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MAGNESIA CEMENTS: OVER A HUNDRED YEARS OLD BUT STILL NOVEL

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MAGNESITE /MAGNESIA

BACKGROUND

Magnesite, magnesia and magnesium compounds are terms used to designate a variety of industrial raw materials which are related by their common main constituent, magnesium, but still very much diversified by their different properties as well as different uses.

The term ♦magnesia♦ in particular refers to the various types of magnesium oxides, which are available in the market. Deadburned magnesia, caustic calcined magnesia and electrofused magnesia are all three magnesium oxides possessing different physical properties and thus addressing to diverse applications.

Magnesia originates from two main sources: Natural and synthetic.



The basic concept and technology of the two production processes are quite different, while the resulting end products are similar, presenting however differences in terms of their respective degree of purity.

Figure 1 presents schematically the production process of magnesite / magnesia / magnesium compounds from natural sources.

Magnesite / magnesia is used in several industrial sectors. It is worth mentioning that contrarily to deadburned magnesia (dbm) which is mainly used as a high duty refractory raw material, caustic calcined magnesia (ccm) addresses to a much wider spectrum of applications, including certain specialized niche markets. Figure 2 summarizes the main magnesite / magnesia fields of application.

Figure 1: Production process from natural sources

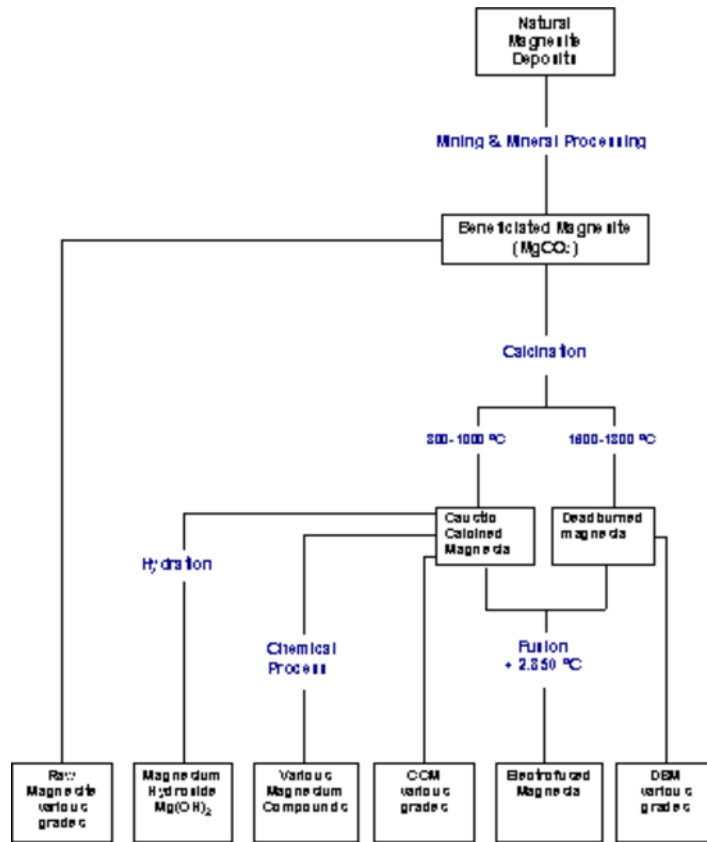


Figure 2: Magnesite / Magnesia Applications

CAUSTIC CALCINED MAGNESIA

- Construction
- Industrial flooring
- Insulating panels

Various Industrial applications:

- Pulp and paper industry
- Abrasives (grinding and polishing wheels)
- Electrofused magnesia
- Steel industry (fluxes, insulating powder, electrical steel)
- Glass industry
- Tanning industry
- Fuel & lubricant additives
- Sugar



Environmental applications:

- Flue gas treatment
- Industrial effluent treatment
- Sewage treatment
- Water purification
- Acid rain
- Waste incinerators

Agricultural applications:

- Animal Feed
- Fertilizers, Soil conditioner

- Chemicals, pharmaceuticals, cosmetics
- Fillers (plastics, rubber, paints, adhesives)

DEADBURNED MAGNESIA

- Refractories
- Magnesium metal
- Welding fluxes
- Heating elements
- Mineral insulated cables



MAGNESITE RAW

- Ceramics
- Fertilizers
- Welding fluxes
- Magnesium metal
- Fluxes for the steel industry
- Fillers



For the sake of completeness of this short prologue on magnesite / magnesia fundamentals the following global figures on production and consumption are presented to the best of our knowledge in order to show the significance of this important industrial minerals sector.

