

A STATISTICAL ANALYSIS OF THE FACTORS WHICH CONTRIBUTE TO THE CORROSION OF STEEL IN OPC AND SILICA FUME CONCRETE.

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Abstract.

The corrosion of embedded reinforcement has been measured in two series of concrete samples made with and without Condensed Silica Fume (CSF) as a partial replacement for the cement. Three different curing regimes were used and samples were tested at three different ages. Measurements of carbonation, electrical conductivity, strength, lime content and chloride, oxygen and water vapour transport were carried out on matching samples.

The results have been analyzed using Analysis of Variance and regression to show which aspects of the materials and methods used to make the samples and which of the measured properties had significant effects on the corrosion. The way in which these effects were modified by the presence of the CSF was also analyzed.

The analysis showed that while the corrosion rate was affected by the water/cement ratio and the curing for all samples the use of CSF significantly increased the sensitivity to poor curing. Also while electrical conductivity and chloride transport were good predictors for corrosion in all of the tests the relative significance of the different predictors was very different for the CSF mixes.

1. INTRODUCTION

The corrosion of reinforcing steel in concrete has caused widespread failure of structures and the selection of materials and methods which will inhibit or prevent the process is therefore a high priority for new works. There is now a substantial body of research which confirms that there are numerous factors related to the materials and methods used in the construction process which may be shown by simple correlation to have a significant effect on corrosion (1). There is, however, a lack of data on the relative importance of the different factors as predictors for the corrosion rate.

The corrosion of steel requires water and oxygen to proceed and is promoted by the ingress of carbon dioxide, chlorides and other chemicals into the concrete. Relationships between the transport properties of concrete and corrosion rates would therefore be expected and many of these have now been proven. Again, however, there is a lack of data on the relative importance of each property.

Condensed Silica Fume (CSF) has now been in use as a partial cement replacement material for some years and its use has been shown by research to have both benefits (2) and disadvantages (3). The essential finding of the research has been, however, that concrete made with CSF is very different from concrete with pure Ordinary Portland Cement (OPC) as a cementitious component. When considering the use of this CSF it is therefore important to determine whether relationships which have been shown to hold for OPC mixes will also hold for CSF mixes. An example of a relationship which holds for OPC mixes but is different CSF mixes is that between electromigration and other transport processes for chloride ions. A high voltage electromigration test is recommended (4) for measuring chloride transport but the use of this test on CSF mixes may lead to misleading conclusions (5).

In this paper a statistical analysis of a set of experimental results on OPC and CSF mixes is presented. The results are from laboratory measurements of corrosion by Linear Polarisation Resistance Measurement and of various transport properties of the mixes. The objectives of the analysis are as follows:

1. To show the importance of the different aspects of the materials and methods used in construction (e.g. the water/cement ratio and the curing conditions) on the corrosion rates.
2. To determine whether the type of mix (CSF or OPC) affects the sensitivity to changes in materials and methods.
3. To show the relative effect of the different transport properties on the corrosion rates.
4. To show the way in which the relative effects of the different transport properties on the corrosion rates are modified by the use of CSF.

2. EXPERIMENTAL METHODS.

2.1. Sample Preparation.

Samples were prepared to the four different mix designs given in Table 1.

Table 1. Mix Designs

Mix	A	B	C	D
Cement (kg/m ³)	344	430	252	315
CSF (kg/m ³)	86	0	63	0
Water/(OPC + CSF)	0.3	0.3	0.46	0.46
Superplasticiser (% of OPC + CSF)	1.4	1.4	1.9	1.9
5-20mm aggregate /(OPC + CSF)	3	3	4	4
Fine aggregate /(OPC + CSF)	1.5	1.5	2.3	2.3

Mortar and paste samples were made with the same proportions but without the aggregates. After casting the samples were covered and kept at 20°C for 24 hours until they were struck. They were then cured using the three different curing conditions given in Table 2. These three curing conditions cover the range of curing environments which would be encountered on a reasonably well managed construction site.

Table 2. Curing Conditions

Curing Condition
(CC) No.

1	20°C and 99% RH until test age
2	Treated with aluminium pigmented curing agent and kept at 20°C for 7 days and then in water at 6°C
3	In water at 6°C until test age

The samples were tested at 3, 28 and 90 days. All combinations of the 4 mixes, 3 curing conditions and 3 test ages were used for the tests giving a total of 36 "sample conditions" which reflect a wide range of possible conditions for site concrete when first exposed to an aggressive environment.

2.2. Sample Testing

The corrosion current was measured and measurements were made of the properties known to influence it (the predictor properties). These predictors were all transport properties except for the lime content and the cube strength. The testing programme is summarised in Table 3

Table 3. Summary of experimental programme

Corrosion measurements

Initial Current
28 Day Current
Current Change

Predictor Measurements

(The abbreviations shown in brackets are used in Figures 7 and 8)

Chloride Transport	Concentration (ClConc)	Measured in sample after gravity assisted ingress
Carbonation	Strain (Strain 18)	Measured on mortar prisms with LVDT
	Prism depth (Depth 18)	Measured with phenolphthalein at 18 days exposure
	Mortar depth (Depth 28)	Measured with phenolphthalein at 28 days exposure
Oxygen Transport	Permeability (K(O ₂))	Measured on sections on mortar cores.
Vapour Transport	(Vapour)	Measured on thin discs of paste.
Electrical Conductivity (Conductivity)		Measured between steel and solution on corrosion. samples
Lime Content	(Lime)	Measured with thermogravimetric analysis of paste samples
Compressive Strength	(Cube Strength)	Measured on 100mm cubes.

Corrosion measurements

Samples containing a mild steel bar were placed in salt solution and the initial corrosion rates and were measured by linear polarisation resistance measurements. The steel was then polarised to +100mV relative to a standard calomel electrode for 28 days and the corrosion rate was measured again. Details of the experimental procedures are reported elsewhere (6,7).

