down the corrosion of the alumina and silica molecules which is caused in the formation of anorthite. These grains should best be small and, many of them rather than few, well developed crystals.

From every consideration of the possible reactions and conditions which occur in this section of the blast furnace, it appears that the consideration of super duty fire clay refractories is justified. There may be a question of whether the hard-fired type is required for the whole bottom as it may be that due to the slow wear of the bottom, the brick are fired to a maximum in service and, thus, the hard burning might be produced in service. If this is the case, it hardly seems justified to pay for the additional burning when it can be accomplished in service at little cost. But aside from this point of view, there should be little question as to the fact that super duty brick should be employed in this section.

Conclusions:

From the many tests which have been run on Missouri Super Duty Brick, comparing them with standard blast furnace refractories, it can readily be seen that the better physical properties which these super duty brick possess indicate that they are more suitable to withstand the action of blast furnace service. Because of these better physical properties, longer blast furnace campaigns should be possible, and although the cost of an installation would be somewhat greater it should readily prove economical and would act as insurance, assuring safer and longer operation on any given campaign.

Fig. 16 - Resistance to CO of "A" $4\frac{1}{2}$ x 9 x 18"

Fig. 17 - Resistance to CO of "A" Inwall Quality

Fig. 18 - Resistance to CO of "A" Top Quality

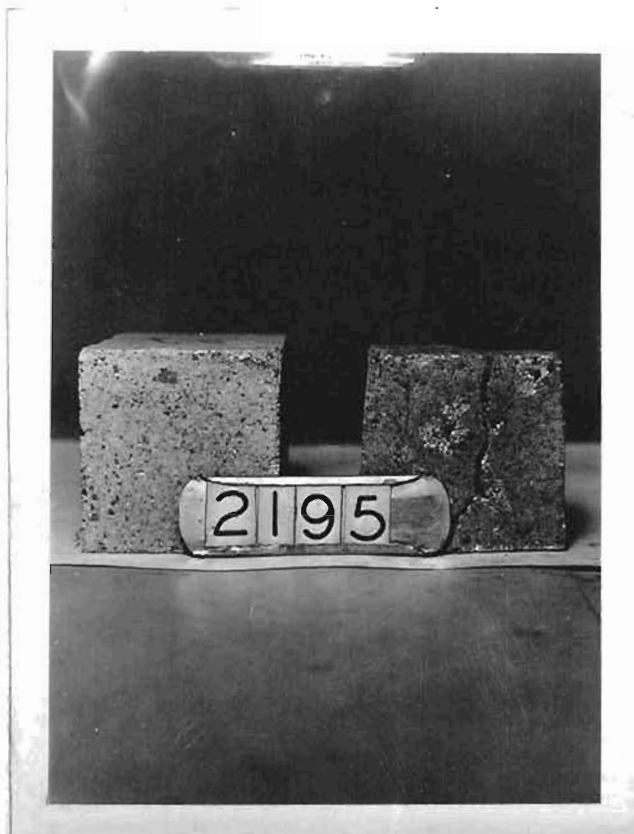

Fig. 19 - Resistance to CO of "B" Inwall Quality

Fig. 20 - Resistance to CO of "B" Hearth & Bosh Quality

Fig. 21 - Resistance to CO of Hard Burned, Super Duty, Missouri fire brick.

