Principles of Metal Corrosion

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1 General

Corrosion is the chemical change or destruction of materials, especially of metallic materials, through water and chemicals; corroding metals can form oxygen compounds (oxidation) or ionic compounds with non-metals.

This can lead to the deterioration of the performance of a building component or an entire system.

Corrosion as such is not as yet a damage. The sole criterion for corrosion damage is the impairment of the function which must be seen in connection to the requirement demanded.

For insulators, the following types of corrosion are of predominant importance:

- contact corrosion,
- surface corrosion,
- tension cracking (stress corrosion cracking).

While low- and non-alloyed steels from loose iron oxide layers, which peel off easily, other materials such as zinc, aluminium and stainless austenitic steel form firm layers of oxidation which protect the material against further oxygen corrosion. These very thin layers (some thousands of a micrometer) are also called “passivating layers”.

If such layers are damaged, they are reconstituted quickly as long as oxygen is present.

In addition to the chemical variation of materials on larger surfaces, the stress corrosion cracking of stainless austenitic steels is of special significance since it causes cracks in the material.

2 Contact corrosion with metals and their compounds

Between different metals certain reactions occur in the presence of electrically conductive fluids (electrolytes), in which the respective less-noble metal is damaged. It is therefore that e. g. rivets made of less-noble metal dissolve. This process is called contact corrosion.

Electrolytes are every type of electrically conductive fluids, e. g.:

- hydrous salt solutions,
- hydrous acids,
- hydrous lyes.

Rain or condensation water can contain hydrous acids.

The distinction between noble and less-noble metals can be made using the so called electro-chemical tension sequence (Table 1).

The table alone does not allow for a deduction concerning the amount of corrosive damage. This is solely decided by the conductivity of the electrolyte.

Additionally, it must be remembered that the order in the tension sequence can change in the presence of certain electrolytes. It is therefore that practical experience must always be considered in connection with Table 1.

The total corrosive damage through contact corrosion is dependent upon:

- the two materials concerned,
- the type of electrolytes present,
- the ambient conditions such as temperature, relative humidity, exposure to dangerous substances,
- the relative surface size of the metals concerned.

The following rules apply:

disadvantageous: less-noble metal surface / noble metal large surface
advantageous: noble metal small surface / less-noble metal large surface.
Example: Connections of aluminium sheets (less-noble) with screws of stainless austenitic steel (noble) are all right. On the other hand, the connection of sheets made of stainless austenitic steel with aluminium rivets cannot be recommended since a corrosive attack concentrates on the small surface of the rivet.

Table 2 shows the incompatibility of different metals between each other and provides an initial indication of the danger of contact corrosion in metal combinations. It does not relieve the need for a precise evaluation of the corrosion situation in the individual case.

Contact corrosion can be avoided or at least be minimised by observing of the following rules:

- The large-surface contact of different materials must be avoided.
- Fixings such as screws, rivets, bands and locks must at least be as noble as the material to be connected.

The corrosive attack is then directed against the less-noble material. It is, however, very minor due to the advantageous ratio of surfaces.

Electrically non-conductive layers can prevent the electrolytic contact corrosion. They must be inserted where dangerous material combinations or surface ratios cannot be avoided. Non-conductive layers are amongst others:

- plastic material,
- plastic bands,
- bitumen coatings.

Contact corrosion can also be prevented through the prevention of an access of electrolytes to the contact point. This is achieved generally by correctly installed coatings.
Table 1: Electro-chemical potentials of some elements and alloys (electro-chemical tension sequence)

Sources: - Dubbel, Taschenbuch für den Maschinenbau, Ausgabe 1982
- Baumgartl, Werkstoffkunde kurz und einprägsam, VEB Fachbuchverlag Leipzig 1971, 4. Auflage

<table>
<thead>
<tr>
<th>Material</th>
<th>Potential (V)</th>
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<td>-3</td>
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<tr>
<td>Increasingly non-noble</td>
<td>.</td>
</tr>
<tr>
<td>Increasingly noble</td>
<td>.</td>
</tr>
</tbody>
</table>

