PITTING CORROSION ON MAGNESIUM ALLOYS : A COMPARATIVE STUDY OF FIELD DATA USING EXTREME VALUE STATISTICAL TECHNIQUES

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ABSTRACT

Galvanic corrosion of the magnesium alloys AZ91D and AM60B combined with different coatings on steel bolts was investigated in field corrosion tests carried out by Volvo Car Corporation. Light metals like magnesium and aluminum are prone to localized corrosion. The risk of perforation was of particular interest. Three circular plates of each alloy were mounted with steel bolts for each of four different types of bolt coating. The assemblies were placed in racks on three trucks in regular use in the area of Gothenburg, Sweden, for two years. Maximum pit depths were measured in eight sectors around the bolts at the end of the two-year period.

A newly developed Extreme Value methodology ([1]) was used to analyze the measurements. For the alloy AZ91D there were no systematic differences between the sectors or assemblies with the same treatments. Also for the AM60B there did not seem to be systematic differences between sectors. However, for AM60B there were statistically significant differences between assemblies with the same treatment for all coatings except for the yellow chromate zinc plating

Pairwise comparisons exhibited several differences between the coatings for the alloy AZ91D. In particular, the aluminum washer offered little protection in dirty environments, and the yellow chromate zinc plating had a significantly smaller risk of perforation, for material thickness exceeding 1.14 mm. When comparing the AZ91D and AM60B alloys, the yellow chromate zinc plating of AZ91D was significantly better at a 95 % confidence level, for maximum pit depth per plate exceeding 1.35 mm.

INTRODUCTION

Reduction of fuel consumption is becoming increasingly important as incentives and legal requirements are being sharpened all over the world. In Europe ACEA (Association des Constructeurs Européens d'Automobiles) promised the European Commission to reduce fuel consumption by 25 % from 1995 to 2008, to 140 g CO_2/km as an average CO_2 emission for the European car fleet. In 2012 the emissions are to be reduced by further 14 % to 120 g CO_2/km. In the US, fuel economy requirements are also becoming increasingly important because of governmental pressure to reduce dependence on imported oil. One way, amongst many others, is the reduction of vehicle mass where each kg means approximately an emission reduction of 0.12 g CO_2/km.

Aluminum as a lightweight material has been used for 20 years in Volvo cars and material knowledge and design restrictions are well known. Magnesium, however, has been used in many concept cars and is widely known as the lightest construction metal, but has up till now not been used in exterior applications in Volvo cars. Knowledge about its corrosion properties is to a large extent still in its cradle. Galvanic corrosion is a major obstacle for the use of magnesium in exterior components (see e.g. [2,3,4,5]).

One difficulty in applied corrosion science has been to find suitable objective evaluation methods, as the morphology and phase distribution of magnesium (and aluminum) casting alloys in the surface region is not homogeneous. Hence corrosion properties, in particular for galvanic corrosion, are influenced by surface factors which may be of the same order of magnitude as the evaluated sectors.

Weighing and weight loss offer no fine tuned comparisons or ways to judge and calculate the severity of the attack. Instead interest focus on extreme pit depths, which may lead to fatigue problems in loaded areas, leakages in housings etc. that can lead to warranty claims. Classical statistical methods such as t-tests and ANOVA techniques are not suitable for pit depth evaluation. On the contrary they may sometimes not be able to identify existing and important effects because important differences in the extreme tails of the distributions may be erroneously interpreted as a large but homogeneous scatter.

The approaches based on Extreme Value (EV) distributions have instead appeared as a successful model for maximum pit depths, see e.g. [6,7,8]. The use of these distributions are supported by two related basic properties:

1. The EV distribution is obtained as the only possible limit (under linear normalization) of the distribution of the maximum of an increasing number of independent and identically distributed random variables.

2. The EV distribution is the only one that is stable under change of block size, i.e. such that if maxima over smaller blocks have this type of distribution, then the distribution of maxima over bigger blocks is of the same type.

A statistical methodology intended as an engineering tool for the analysis of such data was proposed in [1]. This tool was used in the present analysis of the Volvo Car Corporation field test.

Other areas of interest where the extreme value approach is useful are all where penetrative corrosion is an issue, regardless of the material used. This includes e.g. hem flanges, brake pipes, fuel tanks, etc.

The experimental setup and the measurement methods are described in the next section. Then the statistical EV methods are introduced, followed by a presentation of the results. A final discussion and our conclusions are given at the end.

THE EXPERIMENT

EXPERIMENTAL SETUP - The test units used in the study consisted of assemblies of magnesium plates mounted with coated steel bolts according to the experimental setup in table 1. The specimen were fastened onto plastic panels (see Figure 1) in a rack under the chassis, close to the rear wheel (see Figure 2), on three trucks. The trucks were in line traffic use in a similar traffic environment, in the Gothenburg, Sweden, area.

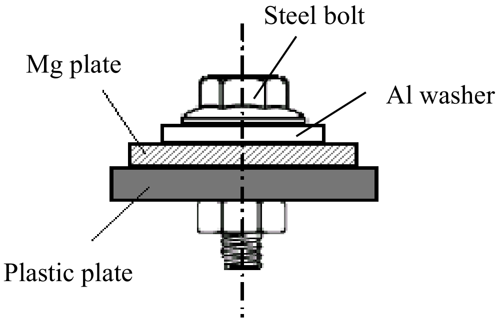


Figure 1: *Assembly of steel bolt/AA6016 washer and magnesium plate used in the field test.*

(a) *(b)*

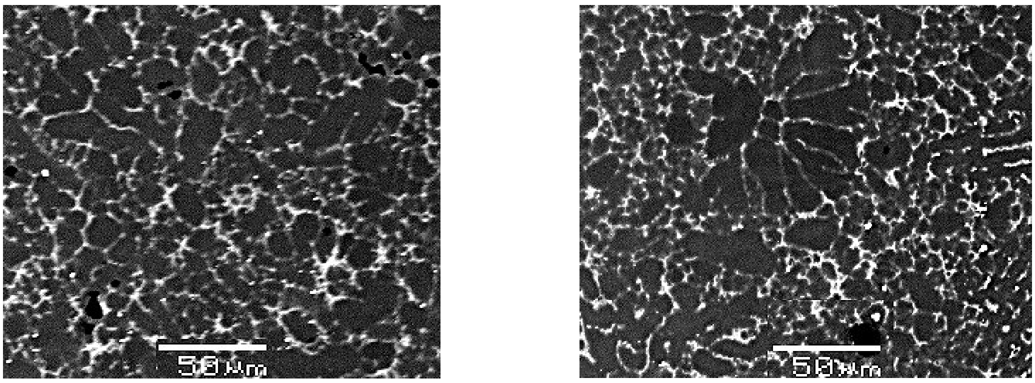
Figure 2: *a) The field test by placing a) plates and bolts under the chassis of a truck.*
b) The corrosion surfaces of plates parallel with the driving direction.

