FIELD TESTS ON THERMALLY SPRAYED ZINC-(ALUMINIUM)-COATINGS ON STEEL

FELDUNTERSUCHUNGEN AN THERMISCH GESPRITZTEN ZINK-(ALUMINIUM)-ÜBERZÜGEN AUF STAHL

EXAMENS EN EXTÉRIEUR DE REVÊTEMENTS ZINC-(ALUMINIUM) THERMO VAPORISÉS SUR ACIER

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SUMMARY

To estimate the corrosion protective effect of zinc spray coatings, produced by means of modern technologies in comparison with hot-dip galvanised coatings, tests were conducted under a variety of test conditions. ZnAl 15 spray coatings were also examined to obtain a direct comparison with frequently observed improved corrosion resistance of hot-dipped aluminium containing zinc coatings.

The investigations show, that using modern spraying techniques an improved corrosion resistance of zinc-sprayed coatings is possible to achieve. In a lot of media it can be selected equally between zinc sprayed and hot-dip galvanized coatings. Furthermore, it was also revealed that, in many situations, ZnAl 15 spray coatings produce a considerably improved corrosion resistance than zinc coatings.

ZUSAMMENFASSUNG

Zur Beurteilung der verbesserten Korrosionsschutzwirkung von mit modernen Techniken aufgebrachten Zinkspritzüberzügen im Vergleich zur Feuerverzinkung wurden in einer Vielzahl baupraktischer Medien Versuche durchgeführt. Zusätzlich wurden ZnAl 15-Spritzüberzüge untersucht, um die vielfach beobachtete verbesserte Schutzwirkung von aluminiumhaltigen Zinkschmelztauchüberzügen im direkten Vergleich überprüfen zu können.

Anhand der durchgeführten Untersuchungen wird deutlich, daß mit modernen Spritztechniken durchaus Spritzüberzüge mit einer verbesserten Korrosionsschutzwirkung hergestellt werden können als mit herkömmlichen Verfahren. In einer Vielzahl von Medien kann durchaus gleichberechtigt zwischen einer Feuerverzinkung und einer Spritzverzinkung gewählt werden. Darüberhinaus konnte gezeigt werden, daß aluminiumhaltige Zinkspritzüberzüge vielfach eine deutlich bessere Korrosionsschutzwirkung aufweisen als Zinküberzüge.

RESUME

Pour apprécier l'amélioration de la résistance à la corrosion de revêtements de zinc appliqués par des techniques modernes de projection par rapport à la galvanisation à chaud, des essais ont été effectués sur différents supports expérimentaux. Des revêtements par projection ZnAl 15 ont été en outre examinés afin de vérifier par comparaison directe l'amélioration maintes fois observée de la résistance à la corrosion de revêtement de zinc par projection contenant de l'aluminium.

Les examens réalisés montrent clairement que la mise en œuvre de techniques modernes de projection permet d'obtenir des revêtements par projection bien plus résistants à la corrosion qu'avec des procédés traditionnels. Sur plusieurs supports, il est possible de choisir indifféremment entre une galvanisation à chaud et un revêtement de zinc par projection. Il a été de plus démontré que les revêtement de zinc par projection contenant de l'aluminium présentent une résistance à la corrosion nettement supérieure à celle des revêtements de zinc.

KEYWORDS: Corrosion, thermal spraying, zinc, zinc-aluminium, aluminium, galvanised steel, coatings.

1 INTRODUCTION

Thermal spraying is a commonly used method of corrosion protection by spraying zinc on steel. In civil engineering, however, hot-dip galvanising is more commonly used for corrosion protection purposes [Johnen, 1981; Hoff, 1997; Oeteren, 1980; Smolka, 1985].

When comparing these two methods, it is assumed that the corrosion protective effect of hot-dip galvanised coatings is better than that of thermally sprayed coatings due to the higher porosity of the latter. Therefore, in the case of spray coatings, an additional organic coating is usually required [DIN EN 22063, 1994; Schulz, 1996]. Nevertheless, modern state-of-the-art technology is able to produce spray coatings with a improved corrosion protection effect [Lester et al., 1995].

