Materials Properties, Use and Conservation: Construction Materials and Binders

Magnesian and gypsum binders

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CIBA Centro per i Beni Culturali
Diagnostica . Rilievo . Tecnologie

Binders classification

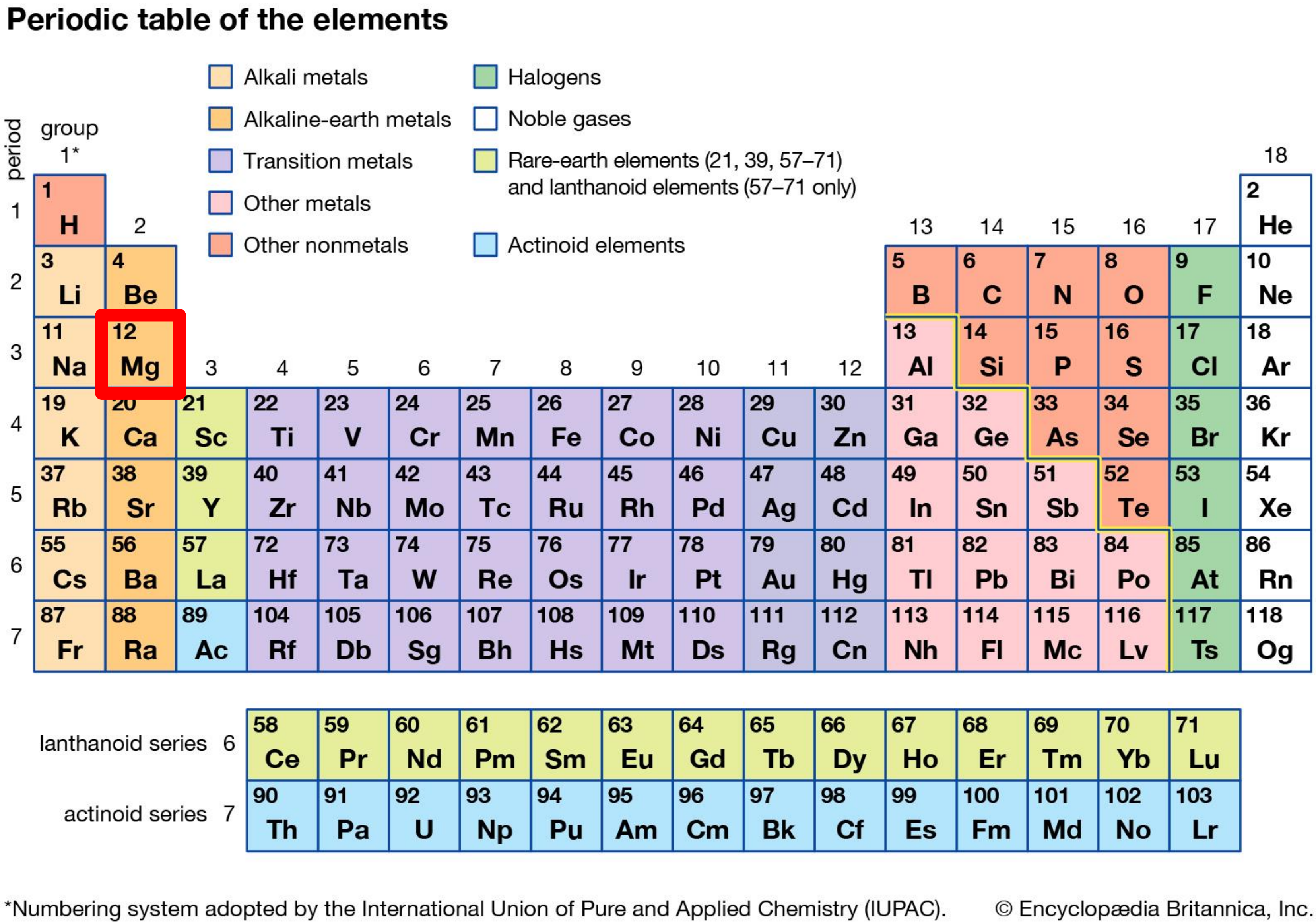
Table 3.6. Main classes of binding compounds produced by pyrotechnology.

Starting reactive material	***Production process***	***Material-water mixture***	***Final product***	***Mineral phases in the hardened aged material***
Lime-plaster (quicklime)	Calcinations of limestone	Slaked lime (lime putty)	Lime plaster	Calcite
		Slaked lime + fine aggregate	Lime mortar	Calcite + aggregate
		Slaked lime + fine aggregate + pozzolan	Hydraulic mortar (Roman opus caementitium)	Calcite, zeolites, C-S-H + aggregate
	Calcination of dolomite	Slaked magnesia-lime	Dolomitic or magnesian plaster	Calcite, brucite, periclase
Gypsum-plaster (plaster of Paris)	Calcination of gypsum	Bassanite (± anhydrite)	Gypsum plaster	Gypsum
		Bassanite + fine aggregate	Gypsum mortar	Gypsum + aggregate
Portland-clinker	Calcinations of limestones+clay	Portland cement paste	Portland cement	Portlandite, C-S-H, calcite
		Portland cement paste + fine aggregate	Portland cement mortar	Portlandite, C-S-H, calcite + aggregate
		Portland cement paste + fine and coarse aggregate	Concrete	Portlandite, C-S-H, calcite + aggregate
		Cement paste + fine aggregate + pozzolan	Pozzolanic Portland cement mortar	Portlandite, C-S-H, calcite, Ca-aluminosilicates