Magnesite / Magnesia Global Figures

- World natural magnesite reserves: 10.000.000.000 mt
- World natural magnesite production: 18.000.000 mt/annum
- World magnesia production /consumption

9.500.000 mt/annum out of which...

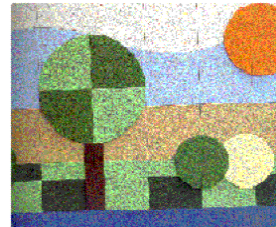
From natural: sources over 80%, dbm: over 80%

From synthetic: sources less than 20%, ccm: less than 20%

MAGNESIA CEMENTS

In 1867 a French engineer named Stanislas Sorel discovered that when active magnesium oxide is added to a solution of magnesium chloride an exothermic reaction takes place and forms magnesium oxychloride, which appears like an extremely strong and hard block.

Investigating further the properties of magnesium oxychloride he realized that, apart from its extraordinary endurance in mechanical strength, it also had an excellent bonding capacity, enabling the binding of various organic and inorganic aggregates.



The first aggregate used was wood shavings (sawdust) and the initial commercial application of this invention was in the construction of flooring, which became known as Sorel cement floor.

The first floors were laid during the 1890s for use in residential and industrial constructions under the name of *xyloolith* (wood stone) or *parquet sans joints* (jointless floor).

Further technical developments followed over the years in terms of the aggregates and additives, as well as the solutions of magnesium salts used, enlarging the spectrum of application of the magnesia cement.

Magnesium oxychloride (MOC)

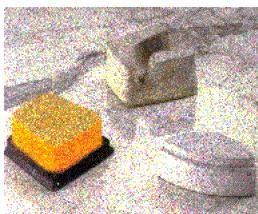
Magnesium oxysulphate (MOS)

Magnesium phosphate (MAP)

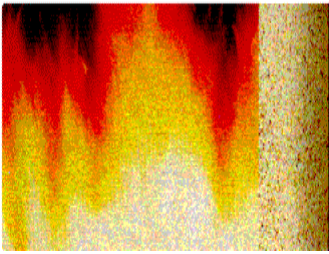
are well known magnesia cements which are mainly used in architectural applications, such as:



- Construction of industrial floors
- Construction of thermal and acoustical insulating panels and other prefabricated building boards



- Grinding and polishing stone



· Fire proofing and special light construction elements

· Plus some lesser applications such as production of special stuccos and manufacture of artifacts.

MAGNESIUM OXYCHLORIDE CEMENT

Chemistry

This cement is manufactured by mixing magnesia with magnesium chloride solutions in well-defined proportions to produce the magnesium oxychloride, which is the bonding phase.

The investigation of the system MgO-MgCl₂-H₂O by some authors¹⁻⁵ highlights the complexity of the Sorel cement chemistry because of the large number of parameters affecting the nature and the quality of the reaction products between magnesium oxide and magnesium chloride solution.

The main bonding phases found in hardened Sorel cement are 5Mg(OH)₂·MgCl₂·8H₂O (form-5: Diag.1) and 3Mg(OH)₂·MgCl₂·8H₂O (form-3: Diag.2). This is in agreement with previous research work³, stating that form-3 and form-5 are the only stable phases in the system MgO-MgCl₂-H₂O (fig.3).

Figure 3: The system MgO-MgCl₂-H₂O

The first, because of its crystallization in well-formed needle like crystals (fig.4) has superior mechanical properties and is formed using a molar ratio of MgO:MgCl₂:H₂O = 5:1:13 according to the global reaction (1). The theoretical formation of form-3 corresponds to a molar ratio of

MgO:MgCl₂:H₂O = 3:1:11 according to the global reaction (2).