In comparison with hot-dip galvanising, metallising reveals numerous advantages: On-site metallisation can be used for large components. Maintenance of corrosion protection surfaces can easily be carried out. In addition, when thermal spraying is used, there is no risk of defects occurring, such as cracks and warping.

Zinc coatings are known to provide good corrosion protection for steel structures under various conditions. However, with the demand for a longer service life in civil engineering structures, use of non-zinc coating materials is becoming increasingly popular. Good results are obtained using aluminium containing zinc coatings. Hot-dipped coatings with 5 Wt.-% or 55 Wt.-% aluminium are commonly used. But aluminium containing coating baths cannot be used for batch galvanising [Nürnberger, 1995]. An advantage of metallising is that it is possible to produce ZnAl-coatings with different aluminium contents.

When zinc is alloyed with aluminium, the corrosion behaviour tends to become more similar to aluminium. At higher aluminium content levels, lower overall attack and increased sensitivity to pitting can be observed. Zinc and zinc-aluminium coatings with smaller amounts of aluminium provide cathodic protection to steel if the coating is partially damaged, removed (e.g. cutting edges) or dissolved [Jailloux et al., 1996; Johnsson et al., 1989; Johnsson et al., 1983; Nagasaka et al., 1985; Schulz et al., 1992].

2 THERMAL SPRAYING

For thermal spraying, the spraying material is melted in a heat source (e.g. fuel gas, electric arc). The molten droplets are then propelled by compressed air and ejected at high velocity onto the substrate to form a coating. The quality of the coating depends on various factors, e.g. heat source type, spraying material, spraying velocity, environmental conditions, temperature of the particles to be sprayed and surface conditions. Adhesion of the metallic coating is based on mechanical action, adhesion, diffusion, chemical bonding and electrostatic forces [Brandl, 1995; Linde AG, 1993; Schulz, 1995; Steffens et al., 1992].

