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BODY COMPOSITION AND PROCESSING OF MAGNESITE
AND OTHER BASIC REFRACTORIES ^{1/}

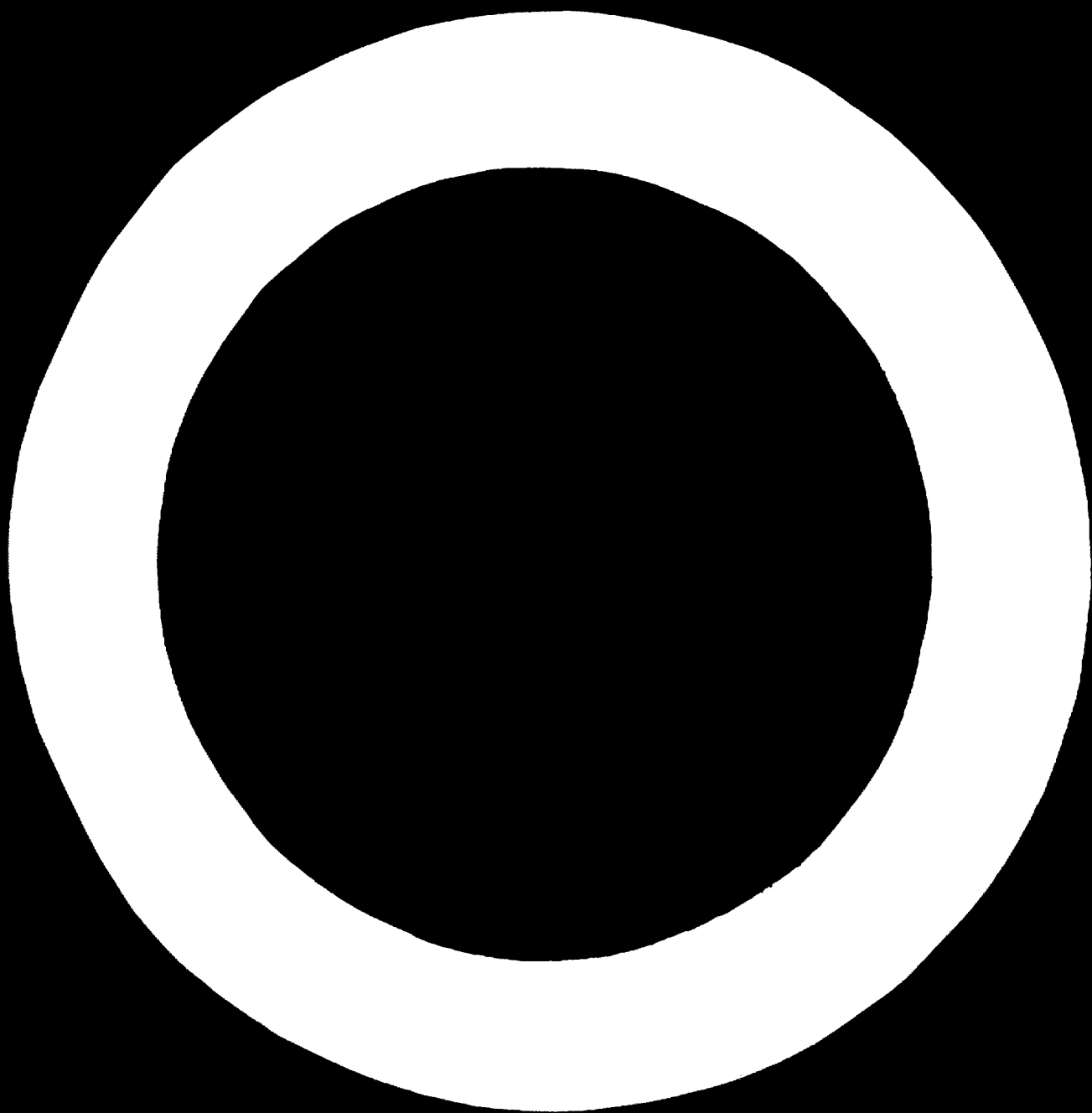
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INTRODUCTION

Magnesia, dolomia, and the materials produced from the mixtures of magnesia with chrome ore fall into the group of basic refractories. They are marked by a high slags resistance at high temperature.

They are used mostly for lining the furnaces and vessels for relining and processing liquid steel. Their production and evolution connected with this industrial branch.

The deep changes in the processes and devices used for steel relining which took place within 15 years ago resulted in a substantial decrease in the specific consumption of basic refractories as well as a rearrangement of the kinds used and enforced rapid progress concerning the properties of the kinds in use.

Basic refractories linings are stressed in the intensified metallurgical processes / high temperatures, variation of temperature, corrosive slags/ to the limit of their abilities given by the physico-chemical character of these substances.

Therefore the development tends to the improvement of mechanical properties at high temperatures, the increase in their density, and the decrease in their porosity.

I. MAGNESIA

A. Mineral composition of sinter-magnesia

The fundamental material for the production of basic magnesia materials is sinter-magnesia. For estimating the quality of sinter-magnesia, particular emphasis is laid upon its mineral composition and density.

In spite of the fact that periclase is the constituent substance of sinter-magnesia, the accessory minerals are responsible for its properties. The amount and composition of accessory minerals affect the formation of liquid molten substance, the amount, viscosity, and temperature of formation of this substance.

The main factor influencing the mineral composition is the molar ratio $\text{CaO}:\text{SiO}_2$. Rigby pointed out that according to this ratio $\text{CaO}:\text{SiO}_2$ two fundamental types of sinter-magnesia could be distinguished, i.e. one with $\text{CaO}:\text{SiO}_2 \leq 2$ and another with $\text{CaO}:\text{SiO}_2 > 2$.

The mineral composition of these fundamental types is in principle presented in Table 1 and Table 2.

Note to Table 1.

M	MgO - Periclase - melting point 2800°C
MF	$\text{MgO} \cdot \text{Fe}_2\text{O}_3$ - Magnesium ferrite - melting point 1750°C
MA	$\text{MgO} \cdot \text{Al}_2\text{O}_3$ - spinel - melting point 2135°C
M_2S	$2\text{MgO} \cdot \text{SiO}_2$ - forsterite - melting point 1890°C
CMS	$\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$ - monticellite - melting point 1490°C
C_3MS_2	$3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ - merwinite - melting point 1575°C
C_2S	$2\text{CaO} \cdot \text{SiO}_2$ - dicalcium silicate - melting point 2130°C

Table 1 : Mineral composition of altered magnesia at the
molar ratio $\text{CaO}:\text{SiO}_2 < 2$

C : S	Minerals present
1	$\text{M}_2\text{S} + \text{CMS} + \text{MF} + \text{MA} + \text{H}$
= 1	$\text{CMS} + \text{MF} + \text{MA} + \text{H}$
1 - 1,5	$\text{CMS} + \text{C}_3\text{MS}_2 + \text{MF} + \text{MA} + \text{H}$
= 1,5	$\text{C}_3\text{MS}_2 + \text{MF} + \text{MA} + \text{H}$
1,5 - 2	$\text{C}_3\text{MS}_2 + \text{C}_2\text{S} + \text{MF} + \text{MA} + \text{H}$
= 2	$\text{C}_2\text{S} + \text{MF} + \text{MA} + \text{H}$

Provided it is valid $\text{CaO}:\text{SiO}_2 > 2$, the formation of minerals in sinter-magnesia depends on various factors, especially with respect to the presence of Al_2O_3 and Fe_2O_3 the content of CaO , Al_2O_3 or Fe_2O_3 is in minimum and in which molar ratio the contents of CaO and Fe_2O_3 or Al_2O_3 are present. Table 2 gives such mineral composition in a simplified form.

Note to Table 2.

C_4AF $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ - brownmillerite - m.p. 1415°C

C_2F $2\text{CaO}.\text{Fe}_2\text{O}_3$ - dicalcium ferrite - m.p. 1435°C

C_3A - CA the series of minerals from $3\text{CaO}.\text{Al}_2\text{O}_3$ to
 $\text{CaO}.\text{Al}_2\text{O}_3$

Table 2.: Mineral composition of sintered magnesia at the molar ratio $\text{CaO}:\text{SiO}_2 > 2$

In minimum is	Minerals present
CaO Al_2O_3 Fe_2O_3	$\text{C}_2\text{S} + \text{C}_4\text{AF} \rightleftharpoons \text{C}_2\text{F} + \text{M} + \text{MF} + \text{H}$ $\text{C}_2\text{S} + \text{C}_4\text{AF} \rightleftharpoons \text{C}_2\text{F} + \text{MF} + \text{C}_3\text{S} + \text{C} + \text{H}$ $\text{C}_2\text{S} + \text{C}_4\text{AF} + \text{C}_3\text{A} \rightleftharpoons \text{C}_1 + \text{M} + \text{H}$

B. Types of starting materials.

The sinter-magnesia is obtained from natural magnesites, sea water or $MgCl_2$ liquors.

The natural magnesites occur in two forms, i.e. crystalline and amorphous. The deposits in CSSR, Austria- the so-called breuneritic magnesites as well as the deposits in Soviet Union and China belong among the crystalline magnesites.

The deposits in Balkan, Near Asia, India, Ural, Australia, and South Africa belong among the amorphous magnesites.

Some less important sources are based on brucite the deposits of which occur in Canada and USA. Typical compositions of some natural magnesites are presented in Table 3 in which only the fundamental components of magnesites are listed.

Table 3 : Typical composition of natural magnetites /weight %/
 calculated for the state without ignition loss

	Cristalline				Amorphous	
	ČSR	ČSR	Austria	Austria	Greece	Jugo- slavia
MgO	84,8	85,5	85,3	86,0	93,6	94,3
Fe ₂ O ₃	8,0	7,0	7,8	3,2	0,1	0,1
SiO ₂	1,2	3,0	3,4	2,9	2,1	0,8
CaO	6,0	3,0	1,8	3,1	2,5	1,1

In sea water magnesium is present in the form of $MgCl_2$ and $MgSO_4$. The content of magnesium is 0,13% on the average, i.e. $1 m^3$ of sea water contains 1.3 kg of magnesium. Table 4 gives the mean content of Mg in the water of various world seas.

The concentration of Mg in small or closed seas is not constant. It varies with the time of day and year, temperature, the depth of sea, etc. In general, the production of magnesium from sea water with a content of Mg less than 0.13% is considered to be improper from the economical point of view.

Another source of MgO are the waste liquors from $MgCl_2$ chemical industry or desalting processes which concerns especially the production of potash from carnallite $/KCl.MgCl_2.6H_2O/$, or kieserite processing.

C. Raw magnesite processing

Before the sintering, the natural raw magnesites are enriched by various dressing methods-among which the dressing in heavy suspensions and flotation are the most important.

The dressing of raw materials in heavy suspensions is one of the oldest methods for obtaining the concentrates and separating them accessory harmful minerals. It is based on different specific densities of the components which can be thus separated from one another. For instance, the properties of following minerals which may be separated in heavy suspension can serve for comparison:

Table 4: Mean content of Mg in sea water

Sea	Mg /‰	Sea	Mg /‰
Red Sea	0,1419	Pacific	0,1298
Persian	0,1411	Indian Sea	0,1296
Adriatic Sea	0,1397	Northern Sea	0,1152
Mediterranean	0,1345	Black Sea	0,0631
Atlantic	0,1302	Baltic	0,0334
Caribbean Sea	0,1300		

Calcite	CaCO_3	2,72 g.cm ⁻³
Dolomite	$\text{CaMg/CO}_3/2$	2,85 g.cm ⁻³
Magnesite	MgCO_3	3,02 g.cm ⁻³

A heavy suspension is prepared by means of various substances, e.g. ferrosilicon, and is adjusted to the demanded and precisely defined value. For instance, if calcite and dolomite should be removed, the density of aqueous suspension of ferrosilicon is adjusted to the value of 2,9 - 3,0. The minerals with lower specific weight remain on the surface of the heavy suspension while magnesite and breunnerite fall into the heavy suspension and thus separate.