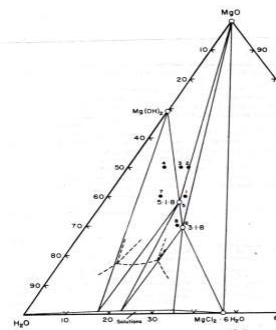
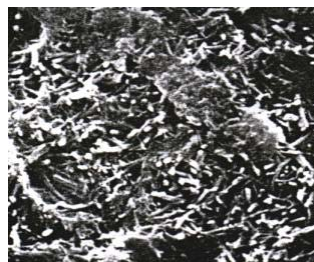
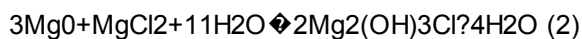
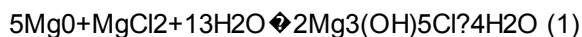


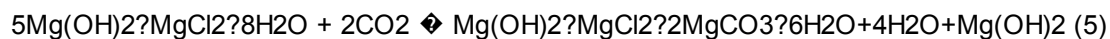
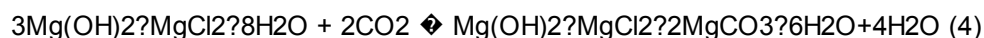
Figure 4: Crystal structure of the MOC (form-5)

A parallel or competitive reaction is the hydration of magnesium oxide due to the presence of excess water according to the chemical equation (3).



The presence of Mg(OH)₂ indicates a low quality magnesium oxychloride and in some cases the form-5 phase is transformed at later stages to the form-3 with mechanical strength decrease. Some authors^{6,7} attribute the late appearance of the form-3 phase to the reaction between the Mg(OH)₂ obtained from reaction (3) and the unreacted MgCl₂ present in the mortar under some conditions. In our experiments we observed this transformation of phases in some caustic magnesia produced from microcrystalline type magnesite (diag.3). Over a period of time, atmospheric carbon dioxide is possible to react with magnesium oxychloride to form a surface layer of Mg(OH)ClCO₃·3H₂O able to limit the Sorel cement's water sensibility (diag.4).

Sorrell and Urwongse state in their investigations³ that «samples with composition near 3.1.8 (form-3) showed a marked tendency to form the chlorocarbonate Mg(OH)₂·MgCl₂·2MgCO₃·6H₂O». Through our own research work on the subject we concluded that the appearance of chlorocarbonate is not correlated with the existence of the form-3 phase and its formation could be possible from both magnesium oxychloride phases (form-3 and form-5) according to the following global chemical equations:



Dry atmospheric conditions eliminate the water produced and favor the chlorocarbonate formation, reaction (5) generates the very white Mg(OH)₂, which could appear as white shadows on the Sorel cement's surface. Cole and Demediuk⁸ also reported that both forms change after long periods of time to the above mentioned basic magnesium chlorocarbonate. The influence of this phase formation on mechanical and other Sorel cement properties has not been investigated yet.

Raw Materials

Both magnesia's physical properties and magnesium chloride solution characteristics in association with various components proportions are the main parameters to obtain magnesium oxychloride cement with suitable properties.

Important raw materials characteristics affecting Sorel cement properties are the following:



Caustic calcined magnesia

Caustic calcined magnesia from natural magnesite is the normal magnesia type used for Sorel cement products. Grecian CCM, because of its unique properties such as whiteness, microcrystallinity, high MgO availability and capability to produce mortars with adjustable setting properties, has a leading position on this market. The most important magnesia's characteristics affecting its performance in this application are:

Microstructure: It is well known that this magnesia's characteristic depends on the raw magnesite used for its production. There are two types of natural magnesite, the macro

crystalline and microcrystalline or cryptocrystalline. Microcrystalline caustic magnesia gives Sorel cements with better mechanical properties and the capability to produce low setting time mortars.

Activity: A complex characteristic depending on many other parameters such as: raw magnesite (macro or microcrystalline), calcination conditions and particle size distribution. Specific surface area (BET), citric or acetic acid activity and iodine number are good indexes of activity.

From our experience as magnesia producers and from a large number of experiments carried out in our R&D center, we concluded that activity is the most important parameter affecting essential Sorel cement properties. Mortars setting time and workability are related to the activity of magnesia. The amount of magnesium chloride solution needed to produce mortars of comparable consistency from a fixed amount of oxide is related to the specific surface area expressing the correlation between microstructure and porosity with material liquid absorption. Figure 5 shows the correlation of the above-mentioned parameters.

Sample	C.Acid. Activity	S.S.A.m2/gr	Liquid Absorpt.	Setting End
1	48sec	49,5	65%	50Min
2	82sec	32,5	60%	85Min
3	110sec	23,8	53,5%	140Min

Figure 5: Physical properties of 3 CCM calcined at different conditions

In previous studies, it is referred that high mechanical strength is developed with low activity oxides. In a mortar with a very active magnesium oxide and in association with the needed excess of water the reaction (3) is favored. The produced $Mg(OH)_2$ not only limits the amount of the good bonding phase form-5 but also with the unreacted $MgCl_2$ favors its transformation in later ages to the form-3 with mechanical strength decrease. Also in some cases these phases transformations could create dimensions stability problems.

