

CORROSION BEHAVIOUR OF NON-FERROUS METALS IN THE ATMOSPHERE
AND IN CONTACT WITH CONSTRUCTION MATERIALS

KORROSIONSVERHALTEN VON NICHTEISENMETALLEN IN DER ATMOSPHÄRE
UND BEI KONTAKT MIT BAUSTOFFEN

COMPORTEMENT A LA CORROSION DE METAUX NON-FERREUX DANS
L'ATMOSPHERE ET AU CONTACT AVEC D'AUTRES MATERIAUX DE
CONSTRUCTION

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SUMMARY

Aluminium and copper as well as its alloys and lead are, besides of zinc as pure zinc, alloyed zinc or galvanized steel, the most important representatives of non-ferrous metals for construction and component elements within construction engineering. These previously mentioned materials are used based on its numerous good qualities [1]. It should be pointed out that depending on the combined effects of exposure to atmosphere and water corrosion mainly takes place. In engineering constructions those metals are also used in immediate contact with concrete, gypsum or gypsum sand mortar, timber, thermal insulating materials and soils. This paper summarizes the corrosion behaviour of non-ferrous metals in view of important applications in engineering constructions.

ZUSAMMENFASSUNG

Aluminium und Kupfer sowie deren Legierungen und Blei sind neben Zink (als Reinzink), legiertem Zink oder verzinktem Stahl die wichtigsten Vertreter der Nichteisenmetalle für Konstruktions- und Installationselemente im Bauwesen. Die Nutzung der genannten Werkstoffe beruht auf zahlreichen wertvollen Gebrauchseigenschaften [1]. Seitens der Korrosion stehen Belastungen durch die Atmosphäre und Wasser im Vordergrund. Im Ingenieurbau werden diese Metalle jedoch auch im direkten Kontakt mit Baustoffen wie Beton, Gips bzw. Gipsandmörtel, Holz, Wärmedämmstoffen und Böden eingesetzt. Der Beitrag faßt das korrosionstechnische Verhalten der NE-Metalle für wichtige Anwendungen im Ingenieurbau zusammen.

RESUME

Aluminium et cuivre ainsi que ses alliages et plomb sont à côté de zinc pur, zinc allié ou acier galvanisé les représentants les plus importants des métaux non-ferreux utilisés pour les éléments de construction et d'installation en génie civil. Les matériaux mentionnés sont utilisés en raison de qualités d'utilisation nombreuses et bonnes [1]. La corrosion est principalement due aux influences de l'atmosphère et de l'eau. En génie civil les métaux sont utilisés en contact direct avec les matériaux comme le béton, le plâtre ou mortier de plâtre, le bois, les matériaux isolants et les sols. Ce rapport décrit le comportement à la corrosion des métaux non-ferreux en vue d'applications importantes en génie civil.

Key-words: corrosion, aluminium, copper, zinc, lead, atmosphere, concrete, insulation material, wood, gypsum, soil.

1 GENERAL CORROSION BEHAVIOUR.

RESISTANCE AGAINST ATMOSPHERIC CORROSION

Based on its position in the electrochemical series aluminium and zinc belong to active metals which, even under absence of oxygen, may react with water under formation of hydrogen. The standard potential, that means the electrode potential in a normal solution of the metal ions concerned were at $-1,66V_H$ or $-0,76V_H$. Lead (standard potential $-0,13V_H$) and copper (standard potential $+0,34V_H$) should in absence of oxygen, only react with strong acids or don't react at all. In presence of oxygen the corrosion resistance should increase based on the standard potential in the order Al - Zn - Pb - Cu. The standard potentials only make indications on the possible electrochemical qualities but not on the kinetic of corrosion process. In fact, the behaviour of aluminium, zinc and lead is determined by the

formation of cover layers which prevent the anodic as well as cathodic corrosion reactions [2]. Therefore, the corrosion behaviour of these materials is much more favourable for a lot of uses in practice than for the more "noble" copper materials.

1.1 Aluminium

In the atmosphere, water and aqueous solutions, aluminium and its alloys are submitted to a weak, facial attack with a formation of oxides and aluminium hydroxide. With the formation of this cover layer the corrosive attack is retarded considerably. This is due to the passivating qualities and the low electron conductivity of the about 0.01 μm thick protection layer [3]; thus, the anodic as well as cathodic partial reactions of corrosion were prevented.

The resistance to corrosion of aluminium [2 - 7] and its alloys depends on the resistance of oxidic and hydroxidic cover layers. During mechanical damaging a spontaneous restoration happens. In water and in the total pH-area relating to atmospheric corrosion the cover layers are insoluble and resistant as well. An important solubility of the cover layers appears relating to a so-called amphoteric behaviour at pH-values <3 and >9 ; in this case aluminium materials behave so active as it corresponds to their position in the electrochemical series. In the more acid and already in the less alkaline areas normally, irregular dissolution of aluminium takes place (Fig. 1).

Based on the already mentioned resistance of the cover layers against diluted acids aluminium materials are only in the atmosphere slightly worn by the sulfuric acid produced by the SO_2 -content in the air. This degradation is done

irregularly in form of small corrosion pits. In the industrial atmosphere, besides the increased SO_2 -content in the air, the coverage with dust and soot particles is important under which sulphuric acid accumulates and as a result the local attack increases.

