

The structure of strongly heteropolar  $\text{KPb}_2$  is dominated by a polyanionic framework of corner-condensed  $\text{Pb}_4$  tetrahedra known as discrete units from more cation-rich  $\text{NaPb} = \text{Na}_4^+ \text{Pb}_4^{4-}$ . The step from an intermetallic phase to a normal valence compound can be even more pronounced. In  $\text{KBi}_{1.2} \text{Pb}_{0.8}$  the  $\text{Bi}_{2.4} \text{Pb}_{1.6}^{2-}$  tetrahedron becomes nearly valence isoelectronic with elemental phosphorus  $\text{P}_4$ , and the Laves-type structure distorts into discrete tetrahedral units [5].

In this short survey we show different classes of Laves phases whose bonding situations range from exclusively multi-center bonds between N atoms via an intermediate situation of two-centre bonds in the N partial structure to the for-

mation of  $\text{N}^{x-}$  anions. No apparent connection is found between the bonding situation common to the members of a class and the location of these members in the near neighbor diagrams except for the last-mentioned salt-like phases.

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## The crystal structure determination of $\text{Mg}_3(\text{OH})_5\text{Cl}\cdot 4\text{H}_2\text{O}$ (F5-phase) from laboratory powder diffraction data and its impact to the analysis of problematic magnesia floors

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In 1867, the French physicist Stanislas Sorel discovered that high quality cement is formed by mixing magnesium oxide with an aqueous solution of magnesium chloride. These so called Sorel cements have a remarkable capacity to bond with and contain other organic and inorganic materials. Many properties of this magnesia cement are superior to those of Portland cement, namely the high fire resistance, low thermal conductivity, high resistance to abrasion etc. The main application for these cements are grindstones, tiles, artificial stone (cast stone), cast floors, and even artificial ivory (e.g., for billiard-balls). On the down side, magnesia cements shows a poor resistance to prolonged exposure to water, making them unsuitable for construction applications or for toxic and hazardous waste immobilization.

During the binding process, ternary magnesium oxychloride phases are formed, which are of key importance for the properties of the

cement. A detailed knowledge of the ternary phase diagram  $\text{MgO}-\text{MgCl}_2-\text{H}_2\text{O}$  is therefore necessary to understand the properties of these cements and to perform any type of qualitative or quantitative phase analysis. So far, four magnesium oxychloride phases are known in this phase diagram:  $2\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 5\text{H}_2\text{O}$  (F2-form),  $3\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 8\text{H}_2\text{O}$  (F3-form),  $5\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 8\text{H}_2\text{O}$  (F5-form), and  $9\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  (F9-form). The only two phases found at a temperature below  $100^\circ\text{C}$  and thus occurring in Sorel cements are the F3- and the F5-phases. The crystal structure of the F3-phase was solved from powder diffraction data in 1953, while that of the F5-phase is unknown. Depending on the production and the setting process, the aging, and environmental influences, with time a typical floor not only consists of the original phases but also of degradation products, of which the most important is a magnesium chlorocarbonate phase (chlorartinite).

The formation of the latter can be explained by the degradation of the F5-phase to the F3-phase according to:  $\text{Mg}_3(\text{OH})_5\text{Cl}\cdot 4\text{H}_2\text{O}$  (F5)  $\rightarrow$   $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$  (F3) +  $\text{Mg}(\text{OH})_2$  and consecutively by carbon dioxide of the air to chlorartinite  $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$  (F3) +  $\text{CO}_2$   $\rightarrow$   $\text{Mg}_2\text{CO}_3(\text{OH})\text{Cl}\cdot 2\text{H}_2\text{O}$  +  $3\text{H}_2\text{O}$ . The massive occurrence of chlorartinite serves as an indicator for problematic floors. We recently succeeded in solving the crystal structure of chlorartinite [1]. The zeolite-like channel structure of chlorartinite acts as a buffer for excess  $\text{MgCl}_2$  in solution, making it very vulnerable for changes in temperature or humidity [2]. Excess  $\text{MgCl}_2$  in solution leads to the occurrence of  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  (Bischofite) or its lower hydrates  $\text{MgCl}_2\cdot 4\text{H}_2\text{O}$ ,  $\text{MgCl}_2\cdot 2\text{H}_2\text{O}$ , or  $\text{MgCl}_2\cdot \text{H}_2\text{O}$ . The crystal structures of the latter three could recently be determined from synchrotron powder diffraction data as function of temperature [3].