The efficiency of this dressing process depends on the size of the entering into dressing. The initial grading used is mostly between 10 to 90 mm. The effect depends on the character of mutual infiltration of the separated minerals. The substances forming heavy suspension are recovered and brought back into the process. The concentrate obtained is processed then into sintered magnesia in sintering furnaces at temperatures over 1700°C.

A more effective enrichment of raw magnesites may be achieved by flotation. This method of enrichment consists in a different surface activity - wettability - of the minerals contained in utilizable component and gangue. The complicated physico-chemical forces effective in the interfaces of three phases, i.e. gaseous /air/ - aqueous - solid /a mixture of separated minerals/ are employed.

The higher selectivity of the dressing by flotation in contrast to the dressing in heavy suspensions - is due to the fact that the particles entering into the flotation process are separated, their grading being in the range

from 0,09 mm to 0,02 mm. A greater amount of fine sludge particles which are smaller than 0,02 mm bonds the flotation agents and impairs the effect of flotation process. Conversely, a greater amount of coarser particles reduces the selectivity of dressing.

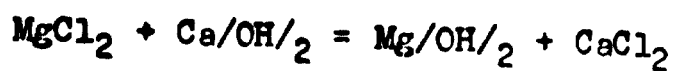
In the flotation process different kinds of flotation agents are used: These agents affect the surface properties of the minerals which are to be separated.

The flotation of magnesites is usually carried out in two stages. The flotation concentrates which have been deprived of flotation agents and water are processed into sintered magnesia by the process described below.

Another method convenient for dressing magnesites after their sintering is the electromagnetic separation. It is used only for crystalline breunneritic magnesites. This method is based on the magnetic properties of magnesium ferrite which arises during firing the isomorphic mixture $MgCO_3 - FeCO_3$. Magnesium ferrite forms a solid solution in periclase which assumes thereby magnetic properties. Other mineral impurities of breunnerite such as dolomite and silicates come into wastes because they are not attracted by magnetic forces.

D. Production of magnesia from sea-water

The sea-water rich in the salts of magnesium is treated firstly with some sulphuric acid, which makes hydrocarbonates decompose. The liberated carbon dioxide is desorbed in towers. By using specially prepared highly pure lime milk, $Mg(OH)_2$ is precipitated from the treated water according to the reaction



The Mg/OH/2 suspension settles-down in several stages in large sedimentation basins and is washed with sweet water. The washed Mg/OH/2 sludge is filtrated on vacuum filters.

The moist filter cake is calcinated at 900 - 1000°C in story furnaces of the HERRESHOFF type. In this way an active MgO is obtained. This product is briquetted and sintered. The principle of this technology is schematically represented in Figure I.

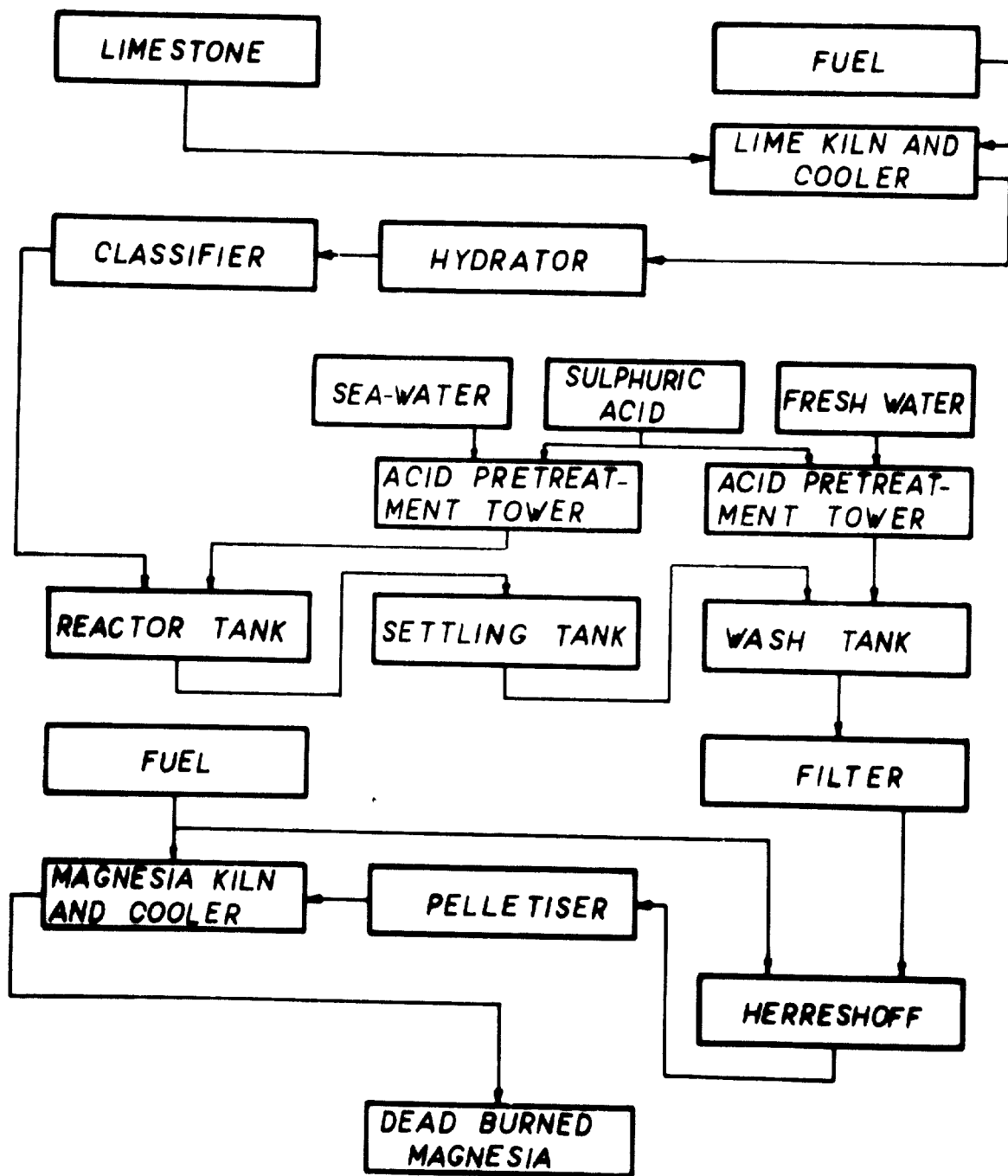
By an analogous process MgO can be obtained from waste salt brines. Calcium sulphate is precipitated and separated by means of calcium chloride. The solution of MgCl2 is precipitated again with lime milk and the precipitate of Mg/OH/2 obtained is further treated as described before.

The solution of MgCl2 may be also processed by thermal decomposition in reactors at about 650°C. MgO and HCl are formed. The light MgO hydrates in several steps and subsequently it is washed with treated sweet water. Thus a filtration cake of Mg/OH/2 is obtained. This cake is processed into sintered magnesia in an equal process like Mg/OH/2 obtained from sea-water.

B. Sinter-magnesia processing from powdered material

The concentrates remaining after the flotation of natural magnesites are grinded before shaping. In order to achieve higher densities it is advisable before grinding to activate the flotation concentrates by calcination at temperatures from 500° to 800°C. The most convenient calcination

FIGURE I. SEA WATER MAGNESIA PROCESS
FLOW DIAGRAM



device is a multiple-hearth furnace. Using a dry briquetting without any binder the briquets are formed in briquetting rollpresses. The higher the density of briquets, the higher density is achieved by sintering.

Whole briquets as well as their fragments exceeding 7 to 10 mm are entered into sintering equipment. The briquets of flotation concentrate sinter in rotary or shaft kilns. The modern shaft kilns make possible a sintering at $2000^{\circ} - 2100^{\circ}\text{C}$.

The sinter-magnesia is processed by crushing, sieving, and milling on various to different grading including a finely milled matrix.

The processing of the light active MgO prepared from sea-water or brines by the calcination of $\text{Mg}(\text{OH})_2$ is in principle analogous to the flotation concentrate processing.

The briquets of calcinated flotation concentrate or MgO have to be sintered immediately after shaping.

F. Typical properties of dead-burned magnesia

Typical properties of dead-burned magnesia are given in Table 5.

The content of B_2O_3 in magnesia from sea-water reaches 0,25%. For the production of first-quality dead-burned various processes removing boron are used. Using these processes the content of that harmful component may be reduced under 0,02% of B_2O_3 .

Further development of the quality of dead-burned magnesia is determined by the demand to reduce to the maximum degree the content of accessory oxides, in particular,

Table 5 : Chemical composition /weight %/ and bulk density /g.cm⁻³/ of dead-burned magnesite

Magnesites		SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	Bulk Density
China	Natural	0,8	7,6	0,4	2,6	88,4	3,30
China	- " -	1,0	5,5	0,3	2,5	90,7	3,35
Austria	- " -	0,9	6,0	0,5	2,7	89,7	3,35
Austria	- " -	1,6	3,5	0,5	2,1	91,9	3,35
Greece	- " -	1,2	0,2	0,2	2,6	95,4	3,30
Turkey	- " -	1,2	0,4	0,5	2,4	95,2	3,30
Sardinia	Sea water	0,6	0,2	0,2	1,2	97,5	3,25
Israel	- " -	0,1	-	-	0,1	99,8	3,40

SiO₂ and Fe₂O₃ at the ratio CaO:SiO₂ = 2 and to increase the bulk density to the values between 3,40 to 3,50 g.cm⁻³.

II. CHROME ORE

Chrome ore is another raw material component necessary for the production of basic refractoriss materials from the blends containing sintered magnesia.

Chrome ores originated from basic and ultrabasic rocks. Their deposits occur mostly in the form of lenticular masses or veins. According to the origin of transformation and conditions of formation there are three fundamental types of chrome ores differing in the composition of spinelic substance and accompanying waste rock

a/ Chrome ores with a high content of Cr₂O₃ and low content of iron oxides. The deposits in Greece, Jugoslavia, Albania, Turkey, Iran and Soviet Union belong to this group.

b/ Ores with a high content of iron oxides and low ratio Cr:Fe. The deposits in Africa, especially Transvaal, India and Vietnam belong to this group.

c/ Ores with a low content of Cr₂O₃ a high content of Al₂O₃. This type of ores occurs in the deposits in Cuba and Philippines.

Typical compositions of the chrome ores of various deposits are presented in Table 6. The spinelic substance of chrome ore is represented by a solid solution of the general formula $R^{+2}O \cdot R^{+3}O_3$, where R^{+2} may stand for MgO and FeO while $R^{+3}O_3$ denotes Cr₂O₃, Al₂O₃, or Fe₂O₃.

Table 6 : Typical analyses of chromium ores from various deposits /%

	USSR Sereenov	USSR Filipov- 28,1	Yugo- slavia	Turkey	Greece	Albania
SiO ₂	4,79	3,29	7,47	3,96	3,75	9,64
TiO ₂	0,20	0,33	0,30	0,33	0,26	-
Al ₂ O ₃	18,00	7,62	18,94	16,40	22,80	10,79
FeO	12,59	4,04	11,19	8,31	14,01	11,60
Fe ₂ O ₃	6,34	12,40	1,00	4,17	0,60	-
CaO	1,60	0,95	0,16	0,18	1,45	0,35
MgO	14,48	12,70	13,02	20,16	17,58	20,28
Cr ₂ O ₃	39,49	56,48	43,47	45,16	37,41	43,56

	Cuba	Phillip- pines	Rhode- sda	Transvaal		
				I.	II.	III.
SiO_2	4,35	2,8	3,58	1,33	1,42	0,68
TiO_2	0,30	-	0,10	0,84	0,85	0,95
Al_2O_3	26,80	29,5	13,85	17,42	12,22	15,78
FeO	8,57	13,9	11,26	20,69	25,12	18,10
Fe_2O_3	8,47	-	3,46	6,07	0,10	8,50
CaO	0,47	0,4	1,01	0,74	0,21	0,46
MgO	18,11	17,3	14,87	9,71	11,45	9,75
Ca_2O_3	30,33	34,4	47,61	42,11	47,50	45,88

Mainly the concentrates of chrome ores from which the accompanying waste rock component has been removed as much as possible are used for the production of refractories materials. The enrichment is achieved by a number of dressing methods. The most effectual are those in which fine grained particles are processed and as we say "the opening grain" sets in. Most technologies of refractories production require grained ores, the size of particles ranging from 0,1 mm to 2,0 mm or 0,5 mm up to 3,0 mm. In this respect the possibilities of the technologies of dressing processes are in opposition to the needs of the technologies of the production of basic refractories materials.

