BONDING MECHANISM OF SOREL'S CEMENT AND MECHANICAL ACTIVATION OF MgO

By

Z. Juhász

Department of Building Materials, Technical University, Budapest

Magnesium oxide, thermally produced from magnesite ($MgCO_3$) and ground to adequate fineness, mixed with $MgCl_2$ or $MgSO_4$ solutions into a paste, yields basic complexes ($3\ MgO \cdot MgCl_2 \cdot 11\ H_2O$ and/or $4\ MgSO_4 \cdot 3\ Mg(OH)_2 \cdot 15\ H_2O$) causing the paste to gradually harden in air. This binder is called after its inventor (1867) Sorel's cement or simply, magnesia cement. Mixed with sawdust, talc, sand, pigment etc. it suits magnesite floors, [1, 2], or, its paste moulded and steam cured yields a refractory material, the so-called chemically bound basic brick [3].

Mg-oxichloride or Mg-hydroxi-sulphate complexes result from a primary topochemical reaction, complicated by the appearance of intermediary complex compounds [4].

This is why the hardening of Sorel's cement, the formation of hardening complexes, depends on several factors: the Mg salt to MgO ratio [5, 6, 7], concentration of Mg salt solution [8, 9, 10], $Mg(OH)_2$ impurities in MgO, w/c ratio, temperature [5, 6] etc.

Both reaction rate and mechanical properties of the hardened paste are greatly subject to *production conditions of magnesia* [10], first of all to the heating temperature of magnesite. Namely below 700°C, MgO becomes a finely crystalline reactive material with 10^{-6} cm crystallites, while at higher temperatures crystals begin to grow at a loss of reactivity.

Magnesia has been demonstrated [11 to 14] to be of a high dispersity degree, metastable, hence it can be made reactive by *mechanical activation*, intensive dry grinding of the relatively coarse systems. Thereby crystallites were shown to be reduced to 3 to 5×10^{-7} cm accompanied by the degradation of the inner crystalline structure (amorphization), resulting, among others, in a lower compaction (sintering) temperature of activated compared to untreated MgO.

The described research work has aimed partly at learning the mechanism of colloid chemical processes during the setting of $MgO/MgCl_2$ and $MgO/MgSO_4$ systems, and partly at determining the effect of mechanical activation on the reactivity of MgO, or briefly, at interpreting processes involved in the hardening of Sorel's cement or of chemically bound basic refractory brick.

1. Experimental

Our tests were made on commercial refractory magnesia (87% of MgO) and on $MgCl_2 \cdot 6 H_2O$ (98%) and $MgSO_4 \cdot 7 H_2O$ (99.5%) salts of technical purity.

1.1 *The setting mechanism was tested by a complex method*:

a) Chemical reaction between MgO and Mg salts took place in an adiabatic calorimeter inside an ultrathermostat at $40 \pm 1°C$.

The calorimeter vessel contained the salt solution, and a closed sample holder the ground MgO. After the system temperature has settled, the magnesia got from the sample holder to the solution (5% suspension) and the reaction heat determined as usual. Exact timing of reaction was provided by continuously checking the electric conductivity of the solution.

b) Reaction and calorimetry completed, suspension was poured into a settling vessel and the *settling rate* of the dispersed part determined, using the set seen in Fig. 1. The settling vessel was placed in a plastic case with a slot as seen in the figure, passing a light beam through the suspension. Light intensity was determined by a photometer zeroed to the pure dispersion medium and to the freshly shaken dispersion (I_{100} and I_0). Since during settling of the suspension, the logarithm of light intensity has empirically been found to decrease
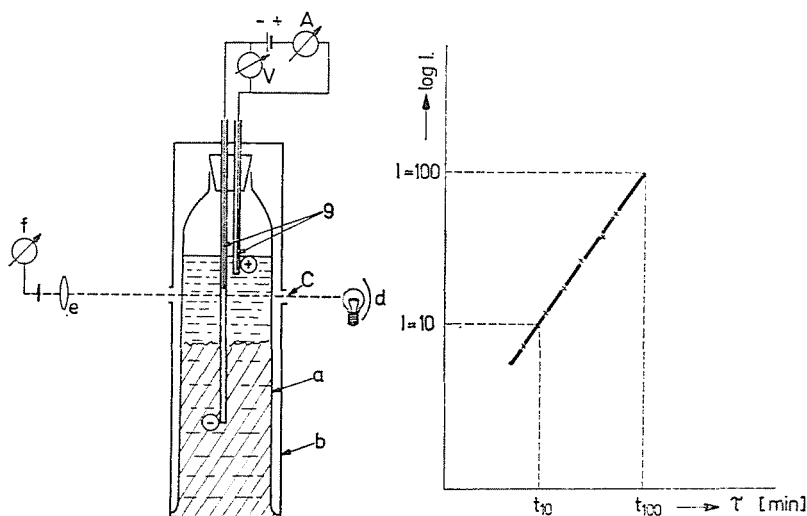