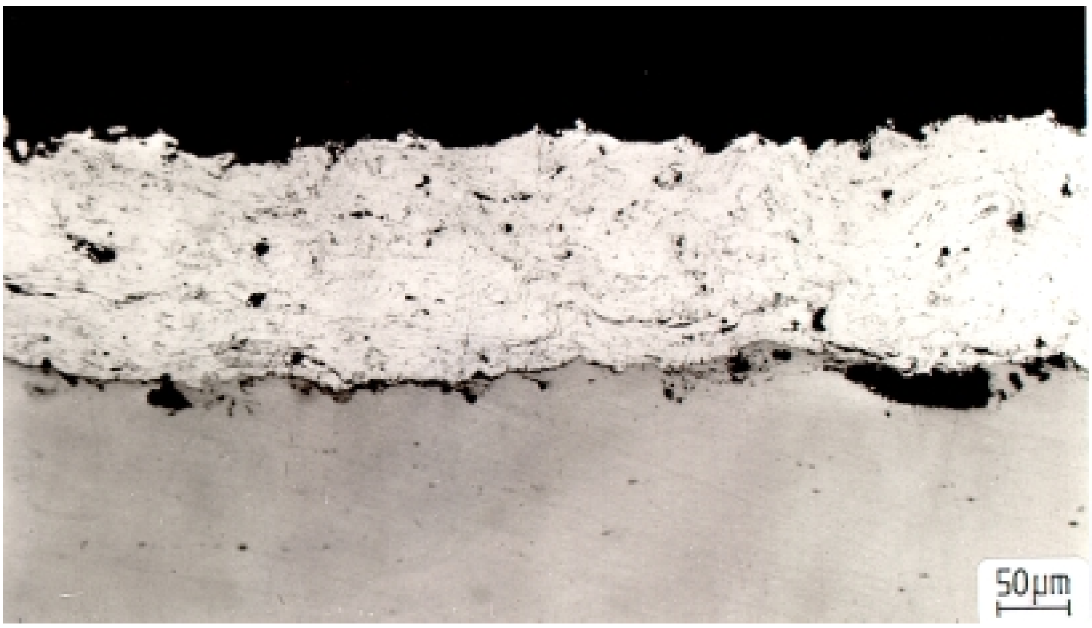

Fig. 1. *Cross section: Arc sprayed zinc coating.*

For corrosion protection with zinc or zinc-aluminium, electric arc or flame spraying is commonly used. Fig. 1 shows a cross section of a typical arc sprayed zinc coating. For comparison purposes, a cross section of a typical hot-dip galvanised coating is pictured in Fig. 2.

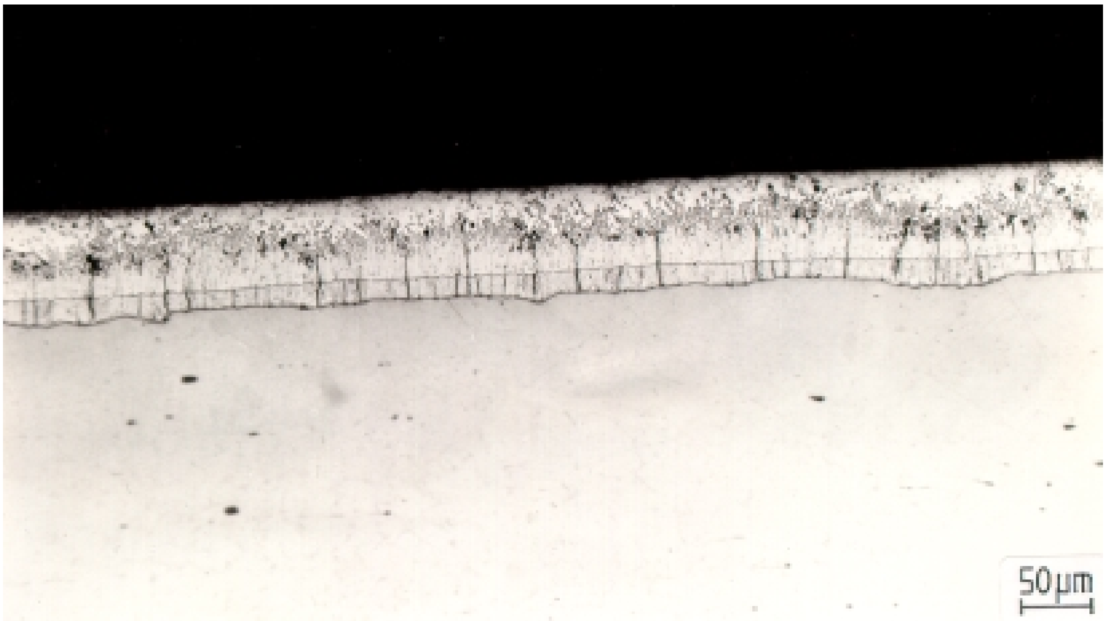

Fig. 2. *Cross section: Hot-dip galvanised coating.*

2.1 Arc spraying

In the arc spraying process, two wire electrodes are automatically fed to the arc zone. The initiated arc between the wire electrodes melts the spraying material (Fig. 3). This process is limited to the use of electrically conducting wires. Under atmospheric conditions, the molten sprayed particles can oxidise depending on the oxygen-affinity of the spraying material. This can result in a more inhomogeneous coating structure, reduced adhesion and/or diminished corrosion resistance. To minimize the oxide formation, it is necessary to use an inert gas or a vacuum chamber.