TEST MATERIALS - The test materials were circular cut high pressure die cast plates of AZ91D and AM60B magnesium alloys, with diameter equal to 46 ± 0.2 mm and original thickness equal to 3.2 ± 0.1 mm. Holes with diameter 10.5 ± 0.1 mm were drilled and coated bolts were mounted (Figure 1). Table 1 summarizes the different alloys and coatings used in the study, with the abbreviations used in this paper. One test unit of each type was fixed on each truck.

Alloys	Bolt coatings
AZ91D (according to AZ91D standard high pressure die cast) AM60B (according to AM60B standard pressure die cast)	Zn+C2 (Zinc plating +yellow chromating) JS2000 (Zinc plating+ silicate conversion layer) Sn/Zn (Zinc-Tin plating electrolytical alloy) JS500+ (Zinc plating+ silicate conversion layer + AA6016 washer)

Table 1: *Abbreviations for the magnesium alloys and surface coatings of steel bolts*

Micrographs of the two magnesium alloys were normal (see Figure 3), and did not explain the observed corrosion behavior.



(a) (b)

Figure 3: *SEM micrographs of a) AM60 and b) AZ91.*

EVALUATION OF CORRODED SPECIMENS - After two years of field exposure, the test units were taken from the trucks, and the bolts were removed. The galvanic induced pitting corrosion was concentrated to the bolt head perimeter (see Figure 4). Before the pitting corrosion depth could be measured, the corrosion products were removed from the surface by pickling the plates in a chromic acid solution, Cr_2O_3 in distilled water, 200 g/l at 80° C for 2 minutes followed by rinsing in water and drying with compressed air.

The pickling process might affect the pitting depth as the acidic reaction of the chromic acid may form hydrochloric acid that readily attacks the magnesium surface. There is at present stage no established better alternative for removing corrosion products of a magnesium surface. The surface of each plate was divided into eight sectors, as shown in Figure 4. A light microscope equipped with a focusing dial was used to measure the maximum pit depth in each sector.

Figure 4: *A magnesium plate with pitting corrosion, divided into eight sub-sections for measuring the maximum pit depth in each of the section.*

STATISTICAL METHODS

In this section we very briefly discuss the statistical extreme value methods used. For a recent and very accessible book on the statistical extreme value analysis see [9]. As mentioned in the previous section, pit depth maxima were measured. In the statistical analysis these measurements were assumed to follow an Extreme Value (EV) distribution (sometimes also called “Generalized Extreme Value distribution”) with a distribution function of the form

$$G(x) = \exp\left\{-\left(1+\xi\frac{x-\mu}{\sigma}\right)^{-1/\xi}\right\},$$

where σ>0, μ and ξ are parameters. The formula is valid for 1+ ξ(x-μ)/σ>0. The parameters μ, σ and ξ are the location, scale and shape parameters, respectively. For ξ negative this distribution is the Weibull extreme value distribution for maxima, which has a finite upper bound at $\mu-\sigma/\xi$. The case ξ positive yields the unbounded Fréchet distribution and for ξ = 0 the formula should be interpreted as the limiting (as ξ tends to 0) Gumbel distribution

$$G(x) = \exp\left\{-\exp\left(-\frac{x-\mu}{\sigma}\right)\right\},$$

which also is unbounded. The parameters μ, σ, and ξ were estimated using the maximum likelihood method (see e.g. [9]). The fit of the EV distribution is studied in Gumbel plots, which show the graph with points;

$$(X_{(i)}, -\log(-\log(\frac{i}{n+1})), i = 1,\cdots,n),$$

where are the observations ordered in ascending order (see e.g. [7]). We used a modified y-scale, which provides the probability of exceeding a maximum pit depth per sector (in %). This probability is 100(1-i/(n+1)) for the (n-i+1)-th largest observation. Sometimes we also added a second y-scale, which gives the expected number of units needed to achieve a given pit depth. In Gumbel plots the data scatter around a straight line if they come from a Gumbel distribution, while a convex curve results when the estimated shape parameter ξ is negative. A concave curve corresponds to positive values of ξ. The methodology developed in [1] for analysis of EV data is used in this paper. Briefly it uses the following steps:

1. A *preliminary study* of the data, to check if the experiment produced – as intended – spatially homogeneous corrosion, and test units which can be considered as replicates if they receive the same treatment.

2. A *separate analysis* for each combination of bolt coating and magnesium alloy, leading to quantitative corrosion predictions.

3. *Pairwise comparisons* of effects of coatings on galvanic pitting corrosion.

RESULTS

1. Preliminary study.

To check a possible influence of the position of the sector relative to the vertical direction of the plate during the test (see Figure 2 b), the sectors were divided into four groups as shown in Figure 5.

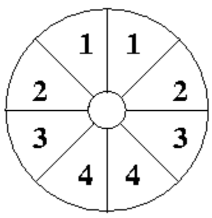


Figure 5: *Numbering of the sectors in terms of their location, with 1 on the top of the plate and 4 at the bottom.*

Figure 6 shows the maximum pit depths per sector plotted on separate lines for the four groups.