Fig. 1. Determination of settling rate and of the charge on the particles. a = settling cylinder with suspension; b = plastic case; c = slot transmitting the light; d = light source; e = lens system; f = photometer; g = electrodes; A = ammeter; V = voltmeter; t = settling time; I = light intensity

about inversely with the settling time, settling times t_{10} and t_{100} for $I = 10\%$ and complete total settlement I_{100}, resp., were directly read off the straight line prolonging the test curve, permitting to express the settling rate as:

$$\frac{\log I_{100} - \log I_{10}}{t_{100} - t_{10}} = v_G$$

and the suspension *stability* as:

$$m_G = = \frac{100}{v_G} \, .$$

c) The next step was to produce an electric field at a voltage drop $1V/cm$ between two second-kind electrodes shown in Fig. 1, timing the settlement rate according to *b)*. Now, positively charged particles settle somewhat faster than in a suspension with no electric field: $v^+ > v_G$. Changing the current direction reduced the settling rate of positively charged particles compared to "free settlement": $v^- > v_G$.

In the actual testing conditions it seemed better to apply a mean settling rate rather than v_G:

$$v = \frac{v^+ + v^-}{2}$$

deducing the charge value from the quotient

$$q^+ = \frac{v^+}{v}$$

truly positive particles being denoted by a positive number while negative charges were affected by a negative q^+. Particle charge was found to be proportional to q^+.

d) After having determined the surface charge the suspension has been filtered, the filtrate and the residue *analyzed* chemically as usual, and the dried precipitate *derivatographed*.

1.2 *Experiments to determine mechanical activity*:

a) The initial MgO grit was dry ground for different times in a laboratory *vibrating mill*. Two grinding series have been made: one *without* surface active grinding admixture, and the other by spraying 0.1% trietholamine on the MgO before grinding to reduce aggregation during grinding.

b) Grinding structure tests involved:
— dispersity degree (grinding fineness) by permeabilimetry [ω cm²/g];

— compactness ξ, voids ratio $\varkappa$ and porosity ε related to inner particle voids of a powder layer compressed by 1 kp/cm² (since $\xi + \varkappa + \varepsilon = 1$, these parameters can be plotted in a triangular diagram = in TPA system);
— "adherence energy" [a in erg/cm²] characterizing cohesion between particles by the compactibility of the powder layer.

(For detailed description of the test method see [15].)

c) The grindings were technologically tested in specimens of the composition:

68% granular magnesia (0.5 to 2 mm)

29% MgO grindings activated in different manners;

3% dry magnesium sulphate.

This dry mix was admixed with 3% of 30% $MgCl_2$ solution, thoroughly mixed, moulded into 5×5 cm cylinders and steam cured under factory conditions. Specimens were tested for compactness, virtual porosity and compressive strength.

2. Test results and evaluation

2.1 *Setting mechanism tests*

2.11. The diagram of *reaction heat* vs. molar ratio of the starting mix Mg^{2+}/MgO (Fig. 2) had a *minimum* at 2 moles of Mg^{2+}, beyond that the reaction heat for $MgSO_4$ is generally lower than for $MgCl_2$.