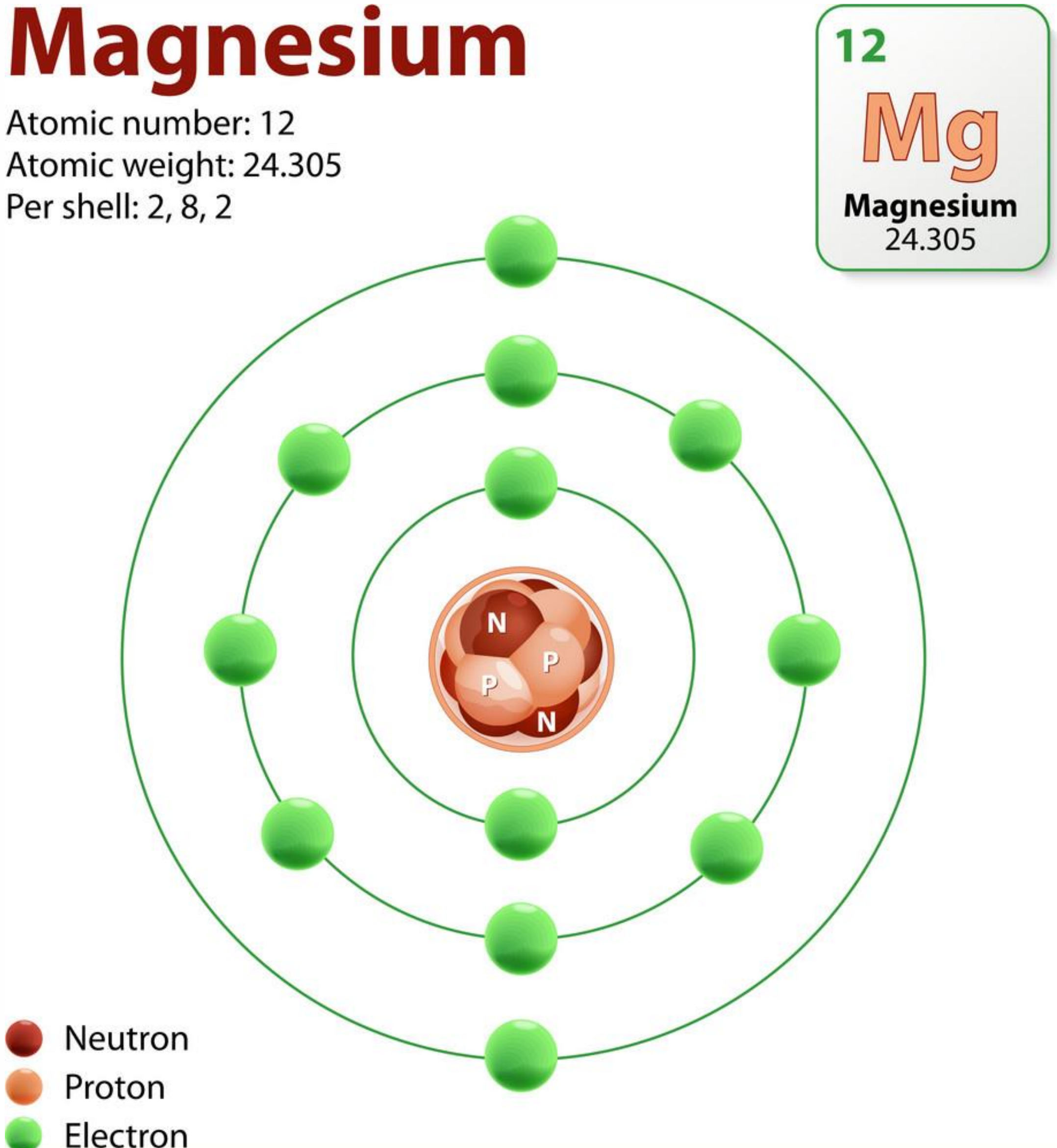
Magnesian binders

If the carbonate contains magnesium, deriving from the presence of magnesian calcite ($Ca_{1-x}Mg_xCO_3$ with $x<0.1$) or dolomite ($CaMg(CO_3)_2$), then the material is a magnesian- or dolomitic-lime. The periclase (MgO) produced together with lime during the firing has a much slower rehydration kinetics with respect to CaO, so that in the magnesian putty both periclase and brucite ($Mg(OH)_2$) are present with portlandite.

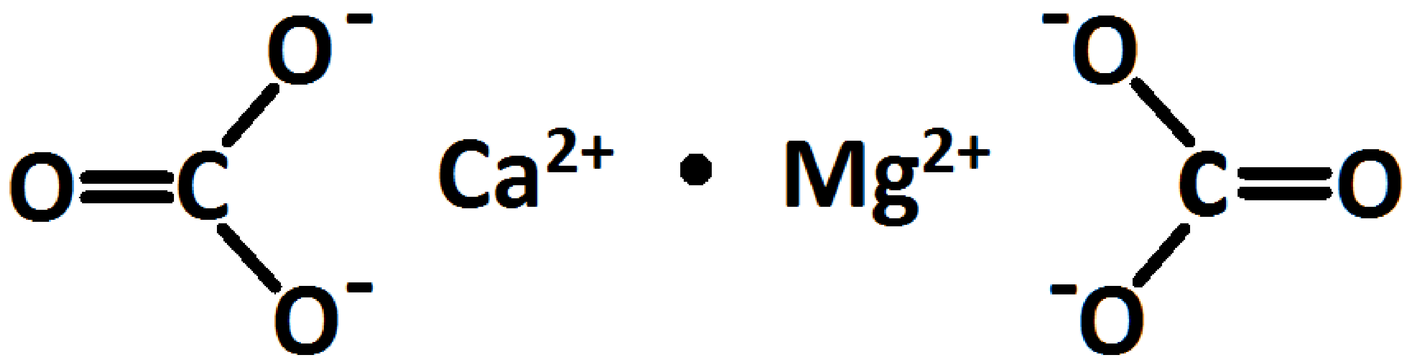
Magnesian binders



Magnesian binders



Dolomite – $CaMg(CO_3)_2$



Magnesian binders

% $CaMg(CO_3)_2$ in carbonate rock:
10% = magnesian limestone
50% = dolomitic limestone
90% = calcareous dolostone
100% = dolostone

1) DOLOMITE CALCINATION:
$CaMg(CO_3)_2$ + heat → $CaCO_3$ + MgO + CO_2 (g). 750°C (30 mins)
$CaCO_3$ + heat → CaO + CO_2 (g). 850°C

2) DOLOMITE SLAKING:
xCaO + xMgO + 2xH_2O → x$Ca(OH)_2$ + (x-y)$Mg(OH)_2$ + yMgO + H_2O

Differences with respect to CALCIC LIMES:

- Lower heat development (contribution of MgO)
- Slower hydration rate (MgO less soluble than CaO)
- Reduced volume increase (MgO crystals absorb less water)
- Brucite ($Mg(OH)_2$), fibrous-acicular crystalline habitus, less plastic behavior than portlandite ($Ca(OH)_2$), lamellar habitus