From the point of view of chemical and physical properties the claims on the quality of chrome ores may be characterized as follows:

Chemical properties: The SiO_2 content of ores ought to be as low as possible. In no case it should be higher than 4% and for better kinds of refractories materials it should be less than 3%. In the case of the ores poor in Cr_2O_3 the low content of this oxide may be compensated by an increased content in Al_2O_3 . The chrome ores with a high content of iron oxides may be used merely in combination with sintered magnesia containing no Fe_2C_3 . They must not be used in combination with breunnerite sintered magnesia.

Physical properties: The chrome ores for refractory materials must be hard. By processing these ores into useful grading which is usually lower than 3 mm the portion of fine grains /under 0,1 mm/ should be as low as possible. Similarly, no additional desintegration of the chrome ore grains put into mixer should take place during the preparation of the pressing mixes from sintered magnesia and

chrome ore.

The need grading chrome ore with minimum content of accessory contaminating silicates will lead no doubt to the processes concerned with the clodding of the fine grained concentrates obtained by the dressing procedures giving these concentrates in grading mostly lower than 0,2mm.

III. REFRACTORY MIXTURES AND GREEN BRICKS PREPARATION

There is a principle which is valid for all basic refractories and demands that the fired bricks as well as other shapes ought to have the lowest possible porosity. This property may be obtained by using a useful grading and adequate forming pressure. The simplest formula indicating the maximum packing of space with particles of different size is

$$y = \frac{x}{x_0}$$

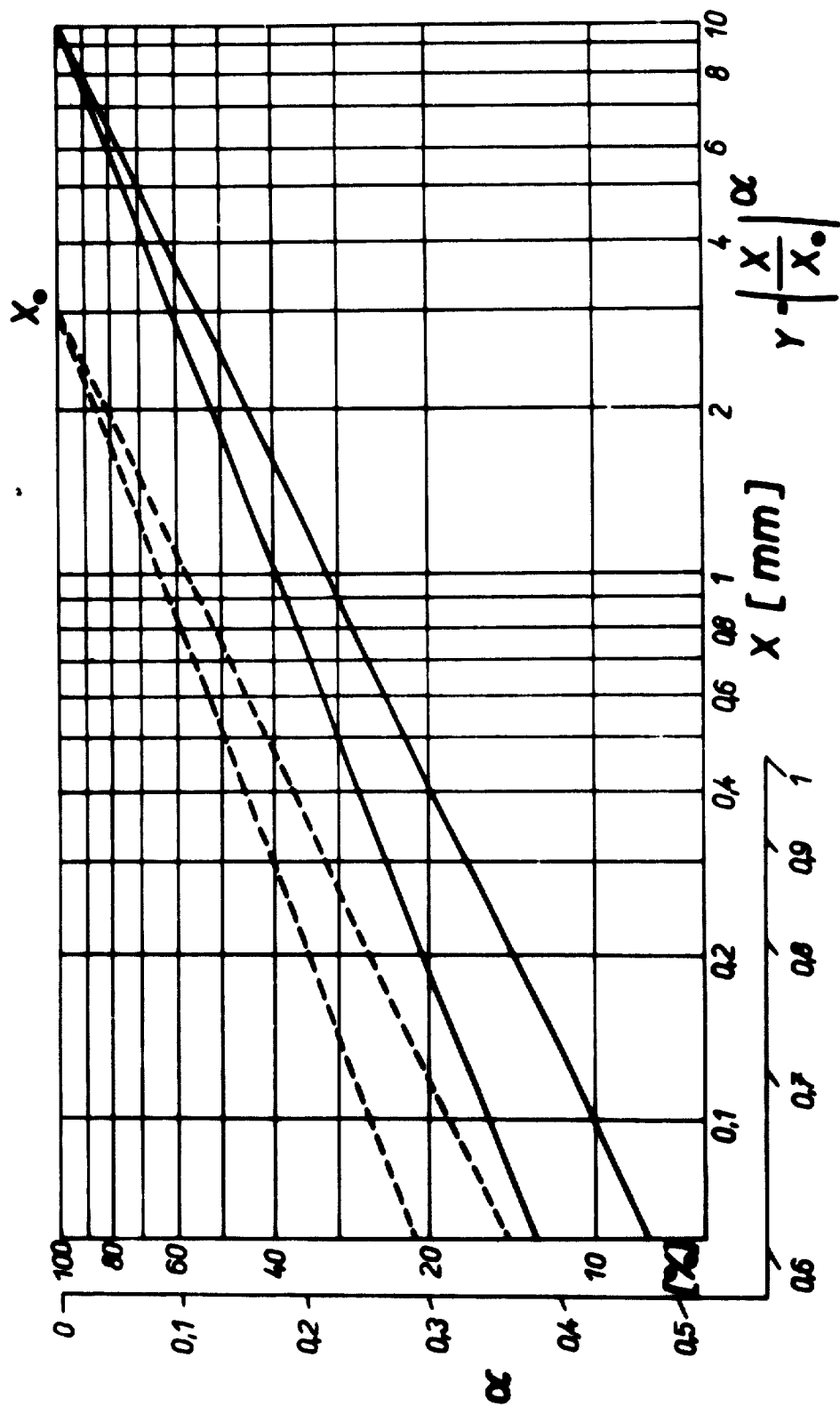
where x is the size of particles

x_0 is the maximum size of particles

y stands for the cumulative percentage corresponding to the grading chosen

The relationship expressed graphically on a bi-logarithmic net gives a straight line, the slope of which yields the exponent λ . For the definition of grading it is sufficient to quote x_0 /maximum grain/ and λ . By using this so-called continuous curve of grading the lowest porosities of green bricks may be achieved provided the value of the exponent λ varies between 0,4 and 0,5 /Diagram I/. In practice the grading of masses with discontinuous curves

DIAGRAM I. GRADING OF MAGNESIA MIXTURES IN AREA OF
MAXIMAL PACKING DENSITY $|\alpha = 0,4 - 0,5 |$



are used. The medium fractions are either missing or suppressed. The grading between 0,2 and 0,5 or even 1 mm are usually regarded as medium fractions. Bifractional bricks consist of two fractions, i.e. fine grained powder and coarse grain portion /0,5 - 4 mm, 0,8 - 4 mm or 1 - 4 mm/. In trifractional masses the first fraction /fine fraction/ is also fine grained powder the second fraction is medium grain /0,2 - 0,5 mm or 0,8 - 1,0 mm/, and the third fraction is coarse grain. The schemes 45/10/45 up to 35/15/50 are usually used. For the forming processes by means of pressure several authors proposed the relationships which express the dependence of the porosity of green bricks on forming pressure.

Among these relationships the most convenient seems to be that-one expressed by the Berežny equation:

$$P_g = a - b \cdot \log . P$$

P_g = green bricks porosity, P = pressing-power, a , b = the constants characteristics of the process/

Provided the pressing-power is small, the term $b \cdot \log P$ is equal to zero and $P_g = a$. The constant a expresses approximately the mass porosity freely poured into a pre-mould and demonstrates the importance of grading in the basic refractory technology.

It should be mentioned that the value of constant "a" depends not only on grading but also on the porosity of coarse particles. The demand that the constituent material for brick production must be of a low porosity is obvious from this equation. The constant b is a function of material. It depends mainly on the hardness and strength of particles, proportion of matrix, size, etc. In general, expresses the

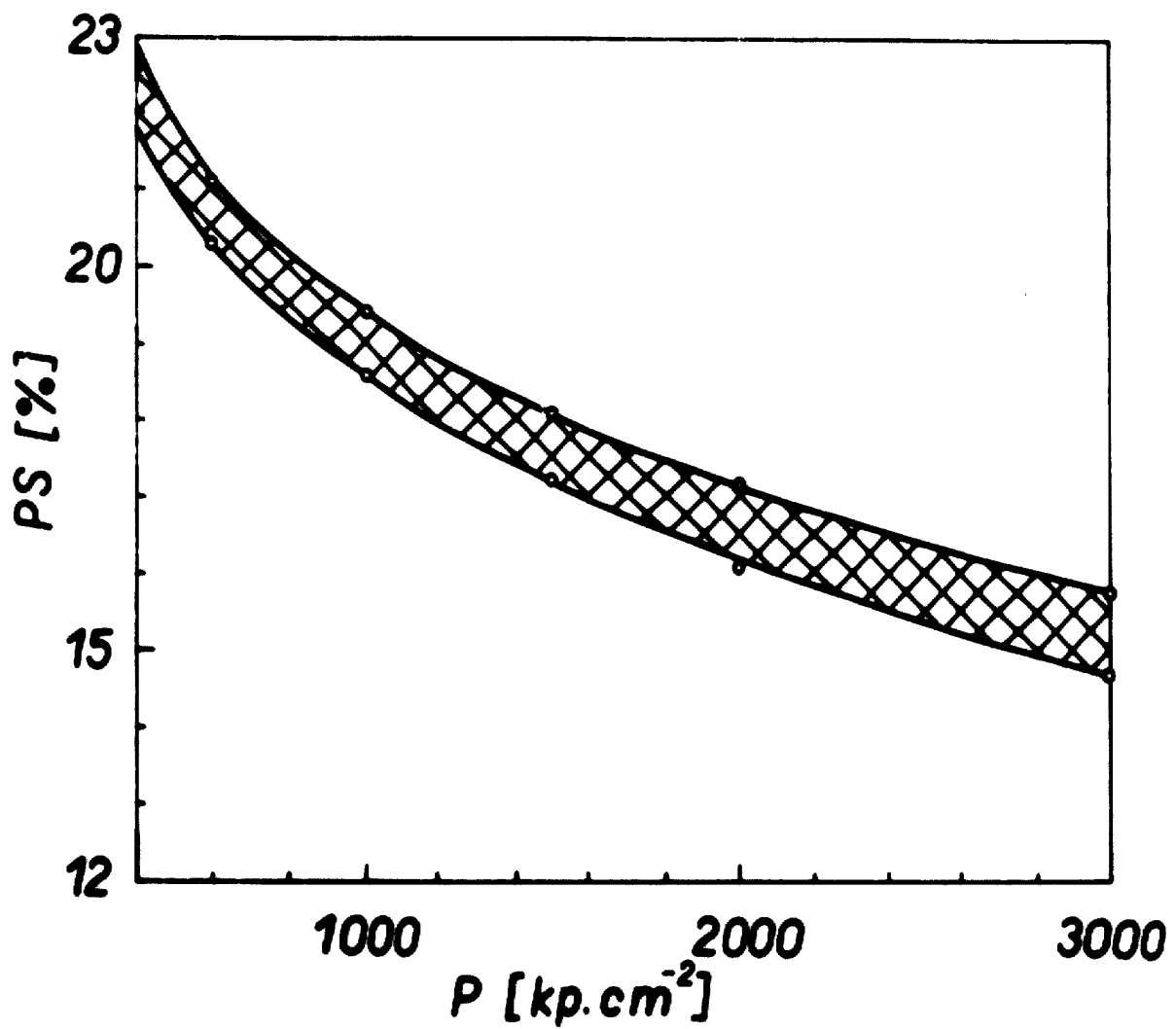
internal resistance and friction walls of mould. It usually depends on the constant a . It is a logarithmic function of pressing-power. In practice this means that the deficiency in the composition of mass cannot be compensated by a manipulation of pressing-power.