Three different data sets were taken forward to the statistical analysis: The initial corrosion current, the 28 day corrosion current and the change in corrosion current. The initial corrosion current was caused by the processes which took place during curing. The 28 day corrosion current is a measure of the ability of the concrete to protect the steel while substantially contaminated with chlorides. The

change in corrosion current is a measure of the ability of the concrete to resist the ingress of chlorides.

Chloride Transport

Chloride transport was measured by placing sodium chloride solution in holes drilled in concrete samples. After exposure the bases of the holes were drilled and dust samples collected from different depths and analyzed for chloride content. Details of the experimental procedure is given in reference 5.

Carbonation.

Mortar samples were exposed to an atmosphere of 90% CO₂ at a pressure of 1 bar at 21°C and 70% RH. The carbonation shrinkage was measured at 18 days after exposure with a comparator using a Linear Voltage Displacement Transducer (LVDT). The carbonation depth of the prisms at 18 days was measured by breaking the samples and using phenolphthalein indicator solution. Further samples were cast in plastic cups and exposed for 28 days before measuring the carbonation depth using the same procedure.

Oxygen Transport

Sections of 25 mm mortar cores were tested for oxygen transport under an applied pressure difference of 1 and 2 bar. Details of the procedure are in reference 8.

Water Vapour Transport.

Thin discs of paste were sealed into the lids of bottles with water in them. The bottles were then placed in controlled humidity environments and their weight loss recorded. Details of the procedure are in reference 8.

Lime Content Measurement

The calcium hydroxide (lime) content was measured using thermogravimetric analysis. Details of the method are given in reference 9

Compressive Strength

This was measured on 100mm cubes.

Data Retrieval

Two readings were obtained for each sample condition for each experiment. The data were collected onto a microcomputer and the average of each pair of readings was used for initial data analysis (10). Subsequently the full data set with all of the independent observations was transferred to a mainframe computer for this analysis.

3. STATISTICAL ANALYSIS

3.1. Initial Calculations.

For a statistical interpretation of regression and analysis of variance it is assumed that the data are normally distributed. The results obtained for corrosion currents were very clearly non-normal and thus unsuitable for analysis. It was observed, however, that the logarithm of the corrosion current was approximately normally distributed. It has been shown (11) that the logarithm of the corrosion current should be linearly dependant on the rest potential and this relationship was found to be accurate for these data (6). There is therefore some theoretical justification in treating the logarithm of the corrosion current as the fundamental parameter and on this basis it was used for the analysis.

3.2 Analysis Of Variance

3.2.1 Method

The effects of mix type, materials and methods on corrosion rates have been studied using the method of analysis of variance. In this analysis both the basic effects and the higher order interactions are analyzed. Thus, for example, in addition to showing that w/c ratio has a significant effect it can also show that changes in w/c ratio make the mix significantly more sensitive to poor curing.

The results of the analysis are given in Table 4.

Table 4. Percentage significance of interactions in Analysis of Variance.

	Initial current	28 day current	change in current
Effects of individual factors			
w/c ratio (0.3 or 0.46)	0.1	0.1	0.1
mix type (OPC or CSF)	0.1	0.1	0.1
age (3, 28 or 90 day)	0.1	0.1	0.1
curing conditions	0.1	0.1	0.1
First order Interactions			
w/c ratio, mix type	-	0.1	0.1
w/c ratio, age	-	1	0.1
w/c ratio, curing	-	0.1	0.1
mix type, age	10	-	5
mix type, curing	0.1	0.1	0.1
age, curing	0.1	-	0.1
Second order Interactions			
w/c ratio, mix type, age	-	5	1
w/c ratio, mix type, curing	10	0.1	0.1
w/c ratio, age, curing	-	10	10
mix type, age, curing	-	-	-

The significance of the effects of the individual factors is expected from previous research which shows that, for example, corrosion rates are affected by w/c ratio. The first order interactions are the most interesting in that, for example, an interaction between w/c ratio and mix type implies that the addition of CSF (change of mix type) changes the sensitivity of the mix to changes in w/c ratio. This is the same as changes in the w/c ratio changing the sensitivity of the mix to changes in mix type.

The main effects are averaged over the interactions so it is important to examine the higher order interaction terms to obtain the full picture. For example, one mix may appear better than another on average, but this may not be true for all ages. The highest order interactions are therefore discussed first in each case.

Where the results are plotted (e.g. Figs 1-6) the vertical bars represent plus or minus half of the least significant difference (12). Consequently bars which do not overlap represent a significant difference between data points.

3.2.2 Discussion

The initial corrosion current.

This is the corrosion current measured immediately after the samples were placed in the salt solution. The measured corrosion was therefore caused by processes which took place during curing, e.g. water penetration and possibly carbonation.

w/c ratio, mix type, curing interaction.

This reaction is significant at the 10% level and the reason for this may be seen from Figure 1. For curing conditions 1 and 2 the CSF mixes are significantly better than the OPC mixes and the low w/c ratio mixes are significantly better than the high w/c ratio mixes. For curing condition 3 (the 5°C condition) there are no significant differences between the mixes except for the low w/c ratio CSF mix. The similarity between the corrosion rates for curing condition 3 could have been caused by the general inhibition of the hydration process preventing the potentially "better" mixes from developing corrosion resistance. The superior performance of the low w/c ratio CSF mix may simply have been caused by self desiccation leaving the steel in a dry environment. It has been shown (9) that at 5°C (curing condition 3) the pozzolanic reaction in the CSF mixes will not have started even at 90 days so it will not have improved the transport properties.

mix type/curing interaction

It may be seen from Figure 1 that changes in mix type from OPC to CSF make the initial corrosion current significantly more sensitive to changes in curing. This shows up as a 0.1% significance for the mix type/curing interaction.

age/curing interaction

This interaction was caused by the procedure for curing condition 2 in which the samples were placed in a cold tank at 7 days and may be seen from Figure 2. The curing condition 2 samples had the lowest current at 3 days because they were dry.