Magnesian binders

3) SETTING AND HARDENING:

$Ca(OH)_2 + Mg(OH)_2 + 2CO_2$ (g) $\rightarrow CaCO_3 + MgCO_3 + 2H_2O$

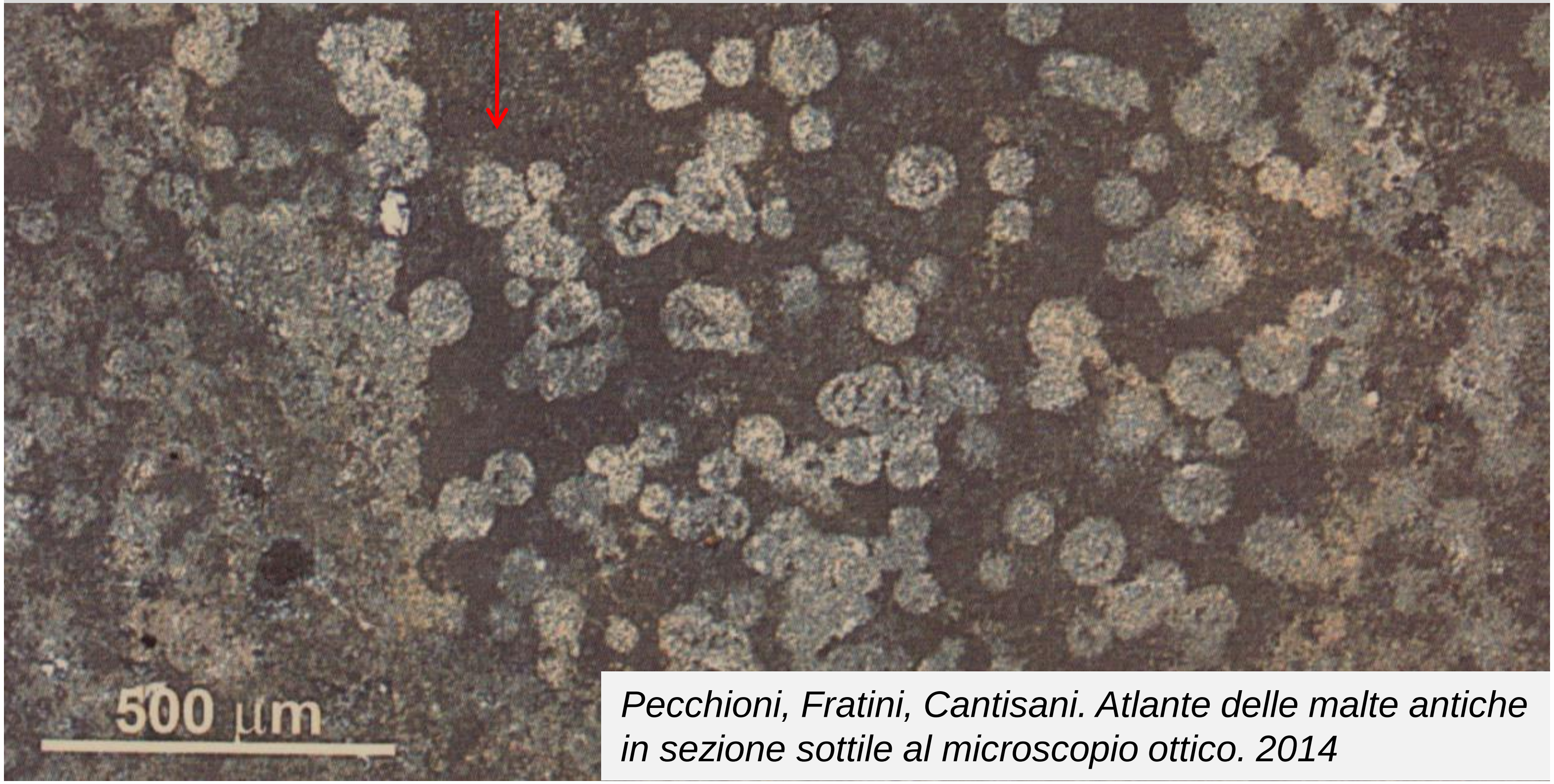
$MgO + H_2O \rightarrow Mg(OH)_2$

Degree of carbonation: 60% magnesian putty
95% calcic putty

Mechanical strength: magnesian putty, good even before carbonation
calcic putty, null before carbonation

