

CORROSION PROTECTION OF STEEL IN SOIL BY SPRAYED ZINC-ALUMINIUM COATINGS

KORROSIONSSCHUTZ FÜR STAHL IN BÖDEN DURCH ZINK-ALUMINIUM SPRITZSCHICHTEN

PROTECTION CONTRE LA CORROSION DE L'ACIER ENTERRE PAR UN REVETEMENT METALLISE DE ZINC-ALUMINIUM

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SUMMARY

Recently, the use of sprayed zinc-aluminium (ZnAl) coatings has been proposed as a protective measure for steel reinforcing strips in Reinforced Earth structures for aggressive soil. Based on long-term tests (20 years) and laboratory experiments, the paper discusses the corrosion behavior of this type of coating. In the long-term tests, protection by ZnAl proves to be superior compared to galvanizing.

ZUSAMMENFASSUNG

Neuerdings wird der Einsatz von Zink-Aluminium Spritzschichten als Korrosionsschutz für Stahlbänder für Bewehrte Erde in aggressiven Böden vorgeschlagen. Die Arbeit diskutiert das Korrosionsverhalten anhand von Langzeitversuchen (20 Jahre) und Laborversuchen. Im Vergleich zu Feuerverzinkungsschichten und reinen Zink-Spritzschichten erweist sich ZnAl in Langzeitversuchen als überlegen.

RESUME

La métallisation par projection à chaud de zinc-aluminium a récemment été présentée comme revêtement de protection des armatures en acier des structures en Terre Armée pour les sols agressifs. A partir d'essais de longue durée (20 ans) et d'essais en laboratoire, cet article examine le comportement à la corrosion de ce type de revêtement. Au cours des essais de longue durée, il a été établi que la protection par le ZnAl est supérieure à la galvanisation.

KEYWORDS: corrosion, underground corrosion, zinc, zinc-aluminium, aluminium, galvanized steel, metallization, soil

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1 CORROSION PROTECTION BY ZINC AND ZINC/ALUMINIUM

One of the most commonly used protective measures for steel in underground structures is hot dip galvanizing. The coating obtained is sufficiently resistant in moderately aggressive soils and provides additional cathodic protection to the steel if the coating is partially damaged, removed (e.g. cutting edges) or dissolved. According to German specifications the coating thickness should be of 85-100 μm , assuring a life time of about 100 years of the structure, if the soil meets certain conditions (resistivity, suitable pH, limited salt-content [Nürnberg, 1991 (1); Bundesminister für Verkehr, 1985 (2)]).

Despite the fact that zinc is among the less noble metals, zinc dissolution is slow because of corrosion by-products forming a protective layer. In soil, formation of protective layers and a resulting significant decrease in corrosion are usually observed after a period of a few months. Bare steel corrodes with a rate three to seven times higher [Nürnberg, 1988 (6)].

In more aggressive soils with higher salt content, the overall corrosion rates are higher and the type of attack may change from uniform to local corrosion with severe pitting, which is especially unfavorable for structural components designed to bear mechanical loads. Therefore, zinc coatings are not recommendable for use in such soils [Nürnberg, 1988 (6); Romanoff, 1957 (17)]. Some alloys, like ZnAl (sprayed and as hot dip coating), tested in the atmosphere, in soils and in salt-spraying tests proved to have a corrosion resistance superior to pure zinc [Johnsson, 1983 (10); Allegra, Dutton, 1986 (13); Nünninghoff, Fischer, 1985 (11); Schulz, Eisengräber, Gorgas, 1992 (15), Nünninghoff, Scepanski, 1987 (14)]. Table 1 gives some results on atmospheric and underground corrosion of galvanized, aluminized and ZnAl-coated steel (Galvalume: 55% Al, 43.5 % Zn, 1.6% Si).