The illustrative example in Diagram 2 shows, that certain rational limits for the height of forming pressure exist. It is obvious, that the application of pressures up to 1000 - 1500 kp.cm^{-2} is effective for magnesia bricks. Above this limit gains in the density of green bricks are not always proportional to the efforts made. A considerable wear of the walls of moulds appear, heavier constructions of presses are needed, the pressing cycle usually gets unduly longer, etc.

IV. REFRACTORIES FROM MAGNESIA

Magnesia materials are used especially for those parts of steel furnaces which are in direct contact with molten metal and slag. This concerns mainly the bottoms of open hearth furnaces, electric arc furnaces, the mixers of pig iron, etc. The special kinds of magnesia refractories with a higher resistance to temperature variation are convenient for the linings of kinder walls of open hearth furnaces while the very dense materials are convenient for oxygen converters and steel-evacuating devices. Very dense magnesia refractories material which are resistant to temperature variations and additionally impregnated with tar are especially convenient for oxygen converters. The impregnation of fired magnesia materials with tar affect favourably the durability provided these refractories are made of

DIAGRAM II. POROSITY |PS| OF GREEN BRICKS
IN DEPENDENCE OF FORMING
PRESSURE |P|



sintered magnesia with a low content of iron.

The service life of magnesia refractories increases with improving thermomechanical properties and density. Therefore the quality of dead-burned magnesia, its mineral purity and density have influence on the properties of these materials. The mineral composition of construction materials is determined by the mineral compositions of the main kinds of sinter magnesia used for their production.

In order to obtain good thermomechanical parameters a low content of liquid phase is necessary. Furthermore, its viscosity given by its composition must be high. Thus this phase forms an isolated intergranular filling among the periclase grains. It does not wet and separate these grains from one another.

The amount of molten silicate phase and its composition depend on the content of SiO_2 . The negative effect of SiO_2 is to be observed e.g. in the decrease in tensile strength at 1500°C exhibited by the magnesia refractories made from the Balkanian sintered magnesia with varying SiO_2 content.

63 kp . cm ⁻³	for the 0,92 % SiO_2	content
15 kp . cm ⁻³	" " 1,45 % SiO_2	"
5 kp . cm ⁻³	" " 1,85 % SiO_2	"
0 kp . cm ⁻³	" " 2,45 % SiO_2	"

It is worth noticing that the increase in the content of SiO_2 did not only raise the content of liquid phase but also caused the composition to change from C_2S through C_3MS_2 to CMS . This means that the viscosity and melting point decreased, periclase got more wetted and the separation of

periclase particles by the effect of liquid phase manifested itself.

The presence of B_2O_3 in magnesia refractories has a very unfavourable effect on their thermomechanical properties. Boron oxide reacts with CaO and MgO and various low-melting Ca and Mg borates, especially C_3B and M_3B are formed. According to the content of B_2O_3 the liquid phase appears even at the temperature of $1200^{\circ}C$, wets intensively periclase and may bring about a full loss of strength at high temperatures.

The content of B_2O_3 exceeding the limit of 0,05% has a negative effect. Provided the sintered magnesia obtained from sea water has not been deprived of boron by a proper process, it contains from 0,2% to 0,3% of B_2O_3 . Davies and Havranek expressed empirically the maximum content of B_2O_3 admissible without harmful consequences by the relationship

$$\% B_2O_3 = \frac{\%CaO + \%SiO_2}{100}^2$$

The negative effect of B_2O_3 is not to be observed provided the ratio $CaO:SiO_2$ is deeply below 1. However in this case, the negative effect of the monticellitic liquid phase manifests itself. As to the ratio $CaO:SiO_2$, it is best if this ratio equals two.

Of course, the thermomechanical properties are also affected by the amount, character and pores size distribution. The less the number of the pores which are discontinuous, closed, and do not separate the periclase particles from one another, the smaller their effect. The pores of small size, closed and present in a small content mitigate

the effect of slags and molten metal. By using a convenient technology involving the correct grading refractory mixture and adding eventually some admixtures stimulating the sintering of dense green bricks at the optimum temperature and sintering mode, the magnesia refractories material showing the actual porosity under 10% may be produced.

The modulus of elasticity of magnesia refractories may be significantly affected by regulating the character of grading of the forming mass for green bricks. Thus the value of the criterion $k = \frac{\sigma}{\epsilon}$ expressing the thermal shock resistance may be raised. This concerns mainly the reduction of the portion of matrix, suppression of fine grain portions /0,1 - 1 mm/ to be the minimum, and increase in x_0 .

The development in the field of burned magnesia refractories tends to the materials with these properties:

Content of SiO_2	0,2 - 1 %
Ratio $\text{CaO} : \text{SiO}_2$	2
Content of Fe_2O_3	0,2 - 3 %
Actual porosity	8 - 14 %
Tensile strength	
at 1500°C	80 - 100 kp.cm ⁻²
at 1550°C	40 - 60 kp.cm ⁻²
K-criterion	8 - 12

In principle, the burned magnesia refractories are produced according to the following technological scheme involving these materials: Bunker with the sinter magnesia of different grading and fine grained matrix, bunker with liquid admixtures - feeding into mixers - preparation of refractory mixture in mixers - half-dry shaping of green bricks in presses - drying of green bricks - firing in tunnel kilns - screening and paletisation - storage of ready products.

V. REFRACTORY MATERIALS FROM DOLOMITES

Dolomite is the most accessible material for the production of basic refractories. It occurs almost in every country. In the calcinated form it served for several decades as lining material for Thomas converters, open hearth furnaces, electric furnaces, etc. Even at present, its use for steel furnaces is not without importance and prospect. Its chemical composition is $\text{MgCO}_3 \cdot \text{CaCO}_3$. After the calcination and loss of water it contains theoretically 41,83% of MgO and 58,17% of CaO. Really the sintered product "DOLOMIA" contains 94,5 - 99,5% of $\text{MgO} + \text{CaO}$. The accompanying oxides, especially Fe_2O_3 , Al_2O_3 and SiO_2 facilitate sintering so that an adequately dense clinker is obtained at relatively low temperatures.

Owing to the intensification of steelmaking processes the demands on the properties of dolomia changed during last 14 years so much that many technologies of the production of grained products and bricks became important only from the historical point of view.

At present, these properties of dolomia are required:

The content of $\text{MgO} + \text{CaO}$ should be at least 97% and in the case of high-quality sorts more than 99%. All accompanying oxides impair the value of product, especially as regards the thermomechanical properties.

The demands on the porosity of dolomia increased substantially. While the porosity of 15-20% was considered to be sufficient for the Thomas converters and some authors of the technologies of linings were of the opinion that so

high porosity was desirable, at present the porosity of 8% is regarded as the highest limit. High-quality kinds of dolomia show the porosity of 1,5% or at most 5%. Unfortunately, only a small part of the dolomites of above properties can be sintered in the form of pieces under formation of a product with low porosity and even the temperature of 2000° is not always high enough. The sintering capacity of dolomites is connected with their structure, the size of crystals, porosity and pores distribution. Very pure dolomites /"low flux"/ are processed in the following manner at first, they are calcinated at a low temperature and the calcination product is ground finely and briquetted without any binder. The briquets are sintered in rotating or shaft furnaces at 1700° - 1900°C. This process yields a dolomia with 1,5% - 3% porosity.

Dolomia bricks

Because of an insufficient resistance of dolomia to the effect of water, tar functioning as a binder is used for the preparation of the forming mixes with a grading to 6 mm or even up to 8 mm. The coarse grained part is usually heated at least to the temperature of 120°C, homogenized in hot steel mixers with the fine grained part and the tar the addition of which amounts to 5% or even 8%. The molding is carried out under pressure from 700 to 1500 kp.cm⁻². The green bricks ought to show a 17% - 20% porosity and the pores should be filled with tar.

In this form the green bricks are usually applied to lining the furnaces and containers for steel making. Sometimes, they are tempered in the absence of air at about

300°C. During this operation the volatile parts of tar are removed and the carbon skeleton remains as a binder.

Ceramically burned dolomia bricks are also used. The firing temperatures correspond to 1400°C - 1500°C according to the content of accessory oxides. As to the process of ceramic firing, the heating to the temperature of Ca(OH)_2 decomposition should be rapid for CaO not to hydrate and make the green bricks break. The burned products are at once impregnated with tar or given hydrophobe packings or coatings. The bricks bond with tar and tempered are storable merely for a limited period of time. They are transported in closed pallets with a filling of calcinated fine dolomite so that the content of water vapour in the space of pallet may be reduced to minimum.

The development in the technology of dolomia refractories tends to the clinkers and bricks with the content of $\text{MgO} + \text{CaO}$ over 99,5% as well as the lowest porosity. The total volume of production or consumption in the future will depend on the economical and raw material conditions in every country and will be always fully connected with steel production.

VI. MAGNESIA - CHROME ORE REFRACTORIES

The bricks of magnesia resist the effect of basic iron slags and melts, but they do not resist to rapid changes of temperature. By introducing the brick production from the mixtures of magnesia with chrome ore, this shortcoming was to a great extent removed. The products of this group became a basic material generally used for lining several kinds of metallurgical furnaces and vessels in those places, where

the bricks of magnesia failed.

The world practice in technology is varied. The proportion of chrome ore is between 10% to 50% in magnesite-chrome bricks and between 51% to 80% in chrome-magnesite bricks. Sometimes it is used in the grading up to 4 mm, the fraction going through the sieve 0,2 /0,5/ being excluded, another time it is used as a matrix with specific surface 0,2 - 1 m²/g. Each of the authors of technologies found reason for his practice in the results of the operation of metallurgical furnaces, some conventionally estimated properties or economic utility eventually in all these three factors.

In order to throw light on the wide problems of the bricks falling in the series magnesite-chrome ore which play an important role in technology, development, and research we may use the well-known simplified relationship which serves as a criterion for the thermal stress resistance at an unilateral heating, cooling and thus for the thermal shock resistance:

$$K = \frac{\sigma_{\text{max}} \cdot a}{E \cdot \alpha}$$

σ_{max} is the strength of brick up to the temperatures at which the refractories material is strained mechanically /kp.cm⁻²/
 a is heat conducting power /m².h⁻¹/ calculated from the formula

$$a = \frac{\lambda}{c_p \cdot \nu}$$

λ is thermal conductivity /kcal.m⁻¹.deg⁻¹/

c_p is specific heat /kcal.kg⁻¹.deg⁻¹/

ν is bulk density /kg.dm⁻³/

E is modulus of elasticity /kp.cm⁻²/

α is the coefficient of thermal dilatation /deg⁻¹/

It follows from the above relationship that for the refractory material of equal mineral composition and current porosities /15-20%/ the thermal shock resistance depends on the value of f , because the other properties involved in relationship /1/ may be considered to be constant.

If the chrome ore into the medium of periclase introduced has brought on intensive change in thermomechanical properties, some of these involved in relationship /1/ must have changed substantially.