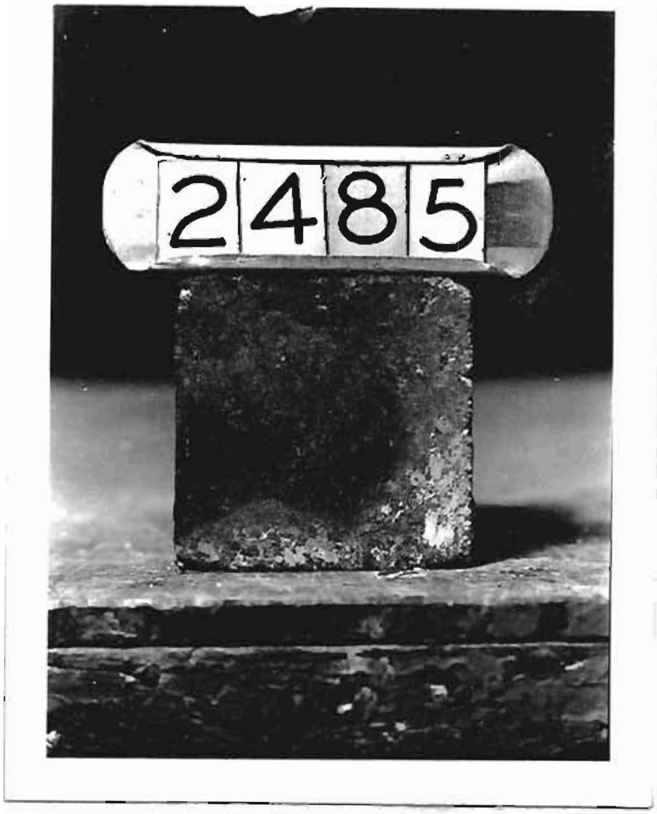

Fig. 22 - Resistance to CO of $4\frac{1}{2}$ x 9 x 18" hard burned super duty fire brick

Fig. 23 - Resistance to CO of "A" Hearth & Bosh Quality

Fig. 24 - Resistence to CO of Missouri First Quality fire brick

Fig. 25 - Resistance to CO of Regular Burn, Super Duty, Missouri fire brick

Fig. 26 - Polished Section
of Super Duty,
Missouri fire brick
Before Reheat
2X

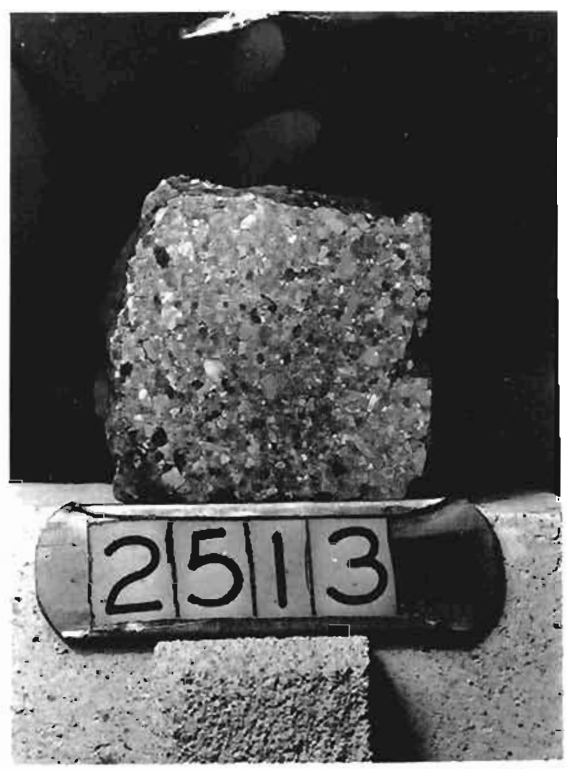

Fig. 27 - Polished Section of
Hard Burned, Super Duty
Missouri fire brick
Before Reheat
2 X

Fig. 28 - Polished Section of Super Duty Missouri fire brick ($4\frac{1}{2}$ x 9 x 18") Before Reheat 2X

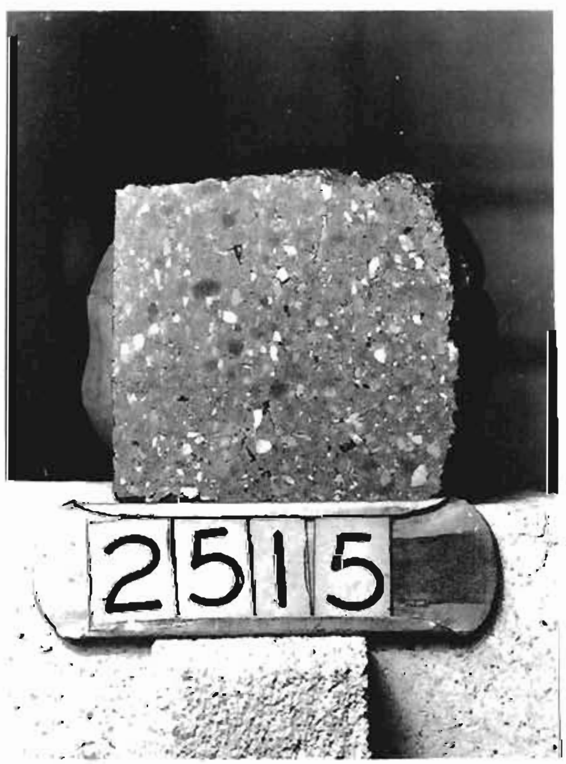

Fig. 29 - Polished Section of Hard Burned, Super Duty, Missouri fire brick ($4\frac{1}{2}$ x 9 x 18") Before Reheat 2X