Magnesian binders

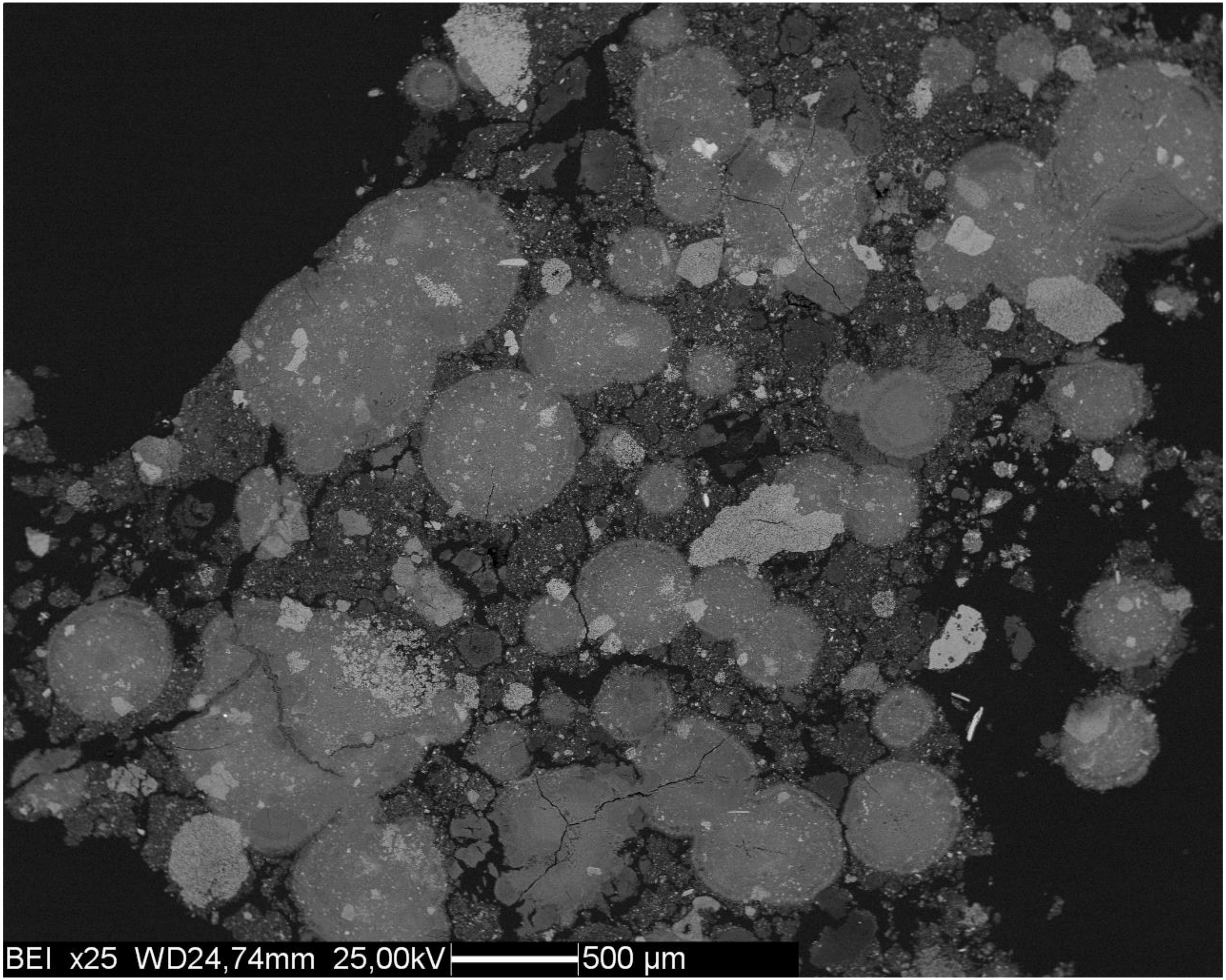
Given the reduced degree of carbonation of the putty, Mg hydrous carbonates can be observed



Pecchioni, Fratini, Cantisani. Atlante delle malte antiche in sezione sottile al microscopio ottico. 2014

Hydromagnesite: $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$
Nesquehonite: $MgCO_3 \cdot 3H_2O$
Artinite: $Mg_2(OH)_2CO_3 \cdot 3H_2O$

Magnesian binders



Gypsum binders

Periodic table of the elements

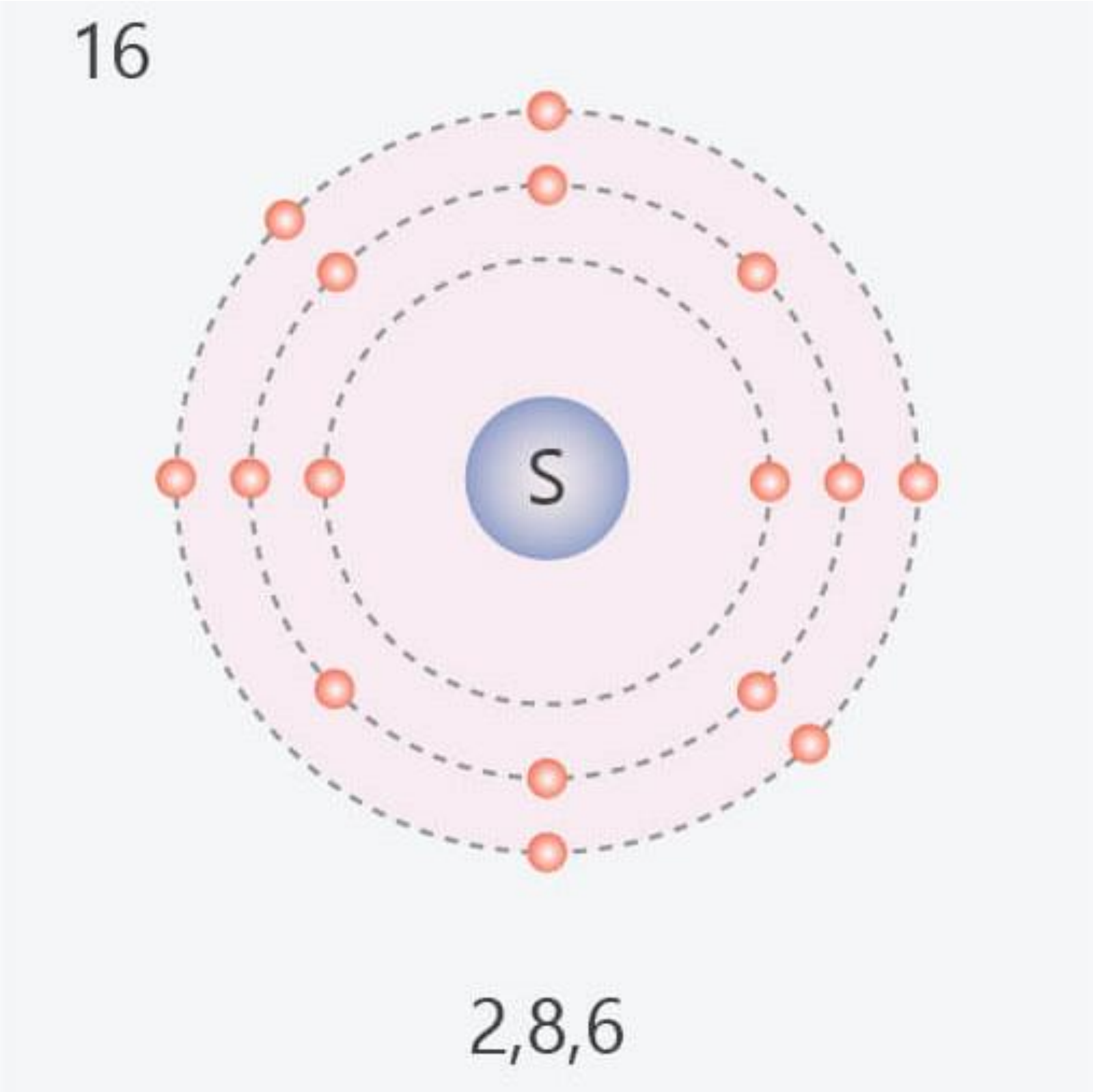
- Alkali metals
- Alkaline-earth metals
- Transition metals
- Other metals
- Other nonmetals
- Halogens
- Noble gases
- Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
- Actinoid elements

period \ group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

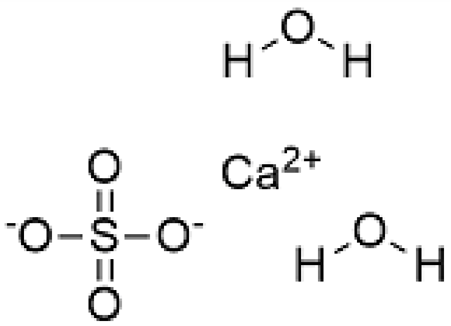
*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