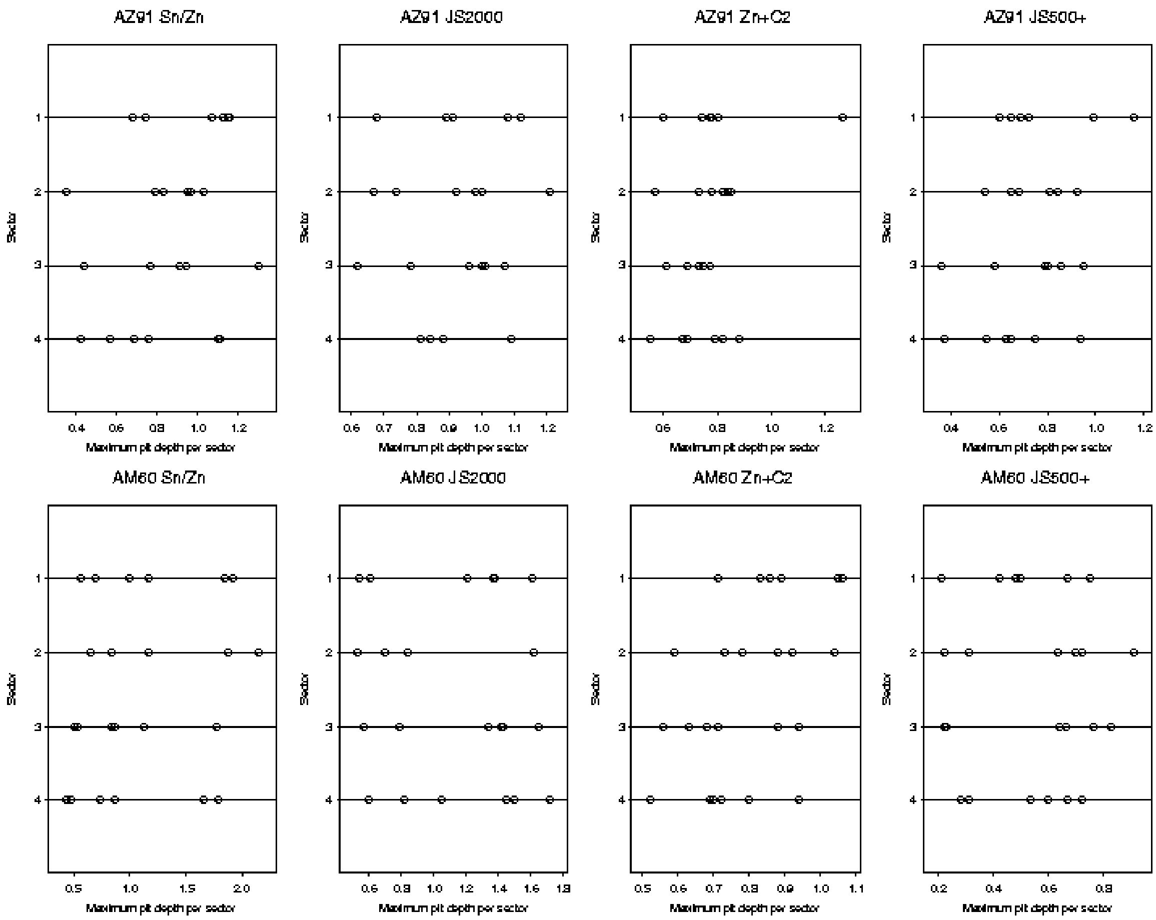


Figure 6: *Maximum pit depth per sector (in mm) for each experiment, split up in 4 sectors according to Figure 5.*

No specific pattern that contradicts spatial homogeneity emerged. These graphical results were corroborated by formal statistical tests. We used both likelihood ratio test and randomization tests adapted to the present context, see [1]. (See also [10] for a general description of these tests). The first row of Table 2 gives the p-values of one of these tests of homogeneity. The results for the other tests are not presented here, as they were similar[1].

	AZ91D Sn/Zn	AZ91D JS2000	AZ91D Zn+C2	AZ91D JS500+	AM60B Sn/Zn	AM60B JS2000	AM60B Zn+C2	AM60B JS500+
Homogeneity	0.77	0.87	0.82	0.90	0.88	0.99	0.47	0.91
Replicates	0.18	0.08	0.53	0.90	0.00	0.00	0.64	0.00

Table 2: *P-values of randomization tests based on the likelihood ratio statistic. The first row concerns the test of homogeneity of the sectors, and the second row shows if plates with the same alloy and coating are replicates. The interpretation of p-values is that, for example, a p-value less than 5% in Row 1 would lead to rejecting the hypothesis of homogeneity at the 5% significance level.*

[1] All the computations have been made using specially developed routines in the statistical analysis software Splus. A specific easy-to-use toolbox is in preparation and will be made available.

The second part of the preliminary study consisted of verifying that the test specimens mounted on different trucks could be considered as similar and produced by the same mechanism, so that the different plates could be handled as replicates in the subsequent analysis.