Fig. 30 - Polished Section of "A" Inwall Quality fire brick Before Reheat - 2X

Fig. 31 - Polished Section of "A" Hearth & Bosh Quality fire brick Before Reheat - 2X

Fig. 32 - Polished Section of "B" Hearth & Bosh Quality fire brick Before Re-heat - 2X

Fig. 33 - Polished Section of "B" Inwall Quality fire brick Before Reheat - 2X

Fig. 34 - Polished Section of Missouri First Quality fire brick Before Reheat - 2X

Fig. 35 - Polished Section of Missouri Super Duty Inwall Quality fire brick After Reheat 2X

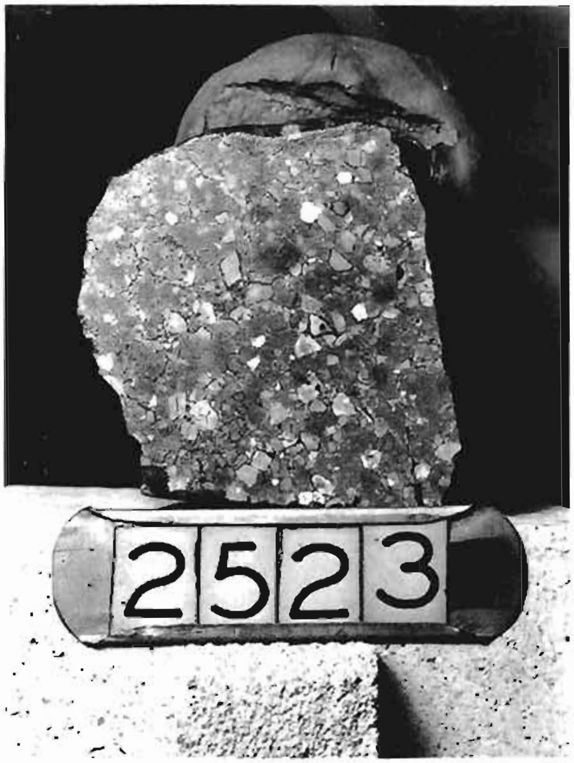

Fig. 36 - Polished Section of Hard Burned, Super Duty Missouri Inwall Quality fire brick After Reheat - 2X

Fig. 37 - Polished Section of Super Duty Missouri fire brick ($4\frac{1}{2}$ x 9 x 18") After Reheat 2X

Fig. 38 - Polished Section of Hard Burned, Super Duty Missouri fire brick ($4\frac{1}{2}$ x 9 x 18") After Reheat - 2X

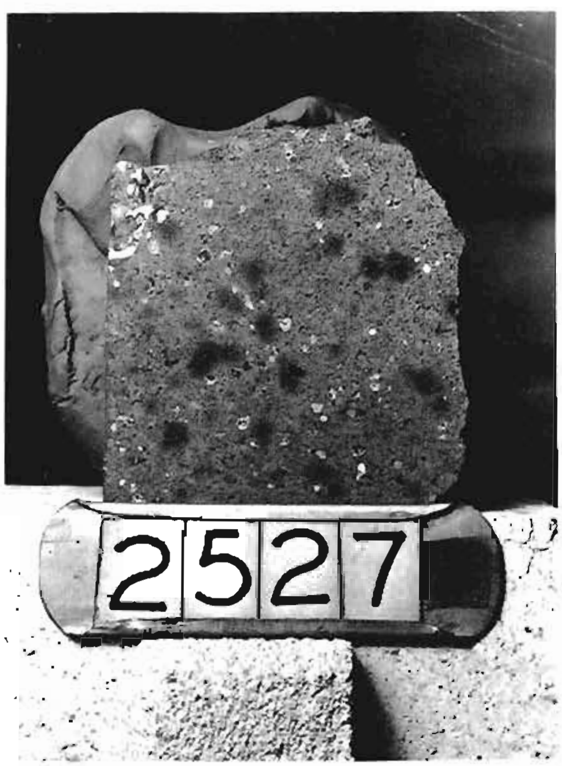

Fig. 39 - Polished Section of "A" Inwall Quality fire brick After Reheat - 2X

Fig. 40 - Polished Section of "A" Hearth & Bosh Quality fire brick After Reheat - 2X

Fig. 41 - Polished Section of "B" Hearth & Bosh Quality fire brick After Reheat 2X