Gypsum binders



Gypsum binders

Gypsum: $CaSO_4 \cdot 2H_2O$



Calcium sulfate dihydrate

Properties:

- High setting speed;
- High hardening speed;
- Hygroscopic material: it absorbs H_2O.

Uses:

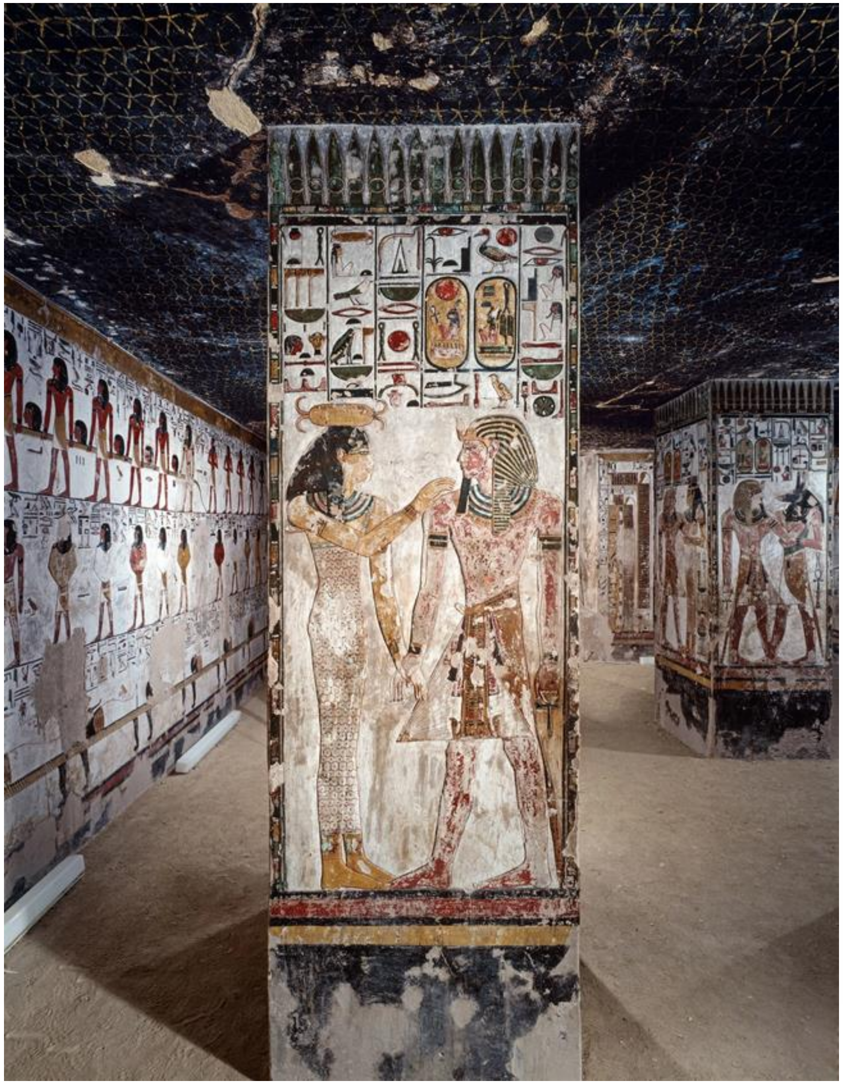
- Binder for masonry (warm climates);
- Binder for interiors;
- Stuccoes, decorations.

Gypsum binders

- Gypsum-based mortars and plasters have been used since ancient times, especially to cover masonry, as decorations, or as a support for mural paintings.
- Due to their setting upon addition of water, gypsum-based binders could be considered the first "hydraulic binder" used by mankind since ca. 9000 years before present.
- Gypsum was the most common binder in Ancient Egypt both for masonry and decorative purposes since Pharaonic times.
- Gypsum plasters were commonly used in the Middle East and in countries around the Mediterranean basin, especially during the Middle Ages (e.g., Islamic Architecture).
- In the area around Paris, gypsum mortars were thoroughly used in gothic buildings such as the Cathedrals of Chartres and Bourgues, which may explain why gypsum-based binders are known as "Plaster of Paris".
- Despite its low strength and poor durability in humid environments, examples of gypsum mortar applications in northern Europe are numerous.

Gypsum binders

MURAL PAINTINGS ON GYPSUM-BASED PLASTERS, ANCIENT EGYPT



Thebes necropolis, tomb of a senior officer of the 18° Nebamun Dynasty (1350 a.C.)

Valley of the Kings, tomb of Pharaoh Seti I (19° Dynasty, 1280 a.C.)

GYPSUM-BASED STRUCTURAL MORTARS AND PLASTERS IN THE ROMAN SITE OF QASR AZRAQ, JORDAN

Tenconi et al. (2018)

Gypsum binders

• The technological bases of **gypsum binders** are very similar to those of lime plaster.

• Gypsum blocks are heated in the kiln to produce the reactive **bassanite** (calcium sulphate hemihydrate), or a mixture of bassanite and **anhydrite** (anhydrous calcium sulphate) if the temperature is too high or the firing time is too long. Anhydrite is commonly not desired because it is much less reactive than bassanite.

• An advantage over lime is that the dehydration of gypsum to bassanite takes place at relatively low temperature (nominally at 128 °C), generally in the range 100-160 °C depending on the water pressure (P_{H2O}), and therefore the production of the plaster of Paris requires much less energy and biomass fuel than lime plaster.

Gypsum binders

However, the gypsum-bassanite-anhydrite transitions are fairly complicated from the kinetic point of view.

