

PERICLASE REFRACTORIES

D. Orderson

INTRODUCTION

Pitch impregnated magnesite bricks are used mainly in the "Basic Oxygen" Steelmaking process. A background of service conditions is necessary to understand what function is required of the refractories, and this is given briefly in chapter 1 to 3.

Chapters 5 to 7 are inseparably related. Chapter 9 is a project in its own right, but is included as background to the work reported in chapter 10.

Chapter 11 consists of PITCH IMPREGNATED PERICLASE investigations which are included as a matter of interest.

REFRACTORIES

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A project for the diploma in Ceramic Technology, Pretoria Technikon.

2. The L.D. Process.
3. Slagmaking Reaction.
4. Materials and Manufacture.
5. Chemistry By:- D. Onderstall
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7. Desirable Properties.
8. Determination of Pore Size Distribution.
9. Grading.
10. Development of an Improved Periclase Brick.
11. Examination of Bricks After Service.

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CULLINAN REFRACTORIES

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CHAPTER 1.

BASIC OXYGEN PROCESSES.

INTRODUCTION

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Chapters 5 to 7 are inseparably related. Chapter 9 is a project in its own right, but is included as background to the work reported in chapter 10.

Chapter 11 consists of extracts from two separate investigations which are included as a matter of interest.

C O N T E N T S .

Chapter	1. Basic Oxygen Processes.
	2. The L.D. Process.
	3. Slagmaking Reaction.
	4. Materials and Manufacture.
	5. Chemistry.
	6. Mechanism of Wear.
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The Rotor Process

The rotor is a large cylindrical vessel which rotates on its axis at about one revolution per minute. It can swing to the side to various positions to charge with iron, lime, scrap and other additives, and it can tilt to discharge. Lime is added several times as the slag builds off during a heat. The oxygen lance is inserted via the south end ports just below the slag-metal contact.

CHAPTER 1.

BASIC OXYGEN PROCESSES.

Steelmaking:

Iron is extracted from the ore in a blast furnace. The ore is mixed with coke and fluxing agents and placed in a blast furnace, where hot air burns the coke. High temperature and reducing conditions result in a two phase melt of metals and oxides. The phases separate by virtue of differential density into iron and slag and are tapped off separately.

To make steel, this "pig iron" must be purged of most of the impurities. Pig iron consists of Fe, Mn, Si, P, C and S. This was done by blowing air through the molten iron via nozzles in the bottom of a Bessemer converter. Later the Open Hearth furnace was developed as an alternative route. The Open Hearth is a regenerative gas fired furnace.

Lime (CaO) is added to the iron and floats on the surface forming slag. The slag slowly reacts with the impurities, absorbing them. Oxidising agents may also be added. The process is slow and the insulating effect of the slag makes it very inefficient.

If O_2 is directly added to the iron, the process becomes highly efficient, rapid and exothermic. Oxygen steelmaking is based on this principle, and several processes have developed since the mid 1950's, when cheap oxygen became available.¹ The various processes are, in broad outline:

1. The Linz Donawitz (L.D.) Process

Oxygen is blown through a water cooled lance at high velocity into an upright vessel. Old Bessemer vessels were used originally. Lime is added in lumps and is only discharged at the end of the 30 minute heat.

2. The L.D./AC Process

Similar to L.D. but slag is replaced once during the heat. This allows pig iron much higher in phosphorous to be treated. Powdered lime may be introduced via the oxygen stream. Variations are called "O.C.P. and O.L.P." process.

3. The Rotor Process

The rotor is a large cylindrical vessel which rotates on its axis at about one revolution per minute. It can swing to the side to various positions to charge with iron, lime, scrap and other additives, and it can tilt to discharge. Lime is added several times as the slag spills off during a heat. The oxygen lance is inserted via the mouth and rests just below the slag-metal contact.

4. The Kaldo Process

The Kaldo vessel rotates about its axis and inclines to charge and tap; the same motions as a concrete mixer. The rotation speed varies during the process, and is much faster than the rotor; up to 40 r.p.m. Slag is made and removed about four times during the heat, which allows an unlimited amount of phosphorous to be removed. The oxygen lance is inserted via the mouth and used similarly to the L.D. process.

Iron oxides removed with the slag are about 11%. The slag composition can be controlled so that there is only 4% iron oxide in the slag, but then it becomes so viscous that it holds up to 30% reduced iron in droplets in suspension.

5. The Ajax Process

The Ajax vessel is a modified open hearth furnace and still uses regenerative gas burners. No scrap metal is handled. Lance practice is similar to that used in the rotor.

6. The Q Bop Process

This process uses a vessel with a removable bottom, similar to a Bessemer convertor. Oxygen is blown through tuyeres in the bottom. The process is similar to argon oxygen decarburisation (AOD).

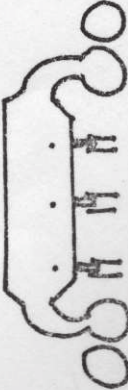
7. Direct Reduction

Highveld steel uses a direct reduction process. Vanadium is removed in a shaking ladle, oxygen lanced. The vanadium-rich slag forms on the bottom of the vessel, below the iron. Silicon is also oxidised at this stage. The iron is then transferred to an L.D. vessel. Since there is no silicon left to produce process heat, ferrosilicon is added to the iron.

The term BOF, or basic oxygen furnace, today refers largely to the LD converter, but all references to BOF's are largely applicable to all the above vessels.

In South Africa and Zimbabwe there are 10 LD converters and one rotor. Further discussion will thus centre on the LD process, which presently makes most of the world's steel.

References: 1, 2, 3, 4, 5 and 6.

Process	Vessel	Motion	Slag	CO	Characteristics
Linz Donawitz		Trunnion	Lumps	usually wasted	Extremely fast Dominant Basic Oxygen Process 30 minute cycle
LD/AC		Trunnion	Lumps and powder deslag twice	usually wasted	Fast, can remove higher P_2O_5 Popular in Europe
Rotor		Rotation tilt and swing	lumps splashes out	Burnt in vessel with secondary air	Vessel is easily accessible for charging, sampling etc. Messy. Few vessels left today.
Kaldo		Rotation and Trunnion	Lumps and powder made ± 4 times	Burnt in vessel with secondary air	Excellent for P_2O_5 removal, but very heavy refractory consumption. A popular process.
Ajax		Tilt	Lumps made once	Burnt with gas flame	Rather specialised, few in operation, no slag handled
QBop		Trunnion	Lumps and powder various stages	Recovered if used with protective gases	A very recent development. Popularity has increased rapidly so far.

CHAPTER 2.

THE L.D. PROCESS.

The L.D. Process was the first basic oxygen process developed and is today the dominant steelmaking process. It started in 1953 at Linz in Austria, and shortly afterwards at Donawitz. L.D. vessels today carry up to 300 tons of iron. The molten metal charge fills only one fifth of the vessel while at rest. Oxygen is blown onto the charge via a water-cooled lance at super sonic velocities. The tip of the lance is never actually below the level of the charge at rest, but at varying positions above the surface. When blowing commences, the metal and slag are churned up very violently into a froth of gas bubbles, slag and metal droplets. This froth almost fills the vessel and the surface contact area between the three phases is extremely large. This allows the reactions to proceed very rapidly, and makes L.D. the fastest steelmaking process, ten times as fast as the open hearth process.⁷

The oxidation of silicon in the metal provides most of the process heat. Lime is added to dissolve in the silica and reduce its viscosity and make to other impurities, particularly P_2O_5 , more soluble in the slag. Barrel

The vessel is blown in an upright position, and can be inclined by trunnions to tap the steel out of the taphole on the cone. Slag is removed by turning the vessel upside-down. Scrap-iron and iron ore may also be added to regulate the temperature or oxygen potential. Carbon is also removed as CO , and is taken off via an exhaust manifold or "hood".



Fig. 1 Cross-section of LD vessel.

Fig. 2 an LD plant layout, from Jackson.

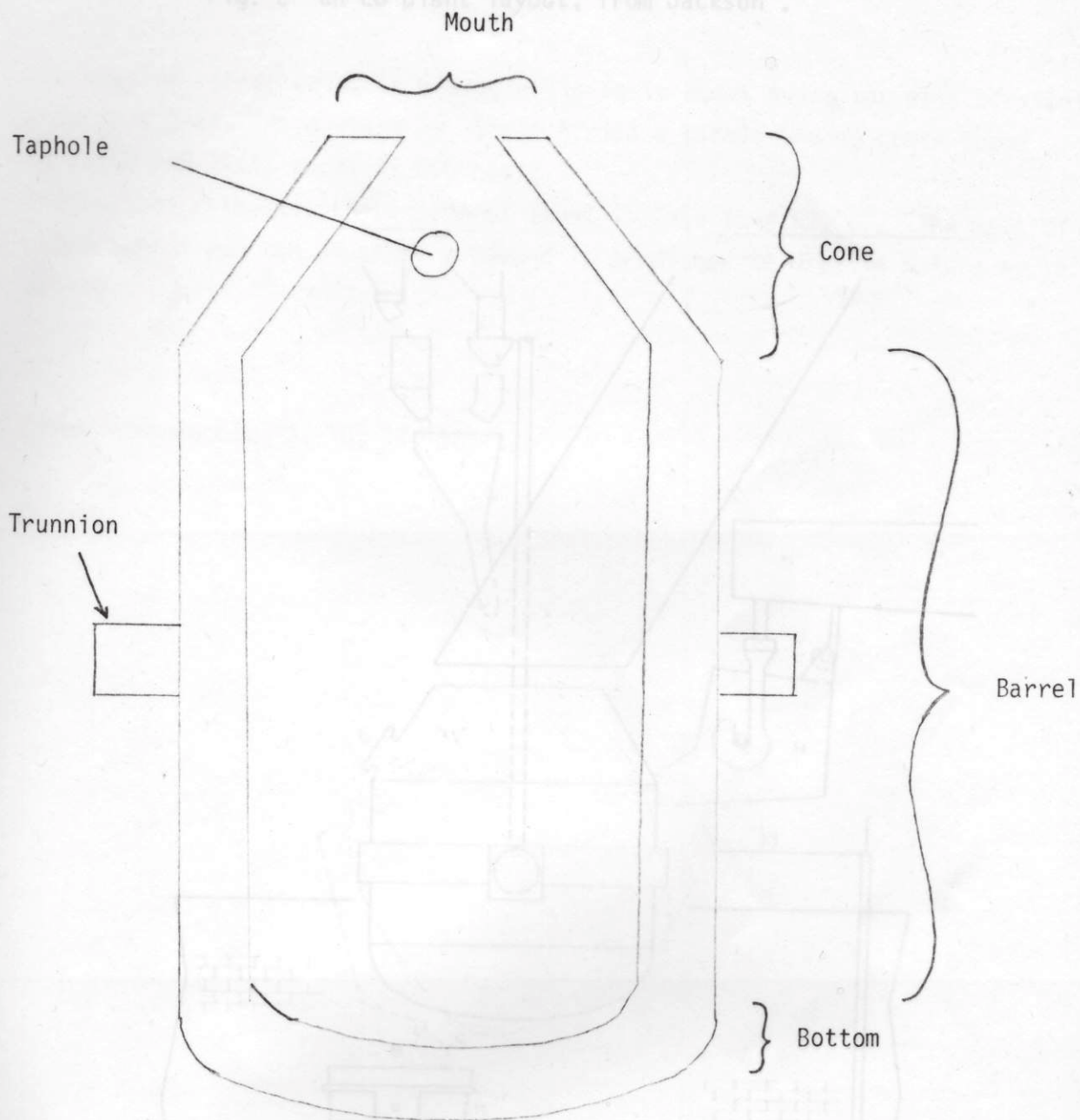


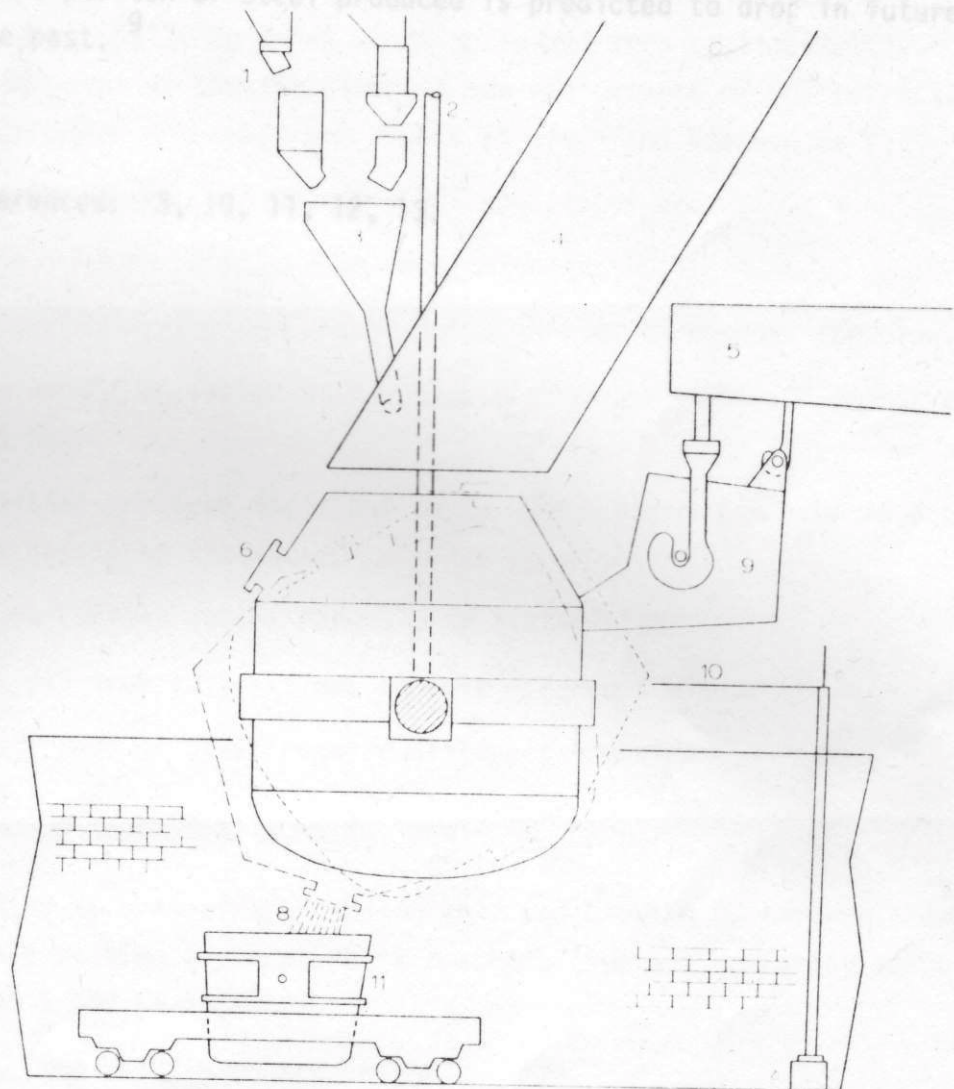
Fig. 1 Cross-section of LD vessel.

Fig. 2 an LD plant layout, from Jackson³.

The mass of refractories in a single lining is about twice the mass of steel made in a heat. At present in South Africa a single lining costs about R150 000 and lasts about 12 000 heats.

The cost of refractories per ton of steel is less than R1.00⁸. The mass of refractories per ton of steel produced is predicted to drop in future as it has in the past.⁹

Other references: 3, 10, 11



1 flux material hoppers; 2 oxygen lance; 3 flux charging chute for limestone, scale, etc.; 4 exhaust hood; 5 hot-metal crane; 6 refining position; 7 charging position; 8 tapping position; 9 hot-metal ladle; 10 charging floor; 11 teeming ladle

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Other references: 3, 10, 11, 12, 13.

1. The impact wear of scrap cannot be simulated.
2. The slag chemistry and percentage melt, changes throughout the blow.
3. The lance height is varied in the course of production, and cannot easily be scaled down.
4. Oxygen partial pressure distribution is poorly known and even if known could not easily be simulated.
5. Temperature cycling occurs randomly in a steel plant.
6. Different pig iron compositions produce different slags.
7. Different grades of steel require different operations.

The LD operation is basically as follows:-

1. A new lining is preheated by adding coke and blowing O_2 through the lance until the operating temperature is reached. (Average operating temperatures are around 1 590 to 1 640°C).
2. Pig iron, lime and fluxes are charged.
3. Scrap iron may be charged.
4. The vessel is returned to the upright position and the lance lowered through the mouth.
5. Oxygen is blown through the lance. (Modern lances generally have 3 orifices). The lance is always above the metal level, but the height may be varied.
6. Reaction takes place after a few seconds. The blow is extremely noisy and operators frequently regulate lance height, O_2 flow rate and time of blow according to the noise level.

SLAGMAKING REACTIONS

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Oxygen steelmaking is a complex process and refractory performance cannot be evaluated on a small laboratory test. An apparatus has been designed to simulate the operation of an LD vessel and a large laboratory rotor with a rammed lining was built by Kriek which performed very satisfactorily.¹⁴ The author has no means of testing directly the performance of BOF refractories. Other slag tests are described by Hubble et al.¹⁵ and Beechan et al.

The problems presented by simulating BOF conditions are:-

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2. The slag chemistry and percentage melt, changes throughout the blow.
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7. Different grades of steel require different operations.

The LD operation is basically as follows:-

1. A new lining is preheated by adding coke and blowing O_2 through the lance until the operating temperature is reached. (Average operating temperatures are around 1590 to 1640°C).
2. Pig iron, lime and fluxes are charged.
3. Scrap iron may be charged.
4. The vessel is returned to the upright position and the lance lowered through the mouth.
5. Oxygen is blown through the lance. (Modern lances generally have 3 orifices). The lance is always above the metal level, but the height may be varied.
6. Ignition takes place after a few seconds. The blow is extremely noisy and operators frequently regulate lance height, O_2 flow rate and time of blow according to the noise level.

7. The vessel is tipped forward and metal and or slag samples taken for analysis when it is thought that the steel is approaching its final composition.
8. Blowing may continue, to lower C, P or S content or to raise the temperature of the steel.
9. Hot metal is teemed into a teeming ladle below, through the taphole.
10. Slag is poured out through the mouth (Tap slag).

The slag charge is basically lime, but nowadays nearly always doloma as well, and flourite or iron ore may also be charged. The main compositional changes of the slag during the blow are:-

1. MgO moves towards its equilibrium concentration.
2. FeO increases.
3. SiO_2 increases, TiO_2 , P_2O_5 increase.

The slag is a cold solid charge and at turndown when the steel is teemed, there is usually some solid lime still present in the slag. The lime will not melt, but only dissolve into the slag as SiO_2 forms from silicon in the metal. This solution is hampered by the formation of a crust of refractory dicalcium silicate around the lime blocks. Flourite is added to dissolve this dicalcium silicate.

The extent of slag attack and consequent wear of the refractories depends on two factors:-

1. The solubility of magnesia in the slag.
2. The total mass of liquid slag.

The solubility of magnesia in the slag increases as the CaO/SiO_2 ratio falls, decreases as the FeO content rises and is not directly affected by CaF_2 content. These direct relationships are not directly applicable to practical steelmaking. For instance, CaF_2 does not have a noticeable effect on MgO solubility, but by dissolving C_2S it releases more CaO into the melt raising to CaO/SiO_2 ratio. This directly makes the MgO less soluble in the melt, but in fact the total mass of molten slag increases as the CaO is released and thus the total mass of MgO soluble in it increases. The same is true of FeO . FeO concentration rises particularly rapidly during a reblow to raise the temperature, and generally a high FeO content is associated with a hot, fluid, highly corrosive tap slag. There are many papers dealing with slagmaking practice.

Generally speaking, the best practice for conserving refractories is to aim at a tap slag which is saturated with MgO . This saturation points is usually

calculated by the operators by their own empirical formulae and doloma is included in the slag charge to provide the necessary MgO . The saturation point is normally in the order of 6 - 8% by weight. For these calculations to be made accurately, various factors must be known:-

1. Chemical composition of the lime charge.
2. Chemical composition of the doloma charge.
3. Blast furnace slag carry over, mass and chemistry.
4. CaO contribution when calcium carbide injection is practiced in the torpedo ladle for desulphurisation.
5. Percentages of silicon and other metalloids in the pig iron.
6. Final chemistry of the steel.

These figures are all available during operation, but the mass of tap slag is not available, and since there is carry over from one heat to the next, loss of refractories and previously carried over tap slag, the mass of slag cannot be directly measured. The mass can also not be calculated from the CaO analysis, as there is usually some solid CaO left in the slag and the analysis is therefore not representative. The best method of calculating slag mass has been found to be that based on a SiO_2 balance.

Unfortunately the viscosity of the slag rises sharply as it reaches the MgO saturation point, and becomes less efficient for the metallurgical process. MgO will actually be deposited by an oversaturated slag. MgO rich slags sometimes build up the bottom of a vessel since the slag cools during teeming. The viscosity of a slag becomes increasingly temperature dependent as the MgO level increases.

Slagmaking practices are similar for all oxygen steelmaking processes, the main differences being:-

1. In rotor vessels and LD/AC the slag may be tapped and charged several times.
2. LD/AC, Kaldo, rotor and Q. BOP use powdered lime additions via the oxygen.

Another aspect of good operation is ensuring that the vessel does not cool down excessively between heats.

A recent development has been the invention of a "sub lance" for taking samples and temperature whilst the blow is in progress.

Lime may be high fired "hard burnt" lime with a coarse crystal structure or a lower fired more highly reactive lime. The latter goes into solution more rapidly and completely and accelerates refractory erosion.

CHAPTER 4.

MATERIALS & MANUFACTURE

Refractory erosion is greatest at the beginning of the blow and the end. (First 12% and last 25%).

It is interesting to note that improved refractories and operating techniques have led to dramatic improvements in lining life. In the early 1950's when the LD vessel was invented, a lining lasted about 40 heats. In 1968 Americans achieved 1004 heats per lining. By 1976, Nippon Steel Corporation had achieved 10110 heats, with gunned maintenance and careful operation.

REFERENCES: 2, 3, 11, 14 to 24.

Between doloma and magnesite, there is another refractory, often called "Magdol". This is often made in Japan, by addition of seawater $Mg(OH)_2$ to doloma to obtain 70% to 75% MgO co-clinker. Indoloma, the MgO and CaO form discrete phases in the clinker, and at the Magdol composition, the MgO phase is sufficiently dominant to completely encapsulate the CaO phase.²⁵ The melting point of doloma is roughly $2300^\circ C$ and magnesite $2800^\circ C$.

Magnesite is obtained from two sources, namely magnesite $MgCO_3$, and from seawater. Seawater magnesite is obtained by reacting the concentrated brine with doloma.



The $Mg(OH)_2$ is calcined at $1650^\circ C$ to $1750^\circ C$ to give "dead burned" magnesite. With higher temperature and firing time, sintering progresses further, yielding larger crystal size and higher density. This gives greater hydration resistance and chemical resistance. Seawater magnesite is very pure. Boron occurs in higher concentrations in seawater magnesite than in that derived from magnesite. As little as 0.1% B_2O_3 lowers the hot modulus of rupture of magnesite brick from $1000^\circ C$ upwards.²⁶ However, B_2O_3 aids sintering and has a beneficial effect on hydration resistance. It is necessary to have some impurities in the raw material to allow the grain to sinter.

Pure magnesite, periclase, can be made by fusion in an electric arc furnace. Silica and iron migrate outwards from the melt. The process is stopped before the whole charge melts. The lump of fused magnesite is removed after cooling and the impurities physically removed from the outside of the lump.²⁷

Natural magnesites vary greatly in composition and mode of occurrence.

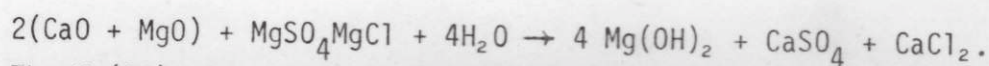
CHAPTER 4.

MATERIALS & MANUFACTURE.

BOF refractories range from doloma to magnesia. Magnesia is more expensive but gives longer life. The choice of refractory is thus a question of economics. Apart from direct cost and availability of the materials, availability of the vessel is a very important factor. In a steelworks operating only one secondary steelmaking vessel, the downtime for relining, causes a complete stop in production, and a longer lining life is thus very important. Magnesite would thus be chosen. The economics are discussed by Hardy.¹⁰

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Natural magnesites vary greatly in composition and mode of occurrence.

The main impurities are silica and lime, and aluminium and iron are normally minor impurities.

The problem of hydration is much more severe in doloma bricks, as CaO hydrates very readily and water based binders cannot be used.

Magnesia refractories for BOF's are made in three ways:

1. Pitch impregnated. The brick is pressed with an organic binder and fired to 1600 - 1800°C and then impregnated with hot pitch.
2. Tar/Pitch Bonded. The material is heated and mixed with hot tar or pitch and pressed into brick.
3. Tar/Pitch Tempered. The above bricks may be coked before being sold. They are fired in a reducing atmosphere and all the volatiles are driven off. Polymerised carbon remains as the binder and imparts considerable strength.

