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Původní práce

THE PREPARATION AND SINTERING OF MgO OBTAINED FROM NATURAL MAGNESITES

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In order to reduce the amount of heat energy in the production of sintered magnesia from natural magnesites of breunerite type using the pyrohydrolysis of magnesium chloride the following modifications were proposed: a) decreasing of CaO *content in the raw material by selective leaching with hydrochloric acid and subsequent pyrohydrolysis of residual* $CaCl_2$; *b) precipitation of calcium salts as* $CaSO_4$ *and reducing decomposition of residual sulphates; c) briquetting of predried* $Mg(OH)_2$ *and sintering without preceding calcination of hydroxide.*

INTRODUCTION

The metallurgical requirements, particularly for bricks for the lining of furnaces and vessels used in the production of steel as well as for the secondary steelmaking processes have necessitated the introduction of the production of sintered magnesia with the content of MgO 98—99.5 % from natural Slovak magnesite of breunerite type containing after annealing:

SiO_2	1—6 %
Fe_2O_3	5—9 %
Al_2O_3	0,4—2 %
CaO	5—12 %
MgO	75—85 %

A process based on the pyrohydrolysis of magnesium chloride obtained by dissolving of the natural magnesite in hydrochloric acid was proposed. After adjustment of the pH to about 6 and filtering off the insoluble residue the solution is concentrated and decomposed in a reactor at the temperature 600—700 °C. The pyrohydrolytic product contains apart from MgO the residues of undecomposed $MgCl_2$ and especially $CaCl_2$ in the concentration corresponding to the proportion of soluble magnesium oxide to calcium oxide in the crude magnesite. The calcium chloride undecomposing in the reactor and the residues of undecomposed $MgCl_2$ are removed from the pyrohydrolytic product with the water washing, during which hydration to $Mg(OH)_2$ takes place. Its drying, dehydration and calcination of the oxide at the temperature 950 °C require a considerable amount of heat energy. The magnesium oxide is briquetted and sintered. The clinker contains 99—99,5 % of MgO and has the porosity 3—6 % (7).

The disadvantage of this process is the high consumption of heat energy which may be as much as 40 GJ per tonne of sintered magnesia when non-calcinated magnesite is used as the raw material. Technologies contributing to the decrease of energy consumption and expenses on the production without detriment of the technical values of the sintered magnesia as regards its chemical and mineral compositions and its density are the conditions of rational realization of production. The methods tried and tested in this work are the subject of the proposed alternatives.

1. SELECTIVE LEACHING OF THE RAW MATERIAL AND PYROHYDROLYSIS OF $CaCl_2$

One of the ways leading to the omitting of calcium salts washing from the pyrohydrolytic product is the reduction of CaO content in the raw material to a such degree which would eliminate the need for its further removal.

It is known that the calcareous component is the first one which is transformed into chloride at dissolving the mixture of magnesite accompanied with dolomite or limestone or dolomite itself in the hydrochloric acid [7]. The "preferential" dissolution was utilized for the selective leaching of natural magnesite accompanied with dolomite for the necessary reduction of the portion of calcium compounds in the magnesite before its entry into the process of the preparation of the magnesium chloride solution. For this purpose hydrochloric acid is used in the amount corresponding to the CaO content with determinated moderate excess. After filtration carbon dioxide is used to precipitate calcium carbonate from the solution using the calcinate from the magnesite. The reaction takes place according to the equation:

$$CaCl_2 + Mg(OH)_2 + CO_2 \rightarrow CaCO_3 + MgCl_2 + H_2O \qquad (1)$$

Magnesium chloride is returned to the process for pyrohydrolysis.

Magnesite from which CaO was eliminated in this way is dissolved in hydrochloric acid. The pH of the solution is adjusted by the addition of calcinate what prevents from passing of salts of iron and aluminium into the solution. The accompanying silicates remain also in the undissolved residue and are separated by filtration The solution obtained in this way is subjected after concentration to the pyrohydrolysis.

The rate of calcium salts selective leaching depends on the degree of dispersion of the raw material. In practice the filtrability requirements of the suspension must be taken into account. Grain size under 150 mesh was verified as satisfactory. The selectivity of leaching depends to a great extent on the concentration of the used acid. The optimum was found to be in the range 12—18 %, which at the same time corresponds to the conditions of acid regeneration after pyrohydrolysis of magnesium chloride.