Depending on the pressure and on the thermodynamic path different forms (**polymorphs**) of bassanite can be formed (**α-, β-, γ-bassanite**), which differ in the thermodynamic and kinetic properties because of structural ordering, microstructural features such crystal size and morphology, and defect density.

- The **α-form** is produced by dehydration of gypsum in conditions of high P_{H2O}, it is commonly fairly crystalline, it requires less water to rehydrate, thus producing a dense plaster with good mechanical properties.
- The **β-form** is produced by dehydration at low P_{H2O} or in vacuum, it is nanocrystalline and has a high surface area, thus requiring much more water to rehydrate into gypsum, and the plaster has consequently more volume shrinkage.
- The **γ-bassanite** is generally produced by slow hydration of anhydrite.

Anhydrite also has several forms depending on the temperature of bassanite dehydration (**α-anhydrite**: 160-200 °C, **β-anhydrite**: 250-300 °C, **γ-anhydrite**: 300-600 °C): the solubility of anhydrite decreases with the temperature of formation.

Above 900 °C the sulphate starts decomposing into CaO and SO_2.

Gypsum binders

• The powderized bassanite (plaster of Paris) is very hygroscopic and needs to be stored in dry places.
• The plaster is used by mixing bassanite and water, causing the dissolution of bassanite (and eventually the associated anhydrite) and the precipitation of gypsum.
• The growth of the gypsum crystal creates the interlocked crystal grid that makes the hardened plaster (Adams et al. 1992).
• The hardening process may be **slowed down** by adding salts that increase the solubility of gypsum, or it may be **accelerated** using a mixture of gypsum seeds and potassium sulphate, favoring nucleation and precipitation. The presence of additives, the relative proportions of bassanite and anhydrite forms in the mixture, their crystal size and morphology, and the temperature of dehydration are the parameters affecting the reactivity and the final type of plaster, i.e. its ability to hydrate fast or slow, its crystallinity and appearance, its workability.

In the case of calcium sulphate the reactions are:

$$\mathbf{CaSO_4 \cdot 2H_2O} \text{ (gypsum)} + \text{heat} \rightarrow \mathbf{CaSO_4 \cdot 0.5H_2O} \text{ (bassanite)} + \mathbf{1.5H_2O}$$ [production of plaster of Paris]

$$\mathbf{CaSO_4 \cdot 0.5H_2O} + \text{heat} \rightarrow \mathbf{CaSO_4} \text{ (anhydrite)} + \mathbf{0.5H_2O}$$ [production of anhydrite]

$$\mathbf{CaSO_4 \cdot 0.5H_2O + 1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O}$$ [quick hydration]

$$\mathbf{CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O}$$ [slow hydration]

Gypsum binders

BASSANITE

1) BURNING 100°<T°(C)<150°C: $CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 1/2H_2O + 3/2H_2O$

α: in humid environment
- Crystalline (acicular or prismatic)
- Higher setting speed
- It requires less H_2O in the mix
- Better mechanical properties

≠

β: in dry environment
- Cryptocrystalline (<1 µm)
- Lower density, high solubility
- It retains more H_2O: greater shrinkage
- Soft, earthy appearance

Gypsum binders

2) BURNING: $CaSO_4 \cdot 1/2H_2O \rightarrow CaSO_4 + 1/2H_2O$

160<T°C<300

SOLUBLE ANHYDRITE

α	β	γ
α: T°C = 160-200°C - Slow setting - Better mechanical properties	β: T°C = 300°C - Poorly hydratable - It hardens only if catalyzed by the addition of salts	γ: 2 polytypes according to the starting hemidrate - They harden in presence of H_2O

3) BURNING 300 <T°C< 600 : HEMIHYDRATE → INSOLUBLE ANHYDRITE ($CaSO_4$)

Stable compound, poorly hydratable, it doesn't set

4) BURNING > 900°C: HEMIHYDRATE → INSOLUBLE ANHYDRITE + CaO

Free lime obtained by sulphate decomposition

5) SETTING AND HARDENING: HYDRATION

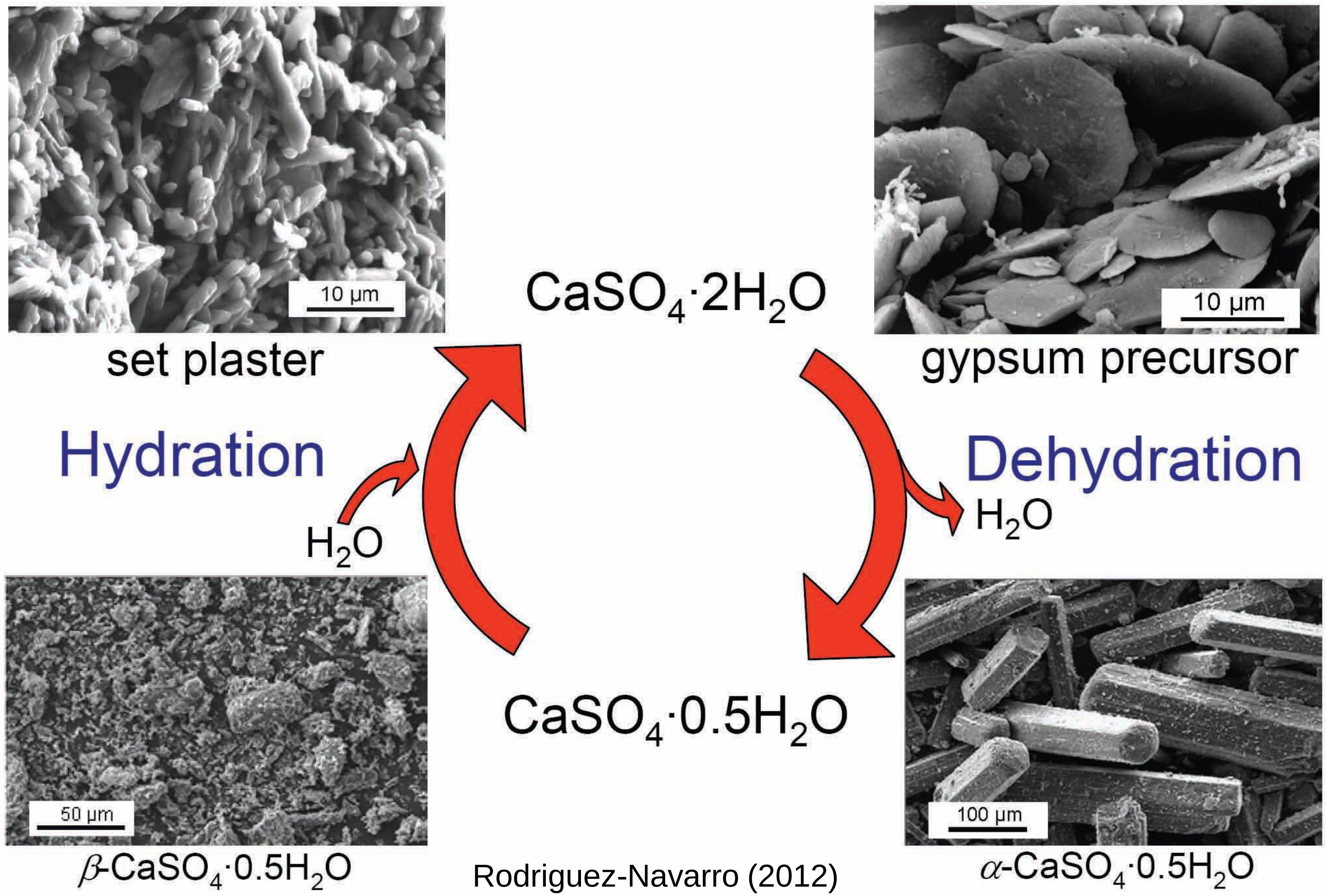
Bassanite ($CaSO_4 \cdot 1/2H_2O$) and anhydrite ($CaSO_4$) solubilize in H_2O and they hydrate with an exothermic reaction.