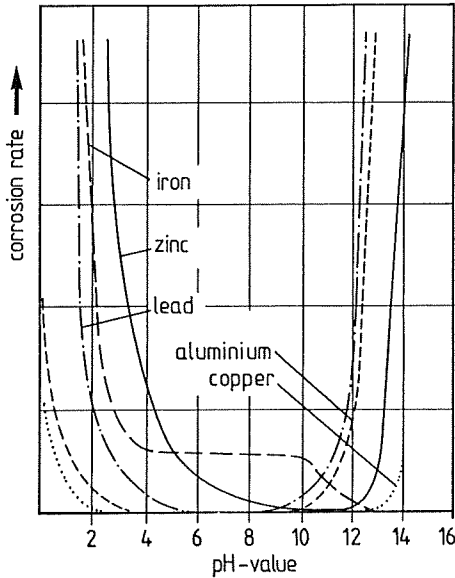


Fig. 1 Effect of pH-value on corrosion rate of construction metals (schematically according to literature)

During atmospheric corrosion in marine environment pitting corrosion appears due to the aerosol content of the air. A remarkably severe corrosion takes place in industrial areas near to the sea [2].

Even under temporary or permanent exposure of aluminium materials to sea water more or less strong local corrosion

(for the qualities not alloyed with zinc) [3], [5] and [8] may be expected.

Finally copper salts precipitated upon Al-surfaces (for mixed structures with copper materials) are representing local corrosion as separations of metallic copper increase the conductivity of the cover layer [2].

Totally, aluminium materials which in the atmosphere or in chlorid-containing water (sea water, deicing salt fog) have, based on the increasing of cover layers in comparison to the so-called "more noble" metals, a good corrosion resistance. E. g. in the atmosphere the corrosion abrasion per year may range, according to the contamination degree and the humidity in the air, between 1 and 5 μm [9] which is very low in comparison to steel (20 - 80 μm). Especially under conditions which are attacking aluminium, as for example acid and chloride containing media, an increasing of corrosion by crevice corrosion (e. g. at butt-joint connections by rivets, screws or not correctly welded joints) may take place [5], [10].

The protective action of the cover layers have its limits where aluminium materials in contact with other metallic, the "more noble" materials which were polarized beyond their pitting potential [3]. In this case of a contact corrosion aluminium is locally attacked, especially if there are aggressive electrolytes, e. g. chlorid-containing waters [5], [10]. Even the cathodic partial reaction which upon aluminium itself is heavily impeded (see above), may be developed the non prevention at the contact material. The metal behaves active according to its position in the electrochemical series and - in case of other necessary conditions for a contact corrosion which were fulfilled [11], - may be more and more attacked by pitting corrosion.

Fig. 2 shows these relations by a comparison of the proper corrosion of AlMg4,5Mn and the corrosion in contact with other materials in sea water. The main danger for the Al-elements contaminated with corrosion lies in the contact with other more noble metals.

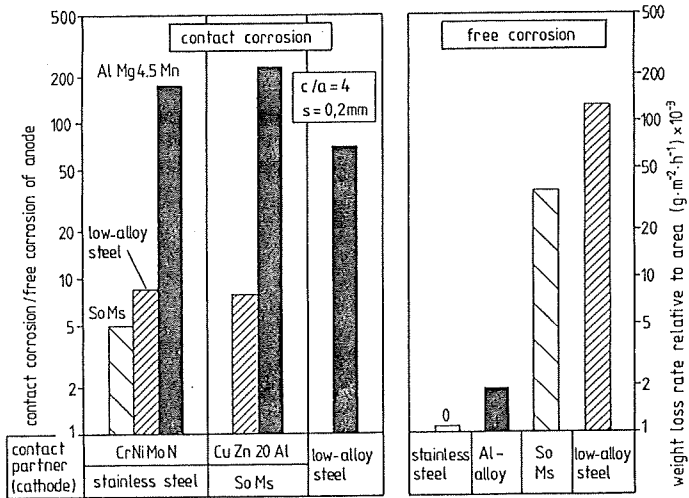


Fig. 2 Corrosion of different materials in continuous immersion zone of North Sea by free corrosion and contact corrosion (Hargarter, Sass)

The resistance to corrosion of aluminium materials in aggressive environment depends on the chemical composition. Normally alloyed metals behave less favourable than unalloyed ones [7], [10]. Foreign crystals of the existing contaminations or alloy elements favour on one side the conductivity of the cover layers (the oxide layers above the structural elements of e. g. copper, iron and silicium, i. e. as mixed oxides are semiconductors) and are moreover able to restrict the passive area (e. g. zinc). Therefore, e. g. copper containing qualities are in aggressive envi-

ronment strongly attacked [5] and are not used in building construction irrespective of its other advantages (high strength). For the previous reasons only the qualities of AlMg, AlMn, and by restrictions the alloy AlMgSi0,5, are used for sea water area [7], [8]. Qualities richer in Si and especially structural alloys of the quality AlZnMg may be more seriously attacked. Especially the alloys AlMg are recommended for the sea water area.

Artificial oxide layers produced by anodic oxidation may improve very considerably the behaviour at weathering and even the resistance to pitting corrosion (for example under seawater attack). But they have only a limited durability in aggressive environment [12]: the dust and soot deposits in combination with a high humidity and the SO₂-content of the air are very critical. Under those conditions chlorides increase that attack. In order to get a good aspect of anodically produced aluminium oxide layers, it is necessary to clean occasionally, especially in industrial areas [13].

1.2 Copper

Copper and its alloys are considered as resistant to corrosion [2], [4], [6], [14]. The corrosion of copper materials is prevented on the one side by cover layers (similar to the conditions for aluminium, zinc and lead); but on the other hand, due to its "more noble" character, it reacts, even when destroyed, only slowly with its environment [15], [16].

In the case of corrosive attack by the atmosphere (e. g. for roofs and coverings) unalloyed copper is used. Pure copper normally is more resistant to corrosion than its alloys. For

a number of applications it is insufficiently strong and therefore contains strong alloyed elements.