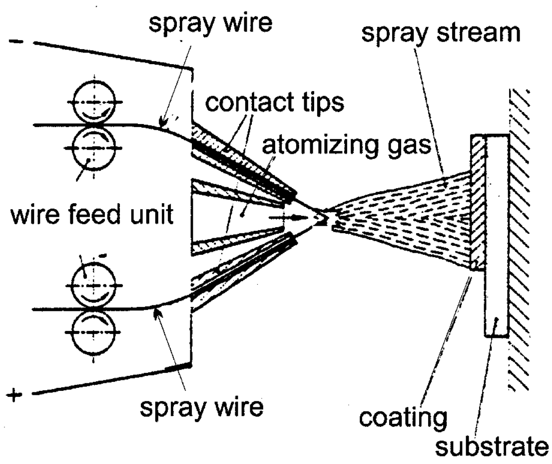

Fig. 3. *Principle of arc spraying*

2.2 Flame spraying

In this process the spraying material is melted in an oxy-fuel-flame and propelled towards the substrate by the expanding gas fuel (Fig. 4). If necessary, atomising air can be blasted in so as to accelerate the spray stream.

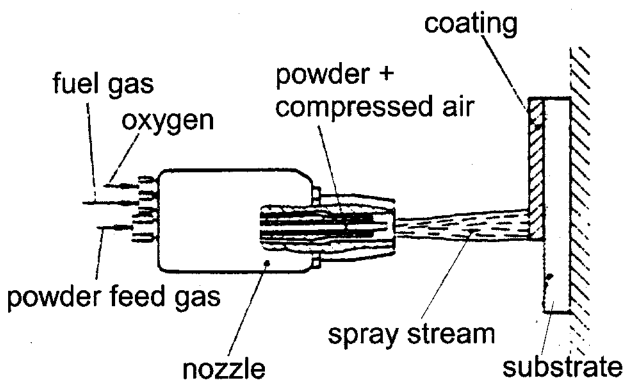

Fig. 4. *Principle of high velocity flame spraying [DIN EN 657, 1994]*

3 EXPOSURE TESTS

Zinc and zinc-aluminium coatings have been tested in a multitude of different atmospheres and media:

- atmosphere
  - rural atmosphere (Stuttgart/FMPA)
  - industrial atmosphere (Duisburg)
  - marine atmosphere (Helgoland)
- humidity chamber (100% rel. humidity, 21°C)
- indoor swimming bath
- sea water (Helgoland)
  - splash zone
  - tidal zone
  - immersion zone
- sandy soil (no salt content)
- concrete (outdoor storage)
  - alkaline concrete
  - chloride contaminated concrete (3% Cl^- / cement weight)
  - carbonated concrete
- gypsum (outdoor storage)
- wet insulating material (rock wool)

Tested samples:

Galvanising process	Spraying material	Average coating thickness	Coating density	Remarks
arc-spraying	zinc	151 µm	7,15 g/cm³	LBS/Zn
arc-spraying	ZnAl 15	154 µm	5,72 g/cm³	LBS/ZnAl
flame-spraying	zinc	138 µm	7,15 g/cm³	HFS/Zn
flame-spraying	ZnAl 15	139 µm	5,72 g/cm³	HFS/ZnAl
hot-dip galvanising		71 µm	7,20 g/cm³	FZ

Table 1. *Tested samples*

<u>Evaluation</u>

After an exposure period of up to 3 years, the corrosion products were removed from the samples by pickling in saturated ammoniumacetate solution and then weighed. Changes in weight are translated into loss of thickness by using the following equation:

$$\Delta d = \frac{\Delta m}{\rho * A} \qquad (1)$$

Δd:	change in coating thickness
Δm:	change in mass
A:	coating area
ρ:	coating density

In the following a thickness increase is called "negative corrosion loss".

3.1 Results after exposure to atmospheric conditions

After 3 years' exposure, ZnAl 15 coatings show an increase or a smaller loss in thickness than hot dip galvanising or zinc metallising in all sorts of atmospheres (rural, industrial and marine atmospheres, humidity chambers and indoor swimming bath); refer to Fig. 5.