Whiteness: Important parameter for the production of light color products.

Particle size distribution: A relatively low particle size is needed for fast and uniform reaction with magnesium chloride solutions to avoid basic reactions after initial setting and the related problems. Suitable: 100% -150 μ m

>80% -75 μ m

Chemical composition: Caustic magnesia with 80-90% MgO is normally used for this application, but with some limitations the impurities content. Important parameter is the available MgO, because some C.C.M such as the Austrian type or other Dolomitic magnesias contain a large amount of MgO combined in other components (Dolomite, Talc?) affecting the stoichiometry and the properties of Sorel cement (figure 6). Free lime also in large amounts (>0,6%) gives an excessive volume change.

Sample	S.S.A (m2/gr)	Available MgO%
GR.MAG: NOR-F	27,6	81,1
STYROMAG: K	26,9	67,8
CHINESE	13,2	70,7

Figure 6: Available MgO on CCM of different origin.

Magnesium chloride is used in various forms such as solution or flakes. The most important parameter is the content in some impurities such as:

$\text{CaCl}_2 \cdot x\text{H}_2\text{O}$ <1%: Higher amount \blacklozenge Volume change weakness

NaCl, KCl <2%:

CaSO_4 <0,5%: # # \blacklozenge Efflorescence problems

Practical Rules

- Use of CCM from Microcrystalline type of magnesite.
- Work on excess of CCM according to the stoichiometry of reaction (1): MgO/MgCl_2 (wt/wt): $\approx 2,20$.
- The MgCl_2 Solution Density should be: 23-25°Be (For floors)
- The working conditions should be precise and stable, as it is a chemical process.
- Avoid extreme weather conditions (Temperature and humidity), which affect both setting properties but also the magnesium oxychloride phase development. Fig. 7 shows the influence of working temperature to the setting time for mixtures prepared and tested according to DIN 273.

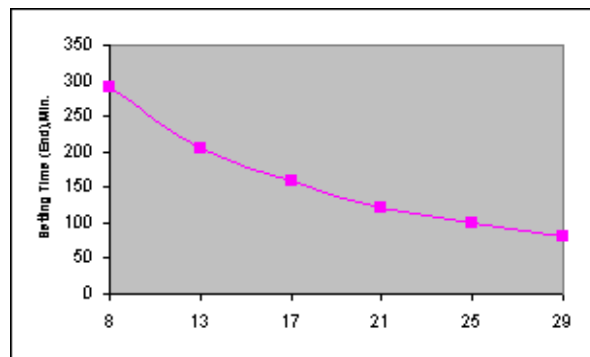


Figure 7: Influence of working temperature to the setting time

Properties

The very good properties of magnesium oxychloride phases (form-5) in association with the properties of the aggregates and other raw materials used allow the production of Sorel cement with unique properties for various applications such as industrial floors. In the following table typical values of Sorel cement compositions for industrial floors and other applications are listed.



PROPERTY	VALUE
Compressive strength	(28 days) 40-100 N/mm ²
Flexural tensile strength	(28 days) 10-17 N/mm ²
Surface hardness	50-250 N/mm ²
E-Module	1-3 10 ⁴ N/mm ²
Thermal conductivity	< 0,7 w/mk
Electrical conductivity	R: 103-105 Ohm
Chemical resistance	<p>Resists to:</p> <ul style="list-style-type: none"> - Organic solvents - Fuels - Oils and grease <p>Not resistant to:</p> <ul style="list-style-type: none"> - Acids - Bases - Water
Specific weight	1,50-2,10g/cm ³
Dimensions stability	$\Delta < 0,2\%$
Surface fluctuation	< 2mm/m

Flame retardant properties

Magnesium oxychloride decomposes at high temperature through several steps. According to the experimental thermal decomposition TGA-DTA diagram (fig 8) a large quantity of energy is absorbed and high amount of water is released (fig 9).

From this point of view MOC could be considered as an inorganic flame-retardant agent on the

same way as the well-known commercial products ATH and Mg(OH)₂ and products with MOC are fire resistant.

