

CORROSION OF METALS IN CONTACT WITH MINERAL BUILDING MATERIALS

KORROSION DER METALLE IM KONTAKT MIT MINERALISCHEN BAUSTOFFEN

CORROSION DES METAUX EN CONTACT AVEC DES MATERIAUX MINERAUX

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ABSTRACT

Metals such as steel, aluminium, copper, zinc and lead in structural engineering get into contact with very different mineral building materials. As a rule, solid phases of the building materials do not attack metals. A corrosive attack only is possible, if the capillary-, pore-, or canal-like cavities, that exist in each building material, contain free water. Further, in case of oxygen-type corrosion, the oxygen that is necessary for the maintenance of the corrosion reaction must be able to rediffuse to the surface of the metal through the cavities of the building material. In addition, conditions that inhibit or destroy passivity have to exist. In all cases of corrosion, there is a complicating effect, if the water dissolves ingredients of the building material that are aggressive against metal or ease the transportation of polluting agents from the environment of the structural element.

In structural engineering, from a corrosion-technical point of view, contacts of metals and mineral building materials, that are produced with cement and gypsum, play an important role.

ZUSAMMENFASSUNG

Metalle wie Stahl, Aluminium, Kupfer, Zink und Blei kommen im Ingenieurbau mit den unterschiedlichsten Baustoffen in Berührung. Die festen Phasen von mineralischen Baustoffen greifen die Metalle im Regelfall nicht an. Ein Korrosionsangriff ist nur möglich, wenn die im Baustoff vorhandenen kapillar-, poren- oder kanalähnlichen Hohlräume ungebundenes Wasser enthalten. Weiterhin muß der für die Korrosion erforderliche Sauerstoff in der Lage sein, von der Oberfläche her durch die Hohlräume des Baustoffes zu diffundieren. Zusätzlich haben Bedingungen zu existieren, welche eine Passivität hemmen oder Pas-

sivschichten zerstören. In allen Korrosionsfällen wirkt sich zusätzlich aus, wenn vorhandenes Wasser korrosionsaggressive Bestandteile aus dem Baustoff löst oder den Transport von Schadstoffen aus der Umgebung zum Metall hin erleichtert.

Im konstruktiven Ingenieurbau spielen aus korrosionstechnischer Sicht Kontakte der Metalle mit zement- oder gipsgebundenen mineralischen Baustoffen eine wichtige Rolle.

RESUME

Les métaux comme l'acier, l'aluminium, le cuivre, le zinc et le plomb sont en contact avec des matériaux très divers dans les ouvrages du génie civil. Les phases solides des matériaux minéraux n'attaquent en général pas les métaux. Une attaque corrosive n'est possible que si de l'eau libre est contenue dans les pores capillaires et les cavités du matériau. De plus la diffusion à travers le système de pores de l'oxygène nécessaire à la corrosion doit être possible. En outre, des conditions inhibant la passivité ou détruisant les couches passives doivent exister. Dans tous les cas de corrosion, la situation est aggravée si l'eau dissout des constituants corrosifs du matériau ou facilite le transport des polluants provenant de l'environnement vers le métal.

Dans les ouvrages du génie civil, le contact entre métaux et matériaux minéraux à base de plâtre et de ciment jouent un rôle important du point de vue de la corrosion.

KEYWORDS: Corrosion, iron, steel, aluminium, copper, zinc, lead, mineral building material, concrete, chloride, magnesia cement, gypsum

1. CORROSION BEHAVIOUR IN BUILDING MATERIALS, THAT ARE COMBINED WITH CEMENT [1-5]

Iron/steel

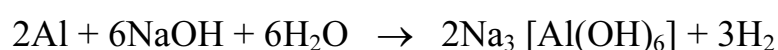
In nearly neutral to weakly basic aqueous resp. sufficiently moist media, that contain oxygen, iron is transformed into iron (II)-hydroxide with the help of water and oxygen and is subsequently oxidised into iron (III)-hydroxide (rust FeOOH)). These rust layers have no corrosion-inhibiting character, at all, and therefore iron/steel is extremely sensitive to corrosion in the system iron/water in a medium pH-region (Fig. 1).