- Caesium
- Lithium
- Calium
- Calcium
- Natrium
- Magnesium
- Beryllium
- Aluminium
- Manganese
- Zinc
- St 1.4300 active
- AlMn
- Chromium
- Iron
- Cadmium
- non-alloyed steel, cast iron
- St 1.4301 active
- Cobalt
- Nickel
- Pewter
- Lead
- CuZn 28 Sn (Ms 71)
- Hydrogen
- Ni 99.6
- St 1.4401, 1.4404 active
- NiCu 15 Fe
- Titanium
- St 1.4301 passive
- NiCu 30 Fe
- St 1.4301, 1.4404 passive
- Antimony
- Bismuth
- Arsenic
- Carbon
- St 1.4006
- Copper
- Oxygen
- St 1.4057
- Palladium
- Silver
- Quick silver
- Platinum
- St 1.4300 passive
- Gold
- Chlorine
Table 2: Contact corrosion with metal combinations (explanations, see page 3)

<table>
<thead>
<tr>
<th>Material considered</th>
<th>Surface ratio</th>
<th>Zinc</th>
<th>Aluminium</th>
<th>Combined with Steel ferritic</th>
<th>Lead</th>
<th>Steel austenitic</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>small</td>
<td>-</td>
<td>A</td>
<td>A</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<td>M</td>
<td>M</td>
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<td>M</td>
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<tr>
<td>Aluminium</td>
<td>small</td>
<td>M</td>
<td>-</td>
<td>M</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>large</td>
<td></td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Steel ferritic</td>
<td>small</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>S</td>
<td>S</td>
<td>S</td>
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<td>large</td>
<td></td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Lead</td>
<td>small</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>-</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>large</td>
<td></td>
<td>M</td>
<td>M</td>
<td>-</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Steel austenitic</td>
<td>small</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>-</td>
<td>M</td>
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<tr>
<td></td>
<td>large</td>
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<td>M</td>
<td>M</td>
<td>M</td>
<td>-</td>
<td>M</td>
</tr>
<tr>
<td>Copper</td>
<td>small</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
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<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
</tbody>
</table>

M: minimum or no corrosion on material considered
A: average corrosion on the material considered, e.g. in very wet atmospheres
S: severe corrosion on the material considered

3 Iron materials (ferritic materials)

Low- or non-alloyed steels do not form a corrosion-resistant, passivating surface layer and must therefore be protected by a coating.

The following are used:
- zinc,
- chromium,
- nickel,
- aluminium,
- paints with anti-corrosion additives,
- plastic materials.

Advice on the choice of corrosion-prevention systems can be found in:
- DIN 55928 "Corrosion prevention of steel constructions through coatings and protective layers",
- AGI Q 151 "Insulation works, corrosion prevention for cold and thermal insulations on industrial installations".

Additionally, the VG 81249, parts 1 and 2, help making decisions for the choice of materials and their behaviour under corrosion, especially in sea water and in sea-water atmosphere.

Prior to coating, existing rust must be removed. This is mainly done by:
- blasting,
- brushing,
- etching.

Paint manufacturers can provide information about coating systems. Coatings – both paints and metallic or plastic protective layers – are mostly susceptible to damage, even if these are microscopically small. These damages can lead to underfilm corrosion and the removal of the protective layer.

Galvanising of steel surfaces is of special importance:
- The impermeable zinc layer is annealed to the steel surface.
- Zinc layers are not susceptible to underfilm corrosion.
- In normal atmospheres, a protective layer of "patinated zinc" is formed which is insoluble in water.

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1 Defence material standard; available in Beuth Verlag, 10772 Berlin, phone: 0049 30 26 01-22 60; fax: 0049 30 26 01-12 60
4 Galvanised steel

Galvanisation of steel components is known as a very reliable corrosion protection. The reliability rests predominantly on the formation of "patinated zinc".

The protective effect of the insoluble "patinated zinc" is, however, limited. Especially near the sea and in industrial environments with severely polluted atmospheres, they are under attack as the "zinc patina" can be transformed into soluble materials by acid rain. These soluble materials are then washed out and away by rain.

This leads in time to the total consumption of the "zinc patina". Consequently, the life cycle of the zinc layer is dependent upon:

- the thickness of the layer,
- the composition of the air.

For the durability of the zinc layer, see Table 3.