Budnikov²⁷ pp. 265 -270 describes in detail the considerations of firing magnesia products.

References: 10, 25 to 30.

CHAPTER 5.

CHEMISTRY.

The ideal composition of a BOF refractory would be pure periclase, with a melting point of $\pm 2800^{\circ}\text{C}$. This would have to be fused cast, as pure periclase grain sinters slowly.

Such a brick would be prone to spalling. Fused magnesia grain is rarely used for economic reasons. A well sintered grain is normally washed out of the brick by slag attack of the more porous matrix long before the grain itself dissolves. In high purity magnesia refractories the full refractory potential of the grain is never realised, and nearly all modern developments are concentrated on improving the matrix.

Periclase as a mineral is very pure, the only oxide which will readily go into solid solution with MgO being FeO , and even then only under certain conditions.³¹

The size of the periclase crystals within the aggregate grains is also of little importance since the large grains are washed out intact into the slag. The chemical purity of the brick is thus relevant only to the slag resistance of the matrix. This resistance to slag attack is determined by the following:

1. Mineralogical composition.
2. Physical structure of the brick.
3. Effects of the carbon.

We are presently concerned only with the mineralogical composition.

Usually SiO_2 and CaO are the main impurities, and their ratio is critically important. The amounts of these oxides should be as low as possible and the molar ratio of CaO to SiO_2 should be 2:1 or greater. If the ratio is correct, dicalcium silicate will form, which is highly refractory. (Melting point $\pm 2150^{\circ}\text{C}$). It is better to have a slight excess of CaO and form some tricalcium silicate and reduce the chance of forming Monticellite or Merwinite. The ideal ratios for different total percentages and firing temperatures are given by Webster and Jackson⁶ p. 238. A brick containing 1% SiO_2 and 1% CaO will form melt at a lower temperature than one containing 2% SiO_2 and 4% CaO . However, after slag penetration, the second brick will contain more melt, since both the SiO_2 and CaO will be dissolved in the slag.

Alumina is usually present in small quantities and nothing can be done about it.

FeO is usually present in small quantities, and in fairly large quantities in Breunnerite, as in Austrian magnesites. FeO goes into solid solution in periclase if fired in an oxidising atmosphere and migrates out in a reducing atmosphere. The FeO in solid solution enhances hydration resistance.³¹

Fig. 3 shows the desirable and undesirable binder phases.³² Further phase diagrams of systems containing MgO can be found in Rait,³⁵ Alper³⁴ and Chesters.³⁰

The binder phases can be summarised as follows, largely from Ford.¹⁵

CaO/SiO ₂ ratio	Silicates	R ₂ O ₃
<1,0	Fotsterite and Monticellite	Spinel MgO Al ₂ O ₃ + MgO Fe ₂ O ₃
1,0	Monticellite	
1,0 < 1,5	Monticellite and Merwinite	
1,5 < 2,0	Merwinite and Dicalcium silicate	
2,0	Dicalcium silicate	Dicalcium ferrite
>2,0	Dicalcium silicate and Tricalcium silicate	

Kriek et al³³ discuss the mechanisms and effectiveness of various oxides as sintering aids and show TiO₂ to be by far the most effective.

CaO-MgO-SiO₂

FIG. 278.—System CaO-MgO-SiO₂ (primary phases and isotherms). Merw—merwinite; Mo—monticellite.

R. W. Ricker and E. F. Osborn, *J. Am. Ceram. Soc.*, 37 [3] 134 (1954).

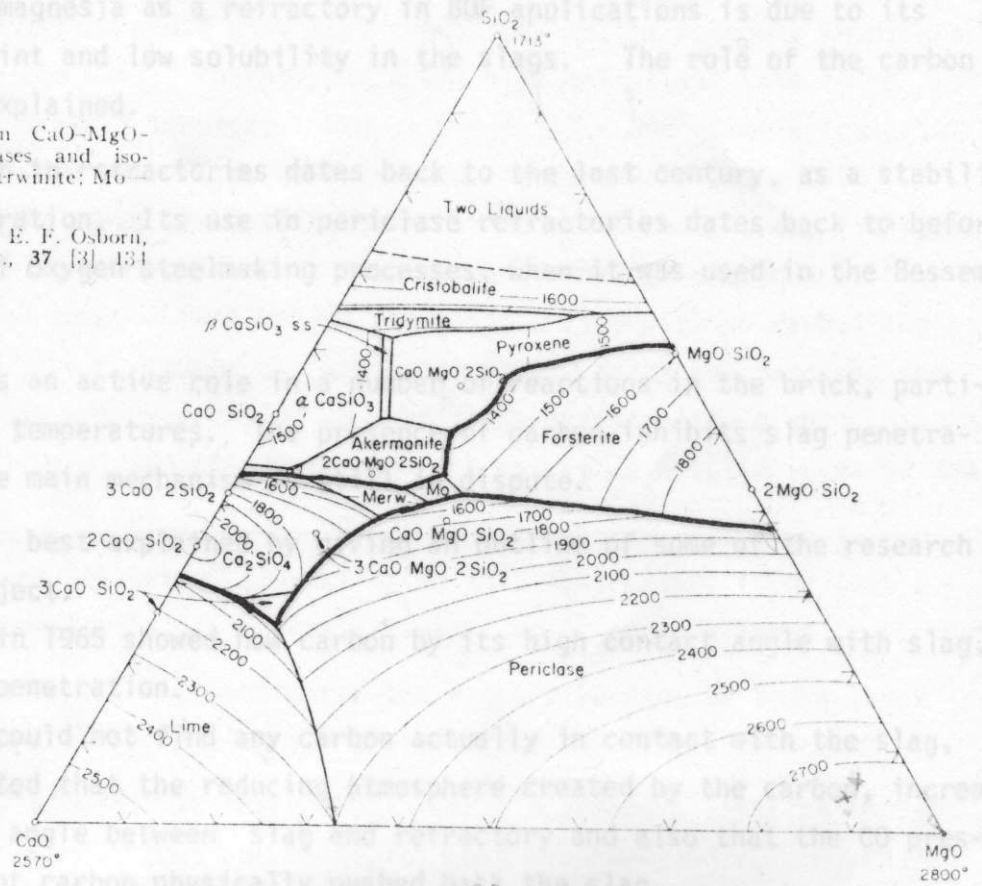
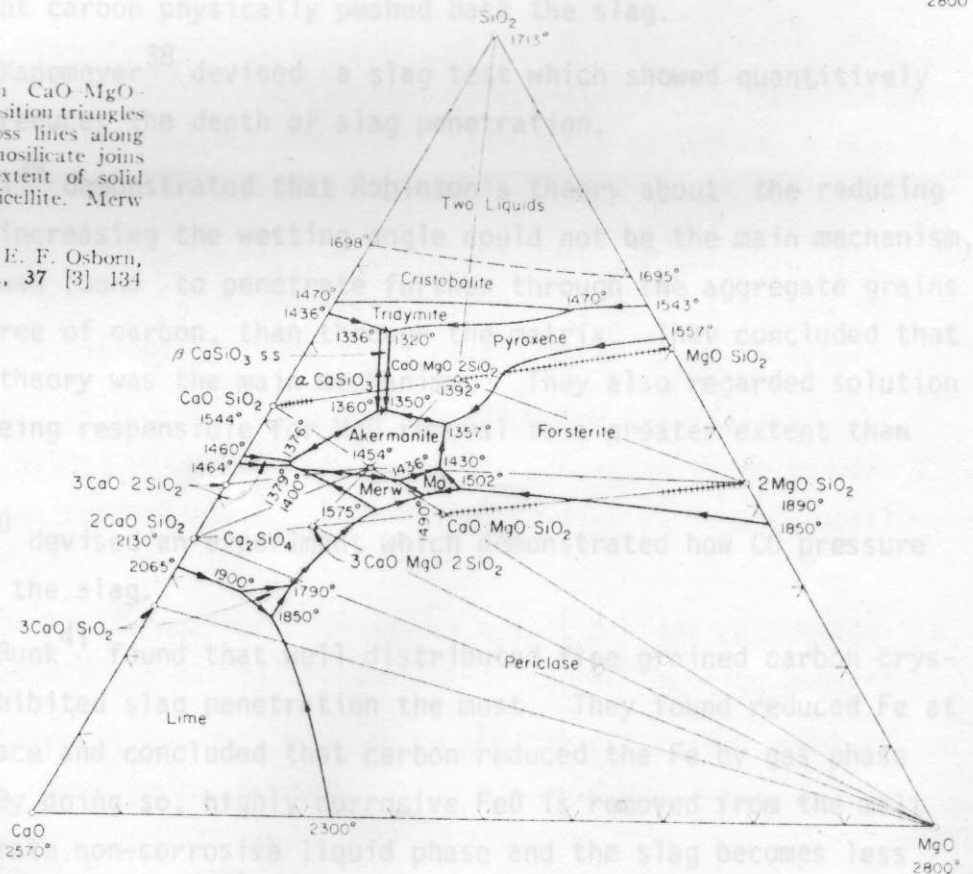


FIG. 279.—System CaO-MgO-SiO₂; showing composition triangles (revised). Short cross lines along metasilicate and orthosilicate joins indicate maximum extent of solid solution. Mo—monticellite. Merw—merwinite.

R. W. Ricker and E. F. Osborn, *J. Am. Ceram. Soc.*, 37 [3] 134 (1954).



MECHANISM OF WEAR.

The success of magnesia as a refractory in BOF applications is due to its high melting point and low solubility in the slags. The role of the carbon remains to be explained.

The use of pitch in refractories dates back to the last century, as a stabiliser against hydration. Its use in periclase refractories dates back to before the invention of oxygen steelmaking processes, when it was used in the Bessemer process.

The carbon plays an active role in a number of reactions in the brick, particularly at high temperatures. The presence of carbon inhibits slag penetration, though the main mechanism is still in dispute.

The theories are best explained by giving an outline of some of the research done on the subject.

1. Barthel³⁶ in 1965 showed how carbon by its high contact angle with slag, stops slag penetration.
2. Robinson³⁷ could not find any carbon actually in contact with the slag, and speculated that the reducing atmosphere created by the carbon, increased the contact angle between slag and refractory and also that the CO pressure of burnt carbon physically pushed back the slag.
3. Hubble and Kappmeyer³⁸ devised a slag test which showed quantitatively how carbon reduces the depth of slag penetration.
4. Herron et al³⁹ demonstrated that Robinson's theory about the reducing atmosphere increasing the wetting angle could not be the main mechanism, since slag was found to penetrate further through the aggregate grains which are free of carbon, than through the matrix. They concluded that Barthel's theory was the main mechanism. They also regarded solution of MgO as being responsible for MgO removal to a greater extent than erosion.
5. Gans et al⁴⁰ devised an experiment which demonstrated how CO pressure pushed back the slag.
6. Herron and Runk⁴¹ found that well distributed fine grained carbon crystallites inhibited slag penetration the most. They found reduced Fe at the brick face and concluded that carbon reduced the Fe by gas phase reaction. By doing so, highly corrosive FeO is removed from the melt into a separate non-corrosive liquid phase and the slag becomes less fluxed.

7. Brezny and Landy⁴² discovered by accident a mechanism hitherto undetected. During coking experiments, they found that the brick had picked up addition SiO_2 . The silica could only have come from the thermocouple housing or the ash in the coal. Thermodynamic calculations showed this to be possible at the temperature involved: $\text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO}$. Similar calculations showed that MgO could also be reduced at temperatures above 1600°C . Since this is above the boiling point of magnesium metal, the liberated Mg would be in vapour phase. This accounts for the presence of the decarburised zone, a zone behind the slagged face with no carbon and high porosity. The Mg vapour diffuses through the brick and is deposited again as MgO wherever the O_2 potential is sufficiently high. This condition exists at the slag face and the result is a solid layer of MgO between the slag and decarburised zone.
8. Pickering and Batchelor⁴³ investigated this further and found that a brick can completely disintegrate if this reaction is allowed to proceed.
9. Leonard and Herron⁴⁴ investigated the factors leading to dense layer formation and its effect on the various types of BOF refractories.
10. Carniglia⁴⁵ showed that there are a number of factors limiting the progress of this reaction, but concluded that the reaction was indeed important.
11. Webster and Jackson²⁶ showed that non-impregnated bricks are susceptible to spalling. They suggest that Fe_2O_3 is reduced to FeO which goes into solid solution with MgO , preventing the formation of low melting point ferrites.
12. Baker et al⁴⁶ showed that the lower partial pressure of oxygen in the A.O.D. process is insufficient to allow the dense layer to form.
13. Baker et al⁴⁷ extended work on the reduction and volatilisation of refractory oxides by carbon, and found the mechanism to be at work with CaO in doloma refractories. They failed to find it in aluminosilicate refractories.*
14. Limes⁴⁸ speculated that the detrimental effect of high FeO content in slags is largely due to its consumption of carbon in being reduced.

The dense layer is now widely accepted and the author has observed two consecutive dense layers formed within a single specimen.

*The author has found several dramatic examples of silica volatilisation and formation of an impervious spheroidal dense layer in aluminosilicate insulating refractories.

The most interesting demonstration of MgO volatilisation is a phenomenon described by Pickering and Bachelor,⁴³ and has been observed at Cullinan Refractories when large pitch impregnated bricks have been refired. If the carbon is not yet burnt out when the temperature is reached where MgO and C become unstable, volatilisation of MgO begins.

The Mg vapour is deposited at the surface of black core of unburnt carbon, eventually sealing it off in the same manner as the slagged face of a brick is sealed off by dense layer formation. Volatilisation continues and the core becomes filled with Mg vapour and CO under considerable pressure. The core expands under this pressure, since the brick is already somewhat plastic at this high temperature. The surface of the brick cracks open and the gas bubble of the core erupts through the crack. The Mg vapour reacts instantly with oxygen in the furnace atmosphere and is redeposited as MgO. A ring of MgO thus forms around the point where the gas bubble bursts, and subsequently more MgO is deposited on top of the ring and this continues, the result being a tube of MgO. The visual appearance of such a brick can be very dramatic. The tube growing from within the crack resembles a sprouting potato. The tube tapers to a fine point as the gas flow slows down, and the tube grows in the direction of gas flow in the kiln.

15. Kriek et al¹⁴ studied the method of wear of rammed magnesia rotor linings. They found spalling in three layer cycles, associated with mineralogical changes caused by migration of oxides within the brick. This type of spalling does not occur in pitch impregnated refractories. The author has reason to believe that the solid state transformation of periclase to magnesioferrite (MgOFe_2O_3) may occur on the brick face. This would be accompanied by a volume expansion which could potentially seal off the surface of the brick and be of considerable significance. This could only be examined by electron microprobe analysis.

MECHANICAL WEAR:

BOF refractories are subject to various types of mechanical wear, and vessel linings are designed with this in mind.

1. Impact breakage by scrap iron: This takes place when the vessel is inclined, and the scrap is dropped in via the mouth onto the area called the charge pad. This area is lined with fired impregnated periclase or doloma bricks.

2. The cone is subject to abrasion by flying particles which pass into the hood. The top of the cone is occasionally lined with fused cast periclase, for its abrasion resistance rather than refractoriness.
3. Spalling on first heat. This is prevented by preheating the vessel with a coke charge and firing it with oxygen through the lance.
4. First, Second and third order peeling. This phenomenon is very pronounced in unimpregnated brick, and has been investigated in detail by Kriek et al.¹⁴ It is caused by mineralogical changes and the development of zones on the brick face. These zones are very narrow in pitch impregnated brick, and although peeling does occur it is not nearly on the same scale.
5. The trunnion area is subject to more mechanical stress than the rest of the vessel, and is usually lined with higher quality brick.

Vessels are designed so that wear will be evenly distributed, and, theoretically, the whole lining should fail at the same time. Linings consist of two parts; the outer safety lining and the inner working lining. When the first holes threaten to appear in the working lining, they are usually gunned. Gunning continues until a considerable portion of the lining is approaching failure. Then the whole working lining is removed and replaced.

It is very difficult to measure the wear on the working lining, and a laser device has been developed to measure the wear from a distant fixed mounting. Measurements are accurate to within 5mm and can be made at any temperature, but are restricted to the floor of the vessel.⁵⁰

Sometimes the metal frame of the cone section deforms if it becomes too hot. This presents difficulties in fitting the brick lining into place. Deformation of the cone cannot be repaired, but can be prevented by water cooling via pipes welded onto the cone.⁴⁹

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DESIRABLE PROPERTIES

When considering the ideal properties of most refractories, it must be remembered that the properties cannot be produced independently; they are related and a compromise has to be found in many cases. For instance, the densest possible brick usually has the greatest resistance to slag attack and the worst resistance to spalling. Other properties are satisfied by the same conditions, i.e. if the highest bulk density is achieved, the highest crushing strength is usually also achieved. Thus it is never necessary to control each property of a particular brick, but only those which are most important, can be controlled, and which determine the other properties. In the case of periclase bricks, the author feels that chemical composition and microstructure are the fundamental properties which control all the others. One cannot be dogmatic about ideal properties, since they vary with different applications and conditions, e.g. a certain brick may perform very well in an L.D. vessel, yet the same brick may tend to spall in a rotor. So the compromise between density and porosity can change for different applications. The "ideal" brick can sometimes be recognised, but is not made, for economic reasons. If the "ideal" brick would last 1000 heats, yet a brick lasting 700 heats could be made at half the cost, it would seem senseless to make the "ideal" brick. This is still an oversimplification, because there are other costs involved. Taking a vessel off line to reline it is extremely expensive and may sway the balance in favour of the more expensive brick.

Ultimately, what is required of a brick is that it should give the lowest cost (of refractories used) per ton of steel produced. Steelmakers are becoming increasingly aware of the importance of good workmanship in lining vessels⁹. In order to obtain a good lining, the bricks must be made to close tolerances of size and shape. Dimensional tolerances can be considered as one of the fundamental physical properties of a refractory.

Webster and Jackson classify the properties of refractories into; physical properties; mechanical properties; chemically quality and cost. Physical and mechanical properties are further subdivided as follows:

	Physical		Mechanical
1.	Porosity and Bulk Density.	1.	Crushing Strength.
2.	Pore size.	2.	Creep in Compression.
3.	Thermal Expansion.	3.	Modulus of Rupture.
4.	Permanent Linear Change on Reheating.	4.	Creep in Torsion or Bend.
5.	Refractoriness.		
6.	Thermal Conductivity.		
7.	Specific Heat.		
8.	Accuracy of size and shape.		

It can be seen that mechanical properties and resistance to slag attack are dependent on physical properties and chemical quality. Note that the only property in the table above that is directly controlled by the manufacturer is accuracy of size and shape. Half of the physical properties are automatically determined by periclase, namely thermal expansion, permanent linear change on reheating (theoretically zero), thermal conductivity and specific heat. Refractoriness is determined by chemical quality. Porosity and bulk density are very important and are within the manufacturer's control. The grain density of the magnesia is important. With fused grain a brick porosity of 12% can be achieved by conventional pressing, whereas with low grain density it may be 20%. The other factor controlling density is the grading.

The last physical property is "pore size".

Pore size varies widely within a brick, and "pore size distribution" would be a better term for the property. The author has evidence that this is still inadequate, and proposes "microstructure" for this property, and further divides this into "bonding", "parting" and "cracking". (See chapter on experimental work).

Several papers 41, 51, 52, 16 and 53 have dealt with the pore size distribution of pitch impregnated periclase refractories. The pores in a brick are interconnected and all conventional bricks are completely permeable. Most of the permeability is due to the larger pores and they are the most detrimental, since they allow slag to penetrate into the brick, and chemical attack proceeds over a very much larger area, causing the brick to wear faster by dissolution of MgO and erosion of grains intact into the slag.

Slag also penetrates the brick via the smaller pores, but it seems to be established now that it is desirable to have fine pores in pitch impregnated periclase bricks. It also seems to be established that this is because the fine pores have a beneficial effect on the retained carbon. According to Herron and Runk⁴¹, fine pores result in well distributed and finely crystalline carbon. Bricks with this structure are shown to have a better resistance to slag. The general conclusion is that total porosity should be as low as can be made by conventional pressing, the pores should be as fine as possible and what pores there are should contain as much carbon as possible. A fine raw material grading results in a fine pore size distribution. High firing temperatures tend to result in elimination of fine pores in favour of larger pores. Finer pores are also said to result in lower hot strength.⁵³ High chemical purity will reduce the extent of sintering and avoid the large pores which form during high temperature firing. Many advances can be expected in the near future in the technology of getting more carbon into the brick. The established technique is to heat the brick and the pitch and immerse the brick in the pitch. This may be augmented by placing the brick in a chamber, evacuating it, running the pitch in and then pressurising it. Even without vacuum and pressure, the brick pores become virtually saturated with pitch. When the brick is heated in service, the volatiles are driven off and the remainder of the pitch becomes coked. Coke oven pitches are known to yield more retained carbon than others, due to their higher initial carbon content and greater percentage of aromatics.^{5,54.}

On coking, the pitch forms liquid crystals, or a "mesophase".⁶⁰ Carbon yield has been improved by adding carbon black or calcium nitrate to the pitch. A novel technique has been proposed by Bradt et al.⁵⁵ This is chemical vapour deposition (CVD) of carbon. A gas, eg. propylene is passed through the brick at the temperature at which it decomposes. The gas decomposes to leave an even coating of carbon on all the surfaces of the brick pores. The crystallites are very small and are orientated with the basal plane facing the centre of the pore. The basal plane is less easily oxidised. The carbon also results in a very considerable increase in strength, particularly at high temperatures. In theory this technique sounds very promising, yet the slag resistance test results were not nearly as impressive.

CHAPTER 8.

Brezny and Fischer⁵⁶ developed a technique for increasing brick life by raising the thermal conductivity. Steel inserts are added before pressing. The steel inserts help to conduct heat away from the slag surface, lowering the hot face temperature. A test panel was mounted in an L.D. vessel and the wear and shell temperature behind the panel were monitored. Early in the campaign the shell temperature was hotter behind the panel, which left the steelmakers unimpressed, but later in the campaign, the wear on the panel was so much retarded that the temperature behind the panel was lower than that of the rest of the shell.

As far as mechanical properties are concerned, hot modulus of rupture has been found to be the most important property. The influence of boron has been discussed under the chapter on chemistry. The microstructure is also important and will be discussed under the experimental work. It is generally believed that a fine pore structure is detrimental to hot strength.⁵³ The CaO/SiO_2 ratio of the binder phases has also been shown to be very important. The correlation between CaO/SiO_2 ratio and hot strength at different oxygen partial pressures was determined by Landy and Brezny.⁵⁷ Reducing conditions generally lead to a lower hot modulus of rupture.⁵² This should be taken into account when testing bricks. Results on non-impregnated periclase bricks cannot be applied to bricks for basic oxygen processes.

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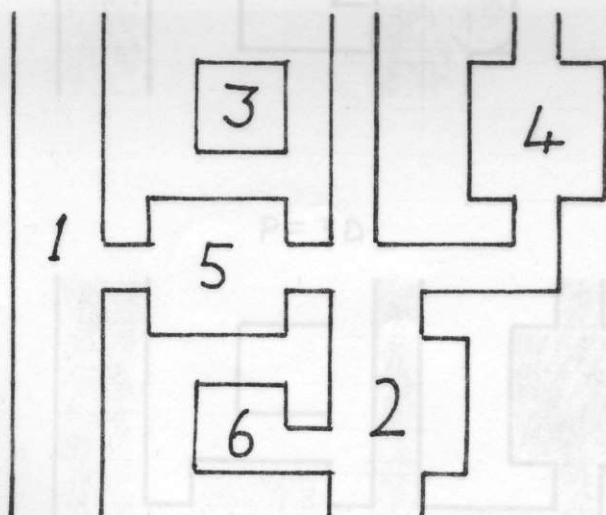
CHAPTER 8.

DETERMINATION OF PORE SIZE DISTRIBUTION

The importance of pore size distribution has been discussed already, but the problems of determining it warrant some consideration. Several methods have been developed for determining pore size distribution.^{64, 65} Most published work on refractories has been done with mercury pressure porosimetry. The other easily applied method which is much less expensive is the water expulsion method. The mercury method is based on the fact that mercury will only penetrate pores of a certain diameter at a given pressure. The diameter of pores penetrated depends on the surface tension of mercury and the contact angle of mercury to the material being tested. These values are discussed in some of the papers referred to. The water expulsion method is based on the force of capillary attraction of water and is again dependent on surface tension and contact angle. Mercury penetration is isostatic whereas water expulsion involves a pressure gradient. It will be shown that the mercury method has an advantage because of this, but both methods have very similar restrictions.