2.12. In pure aqueous systems (Fig. 3) particle surfaces had a positive *charge.*
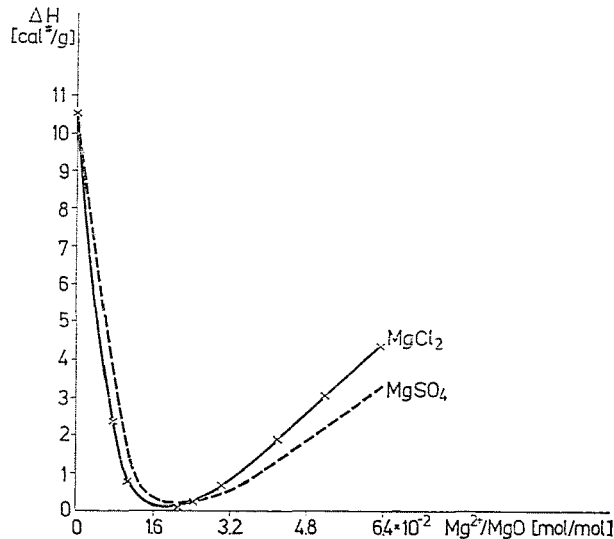
Fig. 2. Reaction energy vs. Mg salt concentration

Notice that *no phenolphtalein* adsorption was observed in clean water when the pigment was admixed to the suspension immediately after wetting MgO, but particles in a suspension stored or heated before pigmented were made bright red by adsorbed phenolphtalein. Increasing the Mg^{2+} quantity, the positive charge is first reduced up to an *isoelectric point* followed by negative charges. For high Mg^{2+} quantities the surface charge decreased.

In high Mg^{2+} suspensions (e.g. above a molar ratio of $5 \times 8 \times 10^{-2}$) *no* phenolphtalein adsorption or particle staining was observed, neither immediately nor after a lengthy warming of the suspension.

2.13. Relation between particle surface charge and *suspension stability* persisted to but a degree (Fig. 3). Though the surface discharge in the range of low concentrations was accompanied by a loss in stability, the lowest stability belonged — rather than to the isoelectric point — to the maximum of negative charge. At and above this concentration the suspension abruptly underwent *coalescence*.

2.14. *Phase analysis* (Fig. 4) concluded by stating the complex compound to develop in the concentration range of minimum surface charges, hence for $MgSO_4$ above a molar ratio of 2.5×10^{-2}, while for $MgCl_2$ for a Mg^{2+} above a molar ratio of $2 \times 10^{-2}/MgO$. Below this quantity of magnesium salt $Mg(OH)_2$
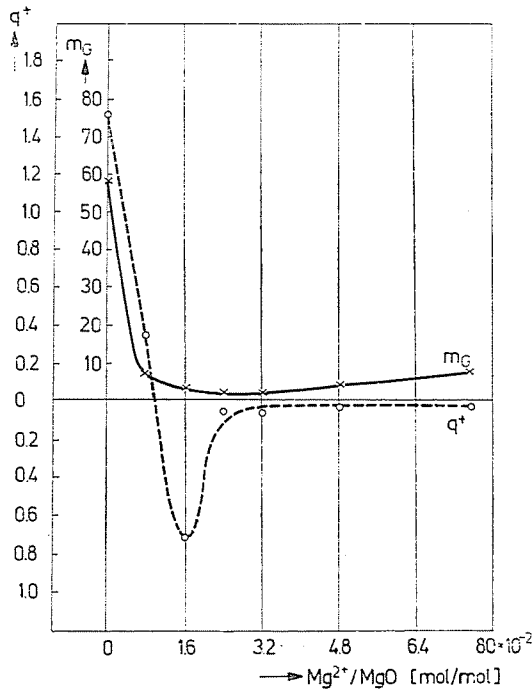

Fig. 3. Particle surface charge q^+ and suspension stability m_G vs. $MgSO_4$ concentration

develops (in conformity with published data) in a quantity increasing until complex formation and decreasing beyond it.