In the atmosphere copper forms a protective layer of red copper oxide Cu_2O . The red brown colour changes by further formation of oxides from dark brown to anthracite grey. From the primary cover layers to secondary cover layers out of acid copper salts are developed in the atmosphere which firmly adhere upon the copper surface and decrease more and more the corrosion rate [16], [18]. They have a greenish colour of different intensity and are called patina. The composition of the colour intensity of patina is regionally different according to the varying atmosphere conditions [15], [16], [18]. In the industrial and rural atmosphere, it is primarily composed of basic copper sulphate $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ and in SO_2 -free towns or rural areas, out of copper carbonate $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. The aggressivity of atmosphere determines the formation rate of patina [17], [18]:

clean mountain air	- 30 years
urban atmosphere	- 8 to 12 years
industrial atmosphere	- 5 to 8 years
marine air	- 4 to 6 years

Even in water a protective Cu_2O -layer is formed which sometimes is covered with green basic copper carbonates.

The formation of patina is a corrosion phenomenon combined with an uniform removal of copper. This surface removal is totally very small because copper in the atmosphere may be regarded as very resistant to corrosion (Fig. 3). According to the aggressivity of the air the annual surface removal is about 1 - 2 μm [9], [15], [16]. For historical buildings within 300 years surface removal of 0,25 mm [16] were measured.

The first formation of patina diluted oxidation products of elements out of copper materials may be separated [16], [18]. The copper sulfates which develop in SO₂-containing air may easily be diluted. For window seats, wall coverings, roof boardings these separations from copper materials may lead to decolorations upon adjacent porous those materials.

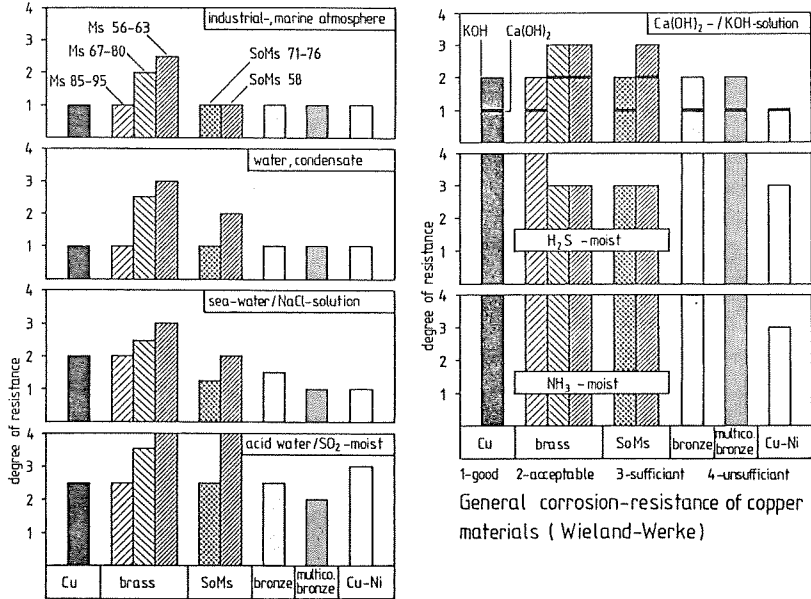


Fig. 3 General corrosion-resistance of copper materials (Wieland-Werke)

Differences in the corrosion behaviour of copper materials are primarily due to special corrosion-promoting elements in the air [15]: it is true that copper resists the sulfur compound in the atmosphere of industrial and rural areas [16], but it is also true that more acid electrolytes are attacking copper materials in presence of oxidizing agents such as oxygen of the air (Fig. 1 and 3); oxidizing

acids such as sulfuric acid itself react aggressively [19]. In the atmosphere there is (based on the relative humidity of the air > 75 %) an attack by SO_2 of the air which increases with its content [15], [16]. Stronger concentrations of sulfur compounds may also lead to damages [17]. This concerns especially chimney cowls out of copper sheets for badly regulated oil-fired central heatings.

Even in the presence of chlorides the attack of copper materials may be increased [15], [19], but this attack is limited in the marine environment as long as the primarily developed copper (I)-chlorid is difficult to dissolve. On the contrary unalloyed copper is slightly attacked in sea water (Fig. 3).

Humid hydrogen sulfide and ammonia are media in which the resistance to corrosion of copper and its alloys may be regarded as insufficient [15], [17], [19] (Fig. 3). Those gases develop in cess pools, clarification plants, stables and sometimes in industrial exhaust fumes. Copper and alloys rich in copper are much more sensible to humid hydrogen sulfide than the high-alloy compounds. Besides of corrosion hydrogen sulfide causes ugly black stains. Ammonia liquids and humid gases attack nearly all copper materials.

In case of corrosion promoting weathering conditions (industrial atmosphere, marine atmosphere) brass, as the cheapest copper alloy, behaves much more unfavourable than copper [15] which means, the resistance to corrosion decreases with an increasing zinc content (Fig. 3). Only β -containing brasses with more than 35 % zinc (less than 65 % copper) shows a moderate corrosion resistance (in aggressive atmosphere). In this case a so-called dezincification appears combined with a selective corrosion attack

of zinc-containing phases and a loss of strength. The brass, especially β -containing brasses, are only partially suited for external applications. In architecture they are preferred for applications in the interior. In diluted acids and very alkaline media ($\alpha + \beta$)-brass were primarily attacked by dezincification (Fig. 3); by increasing chloride content the attack changes from layer-type to plug-type dezincification [14]. β -containing brasses are more and more attacked by dezincification, even with contact to sea water (Fig. 3).