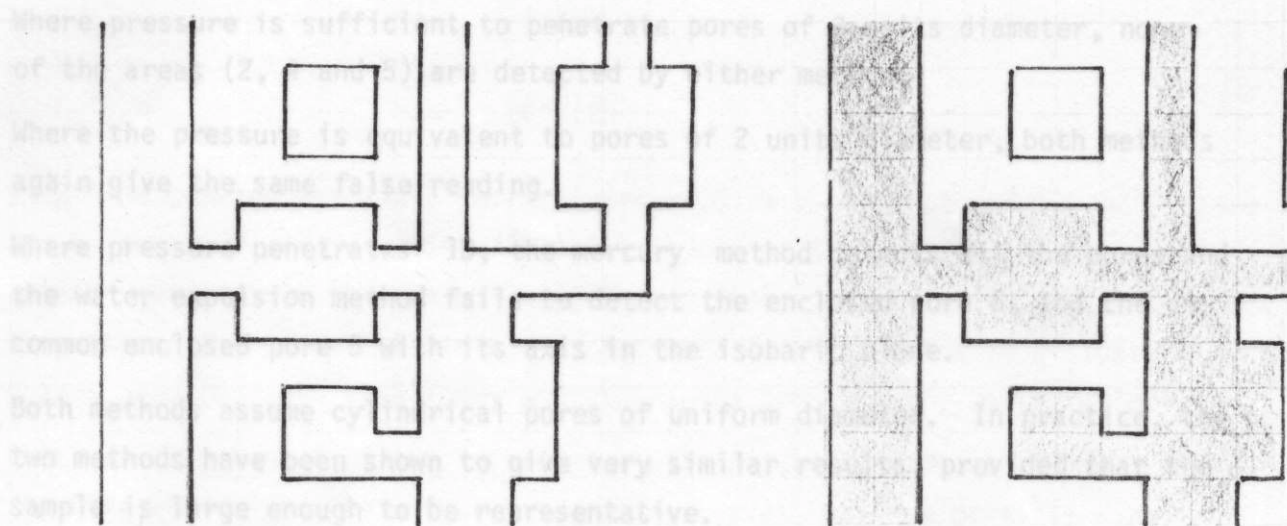
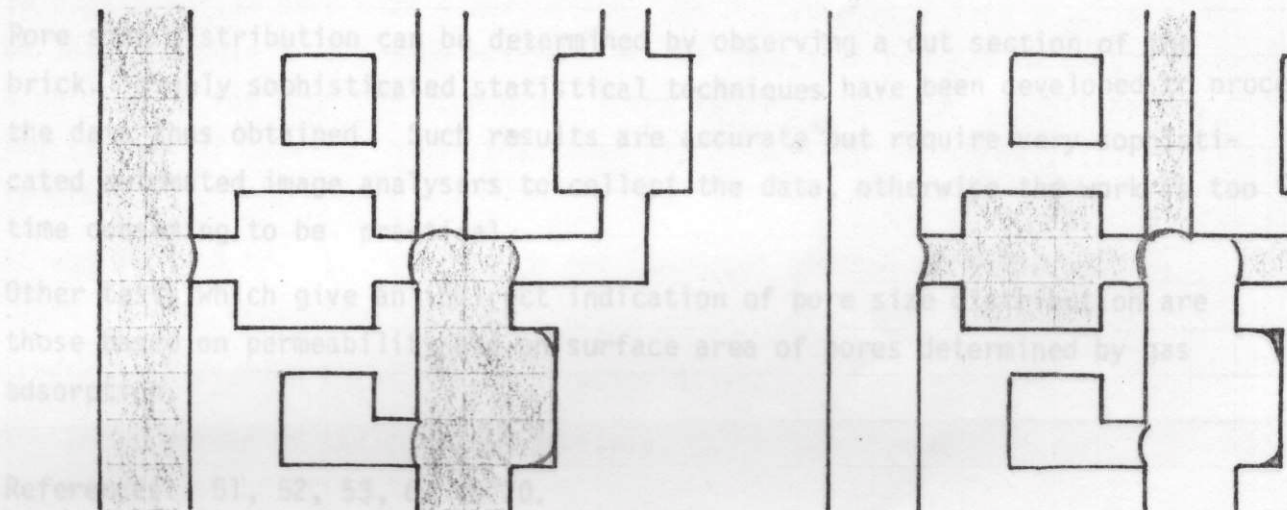
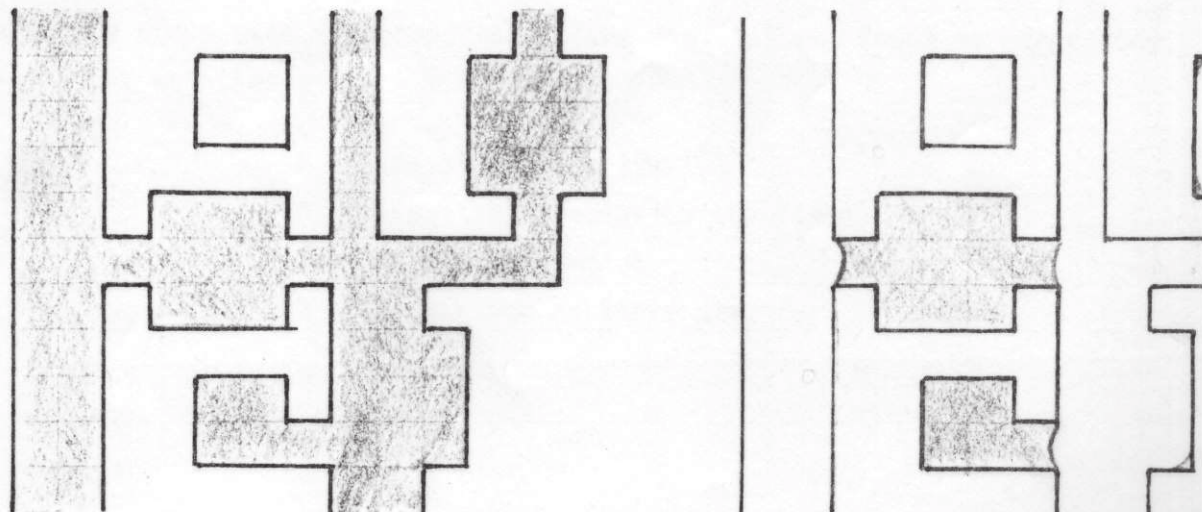
Consider a simplified brick:

- 1: Ideal pore
- 2: Pore of varying diameter
- 3: Sealed pore
- 4, 5 and 6: Enclosed pores.



MERCURY

WATER

 $P = 1D$ $P = 1D$  $P = 2D$ $P = 2D$  $P = 3D$ $P = 3D$ 

Where pressure is sufficient to penetrate pores of 3 units diameter, none of the areas (2, 4 and 5) are detected by either method.

Where the pressure is equivalent to pores of 2 units diameter, both methods again give the same false reading.

Where pressure penetrates 1D, the mercury method detects all the pores and the water expulsion method fails to detect the enclosed pore 6, and the uncommon enclosed pore 5 with its axis in the isobaric plane.

Both methods assume cylindrical pores of uniform diameter. In practice, the two methods have been shown to give very similar results, provided that the sample is large enough to be representative.

The pore size distribution which the tests reveal is thus not the volume of pores of each diameter, but the total volume of the pore structure accessible via that diameter.

Pore size distribution can be determined by observing a cut section of the brick. Highly sophisticated statistical techniques have been developed to process the data thus obtained. Such results are accurate but require very sophisticated automated image analysers to collect the data, otherwise the work is too time consuming to be practical.

Other tests which give an indirect indication of pore size distribution are those based on permeability and on surface area of pores determined by gas adsorption.

References: 51, 52, 53, 61 to 70.

Mixes were designed, adjusting one variable at a time, to determine their effects.

The reference curve used for comparison, (see fig. 1a) was found to correspond roughly to the equation $y = A + (100 - A) \frac{d}{D}$

where
 y = % passing the sieve
 A = a constant regulating the fines
 d = the sieve diameter
 D = the maximum particle diameter in the mix.

CHAPTER 9.

GRADING

Pitch impregnated periclase refractories require a high hot modulus of rupture and a fine pore size distribution. The object of this investigation is to obtain insight into the optimal grading for these properties. A grading based on past experience was rationalised and used as a reference to evaluate other curves and gradings by Bolomey and others and the author's own formulations.

Loose packing densities are tested on a wide range of gradings, using seawater magnesite. The effects of grading curves, maximum particle size and amount of fines are evaluated. The testing procedure is also discussed.

Grading

To obtain a fine pore size distribution, one must use very fine materials, or at least produce a very fine matrix. At the same time one has to ensure a high density for high hot strength. There is very little data published on the subject of grading, other than theoretical work on packing densities of spheres.

It was decided to start the search for the ideal grading by investigating loose packing densities.

Grading curves have three basic characteristics:

1. The diameter of the coarsest particle.
2. The amount of "fines".
3. The shape of the log-cumulative plot.

Mixes were designed, adjusting one variable at a time, to determine their effects.

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where

y = % passing the sieve

A = a constant regulating the fines

d = the sieve diameter

D = the maximum particle diameter in the mix.

This equation is similar to the Bolomey equation, which was used at a later stage. The kink in the above curve cannot be straightened, due to the gradings of the raw materials, which are a natural result of the crushing and milling process. Screening of the - 212 μ m to dust and ball mill fines fractions could not be economically justified, and experimental work was carried out without modifying the plant raw materials, except where fractions used were not available in the plant.

Gradings were calculated using the above curve and maximum particle diameter, varying the percentage fines. The limits selected for fineness were $A = 10$, below which the green bricks are too fragile for handling, and $A = 40$, above which it is thought that the bricks would probably laminate. As it turned out, $A = 40$ produced an excellent brick, with no trace of lamination.

Loose packing densities were tested as follows: A 3kg. mix was made of each grading, and vibrated into a 2 litre measuring cylinder. Mixes behaved differently during compaction, but all trial mixes had reached equilibrium within 40 seconds, except 100% ball mill fines. All densities were measured after 50 seconds of vibration. There are two aspects to the mix behaviour:

1. Cyclic motion: Mixes with very coarse particles and low percentage fines developed a continuous motion, observable at the surface and presumed to continue throughout the container. Material rises in one area of the container and falls in another. By tilting the container towards the upward flowing area the upward motion is shifted to the centre of the cylinder and downward motion to the sides. With this arrangement the motion is slower. It is thought that a higher frequency of vibration may eliminate this convection-like motion, but all available vibrating tables are of the same design. No settlement was observed after vibration and it is presumed that the densities were detrimentally affected by dilatancy.
2. Segregation: Two types of segregation were observed, namely, fines rising to the top, and coarse particles remaining on the top. The highest densities were obtained where no segregation occurred.

A single-sized mix, -4,75mm + 3,35mm, was tested. It reached a density of 1,97g cm⁻³ almost immediately and remained in rapid cyclic motion. Pure ball mill fines reached a density of 1,69 cm⁻³ after 50 seconds and was still compacting to beyond 2,02g cm⁻³ after 6 minutes. A gap graded mixture of 50% -4,75mm + 3,35mm and 50% ball mill fines compacted to 1,69g cm⁻³ interrupting the vibration. (This can be achieved with a 100% ball mill fines as well).

and showed no segregation or motion.

The reference grading and a coarse and fine equivalent were made up, pressed and fired for evaluation of physical and structural properties. 30kg. mixes were made in a foundry sand mixer. (Slow action with no pressure). Bricks of nominal area 230mm X 114mm were pressed at 15mPa, with a pause and pressure release at 13mPa, using molasses as a green binder. Wet green bulk densities obtained were;

A = 10 D = 3: 2,92g cm⁻³

Standard Mix: 2,96g cm⁻³

A = 40 D = 3: 2,94g cm⁻³

The bricks were fired to 1540°C and 1730°C and tested with regard to: Pore size distribution, apparent and true porosities and hot modulus of rupture at 1400°C.

Further gradings were calculated to evaluate the effect of increasing the maximum particle size. The reference curve was used and the fineness index, A, was kept constant at a value of 30. Maximum particle sizes, D, were 3,0mm, 6,7mm and 11mm. Another curve was investigated, namely that of the Bolomey equation. The Bolomey equation is a modification of the Fuller equation, and was developed for cements, where the percentage fines is modified to impart the desired plasticity to the mix. (1).

The Bolomey equation is: $y = A + (100 - A)\left(\frac{d}{D}\right)^{\frac{1}{2}}$

where y = % passing the screen

A = constant regulating the % fines

d = diameter of the screen apertures

D = largest diameter particles in the mix.

In the first series, A values of 10, 20, 30 and 40 were evaluated with D constant at 3mm. In the second series D was raised to 11mm. and A values of 0, 10, and 30 were evaluated.

An exceptionally coarse grading quoted by Chesters. (2) gave a density of 2,70g/cm³ although coarse material segregated to the top. Unfortunately this mix is not likely to give a fine pore structure.

A ternary gap graded mix based on work by Mc Geary, (3), was tried. Where all the other mixes gave consistent results after 50 seconds vibration, this mix gave a range of 2,44g/cm³ to 2,31g/cm³. Cyclic motion was induced by interrupting the vibration. (This can be achieved with other mixes as well).

Conclusions:

After cyclic motion, the density was $2,26\text{g/cm}^3$, and the upper 55% by weight contained coarse material only.

The figures on the following pages show the theoretical curves as solid lines, and any substantial deviations in the experimental mixes as dotted lined. The loose packing densities are plotted against the variable factor for the series. (See fig.s 1 - 7).

Fig. 1. Shows 22% -45 μ m to be the best, when $n = 1$

Fig. 1.a Shows performance of the reference grading.

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Fig. 2. Shows benefit of larger coarse material.

Fig. 3. Shows 22% or less -45 μ m material to be optimal, when $n = 5$

Fig. 4. Shows highest density reached so far, and demonstrates that D-size and A value are mutually dependent for high density.

Fig. 5. Shows Bolomey curve to be inferior to the reference curve for mixes with a high percentage of fines. (Compare Fig. 2).

Fig. 6. Chesters' grading gives the highest density of all. McGeeary's metal sphere packing principles do not perform at all well with loose packing of irregular particles.

In Fig. 1. The density of A = 40 looked suspiciously low, even allowing for the fact that segregation (of fines on top) was observed. The mix was re-calculated revised and tested again with the same result, but 100 seconds vibration gave a higher value, at $2,46\text{g/cm}^3$ (Fig. 1a).

Pure ball mill fines were vibrated and the density achieved was plotted against time in fig. 7. This casts doubt on the validity of the 90 second standard for vibration. Another feature not observable in the rest is segregation of fines to the bottom. This appears to have happened to the McGeeary grading. The phenomenon is reported by Westman and Huggill (4). They describe mixtures of which they placed the coarse material in the bottom of a cylinder and added the fines on top. The density increased to a maximum as the fines penetrated the coarse. A maximum was reached at which no segregation was observable and then the density decreased again. In their test the material is tapped by dropping the cylinder mechanically at 2 second intervals.

It is now clear that there are two different and opposite kind of fines segregation. The first, observed in mixes where there was no circulation, and the fines migrated upwards. The second, only demonstrable in the reference grading after circulation had been in progress. The author discussed the segregation with colleagues and found a wide range of opinions. When asked in a mix of 10% + 30 μ m Magnesite and 90% ball mill

Conclusions:

1. The highest density is generally obtained in the region of 25% -45 μ m mixes.
2. Larger maximum particle size gives the expected higher density.
3. The reference curve gives a higher density than the Bolomey curve.
4. Loose packing densities after 50 seconds vibration are not directly comparable with green bulk densities.

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fig.1.a Shows performance of the reference grading.

fig.2. Shows benefit of larger coarse material.

fig.3. Shows 22% or less -45 μ m material to be optimal, when $n = \frac{1}{2}$

fig.4. Shows highest density reached so far, and demonstrates that D size and A value are mutually dependent for high density.

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finer, would the coarse rise or sink?", the answers varied from "It would float on the top", to "It would sink to the bottom". Such a mix was made, adding the fractions separately. When the coarse was added on the top, it sank during vibration, leaving the upper 25% by weight as pure ball mill fines. It did not sink all the way after 200 seconds, and the lower 40% was still pure ball mill fines. When the coarse was added to the bottom of the cylinder, it rose, leaving 25% ball mill fines on top and the coarse distributed through the lower 75% of the mix. Circulation did not occur on the surface. The result is indeed stranger than anybody's predictions, and indicates the possibility of both types of segregation occurring simultaneously.

The highest density achieved so far is that of the Chesters grading. In an attempt to formulate an equation to generate this curve, one must use the formula: $y = A + (100 - A) \left(\frac{d}{D}\right)^n$ where y = % passing the test screen

A = modulus of fines

d = the screen being calculated

D = Diameter of coarsest particle

n = "Modulus of curvature".

The modulus of curvature which will give the highest density is thought to be dependent largely on two factors:

- 1) Method of compaction.
- 2) Angularity of the aggregate.

Without any experimental proof, the author made the following guesses regarding values of n for "average" refractory materials:

- 1) $n = \frac{1}{2}$ will give the highest densities for water saturated vibrated mixes, ie. castables.
- 2) $n = 1$ will give the highest densities for conventionally pressed materials.
- 3) $n = 2$ will give the highest density for dry, vibrated materials.
(This has no direct refractory application, but could be tried with fettling materials).
- 4) The n value should increase with increasing angularity of grain shape.

Testing of the curve $n = 2$ was disastrous.

fig. 8 Shows that it failed to give a higher density with other factors constant.

fig. 9 Shows that it failed to approach the Chesters grading.

fig.10 Shows the best of each curve, and $n = 2$ still fails.

Figure 1 - Reference curve D = 3.

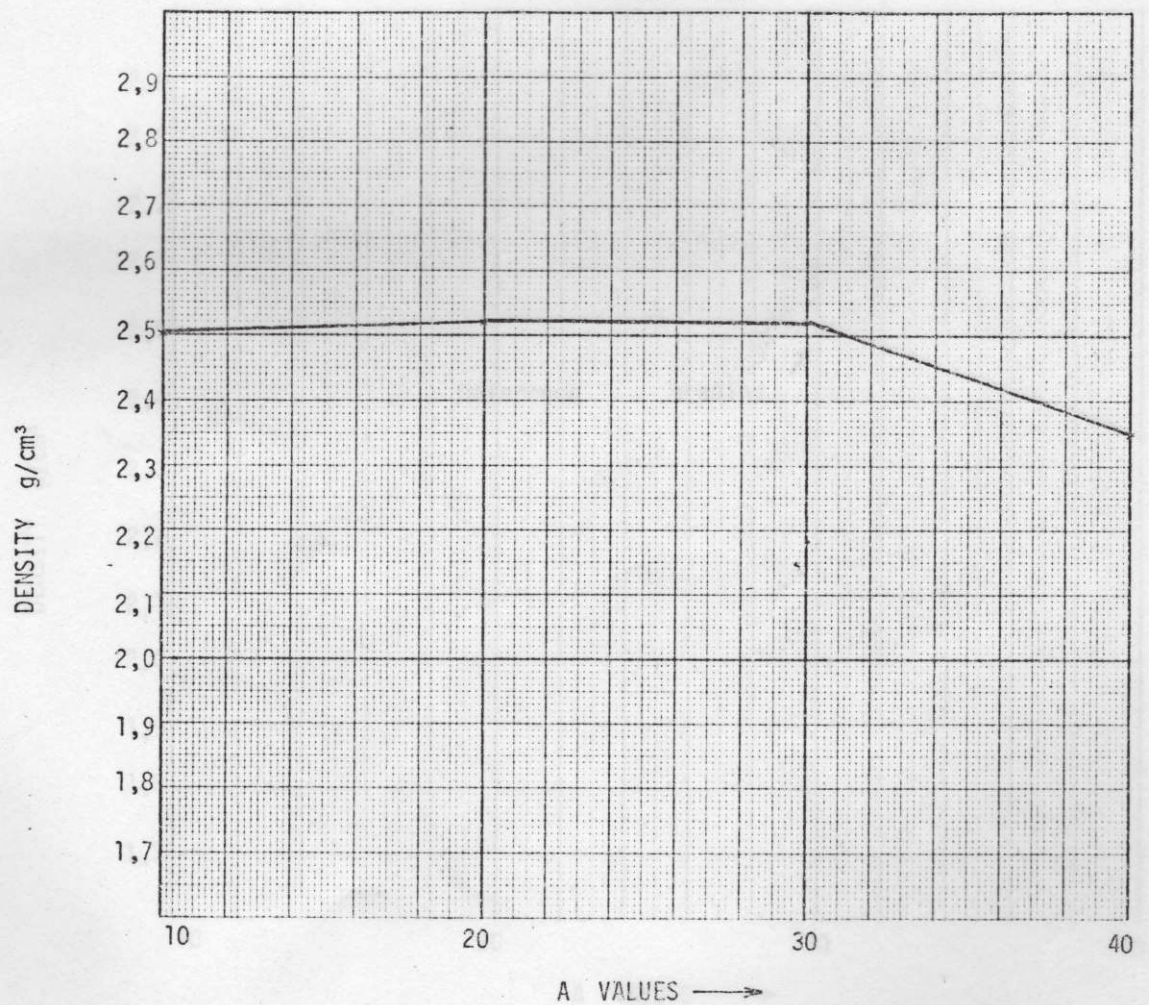
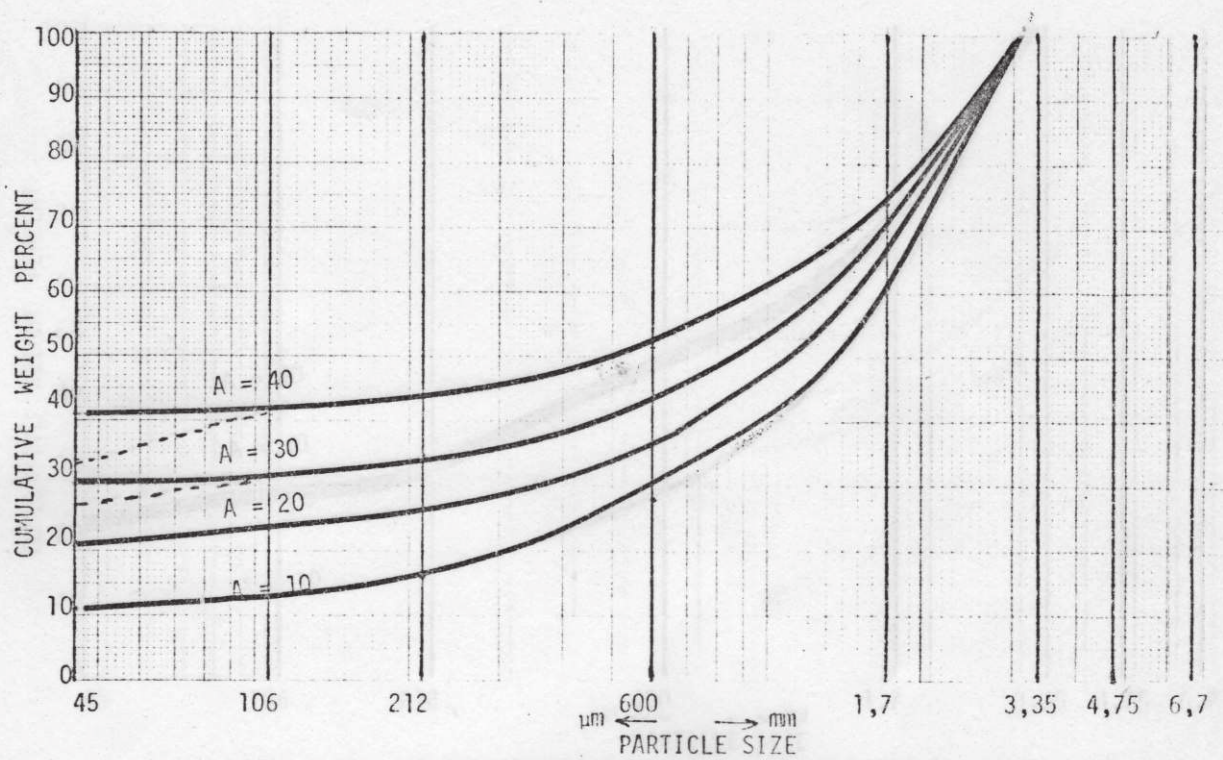


Figure 1a - Rationalised reference curves, $D = 3$ showing original reference grading (thick line).