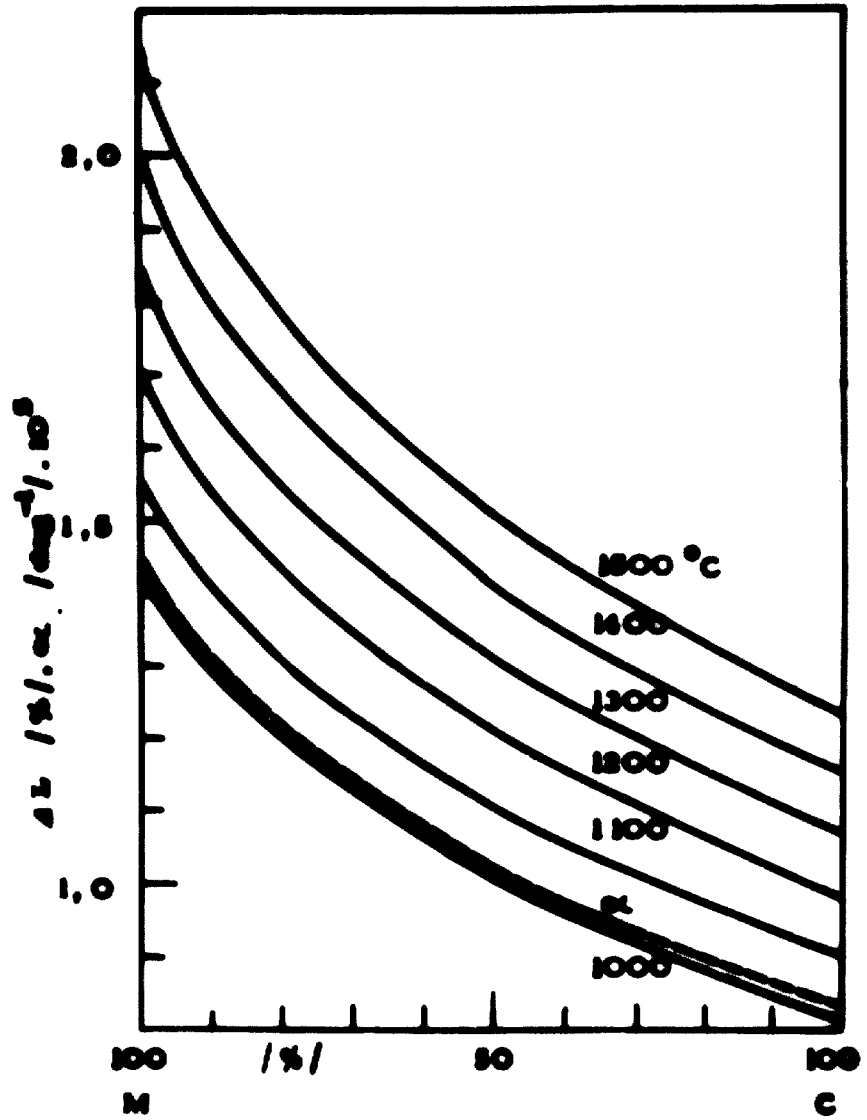
The comparison of the criterial values calculated from known and measured properties of the bodies with different ratio of the above-mentioned basic components enables us to estimate exactly the relative stress strains resistance arising in refractory materials at a unilateral heating, cooling and rapid change of temperature. Thus it will be possible to find out the conditions under which the strains are the smallest and determine the optimum mineralogical composition and texture of the refractories produced from sinter magnesia and chrome ore.

The properties as criteria used are summarized in a few diagrams.

Diagram III. shows the relationship between thermal dilation and the ratio of both constituent components. It is evident that this relationship is not linear. The high thermal dilation of magnesia bricks is reduced significantly even by a relatively small addition of chrome ore.

It is known that the thermal conductivity of magnesia bricks is high and decreases significantly with temperature. By introducing chrome ore into periclase, the thermal conductivity as well as the heat conducting power of all the bricks containing less than 50% of chrome ore decreases considerably at the temperature of 1400°C and more there are no

Diagram III. Thermal dilation $\Delta L/L$ and coefficient of thermal dilatation α series magnesite M - chrome ore bricks



essential differences in this property for the whole series of basic bricks /Diagram IV./.

The character of bending load and tensile strength at the temperature of 1500° which can be regarded as adequate for the evaluation of these properties is shown in Diagram V. The maximum for the materials burned at 1600°C and 1700°C occurs in the region of chrome-magnesit bricks containing 80% of ore.

The strengths at high temperatures are certainly important parameters for appreciating the behaviour of refractories e.g. in the roofs and parts of furnaces which are subjected to thermal stress. They ought, however to be confronted with the moduli of elasticity. Even the values at 20°C show that the effect of chrome ore introduced into periclase is important the most significant being in the composition which contains 20% of ore. Its modulus of elasticity equals one eighth or even one tenth of the value established for magnesia bricks /Diagram VI./. The temperature change is illustrated in Diagram VII. It is worth noticing that the rise of modulus to higher values indicates the strains while the decrease in modulus indicates the relaxation. The bricks with a successively increased portion of ore show an increase in the moduly of elasticity.

If the values of bending strength are correlated with the values of the moduly of elasticity we obtain the view about this criterion which is characteristic of the series of magnesia-chrome ore bricks /Diagram VIII./

For the region of magnesia-chrome bricks the maximum of the criterion values corresponds to the 20% - 30% content of chrome ore while for chrome-magnesit bricks it corresponds to the 70% content of chrome ore.

Diagram IV. Thermal conductivity λ /
series magnesia /M/ - chrome ore bricks

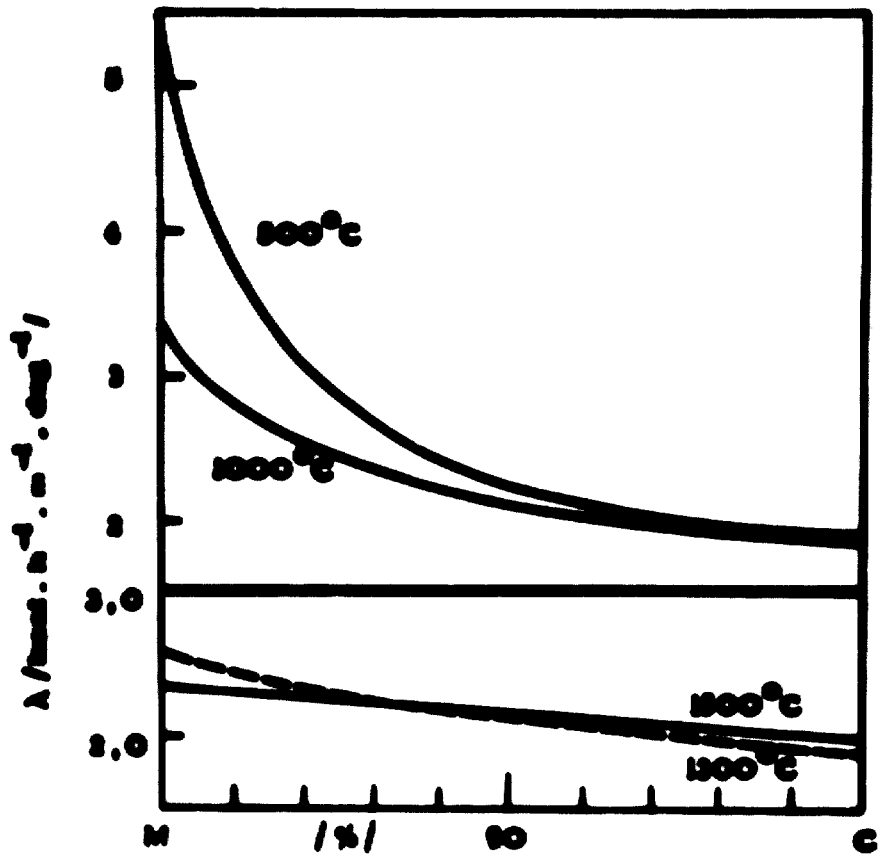


Diagram V. Modulus of rupture / σ_{tc} /
and tensile strength at 1500°C
series magnesia /M/ - chrome ore bricks
burned at 1600°C and 1700°C

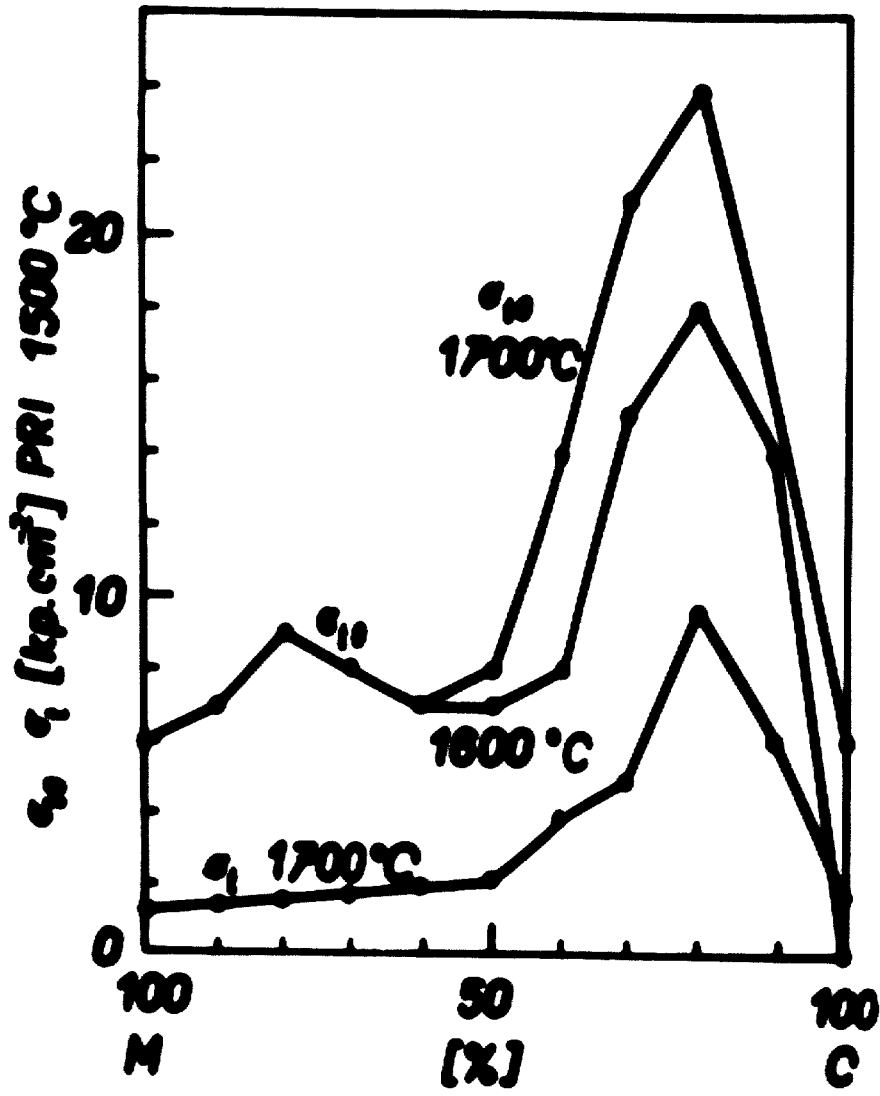


Diagram VI. Modulus of elasticity E_r at 20°C and 1500°C series magnesia /M/ - chrome ore bricks