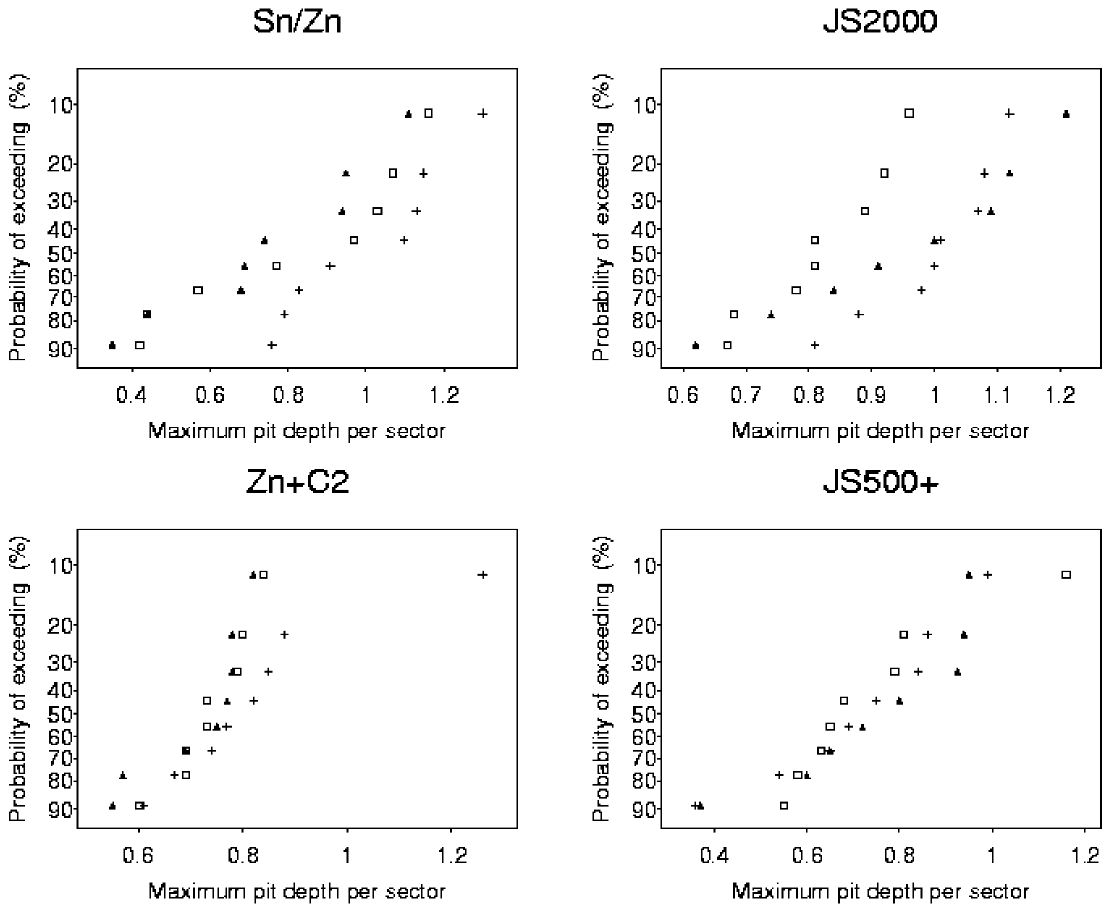


Figure 7: *Gumbel plots of maximum pit depths per sector (in mm). Each graph corresponds to a magnesium AZ91D plate with a given coating. Symbol '▲' corresponds to Truck 1 data, '□' to Truck 2, and '+' to Truck 3.*

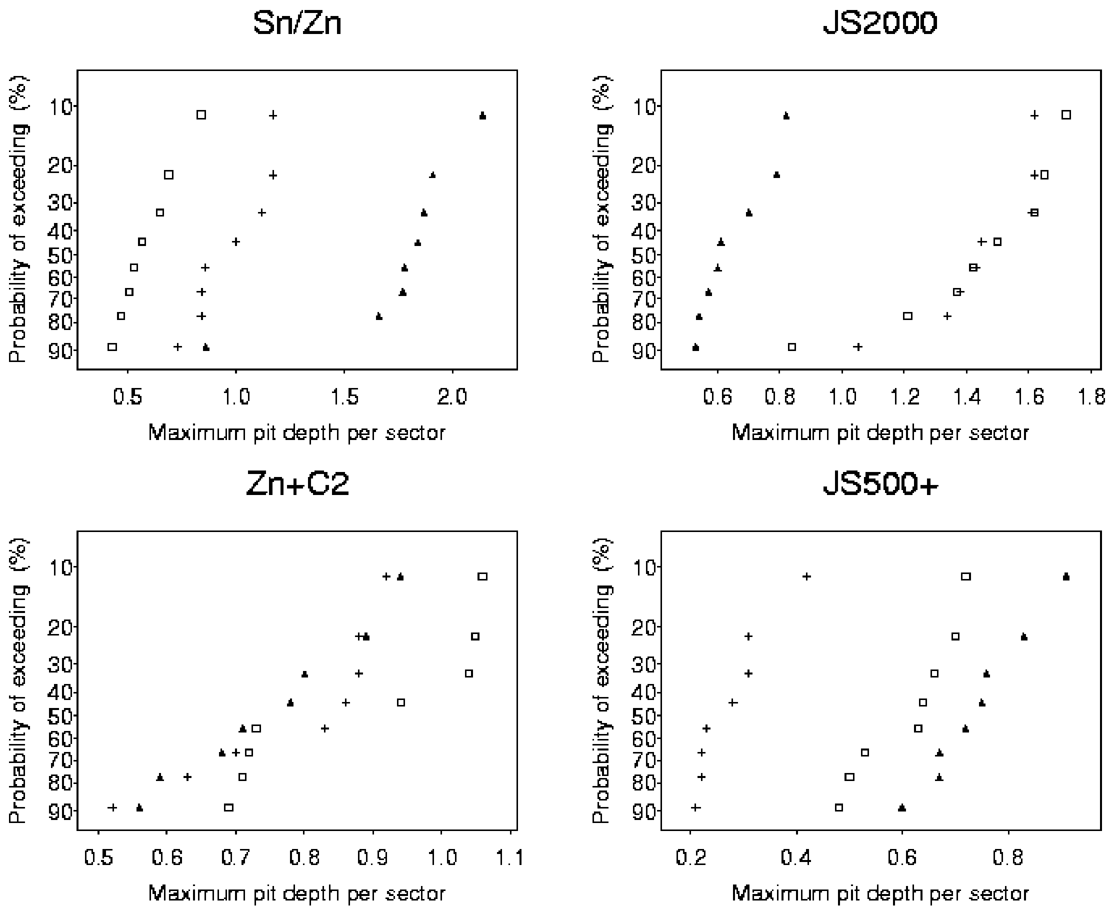


Figure 8: *Gumbel plots of maximum pit depths per sector (in mm). Each graph corresponds to a magnesium AM60B plate with a given coating. Symbol '▲' corresponds to Truck 1 data, '□' to Truck 2, and '+' to Truck 3.*

Gumbel plots for the AZ91D alloy are shown in Figure 7. In all four plots the observed variation between the three plates seem due to chance. Hence this graphical test did not contradict the hypotheses that the plates were replicates.