The method was experimentally verified on magnesite containing after annealing 1.2 % SiO_2, 6.2 % Fe_2O_3, 5.6 % CaO, 87.1 % MgO and on several types of flue dust from rotary sintering furnaces in which magnesite is sintered. Solutions were prepared from which MgO with the content 3—4 % $CaCl_2$ corresponding to 1.5—1.8 % of CaO in the final product was obtained by means of pyrohydrolysis at the temperature 600 °C. But the content of $CaCl_2$ more than approx. 0.8 % is undesirable for the sintering of MgO briquettes to the required densities, same as are the undecomposed magnesium chloride residues, which occur practically always in the pyrohydrolytic product in various amounts. In the dry air atmosphere calcium chloride does not decompose. It evaporates intensively only at temperatures more than 1,300 °C (Fig. 1). But in the presence of water vapour the following reaction may take place:

$$CaCl_2 + H_2O = CaO + 2\,HCl \qquad (2)$$

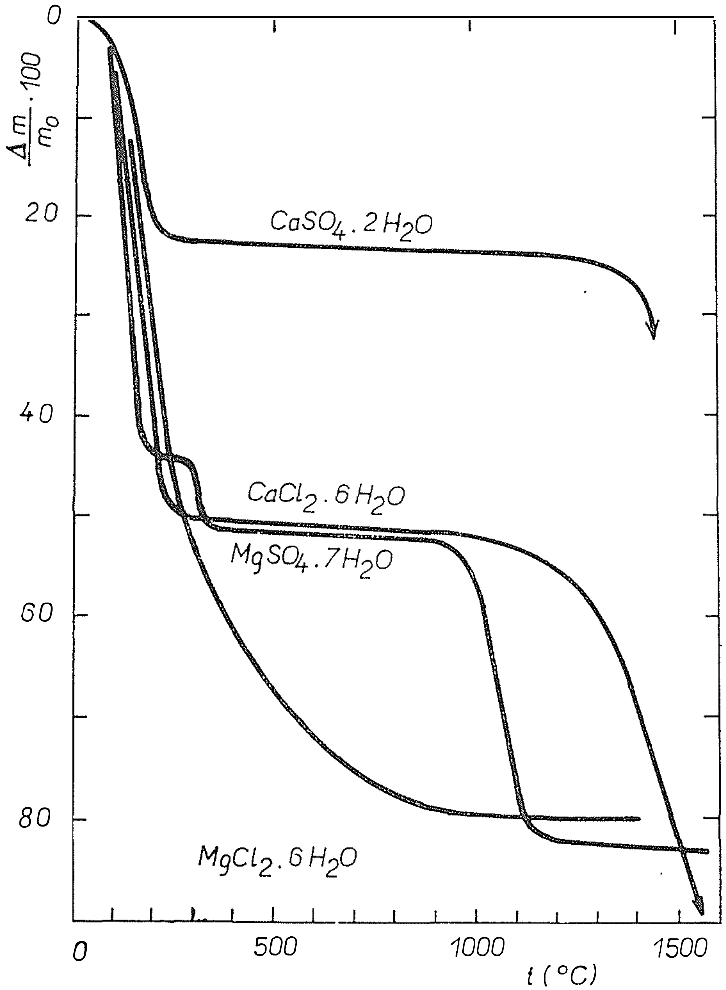

Fig. 1. Thermogravimetric records of the decomposition of magnesium and calcium sulphates and chlorides.

The changes in the free enthalpy of reaction are positive and the equilibrium constant of this reaction has very low values at the temperatures 900—1100 °C, which might be considered for eventual thermal after-treatment of the pyrohydrolytic product [3]. An increase in temperature is undesirable since morphological changes in MgO resulting in excessive porosity of the sintered magnesia obtained by sintering its briquettes would take place [1], [4], [5]. It is also unacceptable to perform the decomposition of $CaCl_2$ in the reactor in which the pyrohydrolysis of $MgCl_2$ takes place, since the reaction necessitates long reactive times. On the other hand ΔG° values in the reaction of decomposition of magnesium chloride reach the minus values already at temperatures 500 °C, which creates the thermodynamic conditions for the course of reaction (2).