The 28 day corrosion current

This was the current measured after 28 days of anodic polarisation in salt solution. The essential feature of the results was that for all ages and curing conditions the CSF mixes performed significantly better than the OPC mixes and the low w/c ratio mixes performed significantly better than the high w/c ratio mixes.

w/c ratio, mix type, curing interaction

It may be seen from Figure 3 that the only mix to be significantly affected by curing conditions was the high w/c ratio OPC mix and this had a lower corrosion current when cold cured. This result would not be expected from observations of the transport properties which were all highest for the cold curing. The low corrosion currents for cold curing would have been caused by the increased ability of the cement paste to adsorb chloride ions into chloro-aluminate phases at early stages in the hydration process (2). In the CSF mixes and the low w/c ratio OPC mix this effect has exactly cancelled out the effect of higher transport properties caused by cold curing. The first order interactions with curing were also caused by these effects, i.e. changes in mix type and w/c ratio significantly change the sensitivity to changes in curing.

w/c ratio, mix type, age interaction

Figure 4 shows this interaction and is very similar to Figure 3. Again the effect of chloride adsorption has cancelled out the reduction in transport with age for the CSF mixes and the low w/c ratio OPC mix and has exceeded it for the high w/c ratio OPC mix.

The change in corrosion current.

This was calculated as the ratio of the final current to the initial current. Thus a value of less than unity (i.e. negative logarithm) indicates a decrease in current during the 28 days.

In this case many of the second order and all of the first order interactions are significant. Figures 5 and 6 show the mix type/w/c ratio/curing interaction and the mix type/w/c ratio/age interaction. It is of note that the effect of chloride binding caused the current to reduce during the test for all mixes except the high w/c ratio OPC mix. The significance of the interactions implies that changing any one of the materials and methods variables will alter the sensitivity to changes in any other.

3.3. Regression

3.3.1 Method

The purpose of the regression analysis was twofold:

- 1 To construct a model for predicting corrosion current from the measured predictor properties, thereby identifying which properties provide the best indication of corrosion.
- 2 To assess the size of the effect of each predictor property on corrosion current. A particular property may be highly correlated with corrosion current yet may have little actual effect on it. This is the distinction between the correlation coefficient and the regression coefficient, or, in simple terms, the difference between how well the line fits the data and how steep the slope of the line is.

Using standard stepwise regression techniques (13) it was found that several of the predictor properties were highly correlated with the corrosion current. However, having fitted one of these properties as a single predictor, the model could not be improved by the addition of a second or further predictors. This phenomenon is due largely to the high correlations existing among the transport properties themselves.

Nonetheless, a comparison of the single predictor models is instructive.

The t-ratio was used to assess the significance of the correlation between corrosion current and each transport property.

Using the regression coefficients (or slopes) to compare the size of the effect of each predictor on corrosion current is complicated by the different units of measurement adopted for each predictor. This difficulty has been overcome by calculating the change in corrosion current predicted by each single predictor model *over the range of samples tested*. The validity of this method of comparison relies on the careful design of the experiment in selecting the range of values for each predictor to reflect the full range of normal site conditions.

It should be noted that for each model used a thorough residual analysis was conducted to check for the possibility of non-linearity or heteroscedasticity. A normal probability plot was used to test for normality of residuals. In the case of Oxygen permeability these diagnostic checks indicated that a logarithmic transformation of the predictor was necessary.

3.3.2 Results.

The effects of the predictors and their t-ratios are given in Table 5 for the initial corrosion current and Table 6 for the 28 day corrosion current. The effects are shown in Figures 7 and 8 (note that the scales are different). In these figures the predictors are labelled using the abbreviations from Table 4.

3.3.3 Discussion.

The cube strength was the only predictor which had a negative coefficient, i.e. high strength indicated low corrosion as expected. The effect of oxygen transport as a predictor is not justified directly in this instance because the corrosion was shown to be anodically controlled (6) but it serves as a general measure of transport in the concrete.

The Initial Current

For the OPC mixes 5 of the 9 predictors were not significant. None of the measurement of carbonation (Strain 18, Depth 18 and Depth 28) or the vapour transport or the lime content were significant. The most significant predictor was the electrical conductivity because none of the transport properties will have been significant before exposure. The remaining significant predictors are chloride transport (Cl conc), oxygen permeability (log K(O₂)) and cube strength which are only significant because they measure the general "quality" of the concrete. The effect of the four significant predictors on the corrosion current is very similar implying that changes in any of them would indicate the same change in corrosion current.

For the CSF mixes the lime content becomes the most significant predictor and also has the greatest effect. The authors have proposed an explanation for the conduction of direct current in CSF concretes (5) which suggests that it is substantially controlled by the amount of lime present. The high

INITIAL CORROSION CURRENT

SILICA FUME CONCRETE

Property	effect	t-ratio
Strain 18	NS	
Cl conc	1.124	3.13
Log K(O ₂)	NS	
Cube strength	1.596	-5.31
Depth 18	NS	
Depth 28	NS	
Conductivity	1.061	3.86
Lime	1.689	6.05
Vapour	0.798	2.39

OPC CONCRETE

Property	effect	t-ratio
Strain 18	NS	
Cl conc	0.611	2.92
Log K(O ₂)	0.456	2.28
Cube strength	0.584	-2.64
Depth 18	NS	
Depth28	NS	
Conductivity	0.57	3.38
Lime	NS	
Vapour	NS	

5% critical t-value is 2.032
 1% critical t-value is 2.728
 0.1% critical t-value is 3.601

Table 5

28 DAY CORROSION CURRENT

SILICA FUME CONCRETE

Property	effect	t-ratio
Strain 18	0.595	2.27
Cl conc	0.550	2.22
Log K(O ₂)	0.803	3.98
Cube strength	NS	
Depth 18	NS	
Depth 28	NS	
Conductivity	0.641	3.51
Lime	NS	
Vapour	0.586	2.77

OPC CONCRETE

Property	effect	t-ratio
Strain 18	4.303	5.17
Cl conc	3.577	5.80
Log K(O ₂)	3.533	6.72
Cube strength	3.431	-4.98
Depth 18	2.921	3.02
Depth 28	2.574	6.79
Conductivity	2.572	4.45
Lime	2.564	2.98
Vapour	1.806	2.30

5% critical t-value is 2.032
 1% critical t-value is 2.728
 0.1% critical t-value is 3.601

Table 6

significance of the lime content is therefore due to a combination of its effect on the electrical conductivity and its depletion as the pozzolanic reaction of the CSF proceeds and the transport properties decrease. This high significance of lime content implies that the pozzolanic reaction is not depleting the lime sufficiently to affect the alkalinity of the steel because this would cause corrosion to increase as the lime content decreased giving a negative t-ratio. The high significance and effect of the cube strength (greater than all of the remaining transport properties) was unexpected.