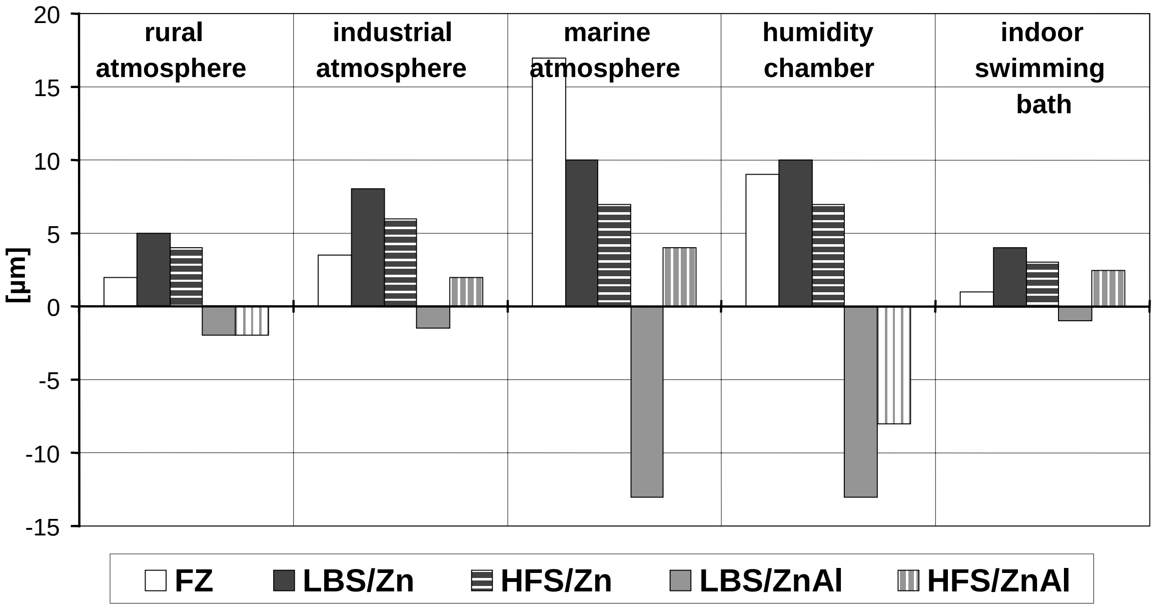

Fig. 5. *Change in thickness in different atmospheres after 3 years´ exposure.*

For zinc (hot-dip galvanised or metallised), the loss of thickness is in the order of rural to industrial to marine atmospheres. Because of the relative small loss of thickness under atmospheric conditions, the changes in thickness of the various zinc-coatings can be grouped in the same order of magnitude.

3.2 Results after exposure in sea water

It is clear that ZnAl 15 and Zinc react differently in sea water. The corrosion resistance of ZnAl 15 is obviously superiour to thoes of pure zinc (Fig. 6). In the tidal zone and immersion zone, zinc coatings show a significant loss of thickness. Owing to the thinner coating, the hot dip galvanised coating is nearly completely dissolved after 3 years of exposure. The results in the splash-zone are similar to those in the marine atmosphere.