Other copper alloys as special brasses, bronzes and Cu-Ni-alloys are resistant under certain atmospheric influences [15]. But the surface loses its bright aspect due to the formation of oxide layers. There is a high resistance against the attack by chlorides, e. g. in sea water (Fig. 3).

Stress corrosion may appear upon copper materials. The general sensitiveness of the alloys increases by increasing content of alloy additives; brass with < 80 % Cu and special brass SoMs 58 [20] are most susceptible to stress corrosion. The resistance of bronzes and especially Cu-Ni-alloys with > 10 % Ni are sufficient. Stress corrosion is especially produced by nitrides and ammonium salts in presence of oxygen and humidity [20]. In the most of cases, small traces in the atmosphere are sufficient. Damages appeared for example upon brass connection nuts of heatings, gas flasks, refrigerating conducts and for condensers for which ammonium ions have been separated from the insulating material by water of condensation [21]. Damages also occurred upon brass screws for fixing facings of façade walls. Even pure copper doesn't good resist against stress corrosion [20]. A crack formation was stated for example upon unductile tubes with inherent stress which for thermal

insulation have been insulated lateron [21]. Due to penetrating humidity, ammoniac has been liberated from the insulating material.

Copper materials, itself, as noble structural metals, which are used in connection with other metals, are not strongly attacked by contact corrosion. However, they are able to increase corrosion upon other structural materials, for example galvanized steel and aluminium. A stronger corrosion attack occurred for example upon drip flaps according to segregated copper salts [17].

1.3 Lead

The corrosion of lead by water and other atmospheric influences is determined by the formation of protection layers [2], [4], [22]. Similar to zinc (chapt. 1.4) the protecting cover layer in the atmosphere is composed of basic carbonate. At the beginning its aspect is grey, and after some years is dark grey. In opposition to zinc there is nearly no abrasion by the SO_2 in the air. The sulfuric acid, which develops in humid air, produces upon the surface hardly soluble lead sulfate with the character of a protective layer. Even hydrochloric acid and chlorides don't cause a significant corrosion of lead because the lead chloride produced is also difficult to dissolve. On the contrary, e. g. acetic acid attacks already in a weekly acid area ($\text{pH} < 6$) because freely soluble acetates appear.

According to the investigations of [9] the mean annual surface removal of lead in the atmosphere are about 1 to 2 μm ; other investigations [22] gave still lower values.

Similar to zinc (chapt. 1.4) lead behaves unfavourable (especially newly rolled lead sheet) by permanent humidity exposure under exclusion of air, e. g. under the influence of condensed water [2], [22], no protection lead carbonate layers can be formed on the contrary rather an easily soluble lead hydroxide is developed.

In alkaline electrolytes lead is very heavily attacked under formation of easily soluble plumbite and, thus, is not resistant [23]. Therefore, lead corrodes more and more at high (> 9) and low pH-values. The aggressivity in the acid area depends mainly on the solubility of the appearing lead salts [4]. E. g. in acetic acid (easily soluble acetates) corrosion takes place already at $\text{pH} < 6$ (Fig. 1) and in (diluted) sulfuric acid (heavily soluble sulfates) only at $\text{pH} < 3$.

1.4 Galvanizations, zinc

Such as the already mentioned metals in certain media, zinc develops cover layers out of corrosion products which prevent corrosion of zinc (abrasion of zinc) [4], [24], [25]. For galvanizations the coatings show the characteristics of passive and active protection against corrosion. They protect the steel against corrosion promoting materials and protect cathodically the free areas of the steel surface, when the conductivity of the attacking medium is sufficient. It should be pointed out that zinc protects steel, if the cover layers form in the corresponding medium and weather, (taking into account local changes) are staying stable. As for galvanizing the same conditions are valid for zinc as well.

At the atmosphere primarily zinc oxide is formed which under the influence of the humidity of the air transforms to zinc hydroxide. These reaction products have a much lower protective action than, for example, the oxide layers upon aluminium. For zinc as for lead the proper protective action is produced by a protective layer which forms with the carbon dioxide of the air. These cover layers, which develop in waters and soil containing carbon dioxide, in essential originate from basic zinc carbonate and are well-adhesive, and self-curing after injuries and very badly soluble in water. According to the humidity content of the air they are produced within a few days to weeks. In acid and more alkaline media the cover layers start to dissolve (amphoteric behaviour) (Fig. 1); in very alkaline solutions the zinc carbonates are transformed into easily soluble zincates [25]. Therefore, zinc is appropriate for the protection under light corrosive attacks of the atmosphere and the water. In alkalic media zinc is more resistable than e. g. aluminium and lead, because the formation of soluble zincates have much higher locally concentration of OH^- -ions than for the formation of aluminates and plumbites.

During outdoor weathering of galvanized steel or zinc the type of atmosphere and the local climatic conditions have an influence upon zinc corrosion [24], [25] (Fig. 4). Zinc is uniformly removed. Especially the sulphur dioxide content of the air increases the rates of the weight loss [26], because sulphur acid, produced at increased humidity of the air, dissolves even highly diluted zinc carbonates. Therefore, zinc is to be removed in industrial atmosphere. The corrosion of zinc by bitumen [27], which may appear by the contact of galvanized elements (for instance gutters) with bituminous felts upon roofs with low inclination, is due to the attack of acid waters. Acid components may be separated from bitumen by oxidation and destroy galvanized elements or

zinc [24], [28]. In such cases zinc has to be protected by a painting cover (see below).