Fig. 42 - Polished Section of "B" Inwall Quality fire brick After Reheat - 2X

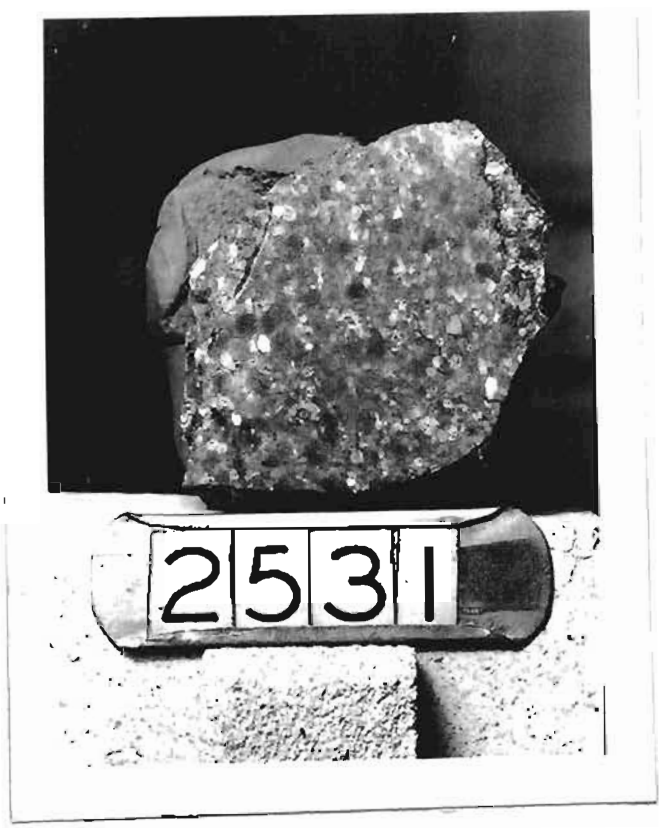

Fig. 43 - Polished Section of Missouri First Quality fire brick After Reheat - 2X