The 28 day Current

The OPC mixes generally performed as expected with every predictor being significant. Having been insignificant for the initial current the carbonation strain has become the second most significant predictor and the oxygen permeability the most significant. The conductivity remains significant but has been overtaken by many transport properties. Figure 8 shows the effects in decreasing order showing the carbonation strain to have greatest effect and the chloride transport next. Because the exposure took place in chloride solution the chloride transport would have been expected to be greatest but all of these properties are highly correlated.

The CSF mixes showed significantly lower changes in corrosion current because their corrosion currents were generally significantly lower. An important observation was that, in contrast to the result for the initial current, the cube strength was not significant as a predictor. This implies that producing high strength mixes with CSF is not a route to durability of embedded steel in a chloride environment. The lime content was also not significant. The failure of the two measures of carbonation depth to work as predictors was caused by the very low (and often nil) depths observed.

4. CONCLUSIONS

1. The use of CSF in concrete makes it significantly more sensitive to changes in curing. This interaction was significant at the 0.1% level for all of the corrosion measurements used in this work.
2. After exposure to chlorides all of the samples made with CSF concrete nevertheless had significantly lower corrosion than corresponding samples without CSF.
3. The single predictor models of corrosion current could not be improved by including a second predictor. This occurred because the transport properties in concrete are all highly correlated and implies that measuring one of them will yield all of the available information about corrosion.
4. The predictive models for corrosion in CSF concrete were very different from those for OPC concrete. In particular after exposure to chlorides the very high significance of many transport properties and compressive strength for OPC was not present for CSF.
5. The electrical conductivity and the chloride transport were the only two predictors which were significant for all situations and the conductivity was more significant than the chloride transport in three out of four.

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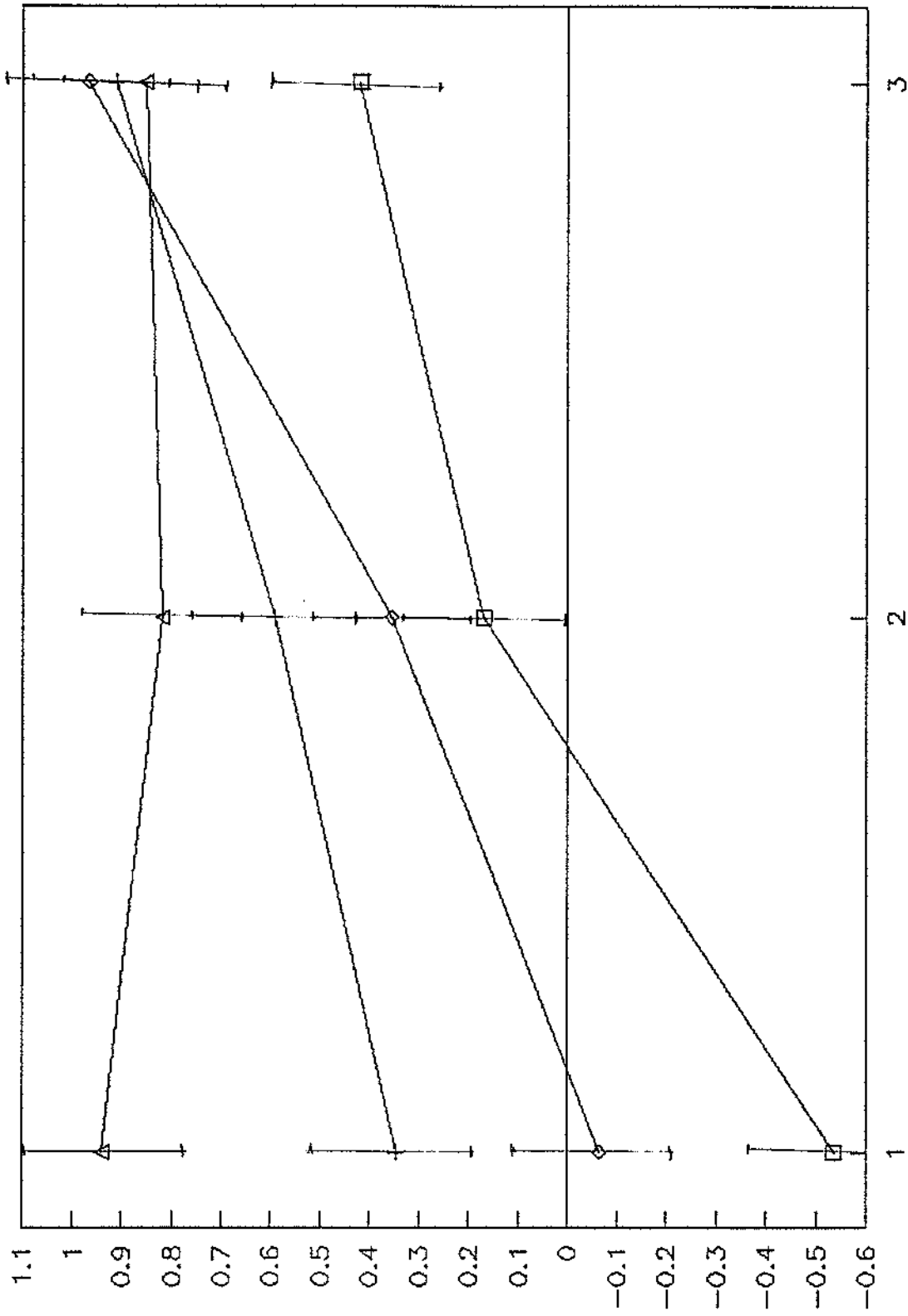
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INITIAL LOG CORROSION CURRENT