	rural atmosphere	urban atmosphere	marine atmosphere	industrial atmosphere	different soils
hot dip aluminized		0,2 $\mu\text{m}/\text{year}$ (after 8 years)	0,8 $\mu\text{m}/\text{year}$ (after 8 years)	0,5 $\mu\text{m}/\text{year}$ (after 8 years)	
	0,1 $\mu\text{m}/\text{year}$ (after 13 years)		0,2 $\mu\text{m}/\text{year}$ (after 13 years)	0,1 $\mu\text{m}/\text{year}$ (after 13 years)	0,6 $\text{g}/\text{m}^2 \text{ year}$ (after 8 years)
Galvalume (55%Al/43,5 %Zn/1,6%Si)		0,2 $\mu\text{m}/\text{year}$ (after 8 years)	0,4 $\mu\text{m}/\text{year}$ (after 8 years)	0,5 $\mu\text{m}/\text{year}$ (after 8 years)	23,5 $\text{g}/\text{m}^2 \text{ year}$ (after 2 years)
	0,3 $\mu\text{m}/\text{year}$ (after 13 years)		0,6 $\mu\text{m}/\text{year}$ (after 13 years)	0,3 $\mu\text{m}/\text{year}$ (after 13 years)	4,4 $\text{g}/\text{m}^2 \text{ year}$ (after 8 years)
thermal sprayed zinc					14 $\mu\text{m}/\text{year}$ (after 19 years)
hot dip galvanized		1,5 $\mu\text{m}/\text{year}$ (after 2 years)	2,2 $\mu\text{m}/\text{year}$ (after 2 years)	4,6 $\mu\text{m}/\text{year}$ (after 2 years)	175 $\text{g}/\text{m}^2 \text{ year}$ (after 2 years)
	1,1 $\mu\text{m}/\text{year}$ (after 13 years)		1,4 $\mu\text{m}/\text{year}$ (after 12 years)	1,9 $\mu\text{m}/\text{year}$ (after 9 years)	19,8 $\text{g}/\text{m}^2 \text{ year}$ (after 8 years)
					15 $\mu\text{m}/\text{year}$ (after 19 years)

Table 1: [Johnsson, Kucera, 1988; Johnsson, Kucera, 1982; Johnsson, 1983; Allegra, Dutton, Homayon, 1986; Jailloux, 1996]

The corrosion resistance of the ZnAl in atmosphere and also in aggressive soils, obviously superior to those of both pure components (zinc and aluminium) is supposed to be the result of synergistic interactions of the corrosion mechanisms of the two metals, which are not completely understood at the time.

About half a century ago, the application of molten metals by spraying has been developed as an alternative to hot dip coating. These coatings consist of small droplets of metal, solidified in contact with the cold support and giving a certain porosity to the cover. The results to be discussed in this paper refer to „DUNOIS“ (trade name ZINACOR®850), a sprayed ZnAl coating containing 15 wt.-% aluminium and 85 wt.-% zinc.

2 EXPOSURE TESTS

In France different zinc-based coatings have been tested in selected soils (tab.2), in boxes sealed with plastic sheet. After exposure up to 19,4 years, the samples were cleaned of corrosion by-products by pickling in saturated ammoniumacetate solution and weighed. Losses in weight are translated into loss of thickness by using equation 1:

$$\Delta d [\text{cm}] = \frac{\Delta m [\text{g}]}{\delta [\text{g} / \text{cm}^3] \times A [\text{cm}^2]} \quad (1)$$

Δd : change in thickness

Δm : change in mass

A: area of coating

δ : density: δ (zinc) = 7,1 g/cm³ / δ (ZnAl) = 5,8 g/cm³

Evaluation of the 19,4 years old samples was performed both at the FMFA and LCPC* for control with results being in good agreement.

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Tested samples:

- AG80: hot dip galvanized steel; coating thickness about 80 μm
- MZ: zinc metallized (thermal sprayed); coating thickness about 80 μm
- MZA: Dunois metallized (thermal sprayed); coating thickness about 80 μm

Soils:

	pH	resistivity [Ωcm]	water content [wt.-%]	Cl ⁻ [ppm]	SO ₄ ²⁻ [ppm]
A	7,35	463	10	41	4671
B	7,9	2075	10	10	320
C	7	1050	3	547	324
D	7,85	3950	11	8	41
E	7,8	1825	7	23	156

Table 2: Parameters of soils

The resistivity was measured in standard conditions, i.e. after one hour of saturation with distilled water. The salt content was determined by an elution analysis by using an eluate of 200g soil and 200 g distilled water.

2.1 Results of the container tests

The loss of thickness vs. exposure time is given in figures 1 to 5.

Dunois (ZnAl) shows a smaller loss in thickness than hot dip galvanizing or zinc metallizing in all sorts of soils. In the most aggressive soil A, the different behaviour of ZnAl and Zn is most obvious. In this soil, the 80 μm zinc-coating, either hot dip galvanized or metallized, is completely dissolved after three and six years respectively, whereas the loss of thickness for Dunois

is less than 15 μm after nearly 20 years. This means a surface removal of less than 1 $\mu\text{m}/\text{year}$ (0,6 μm) for Dunois.