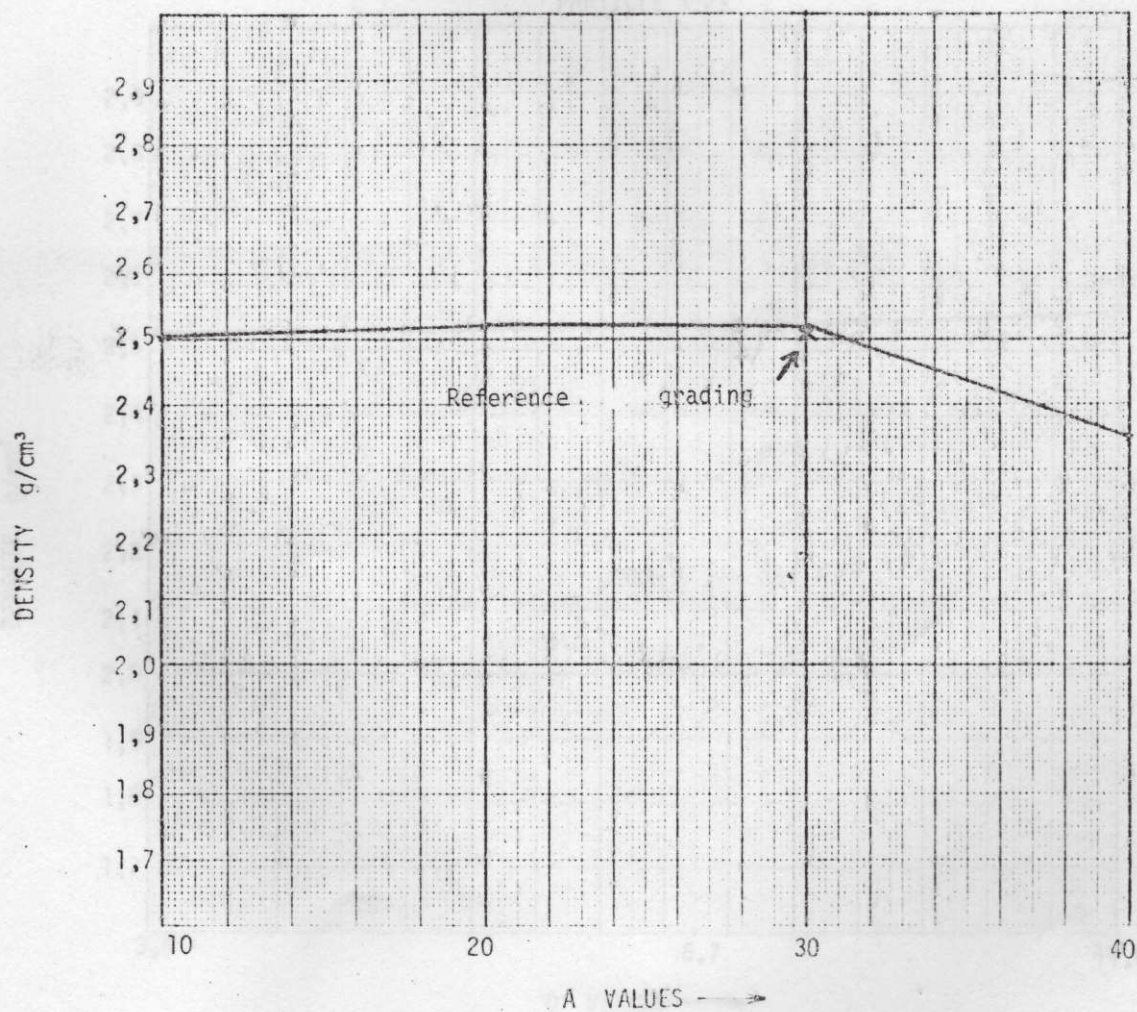
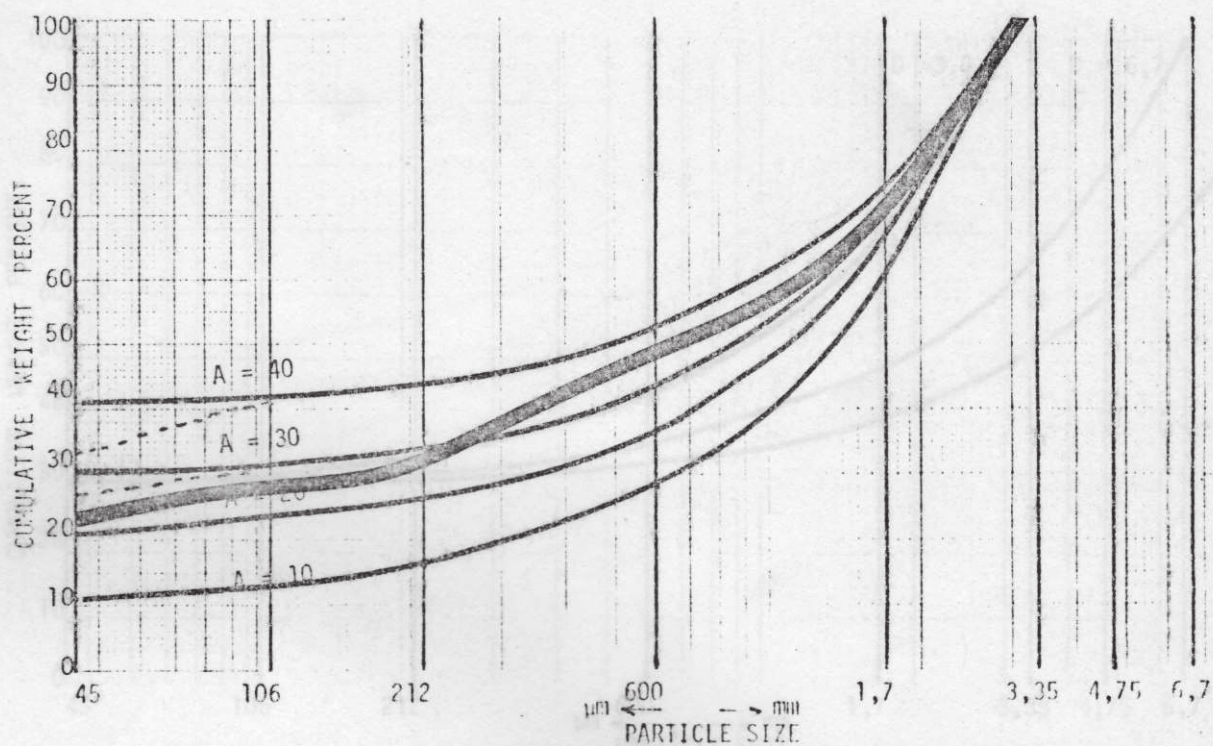


Figure 2 - Reference curve = A 30

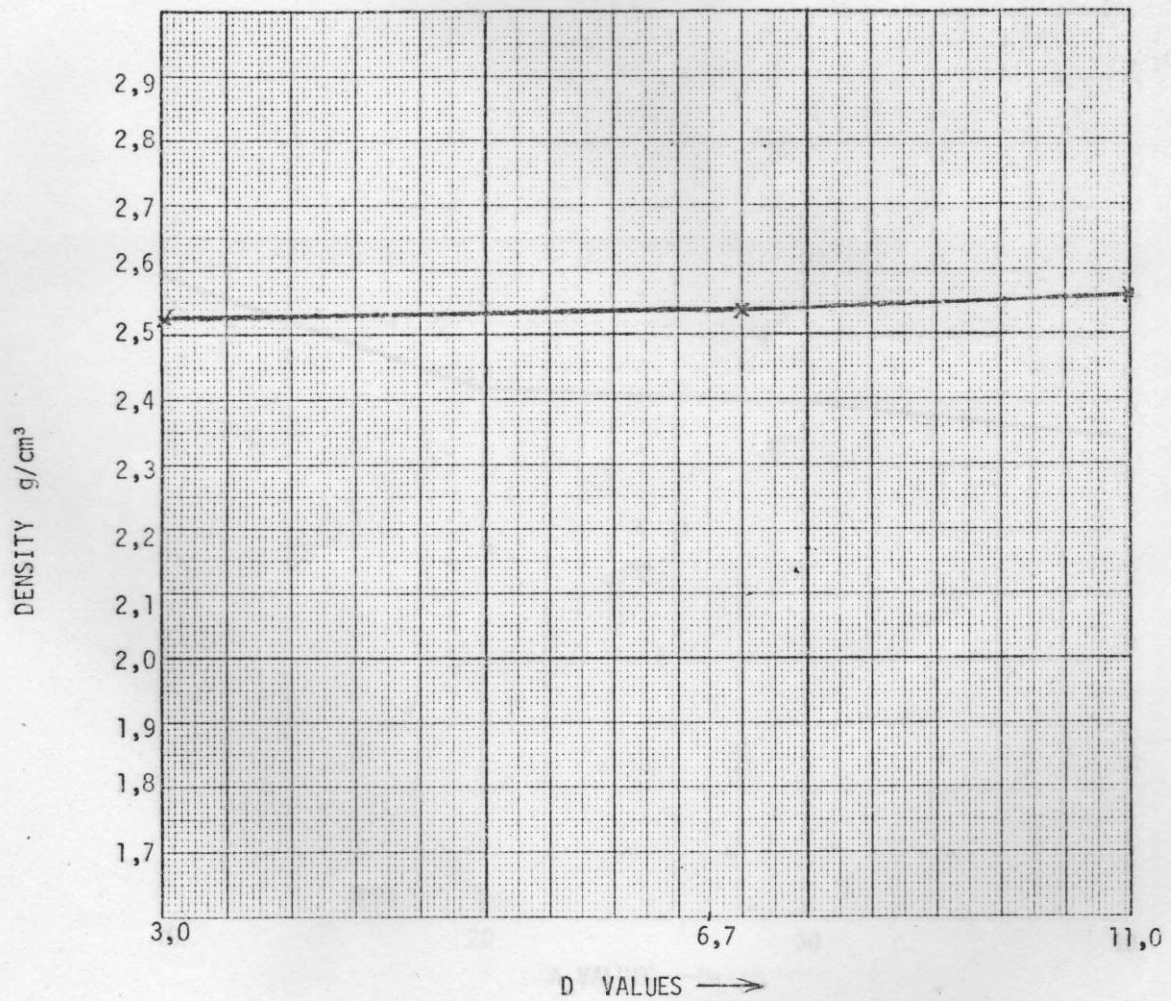
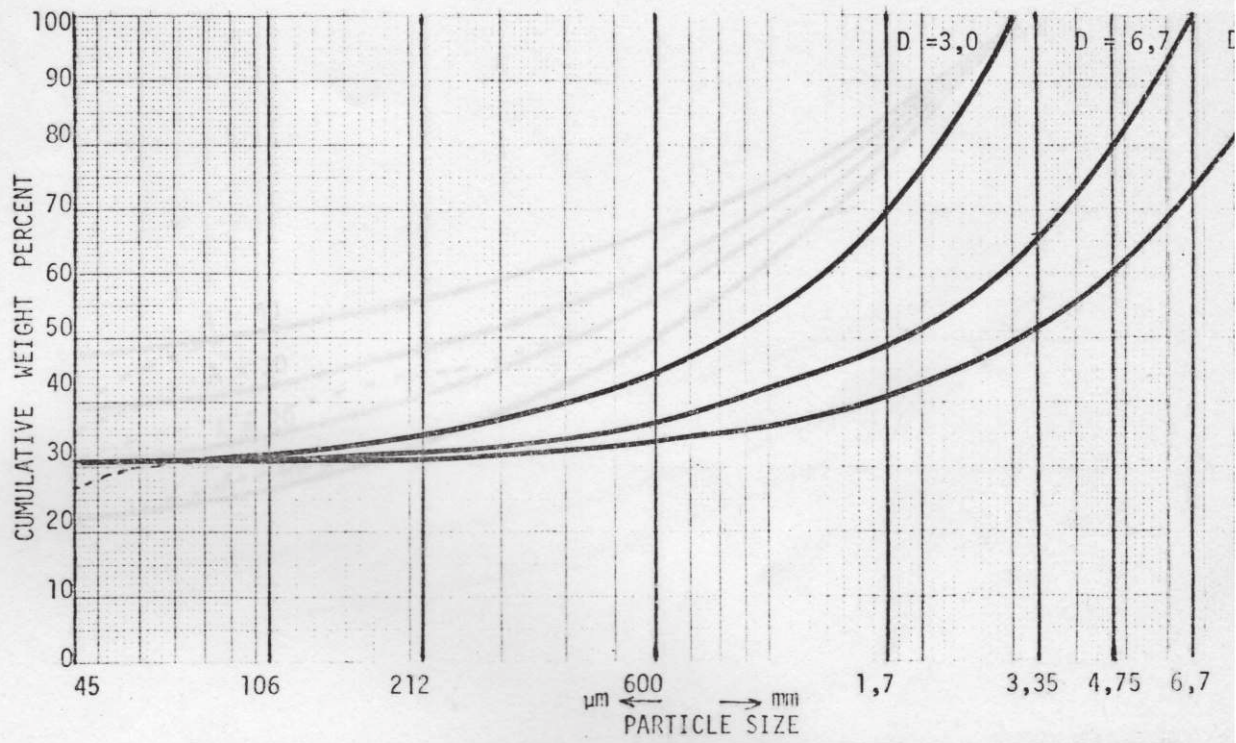


Figure 3 - BOLOMEY CURVE D = 3

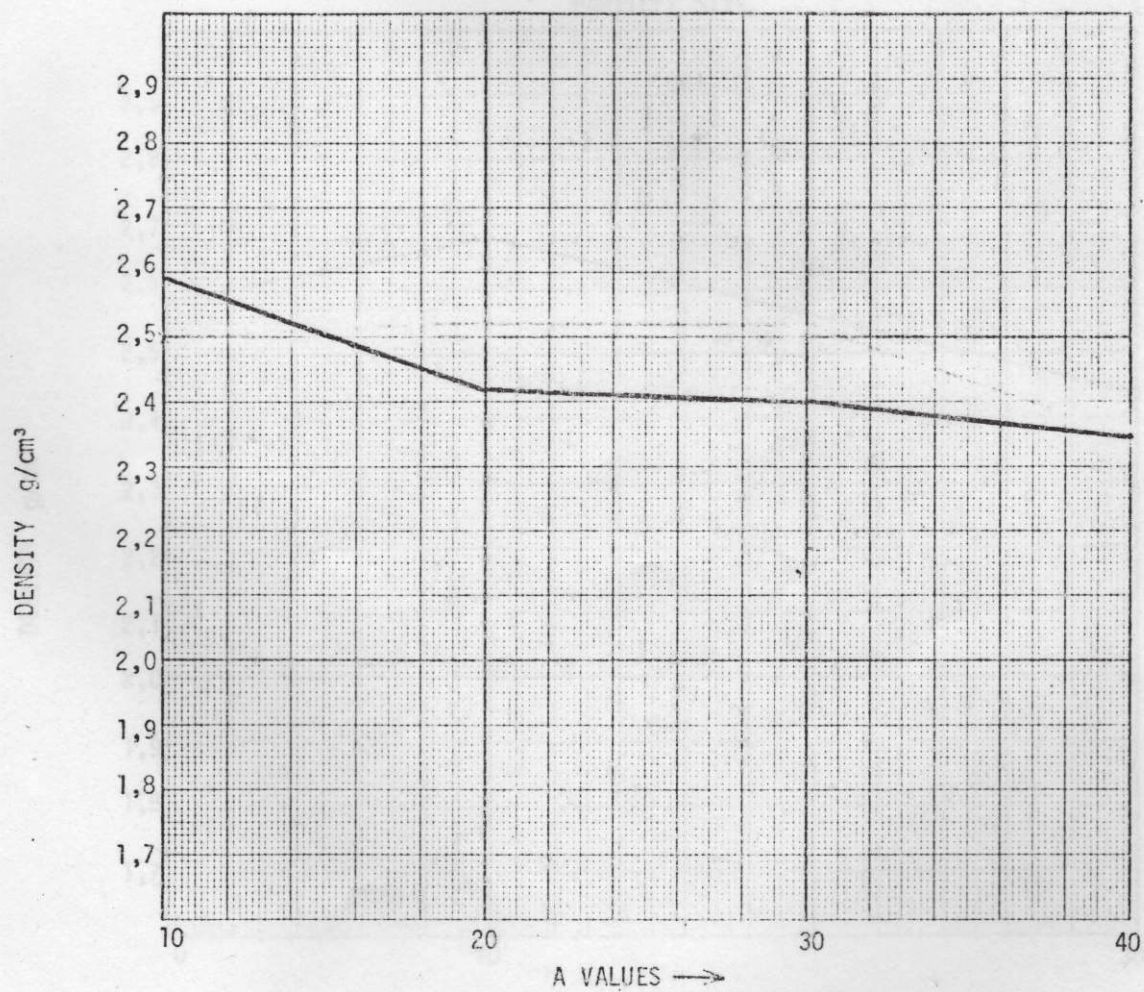
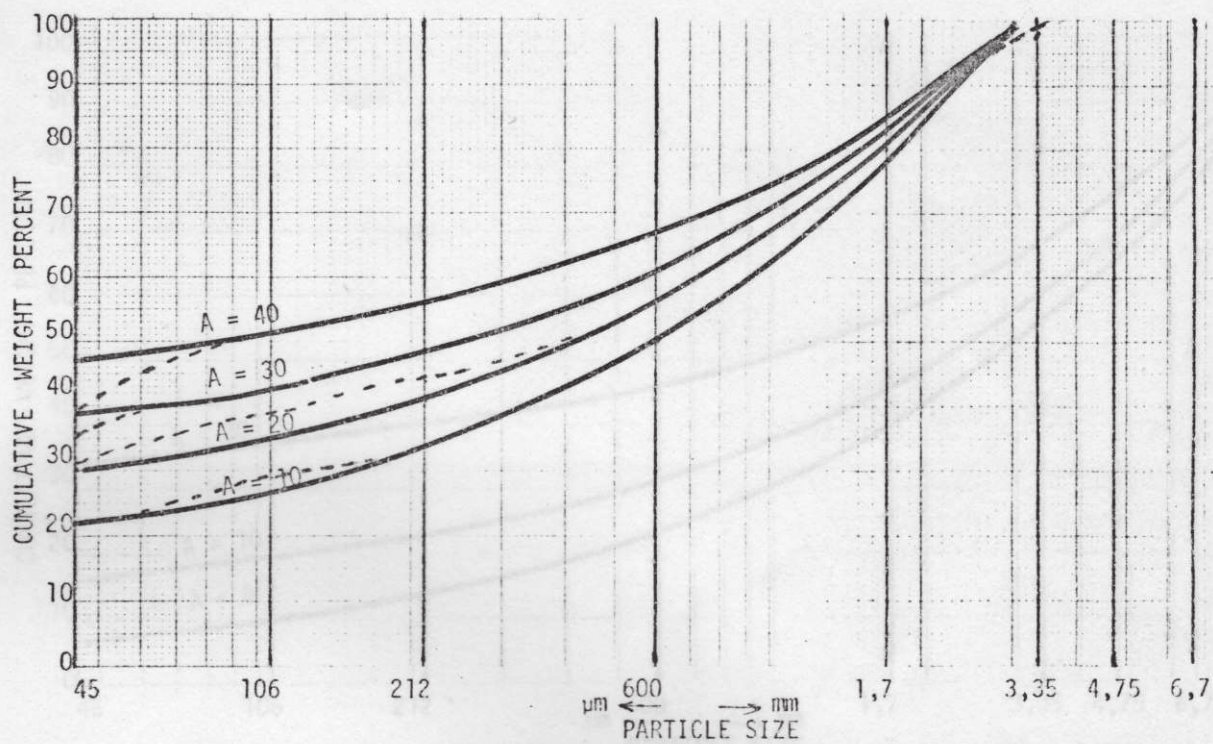


Figure 4 - BOLOMEY CURVE D = 11

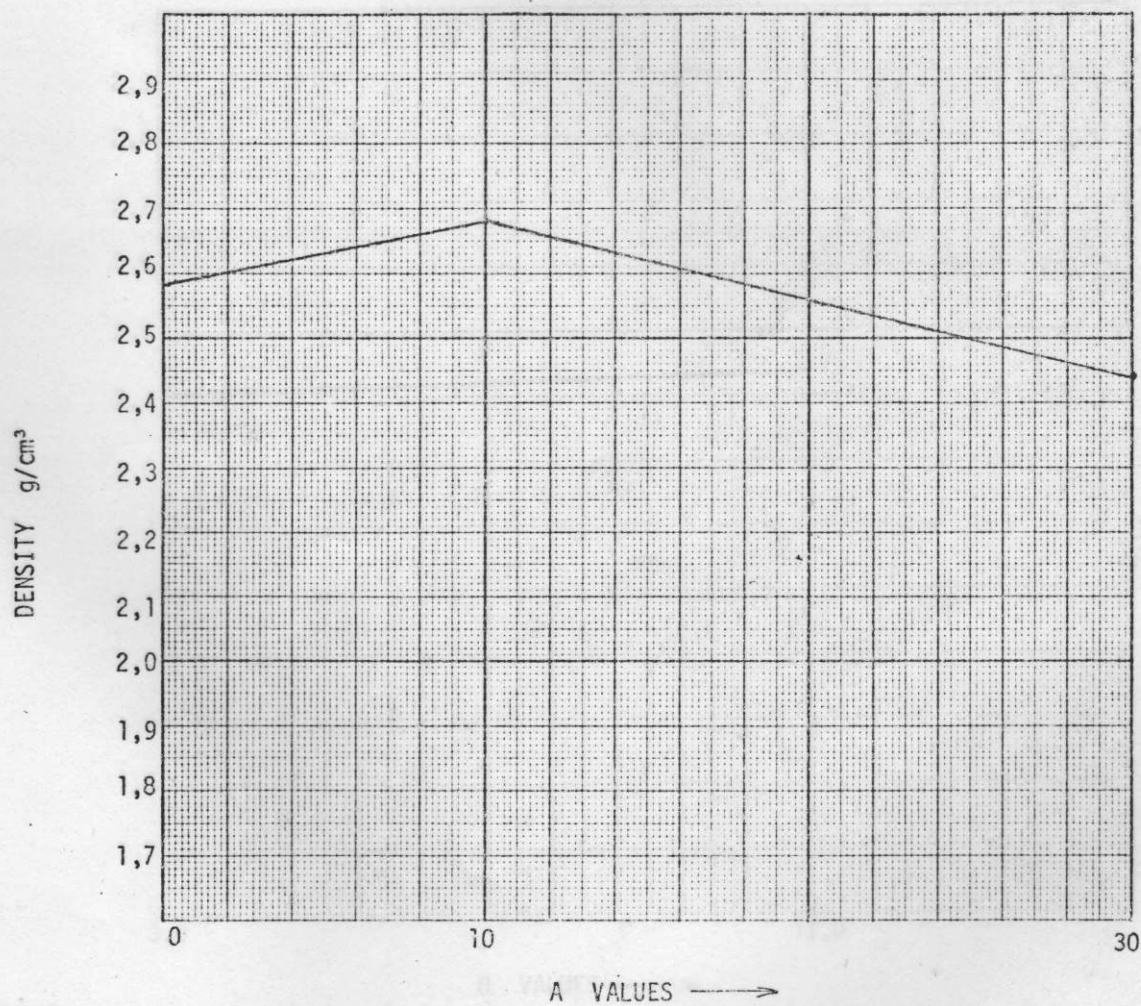
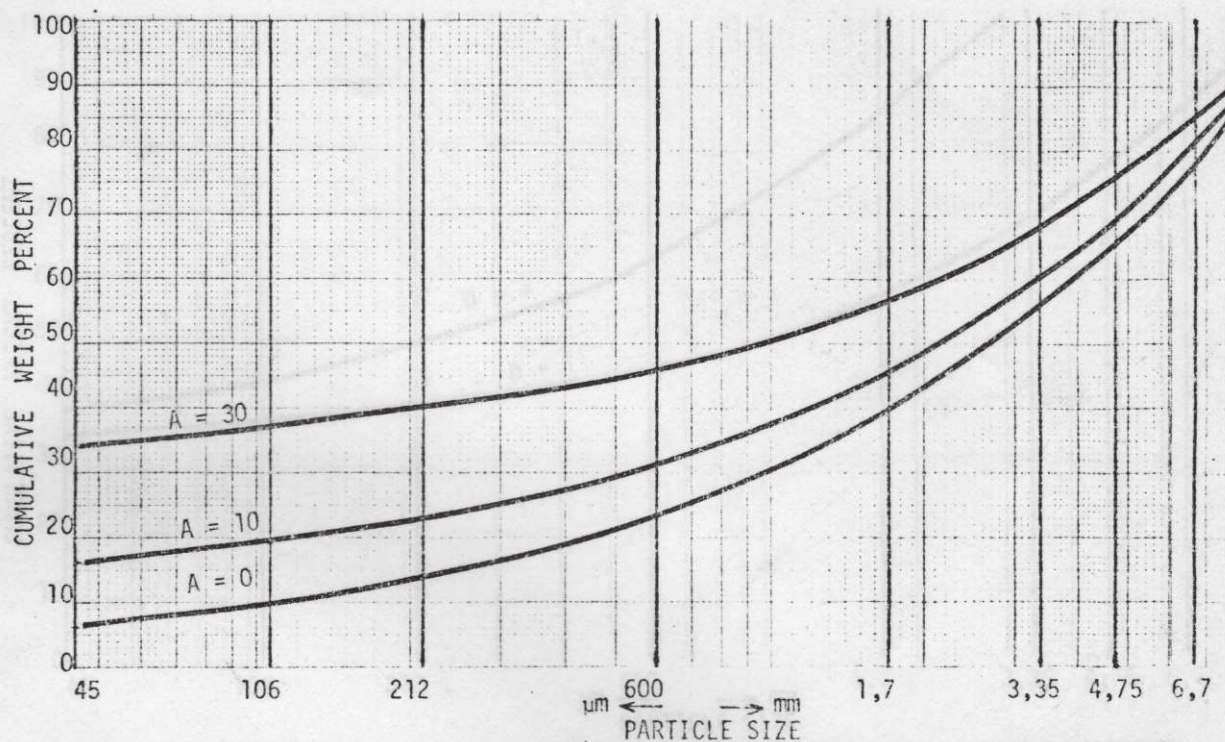