In Portlandcement-mortar/concrete steel is protected against corrosion because of the contact with the highly alkaline concrete pore water. As a result of the strongly alkaline reaction during the hydration of cement, concrete has a large proportion of alkaline ingredients. The pH-value of the aqueous phase of normal concrete is about 12.6 to 13.8 depending on the content of ingredients in the cement, that have strongly basic characteristics (K_2O , Na_2O). In the region of $pH \geq 11.5$, the steel surface is passive, if there are no ingredients that are aggressive against steel and destroy passivity (causing pitting corrosion), which is combined with a complete inhibition of the anodic partial reaction. The passivating layer of hydrated iron oxide is 2 to 20 mm thick. The corrosion-protective effect of the concrete for an embedded steel is cancelled in case of a short-fall of the above-mentioned pH value. However, it is not till below pH 9.0 that a strong corrosion starts, as e. g. after a carbonation of the concrete with a neutralisation of all alkaline ingredients. In addition of this, the cement stone must have as much free water in its pores as possible and oxygen from the structural element must get through the concrete to the steel because of diffusion.

ALUMINIUM [6]

The generally good corrosion behaviour of aluminium with its very negative standard electrode potential ($-1.66 V_H$) is caused by the development of passivating oxidious and hydroxidious coatings. In the pH range between 4 and 9, these coatings are largely insoluble. Because of this fact, aluminium materials are distinguished by a good resistivity in nearly neutral to weakly acid aqueous media and in humid air, thus in atmospheric corrosion conditions, too. Hence follows i. a. the privileged application of aluminium in constructional engineering.

Aluminium is an amphotere metal. Because of that, the protective effect of the coating is lost as a result of its disintegration in more strongly acid and alkaline media. Aluminium and its alloys are mainly attacked by general corrosion in this region and the application of these materials does not come into question in that cases. A noticeable disintegration in alkalis already takes place in the more weakly alkaline region above pH 9 (Fig. 1). Aluminium materials then are as active as you would expect it from their position in the electrochemical series and, even at the absence of oxygen, react under evolution of hydrogen and formation of aluminates with high solubility:



If there is a longer contact with moist Portlandcement building materials, aluminium and its alloying are thus attacked through a reaction with the free alkali hydroxides of the cement stone pores solution because of general corrosion.

Fig. 2 on the left (side) compares the corrosion reaction of aluminium with that of other structural metals in wet cement mortar. In cement mortar and concrete, the corrosion increases due to rising moisture. Considerable loss of mass especially occurs in case of wet storage (Fig. 3). Extremely voluminous corrosion products, that can burst and spall off the concrete cover, develop. It has to be considered that, depending on time in formwork and dry-out conditions, hardening building materials often only give off their excess water very slowly, so that considerable corrosion damages can already occur in fresh concrete until the standardization of a low equilibrium moistness. According to the information given in [5], the corrosion in Portlandcement mortar is like 1 : 6 : 25 referring the state dry : moist : wet. Fig. 3 illustrates that the intensity of an attack decreases with time, since the corrosion products, that develop, impede the transportation of alkalis to the corroding surface.

Anodically produced anodization layers (Eloxal) are also attacked by moist alkaline-reacting building materials and in this case do not offer efficacious protection. To preclude corrosion damages through contact with moist alkaline building materials, aluminium has to be additionally protected by proper organic coatings.

In metals, that are susceptible to alkalis, like aluminium and its alloys, a growing corrosion risk results from an increasing pH value of a building material. So far, the aluminium corrosion can also be limited by the choice of an adequate binding agent (Fig. 4). Concretes, that, depending on their production, only have a small alkalinity, e. g. autoclavely treated pore concrete (gas concrete), are not to be classified as aggressive in respect of structural metals, that are susceptible to alkalis, such as aluminum. In aluminum materials, a carbonation of the building material will have a corrosion-protective effect, too.