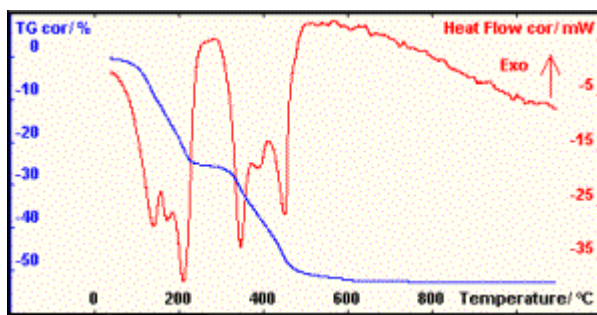


Figure 9: Thermal decomposition of pure MOC (form-5 phase)

Product	Al(OH) ₃	Mg(OH) ₂	MOC
Water content/loss on ignition	34,5%	31,0%	44,1%
Decomposition temperature	>200°C	>340°C	70-500°C
Enthalpy of decomposition (at decomposition temperature)	1051 J/g	1316 J/g	1671J/gr

Figure 8: MOC: Flame retardant properties

SOREL CEMENT FLOORS

Due to their exceptional properties, which we will try to synthesize here below, Sorel cement floors have been widely adopted as an optimum solution in industrial constructions.

In certain industrial sectors and / or cases, sorel cements floors constitute the unique solution to the extent that they fulfill a multitude of requirements. Multifloor buildings, reconstruction of old and decrepitated cement floors, are just a few examples.

It is also important to point out that various types of Sorel cement floors are presently offered aiming at meeting specific customer requirements. This variety is achieved by differentiating the basic Sorel cement composition and also by altering the combination and the proportions of the various aggregates and special additives used.

To mention an example Sorel cement floors exist with low thermal conductivity close to wooden floors.

Panorama of Sorel cement floor properties

The functional point of view:

Sorel cement floors are functional because:

- They have excellent adhesion and they can be quickly laid on any substrate, new or _old
- They are self leveling

- Their thickness can be from less than 5mm to over 5cm
- They acquire high early strength
- They are uniform in their mass and joint less
- They do not need wet curing
- They require low maintenance and are quickly and simply repaired.

The performance / specifications points of view:

Sorel cement floors have controlled performance because:

- They are highly resistant to shocks, can receive heavy weight and are practically wearless, because of their high compression and flexion strength as well as abrasion resistance
- They are resistant to fuels, solvents, grease, non acidic oils and paints
- They have excellent electrical and low thermal conductivity
- They are incombustible and fire resistant

The ecological and comfort point of view:

Sorel cement floors are ecological because:

- They are non toxic, inorganic, dust free and odorless
- They have good acoustical properties
- Their surface is smooth, warm and non-slippery
- They present insecticide properties and they discourage bacteria and fungi growth
- They are available in a wide variety of colors

Precautions and Limitations

MOC is corrosive therefore metallic parts have to be protected, when they adjoin with it. However its major limitation comes from its non-resistance to prolonged contact with water. Consequently it cannot be installed in exterior constructions and also in areas, which need repeated water flow cleaning.

Sorel Cement Floor Applications

As we said before Sorel cement floors have been initially used in residential and industrial constructions. It is worth mentioning that the floors of the first wagons of the Paris Metro were laid with Sorel cement, thanks to their resistance in shocks and continual vibration. Another specialized application was in shipbuilding for the interior decks of war and merchant vessels.

Today Sorel cement industrial floors constitute an economical solution for a wide range of industrial sectors:

· Automotive



· Aircraft, armament
_and aerospace



· Electrical and mechanical



· Printing

· Electronics



· Pharmaceutical

· Plastics

· Clothing textile



· General warehouses

· Furniture



Sorel Cement Floor Markets

Central Europe constitutes the main market, where Germany has been traditionally the leader.

The average size of the European market for the last decade, is estimated at 3.5 million m²/annum, with a peak period of 4.5 million m²/annum in 1991-1993.

Tough competition prevails in Sorel cement floors markets, which causes pressure on market prices.

Competition comes both from internal antagonism between Sorel cement floors laying companies fighting for market share and also from less expensive floors.

As a consequence market prices have dropped during the last years at a current average level of around 12 EUR/m². Moreover, for large sites, prices below 10 EUR/m² have been reported.

There is a niche market for Sorel cement floors in the US for residential as well as commercial and industrial flooring. This market is estimated at 1.5 million m²/annum.