Figure 5 - BOLOMEY CURVE A = 30

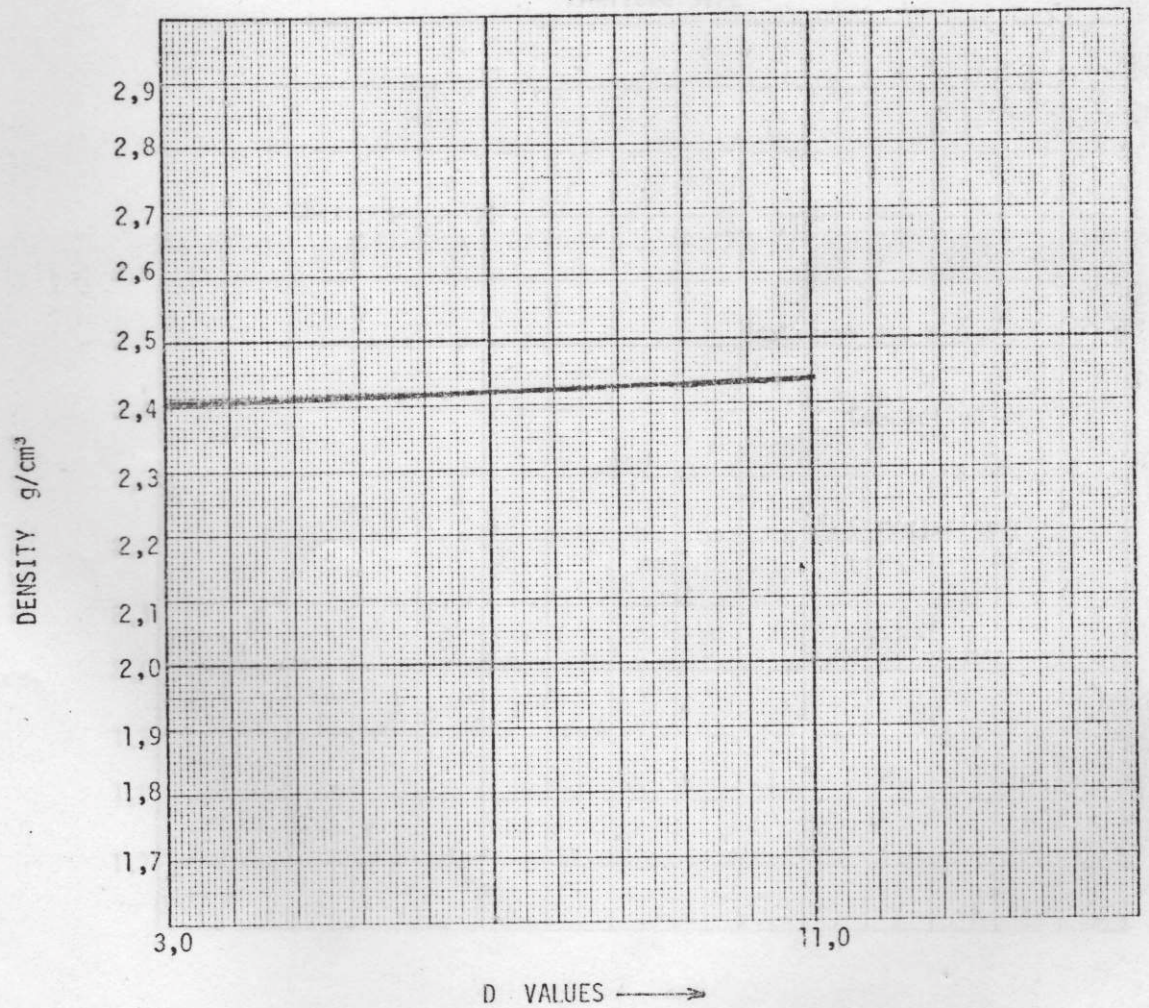
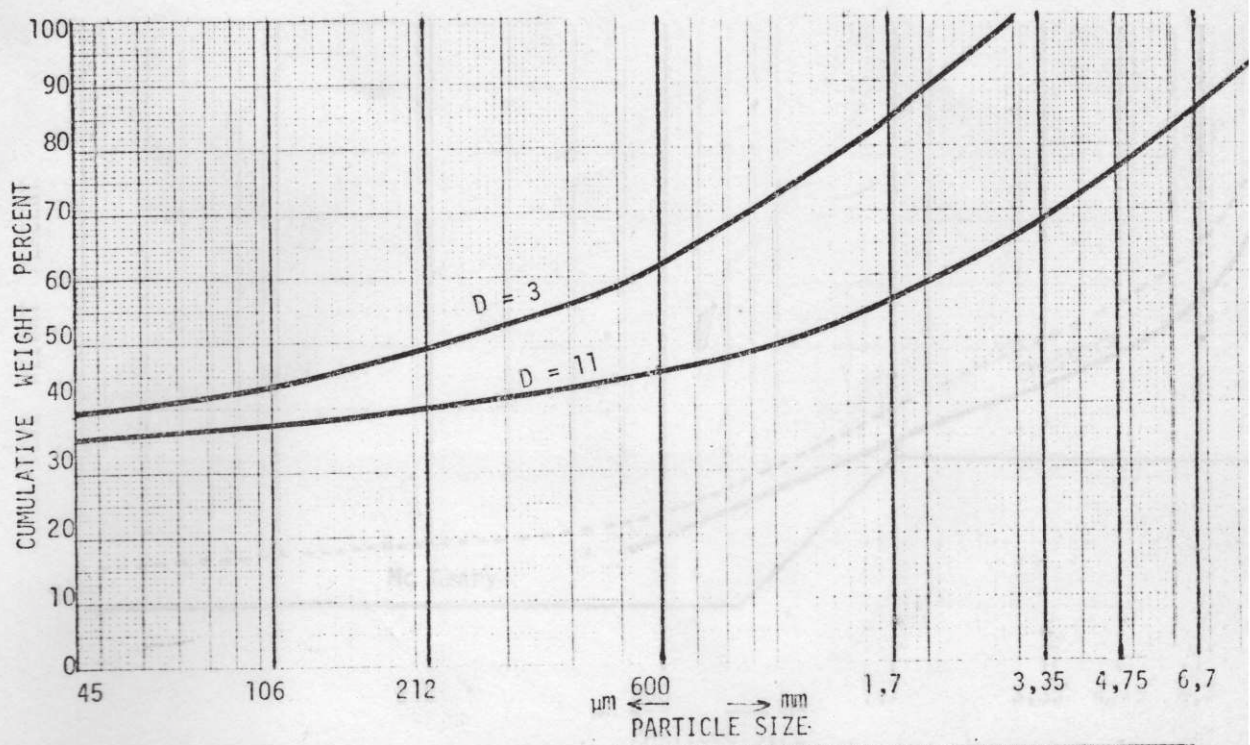


Figure 6 - Chesters and McGeary gradings.

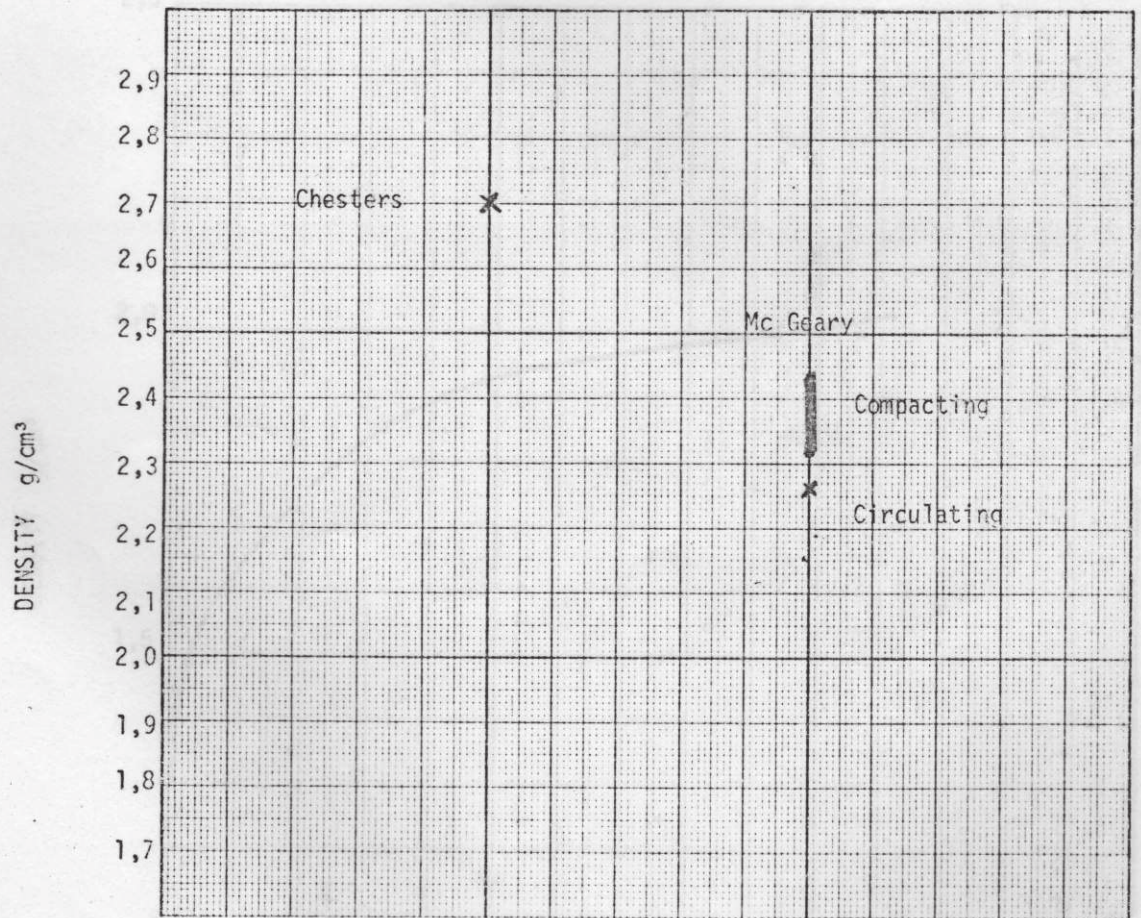
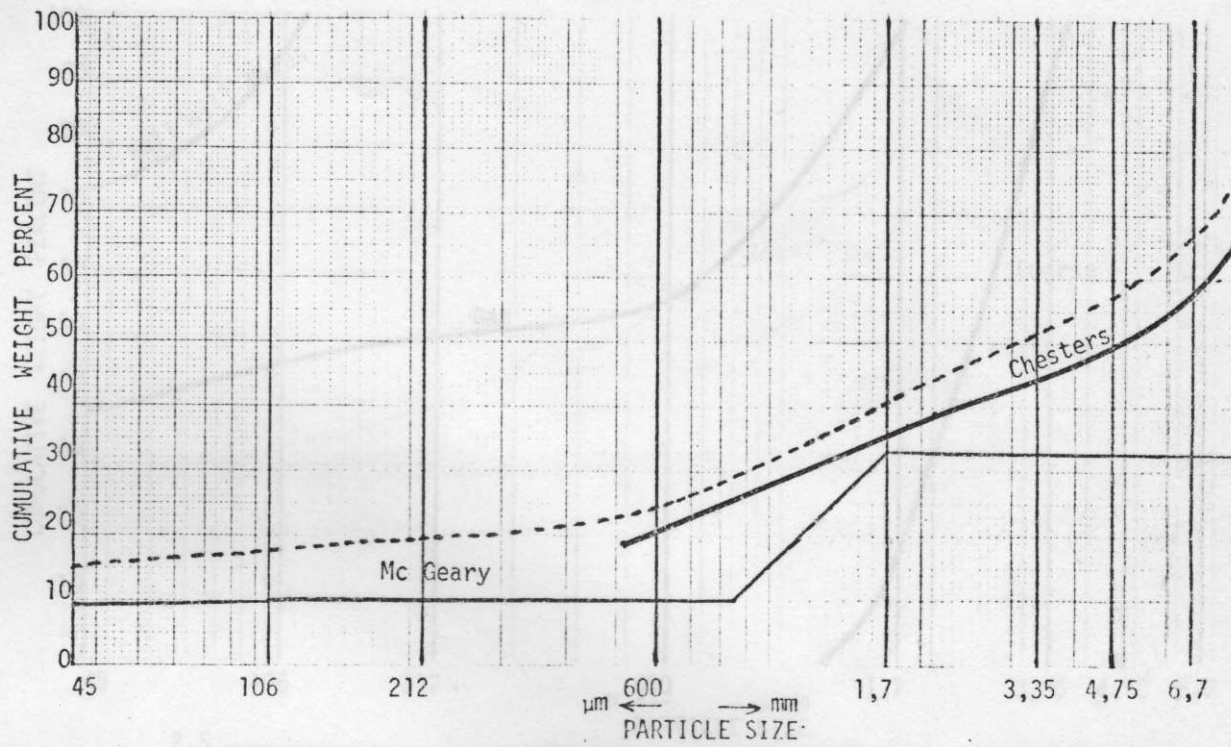


Figure 7 - Evaluation of curves

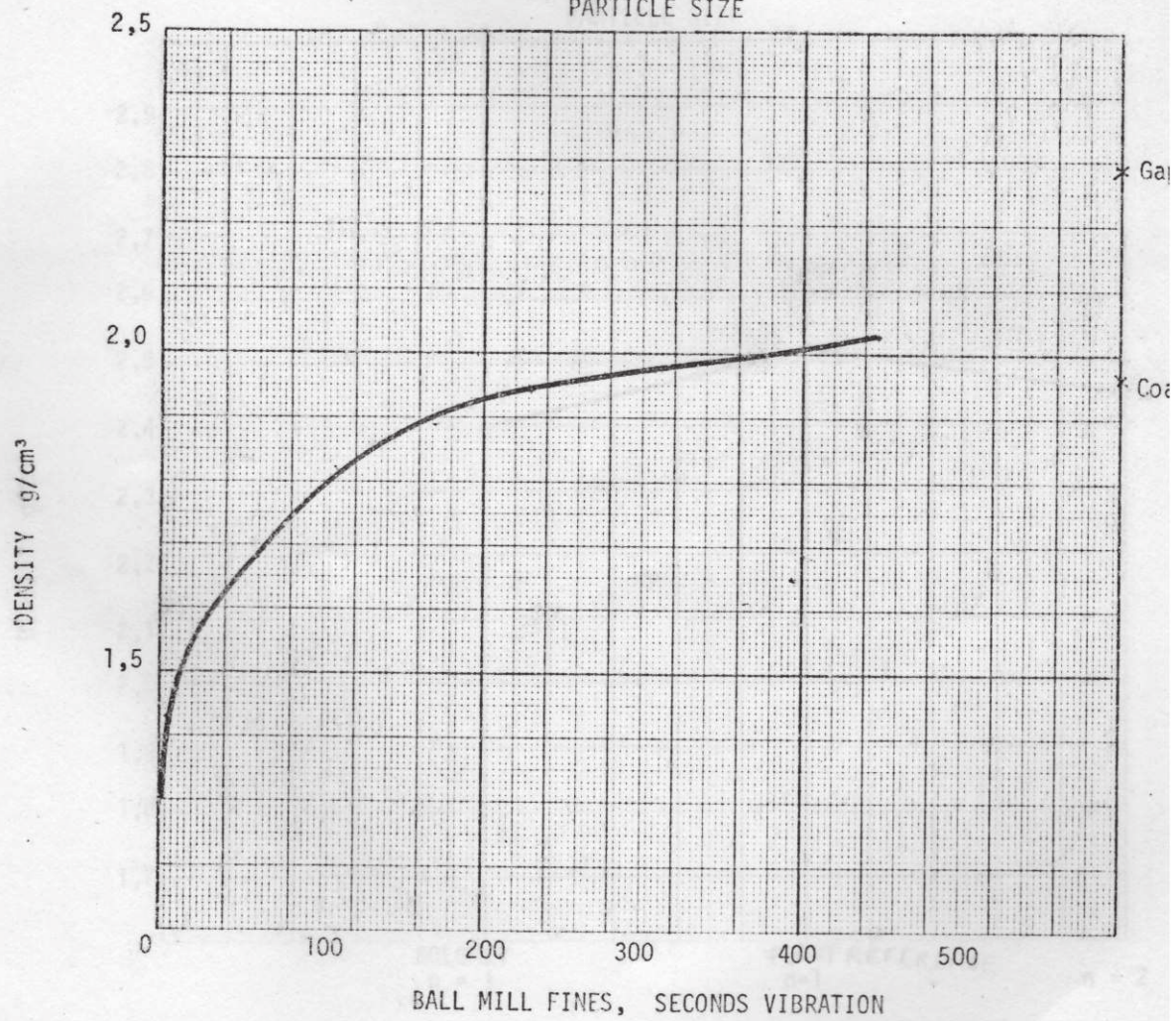
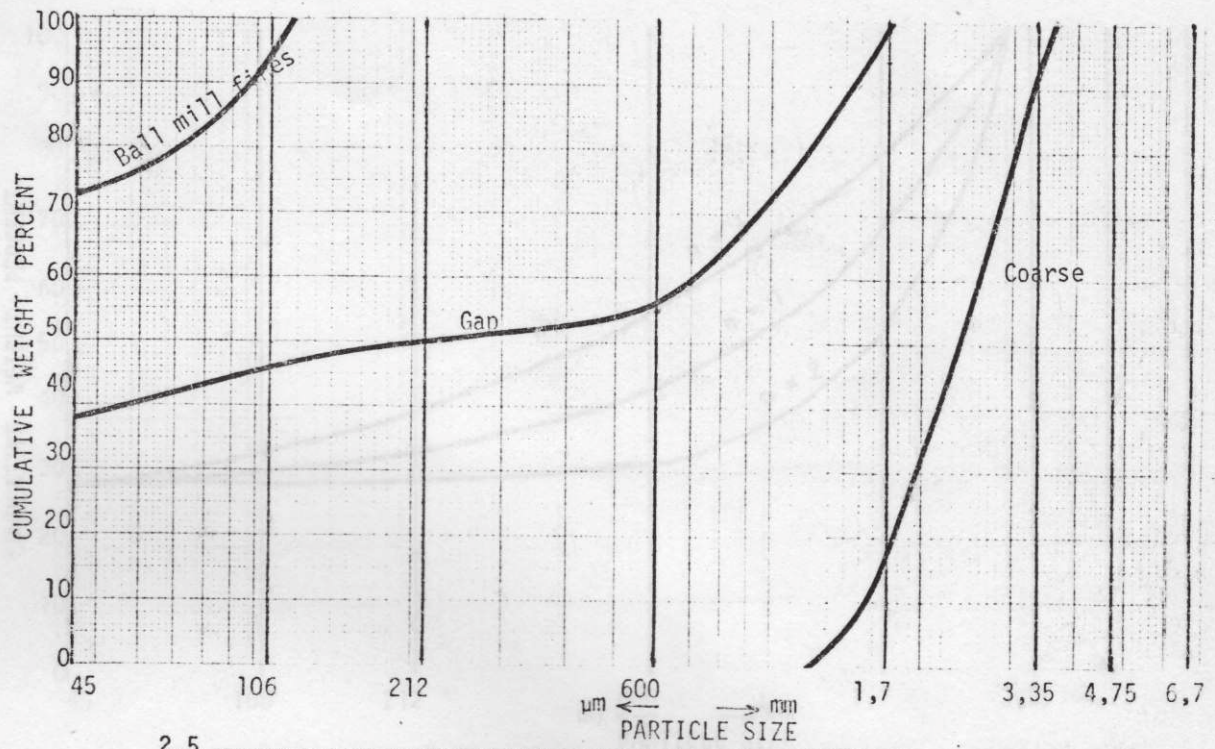


figure 8 - Evaluation of curves

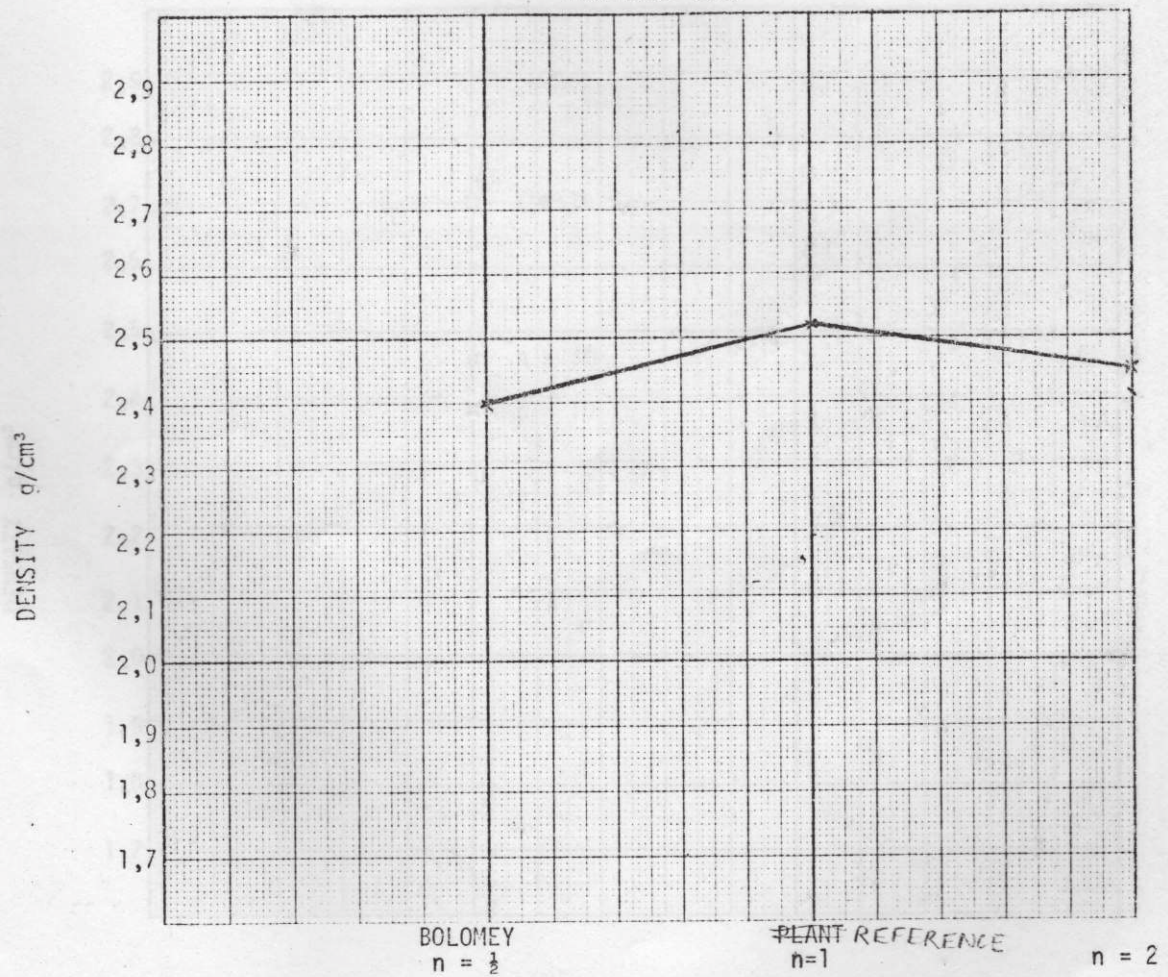
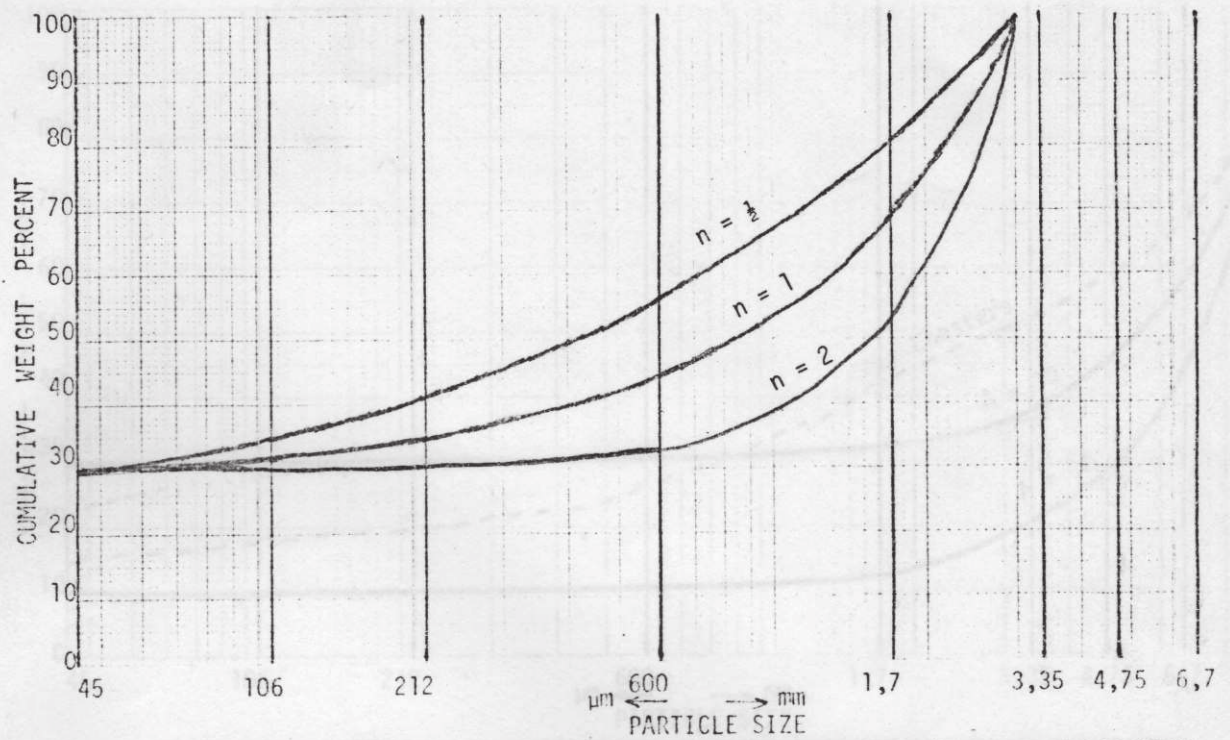