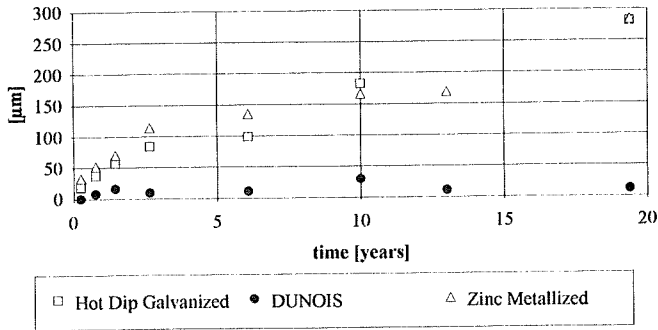


Fig. 1: Loss of thickness in soil A

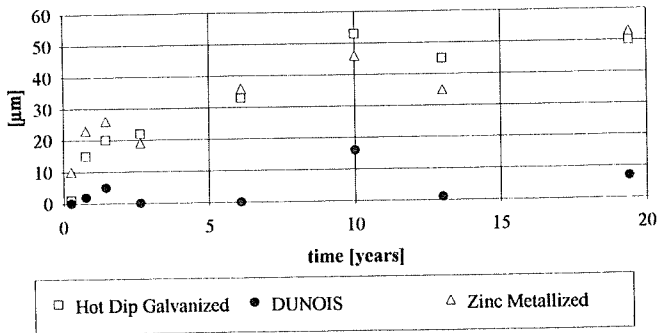


Fig. 2: Loss of thickness in soil B

The free corrosion potential of the Dunois-coated samples was found to be lower compared to pure zinc. In table 3, the free corrosion potentials vs. saturated calomel electrode after 19.4 years are given. The higher potentials (soils A and C) indicate an already dominating effect of bare steel.

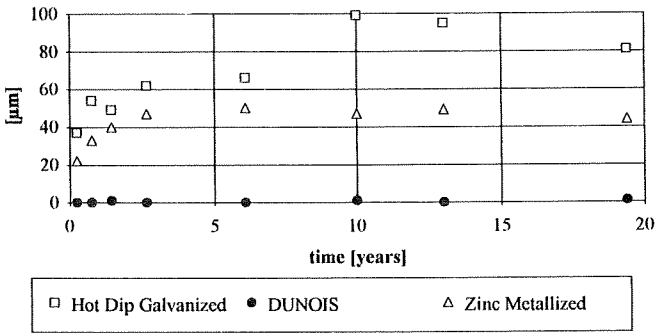


Fig. 3: Loss of thickness in soil C

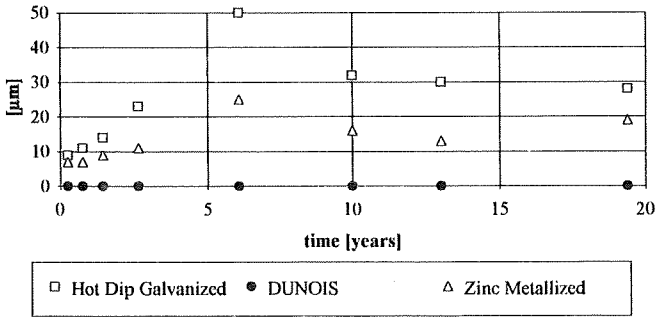


Fig. 4: Loss of thickness in soil D

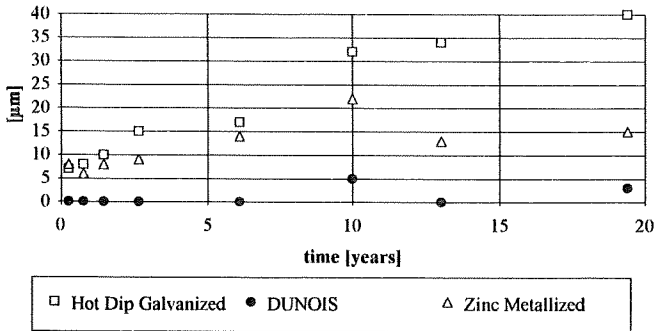


Fig. 5: Loss of thickness in soil E

	Soil A potential [mV/SCE]	Soil B potential [mV/SCE]	Soil C potential [mV/SCE]	Soil D potential [mV/SCE]	Soil E potential [mV/SCE]
AG80 (hot dip Zinc)	-622	-731	-608	-775	-855
MZ (sprayed Zn)	-542	-885	-628	-884	-857
MZA (Dunois)	-784	-905	-923	-885	-930

Table 3: free corrosion potentials after 19.4 years; measurements before removal of samples from the test-boxes

3 LABORATORY TESTS

3.1 Electrochemical tests

Electrochemical tests, such as corrosion potential/time-measurements and potentiodynamic polarization tests, have been performed on soil solutions, simulating the liquid phase of soil A used in the exposure tests. For "soil-solution A", 41 ppm chloride (added as NaCl) and 4761 ppm SO_4^{2-} (added as Na_2SO_4) were used. The tested specimens were isolated sprayed zinc and ZnAl coatings, pickled in 5% acetic acid for 3 minutes before measuring. Platinum was used as counter-electrode.