However, for the AM60B alloy in Figure 8, the plots for the three coatings Sn/Zn, JS2000, and JS500+ exhibit differences between plates which seem larger than can be expected from random variation alone. It was hence hard to believe that plates were replicates in these cases. For AM60B combined with the Zn+C2 coating plates, however, did seem to be replicates. The results from the graphical tests in Figures 7 an 8 were confirmed by formal statistical tests: p-values for randomization tests based on the likelihood ratio test statistic are reported in Table 2, second row.

To summarize, the preliminary study revealed, firstly, that corrosion was homogeneous around the bolt, for all combinations of alloy and bolt coating. It appeared secondly that the variability of corrosion was different for the two alloys: the AZ91D plates were similar for all three trucks, while the AM60B results depended significantly on which truck they came from, except for the combination with the Zn+C2 coating.

2. Analysis of each experiment separately.

As discussed in the previous section five combinations (all combinations of bolt coating with AZ91D, and Zn+C2 coated bolts combined with AM60B) passed the preliminary tests of homogeneity and replication of experimental conditions. Thus the measurements originating from each of these five combinations were pooled into datasets of size 24. In the present section these data sets are analyzed one by one.

Next we choose either a Gumbel or an EV distribution for each combination. As an example, Figure 8 contains Gumbel plots with a fitted Gumbel distribution and with a fitted EV distribution, both with 95% confidence intervals obtained by the delta-method (see [1] for more details), for the AZ91D and Sn/Zn combination.

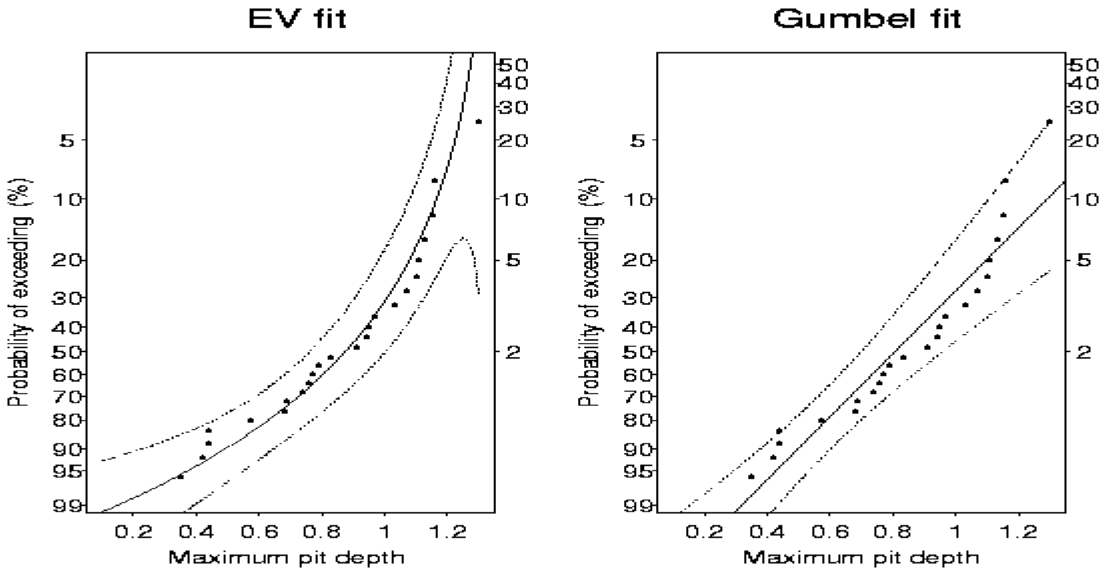


Figure 8: *Gumbel plots with Gumbel and EV fits of maximum pit depths per sector, for AZ91D with coating Sn/Zn.*

The choice between an EV distribution and a Gumbel distribution was made from plots like Figure 9 and from a statistical likelihood ratio test. The best fitting distribution for each experiment is shown in Gumbel plots, see Figures 10 and 11. In the figures the observations were in addition transformed to show the distribution of the maximum per plate rather than per sector, since plate is the meaningful unit.

The best fit for AZ91D alloy with Sn/Zn coating was given by the EV distribution. (p-value=0.01), whereas the Gumbel fit was best for the other four experiments (namely AZ91D-JS2000, AZ91D-Zn+C2, AZ91D-JS500+, and AM60B-Zn+C2 with corresponding p-values 0.06, 0.95, 0.09, 0.13).

The Gumbel plots in Figures 10 and 11 provide answers to many basic quantitative questions on a given experiment. E.g. the answer to "What is the expected number of perforated units if one has 1000 units of AZ91D Zn+C2 with 1.2 mm thick plates", is obtained from Figure 10 by reading that the probability of a pit depth exceeding 1.2 mm is 0.063, so that the answer is 1000 x 0.063=63. One should preferably complement this point estimate by a 95%-confidence interval, which similarly can be read from the graph to be (23,166). The delta-method produces quite wide confidence intervals, especially for such extreme quantiles. A better alternative might be a method based on profile likelihood, see e.g. [9]. One can also get the answer to "How thick should be the plate to have an expected number of perforated units out of 1000 to be at most 10". Reading the x-value corresponding to the probability 10/1000=0.01 from the graph yields the answer 1.39 mm.

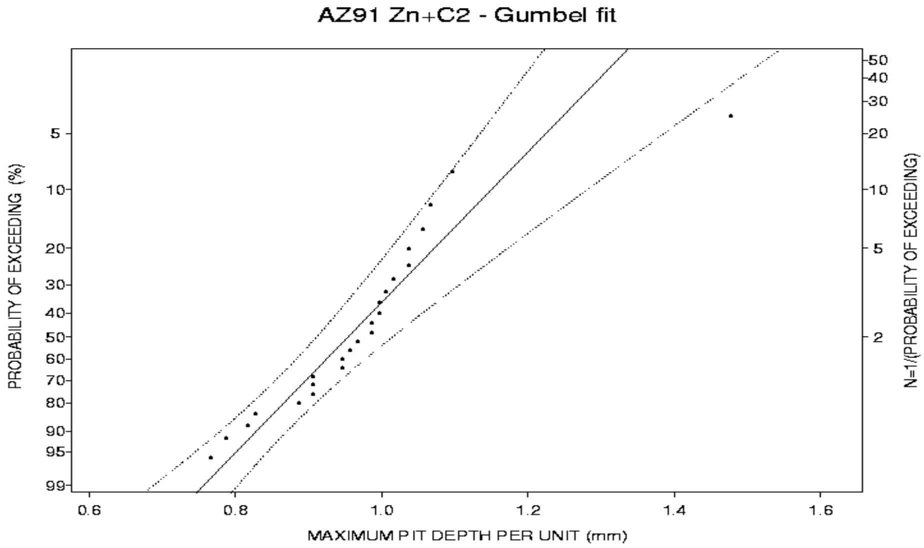


Figure 10: *Gumbel plot with Gumbel fit for the maximum pit depth per unit (in mm).*