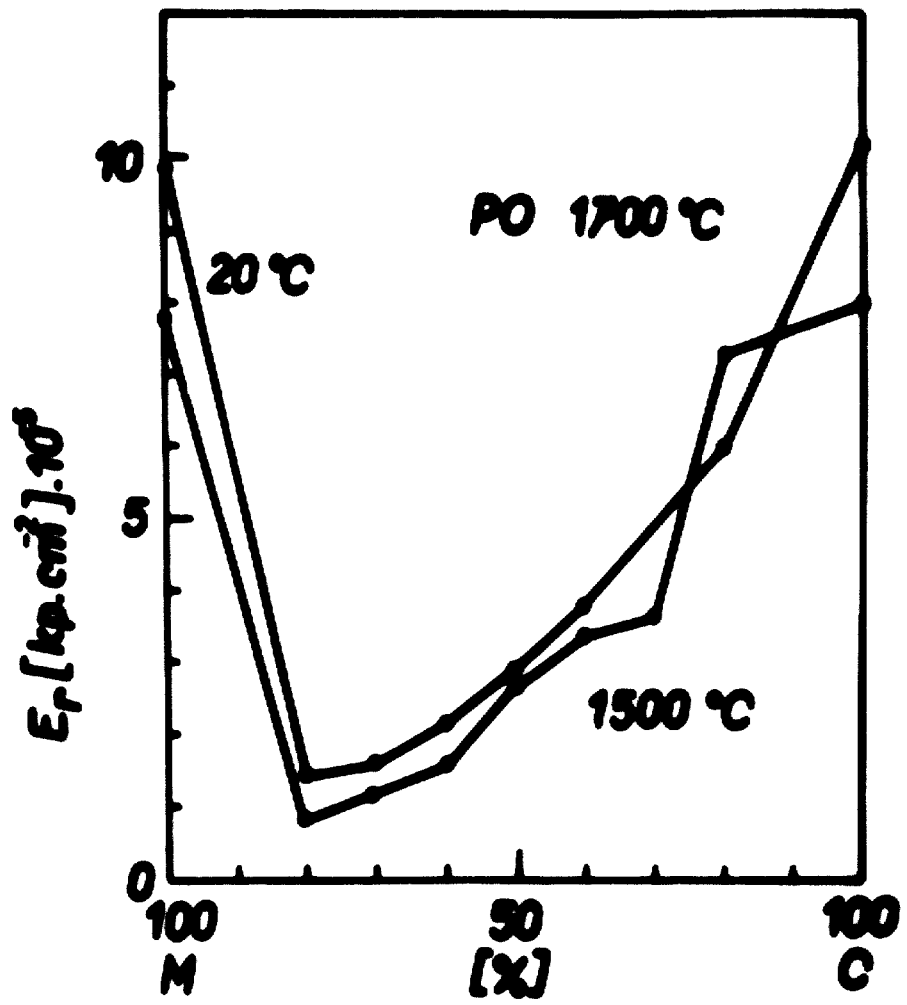


Diagram VII. Modulus of elasticity E_r / series magnesia-chrome ore bricks at temperature 1500°C /curves numbers mean the chrome ore contents in bricks/

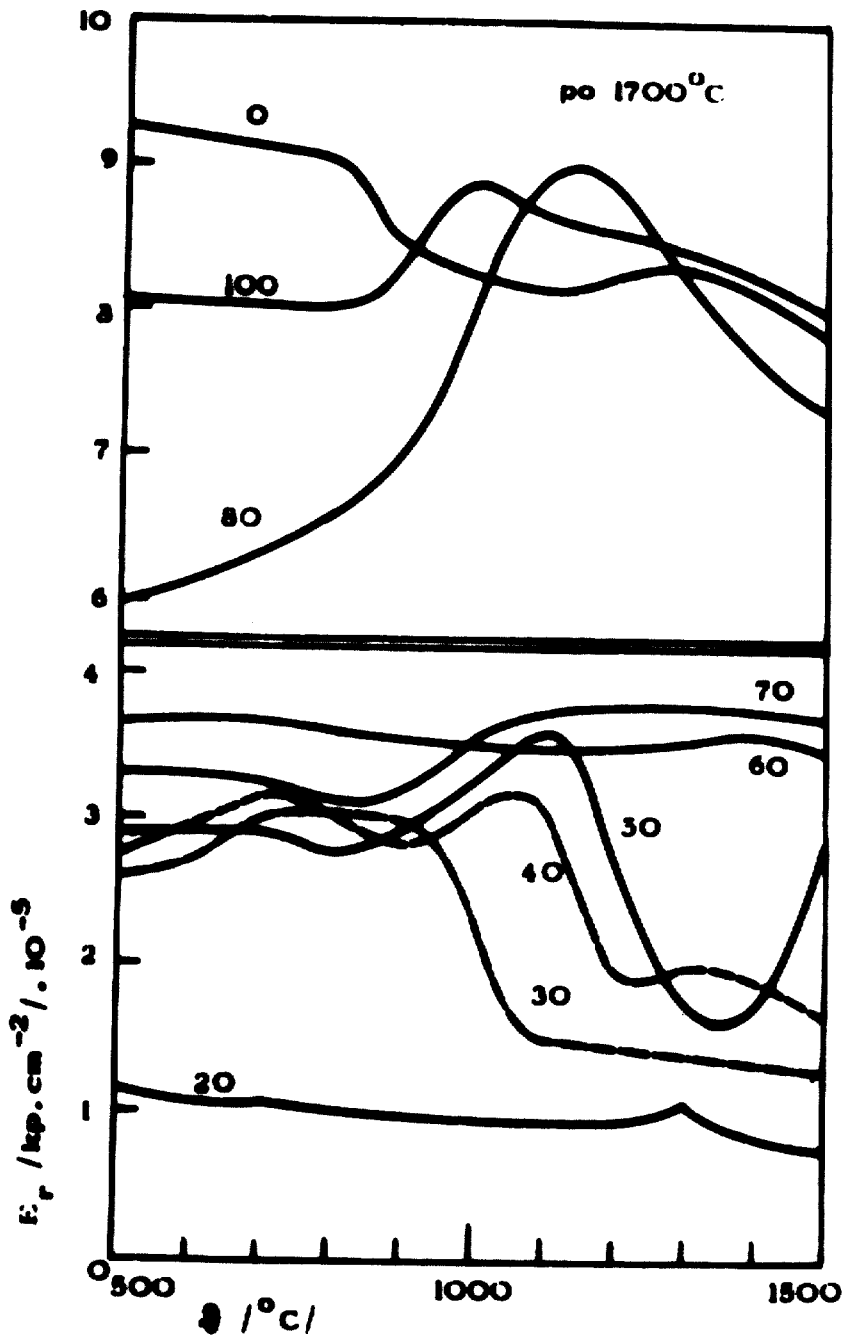
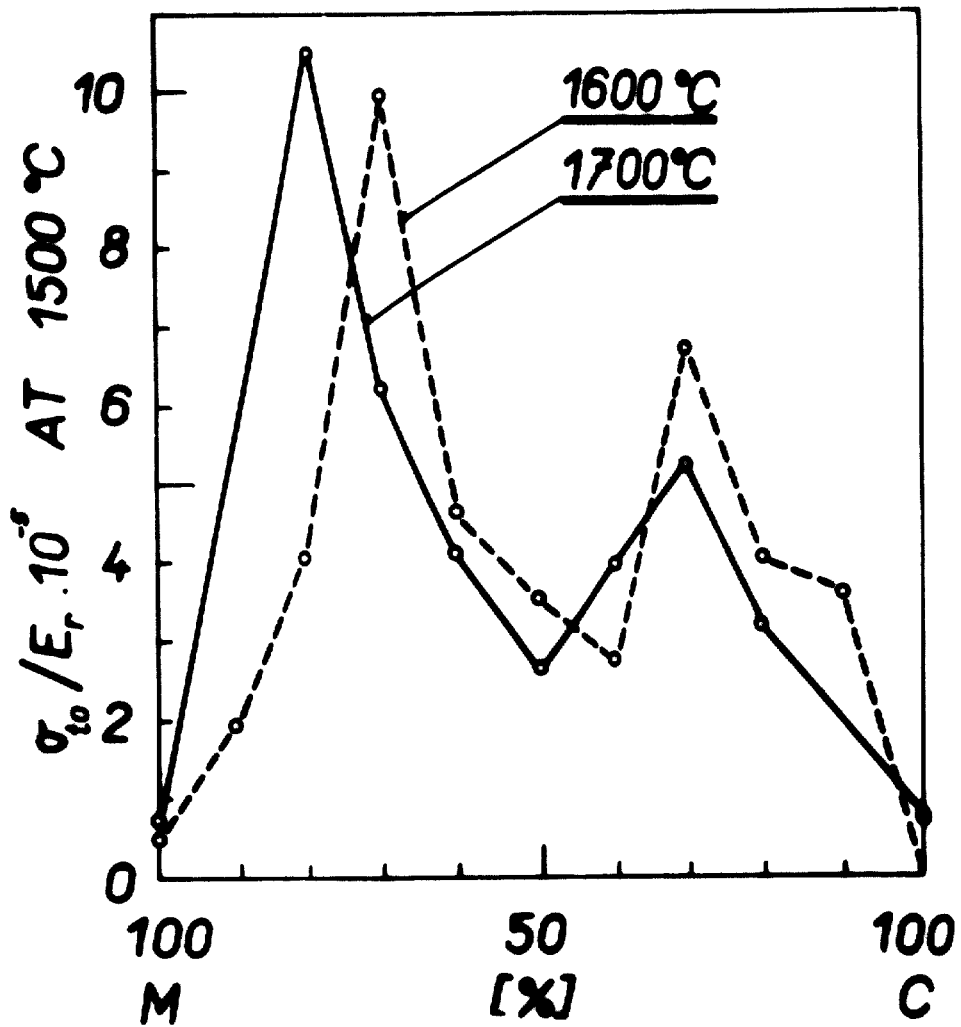


DIAGRAM VIII. MODULUS OF RUPTURE / MODULUS OF ELASTICITY $\sigma_{10}/E_r \cdot 10^{-5}$ / AT 1500°C OF MAGNESIA |M| - CHROME ORE BRICKS BURNED AT 1600° AND 1700° C



It remains to reply to the question which form of chrome ore should be used as a component of mixtures. The reply to this question is interesting with respect to the magnesit-chrome bricks containing less than 50% of ore.

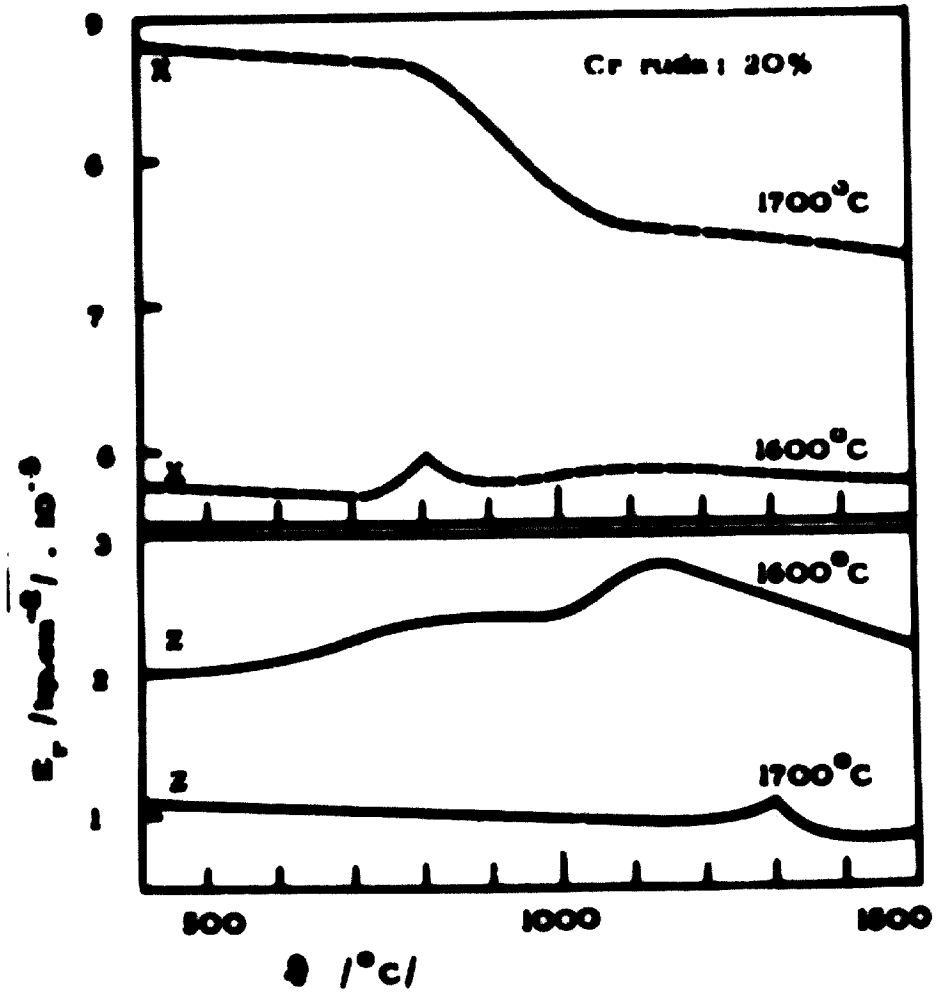
In Diagram II. the moduly of elasticity of bricks with 20% ore are presented. The ore was used as a matrix. It appears that spinel as a fundamental component of ore does not produce the desirable decrease in the moduly of elasticity with respect to the bricks of magnesia because it predominately dissolves in periclase. Therefore the application of coarse grain ore is more advantageous.