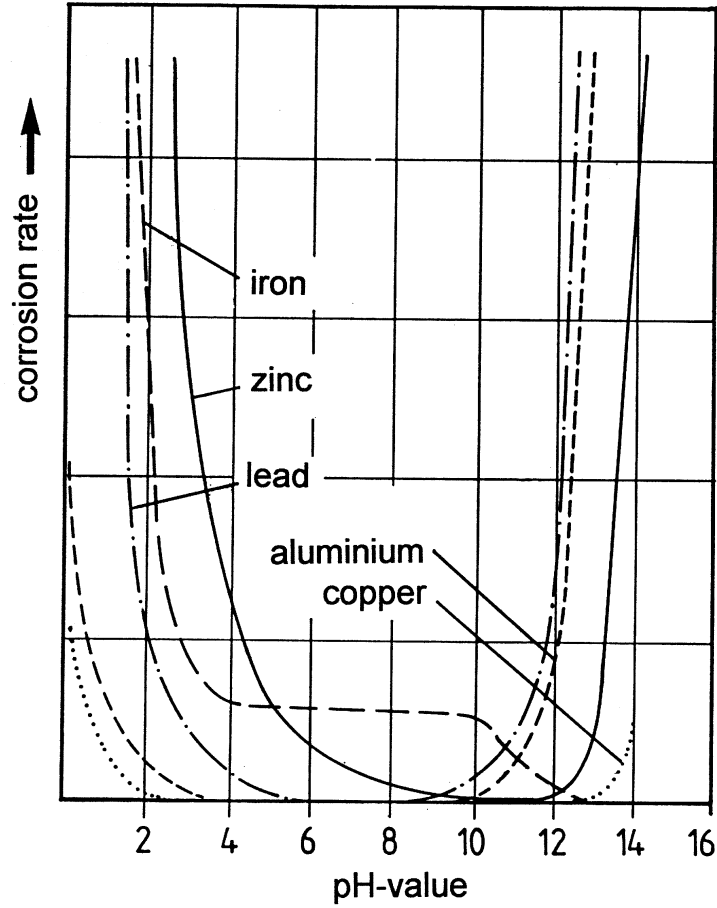


Fig. 1: Corrosion rate of metals in dependence on the pH value; reference data from a structural point of view [1]

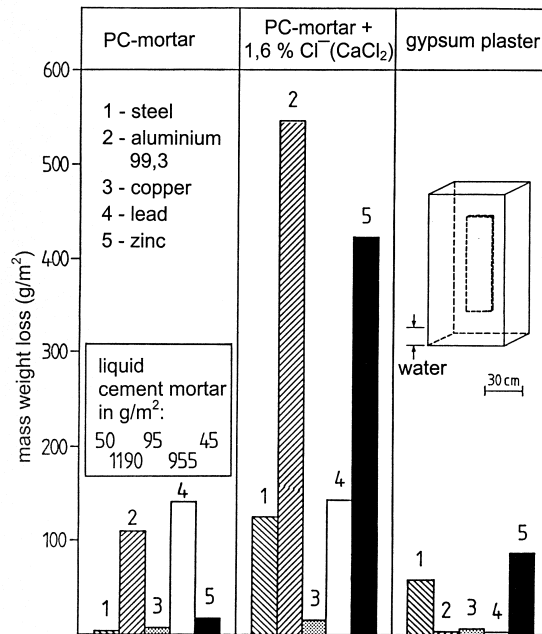


Fig. 2 Loss of mass of metals after twelve months of storage in moist building materials (the mortar prisms plunged 2cm into the water during the testing) and in structural aqueous cement solutions (numerical data) (in [1] according to the results of [2])