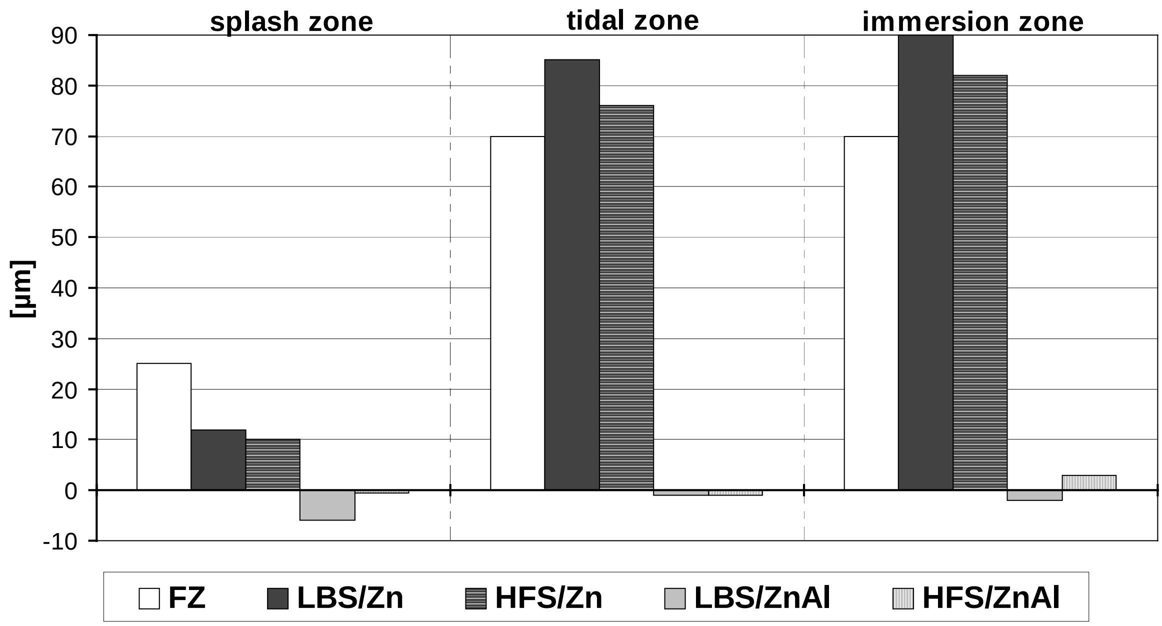

Fig. 6. *Change in thickness in sea water after 3 years of exposure*

3.3 Results after exposure in concrete

The results of contact with concrete show that ZnAl 15 is less resistant to corrosion because of the reduced alkali resistance due to the aluminium content. In highly chloride-contaminated concrete, corrosion loss of zinc coatings (min. 75 µm) is also significant (Fig. 7).