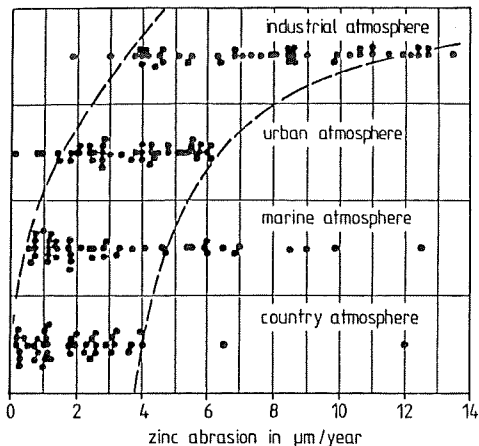


Fig. 4 Atmospheric corrosion of zinc coating (literature interpretation according to Schikorr)

The influence of chloride ions (e. g. aerosoles in the air, sea water) upon zinc corrosion is very low, because zinc, based on the qualities of its compounds, shows no clear tendency to form stable local elements [29]. For example liberation of copper ions from separations of copper elements increase the conductivity of the cover layer and produce a clear pitting corrosion. In sea water the surface-removal rate of zinc according to the conditions of attack are at about 8 - 12 $\mu\text{m/a}$.

In comparison to the conditions for lead, increased corrosion phenomena may also appear for zinc if the access of air to the surface is prevented and the formation of carbonatic cover layers is stopped. In case of an insuffi-

cient aeration soluble $Zn(OH)_2$ is produced without any protective qualities. An attack with production of voluminous corrosive products (white rust) [25] occurs. Under a longer exposure to humidity (especially condensed water) a rapid destruction of galvanized elements or zinc elements may be expected. Known damages [24] are due to moist from construction or use. For example important damages appeared upon the unaerated bottom side of the roof sheating of warm roofs above humid rooms; also after a permanent contact with humid elements [30], [31] (see chapt. 4).

Upon the castings out of ZnAlCu exposed to long-term attack by condensed water intercrystalline corrosion may appear especially if the additions of tin, lead and cadmium determined by the standard are exceeded [24]. In engineering constructions damages appeared among others upon window benches due to structural humidity.

Galvanized elements in contact with so-called noble materials such as copper or stainless steel were under certain circumstances increasingly attacked by contact corrosion [11] but still less than e. g. aluminium (Fig. 2). Fig. 5 illustrates that the increasing of corrosion by contact corrosion in comparison to the self-corrosion of zinc grows by increasing aggressivity of the environment. An important attack of zinc only takes place after wetting the contact area with chlorid-containing water.

Elements out of galvanized steel are commonly used in aggressive environment, in which protection against corrosion of zinc itself is limited, in combination with organic coatings [32]. However, coatings must comply with the zinc surface and be sufficiently permeable for carbone dioxide so that underneath the coating corrosion-preventing

cover layers may be developed. Otherwise, the coatings may be peeled off [2].

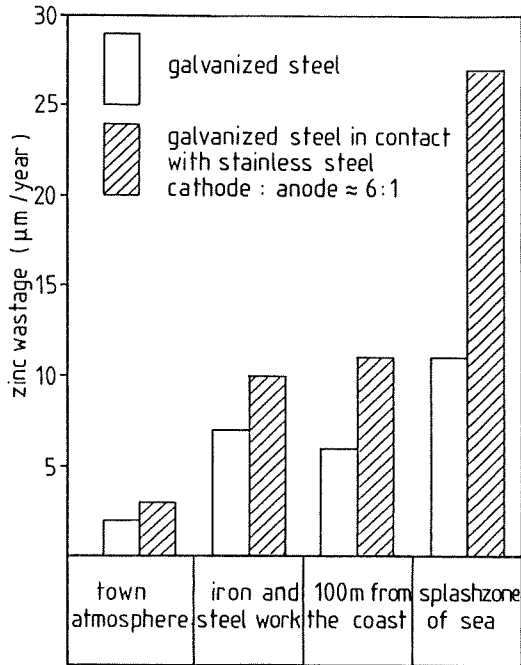


Fig. 5 Corrosion of galvanized steel elements in contact with stainless steel

2 RESISTANCE TO ALKALINE MATERIALS

Normally, compact stages of construction materials do not attack metals. A corrosive attack is only possible if the capillary-, porous- or channel-shaped cavities contain free water and, owing to the cavities, oxygen, which is necessary for maintaining the corrosive reaction, may diffuse to the

metal surface. Furthermore, there must be conditions which obstruct or even destroy passivity. In all corrosion cases the situation becomes more serious if water separates aggressive components from the material or favours the transport of pollutants from the element environment.

2.1 Corrosion in concrete or cement mortar

In materials under alkaline reaction aluminium materials are strongly attacked by surface corrosion due to the amount of moisture in the material. According to the indications in [33] corrosion in pc-mortar in the case of dry : humid : wet behaves as 1 : 6 : 25. Therefore, corrosion is more severe in presence of an increased water content in the pore system of the cement stone [23], [33], [34] (Fig. 6). The oxide layer dissolves and aluminium reacts under formation of hydrogen. In order to prevent corrosion damages [35] by contact with humid alkalic materials, aluminium has to be protected additionally by appropriate coatings (e. g. bitumen or tar epoxy resin combinations) [33], [34]. Even oxide-layers produced by anodic reaction (anodic oxydation) are attacked by alkaline materials [2], [6], [33] (especially for painted layers), which produces ugly spots. Therefore, visual areas of anodically oxidized parts (e. g. window frames) have to be protected by covering with detachable foils against damages during the construction phase due to pollutions by alkaline materials.

Copper and its alloys, if completely embedded into alkaline materials, are normally not attacked [6], [17], [23], [24], [36] (Fig. 6). Using cements with a higher alkalinity (especially brasses with an increased content of zinc) are insufficiently resistant. In alkaline solutions the resistance decreases in the order $\text{Ca}(\text{OH})_2$ - KOH - NaOH (even

with increasing of pH-value) (Fig. 3). ($\alpha + \beta$)-containing brass is more attacked in alkaline materials because of its dezincification.