The MECHANICAL RESISTANCE of gypsum comes from its crystallization into thin, elongated crystals that form a compact, fibrous web.

Hemihydrate: it needs less water;
it completely reacts with water;
Better mechanical strength of the hardened product

FINAL PRODUCT: $CaSO_4 \cdot 2H_2O$, 0.2% solubility

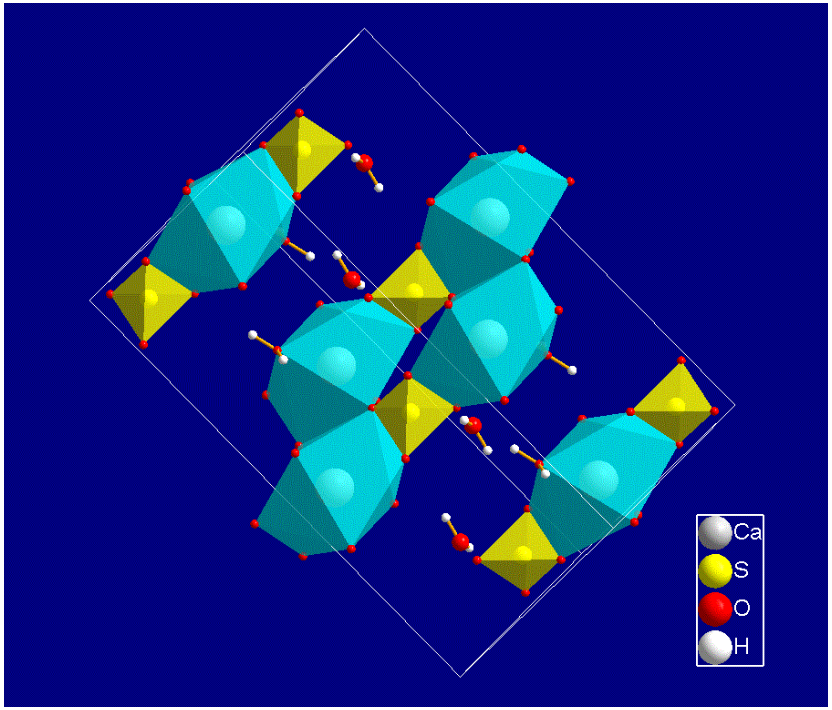
The gypsum cycle



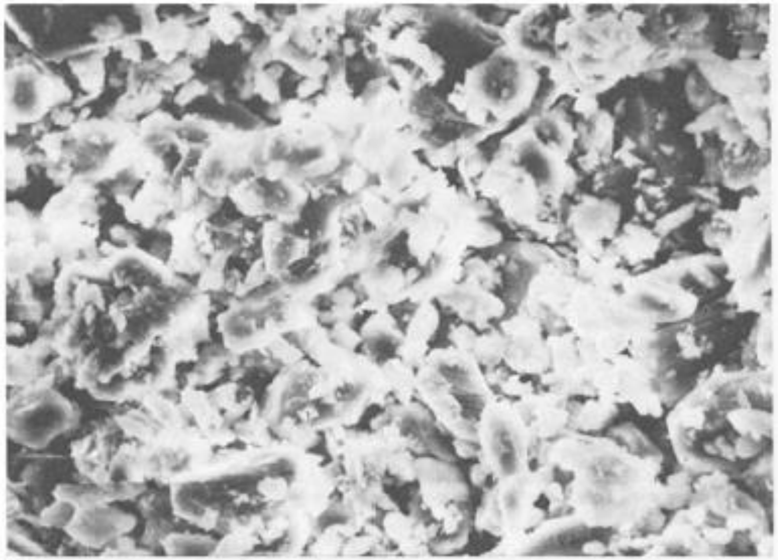
Rodriguez-Navarro (2012)

GYPSUM STRUCTURE AND CRYSTAL HABIT

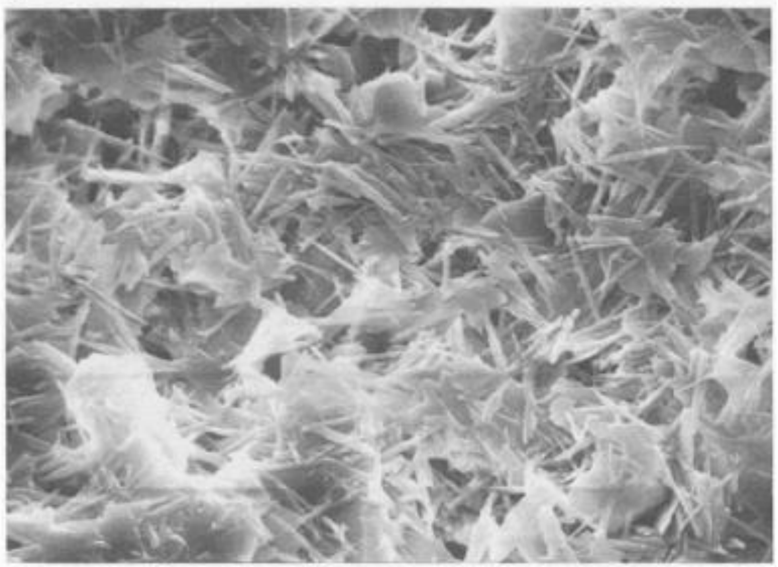
It has a parallel layered structure of $(SO_4)^{2-}$ ions strongly bound to Ca^{2+} (Coordination Number = 8) interspersed with H_2O molecules. Therefore, gypsum has excellent cleavage according to (010).