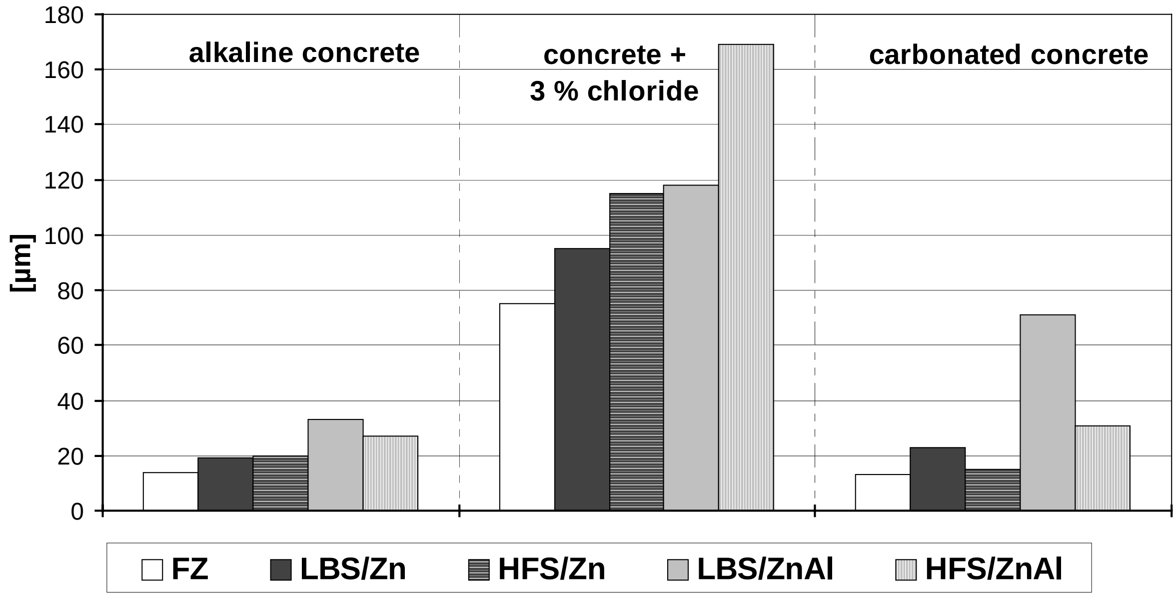

Fig. 7. *Change in thickness after 3 years´ exposure to concrete (outdoor storage).*

3.4 Results after exposure to sandy soil, gypsum and wet insulating material

After three years of exposure to sandy soil, gypsum (outdoor storage) and moist insulating material (rock wool), ZnAl 15 proves to be more corrosion resistant than zinc (Fig. 8). This behaviour is most obvious after exposure to gypsum and wet insulating material. In the case of zinc coatings (hot-dip galvanised and metallised), the thickness loss is in the range of at least 52 µm. Here, it is remarkable that the hot-dip galvanised coating shows the most severe thickness loss. In contrast, the ZnAl 15 coatings show a significant thickness increase.

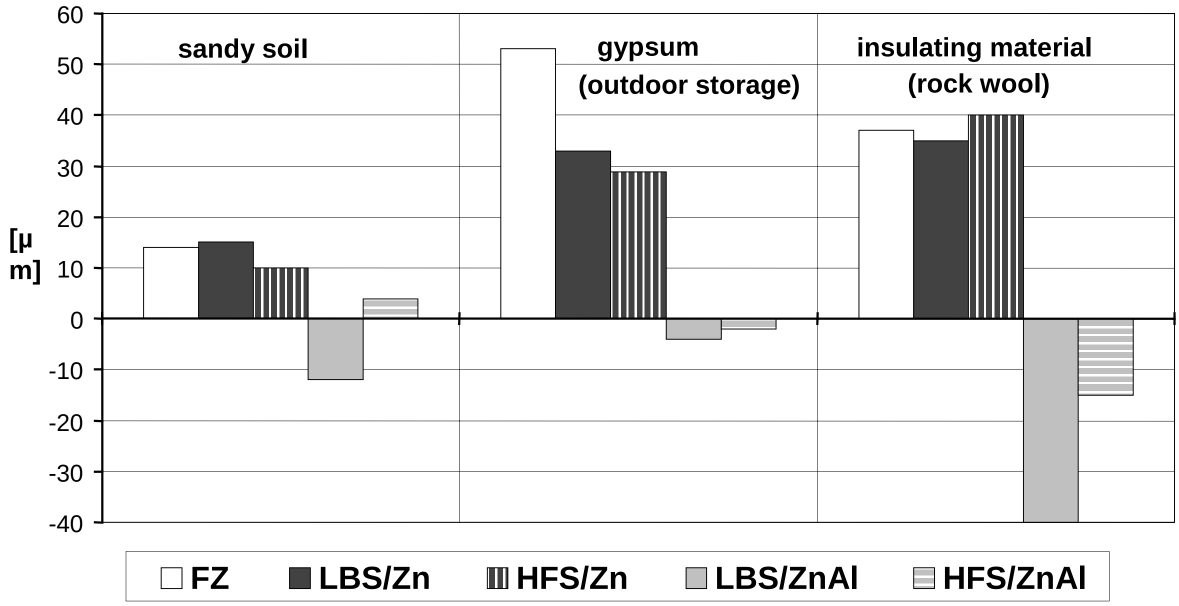

Fig. 8. *Change in thickness in sandy soil, gypsum (outdoor storage) and wet insulating materials (rock wool) after 3 years' exposure.*

4 DISCUSSION

A comparison of the corrosion behaviour of the different coating systems (coating material, coating procedure) is presented in Table 2.