In humid alkaline materials lead in comparison to aluminium is very susceptible to corrosion [2], [22], [23] (Fig. 6). Even a direct contact with moist concrete and mortar should be avoided by an insulating intermediate layer. In concrete or mortar, lead could be protected with e. g. bituminous insulating layers.

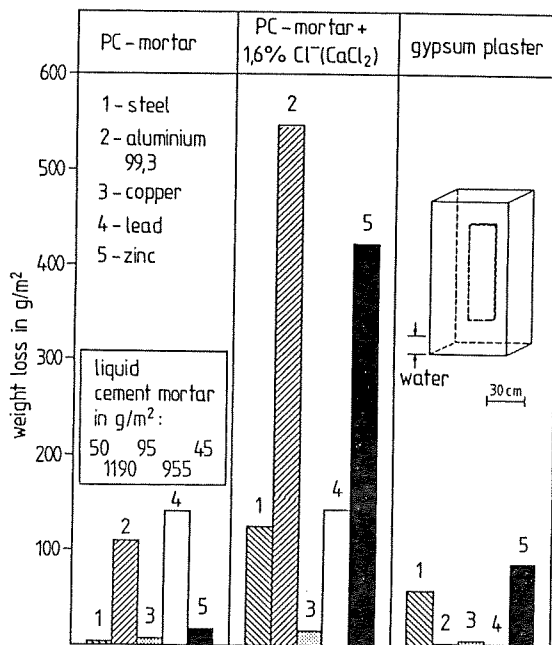


Fig. 6 Weight loss of metal plates for construction metals in specified mortar following wet exposure after 12 months (Bukowiecki)

Zinc or galvanic steel is slightly more attacked in alkaline materials than copper materials but much less than aluminium and lead (Fig. 6) [23], [24]. In cement mortar and concrete there are reactions between zinc and calcium hydroxide, by which cover layers of calciumhydrozincate develop. Until the moment of the formation of the cover layers the zinc layer corrodes, by which, in the first 1 to 2 years, about 10 μm are removed. Following that, zinc corrosion is practically stopped [25], [30], [31]. During the initial corrosion of zinc there may be a temporary formation of hydrogen. The initial development of hydrogen in the still green concrete endangers high-strength galvanized steel parts in view of hydrogen-induced stress cracking corrosion [37]. Using alkali-containing cement and pH-values of the concrete/mortar > 13.3 the formation of cover layers is prevented and the corrosion of zinc increases [38].

Galvanizing is used in concrete construction as an additional protection against the corrosion of reinforcing steel [30], [31], [37], [39]. This may be an advantage in comparison to ungalvanized reinforcing steel if a carbonation of concrete may be expected (Fig. 7).

In the case of a partial embedment of non-iron metals zinc, galvanized steel and copper materials are strongly attacked in the transition area material/air than in the material. However, this is not valid for aluminium and lead [23] which are susceptible to alkalines.

Chlorides in mortar/concrete, which resulting from salts penetrated lateron, intensify the corrosive attack especially of aluminium and zinc or galvanized steel, but not for lead and only slightly for copper materials [23], [33] (Fig. 6). In the presence of chlorides there is rather a wide to deep pitting corrosion attack. For zinc or

galvanized parts a sudden increase of zinc corrosion may be expected if the chloride contents surmount about 1,5 weight-% related to the cement weight [30], [39]. In high chloride containing solutions, even copper is destroyed. Damages were known upon copper foils used for sealing bridge lanes against the attack of thawing salts and jointing sheets of bridges.

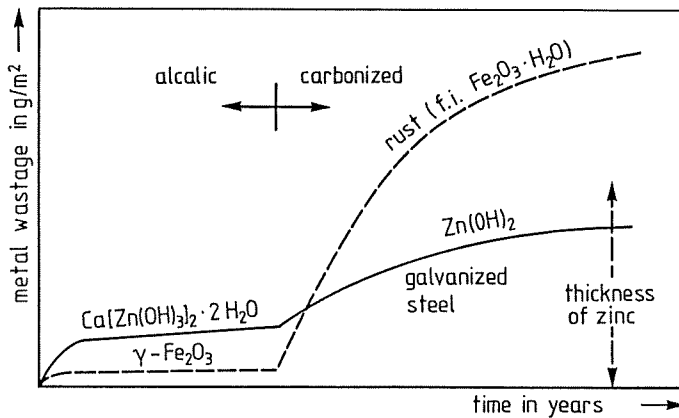


Fig. 7 Corrosion of galvanized and not galvanized steel in concrete (schematically) (Nürnbergger)

Even non-alkaline materials may increase corrosion of non-ferrous metals if they contain chlorides, as it is the case for the use of magnesium cement (e. g. lightweight slabs, magnesium oxichloride floors), [23]. The main reasons for aggressivity is mainly due to the fact that MgCl_2 in the magnesium cement has very hygroscopic qualities. Especially zinc and galvanized parts and less aluminium, copper and lead are attacked.

2.2 Corrosion by cement mortar and concrete extracts

Upon construction sites it often takes place that the construction metals are wetted with cement precipitations of watery extracts which were, for a longer time, in contact with hardened mortar or concrete. They may contain components of cement stone in diluted form and therefore react in the alkaline direction. In such watery precipitations or solutions especially aluminium materials and lead behave much more unfavourable than in humid, solid materials [2], [23], [34] (Fig. 6). But zinc and copper are much more attacked. The corrosion behaviour in alkaline solutions may not be compared with that in solid structural phases.