In a typical Sorel cement, about 2/3 of the cement consist of inert filler materials, with quartz sand as the dominant phase. Depending on impurities of binder and filler and on the pigments used, a whole list of minerals (most of them having known crystal structures) are found, e.g., calcite, aragonite, hematite, magnesite, feldspar, talcum, muscovite, etc. It is known that the binder of a perfect floor, prepared with high quality materials (e.g., high magnesium oxide reactivity) in equilibrium conditions, consists exclusively of F5-phase. Once the F5-phase is transformed at later stages to the F3-phase and subsequently to chlorartinite, the mechanical strength decreases considerably. In general, the use of inferior components and/or excess water leads to various problems such as the occurrence of cracks in expanding or contracting floors, decoloring, crumbling floors etc. To investigate these phenomena, it is crucial to know the mineralogical composition of these floors quantitatively. Although wet chemical analysis provides some insight in the distribution of elements, the mineralogical composition is much more meaningful. In order to control

the production or to evaluate structural damage in the construction business, a full quantitative phase analysis (QPA) using the Rietveld method is necessary, for which the knowledge of the crystal structures of the components is essential.

The only major constituent with an unknown crystal structure is the F5-phase. Since single crystals of a suitable quality for single crystal analysis were difficult to grow, we decided to investigate its crystal structure from high resolution laboratory powder diffraction data. Using this structure in a practical application, a full quantitative phase analysis of two problematic unintentionally bleached magnesia floor was performed, revealing possible causes for the technical failure.

The crystal structure of  $\text{Mg}_3(\text{OH})_5\text{Cl}\cdot 4\text{H}_2\text{O}$  (F5-phase) was solved from a high resolution X-ray powder diffraction pattern of a synthetic binder, employing the global optimization method of simulated annealing (SA) as implemented in the program TOPAS. The crystal structure of the F5-phase consists of infinite triple chains of almost regular  $\text{MgO}_6$  octahedra running along the *b*-axis and intercalated disordered chlorine ions and water molecules (or hydroxyl groups) (Fig. 28). The octahedron in the middle of the triple chain shares 6 out of 12 edges and all 6 corners with four neighboring octahedra. The outer octahedra share 4 edges, 3 corners with two, and 2 corners with one neighboring octahedron. Thus, one can distinguish between  $\text{OH}^-$  and  $\text{OH}_2$  by applying Pauling's rules. The protruding corners of the octahedron must be occupied by  $\text{H}_2\text{O}$ , while the corners shared by three octahedra can only be occupied by  $\text{OH}^-$ . The corners shared by just two octahedra can be occupied by  $\text{H}_2\text{O}$  or  $\text{OH}^-$ . For reasons of charge neutrality, two alternatives remain. If the channels are occupied by disordered chlorine ions and hydroxyl groups, a hydroxyl group sits statistically on every fourth corner shared by two octahedra. Alternatively, if the channels

(similar to those in the F3-phase) are occupied by chlorine ions and water molecules, corners shared by two octahedra are occupied alternately by water molecules and hydroxyl groups. The triple chains thus are formed by one  $\text{Mg}(\text{OH})_6$  and two  $\text{Mg}(\text{OH})_3(\text{OH}_2)_3$  or  $\text{Mg}(\text{OH})_4(\text{OH}_2)_2$  octahedra. Additionally, hydrogen bonds increase the stability of the crystal structure.