Table 3: Durability of zinc layers

| Zinc layer group acc. DIN EN 10142 | Zinc layer (g/m²) both surfaces together | Zinc layer thickness µm minimum per surface | Durability in years: | | | |
|-----------------------------------|------------------------------------------|---------------------------------------------|----------------------|---------------------|----------------------|
| 275                               | 275                                      | 8                                           | Rural atmosphere²    | See atmosphere      | Urban atmosphere      | Industrial atmosphere |
| 350                               | 350                                      | 17                                          | min.                 | max.                | min.                 | max.                  |
| 450                               | 450                                      | 22                                          | 13.25                | 29                  | 4.5                  | 12.75                 | 5                    | 11.25                | 2.75                 | 5.75                  |
| 600                               | 600                                      | 29                                          | 18                   | 39                  | 6                    | 17                   | 6.75                 | 15.25                | 3.75                 | 7.5                  |

¹ according DIN 18421 = VOB Part C, required as minimum value
² rural atmosphere is non existent in Central Europe

Galvanised components are susceptible to moisture in the absence of air. This specifically applies to fresh galvanising. Then, no zinc patina is formed, but instead so called white rust which may lead to the destruction of the zinc layer.

This product of zinc corrosion, which in unfavourable circumstances can form very quickly, frequently in a few hours, severely attacks the zinc surface.

Chromating offers a short-term protection against white rust. Galvanised sheets, transported in packs can only be protected against white rust by preventing condensation on cold metal surfaces (especially in winter). Well aired stacking is recommended.

The galvanised parts are well protected against small damages of the zinc layer and on cutting edges of sheets. However, the protection is not as durable as on the uncut surfaces.

Advice is given in publications of the Deutsche Verzinkerei Verband (DVV)
Breite Straße 69, D-40213 Düsseldorf, Germany

Sheets with an anti-corrosion layer of an aluminium-zinc alloy (55% aluminium, 43.4% zinc, 1.6% silicon) possess a significantly better durability than sheets with an equally thick coating of pure zinc.

Trade names are:
- Aluzinc (Europe),
- Galvalume (USA),
- Zincalume (Australia).

The service temperature limit for galvanised sheets is about 230 °C, for aluminium-zinc sheets about 315 °C.

Galvanised sheets must possess a minimum zinc coating of 275 g/m² (both surfaces together). A minimum of 40% of this total coverage must be on the less-well coated surface.
Fixings for galvanised sheets are galvanised or cadmium-coated or made of stainless austenitic steel.

Through an additional layer of paint or plastic, the durability of galvanised surfaces can be increased further.

5 Stainless austenitic steels

Stainless austenitic steels form a protective passivating layer with oxygen from the air. Without oxygen, this layer is not formed and corrosive attack can occur.

The stainless austenitic steels are the better corrosion-resistant, the smoother the surface. However, they can be attacked by rust from somewhere else and be destroyed. Such rust can be caused by:

- handling of non-alloy steel and stainless austenitic steel with the same tools,
- welding splashes,
- swarf, iron dust.

Stainless austenitic steel is normally vulnerable to halogenated solvents. These are solvents containing chlorine, bromine, iodine or fluorine.

Example: In public swimming halls with chlorinated water the air also contains chlorine and can cause damages to stainless austenitic building components. The result of the corrosive attack of the chlorine increases when these components are under tension stress.

This is called stress-corrosion cracking (tension cracking) which can destroy building components as a result of crack formation in a very short time. For the use of stainless austenitic steel for supporting parts in chlorine-containing atmospheres, see Zulassungsliste des DIBt (list of admissible materials, issued by the Deutsches Institut für Bautechnik, Kolonnenstraße 30, 10829 Berlin – Germany, telephone 0049 30/78730-0; fax: 0049 30/78730-320).

Tension cracking occurs with stainless austenitic steel if the following conditions combine:

- tension stress at the surface, this can already be caused by production-related internal tensions;
- the pressure of, especially, chloride ions;
- moisture;
- elevated temperatures, even if these occur only for short periods.

Investigations show that damage through stress corrosion cracking in stainless austenitic steel practically never occurs at temperatures below 50 °C.

Since the presence of chloride ions is dependent upon several factors, such as the atmosphere and the chloride ion content of the insulation materials, objects made of stainless austenitic steel should also be protected from corrosion. Coating systems containing metallic zinc or aluminium must not be used. Surfaces must be cleaned prior to the coating and they must be free of fat, dust or acids. They should be roughened by blasting with non-metallic blasting means, free of iron, e. g. glass beads.

Narrow gaps must be avoided, especially with constructions made of stainless austenitic steel, since here the oxygen access is limited (gap corrosion). This can be achieved for example by welding. The appropriate welding additives must be taken care of when welding stainless steels.