3 RESISTANCE AGAINST GYPSUM AND GYPSUM SAND MORTAR

As for gypsum and gypsum sand mortar a lot of dihydrate crystal ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) develop with the setting of the liquid paste. Based on the normally high excess of mixing water, porosity of gypsum mortar is very high. If gypsum mortar is kept humid the pores are filled with a saturated calcium sulphate solution. As this salt is stimulating corrosion in neutral materials, gypsum mortar attacks zinc in connection with humidity [23], [30] (Fig. 6). For relative humidities of the air $< 99\%$ gypsum mortar dries completely and does no longer produce any corrosion of zinc.

In Fig. 8 the behaviour of zinc coatings in permanently humid and in dried gypsum is compared. In the last case gypsum was kept humid only for 0.5 months and afterwards stored at 70% relative humidity of the air. In the dry gypsum zinc corrosion was rapidly stopped. Taking into consideration that gypsum normally dries out quickly and even in unfavourable cases of corrosion in practice rarely

moistens thoroughly for a longer time, the conclusion may be drawn that the danger of corrosion of galvanized parts is actually much lower than it has to be concluded from laboratory tests with humid gypsum (Fig. 6).

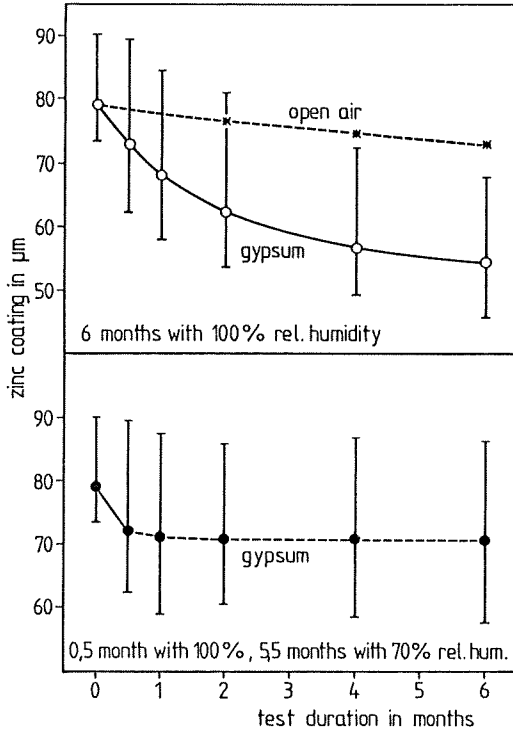


Fig. 8 Zinc coating of hot-galvanized round-wires after exposure to gypsum plaster

Already less alkaline cements, e. g. blast furnace cement and especially high alumina cement produce for aluminium and lead a lower corrosion than for materials combined with Portland cement [22], [23]. The naturally reacting gypsum materials hardly attack these materials susceptible to

alkalis [2], [6], [23], [33] (Fig. 6). As for lead gypsum produces hardly soluble lead sulfates which prevent abrasion. As for aluminium humid gypsum favours, only to a limited extent, pitting corrosion [33]. Copper also is almost resistant to humid gypsum [17], [23].

4 RESISTANCE AGAINST THERMAL INSULATING MATERIALS AND TIMBER

Timber and thermal insulating materials normally do not contain special pollutants which are dissolved after access of water. Because of the numerous cavities (especially for open-cell thermal insulating materials) those materials absorb the penetrating water and retain it according to capillary action. Therefore, these materials favour the corrosion at covered metal parts [21]. In order to avoid in these cases damages by corrosion the entry of humidity has to be prevented by appropriate insulations.

Further, the following particular qualities of timber are still known [40]: timber contains portions of acetic acid which, due to the entry of humidity and moreover by increasing temperature, are liberated and according to the type of timber, diminish the pH-value of the liquid phase to values between 3.3 and 5.3. Acetic acid becomes active at a direct contact with humid timber and metal and in the vapour phase above the timber surface, because the acid is volatile.

For initiating corrosion processes at a direct contact metal/timber a humidity of timber of more than 16 - 18 % is necessary. Such contents appear at mean relative humidities of the air of 75 - 80 %. But only much higher humidities of the air and direct access of water to the timber surface

favour increased corrosion as in this case timber presents free water. This is the case above 30 mass-% water in the timber: underneath this value the water is liberated in the fibers and accumulated above in the cavities. Even the corrosive action of certain timber protection chemicals takes place only by increasing humidities of timber; but their corrosion-promoting influence is often overestimated.

Increasing of corrosion in connection with humid thermal insulating materials became especially known for galvanized parts (cold-water-tube enveloped with glass wool, shield sheets of thermal insulating slabs out of stone wool upon reactor security vessels) [30], [31]. Because of wetting with permanent humidity and the resulting prevented entry of air no protecting carbonate cover layers have developed. Other construction materials such as aluminium and copper materials may only be attacked by corrosion in humid insulating materials if they contain polluting agents.

Humid insulating materials favour however the formation of cells at a contact with embedded parts (e. g. galvanized steel) with more noble metal parts (e. g. copper materials, steel in concrete) if these parts are connected electrically among eachothers [11].

In view of the behaviour under corrosive attack in connection with timber the following series of increasing resistance may be established for connection metals [40]: unalloyed steel, aluminium. Under outdoor exposure the following corrosive removal in connection with timber may occur:

unalloyed steel	:	zinc	:	lead	:	copper(brass)	:	aluminium
35	:	9	:	4	:	3	:	1

The absolute value for unprotected steel reaches as an annual mean value 11 $\mu\text{m/a}$. In frequently wet timber or at permanent contact with humid timber it has to be started from a stronger removal. This is especially valid for zinc and galvanized parts in which the comparison to the conditions in humid insulating materials no protecting cover layer may be developed, e. g. in [30], [31] reports are given about those damages. Removals of several tenth millimeters zinc per year occurred upon titanium zinc roof in permanent contact with a wet timber sub-structure.