Also the tendency was manifest that for a highly concentrated suspension (hence for a low Mg^{2+}/MgO molar ratio), particles had a positive charge, while a thin suspension contained negative charged particles, with the demonstrable presence of sulphato- and chloro-complexes. To have negative charged particles in paste consistency, the $MgSO_4$ or $MgCl_2$ of the medium had to be greatly raised. Using a *mix* of $MgSO_4$ and $MgCl_2$ in the tests always resulted in a chloro-complex — even for 3 : 1 ratios of $MgSO_4$ to $MgCl_2$ in the mix. Though, for pure salts with identical Mg^{2+}/MgO molar ratios, chloro-complex quantities always exceeded sulphato-complex ones (twice for high Mg^{2+} concentrations). 2.15. *Hardening* was exclusively observed in the presence of a chloro-complex or sulphato-complex. No permanent strength was found in lack of complex compounds. Specimen compressive strength increased about linearily with the quantity of complexes.

The presented experimental data hint to the following phenomena (see also Fig. 5):

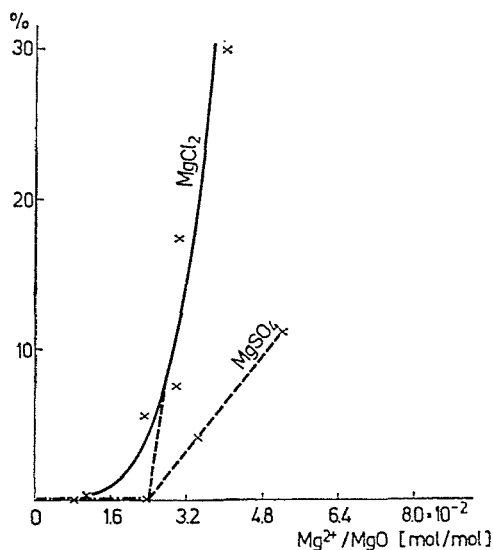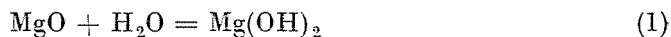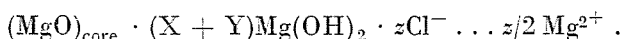In a *pure aqueous* solution, because of the known MgO reaction:

$$MgO + H_2O = Mg(OH)_2 \tag{1}$$

$$Mg(OH)_2 = Mg^2 + 2(OH) \tag{2}$$

Fig. 4. Reacting complex salt percentage in the filtrate vs. Mg^{2+} concentration

particle surface layers develop an electric double stratum with inner, positive armature (plotted schematically in Figs 5*a,b*), leading to the symbol of micellar structure:

$$(\text{MgO})_{\text{core}} \cdot x\text{Mg(OH)}_2 \cdot y \; \text{Mg}^{2+} \ldots 2y(\text{OH})^- \; .$$
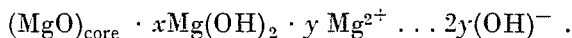
Solving *little* MgSO_4 or MgCl_2 salt in the dispersing medium reduces both hydrolysis according to reaction (2) and the electric charge on the particle as much as to the isoelectric point (Fig. 5*c*).

After the isoelectric point, *re-charging* and perfect reduction of surface hydrolysis come about, owing to the binding of Cl^- or SO_4^{2-} ions parallel to the formation of the micellar structure:

$$(\text{MgO})_{\text{core}} \cdot (\text{X} + \text{Y})\text{Mg(OH)}_2 \cdot z(\text{SO}_4)^{2-} \ldots 2 \; \text{Mg}^{2+}$$

$$(\text{MgO})_{\text{core}} \cdot (\text{X} + \text{Y})\text{Mg(OH)}_2 \cdot z\text{Cl}^- \ldots z/2 \; \text{Mg}^{2+} \; .$$

Further increasing Mg^{2+} in the dispersion medium involves the reduction of the electric charge on the outer layer, reducing in turn the double layer safeguarding the suspension stability to a degree to bring about *intensive coalescence*. This process (of coalescence) is equivalent to the formation of chemical bond leading to complex compounds, namely only closely adjacent surfaces can enter a *bridge bond* type $\text{SO}_4-\text{Mg}-\text{SO}_4$ or $\text{Cl}-\text{Mg}-\text{Cl}$ providing for particle intergrowth, hence for strength development (Fig. 5*d*). Interface points of particles intergrown upon the reaction give rise to the known *complex compounds* — related to coalescence.