Welding leads to structural changes in the vicinity of the welded seam. Especially in an acid environment, this leads to risk of corrosion. Welding colours and welding splashes must be removed after completion of the welding. This can be done with the aid of:

- brushes of stainless steel wire,
- grinding discs free of iron oxides,
- mordant solutions or mordant pastes.

When employing mordant solutions and mordant pastes, manufacturers' recommendations must be heeded!

Fixings such as screws, rivets and bands must also be of stainless austenitic steel.
Extensive advice about the qualities of stainless steel can be found in the following publications:

- Edelstahl rostfrei – Eigenschaften, Verwendung.
- Die Verarbeitung von Edelstahl rostfrei.
- DIBt, Zulassungsliste Bauteile und Verbindungsmittel aus nichtrostendem Stahl (Z. 30.44.1).

These publications can be ordered at: Informationsstelle Edelstahl Rostfrei
Postfach 10 22 05, 40013 Düsseldorf – Germany
telephone: 0049 30/829-504, fax: 0049 30/829-200/-231.

Additional information can be found e. g. in DIN 17440.

6 Aluminium

Aluminium covers itself with a tight, passivating oxide layer in the open air react in a similar manner as zinc or stainless austenitic steel. If this is mechanically damaged or removed with mordant, a spontaneous re-formation occurs when oxygen is present.

This oxide layer provides a secure protection of the metal under it from further oxidation and is also the reason for the outstanding weather resistance and durability as opposed to a large number of inorganic and organic substances.

This is why aluminium even resists aggressive industrial atmospheres as long as they are dry. With high relative humidities and large temperature changes, dew drops condense on the aluminium surface in which gases and salts can dissolve.

If these dew drops stay long enough on the surface, the oxide layer and the aluminium under it are attacked at these points. The aluminium is converted to aluminium hydroxide which marks the places of such corrosive attacks in the form of white blossoms.

If dust and soot is present, a light-, respectively dark-grey covering layer is formed. As this layer thickens, the corrosive attack finally is halted.

The natural oxide layer does not provide sufficient protection against corrosive attack in every case. Through anodisation, the protective layer can be increased.

In permanent contact with sea water, all aluminium alloys are attacked more or less severely. A number of magnesium or silicon containing aluminium alloys are, however, considered as sea-water resistant. Amongst these are AlMg₃, AlMg₄,₅Mn, AlMgSi₁. In marine atmospheres, an additional protective painting is recommended.

- At the contact point between steel and aluminium, corrosion on the aluminium occurs in the presence of an electrolyte. The combination of galvanised building components is, on the contrary, normally all right since zinc and aluminium are very close to each other in the chemical tension sequence. The contact between lead and aluminium must be avoided because of their large difference in the electrical tension sequence. This can be achieved by coatings such as bitumen.

- Aluminium and copper have an even larger difference from each other in the tension sequence. Therefore, their direct contact is especially critical and must definitely be avoided.

- Some insulation materials, e. g. calcium silicate, concrete and plaster, especially when wet, eat into aluminium. In this case, a barrier by coating or intermediate layer, such as plastic film or kraft paper, is absolutely needed.

- Fixing means for aluminium sheets should be of stainless austenitic steel.

Similar to corrosion-protected steel sheets with zinc or aluminium/zinc coatings, aluminised steel sheets are on the market which combine the surface properties of aluminium with the stability of the steel sheet.

7 Protection against corrosion

The standard directives for insulation work on industrial installations give the following information regarding the anti-corrosion needed:
For cold insulation, the object must be corrosion-protected (DIN 4140, edition 1996, chapter 6.2.2). Objects of metallic materials must be corrosion-protected (AGI Q 138 "Polyurethane (PUR) in-situ foam, water/CO\textsubscript{2}-blown, for thermal and cold insulations in industrial installations – Properties, fabrication, execution of insulation systems", chapter 5.4).

With objects made of e. g. stainless austenitic steel or copper, it must be checked in each individual case whether or not corrosion protection can be dispensed with (AGI Q 03 "Insulation work on industrial installations – Execution of thermal and cold insulations", chapter 3.2.2).

To insulate an object, the anti-corrosion measures needed must have been completed (AGI Q 03, chapter 3.1).

Water in the insulant leads to corrosion damage. The ingress of moisture into the insulant is therefore to be prevented by appropriate means (AGI Q 03, chapter 3.2.2).