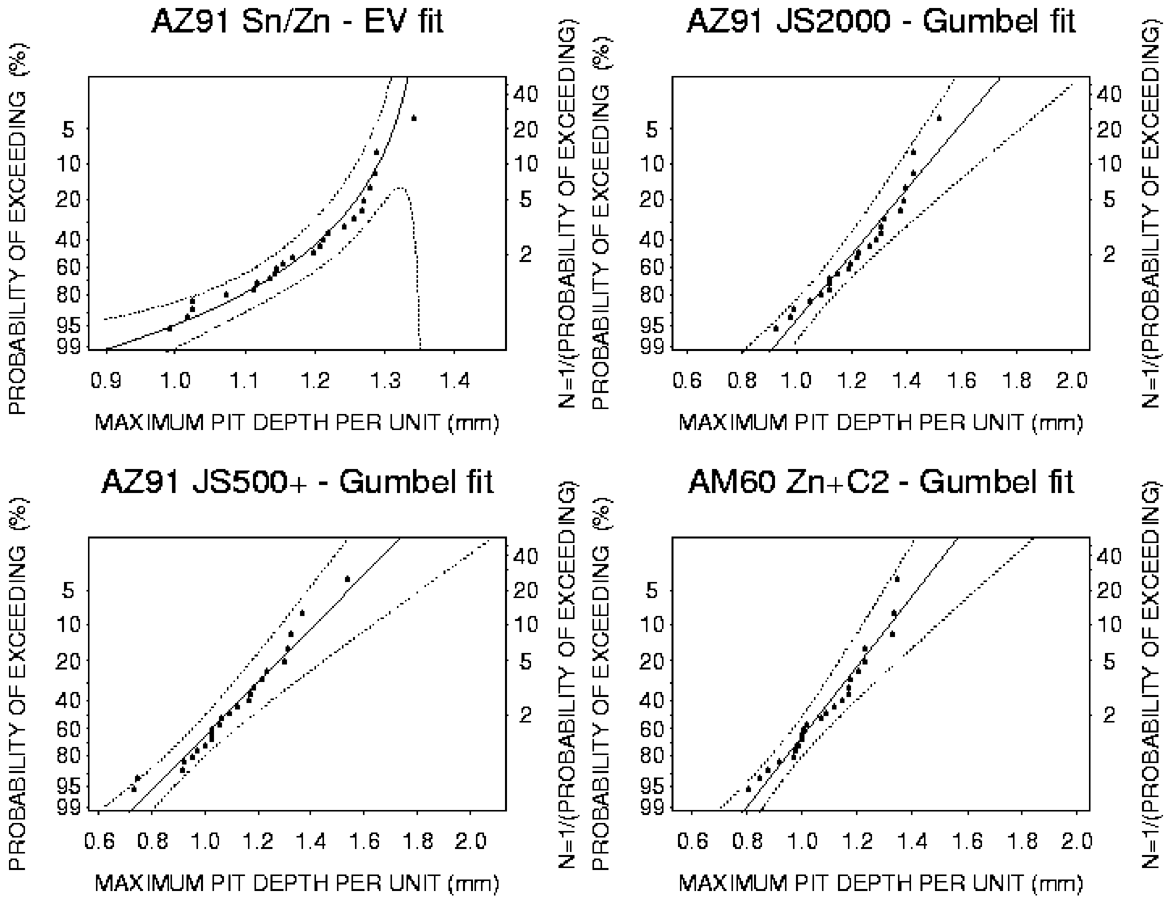


Figure 11: *Gumbel plots with EV fit or Gumbel fit for the maximum pit depth per unit (in mm).*

3. Pairwise comparisons of experiments

In this section, we make pairwise comparisons between the five combinations of alloy and bolt coating which passed the tests in the preliminary study. A complicating feature of the comparisons was the possibility that one combination could have many relatively shallow pits, while another could have few, but deep, pits. Then the former combination would be preferable for thick plates, and the latter for thinner plates. We have let the comparisons depend on the pit depth considered.

A preliminary step was to check via a likelihood ratio test if the shape parameters could be considered as equal, in the pairs where the Gumbel distributions didn't give the best fit. Tests at the 5 % level did not reject the hypothesis of the equality of shape, except for the pair (AZ91D Sn/Zn, AZ91D Zn+C2). Hence, the EV distributions for two combinations -- say Experiment 1 and Experiment 2 -- with parameters (ξ_1, σ_1, μ_1) and (ξ_2, σ_2, μ_2) were fitted by maximum likelihood, under the constraint of the same shape $\xi_1 = \xi_2$, for all the pairs except (AZ91D Sn/Zn , AZ91D Zn+C2). For this pair, shape parameters were allowed to be different. When a Gumbel fit was better than the EV fit both for experiment 1 and for experiment 2, Gumbel distributions with parameters (σ_1, μ_1) and (σ_2, μ_2) were used, and fitted by maximum likelihood. This was the case as soon as the experiment AZ91D Sn/Zn was not involved in the comparison.