Development of the complex responsible for cement hardening is preconditioned by fast coalescence of negative charged particles in the presence of Mg ions suiting bridge bond. Recharge of particles of originally positive surface charge and coalescence need a high Mg^{2+} concentration. Thus, also cement strength begins only to grow at a high $\text{Mg}^{2+}/\text{MgO}$ ratio.
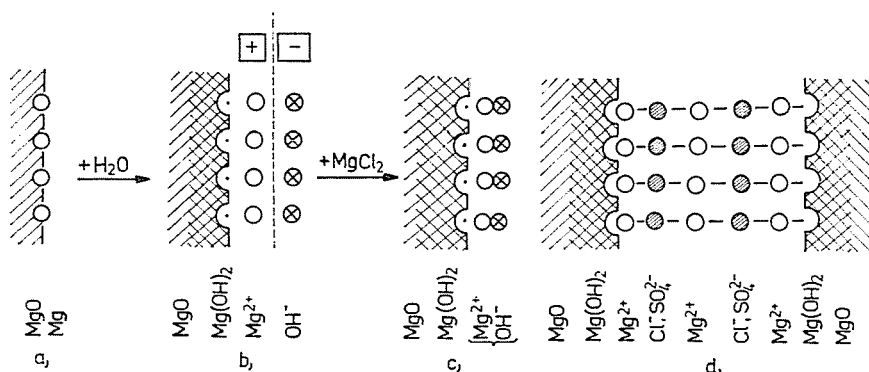

Fig. 5. Schematic interpretation of surface complex formation

2.2 *Mechanical activation test results*

2.21. Grinding characteristics have been plotted in Fig. 6, showing:

— *specific surface* to monotonously increase with activation time. Trietanol-amine (TEA) admixture somewhat improved the grinding dispersity degree (Fig. 6*a*);

— *adhesion* between particles activated without TEA to vary according to a minimum-maximum curve. For a 1 to 3 h activation, adhesion exhibited a sharp maximum. Grinding with TEA monotonously reduced adhesion with activation time (Fig. 6*b*);

— *grinding structure* to vary in the TPH system (Fig. 6*c*), compactness ξ tending to decrease with the increase of activation time (indicated by arrows) in both grinding tests. Within this range, however, a shorter grinding time is accompanied by more porous particles ε in activation zone I, indicating the development of *loose bulks*. A protracted grinding zone II involves decrease of ε and increases voids ratio $\varkappa$, hence *compact bulks* come about.

2.22. *Specimen compactness* increased with grinding time, more exactly, in both test series, the virtual porosity of specimens monotonously decreased with grinding time.

2.23. In grinding times I and I', the *compressive strength* of specimens increased about linearily with grinding fineness ω and monotonously decreased with virtual porosity ε_l. In zones II and II', however, curves of both test series deviated, and for the same fineness degree or virtual porosity achieved by a surface active admixture, the strength was higher than without.

2.24. All in all, both activation tests involved an important increase of binding force.
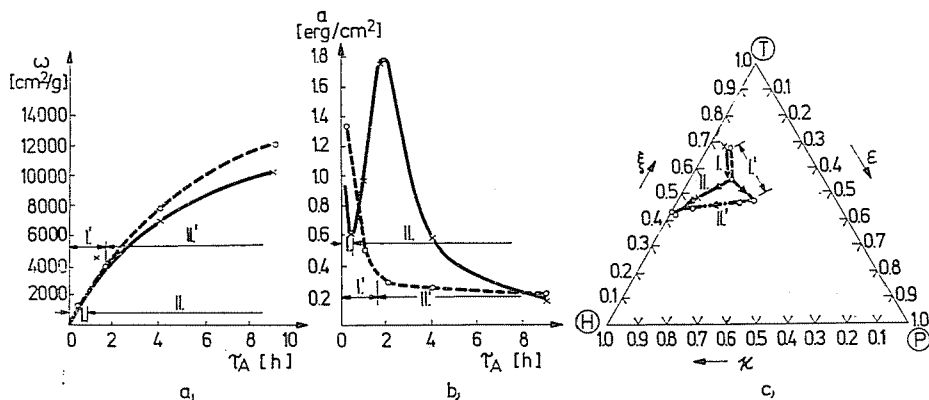