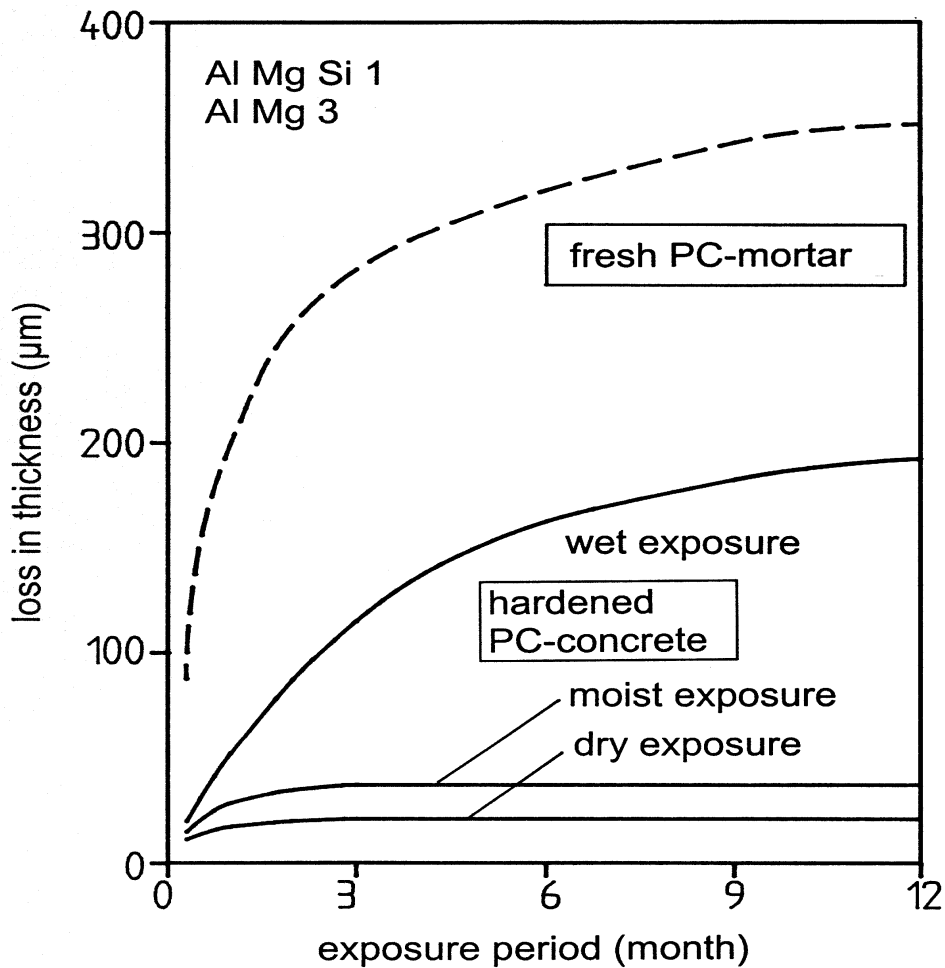


Fig. 3: Corrosion behaviour of aluminium alloys in alkaline building materials resp. media
(in [1] according to the results of [2])
wet storage: concrete, partially plunged into water,
moist storage: concrete in 95 % relative humidity,
dry storage: concrete in 65 % relative humidity

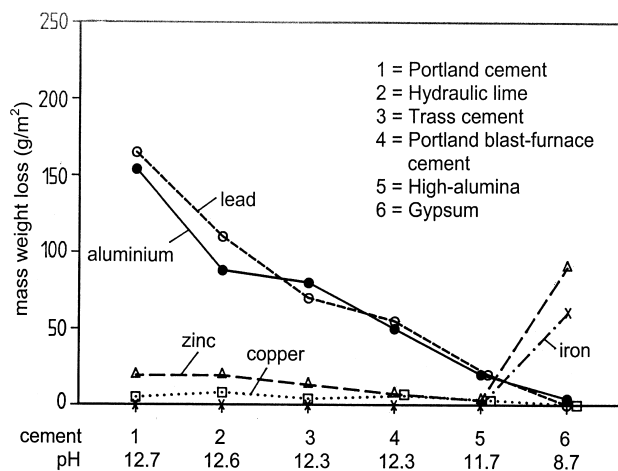


Fig. 4: Loss of mass of metals after twelve months of storage in wet mortar with various bonding agents (testing arrangement as shown in Fig. 2)
(in [1] according to the results of [2])

Copper

On one hand, the excellent corrosion resistivity of the copper materials depends on the "noble" character (positive standard electrode potential of $+0,34V_H$) and on the ability to form protective layers in many normal media, chemicals and on contact with building materials. In water and neutral salt solutions, copper materials have a very good resistivity in a wide pH range (Fig. 1). In diluted (non-oxidating) acids and in the alkaline region, copper, above all, is superior to other non-iron metals. Copper and its alloys are solely inapplicable, if the formation of the protective layers is hampered and the material is heavily attacked through a formation of complex salts, e. g. at contact with ammonia and ammoni-alkaline solutions.

The layers made of slightly soluble copper (I)-oxide, that have primarily formed (in the air), are virtually insoluble in alkalis. Copper and its alloying do therefore only undergo a negligible uniform removal by corrosion, in case of an embedding in moist concrete or cement mortar (Fig. 2 on the left and Fig. 4). In case of an application of cements with higher alkalinity (pH value of the cement stone pores solution > 13.3) copper, but especially brasses (e. g. CuZn 37), that are rich of zinc, are not sufficiently resistant.