Estimating the corrosion rate the thickness loss value after 3 year´s exposure is divided by 3. In the case of thickness increase the corrosion rate is indicated as "0".

Sprayed coatings (especially ZnAl 15) in some cases proved to be thicker after exposure even after cleaning and pickling. The explanation of the phenomen is "inner corrosion", meaning an increase of porosity due to deposition of corrosion products in the pores of the coating.

	LBS/Zn	**LBS/ ZnAl**	**HFS/ Zn**	**HFS/ ZnAl**	**FZ**
rural atmosphere (Stuttgart)					
industrial atmosphere (Duisburg)					
marine atmosphere (Helgoland)					
humidity chamber (100% rel.H., 21°C)					
indoor swimming bath					
splash zone (Helgoland)					
tidal zone (Helgoland)					
immersion zone (Helgoland)					
sandy soil					
alkaline concrete (outdoor storage)					
carbonated concrete (outdoor storage)					
chloride cont. concrete (3 wt.-% Cl^- rel. to cement content, outdoor storage)					
gypsum (outdoor storage)					
wet insulating material (rock wool)					

corrosion rate: <1µm/a

corrosion rate: 1-5 µm/a

corrosion rate: 5-15 µm/a

corrosion rate: >15 µm/a

Table 2. *Corrosion rates of metallic coatings after three years' exposure.[Zecho, 1999]*

The real "corrosion loss" in such cases had to consider this by quantitative analysis of porosity before and after exposure by means of image analysis on metallographically preparated cross sections of the samples. But it is to notice, that there exist no clear correlation between exposure period and thickness increase. Therefore, determining the remaining metal content of the coating after exposure would supply more exact results in order to be able to estimate the remaining corrosion protective effect of the coating [Zecho, 1999].

Comparison: Hot-dip galvanised vs. Thermally sprayed zinc coatings

A similar magnitude of thickness loss is revealed for the corrosion rates of hot-dip galvanised and thermally sprayed zinc coatings. There is no significant difference between the corrosion behaviour of hot-dipped and metallised zinc coatings. This shows that modern state-of-the-art technology is able to produce spray coatings with a improved corrosion protection effect.

Effect of spraying methods on corrosion loss

The spraying methods used here (electric arc spraying, high velocity flame spraying) do not have any significant effect on the corrosion loss of the zinc- and ZnAl 15 coatings. Only the thickness increase of the ZnAl 15 coatings tends to be higher in the case of electric arc spraying.

Effect of coating materials on corrosion loss

As far as coating materials are concerned, it can be seen, that in several media, ZnAl 15 displays different corrosion behaviour when compared with zinc.

Under mild conditions such as in a rural, industrial and marine atmosphere as well as in the humidity chamber and splash-zone, ZnAl 15 shows less corrosion loss than zinc and sometimes a thickness increase. However, it should be noted that in the above-mentioned atmospheres, the corrosion loss of zinc is also low.

In sea-water (tidal zone / immersion zone), ZnAl 15 shows significantly lower corrosion rates than zinc (zinc-sprayed and hot-dip galvanised coatings). The corrosion loss in the case of the zinc coatings (min. 70 µm) after three years' exposure is very high. ZnAl 15, on the other hand, shows a thickness increase. Similar behaviour can be observed in gypsum and wet insulating materials.

As expected, the corrosion rate of ZnAl 15 in concrete (alkaline medium) is considerably higher than that of zinc. In chloride-contaminated concrete, the corrosion loss of zinc coating is also extremely high (max 115 µm) but the corrosion loss of ZnAl 15 is higher still (up to 170 µm).

Summary

The investigations show that when exposed to various atmospheric conditions, zinc-sprayed and ZnAl 15 sprayed coatings as well as hot-dip galvanised coatings can be recommended. ZnAl 15 coatings should be prefered in sea-water as well as in gypsum and wet insulating materials. In these media, zinc cannot be used without additional corrosion protection (e.g. organic coating).

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