If $G_1(x)$ and $G_2(x)$ denote the corresponding EV distribution functions, Experiment 1 was considered better than Experiment 2 for a given pit depth x, if the tail functions $\overline{G}_i(x) = 1 - G_i(x)$, i=1,2, satisfied $\overline{G}_1(x) \leq \overline{G}_2(x)$. Equivalently Experiment 1 was considered better if the ratio of the return periods for Experiment 1 and for Experiment 2, i.e. $\overline{G}_2(x)/\overline{G}_1(x)$, was greater than 1. Figures 12 and 13 show the estimates of this ratio as a function of the maximum pit depth (x) per unit.

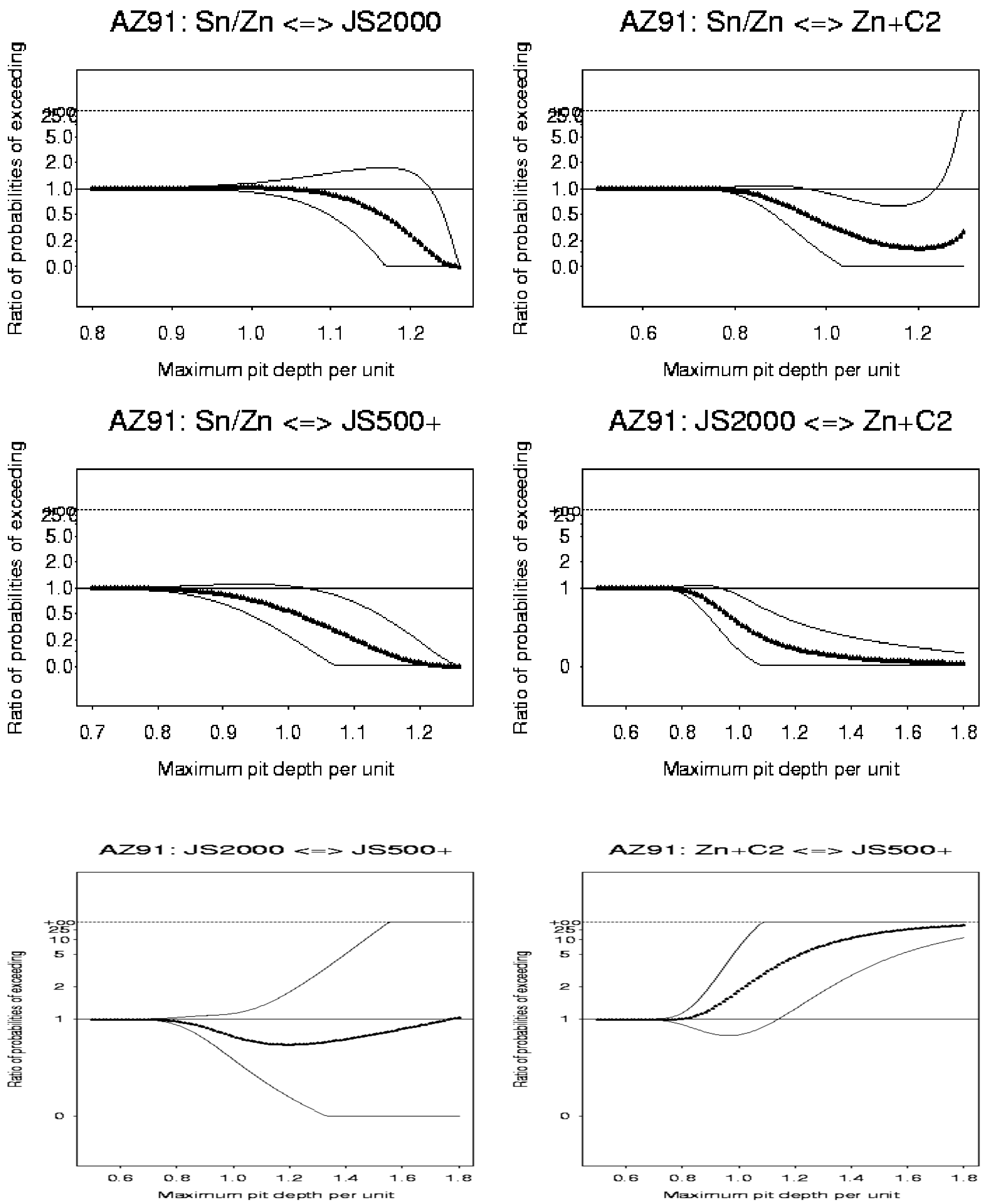


Figure 12: *Estimates of the ratio of the probabilities of exceeding in terms of maximum pit depth per unit (….) with associated 95% confidence interval (----) obtained by the delta-method. Comparisons of the different coatings for the AZ91D alloy.*