Zinc [7-10]

Zinc, like aluminum, is characterized through a negative standard electrode potential ($-0,76V_H$) and because of this thermodynamic characteristic it is a metal that is susceptible to corrosion. Zinc, however, also forms protective coatings made of solid corrosion products in many normal media and in building materials by a reaction with its environment.

Zinc as well is an amphotere metal and therefore is not resistant in both acid ($< \text{pH } 5$) and alkaline regions ($> \text{pH } 12$) (Fig. 1). In more alkaline solutions zinc hydroxide, which is transformed into readily soluble and non-protective zincates by a reaction with the alkaline compound, develops under a formation of hydrogen. In alkaline concrete with pH values of the pores solution of the cement between 12.6 and 13.8 (application of alkali-enriched cements) a galvanization should be susceptible to corrosion because of the amphotere reaction. In fact, however, it is determined that at least for pH values ≤ 13.3 the dissolution rate of zinc under formation of hydrogen quickly diminishes, what can be explained by passivation. If Ca(OH)_2 exists besides Zn(OH)_2 , a further corrosion product, the slightly soluble calciumhydroxozinkat $\text{Ca} [\text{Zn(OH)}_3]_2 \cdot 2\text{H}_2\text{O}$, de-

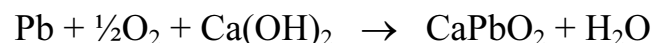
velops, which is held responsible for the passivation of zinc in concrete by some researchers. Because of that, zinc is uniformly attacked in alkaline building materials a little bit more than copper materials, but much less than aluminum and lead (Fig. 2 on the left and Fig. 4). Above the said critical pH value of 13.3, the passivability is certainly more and more restricted in case of a rising alkalinity and the zinc corrosion increases very much. In carbonated concrete the corrosion rate can, indeed, be a little higher than in alkaline concrete, but it is considerably lower than e. g. of steel. Because of that, e. g. galvanized reinforcing steels are applied to, if a premature carbonation has to be expected.

Heightened contents of chromium in the cements have an advantageous effect on the zinc corrosion in the alkaline region. They promote a rapid initial passivation of the zinc.

Lead [11]

Lead is relatively “noble“ in regard to corrosion, because of its position in the electrochemical series – the standard electrode potential is $-0,13V_H$. However, lead also owes its good corrosion resistivity to the ability to form impervious, tightly adherent and slightly soluble coatings made of lead compounds in dependence on the attacking medium.

Lead ranks among the amphotere metals that can be dissolved not only in acids but also in alkalis (Fig. 1). In alkaline electrolytes, lead is heavily attacked above pH 9:



This way, primarily developing lead hydroxides are transformed into readily soluble plumbate, mainly calciumplumbat. Because of that, lead, comparable to aluminium, is very susceptible to corrosion in moist alkaline building materials (Fig. 2 on the left). An intensified attack results from the increasing pH value of a aqueous phase of a building material (Fig. 4). The high rate of attack of the mainly uniform corrosion decreases with time and the removal of metal declines with subsiding moistness of the building material.

In wet concrete resp. mortar, lead can be protected e. g. through an isolation with thick bituminous coatings, plastic sheets or the like.

2. REACTION IN CASE OF A CONTACT WITH AQUEOUS CEMENT SOLUTIONS AND ALKALINE WATERS [1,2]

In practical constructing it occasionally happens that structural metals are moistened with aqueous cement solutions (fresh concrete) or with such aqueous extracts that were in contact with hardened mortar or concrete for a longer time. The latter can contain parts of the cement stone in a dissolved state, then, and thus react alkaline. In such media especially aluminum materials and lead behave even much more disadvantageous than in moist, solid building materials (v. numerical data in Fig. 2), in the course of which the corrosion hardly slows down. In zinc and copper as well, a much stronger attack than in hardened wet building material can be determined. The corrosion reaction in alkaline solutions can thus not be compared to that in solid phases of a building material. In case of a contact of the metals with alkaline-reacting electrolytes, irregular alterations in colour can already occur after a short-time attack, that under certain circumstances strongly affects the exterior of construction elements.

3. CORROSION PERFORMANCE IN CHLORIDE CONTAINING ALKALINE BUILDING MATERIALS [1-3,6]

Chloride ions in sufficiently moist mortar/concrete, normally resulting from salts, that have subsequently penetrated, will cause pitting corrosion and wide pitting in **steels**, that are embedded and in a passive state, from a content of chloride of about 0.5 up to 1.0 M.-% (referring to the content of cement) (Fig. 2). Besides the content of chloride, the intensity of a chloride-induced corrosion depends on further parameters of the concrete (pH value and kind of steel, aeration and content of water).