The kinetics of the calcium chloride decomposition at various partial water vapour pressure and at various temperatures were investigated in the through-flow atmosphere on MgO sample containing 3 % of calcium chloride. There were determined:

— the dependence of the conversion on time at temperatures 900, 1000 and 1100 °C at constant partial water vapour pressure 6.7 KPa (Fig. 2);

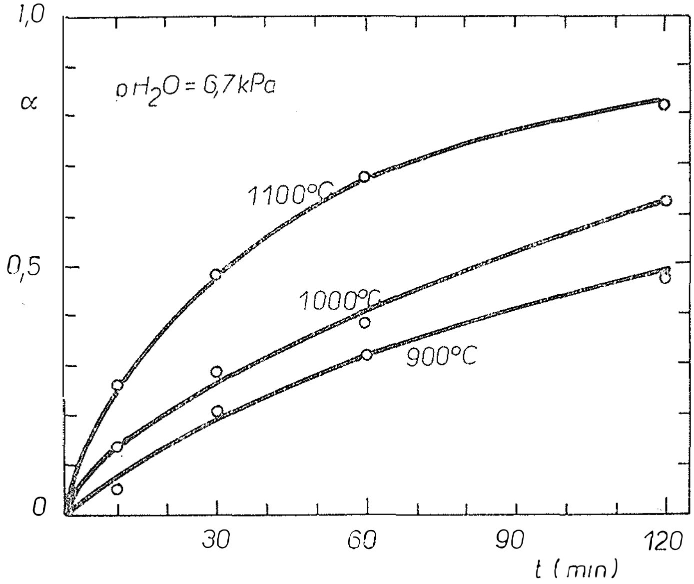

Fig. 2. The dependence of conversion α on time t at constant p_{H_2O} *and temperature t.*

— the dependence of the conversion on partial water vapour pressure at constant time and temperature (Fig. 3).

It follows from recorded dependences that:

The increase of partial pressure of H_2O more than 6.7 KPa, what was the lowest tested value, does not have any great effect. The reaction can be influenced more effectively by an increase of temperature and prolongation of time of reaction.

If the time 30—60 min. is taken as the actual time during which the material remains in any industrial calcinator, then the temperature 1100 °C is required to achieve high degree of $CaCl_2$ conversion. The combustion products contain approx. 18 % (vol.) of water vapour at the combustion of natural gas without excess of air.

On the basis of the results obtained the following modifications of the production of MgO and sintered magnesia can be made: The magnesite is subjected to selective leaching before its entry into decomposition with hydrochloric acid thus reducing the CaO content to level 1—1.8 % calculated after ignition. The pyrohydrolytic product is subsequently annealed at the temperature approx. 1100 °C in the atmosphere containing around 10 % volume of water vapour in order to remove residual magnesium chloride and decompose calcium chloride by pyrohydrolysis. The obtained oxide is briquetted and the briquettes are sintered at the temperature 1700—1900 °C.

The washing of the accompanying salts is eliminated as well as the consumption of energy for the water evaporation and the hydroxide decomposition in contrast to the originally proposed process.

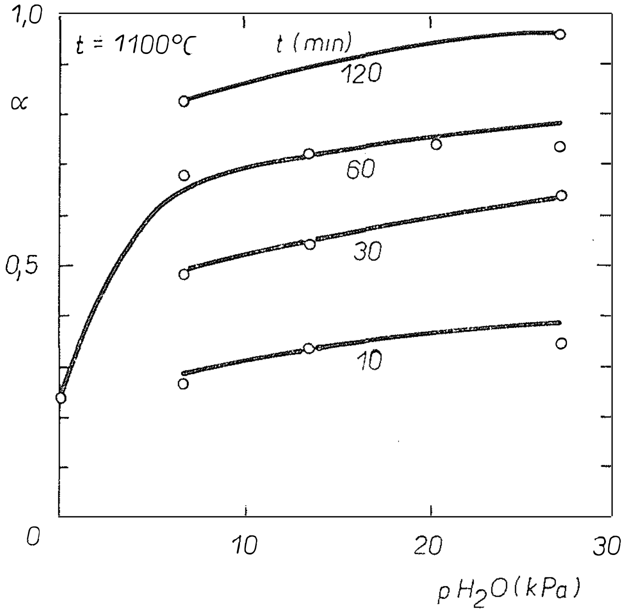

Fig. 3. Conversion α vs. p_{H_2O} at constant time t and temperature t.