Fig. 6. Structure characteristics of MgO grindings: ω = specific surface; a = adherence energy ξ = compactness; ε = porosity; k = voids ratio, τ_A = grinding time.
———— no admixture;
- - - - - TEA-admixed

Activation tests have led to the following conclusions:

A higher dispersity degree (mechanical dispersion [16]) increases strength by reducing the particle size and thereby increasing the number of contact points inside the binder, hence of the active surface centres likely to develop bridge bonds or complex compounds. *A higher dispersity degree improves the binding force.*

Freshly broken surfaces developed in grinding solids normally exhibit denser active centres than do earlier developed surfaces (surface activation [16]), important not only for the higher reactivity in topochemical processes but for inducing and facilitating *adherence* and *intergrowth* of particles (aggregation and agglomeration [17]), reducing, in turn, the specific surface, hence the reactivity. In grinding zone II, the equilibrium between dispersion and the counteracting agglomeration results in a "final strength" little changing with grinding time. Reducing agglomeration by a surface active grinding admixture results in a higher specific surface and specimen strength for the same grinding time.

Also the test result of higher binding force of grindings of the *same specific surface* upon reducing agglomeration by a surface active admixture suggests agglomeration to principally affect *active centres* on freshly broken surfaces released by mechanical activation so that agglomerating particles mutually cover each other's active surface elements. This *cover effect reduces grinding reactivity* in complex development processes responsible for the binding force of Sorel's cement, just as the strength of specimens compared to that expected from the specific surface area. Reducing the agglomeration by a surface active
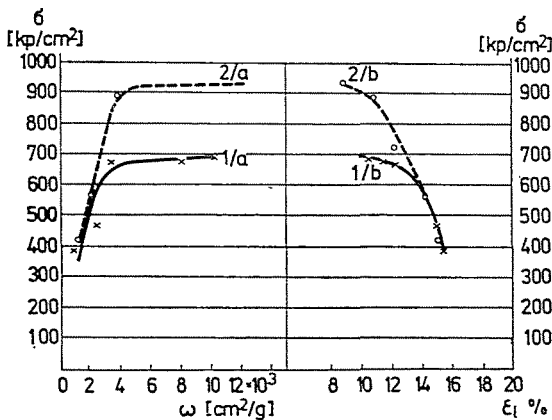

Fig. 7. Compressive strength of refractory bricks vs. binder grinding fineness ω and virtual porosity ε_1
——— no admixture
- - - - - TEA-admixed

grinding admixture hinders the cover effect, releasing active centres fitting the development of complexes. This process is manifest by the improvement of binding force and in specimen strength increase.

3. Conclusions

Chemical processes involved in the hardening of Sorel's (magnesia) cement have been examined for different $MgO/MgCl_2$ and $MgO/MgSO_4$ ratios. Surface charges of MgO particles, stability of thin suspensions, reaction heat of chemical processes between MgO and Mg salts, as well as the composition of the product have been determined.

A *double layer* has been found to develop on Mg particle surfaces in aqueous medium and in thin Mg salt solutions, with positive inner, and negative, OH^- outer armature. Increasing the Mg salt concentration reduces the charge on the double layer to an isoelectric point, and then causes it to *recharge*. In high Mg concentrations the charge on the recharged layer gradually *discharges* accompanied by an abrupt *coalescence* of the suspension. Now, (surface)$-$Cl$-$ Mg$-$Cl (surface)- or (surface)$-SO_4$Mg$-SO_4-$(surface)-type bridge bonds arise, concomitant to the development of the known chloro- and sulphato-complexes, these latter being responsible for the binding force of hardened cement.

Also the effect of mechanical activation of MgO on the strength of basic refractory bricks has been investigated, determining the structure of MgO grindings activated for different times in a vibrating mill, the virtual porosity and strength of activated MgO bricks.

A higher dispersity degree was found to improve the binding force of MgO, by increasing the contact areas between particles, important for bridge bonds to develop.