Gypsum binders



A



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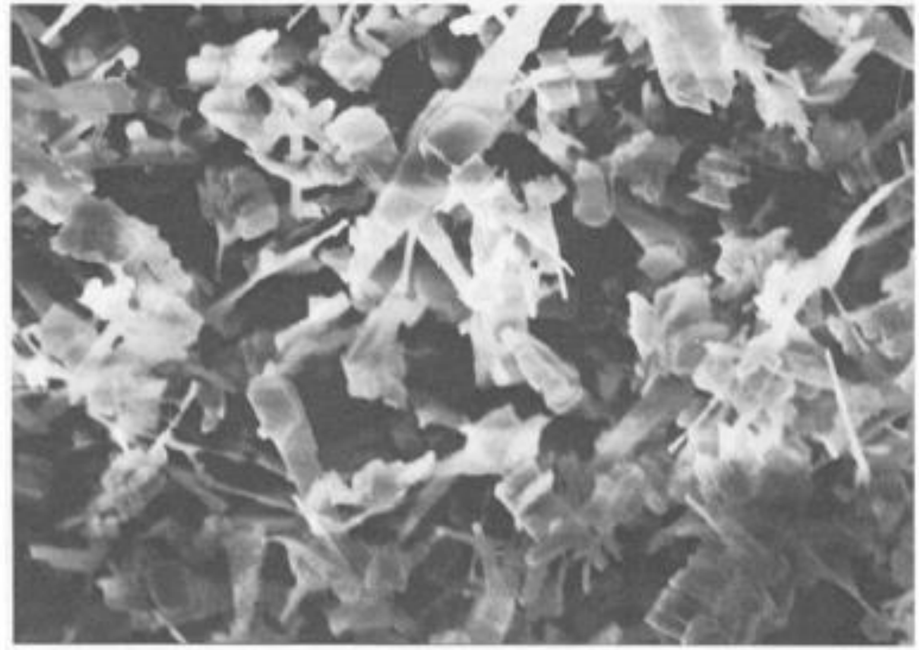

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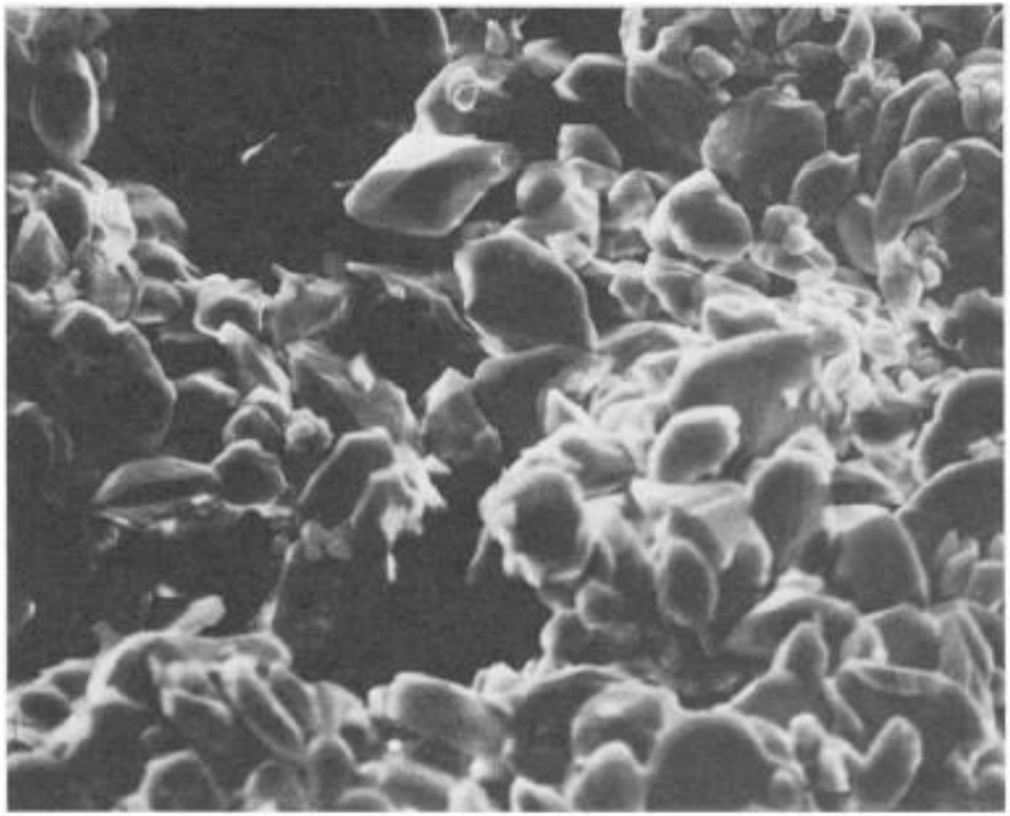
Figure 1. Gypsum microstructures. A) Ground gypsum rock (Colorado) consists of chunky grains with sharp edges and fractured surfaces (770×). B) Gypsum plaster consists in large part of fine lath-like crystals (1540×). C) After "pressure cooking" in an autoclave for two hours at 150 psi to simulate long exposure to occasionally moist conditions, there is grain coarsening and the crystals are more blocky (1540×).

Gypsum binders

Figure 8. Microstructure of a gypsum plaster ball from Abu Hureyra with faceted grains developed over time by a grain-coarsening process (850×). Other areas contained more typical elongated laths as shown in Figure 3.



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