□ sf/0.3 + cont/0.3 ◇ sf/0.46 △ cont/0.46
 CURING

Fugl

INITIAL LOG CORROSION CURRENT

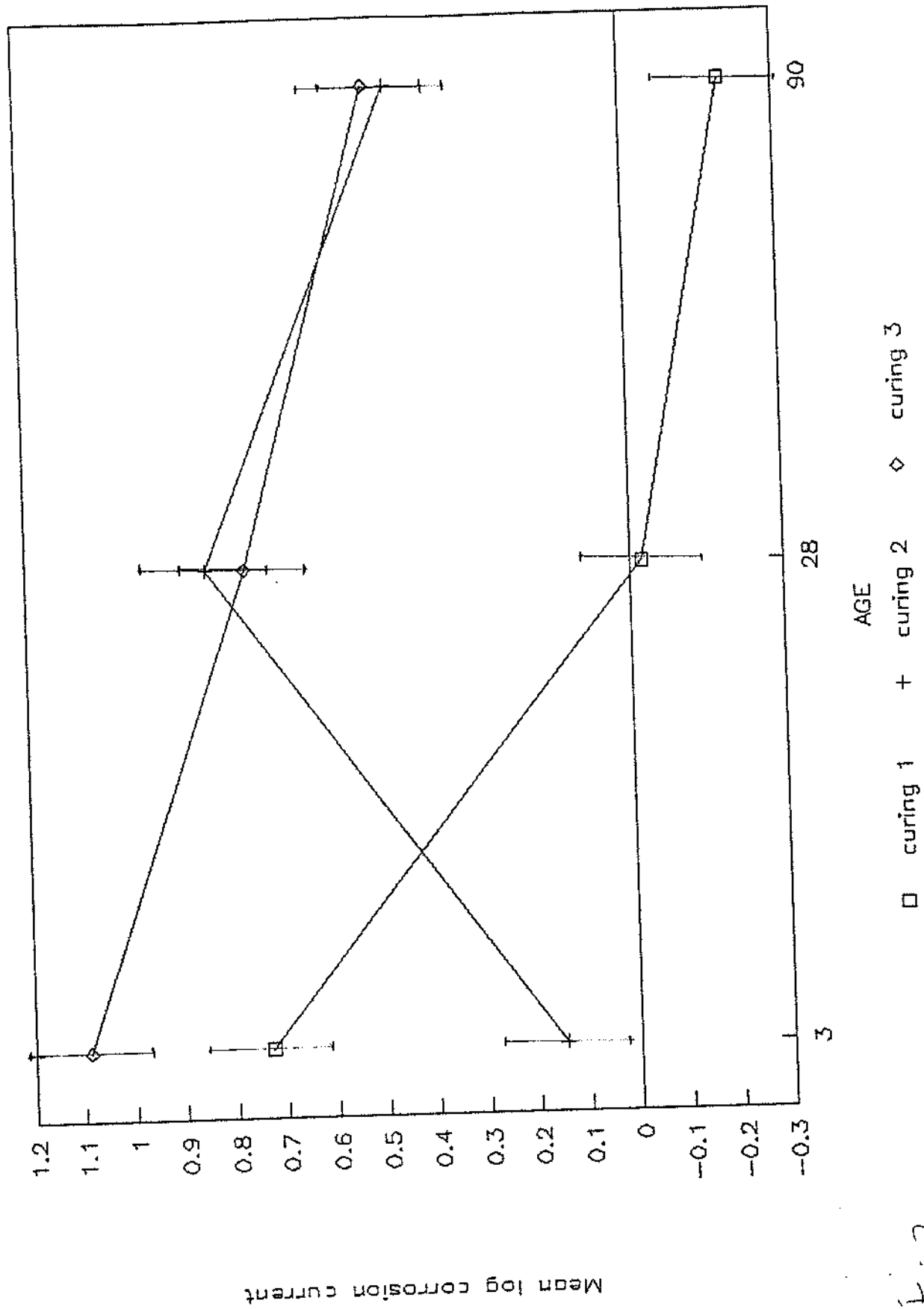
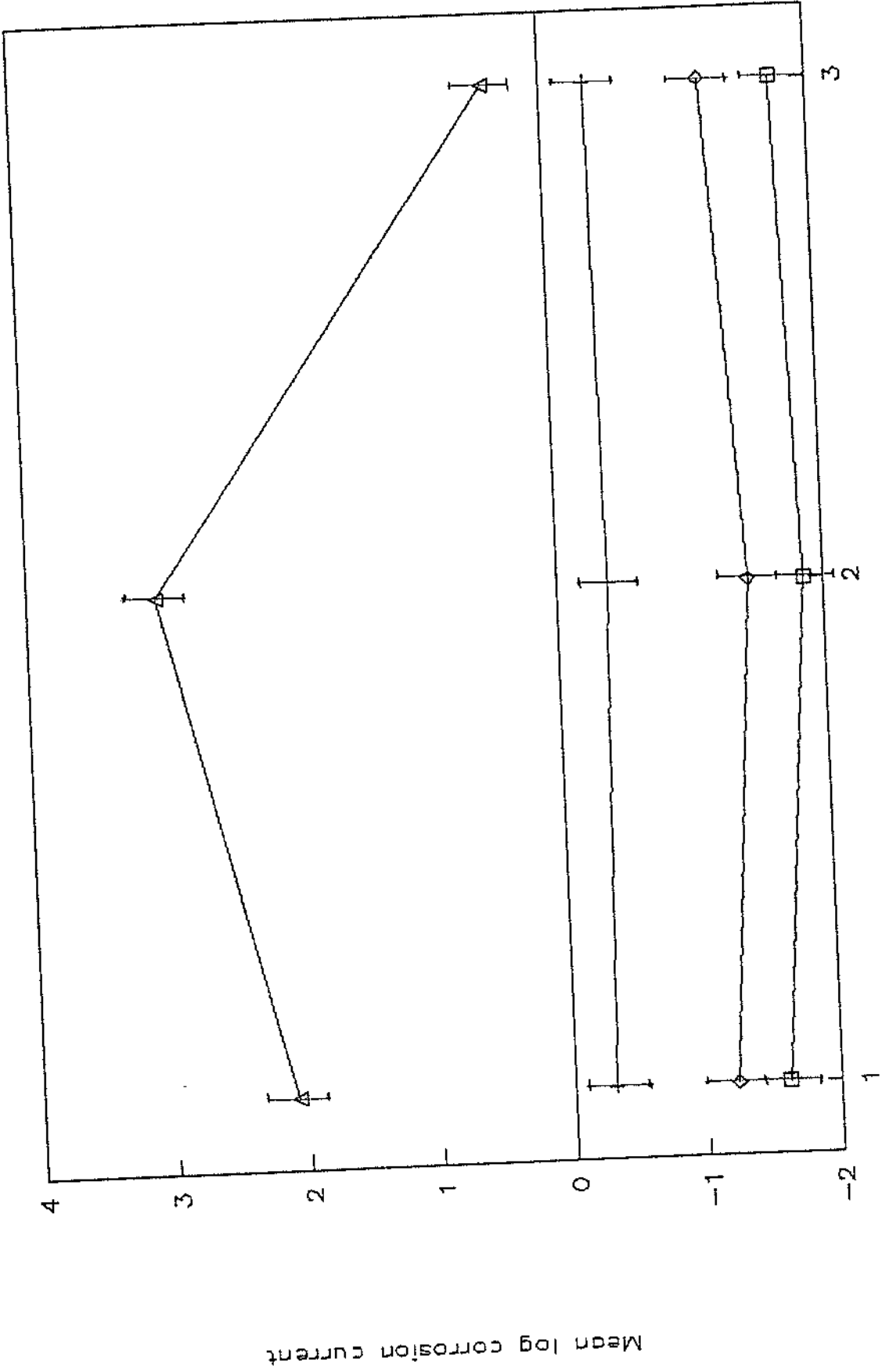