Price levels are reported to be in the range of 20 USD/m², which is substantially higher, compared to the prices applied in Europe.



MAGNESIA CEMENT BONDED GRINDING AND POLISHING WHEELS

Although this application is not directly related to the architectural sector a quick reference on the subject is considered to be useful for the completeness of this presentation.

Due to its very high bonding strength MOC cement is largely used in the manufacture of grinding and polishing stones.

In this application MOC cement is used to bond SiC grains. The main end-users are the marble, granite and mosaic processing industries.



Despite the strong competition with diamond discs and other resin bonded tools, an increased

demand of MOC cement based polishing stones has been witnessed during the last years thanks to the development of the \diamond gres porcelanato \diamond type of ceramic tiles.

Another interesting and developing application is in the manufacture of special millstones for rice peeling where the ecological properties of MOC cement are highly appreciated.

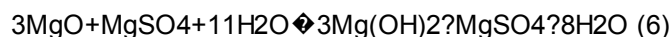
MAGNESIUM OXYSULFATE CEMENT (MOS)

The second well-known magnesia cement is the magnesium oxysulfate cement, which is formed by the reaction of magnesium oxide with magnesium sulfate solutions to produce a very good bonding phase. Mechanical strength and abrasion resistance are much better than those of Portland cement but not as good as MOC cement.

The main phases that we identified on a lightweight-insulating panel based on magnesium oxysulfate cement are the following:

- MgO: main phase
- $3\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 8\text{H}_2\text{O}$
- $\text{Mg}(\text{OH})_2$
- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- Impurities from raw materials

From the above results we conclude that the bonding phase corresponds to the stoichiometry of the global reaction (6), the MOS cements on this main application are formulated with large magnesium oxide excess and secondary reaction (7,8) takes place.



Relatively low quality caustic calcined magnesia is used for this application but the role of some impurities and the stable quality, due to the industrialized production process are important parameters.

On the same way as MOC this magnesia cement exhibits very good flame retardant properties.

MAGNESIA CEMENT PANELS

The principal industrial application of magnesium oxysulphate cement is in the manufacture of lightweight insulating panels.

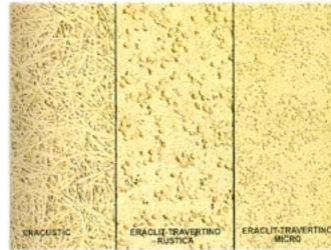
The basic technology consists of impregnating wood shavings with MOS cement in a mixer. The mixture is then molded, pressed in order to give the desired density of the panel. Then is desiccated and cured either at ambient conditions or at high temperature in ovens. Lastly the surface is finished before the panel is ready for delivery.

All these stages are of capital importance for the quality of the end product.

Several manufacturing techniques have been developed, including a patented continuous production process.

The main characteristics of these building boards are:

- Light weight and dimensional stability
- Thermal insulation
- Acoustical insulation and sound absorption
- Mechanical strength compression and flexion
- Fire resistance
- Ecological



A large variety of types of MOS panels exist in terms of:

- Different thickness from 10 to 100 mm
- Different densities from 350 to 650 kg/m³
- Different combinations of insulating materials
- Different surface treatment and finishing



The above parameters and their combination create vast possibilities for the production of different types of panels, which satisfy specific requirements in several applications.

Figure 10 summarizes the typical properties of the magnesia-bonded panels produced by ERACLIT VENIER SPA in Italy

Properties	Values
Dimensional / Stability	$\Delta < 0,05\%$
Thermal insulation	$\lambda = 0,072 \text{ w/mk}$
Acoustical insulation	58 db ISO R717:154 mm

Sound absorption	up to $\alpha_m=0,88$: 125e. 4000HZ
Specific weight	350-650 kg/m ³
Vapor permeability	$\mu= 4-10$
Flexure strength	up to 5 N/mm ²
Compressive strength	up to 0,7 N/mm ²
Fire resistance	up to REI 180
Applications conditions	up to 200° and R.H. 100%

Figure 10: Typical properties of Magnesia bonded panels

MOS Panels Applications

MOS panels can be applied, horizontally, vertically and to ceilings and therefore can be used for floor, wall/frame and roof insulation.

Thanks to their multifunctional and ecological properties, MOS panels are used in every type of civil construction, including the residential, public, professional and industrial sectors.



Houses, schools, gymnasiums, theaters, offices and a number of industrial constructions are a few examples.