Fig. 6 shows the free corrosion potential vs. time for zinc, ZnAl and pure aluminium, measured in soil-solution A. The alloy potential is not significantly different from the pure zinc potential within a period of about 3 months. The potential of pure aluminium is always more positive.

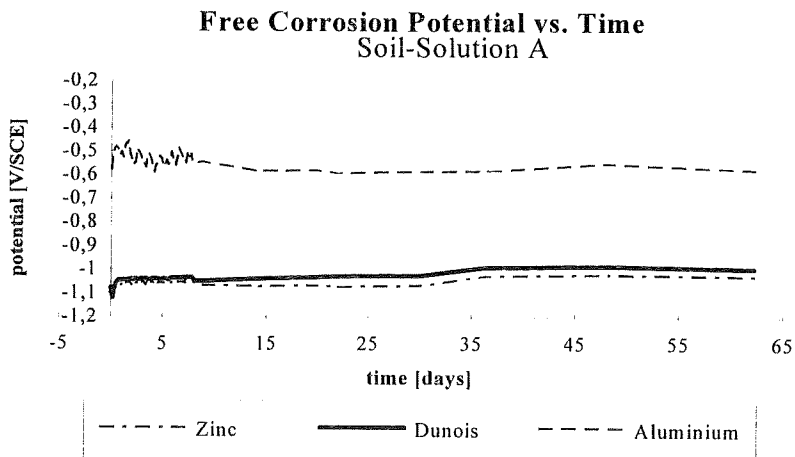


Fig. 6: Free corrosion potential vs. time

Current/potential plots measured in solutions exposed to air are given in figs. 7 and 8, indicating a zinc-like behavior of the Dunois coating far apart from the passive behaviour of pure aluminium with a pitting-induced increase of current at higher potentials (not included in the diagram). Plots measured in deaerated solutions are not significantly different, and so far do not allow an interpretation with respect to the kinetics of the cathodic reaction.

Current Density - Potential - Curves in Soil A (water saturated)