2. PRECIPITATION OF CALCIUM SALTS AND DECOMPOSITION OF $CaSO_4$

Another possible way of reducing the calcium salts content in the product of $MgCl_2$ pyrohydrolysis is to precipitate Ca^{2+} ions from the solution by means of magnesium sulphate or sulphuric acid in the form of $CaSO_4$ separated from the solution with the filtration. The solubility of calcium sulphate is not negligible. Therefore the pyrohydrolytic product contains $CaSO_4$ and $MgSO_4$ in the concentrations negatively influencing its sintering into a dense clinker [2].

Calcium sulphate decomposes in the air atmosphere only at temperatures 1300 to 1500 °C (Fig. 1). Annealing of the pyrohydrolytic product at temperatures more than 1100 °C cannot be considered because of the MgO deactivation. The decomposition of calcium sulphate at temperatures less than 1000 °C can be realized in the atmosphere of hydrogen or another reducing gas [6].

In industrial use it is possible to obtain the reducing atmosphere in the annealing furnace by means of the incomplete combustion of natural gas. At the combustion of methane carbon oxide is produced according to the reaction:

$$2\,CH_4 + 3\,O_2 \;=\; 2\,CO + 4\,H_2O \tag{3}$$

It has been found that the decomposition of $CaSO_4$ in the combustion products of methane takes place at the temperatures slightly more than 800 °C in two stages according to the reaction:

$$\begin{aligned} CaSO_4 + 4\,CO &= CaS + 4\,CO_2, \\ CaS + H_2O &= CaO + H_2S\ . \end{aligned} \tag{4}$$

The content of SO_3 decreased from 2.6 % to 0.07 % after 45 min of calcining of the MgO sample in the atmosphere of reducing combusted methane at the temperature 875 °C, while no decrease was recorded in the atmosphere of the products of the complete CH_4 combustion [8].

On the basis of the experimental results further alternative technology for the production of MgO and its processing to the sintered magnesia can be suggested [8]. In the solution of $MgCl_2$ obtained by dissolving of natural magnesites Ca^{2+} ions are precipitated with $MgSO_4$ or H_2SO_4. The product of pyrohydrolysis then contains Ca in the form of calcium sulphate in the concentration 1—1.5 %, magnesium sulphate as the precipitating agent used in slight excess and residues of undecomposed magnesium chloride. Lower densities are recorded at sintering of products prepared with the isostatic pressings under 100 MPa at various temperatures than it is in the case of the oxide without these accompanying products removed from it with washing (Fig. 4). In the annealing furnace the calcium sulphate is then decomposed into CaO

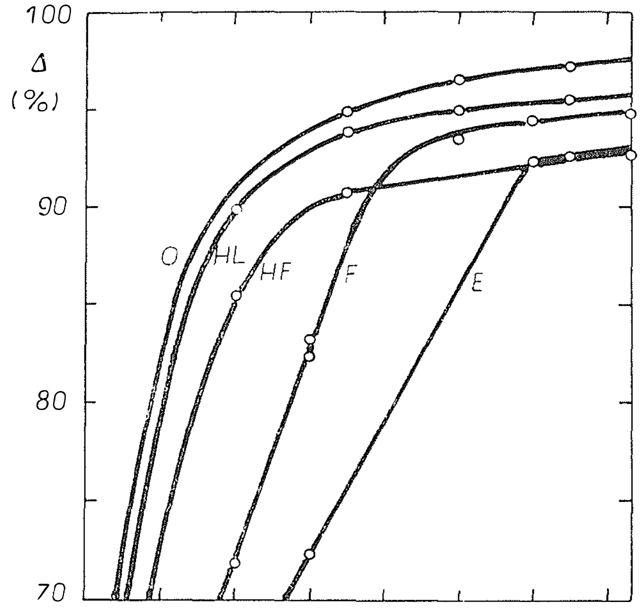

Fig. 4. Dependence of sample density Δ on firing temperature t; E, F — MgO from pyrohydrolysis (containing sulphates), HF — Mg(OH)₂ cake from a high-pressure filter, HL — Mg(OH)₂ pressed under pressure of 100 MPa, O — MgO pressed under pressure of 100 MPa.