Figure - 9 $n = 2$ $D = 11$

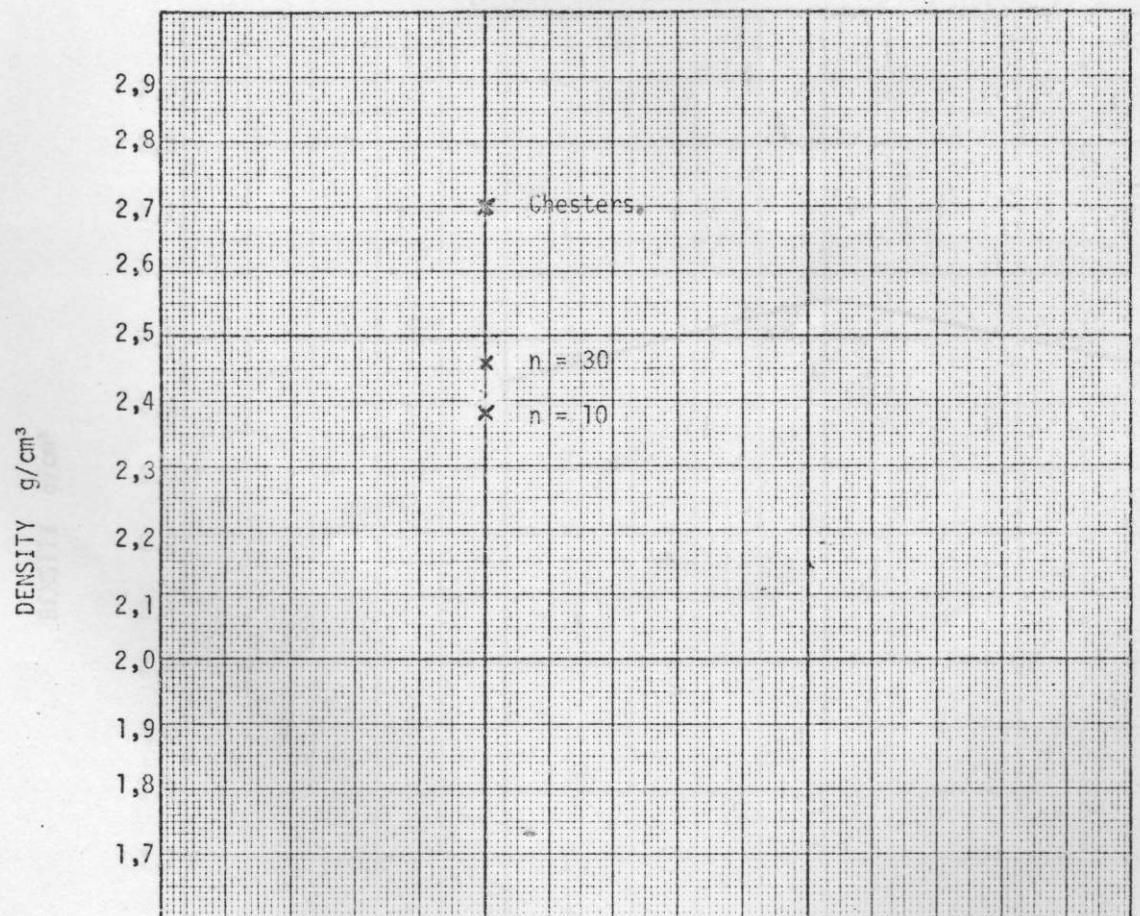
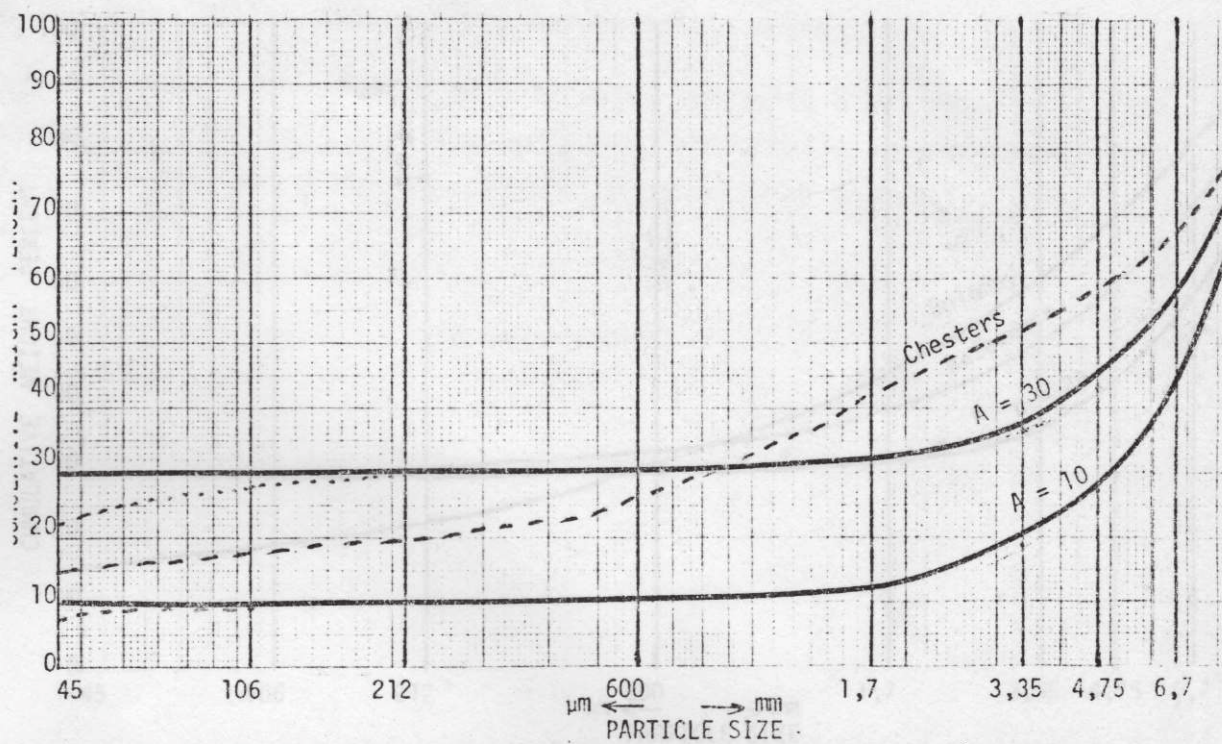
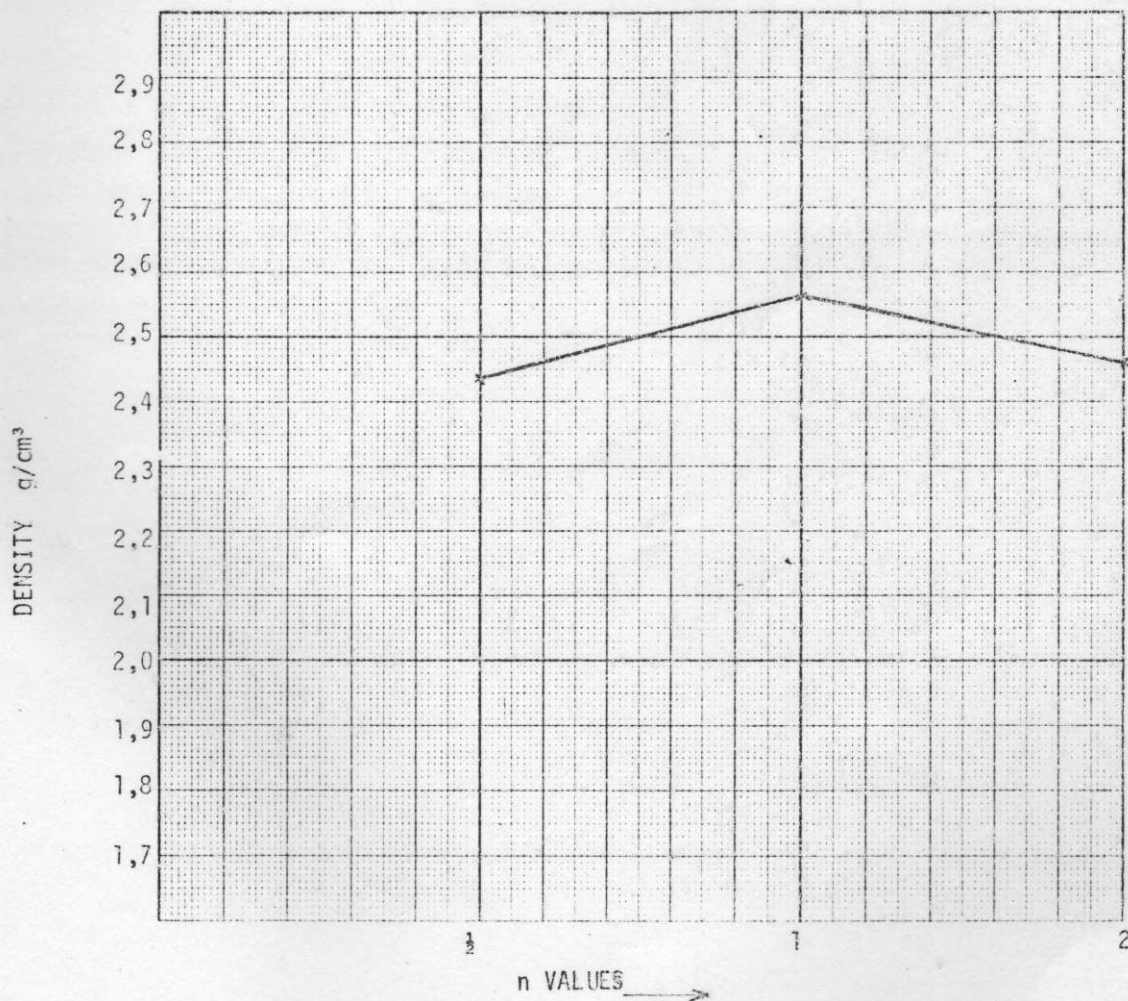
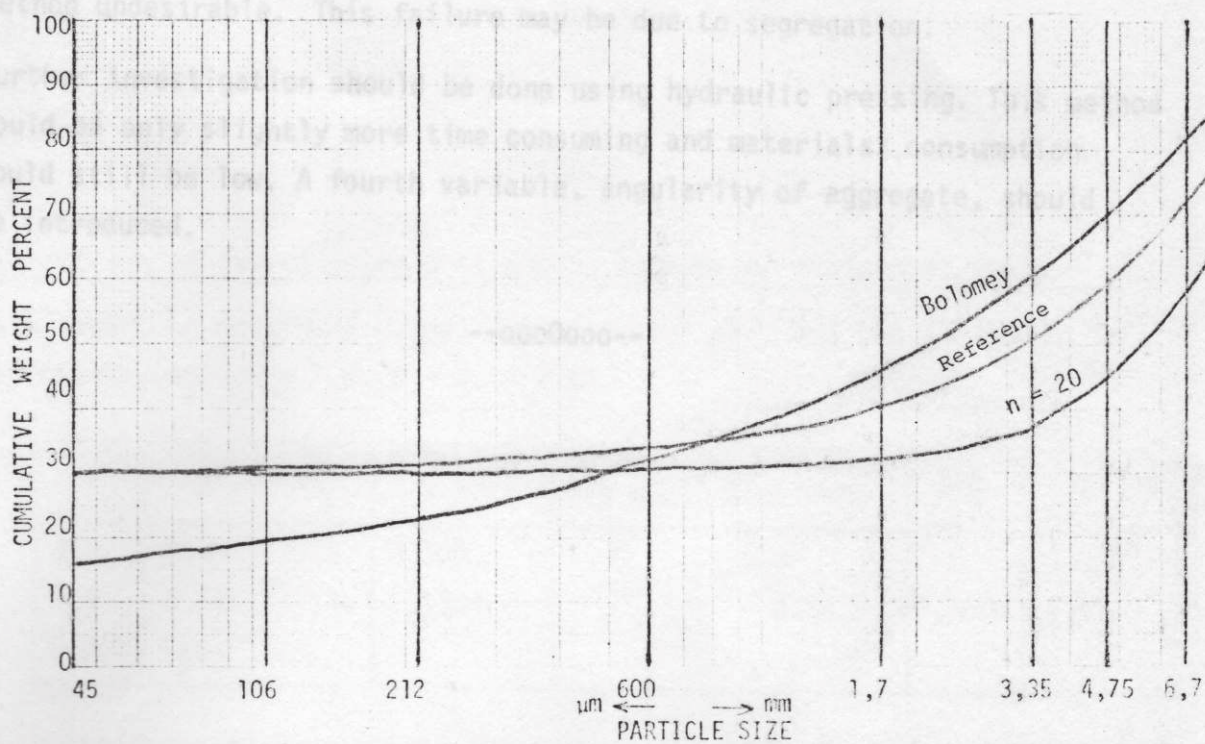


Figure 10 - Densest gradings from each curve



The author's curve fails to provide a unified theory for designing dense packing gradings and the problems encountered in testing loose packing densities are so great as to render further investigation via this method undesirable. This failure may be due to segregation.

Further investigation should be done using hydraulic pressing. This method would be only slightly more time consuming and materials consumption would still be low. A fourth variable, angularity of aggregate, should be introduced.

Calculation of curves where n is not an integer or reciprocal thereof

This cannot be done on a normal ~~calculator~~, but can be done using logarithms, eg. $n = 1.5$, $D = 3$, $A = 25$.

d	$\frac{d}{D}$	$100\frac{d}{D}$	+ve log $\times n$	integer $\times n$	sum of last 2 columns	log	antilog
3.0	1	1,000	0.0000	0	0	0	1.000
1.7	0.567	1,7536	1.1304	1.5	- 0.3696	1.6304	0.4270
0.600	etc.	etc.					

Now substitute these values in the general equation, $y = A + (100 - A) \left(\frac{d}{D}\right)^n$
 $y = 25 + 75 \left(\frac{d}{D}\right)^{1.5}$

for 3.0 : $25 + 75 (1) = 100\%$ passing 3.0mm

for 1.7 : $25 + 75 (0.4270) = 57\%$ passing 1.7mm.

$\therefore 100 - 57 = 43\%$ retained on 1.7mm screen etc.

The values are now rationalised into mix proportions from screen analyses of raw materials.

~~calculator~~

Development of an Improved Pitch Impregnated Periclase Brick.Introduction:

Recent literature on the optimal properties for pitch impregnated magnesia refractories is outlined in Chapter 7. An attempt was made to produce a brick conforming to these properties, with particular attention to pore size distribution and retained carbon yield after coking.

APPENDIXCalculation of curves where n is not an integer or reciprocal thereof

This cannot be done on a normal pocket calculator, but can be done using logarithms, eg. $n = 1,5$, $D = 3$, $A = 25$.

d	$\frac{d}{D}$	$10 \log \frac{d}{D}$	+ ve log x n	integer x n	sum of last 2 columns	log	antilog
3,0	1,	1,000	0,0000	0	0	0	1,000
1,7	0,567	1,7536	1,1304	1,5	- 0,3696	1,6304	0,4270
0,600	etc.	etc.					

Now substitute these values in the general equation, $y = A + (100 - A) \left(\frac{d}{D}\right)^n$
 $y = 25 + 75 \left(\frac{d}{D}\right)^{1,5}$

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1. Pore size distribution.
2. Apparent and true porosity. (Tested separately).
3. Hot modulus of rupture at 1400°C.
4. Optical microscopy.

Development of an Improved Pitch Impregnated Periclase Brick.Introduction:

Recent literature on the optimal properties for pitch impregnated magnesia refractories is outlined in Chapter 7. An attempt was made to produce a brick conforming to these properties, with particular attention to pore size distribution and retained carbon yield after coking. Pore size distribution was altered by modifying the brick grading and firing temperature. Fired, impregnated bricks were coked and impregnated again in an attempt to improve retained carbon yield.

Effect of Grading

To establish the effect of grading on structure and physical properties, three gradings were used. The gradings are derived from the "reference" curve described in chapter 9. Their n value is thus 1.

3,35mm was chosen as the D value, and A values are; fine = 40, medium = 25 and coarse = 10.

The mixes were made in a foundry sand mixer, adding first +212 μ m fraction then the bulk of the molasses and then the -212 μ m fractions. Finally more molasses was added to reach the correct "feel" of the mix. The mixes were pressed into a 230 X 114mm die to make 6kg. bricks on a hydraulic press. The bricks were pressed at 13MPa with a pause and release, then 15MPa. The wet green bulk densities thus obtained were:

Fine: 2,94cm⁻³
 Medium: 2,96gcm⁻³
 and coarse: 2,92gcm⁻³.

The bricks were dried and fired to 1720°C and 1540°C respectively. (fig.10

The specimens were tested with regard to

1. Pore size distribution.
2. Apparent and true porosity. (Tested separately).
3. Hot modulus of rupture at 1400°C.
4. Optical microscopy.

Fig.10.1 Firing curves

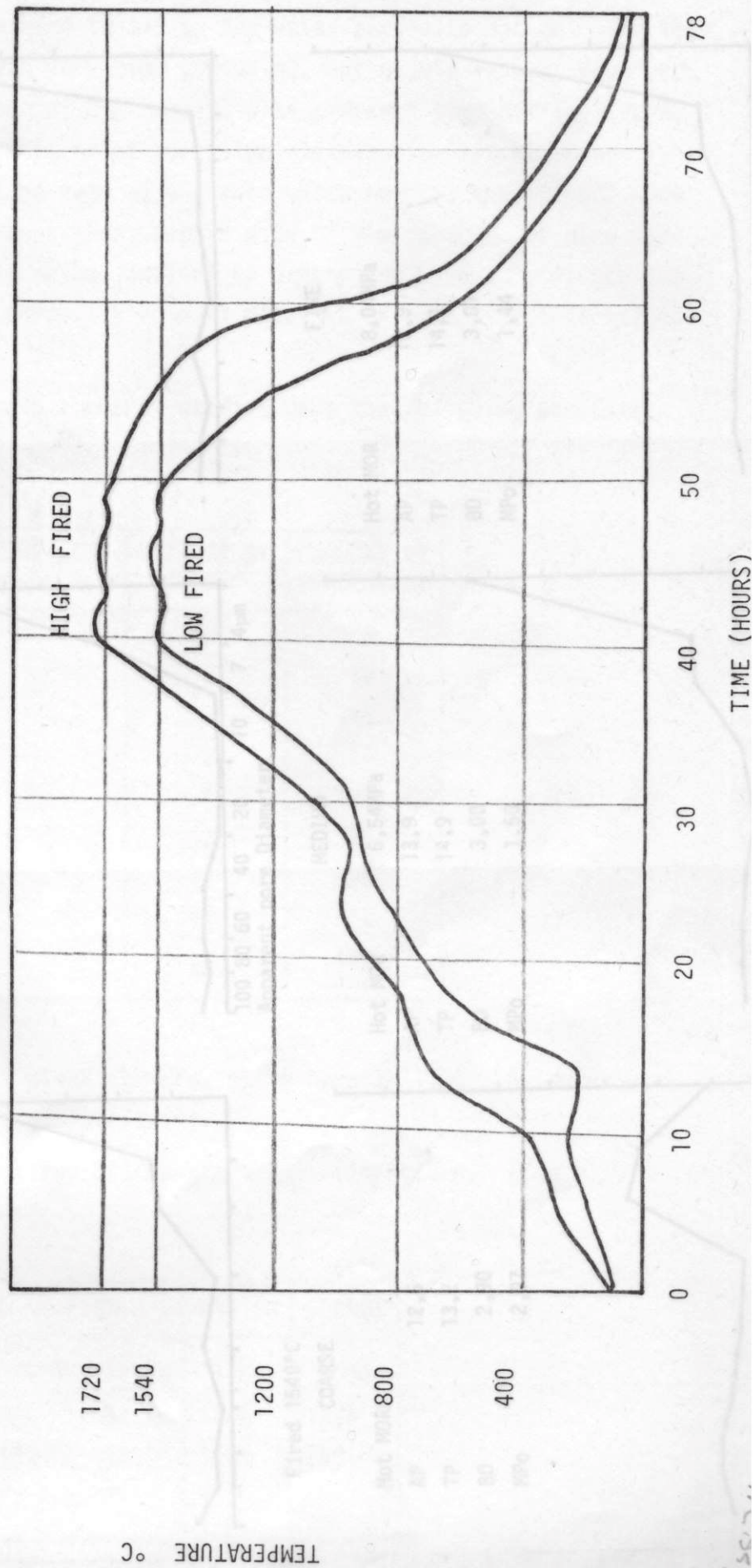
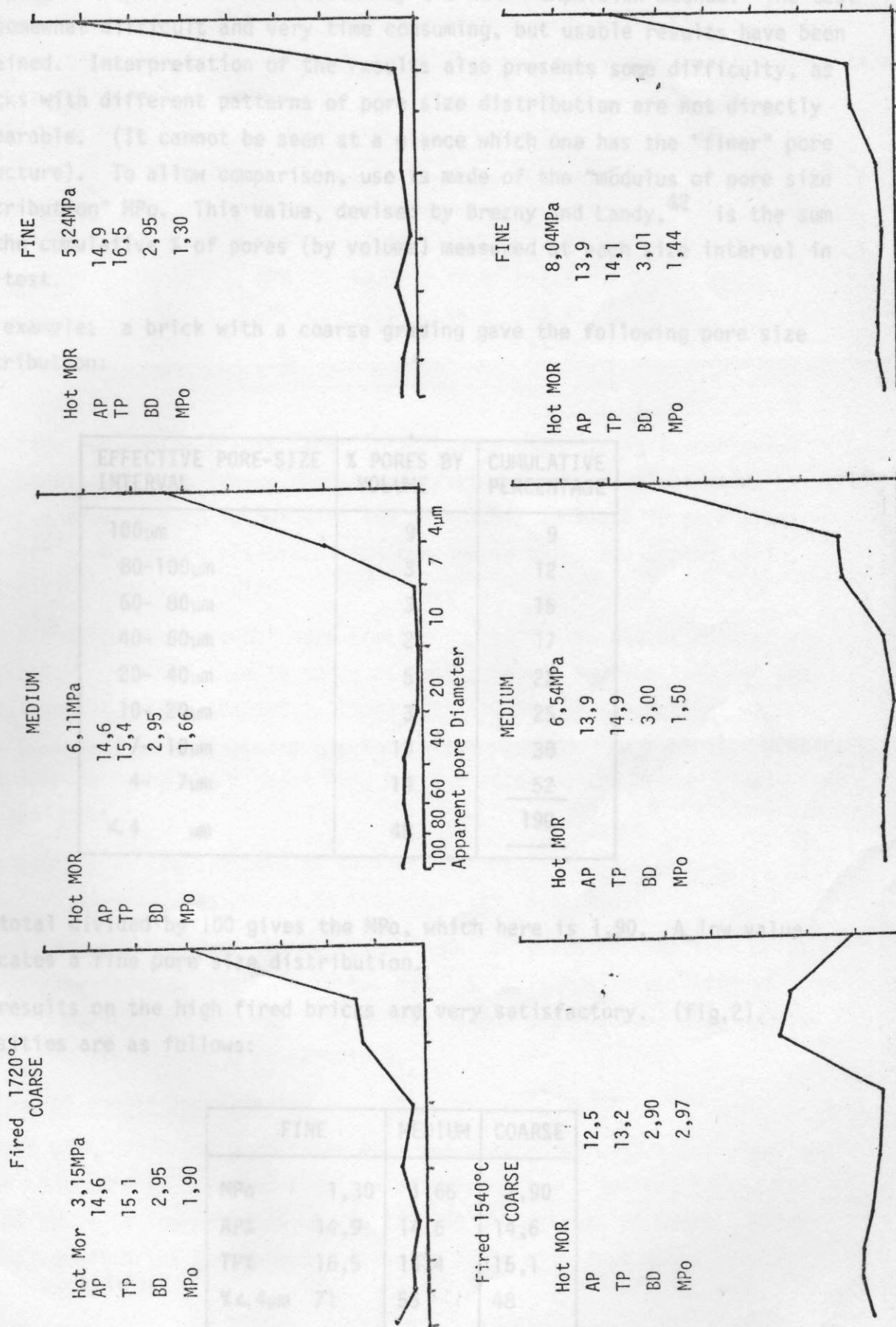


Fig.10.2 - Effect of grading and firing temperature on pore size distribution



Pore Size Distribution

Pore size distributions were tested by the water expulsion method. The test is somewhat difficult and very time consuming, but usable results have been obtained. Interpretation of the results also presents some difficulty, as bricks with different patterns of pore size distribution are not directly comparable. (It cannot be seen at a glance which one has the "finer" pore structure). To allow comparison, use is made of the "modulus of pore size distribution" MPo. This value, devised by Brezny and Landy,⁴² is the sum of the cumulative % of pores (by volume) measured at each size interval in the test.