An intermediate layer may (...) be needed to prevent contact corrosion when different metals are combined (AGI Q 03, chapter 3.5.2).

The AGI working document Q 151 summarises anti-corrosion systems for non-alloyed, respectively low-alloyed steels and for stainless austenitic steels in tables 1 and 2:

### Table 4: Anti-corrosion-systems or non-alloyed / low-alloyed steels

Source: AGI working document Q 151, edition 01/1991

<table>
<thead>
<tr>
<th>Surface temperature of the object</th>
<th>Total system</th>
<th>Surface preparation acc. DIN 55928 part 4, standard cleanliness</th>
<th>Metal coating</th>
<th>Set layer thickness</th>
<th>Fundamental coating</th>
<th>Set layer thickness</th>
<th>Final coating</th>
<th>Set layer thickness</th>
<th>Complete system</th>
<th>Set layer thickness</th>
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<tr>
<td>No.</td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Spray galvanisation</td>
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<td>1.2</td>
<td>Sa 2 ½</td>
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<td>-</td>
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<td>Zinc dust</td>
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<td>Epoxid resin, two components (EP)</td>
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<td>160</td>
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<td>1.3</td>
<td>Sa 2 ½</td>
<td>-</td>
<td>-</td>
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<td>Polyurethane, two components (PUR)</td>
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<td>1.4</td>
<td>Sa 2 ½</td>
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<td>-</td>
<td>Epoxid resin, two components (EP)</td>
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<td>80</td>
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<td>160</td>
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<td>Sa 2 ½</td>
<td>-</td>
<td>-</td>
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<td>Zinc dust</td>
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<td>Polyurethane, two components (PUR)</td>
<td>Ironmica</td>
<td>80</td>
<td>160</td>
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<tr>
<td>+140 up to +450</td>
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<td>1.6</td>
<td>Sa 2 ½</td>
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<td>1.7</td>
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<td>-</td>
<td>-</td>
<td>Vinlychloride-Copolymerisate (PVC)</td>
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<td>Ironmica</td>
<td>80</td>
<td>160</td>
</tr>
</tbody>
</table>

1) If blasting is not possible due to service conditions, the following anti-corrosion systems are possible. Attention: The corrosion protection is diminished!
Table 5: Anti-corrosion systems for stainless austenitic steels

Source: AGI working document Q 151, edition 01/1991

<table>
<thead>
<tr>
<th>Surface temperature of the object °C</th>
<th>Total system No.</th>
<th>Prior to mounting the object</th>
<th>After assembly of the object</th>
<th>Total system Set layer thickness</th>
<th>Fundamental coating</th>
<th>Final coating</th>
<th>Total system Set layer thickness</th>
<th>µm</th>
<th>µm</th>
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</thead>
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<tr>
<td>-80 up to +120</td>
<td>2.1</td>
<td>Air blasting, mordant</td>
<td>Polyurethane, two compo-</td>
<td>Zinc phosphate</td>
<td>80</td>
<td>Polyurethane, two compo-</td>
<td>Iron-mica</td>
<td>80</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>Air blasting, mordant</td>
<td>Epoxid resin, two compo-</td>
<td>Zinc phosphate</td>
<td>80</td>
<td>Epoxid resin, two compo-</td>
<td>Iron-mica</td>
<td>80</td>
<td>160</td>
</tr>
</tbody>
</table>

Note: For insulated objects, two layers are considered sufficient according to the above tables. DIN 55928 "Corrosion protection of steel works through layers and coatings" requires three layers.
This FESI Document provides a general discussion of the technical issues mentioned therein. It does not replace detailed calculations and assessments of prevailing physical conditions in complicated building tasks. Readers are therefore advised to seek assistance from their technical advisory bodies in case of complicated and/or complex questions.

Other FESI Documents:

01: Insulation work on industrial plant – Ancillary work calculation  
(September 1986)

02: Rules for carrying out thermal insulation work (working temperature higher than ambient temperature)  
(June 1988)

03: Rules for carrying out thermal insulation work (working temperature lower than ambient temperature)  
(January 1993)

04: Working manual: System for measurement and recording for industrial insulation cladding)  
(February 1995)

05: Problems associated with the warranty of specified surface temperatures  
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06: High profitability through ecologically based insulation thicknesses  
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07: Heat insulation of refrigerated premises and buildings – Technical clauses  
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