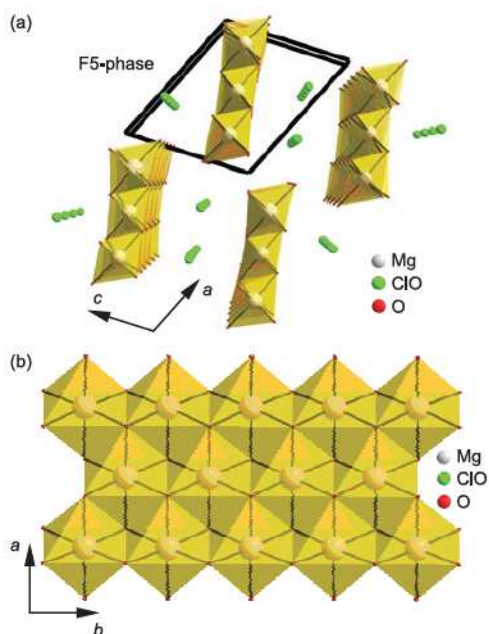


Figure 28: Perspective view of the crystal structure (a) and of the triple chain with one  $\text{Mg}(\text{OH})_6$  and two  $\text{Mg}(\text{OH})_4(\text{OH}_2)_2$  octahedra (b) as building units of  $\text{Mg}_3(\text{OH})_5\text{Cl}\cdot 4\text{H}_2\text{O}$  (F5-phase) at  $T = 295$  K in a central projection (camera distance of 35 cm) down to the crystallographic  $b$ -axis. Oxygen positions are in red, chlorine positions are in light green and magnesium position are in yellow.

With the structure determination of the F5-phase, the crystal structures of all significant binder phases occurring during or after the formation process of Sorel cements are finally known. These phases are: Periclase, brucite, bischofite and its lower hydrates, F3, F5, and chlorartinite. The mineralogical composition of a Sorel cement can now be determined routinely to high precision using quantitative phase analysis (QPA) by the Rietveld method. Such an analysis can be used to determine the quality

of a magnesia floor and to determine the causes of cracks and decoloring effects caused by late crystallization. For a practical test, two magnesia floors (colored with iron oxide pigments) which were exhibiting unwanted bleached spots were selected. Floor (1): Industrial quality magnesia floor MA C50 in anthracite color installed in a production plant in southern Germany in 2006. Light grey spots of diameter 10–200 cm occurred 4–8 weeks after installation of the floor without obvious causes. Floor (2): Industrial quality magnesia floor MA C50 in yellow color installed in 2007 in a showroom of a manufacturer of magnesia screeds. White spots occurred within few minutes after pouring and fast removing water on the floor for cleaning purposes (Fig. 29).



Figure 29: Core drill samples of a yellow magnesia floor from southern Germany. The yellow colour was achieved by mixing iron oxides into the  $\text{MgO}$  powder. Left: Correctly colored sample. Right: Bleached sample.

For the analysis of the magnesia floors, four samples were taken. Sample (1a): interior of floor (1); sample (1b): decolored surface of floor (1); sample (2a): correctly colored surface of floor (2); sample (2b): decolored surface of floor (2). In the case of sample (1), there is a huge difference between the mineralogical compositions of the surface (Fig. 30(a)) and of the interior of the floor (Fig. 30(b)). While the interior shows the expected composition of an equilibrated magnesia floor with F5 as the only binding phase, the surface is characterized by a thin layer of calcium carbonate in different crystalline forms and the decomposition products of the F5-phase, namely the F3-phase and chlorartinite. This can be taken as evidence that

the floor had been correctly laid but that the surface had been quite likely exposed to excessive water during the curing process of the floor.