At conclusion it is worth noticing that the presented examples hold good for magnesia or at low temperature burned magnesite and chrome ore of a certain kind. In technology the optimum conditions have to be set in conformity with a described procedure for every constituent material used.

There is no doubt that the strengths at high temperatures will be always a basic indicator of the technical value of burned magnesit-chrome bricks. They depend in the first place on the content of accessory minerals silicates - so as it is valid for the bricks of magnesia. In the second place they depend on the kind how the coarse grains of spinel /chrome ore/ are bound to the periclase medium, i.e. the grain of periclase. Direct-bond can be obtained only by firing at high temperatures, namely 1700° - 1780°C . These direct-bonded bricks are characterized mainly by a high firing temperature and represent the last stage of development.

At conclusion it should be mentioned that the maximum of the direct-bonds spinel-periclase is achieved by briquetting and sintering a magnesia-chrome ore mix at

Diagram IX. Moduly of elasticity E_T to temperature 1500°C
series magnesia-chrome bricks /80/20/
that x chrome ore as matrix
s bricks with chrome ore as coarse grains



temperatures up to 2200°C in shaft kilns. This spinel clinker which already contains direct-bond is then used as basic material for the production bricks of high quality. The green bricks are either ceramically bonded or chemically bonded and metal-cased they are used in metallurgical furnaces.

The above considerations established the principles for the technology of bricks of the series magnesia-chrome ore. It should be pointed out that the portion of matrix in mixtures is 25-40%, the medium grading /0,2 - 0,8 mm/ is usually missing, or its portion does not exceed 20% while the coarse grading fraction 0,8 - 3/4/ mm forms the basic skeleton of the batch of green bricks or bricks.

The trends for the future are characterized by the use of magnesia with minimum content of SiO₂ /less than 0,2%/ and chrome ores as concentrates containing 2% of SiO₂ at the most or even less than 1,5%.

Some typical properties of bricks are summarized in Table 7.

VII. FUSED BASIC REFRACTORIES

High density and volume stability at high temperatures are the main reasons for the production of fused basic refractories. According to the production method there are two main kinds of products.

Basic rebonded refractories with fused grain. These materials are produced so that sintered magnesia or its mixture with chrome ore is molten in the arc of electric furnace at 2850° - 2350°C. The melt is allowed to cool in the furnace. The set block of 2-10 tons weight is fragmented, crushed and finished to the grading up to about 5 mm. The

Table 7 : Properties of magnesite - chrome bricks

	USA	USA	G.B.	USSR
SiO ₂ [S]	2,0	2,0	1,6	1,2
Al ₂ O ₃ [S]	17,1	20,7	15,0	10,8
MgO [S]	62	49,5	63,5	75,4
MOR, 1500°C [kp.cm ⁻²]	50	55	63	45
Apparent porosity [S]	16,0	19	15,0	19
Volume change at 1700°C after 5 h [S]	+0,1	+0,3	+0,4	-0,1

fractions obtained and the fine grained material prepared by milling in ball tube or other mills is used for the preparation of the mixture which is pressed in an usual manner and burned at 1650° - 1750°C .

These products distinguish themselves by a high density, strength at high temperatures, volume stability as well as a low value of creeping. In spinelic bricks the content of chrome ore is usually either 20-40% or 50-70%. The bricks are used especially for lining the containers for vacuum degassing of steel, for the linings of the stressed parts of electrical furnaces etc.

The ramming mixture consisting of fused grain is successfully used for the electrode centres in the roofs of electric furnaces, induction furnaces, containers for steel evacuation, and other places of metallurgical furnaces where the shaped bricks are to be replaced in the places stressed thermally.

Fused and cast basic refractories. Magnesia or a mixture of magnesia and chrome ore is molten in an electric arc furnace and cast into the ingot form and subsequently allowed to cool there at a controllable rate. The cold ingots are then cut with diamond charged saws into the parts with needed dimensions. As the melting process as well as working is expensive, these materials represent the most expensive, basic refractories. Their open effective porosity is practically equal to zero. Therefore they exhibit the highest resistance to corrosion. On account of the high modulus of elasticity they show a relatively low spalling resistance. They may be, therefore, used in those parts of furnaces where the temperature variations are neither frequent nor great. The bricks with a 20-30% portion of chrome ore prove their worth especially in electric furnaces in the places most exposed to the effect of slags. Anyway, their high price

prevents the extension of their use in to-days technology. Their composition depends on the chemical composition of magnesia and chrome ore as well as the ratio of the amounts of these substances in the mixture.

VIII. CHEMICALLY - BONDED REFRACTORIES

An important position in the production and use of basic refractories belongs to the chemically bonded - non fired basic refractories. In principle, they may be used for steel-, cement-, and other furnaces like fired basic refractories.

The chemically bonded refractories produced, comprise magnesite, magnesite-chrome, chrome-magnesite, and chemically bonded chrome materials. The technology of their production does not differ substantially from the production of fired materials. Since their firing does not take place at the producer's, but this process is accomplished on the place of their service in lining, it is necessary to respect this circumstance. Attention must be given to the fact that the properties of the chemically bonded basic refractories ought to resemble the properties of fired refractories, in particular, as regards the cold strength, small changes in dimensions at high temperature, and sufficient density of green bricks.

These properties are achieved by a convenient choice of grading of forming mixture and use of the binders forming chemical bonds which provide a strong binding of individual components of the material without any use of ceramic firing. Sulfite waste liquor, magnesium sulfate and chloride, boric acid, and alkaline polyphosphate serve as bonding agents. The origination of chemical bonds in green bricks takes place

during the drying process. Therefore the demands on the drying of the green bricks of the chemically bonded refractories are higher than the demands on the drying of the green bricks for firing. Sometimes, the hardening process continues in a CO_2 atmosphere.

In most cases, the chemically bonded refractories are pressed into metal-cases, wrapping the shaped bricks from four or two sides. The chemically bonded refractories are also to a lesser extent produced without any metal-case for some places of use. For instance for the use in the places where the linings are exposed to higher demands on the spalling resistance a reinforcement-metal is pressed in and divides the inside of green bricks mostly in three parts. The refractories, which hung during the installation of lining, e.g. for main arches of open hearth furnaces, etc. are produced already with a suspender mostly of fireproof steel.

The metal-cases of chemically bonded refractories show several merits. They protect the shaped bricks against damage during transport and manipulation, facilitate the assemblage of lining and no other metal inserts are to be put among the shape bricks. Moreover, they are equipped with suspenders. This merit manifests itself especially in the case of panel linings. At working temperature the metal-cases oxidize, react with MgO of the material under formation of magnesia ferrite and the complex magnesiaferrite-magnetite and thus make the lining monolithic and fulfil the function of mortar.

The chemical bonds obtained by the majority of binders vanish in the region of so-called transition temperatures, i.e. 600°C - 1200°C where ceramic bonds have not arisen, yet. Then the refractories loose mechanical strength at these temperatures and are not able any more to resist to the me-

chanical stress exerted on the lining. Therefore, if chemically bonded refractories are used for those places of lining which are exposed to a mechanical stress at these temperatures, it is necessary to raise the so-called "transition strength" by using some binding agents such as alkaline polyphosphates or powdered metal admixtures, e.g. FeCr or Fe. Simultaneously the presence of these admixtures raises the volume stability of refractories at high temperatures. Appropriate "transition strength" of chemically bonded refractories are necessary especially for the products used for the construction of roof linings. In this case the temperature acting on the refractory material decreases with the distance from the working area of lining. The refractory material therefore exhibits the character of fired material in the working, i.e. hot part and the character of chemically bonded material in the cool part of furnace. In the region of above-mentioned "transition temperatures" a spalling and immoderate abrasion would occur because of the loss of strength and mechanical stress.

If a high volume stability of chemically bonded refractories is to be attained sintered magnesia with a low content of accessory contaminating oxides, in particular SiO_2 and high density must be used for their production. Equally the lowest possible content of SiO_2 is required for the chrome ore used which should not contain any particles smaller than 0,2 mm.

The use of spinelic clinkers produced from a magnesia-chrome ore mixture, in the form of the briquets sintered at about 2000°C represents a new trend in the production of chemically bonded magnesia-chrome and chrome - magnesia materials. These chemically bonded refractories show the best performance.

In principle, the chemically bonded basic refracto-

ries ought to fulfil the demands on these properties:

cold crushing strength		min. 400 kp.cm ⁻²
tensile strength at	20°C	min. 80 kp.cm ⁻²
	at 950°C	min. 30 kp.cm ⁻²
	at 1260°C	min. 20 kp.cm ⁻²
	at 1500°C	min. 10 kp.cm ⁻²

Open apparent porosity after annealing
at 1100°C/2 h max. 19%

Linear shrinkage at 1700°C/5 h as a
characteristic of the volume stability
at high temperatures max. 1%

IX. MONOLITHIC MATERIALS

Unshaped basic materials form a wide range of refractories, from which some are gaining still more importance.

An individual place occupy ramming and casting materials for making and repairing bottoms, as well as oblique parts of walls of OH-furnaces and electric archkilns. They are made from magnesia, dolomagnesia or dolomia. Are present their consumption amounts to 6-25 kg per ton of steel made in OH-furnaces, tandem furnaces, electric arc kilns respectively. They are supplied in regulated grading usually up to 8 mm. Their basic requirements are easy sintering due to properly chosen mineralogical composition and a sufficient high part of fine fractions amounting to 40-45%.

In order to prevent the raise of dust during manipulation they usually add a small amount of mineral oil to the fine fractions.

It is necessary to state that the life of i.e. OH-furnace bottoms depends mainly on the MgC content in the volume unit of the bottom. Just therefore consumption depends mainly on the MgC content in the supplied product.

Consumption development of the abovementioned materials will depend on the steel production trend in OH-and electric arc furnaces.

In another group belong ramming and casting materials for more kinds of steelmaking furnaces and vessels as induction kilns, parts of electric furnace roofs, vessels for vacuum degassing and others.

For induction kiln prove to be suitable magnesia materials with corundum or chrome ore addition, for vacuum vessels materials made from a mixture of electrically fused magnesia and chrome ore, for electric furnaces chrome-magnesite and magnesite-chrome materials.

As bonding agent for materials which are rammed wetted or are cast, they use mainly magnesia sulphate, chromic acid, alkaline condensed phosphates, water glass and others,

At present the use of gunning materials is strongly growing. The use of materials gunned onto place, which have to be repaired, in form of water suspensions decrease. A progress mean grading materials which are moistened at the nozzle of the lance by which they are gunned.

They are gunned cold and also hot and form a compact and stable layer, not only on horizontal surfaces, but on oblique and vertical areas too, as well as on roofs. It is necessary that the materials have an adequate adhesion to the walls and a cohesion between themselves.

The density of the layer is attained by an adequate grading and the density of coarse grains. The question of

the bond is remarkably important. Respective bonds have to be made in accordance with the character of composition, temperature of lining on which they are applied as well as its composition. In the last time different kinds of phosphates, water glass, chromates in combination with plastifying agents as i.e. bentonite, derivatives of cellulose, sulphates and many others are used.

It is expected that the process of repairing BOF with grading materials from magnesia, dolomagnesia and dolomia will develop and extend and the consumed quantities of these materials will be very interesting to the producers of refractory materials.