In structural elements made of **zinc** or in galvanizing with, apart from that, a nearly passive reaction, a desultory increase of a corrosion in the alkaline building material has to be expected, if the contents of chloride exceed about 1.5 M.-% related to the cement weight. The higher critical content of chloride in comparison to steel results from the fact that chloride ions are partially bound as slightly soluble basic zinc chlorides.

In the presence of chlorides in the concrete/mortar a serious susceptibility to wide pitting exists for the **aluminum**, that anyway is sensitive to a corrosive attack. An addition of chloride even multiply intensifies the corrosion removal in the alkaline building material (Fig. 2). Even the smallest additions of chloride are corrosion-promoting.

The **lead**, that is also strongly corrodible in the moist alkaline building material, does not sustain an aggravation of corrosion in the presence of additional chlorides (Fig. 2). This can be explained by the formation of slightly soluble reaction products with a protective effect.

Copper is also largely unsusceptible to an influence of chloride salts, since the primarily developing copper (I)-chloride is slightly soluble.

4. CORROSION BEHAVIOUR IN CASE OF CONTACT WITH BUILDING MATERIALS CONTAINING MAGNESIA CEMENT [2,12]

A number of building materials as e. g. stone wood (for flooring) and light building boards are made of wood-shavings, that contain magnesia cement as a bonding agent. Magnesia cement is tempered by mixing lightly burnt magnesite and concentrated magnesium-chloride solution and hardened under formation of a compound of low solubility (probably $3\text{MgO} \cdot \text{MgCl}_2 \cdot 11\text{H}_2\text{O}$). The pores of the building material are filled with a magnesium-chloride solution. If the building materials that are bound with magnesia cement, get into contact with metals, they can heavily attack them. Above all, iron (steel) and zinc resp. galvanized steel, and not so much aluminum, copper and lead, are attacked.

The distinct aggressiveness of such building materials is explained by the strong hygroscopic character of the magnesium-chloride (pores containing magnesium-chloride do not dry up at relative humidity $> 32\%$) on the one hand and the corrosion-promoting characteristics of concentrated chloride solutions on the other. Because of that, corrosion is already possible in a comparatively dry environment.

In case of a reaction of the moistness that always exists in stone wood floorings, with magnesium chloride, e. g. in warm pipe walls, hydrochloric acid is split off and the pH value is reduced. This way, very aggressive corrosion conditions are created for the steel pipes and pipes made of unalloyed steels or galvanized steels may, because of that, not be laid in stone wood floorings without external protection.

5. CORROSION BEHAVIOUR IN CASE OF CONTACT WITH GYPSUM PRODUCTS [1-3,6,12]

Structural gypsum (e. g. gypsum mortar), that is mixed with water, forms a union of needle-shaped dihydrate crystals $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, as soon as the fluid pulp reacts. Because of the usually high surplus water resulting from fresh gypsum, the porosity of the hardened building material is quite high. If the hardened gypsum products (gypsum plasters, gypsum pasteboards, gypsum wall-construction boards) are kept moist, the pores are filled with a saturated calcium-sulphate solution. Since this salt has a corrosion-stimulating effect in neutral building materials, gypsum/gypsum mortar does attack **zinc** and **iron (steel)** very strongly in combination with humidity (Fig. 2 on the right and Fig. 4). Steel pipes and galvanized steel pipes, that are in contact with gypsum, which was moistened long-term, are attacked by thick rust products and can already be destroyed after few years. At relative humidity of $< 99\%$ gypsum mortar completely drains with time and does not cause steel corrosion and zinc corrosion any more.

Aluminum materials and **lead** in general are not likely to be attacked by the more neutrally reacting gypsum building materials. In case of lead, gypsum forms slightly soluble lead sulfates, that hamper the surface removal. In aluminum, that is free of copper, moist gypsum promotes a limited pitting corrosion. Though, aluminum alloying, that contains copper, sometimes corrodes quite intensive in wet gypsum.

Copper materials are largely resistant to gypsum, too, because the surfaces are coated with an oxide film that is stable to sulphate.

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