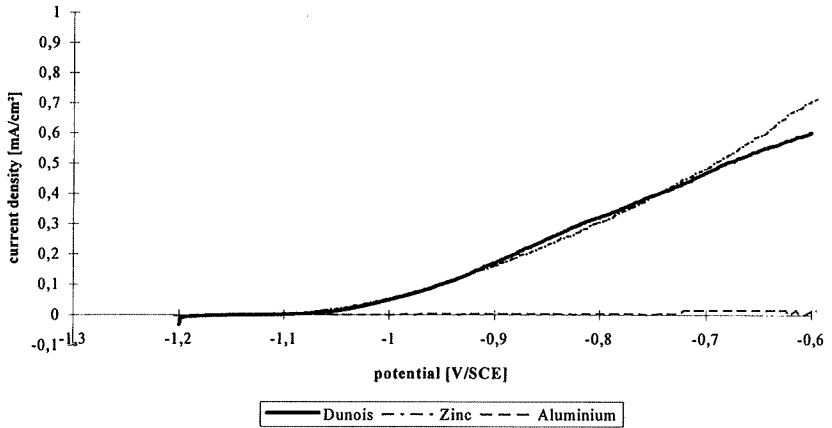


Fig. 7: Current/potential plot measured in soil A

Current Density - Potential - Curves in Soil-Solution A

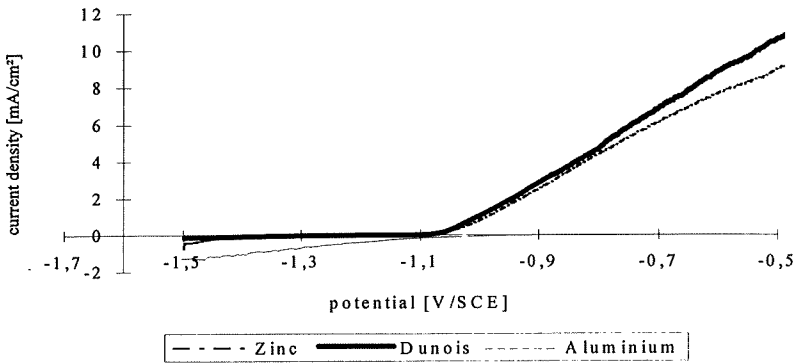


Fig. 8: Current/potential plot measured in soil-solution A

3.2 METALLOGRAPHIC AND CHEMICAL ANALYSIS

Fig. 9 shows a cross section of a ZnAl thermal sprayed coating with a thickness of about 150 μm . In fig. 10 and 11, Dunois-coatings (original thickness of 80 μm) are shown after 20 years of exposure in soils D and A. Soil D is the least aggressive, soil A amongst the most aggressive used in the exposure tests.