and gaseous H_2S in the reducing atmosphere with the content of CO and H_2O already at temperatures 850—900 °C. If the temperature 1000—1100 °C is used, MgO is obtained in the morphologically optimal form guaranteeing high densities of magnesia

[1], [5] after sintering the briquettes. Besides there occurs in the presence of water vapour the decomposition of calcium chloride. It makes possible to obtain the product with the low content of CaO, chlorides and sulphates. Washing of the pyrohydrolytic product can be omitted since it can be briquetted directly and the briquettes can be sintered to the magnesia with the high density.

3. SINTERING OF BRIQUETTES MADE FROM $Mg(OH)_2$

The cake of magnesium hydroxide is obtained with the filtration after washing the accompanying salts from the product of pyrohydrolysis. Its properties depend on filtration conditions. The cake from vacuum filter contains 45—55 % water. Sintered magnesia with the porosity 15—18 % is obtained after sintering at temperature 1800—1900 °C. Dehydration to moisture 35—40 % was obtained under the pressure 1.2 MPa and porosity 11—13 % [1,7] after sintering under conditions similar to those in the precious case.

Interesting results were achieved by dehydration in the isostatic tube filter under the pressure 14 MPa, namely moisture of the cake 23—25 % and porosity 7—9 % after sintering [1]. Magnesia with the porosity 4.5—5.5 % was obtained after pressing of hydroxide with the water content 7 % under the pressure 100 MPa and sintering of compacts.

For comparison the porosities of magnesia after sintering at temperatures 1200 to 1850 °C from variously prepared compacts and various original materials were examined (Fig. 4).

The highest densities after every sintering temperature in the given region were achieved from the compacts of oxide prepared from hydorxide by annealing at 950 °C.

It is interesting that the porosity 5 % was obtained already by sintering at the relatively low temperature 1550 °C. In the same conditions of sintering higher porosities of magnesia were achieved from compacts prepared from hydroxide with the moisture 7 % pressed under the pressure 100 MPa.

Magnesia prepared with the sintering of cake from the isostatic filtration under the pressure 14 MPa has the lowest density. The reason is the highest porosity of cakes and products after sintering at 1200 °C, what is in the final view relatively the most unfavourable initial state. Despite of this fact the porosities after sintering at 1850 °C are only very slightly below the limit of demanded densities.

Curves *E*, *F* (Fig. 4) show objectively the retarding effect of residual salts ($CaSO_4$, $MgSO_4$) on the sintering of compacts prepared from the pyrohydrolytic product according to the alternative 2 without their removal.

On the basis of previous works briquetting of magnesium hydroxide and sintering of briquettes were performed. Laboratory briquetting press with following parameters was used:

cylinder diameter	300 mm
peripheral velocity	0.1 m . s^{-1}
press power	7.10^4 N . m^{-1}
moisture of hydroxide	7 %
volume of briquettes à	14 cm^3

The volume density of briquettes was 1530 kg . m^{-3}.

The porosity 5.3 % of magnesia was obtained after sintering for 1.5 h at 1850 °C.

It can be concluded from the experiments that it is technically possible to perform the briquetting of hydroxide and to realize the dehydration and sintering of briquettes in a single sintering apparatus. The advantage of this process is the greater simplicity of the technological apparatus. The use of relatively complicated calcining furnace requiring the keeping of calcining regime of the technically narrow area is eliminated. A further advantage is the great improvement in the briquetting ability of hydroxide in comparison with oxide, even though in the case of hydroxide larger amount is required for briquetting.

Sintered magnesia with sufficient density is produced by sintering at the temperature 1850 °C in generally used shaft kiln.