Fig. 2.

28 DAY LOG CORROSION CURRENT



□ sf/0.3 + cont/0.3 ◇ sf/0.46 △ cont/0.46
 CURING

Fig 3

28 DAY LOG CORROSION CURRENT

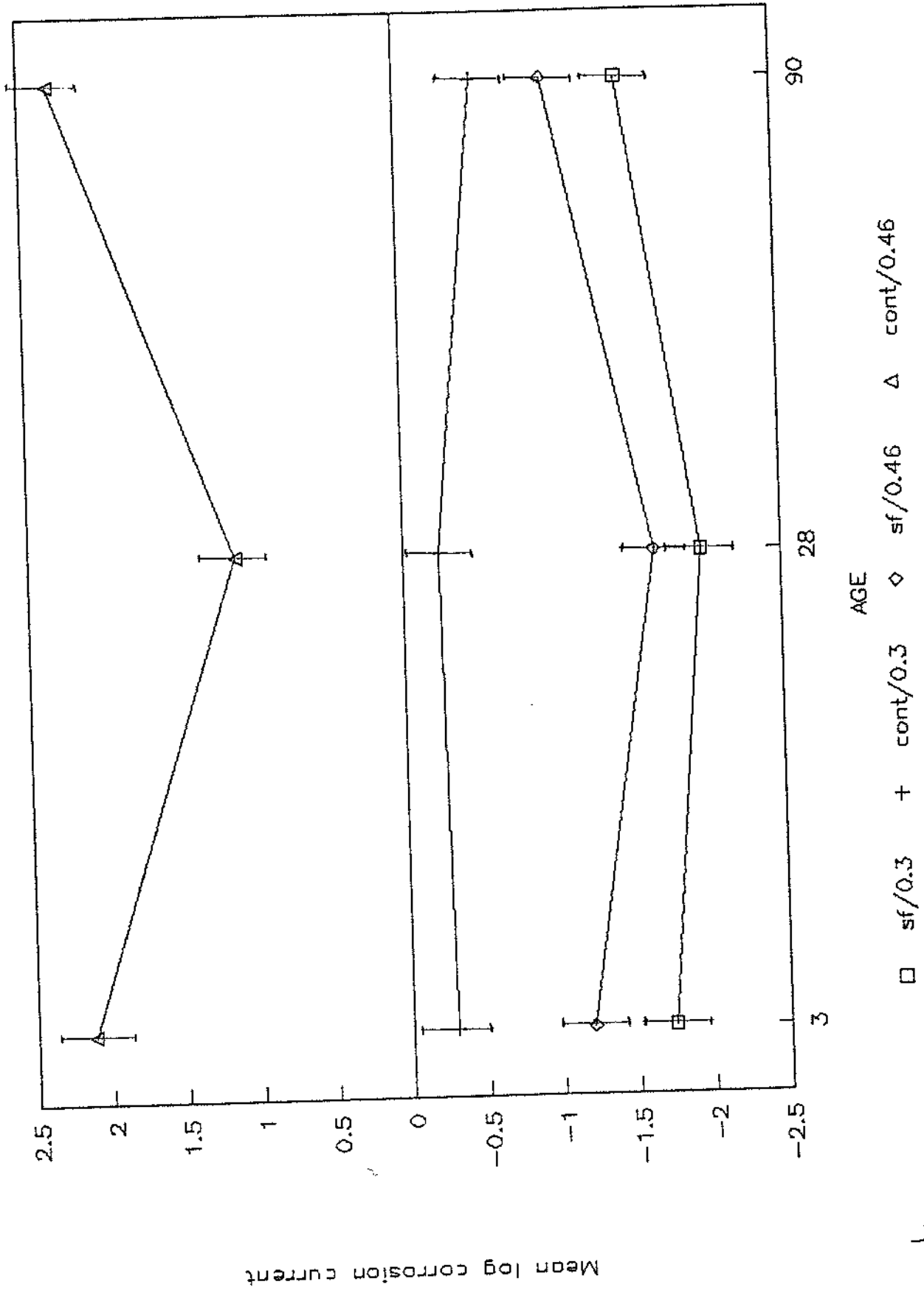
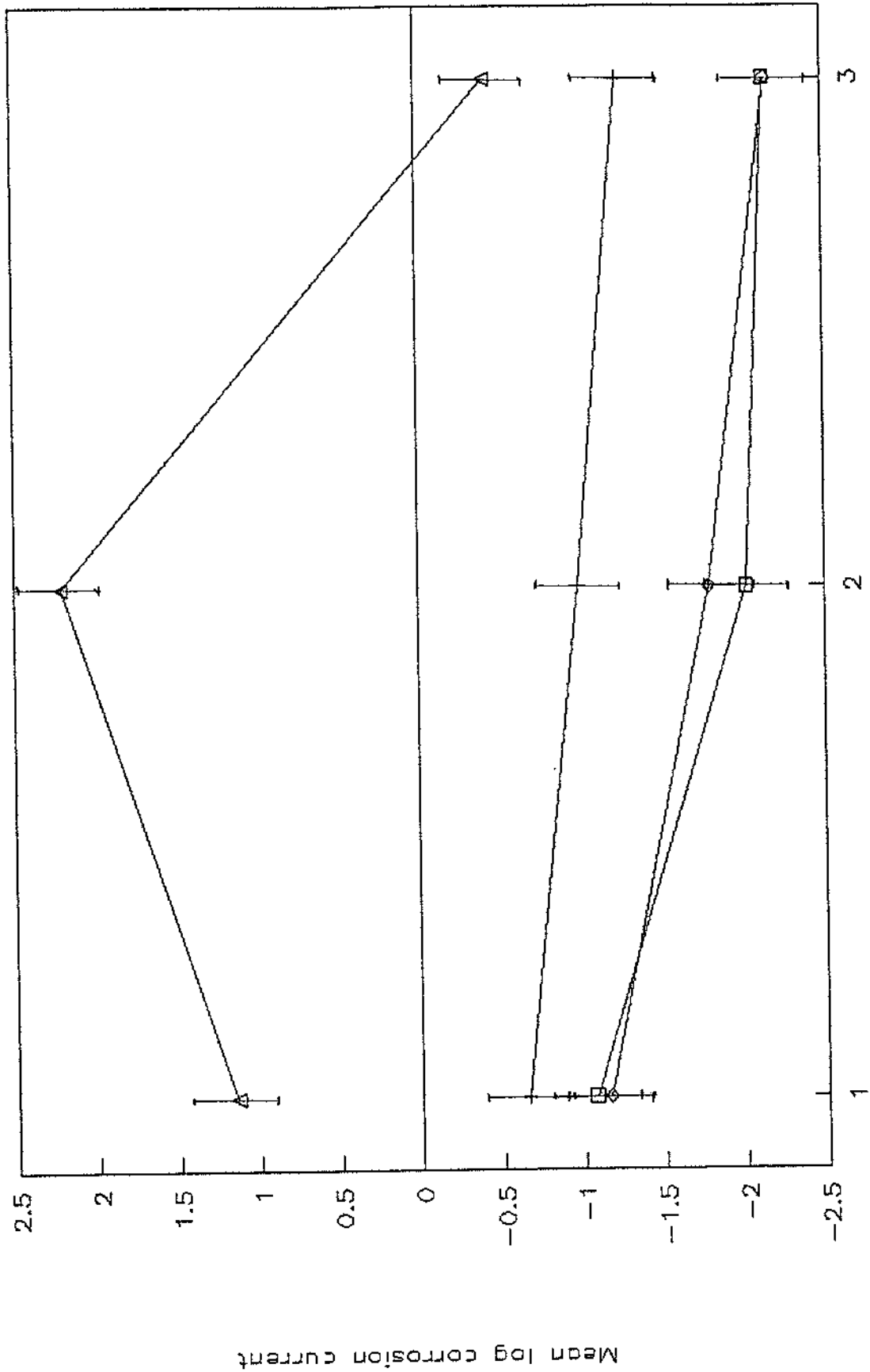