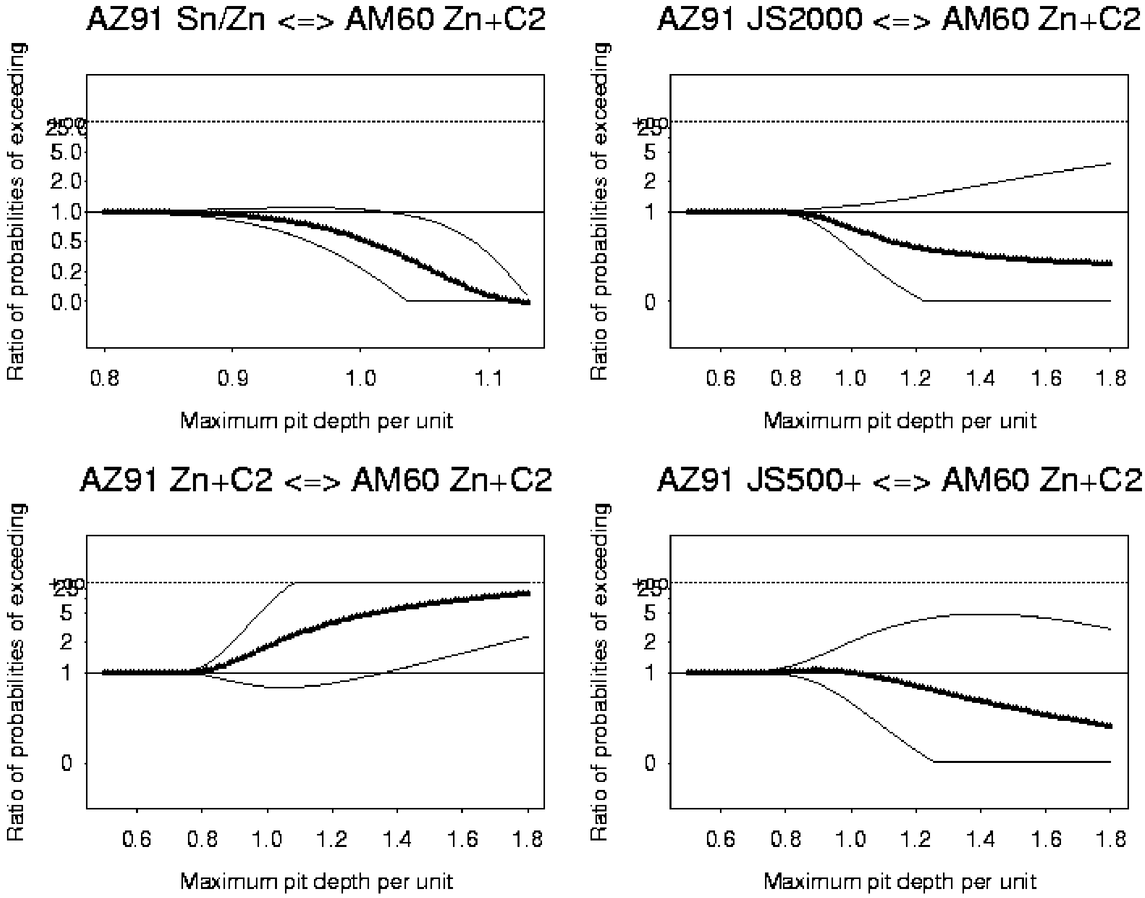


Figure 13: *Estimates of the ratio of the probabilities of exceeding in terms of maximum pit depth per unit (….) with associated 95% confidence interval (----) obtained by the delta-method. Comparisons between the AZ91D alloy and the AM60B alloy.*

From Figure 12 was concluded that for the AZ91D alloy, the Zn+C2 coated bolts had the best corrosion behavior. Specifically, the Zn+C2 coating performed significantly better than Sn/Zn for maximum pit depths per plate in the interval 0.96 mm to 1.23 mm, at the 95% confidence level. Similarly it was significantly better than JS2000 for maximum pit depths greater than 0.98 mm and better than the JS500+ coating with added aluminum washer for pit depths greater than 1.14 mm.

Of the remaining comparisons for the AZ91D alloy, the only clear significant result was that the JS500+ coating with added aluminum washer was better than Sn/Zn for maximum pit depth per plate greater than 1.03 mm, still at the 95% confidence level. Generally, for AZ91D the Sn/Zn coating seemed to have the worst corrosion behavior.

From Figure 13 can be seen that the best AZ91D combination, i.e. the AZ91D alloy combined with Zn+C2 coated bolts was significantly better than the AM60B alloy combined with Zn+C2 coated bolts for maximum pit depths exceeding 1.35 mm. Further, AZ91D combined with Sn/Zn was worse than AM60B combined with Zn+C2, for pit depths larger than 1.02 mm. The remaining two comparisons between the alloys did not show significant differences.

CONCLUSIONS AND DISCUSSION

• Preliminary analysis indicated that corrosion was not influenced by sector position, and that AZ91D test units with the same bolt coating were replicates. Also AM60B test units with Zn+C2 coated bolts were replicates. However, for the other AM60B experiments corrosion behavior was different for different plates.

The trucks were run in similar conditions. Since in addition AZ91 test units with the same bolt coating were replicates, it was not believed that corrosion differences between AM60B test units with the same bolt coating was caused by differences between trucks.

The plates were produced by a high pressure die casting process with a rather rapid cooling rate. This can cause cold flows and surface segregation and lead to areas rich in β-phase ($Mg_{17}Al_{12}$). The β-phase is eutectic and hence these areas are more corrosion resistant. The AM60B alloy has less β-phase. This may lead to surface segregation of the same order of magnitude as the evaluation sectors. In turn this may cause different corrosion behavior of different AM60B plates and may explain the failed replicate tests. One way to avoid such problems in future experiments could be to increase the number of test objects and use wider angle sectors.

The AZ91D alloy has a higher aluminum concentration and may have more homogenous β-phase surface (Skin effect), and hence similar corrosion resistance for all plates.

• The corrosion attacks were too severe to be acceptable for use in dirty environments.

One way to reduce C_d-values ("air resistance"), and hence fuel consumption, is to make the car underbody smoother by the use of underbody panels. This makes the underbody both cleaner and less wet, and hence drastically improves the corrosion environment. It may hence make possible uses of magnesium in underbody applications which are not acceptable in today's cars.

• The aluminum washer offers little protection in dirty environments.

The dirt functions as a thick electrolyte and conducts ions too much. The chemical reaction between aluminum and magnesium yields a steady state potential. This potential lowers at high alkalinity, which occurs naturally at a corroding magnesium surface. Aluminum washers do not function as corrosion protection in dirty environments, contrary to expectation.

• The Zn+C2 bolt coating gave the best corrosion protection on the AZ91D alloy, and the Sn/Zn coating the worst. The AZ91D alloy with the Zn+C2 bolt coating had less serious corrosion than the AM60B alloy with the same bolt coating.

• The extreme value methodology ([1]) provided a useful way to check experimental conditions, to analyze corrosion behavior in individual experiments, and to compare results from different pitting corrosion experiments.

It is hard to foresee which factors will influence corrosion experiments (e.g. the cold flows on AM60B). It is then important to be able to check a posteriori for such influences, both to improve subsequent experiments and to permit a correct analysis. This is also a reason to increase the number of replicates in experiments: with more replicates it may be possible to compensate for unforeseen factors.

In this paper the extreme value methodology has been used to evaluate an experimental study of galvanic corrosion on magnesium plates. However, it is equally applicable to field tests or warranty data and to localized corrosion on other materials, such as aluminum (or even iron) and for many kinds of components, like hem flanges, housings, etc.

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