CONCLUSION

Methods of decreasing the consumption of heat energy in the production of sintered magnesia with the content of MgO 98—99.5 % from natural magnesite using pyrohydrolysis of magnesium chloride were proposed. In the first alternative the raw magnesite is subjected to selective leaching with HCl, which reduces the CaO content to the final level. The residual chlorides in the pyrohydrolytic product are decomposed after treating at the temperature 1000—1100 °C in the atmosphere containing water vapour. In the second alternative the calcium salts are precipitated from the solution as calcium sulphate. The residual sulphates are decomposed by annealing in the reducing atmosphere. In both cases the obtained product is briquetted and sintered to the required density. In the third alternative the calcium salts are washed from the pyrohydrolytic product and the pure hydroxide is not calcinated but predried, briquetted and the briquettes are sintered at the temperature 1850 °C. In the first two alternatives the saving 8.8 GJ/*t* of magnesia is reached, in the third one the erection and operation of special calcining furnace is eliminated.

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PRÍPRAVA A SLINOVANIE MgO ZÍSKANÉHO Z PRÍRODNÝCH MAGNEZITOV

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Pyrohydrolýza $MgCl_2$ sa používa v priemysle na výrobu MgO, z ktorého je možno získať magnéziový slinok vysokej čistoty. Nevýhodou procesu je vysoká spotreba energie. Predkladajú sa tri alternatívne riešenia problému: a) Zníženie obsahu zlúčenín vápnika vo východzom ma-

teriáli selektívnym rozpúšťaním v kyseline chlorovodíkovej. b) Zrážanie solí vápnika z roztoku $MgCl_2$ síranom horečnatým alebo kyselinou sírovou a rozklad zostatkových síranov v produkte pyrohydrolýzy žíhaním v redukčnej atmosfére. c) Vypieranie sprievodných solí vodou a slinovanie brikiet hydroxidu horečnatého po jeho čiastočnom vysušení. Realizáciou je možné docieliť úsporu 8,8 GJ/tonu slinutej magnézie.

Obr. 1. Termogravimetrické záznamy rozkladu síranov a chloridov horčíka a vápnika.
Obr. 2. Závislosť konverzie α od času pri konštantnom p_{H_2O} a teplote t.
Obr. 3. Závislosť konverzie α od p_{H_2O} pri konštantnom čase t a teplote t.
Obr. 4. Závislosť hutnosti Δ vzoriek na teplote výpalu t.
E, F — MgO *z pyrohydrolýzy (s obsahom síranov),*
HF — *koláč* $Mg(OH)_2$ *z vysokotlakového filtra,*
HL - $Mg(OH)_2$ *vylisovaný tlakom 100 MPa,*
O MgO *vylisovaný tlakom 100 MPa.*

ПРИГОТОВЛЕНИЕ И СПЕКАНИЕ MgO, ПОЛУЧЕННОЙ ИЗ ПРИРОДНЫХ МАГНЕЗИТОВ

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Пирогидролиз $MgCl_2$ применяется в промышленности для производства MgO, из которой можно получать магнезитовый клинкер высокой чистоты. Недостатком процесса является большой расход энергии. Предполагаются три альтернативные решения проблемы: а) понижение содержания соединений кальция в исходном материале селективным растворением в хлористоводородной кислоте, б) осаждение солей кальция из раствора $MgCl_2$ сульфатом магния или серной кислотой и разложение остаточных сульфатов в продукте пирогидролиза отжигом в восстановительной среде; в) вымывание сопутствующих солей водой и спекание брикетов гидрата окиси магния после ее частичной сушки. Проведением можно достичь экономию 8,8 GJ/t спекшейся окиси магнезии.

Рис. 1. Термогравиметрические записи разложения сульфатов и хлоридов магния и кальция.
Рис. 2. Зависимость конверсии α от времени t при постоянном pH_2O *и температуре t.*
Рис. 3. Зависимость конверсии α от pH_2O *при постоянном времени t и температуре τ.*
Рис. 4. Зависимость плотности Δ проб от температуры обжига t, E, F — MgO *из пирогидролиза (с содержанием сульфатов), HF* — *кек* $Mg(OH)_2$ *из фильтра, работающего под высоким давлением, HL* — $Mg(OH)_2$ *отпрессованная под давлением 100 MPa, O* — MgO, *отпрессованная под давлением 100 MPa.*