In addition, reactivity and binding force are also increased by the development of surface elements of higher activity on freshly broken surfaces. A protracted grinding is, however, accompanied by the phenomenon of agglomeration, impairing specimen strength partly by reducing the specific surface area, and partly by inactivating high-activity centres — important for the binding force, — to complex formation, because of a *cover effect*. Reducing agglomeration by a surface active admixture much increases the cement binding force.

Summary

Chemical processes involved in the hardening of Sorel's (magnesia) cement have been examined for different $MgO/MgCl_2$ and $MgO/MgSO_4$ ratios. Surface charges of MgO particles, stability of thin suspensions, reaction heat of chemical processes between MgO and Mg salts, as well as the composition of the product have been determined.

Also the effect of mechanical activation of MgO on the strength of basic refractory bricks has been investigated, determining the structure of MgO grindings activated for different times in a vibrating mill, the virtual porosity and strength of activated MgO bricks.

A higher dispersity degree was found to improve the binding force of MgO, by increasing the contact areas between particles, important for bridge bonds to develop.

References

1. KILIÁN, J.: Building Materials.* University Notebook 1972.
2. Hungarian Standard MSz 4249—53.
3. KISMARTY, L.: Refractories.* Műszaki Kiadó, Budapest, 1956.
4. VYDRODOV, I. P.: X-ray Diffraction Study of the Kinetics of Hardening of Magnesium Oxychloride and Gypsum.** Tr. Kubansk. Selshokhoz Inst. (1963) pp. 50—55.
5. BERG, L. G.—ALTYKIS, M. G.—ZHURAVLEVA, I. P.: Hardening of Magnesia Cements Sealed by Magnesium Sulfates.** Izv. Vyssh. Ucheb. Zaved. Khim. Teknol. (1967) pp. 905—909.
6. BENKEL, E.: The Setting Process of Magnesia Cements. Fraunhofer Ges. F. Angew. Forsch. E. V. (1961) pp. 95—98.
7. PETUKHOVA, G. M.: Composition of Magnesia Cement.** Vopr. Sovrem. Stroit. i Arkh. (1964) pp. 470—476.
8. SMIRNOV, B. I.—SOLOVEVA, E. S.: Physico-Chemical Study of the Mechanism of Hardening of Magnesia Cement.** Fiz. Khim. Mekk. Pocho. Gruntov. Glin. Stroit. Mater. (1966) pp. 429—444.
9. SMIRNOV, B. I.—SOLOVEVA, E. S.—SEGALOVA, E. E.: Chemical Reaction of MgO with $MgCl_2$-Solutions of Various Concentrations.** Zh. Prikl. Khim. (1967) pp. 505—515.
10. MEYER, B. J. (Editor): Gmelin's Handbuch der anorganischen Chemie. Verlag Chemie, Weinheim 1959.
11. SCHRADER, R.—KNESCHKE, G.: Mechanische Aktivierung von Magnesiumoxid für die Sinterung. Silikattechnik. H.6. (1968). p. 19.
12. KNESCHKE, G.—ZACHMANN, L.: Der Einfluß einer Desintegratormahlung auf die Sinterfähigkeit von Magnesiumoxid. Silikattechnik 24 (1973) pp. 118—121.
13. SCHLEGEL, E.—MORGNER, J.: Die Sinterung von CaO und MgO aus Pulvern mit unterschiedlichen Eigenschaften. Silikattechnik, 22 (1971) pp. 48—53.
14. REINHARDT, H.—KNESCHKE, G.—HARJES, W.: Einfluß der Feinstmahlung auf die Sinterung von Magnesiumoxid. Silikattechnik 24 (1973) p. 117.
15. JUHÁSZ, Z.: Description of Building Materials by Inner Morphology.* Építőanyag No. 6, 1977.
16. JUHÁSZ Z.: Mechanochemische Aktivierung von Silikatmineralien durch Trocken-Feinmahlen. Aufbereitungstechnik H. 10 (1974) pp. 558—562.
17. OPOCZKY L.: Report of the Working Committee of Colloid Chemistry of the Hungarian Academy of Sciences, 1976.

Dr. Zoltán JUHÁSZ, Sen. Res. Worker, H-1521 Budapest

* In Hungarian
** In Russian