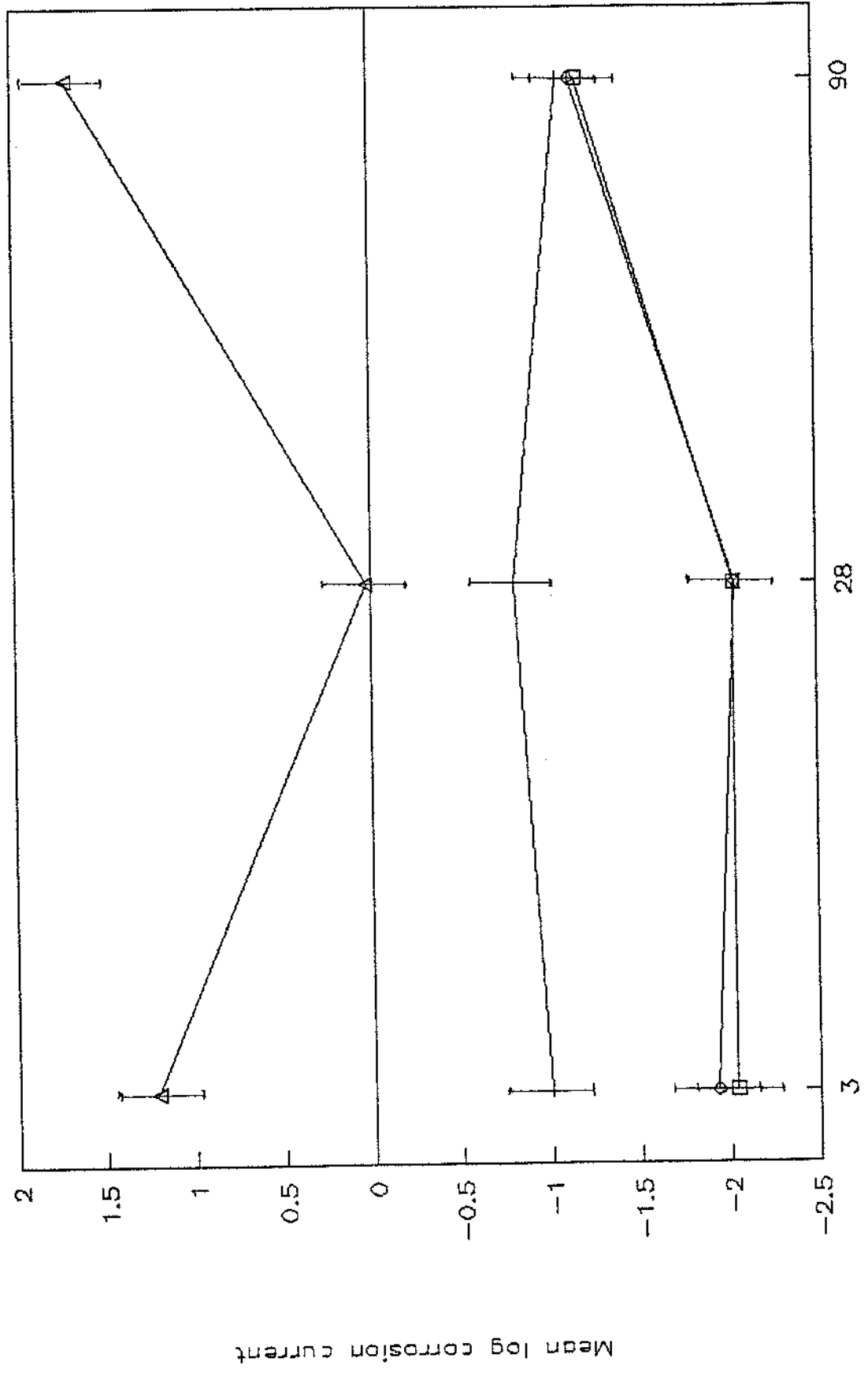
Fig 4

LOG RATIO CORROSION CURRENT



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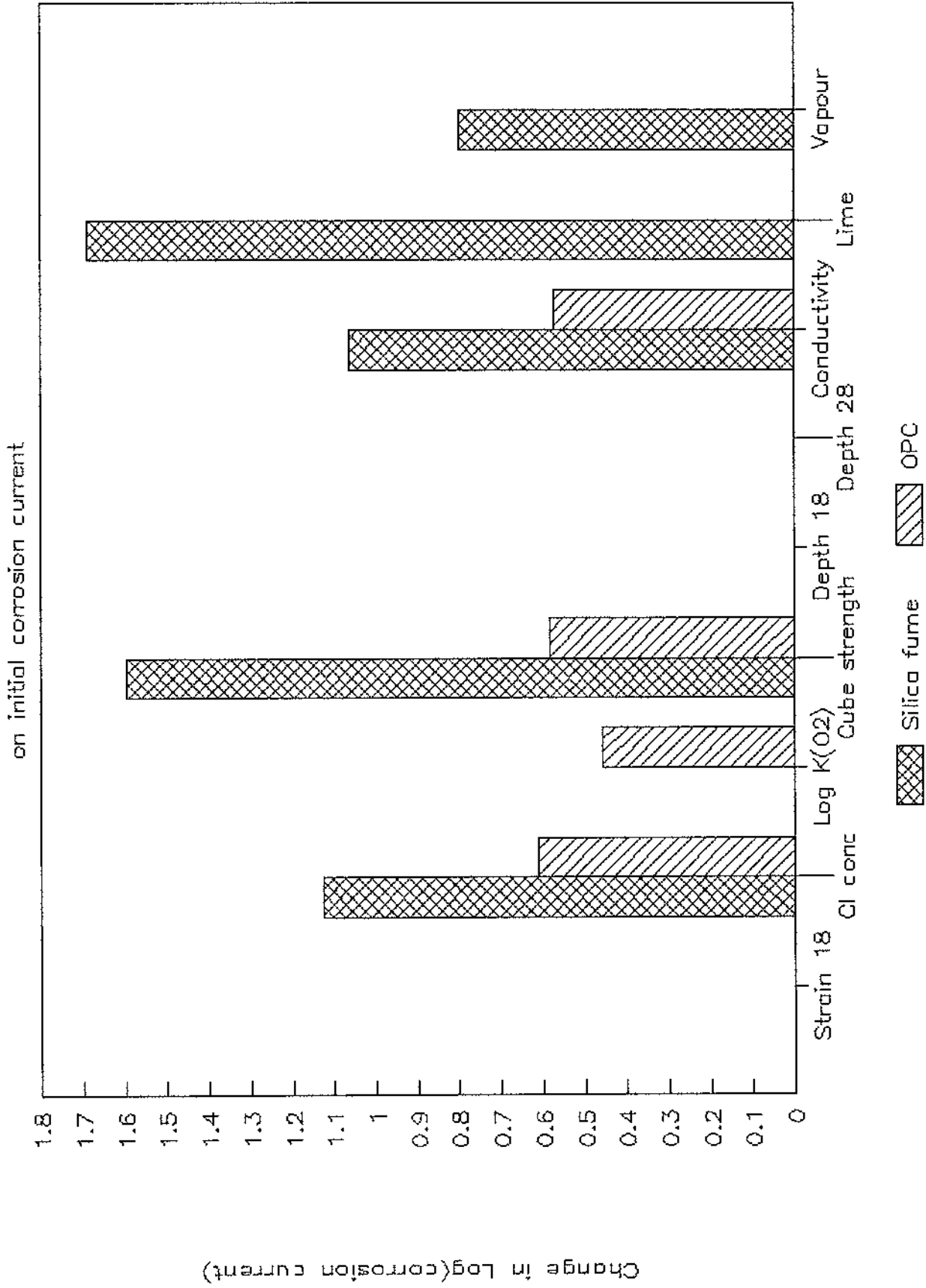
LOG RATIO CORROSION CURRENT



AGE ◇ + cont/0.3 sf/0.46 △ cont/0.46

Fig 6

EFFECT OF TRANSPORT PROPERTIES



EFFECT OF TRANSPORT PROPERTIES

on 28 day corrosion current