Under certain conditions (see above) in humid timber an increasing of liberated acetic acid cannot be excluded, e. g. upon zinc surfaces and possibly upon aluminium and especially upon lead. Acetic acid attacks lead in already low concentrations [2] (see chapt. 1.3). For impregnated timber in special cases the danger of corrosion may be higher if specific metal-salt-combinations exist [40]:

copper/ammonium salts

zinc, aluminium/chlorides, copper salts

5 RESISTANCE IN SOILS

For metal parts out of aluminium, zinc or galvanized parts and lead but not copper materials embedded in the soil, corrosion is stronger in non-aerated soil than in aerated soil (Fig. 9) [41], [42]. The behaviour of these materials, thus, corresponds to that of unalloyed steels. For a decreasing aeration of the soils the capacity to form a cover layer decreases and the earth conductivity increases. Therefore, the corrosion rate increases. The aeration capacity of a soil decreases with an increasing proportion

of fine parts and water. Futhermore, the soil conductivity increases with increasing salt content and temperature [43].

For Al-alloys free of copper the loss of weight in soils is relatively low [41], [42], [43]; however aluminium is attacked by pitting corrosion, especially in badly aerated and often humid soils (Fig. 9). Copper containing aluminium alloys behave as unfavourable as steel; in soils of all type corrosion attack differs very much [41], [42].

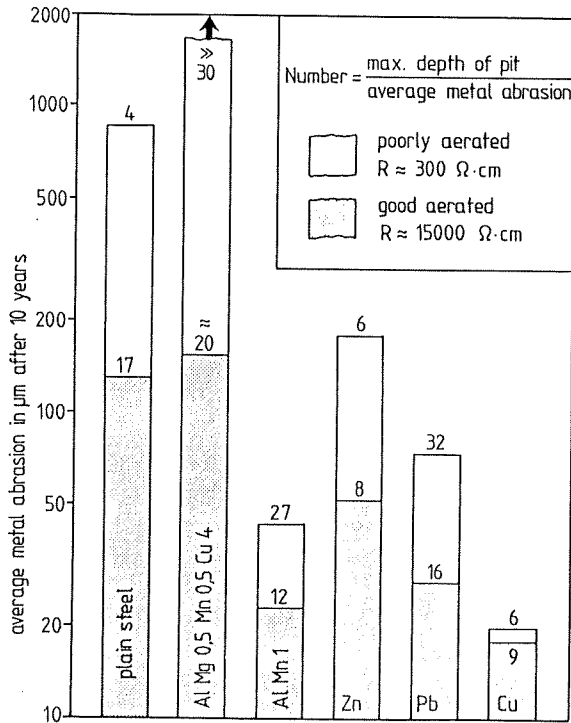


Fig. 9 Corrosion of construction metals in ground (Romanoff)

Fig. 9 illustrates the corrosive behaviour of zinc in comparison to other metals. Only in a moderately to well aerated soil galvanization as a protection against corrosion is appropriate. In acid soils ($\text{pH} < 4,5$) corrosion rate is higher than in nearly neutral soils. But even under conditions, under which zinc is abraded quickly, galvanization still offers advantages [30], [43]. While ungalvanized steel normally may be attacked by extreme pitting corrosion, galvanized steel, even after zinc removal, is abraded uniformly. In an area free of zinc, steel is protected cathodically.

Copper and copper alloys were rarely used in immediate contact with the soil, although the corrosion danger is very low and the annual rates of removal in aerated as well as unaerated soils reach only a few μm [36], [41], [42] (Fig. 6). The most strongly abrasion by corrosion only occurs in slag-containing or acid, even also sulfid-containing soils [42]. In [36] maximum values of a mean abrasion of $40 \mu\text{m/a}$ are measured. Brass behaves somewhat more favourable in soils than pure copper [41]. In acid soils a dezincification appears. But the general behaviour is still more favourable than e. g. several aluminium materials of galvanized steel.

Lead in soils is normally attacked exclusively by wide pitting, especially in low aerated soils [42] (Fig. 9). An increasing of abrasion takes place especially in acid soils; lead e. g. is attacked by humic acids.

For all metals with amphoteric behaviour, but especially for aluminium and lead, alkalic soils increase the abrasion by corrosion [42]. Even high contents of salt, especially chlorides, increase the irregular attack (with the exclusion of lead). For galvanized steel extensive investigations have

been carried out by [43], [45]: it was stated that increasing of chloride contents in the soil increase only the initial corrosion of zinc. Cover layers formed are sufficiently stable against salts penetrating lateron.

6 SUMMARY

The most important qualities of steel structural were summarized in Fig. 10.

material	elektrochem. property	atmos-phere	wetness	chloride	alkaline	ground	
						aerated	unaerated
plain steel	active	-	-	-	+	0	-
Cr-Ni-steel	noble	+	+	0	+	+	+
weather resistant steel	active	+ / 0	-	-	+	+ / 0	-
galvanized steel	active	+ / 0	- 1)	0	0	+	-
pure zinc, titanium zinc	active	+ / 0	- 1)	0	0	+	-
aluminium	active	+	+	-	-	+	-
copper	noble	+	+	+ / 0	0	+	+
lead	active/noble	+	- 1)	+ / 0	-	+	0
+ resistant	0 conditionally resistant		- no resistant		1) poorly aerated no CO ₂ -access		

Corrosion behaviour of construction metals

Fig. 10 Corrosion behaviour of construction metals

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