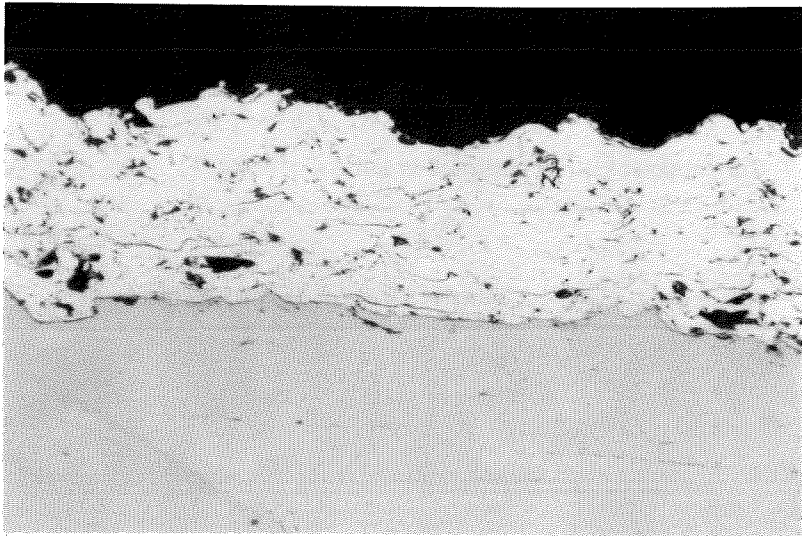


Fig. 9: New specimen

260x

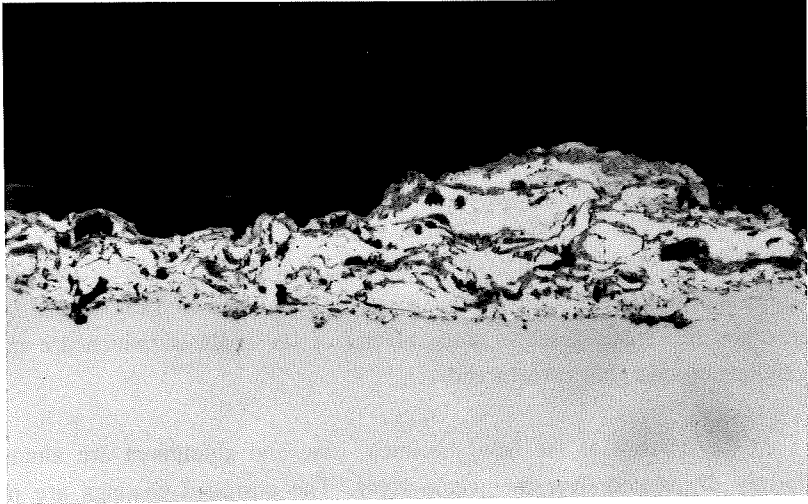


Fig. 10: Dunois after 20 Years of exposure in soil D

260x

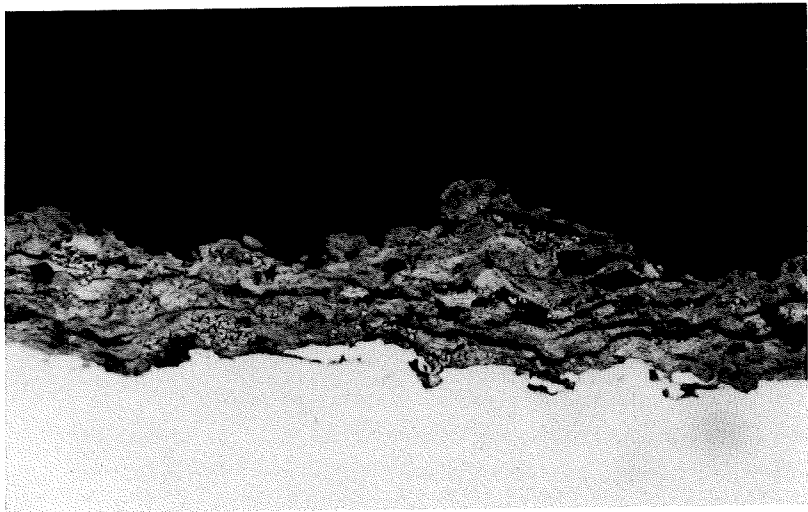


Fig. 11: Dunois after 20 Years of exposure in soil A

260x

While the original coating is relatively compact with a few pores, the corroded coating is changed in structure: porosity is higher and dark layers are visible around the metal droplets. This effect of "inner corrosion" is most obvious in fig. 11, where irregularly distributed dark layers of corrosion products are dominating. Nevertheless, the coating seems to be macroscopically nearly undamaged.

EDX-Analysis on sections of coatings have been carried out to analyze the zinc and aluminium distribution in "new" ZnAl and in Dunois-coatings after exposure. Table 4 shows some results of the analysis, which are not exactly quantitative, but reveal trends.

In the coating of the new specimen, zinc and aluminium are almost uniformly distributed over the whole layer. The corroded coatings are no longer homogeneous (see spot analysis results). There are regions containing nearly exclusively zinc. Besides, there are regions with a clearly lower zinc-content than in the new specimen. Conspicuous is the high oxygen-content where the zinc content is lowest. In chloride- and sulfate-containing soils, chlorine and sulfur are locally enriched in the regions with high oxygen concentration. After exposure to aggressive soil, zinc depletion of the whole layer is observed.

EDX-Analysis on some specimens of the electrochemical tests show, that after anodic polarization, an enrichment of aluminium can be found in the outer layer of the coating. X-ray-diffraction analysis shows very poorly crystallized species both in exposure- and laboratory-samples, not allowing a precise identification.

	Zinc [wt-%]	Aluminium [wt-%]	Oxygen [wt-%]	Chlorine [wt-%]	Sulfur [wt-%]
new coating (over- all)	79	19	2	/	/
	75	22	3	/	/
	78	20	2	/	/
	79	19	2	/	/
	76	20	4	/	/
	77	20	3	/	/
specimen after exposure in soil C (19.4 years; local)	94	5	1	/	/
	59	18	21	2	/
	29	26	44	1	/
specimen after exposure in soil A (19.4 years; local)	88	9	3	/	/
	55	21	23	/	1
	32	33	34	/	1
	44	8	44	/	4
specimen after exposure in soil A (19.4 years) (over- all)	38	26	34	/	2
	52	22	22	/	1
	42	23	33	/	2
	38	22	38	/	1
specimen after exposure in soil D (19.4 years) (over- all)	66	18	15	/	/
	60	19	21	/	/
	61	20	19	/	/
	54	21	25	/	/

Table 4: Some results of the EDX-Analysis

4 DISCUSSION

Regarding the criteria optical aspect (compactness, visible attack), gravimetrically determined thickness-loss and protection of the steel surface, exposure tests show that thermally sprayed ZnAl is evidently superior to pure sprayed zinc and galvanizing. Nevertheless, the layer changes with time in composition and structure. A certain loss of zinc (not so much in aluminium) and accumulation of oxygen-rich components within the whole layer is noticed. This "inner corrosion" - effect is specific to sprayed ZnAl. The protective properties are not affected by the phenomenon within the 20 years of exposure. A zinc-like behavior (see corrosion potential measurements) of DUNOIS and full protection of the steel can still be found even in the most aggressive soil, where pure zinc and galvanized coatings are completely corroded and the steel itself is attacked. An explanation has to be sought for in the combined effect of cathodic protection of aluminium-rich phases by selective corrosion of zinc, compact corrosion products and metallic inclusions acting as a diffusion-barrier and the buffering effect of Al and Zn-hydroxides. These effects can not be reproduced in short-time laboratory tests, where corrosion of the outer layer with enrichment of aluminium is the dominating effect, different from the slow and rather homogenous „inner“ corrosion observed in field tests. Regarding the practical aspects of corrosion protection of steel, the performance of ZnAl-coatings will be satisfactory in a large variety of soils. The protective properties after complete consumption of metal within the coating remains to be fully explained by future research.

5 REFERENCES

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