For example; a brick with a coarse grading gave the following pore size distribution:

EFFECTIVE PORE-SIZE INTERVAL	% PORES BY VOLUME	CUMULATIVE PERCENTAGE
100 μ m	9	9
80-100 μ m	3	12
60- 80 μ m	3	15
40- 60 μ m	2	17
20- 40 μ m	5	22
10- 20 μ m	3	25
7- 10 μ m	13	38
4- 7 μ m	14	52
< 4 μ m	48	190

The total divided by 100 gives the MPo, which here is 1,90. A low value indicates a fine pore size distribution.

The results on the high fired bricks are very satisfactory. (fig.2). Porosities are as follows:

	FINE	MEDIUM	COARSE
MPo	1,30	1,66	1,90
AP%	14,9	14,6	14,6
TP%	16,5	15,4	15,1
% < 4 μ m	71	55	48

Effect of firing temperature

The results of the low fired samples are not interpretable at present, (fig.3 Books, Herron and Beechan,⁵¹ show that the pore size distribution becomes coarser at higher firing temperatures. This was not demonstrated. Porosities are as follows.

	FINE	MEDIUM	COARSE
MPo	1.44	1.50	2.97
AP%	13.9	13.9	12.5
TP%	14.1	14.7	13.2
% 4 μ m	61	56	11

The fine and medium bricks show little change with firing temperature. All porosities drop (where they were expected to rise). The coarse brick shows a greater drop in porosity and a dramatic increase in pore size. Another cored sample was taken from the coarse brick and tested again, but gave a similar result.

These results are somewhat more similar to those obtained by Webster and Jackson,²⁶ (fig.4) than to those of Books, Herron and Beechan, but they still appear rather suspect. (Note that the MPo of Webster and Jackson's coarse sample is practically the same after high and low firing). Webster and Jackson found the highest MOR, hot and cold, on the higher fired, fine graded brick.

Hot modulus of rupture results were as follows:

Fine: 8.04 MPa. Medium: 6.54 MPa. Coarse: 3.35 MPa.

These values are higher than those obtained at 1720°C. The fine brick shows a substantial increase in hot MOR. This is consistent with its lower porosity, and according to Books, Herron and Beechan, also consistent with its coarser pore structure.

Effect of double impregnation

Bricks with different porosities were impregnated through a tar plant and then sent through a second time for reimpregnation. Heating in the tar plant prior to impregnation was at 220-240°C and lasts 24 hours. After reimpregnation the bricks were heated to 300°C with four hours soak.

Retained carbon percentages:

	Seawater MgO	Natural MgO	Low Grade MgO	Average
Once impregnated	2,05	2,18	1,62	1,95
Twice impregnated	2,47	2,19	2,88	2,51
Difference	0,42	0,01	1,26	0,56
% Increase	17,00	1,00	44,00	22,00
% AP	18,50	17,20	23,70	
Carbon Porosity ratio:				
Once impregnated	11,10	12,70	6,80	10,20
Twice impregnated	13,40	12,70	12,20	12,80
% Increase	21,00	0,00	83,00	25,20
MPo	2,06	2,82	3,47	

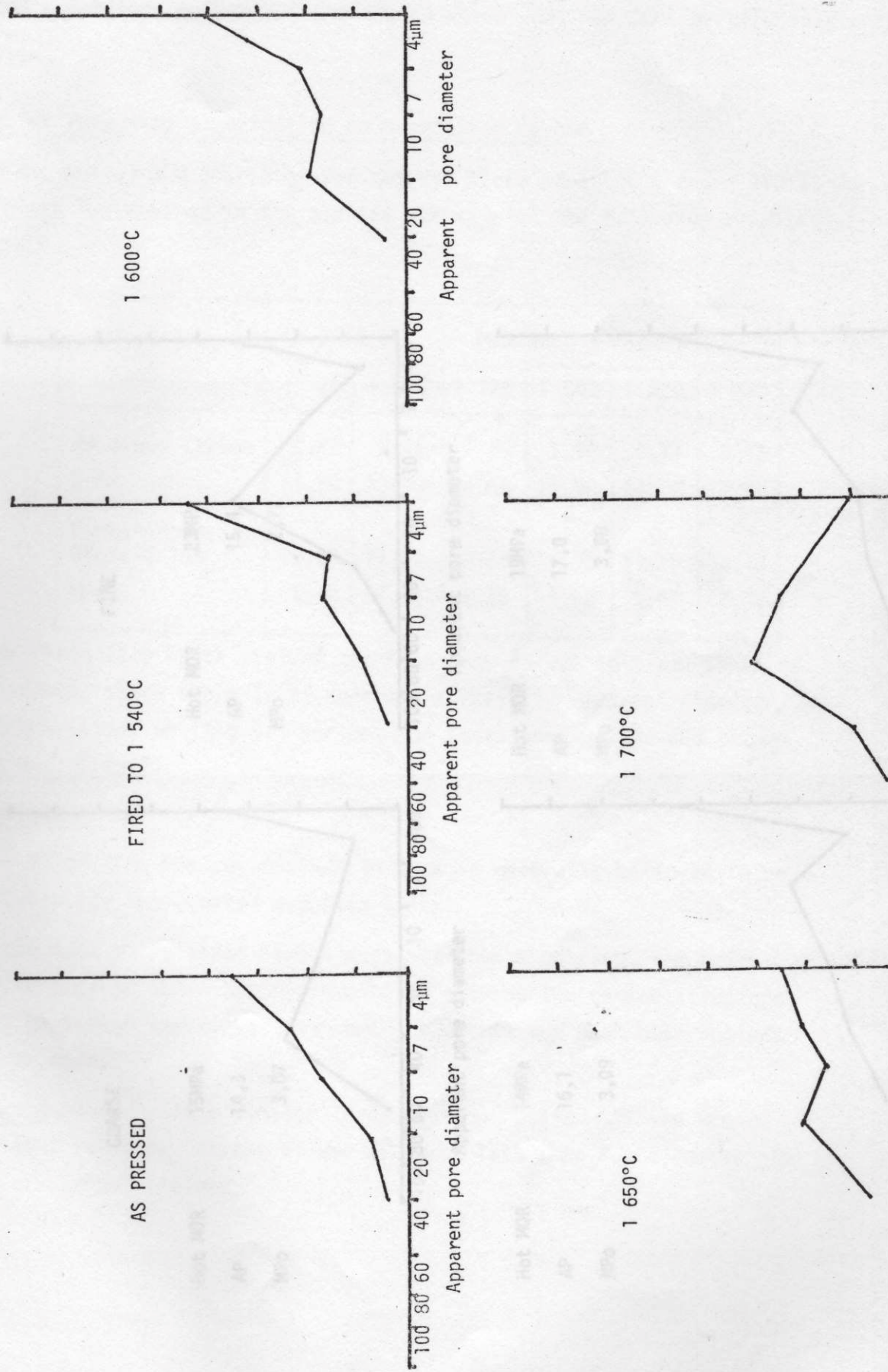
The carbon porosity ratio is a property investigated by Beechan, Padfield and Steger.¹⁶ It is the % retained carbon, divided by the apparent porosity. A value of 25% increase in carbon porosity ratio would predict a decrease in slag attack of 13%. 83% Increase predicts 63% less slag attack, but the brick structure yielding this increase is too coarse to give reasonable slag resistance. The conclusion is that double impregnation is probably not economically feasible. No economic data has been consulted at present.

Pitch impregnation leads to a finer effective pore size distribution. This result is thought to be misleading, and the probable explanation is that access pores are reduced in size and the volume of sample accessible by fine pores after impregnation increases because the large pores are more "enclosed". An "enclosed" pore is a large pore which is not sealed, but only accessible via smaller pores. It is thus reflected on the test results as a fine pore.

Effect of Grade of Pitch used

An impregnation apparatus has been built to test different pitches and impregnation parameters. The apparatus broke down due to carbonisation of the pitch in the transfer pipes. The apparatus has been redesigned and is presently being modified.

Figure 10.3 - Modified from Books, Herron and Beechan. Effect of firing temperatures on grading.



Before failure, one impregnation with a new pitch was carried out and yielded a retained carbon value of 2,42% which does not look particularly promising.

Effect of Pore Size distribution on retained carbon

The fine, medium and coarse graded bricks, fired at 1 540°C and 1 720°C, were pitch impregnated in the old tar plant, with the following results:

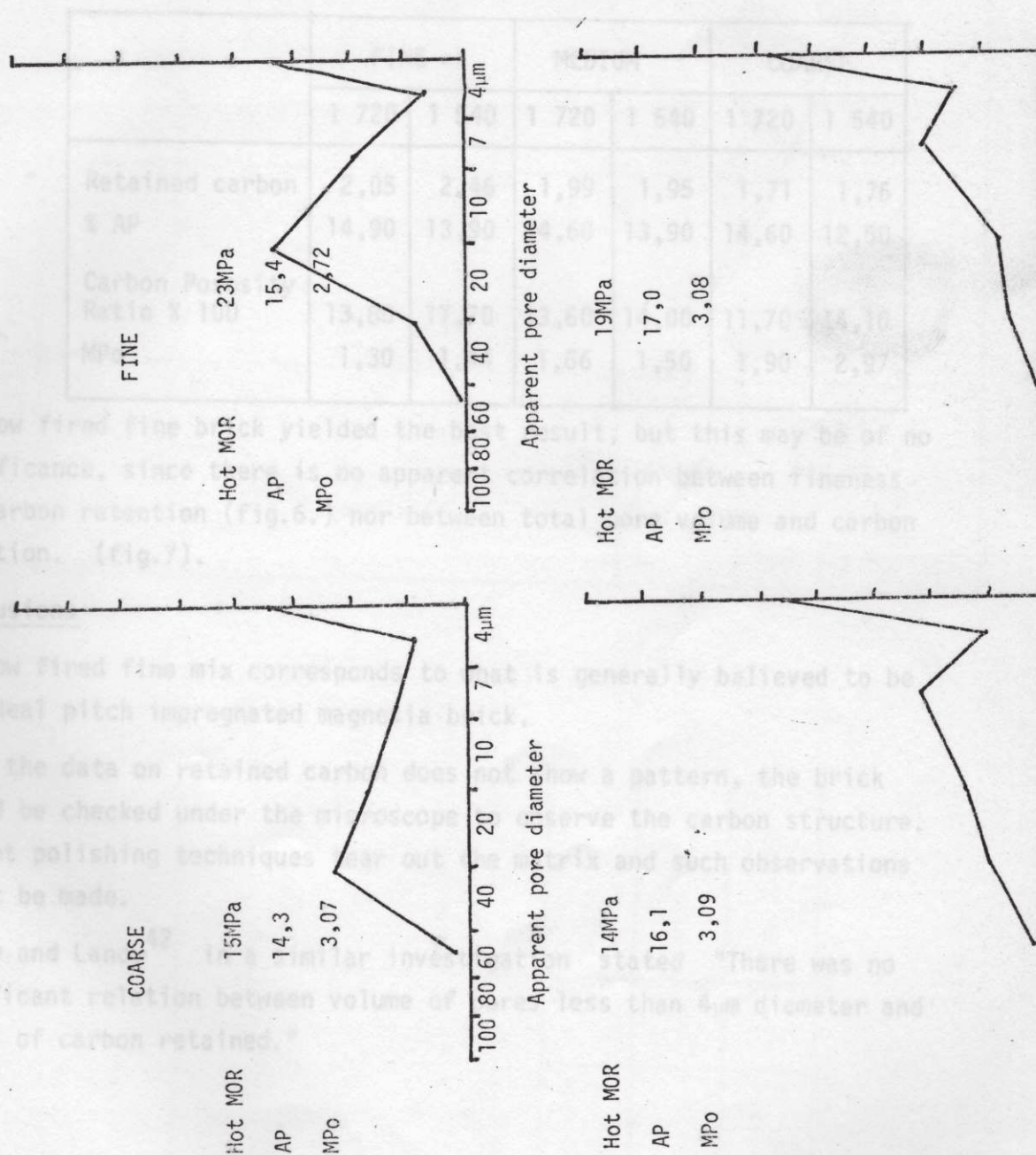


Fig. 10.4 - Reproduced from Webster and Jackson 26

Before failure, one impregnation with a new pitch was carried out and yielded a retained carbon value of 2,42% which does not look particularly promising.

Effect of Pore Size distribution on % retained carbon

The fine, medium and coarse graded bricks, fired at 1 540°C and 1 720°C, were pitch impregnated in the old tar plant, with the following results:

	FINE		MEDIUM		COARSE	
	1 720	1 540	1 720	1 540	1 720	1 540
Retained carbon	2,05	2,46	1,99	1,95	1,71	1,76
% AP	14,90	13,90	14,60	13,90	14,60	12,50
Carbon Porosity Ratio X 100	13,80	17,70	13,60	14,00	11,70	14,10
MPo	1,30	1,44	1,66	1,50	1,90	2,97

The low fired fine brick yielded the best result, but this may be of no significance, since there is no apparent correlation between fineness and carbon retention (fig.6.) nor between total pore volume and carbon retention. (fig.7).

Conclusions

The low fired fine mix corresponds to what is generally believed to be the ideal pitch impregnated magnesia brick.

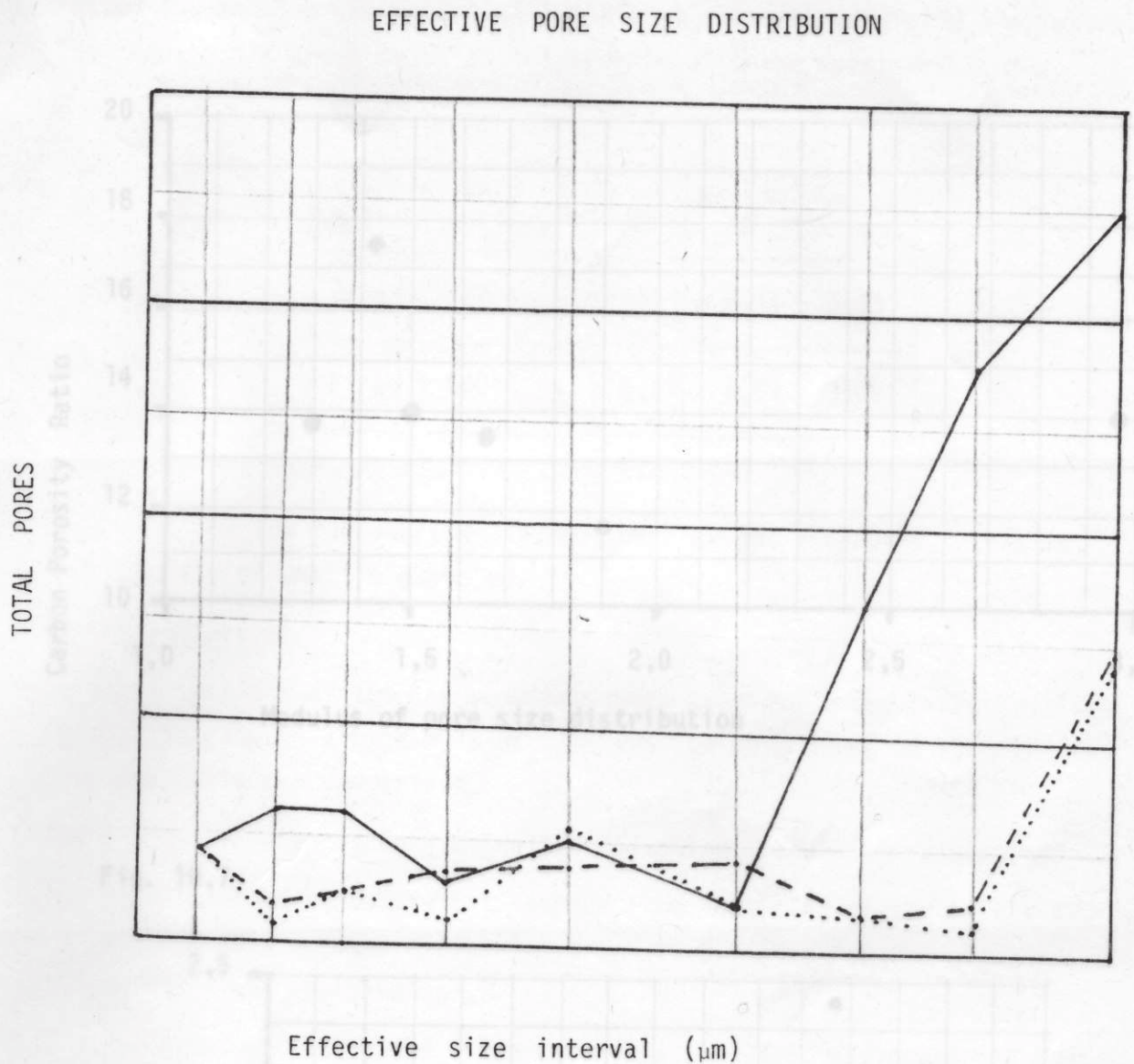
Since the data on retained carbon does not show a pattern, the brick should be checked under the microscope to observe the carbon structure. Present polishing techniques tear out the matrix and such observations cannot be made.

Brezny and Landy⁴² in a similar investigation stated "There was no significant relation between volume of pores less than 4 μ m diameter and amount of carbon retained."

	MPo	2,06	2,62	3,47
Impregnated	AP	6,7		13,5
	MPo	2,93		5,73
	RC	2,05		1,62
Twice Impregnated	AP	5,64	8,9	6,33
	MPo	2,36	2,16	2,70
	RC	2,47	2,19	2,80

Fig. 10.5 Medium, Fired 1 720°C

— Fired
 - - - Once Impregnated
 Twice Impregnated



		Seawater	Natural	Low Grade
Fired	AP	17,4	17,2	23,7
	MPo	2,06	2,82	3,47
Impregnated	AP	6,7		13,5
	MPo	2,93		5,73
	RC	2,05		1,62
Twice Impregnated	AP	5,64	8,9	6,33
	MPo	2,96	2,10	2,70
	RC	2,47	2,19	2,88

All values are calculated as % AP after firing.

Fig. 10.6

Hot Modulus of Rupture

Unimpregnated specimens measuring 150mm X 25mm were cut from the bricks and tested for modulus of rupture at 1 450°C in a normal oxidising atmosphere. The results are shown below as the average of three specimens in MPa.

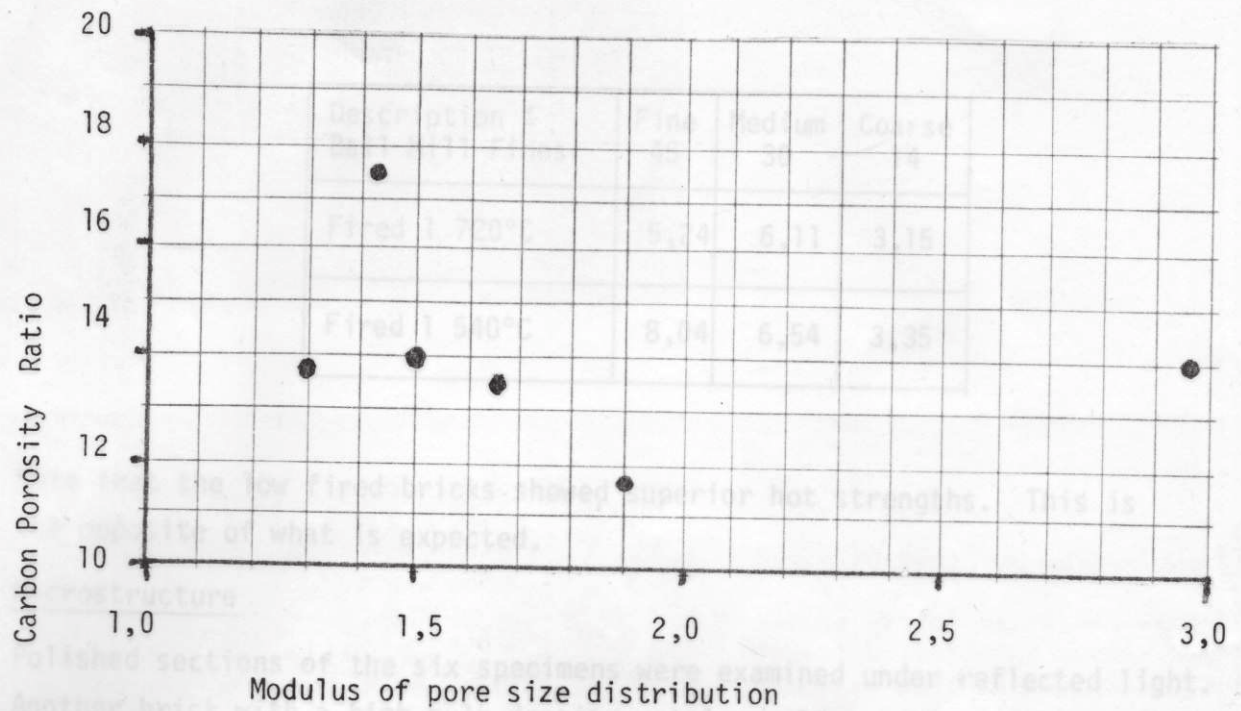
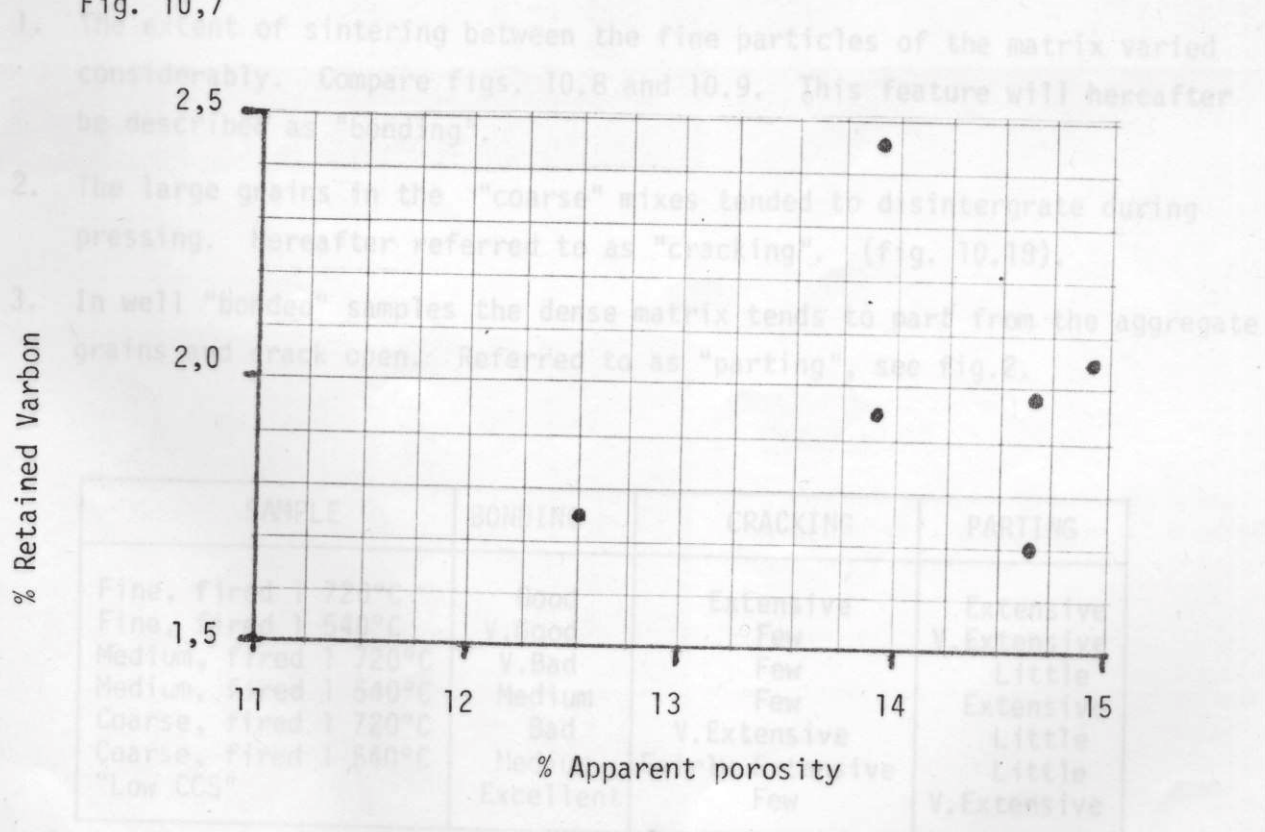


Fig. 10,7



Hot Modulus of Rupture

Unimpregnated specimens measuring 150mm X 25mm were cut from the bricks and tested for modulus of rupture at 1 450°C in a normal oxidising atmosphere. The results are shown below as the average of three specimens in MPa.