It is worth mentioning some special applications of particular interest.

- Permanent mould for concrete structures
- Cheap building board for light and anti seismic constructions
- Fire protection of metallic structures

MOS Panels Markets

In Europe MOS panels are produced in Italy and Austria and the total European production is estimated at 350.000 m³/annum.

Market could be characterized as stable, although pressure on prices exists on the low-end applications, coming from lower quality-cheaper price cement panels.

There is a wide range of prices depending on each specific type of panel. However a price idea of a standard MOS panels is: 180 EUR/m³

MOS panels are also produced in the US for niche market applications mainly taking advantage of their ecological and fire proofing properties.

Magnesium phosphate cement (map)



This type of magnesium cement is formed by reacting magnesium oxide with a soluble phosphate. A solution of an agricultural grade ammonium phosphate can be used for this purpose.

MAP possesses all the fundamental properties of MOC, while in addition it has excellent water and freeze thaw resistance.

Due to its very rapid setting and high early mechanical strength, MAP constitutes an ideal patching mortar for fast repairing of roads, aircraft runways and other constructions where an immediate restoration of the site into use is required. It is reported that the areas repaired with MAP cement can be reused within less than one hour. One high added value application for the MAP cement is its use as binder in dental refractory cements.

The ammonium phosphate, either the mono or dibasic salt is used in some known applications to form the MAP cement and the main bonding phase is considered to be the $Mg(NH_4)PO_4 \cdot 6H_2O$.

Due to the very low setting time of magnesium phosphate cement dead burned magnesia (DBM) or electro fused is used. In some cases, retardants such as borax or boric acid are used to afford a workable setting time.

MAP mortars constitute a field of research where major developments are to be expected.

CONCLUSIONS

The fundamental technology of magnesia cement is over a hundred years old and its merits have been implemented in the architectural markets especially through its main two applications i.e. the industrial flooring and the insulating panels.

It is our belief that magnesia cements and especially their applications in industrial flooring need a more active, extrovert and coordinated marketing effort. This effort, to be more efficient, should involve all interested parties including the floor and panel manufacturers as well as the raw materials producers and processors.

A second factor, of equal importance for the further development of the magnesia cement markets, should be the undertaking of R&D efforts aiming at higher standardization of the magnesia cement technology. Such developments should include the improvement of the water resistance of MOC cements.

Our company, being a traditional leading supplier of the magnesia cement markets, has undertaken the initiative to promote such actions in close cooperation with our customers, using our R&D potential and marketing capabilities.

References

1. F.C.Happer, ♦Effect of calcination temperature on the properties of magnesium oxides for use in magnesium oxychloride cements♦, J. appl.Chem., Vol 17, 9-10, (1967).

2. B.Matcovic and all., ♦Reaction products in magnesium oxychloride cement pastes♦, J. Am.Ceram.Soc., 60(11-12), 504-507, (1977).
3. L.Urwongse and C.A.Sorrell, ♦The system MgO-MgCl₂-H₂O at 23°C♦, J. Am.Ceram.Soc., 63(9-10), 501-4, (1980).
4. C.A.Sorrell, C.R.Armstrong, ♦ Reactions and equilibria in magnesium oxychloride cements♦, J. Am.Ceram.Soc., 59(1-2), 51-54, (1976).
5. PH.Matray, P.Hmelin, ♦Etude de l♦ influence du rapport MgO/Sol sur les proprietes des liants magnesiens♦, Materials and Structures, 24, 106-114, (1991).
6. E.S.Solovleva, B.I.Smirnov, E.E.Segalova, P.A.Rebinder, ♦Physicochemical features of hardening of magnesium oxychloride cement. Kinetics of formation of disperse hardening structures on interaction of magnesium oxide, with magnesium chloride in aqueous medium♦, Kolloidn.Zh., 30(5), 754-60, (1968).
7. B.I.Smirnov, E.S.Solovleva, E.E.Segalova, P.A.Rebinder, ♦Physicochemical features of hardening of magnesium oxychloride cement. Kinetics of formation of disperse hardening structures on interaction of magnesium oxide, with magnesium chloride in aqueous medium♦, 31(3), 440-45, ibid (1969).
8. W.F.Cole and T.Demediuk, ♦X-ray, Thermal and Dehydration studies on magnesium oxychlorides♦, Aust.J.Chem., 8(2), 234-51, (1955).