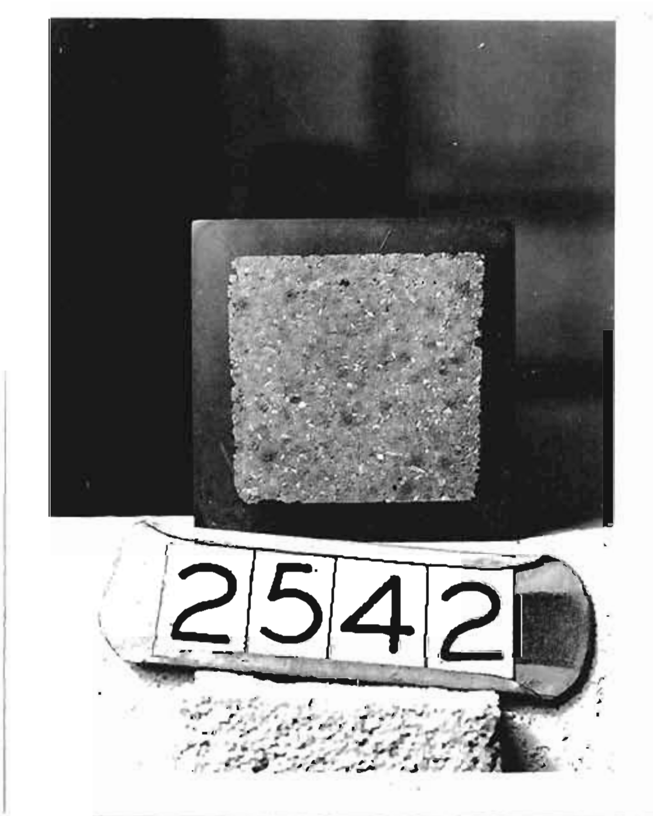

Fig. 44 - Polished Section of "A" ($4\frac{1}{2}$ x 9 x 18") Before Reheat - 2X

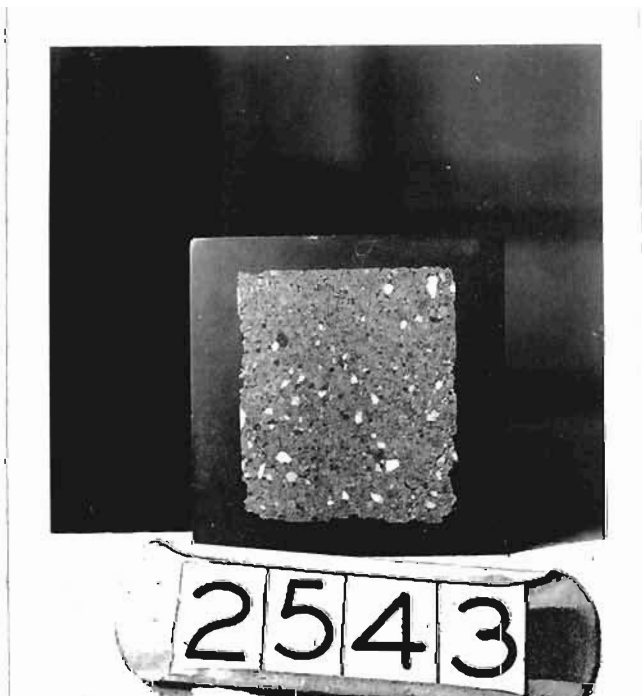

Fig. 45 - Polished Section of "B" ($4\frac{1}{2}$ x 9 x 18") Before Reheat - 2X

Fig. 46 - Polished Section of "C" ($4\frac{1}{2}$ x 9 x 18") Before Reheat - 2X

Fig. 47 - Polished Section of "A" ($4\frac{1}{2}$ x 9 x 18") After Reheat - 2X

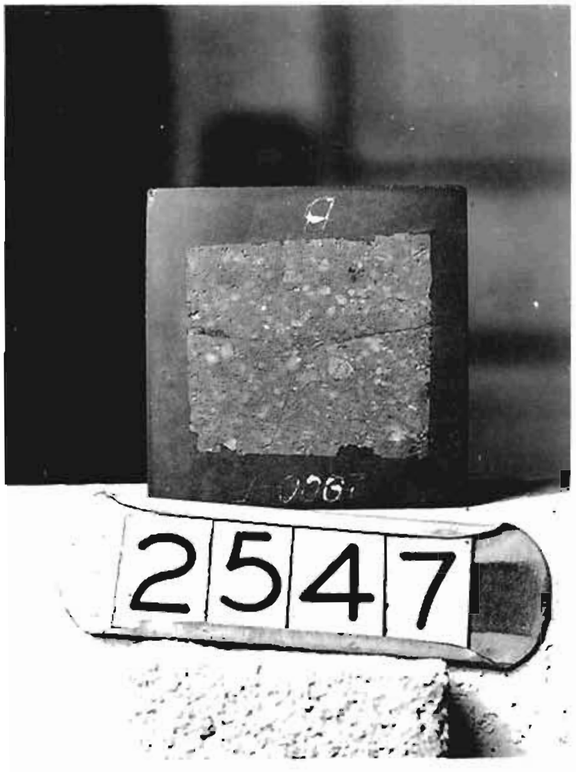

Fig. 48 - Polished Section of "B" ($4\frac{1}{2}$ x 9 x 18") After Reheat - 2X

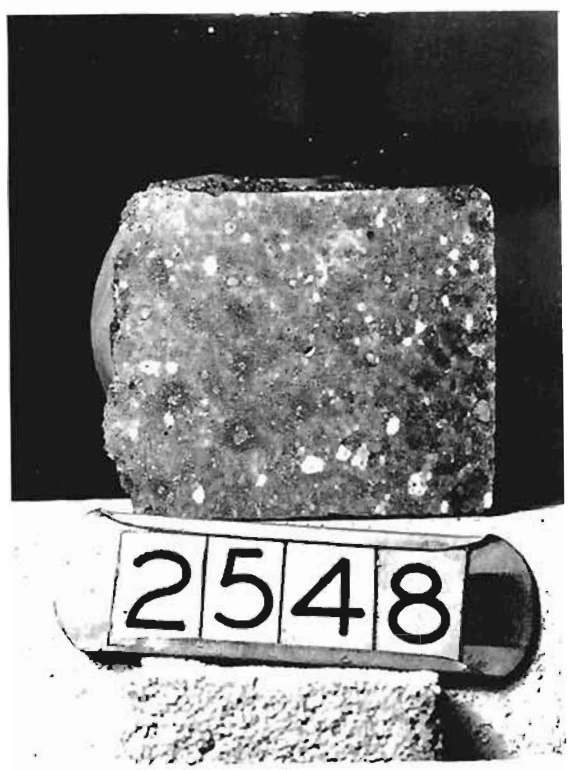

Fig. 49 - Polished Section of "C" ($4\frac{1}{2}$ x 9 x 18") After Reheat - 2X

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