Description % Ball Mill Fines	Fine 45	Medium 30	Coarse 14
Fired 1 720°C	5,24	6,11	3,15
Fired 1 540°C	8,04	6,54	3,35

Note that the low fired bricks showed superior hot strengths. This is the opposite of what is expected.

Microstructure

Polished sections of the six specimens were examined under reflected light. Another brick with a high bulk density yet low cold crushing strength was also available for comparison.

Apart from differences in grading the following features were observed:

1. The extent of sintering between the fine particles of the matrix varied considerably. Compare figs. 10.8 and 10.9. This feature will hereafter be described as "bonding".
2. The large grains in the "coarse" mixes tended to disintergrate during pressing. Hereafter referred to as "cracking". (fig. 10.10).
3. In well "bonded" samples the dense matrix tends to part from the aggregate grains and crack open. Referred to as "parting", see fig.2.

SAMPLE	BONDING	CRACKING	PARTING
Fine, fired 1 720°C	Good	Extensive	Extensive
Fine, fired 1 540°C	V.Good	Few	V.Extensive
Medium, fired 1 720°C	V.Bad	Few	Little
Medium, fired 1 540°C	Medium	Few	Extensive
Coarse, fired 1 720°C	Bad	V.Extensive	Little
Coarse, fired 1 540°C	Medium	Fairly Extensive	Little
"Low CCS"	Excellent	Few	V.Extensive

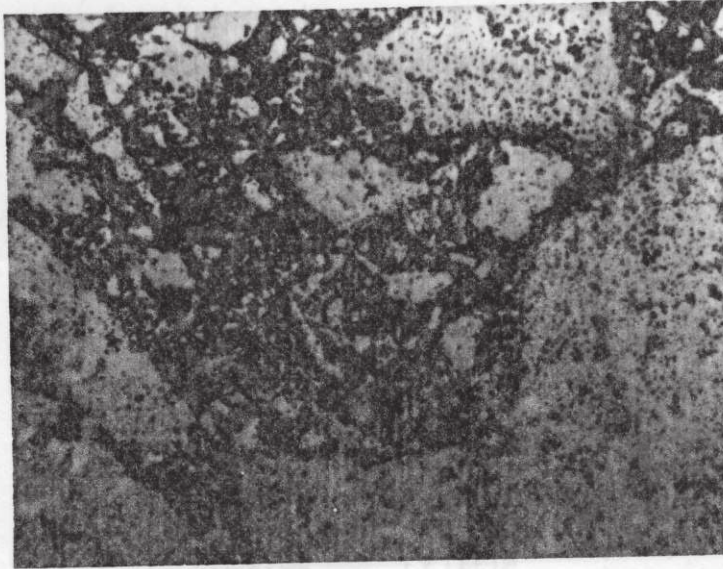


Fig. 10.8

A coarse graded brick, showing low density, poorly bonded matrix.

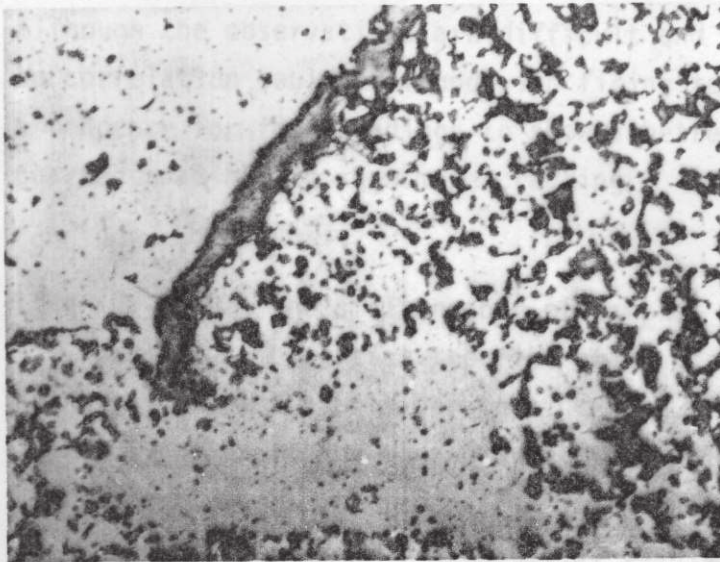


Fig. 10.9

A fine graded brick, showing the dense, well-bonded matrix, adhering well to one grain, but parting from the other grain.

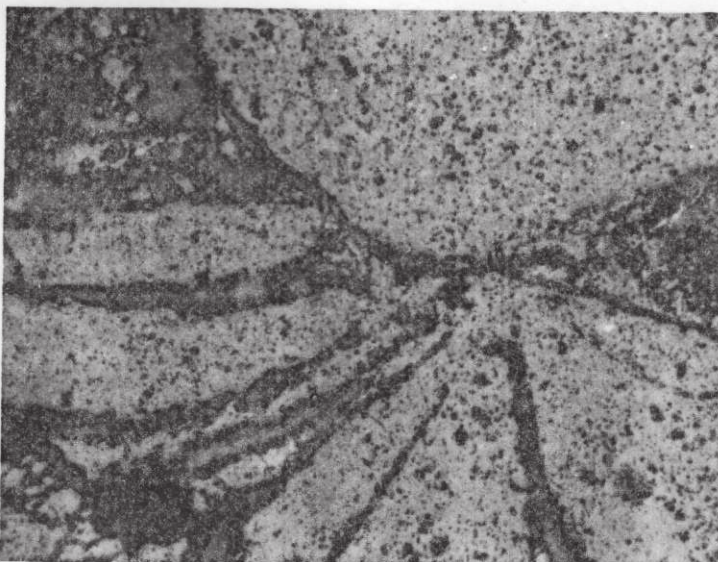


Fig. 10.10

A coarse graded brick, showing a grain which has been shattered during pressing.

The only clear pattern seen in these results is a direct correlation between bond development and parting. The observation can be arranged in order of magnitude as follows:

Matrix Bond	Extent of Parting	Sample
Excellent	very extensive	"Low CCS"
Very good	very extensive	Fine, fired 1 540°C
Good	Extensive	Fine, fired 1 720°C
Medium	Extensive	Medium, fired 1 540°C
Medium	Little	Coarse, fired 1 540°C
Bad	Little	Coarse, fired 1 720°C
Very Bad	Little	Medium, fired 1 720°C

Although the observations are difficult and subjective, they are reproducible. No correlation could be found with firing temperature or grading, except for a tendency for fine gradings to show a better bond but more parting and coarser gradings to show more cracking.

Conclusions

It appears that the small number of samples yields inconsistent results. It would seem possible that the fine grading is still too coarse to allow the brick to contract evenly during sintering. The coarse aggregate particles may be in contact, and thus prevent the whole brick from contracting, and the matrix tears apart as it densifies. Theoretically, a still finer brick would eliminate this problem and also cushion the coarse grains to prevent cracking. Such a brick may present considerable problems with lamination during pressing, but a trial could be very informative.

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CHAPTER 11

EXAMINATION OF BRICKS AFTER SERVICE.

Unfortunately it was not possible to test any of the experimental bricks in service or in simulated service experiments. Extracts from reports on used pitch impregnated periclase bricks are included here to illustrate some of the phenomena observed.

The first report concerns a brick which performed well in an L.D. vessel:

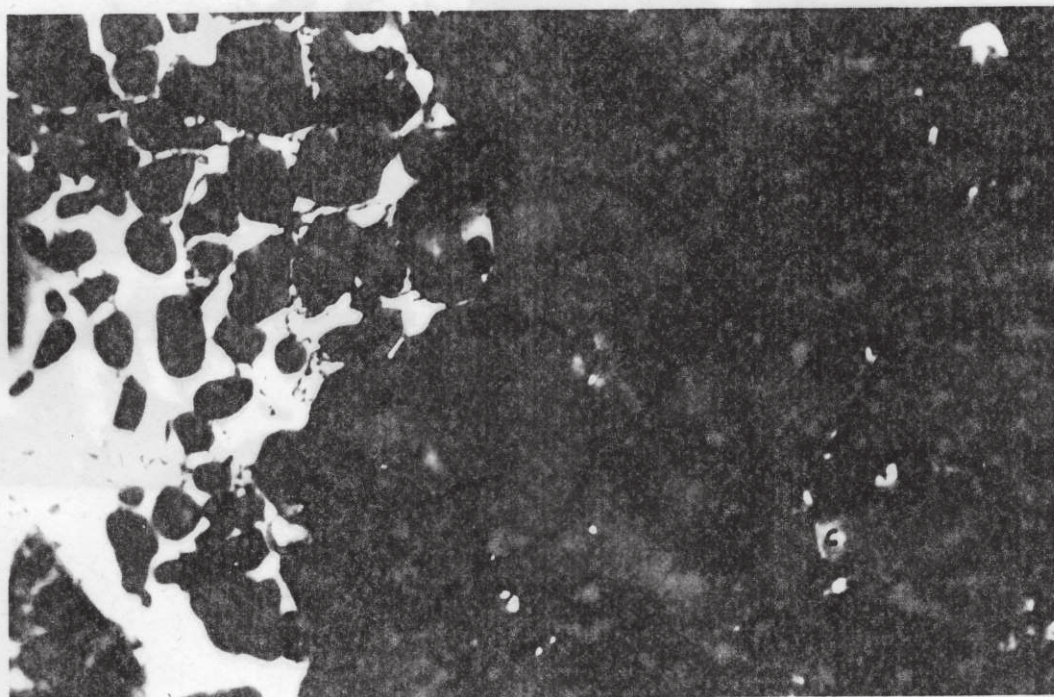
Slag Resistance

Various reactions involving the retained carbon from the pitch impregnation inhibit slag penetration. A very important reaction is the volatilisation of MgO : At high temperature MgO and carbon are thermodynamically incompatible and MgO is reduced by the carbon, releasing Mg metal vapour and CO . This reaction depletes the MgO in the matrix, weakening the structure in the area behind the hot face in what is known as the decarburised zone.

The Mg vapour will be deposited wherever the oxygen partial pressure is sufficiently high. The oxygen partial pressure increases towards the hot face and the Mg vapour is deposited at the slag/brick interface as MgO . Ideally, this deposition will completely seal the brick pores and present an impervious MgO surface to the slag, preventing slag penetration. The impervious layer is not formed in all bricks in L.D. applications, but the MgO volatilisation is strictly temperature controlled. Therefore the dense layer formation is very important. If it forms it is highly beneficial in preventing slag penetration, and if it does not form, the MgO volatilisation in the decarburised zone continues unimpeded, weakening the brick and opening the pores to slag penetration.

Fig.1 shows an area of the used brick where the densification has progressed well. On the left is the slag, the bright phase, with undissolved periclase crystallites in it. Through the centre is the dense layer, which at this point is perfectly impervious. On the right is the decarburised zone. Here the bright spots are carbon (coked pitch), C, the light grey areas are the periclase, M, crystallites and the darker grey areas between them are dicalcium silicate, S. The indistinct black areas are pores, P. Fig.2 shows the matrix farther back in the brick. Carbon is more abundant here but no structural difference in the matrix can be seen. The carbon is in randomly distributed lumps in the matrix.

FIG. 1



SLAG

DENSE ZONE

DECARBURISED ZONE

FIG. 2

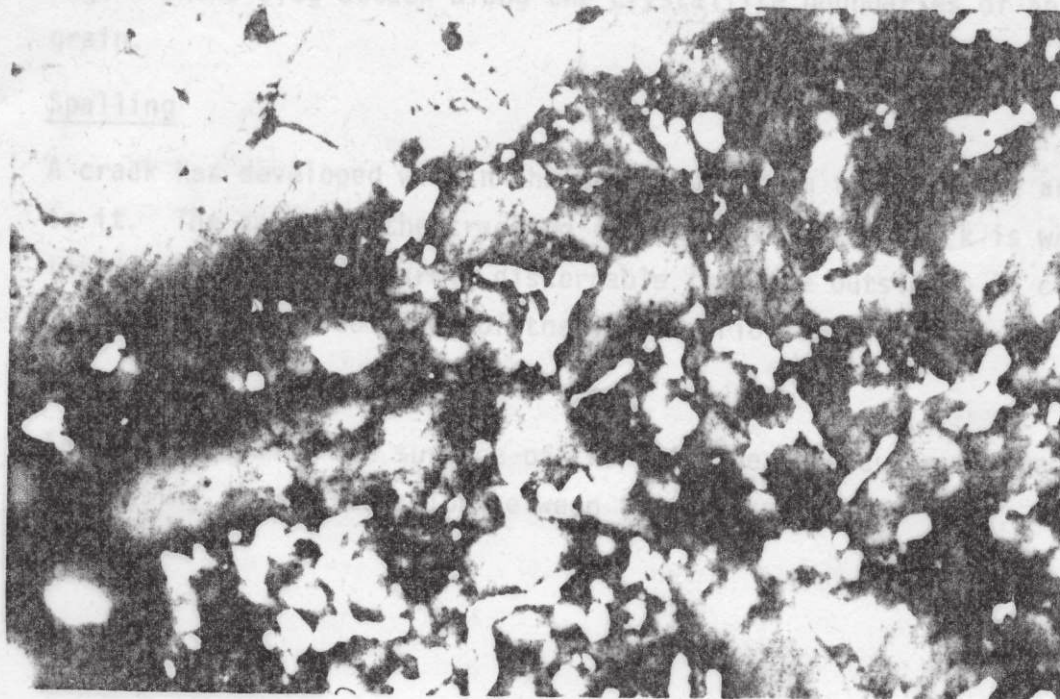
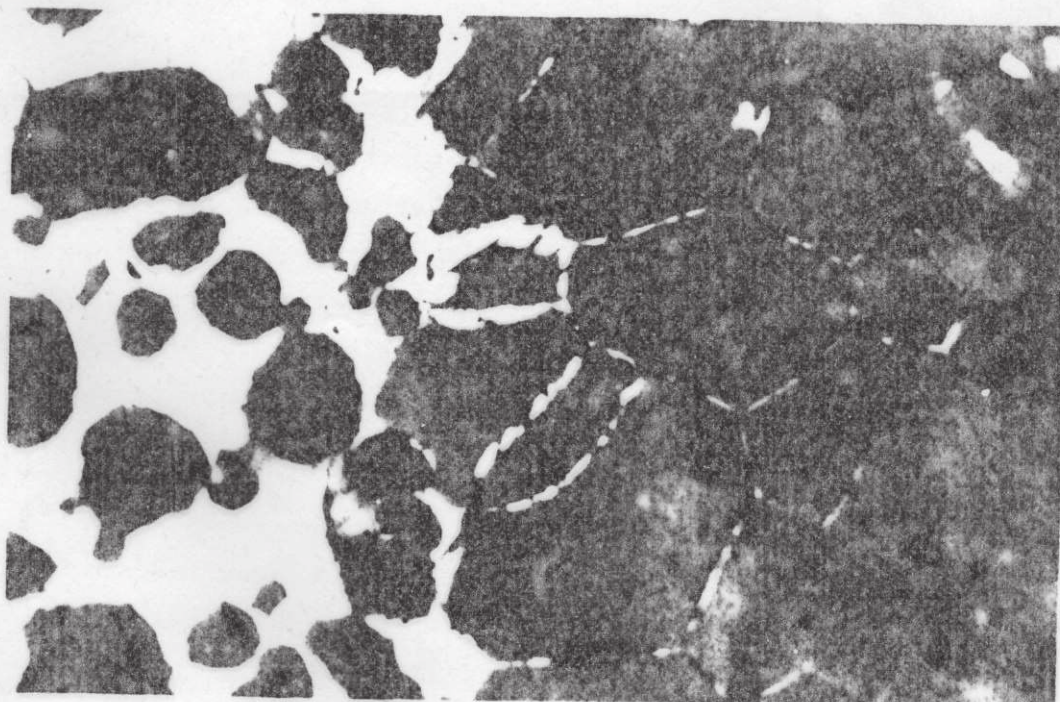


FIG. 3



The second report involved a brick which burnt through early. The

Fig. 3 shows slag attack along the crystallite boundaries of an aggregate grain.

Spalling

A crack has developed within the brick 50mm from the hot face and parallel to it. The cause of the cracking is not known. The crack is well developed inside the brick but barely discernable from the outside. It could have developed during cool down of the vessel prior to wrecking.

Iron Penetration

Iron was found on the surface of the brick perpendicular to the slag face, indicating iron penetration between the bricks.

The structure of the outer layer is typical of that formed by Mg vapour deposition. The outer surface is continuous and the density decreases from the surface inwards. Iron droplets of reduced iron are sometimes encountered on the slag/brick contact in BOF refractories. These droplets are generally considered to have formed secondarily, i.e. slag iron oxides have been reduced by the carbon in the brick. It has been shown that this reaction consumes a great deal of carbon. This sample has a large volume of iron droplets and in places there is a thick (2-3mm) layer of iron in contact with the brick. However, the brick does not seem to be excessively depleted in carbon.

The photographs show all the features mentioned above, and in addition they show what is thought to be the formation of magnesioferrite from the slag.

An X-ray diffraction trace was run on the slag and yielded surprising and disappointing results. Although several phases are identifiable even in the photographs, only two were visible on the trace, namely dicalcium ferrite (anisotropic) and periclase. The periclase peaks were extremely low. The slag from a recently investigated brick was compared. It also yielded only dicalcium ferrite and periclase, but the periclase peaks were high, as expected.

Chemical Analysis of Slags

For many reasons, a slag sample cut off a BOF brick should not be considered representative of anything, yet the results are so extremely different as to justify their inclusion.

The second report involved a brick which burnt through early. The photographs and mineralogical discussion are included here:

Slag Face Microstructure

The dense layer which forms by vapour phase transport of Mg can be seen in most parts of the contact. In some parts there appear to be two consecutive dense layers, the outer one having been breached by the slag. The area between the dense layers contains an anisotropic slag phase, and is severely depleted in MgO.

The structure of the outer layer is typical of that formed by Mg vapour deposition: The outer surface is continuous and the density decreases towards the brick. (see photographs).

Small droplets of reduced iron are sometimes encountered on the slag/brick contact in BOF refractories. These droplets are generally considered to have formed secondarily, i.e. slag iron oxides have been reduced by the carbon in the brick. It has been shown that this reaction consumes a great deal of carbon. This sample has a large volume of iron droplets and in places there is a thick ($\pm 1\text{mm}$) layer of iron in contact with the brick. However, the brick does not seem to be excessively depleted in carbon.

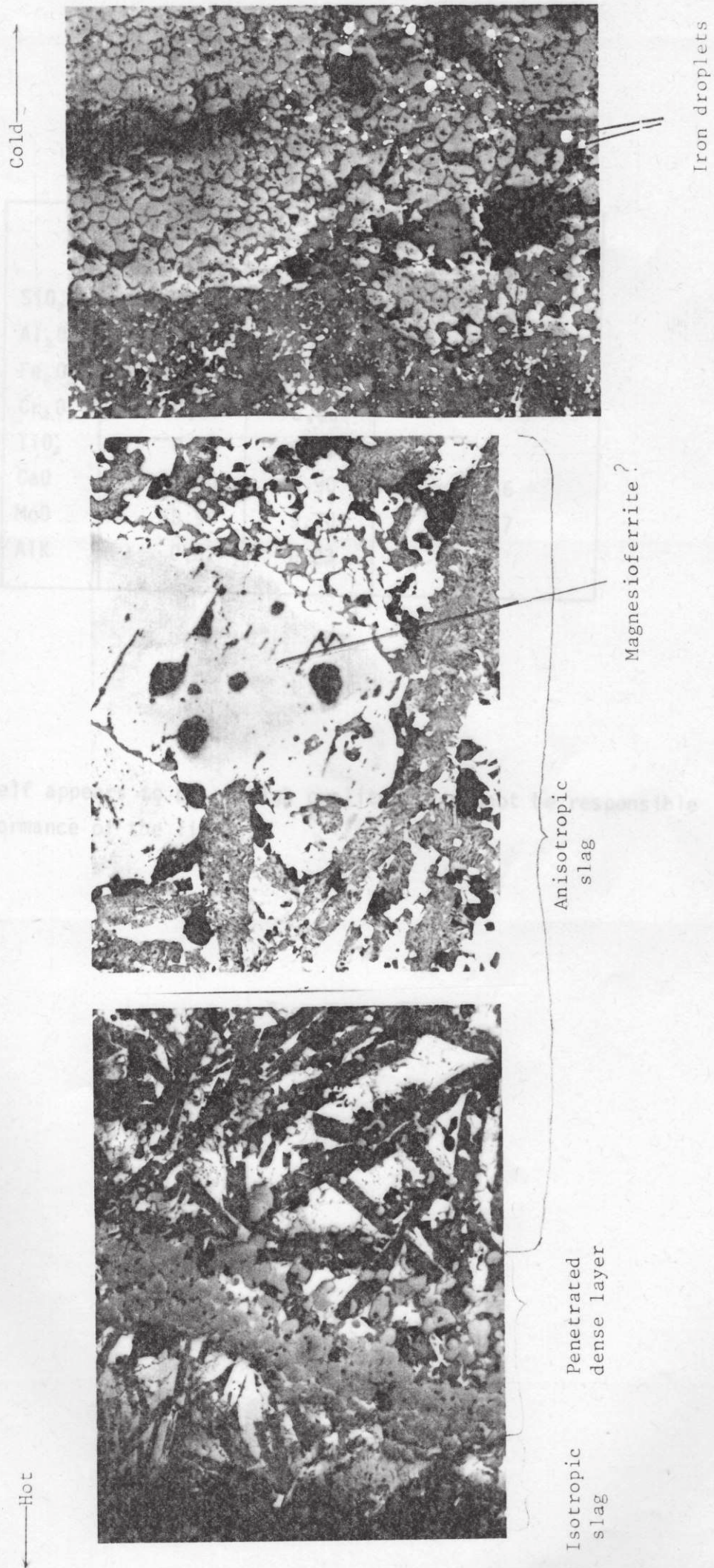
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Chemical analysis of Slags

For many reasons, a slag sample cut off a BOF brick should not be considered representative of anything, yet the results are so extremely different as to justify their inclusion.

PF MICROGRAPHS OF SLAGGED FACE



	Other Slag	This Slag	Typical Pure Slag
SiO ₂	2,40	17,40	11,4
Al ₂ O ₃	0,30	0,50	-
Fe ₂ O ₃	19,60	23,20	26,9
Cr ₂ O ₃	0,31	0,36	-
TiO ₂	0,26	1,06	-
CaO	23,10	46,90	39,6
MgO	50,96	9,70	7,7
AlK	0,07	0,23	

Conclusions

The brick itself appears to be of high quality and cannot be responsible for poor performance of the lining.

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