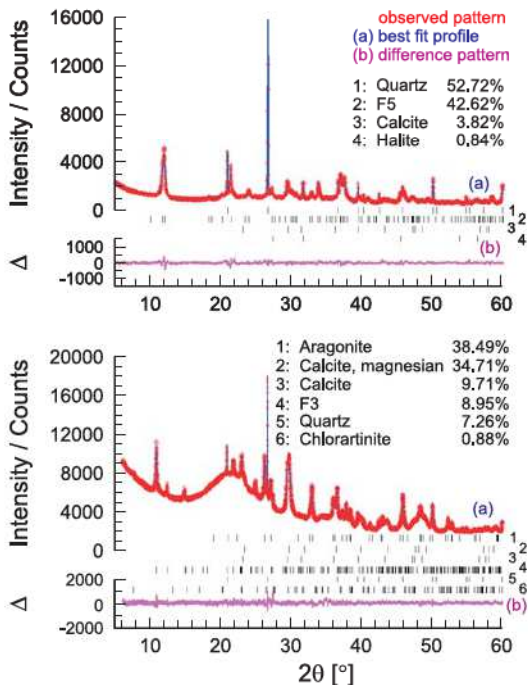


Figure 30: Rietveld plot of a sample taken from the interior (a) and from the surface (b) of a black magnesia floor at  $T = 295$  K from southern Germany.

The F5-phase transformed to the F3-phase and subsequently to chlorartinite while calcium ions (the amount of reactive calcium within natural magnesium oxide and magnesium chloride varies for different batches and is usually quantitatively analyzed by the manufacturers of the Sorel cement) were transported to the surface and reacted with  $\text{CO}_2$  from air to form different polymorphs of calcium carbonate. The situation for sample (2) is entirely different, pointing to a problem with the starting materials. The samples from the correctly colored and from the decolored surface, both reveal a substantial amount of gypsum (8% for (2a) and 28% for (2b)). It can be assumed that gypsum as an undesired component was already present in the raw material before the floor was laid. Due to its good solubility, the concentration of gypsum in water is enriched in the liquid water during the drying process and brought to the surface

by capillary action. When the water evaporates, a thin film of gypsum (and bassanite) is deposited on the surface of the floor. Depending on the local concentration, severe bleaching occurs (Fig. 31).

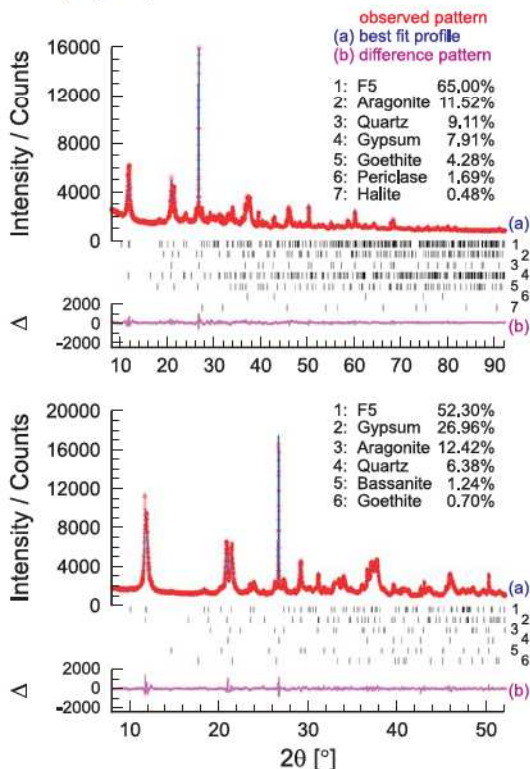


Figure 31: Rietveld plot of samples taken from the surfaces (a) of a correctly colored and (b) of a bleached yellow magnesia floor.

From Figs. 30 and 31 it is evident that the peak overlap between the F5-phase and the components responsible for damages by bleaching is severe, making the knowledge of the crystal structure of the F5-phase a prerequisite for a successful QPA. Together with the finally available crystal structure of the F5-phase, such a full quantitative phase analysis will allow an efficient quality control of Sorel cements.

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