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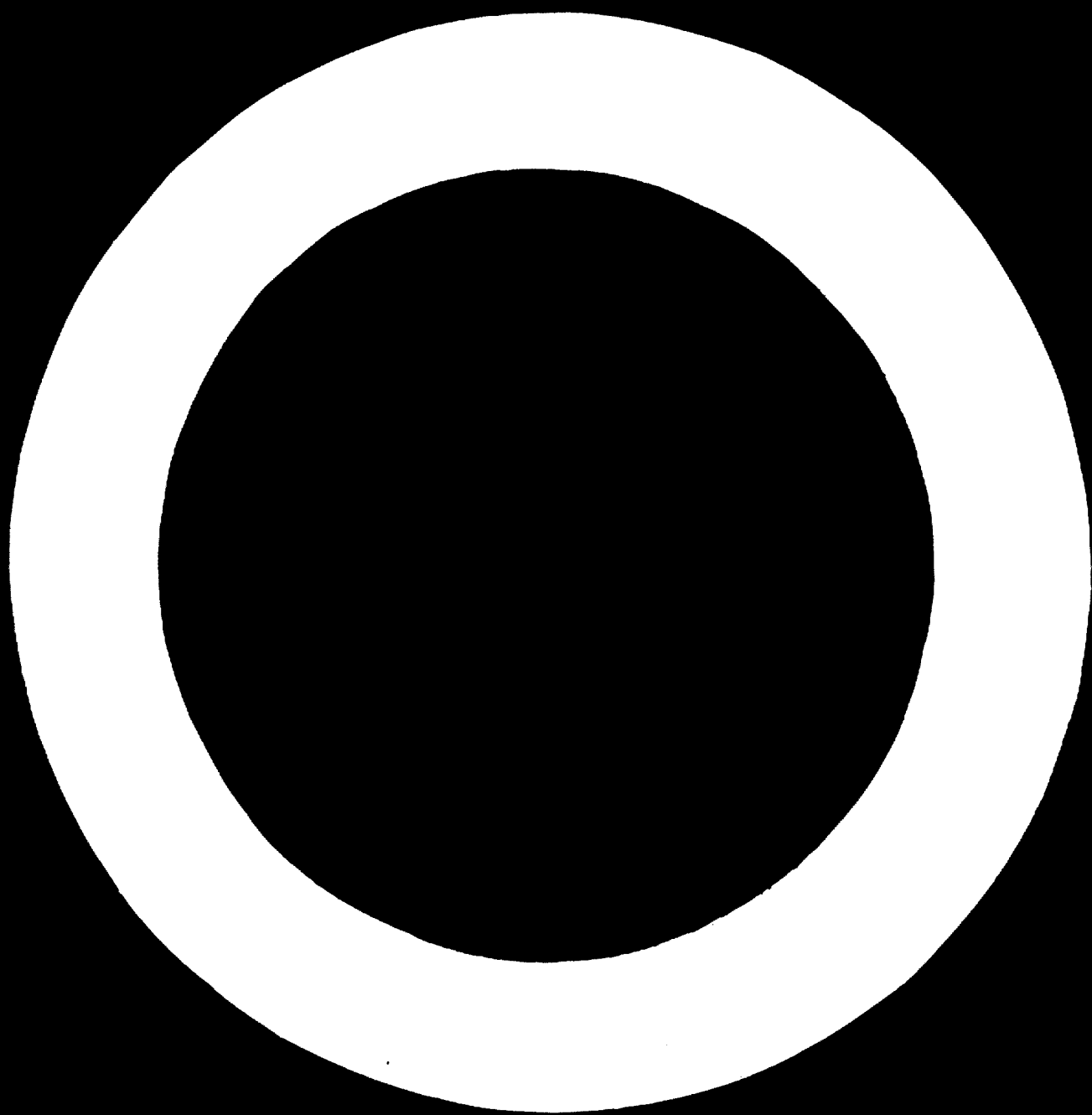
BODY COMPOSITION AND PROCESSING OF MAGNESITE AND OTHER BASIC REFRACTORIES ^{1/}

J. Staron *

SUMMARY

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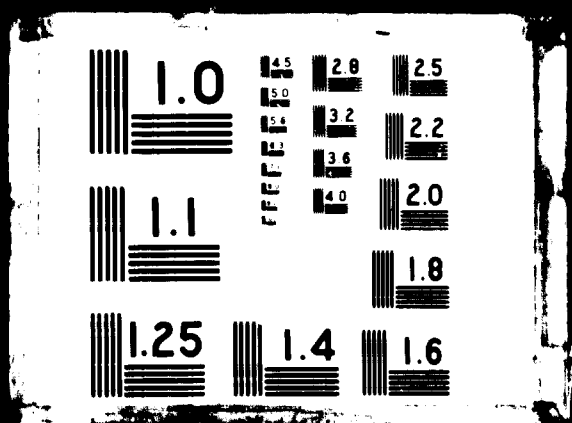




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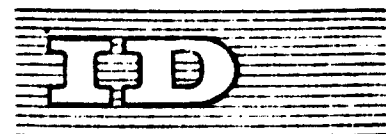
The sources, preparation and dressing of fundamental raws for processing basic refractories including the principles of processing, types and properties of these are described.

The types and properties of sintered magnesite, sintered dolomite and chrome-ores are mentioned. Demands of chemical composition, density and grading of fundamental materials are defined. Attention is given to the influence of impurities as SiO_2 , Fe_2O_3 , B_2O_3 and to the CaO/SiO_2 ratio in fundamental materials and its mixtures on the properties of basic refractories.

Burned and chemical bonded magnesite and chrome-magnesite bricks, basic rebonded fused grain bricks, fused-cast bricks and dolomite bricks are described. The characteristic properties and the dependence some of these properties on the proportion of the fundamental constituents content, temperature, and s.c. are mentioned. From the point of view of measuring physical and thermomechanical properties, are the bricks' qualities judged.

The author's observations on the further development and raising of basic refractories quality are discussed. Demands on quality and service life of basic refractory linings rise in dependence with new technological steelmaking processes.

In the last chapter of present paper the monolithic basic materials are discussed.



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11 - 28 junio 1974

COMPOSICION Y ELABORACION DE LA PASTA PARA PRODUCTOS DE
MAGNESITA Y OTROS PRODUCTOS REFRACTARIOS BASICOS^{1/}

J. Staron*

RESUMEN

En la monografía que aquí se resume se describen las fuentes y la preparación mecánica de las materias primas fundamentales para la elaboración de productos refractarios básicos, inclusive los principios de elaboración, los tipos y sus propiedades.

Se señalan los tipos y propiedades de la magnesita sinterizada, de la dolomita sinterizada y de los minerales de cromo. Se definen las exigencias relativas a la composición química, la densidad y la composición granulométrica de las materias primas fundamentales. Se dedica atención a la influencia que ejercen sobre las propiedades de los productos refractarios básicos la presencia de impurezas como el SiO_2 , el Fe_2O_3 y el B_2O_3 , así como la razón CaO/SiO_2 , en las materias primas fundamentales y sus mezclas.

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1/ Las opiniones que el autor expresa en este documento no reflejan necesariamente las de la Secretaría de la ONUDI. La presente versión española es traducción de un texto no revisado.

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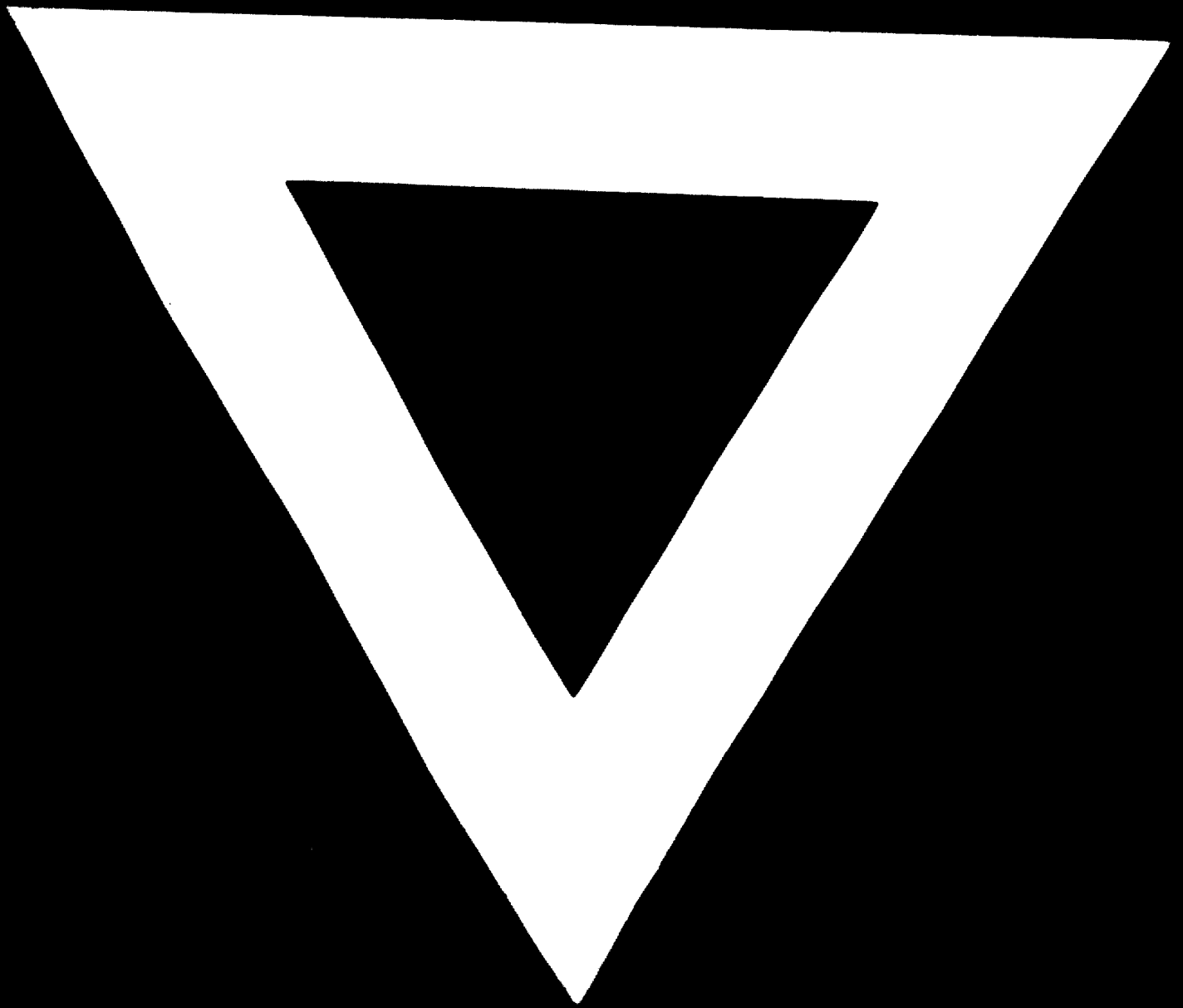
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Se describen los ladrillos de magnesita calcinada y ligada químicamente, así como los de cromo-magnesita, los ladrillos básicos de grano fundido y religados, los ladrillos colados por fusión y los ladrillos de dolomita. Se enumeran las propiedades características y el grado de dependencia de algunas de esas propiedades respecto de la proporción, temperatura, etc., de los constituyentes fundamentales. Se juzgan asimismo las cualidades de los ladrillos desde el punto de vista de sus propiedades físicas y termomecánicas.

Se analizan las observaciones del autor sobre futuras innovaciones y el mejoramiento de la calidad de los materiales refractarios básicos, teniendo en cuenta que las exigencias sobre calidad y duración de los revestimientos con materiales refractarios básicos aumentan a la par de los nuevos procesos tecnológicos de la siderurgia.

En el último capítulo de la monografía se estudian los materiales básicos monolíticos.





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