

Instant performance verification after electrochemical chloride extraction by enhanced corrosion testing

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Abstract. Electrochemical chloride extraction (ECE) is meant to re-establish the corrosion protection of concrete for the embedded reinforcement by removing chloride non-destructively and by enhancing the alkalinity of the rebar surrounding concrete. Both effects depend on various parameters, such as concrete cover, rebar spacing, chloride profile (especially if chloride ingress is deeper than the outside rebar layer) and concrete permeability. Often these parameters require long or multi-stage treatments, which basically can achieve any desired target level of chloride profile and impressed charge, but become a costly solution after a while. The acceptance criteria mentioned in CEN TS 14038-2 clause 8.6 refer to the achieved chloride content and to the amount of impressed charge, which are the conventional, easy measurable, but not direct parameters for evaluating the corrosion activity. A third parameter – the re-measurement of potentials for assessing (intended) low potential gradients and more positive average potentials – requires some weeks to months of depolarization and evaporation of water, before such a measurement can be applied successfully. A promising approach for an instant performance testing after an ECE treatment has been made on several occasions with follow-up measurements of electrolyte resistance, polarization resistance and corrosion current. Convincing changes towards significantly lower corrosion activity could be obtained (and compared to known classified values) – regardless of sometimes high residual chloride and very wet concrete. These data could be verified when re-assessed after some weeks, so enhanced corrosion measurements seem to be a useful tool for either establishing that the designed treatment time has been sufficient or to check on possible earlier termination of the treatment during a running ECE.

1 Introduction

During the past 8 years enhanced corrosion measurements (AC impedance, galvanostatic pulse measurement, linear polarization and Tafel polarization) have been increasingly used in corrosion survey projects of CITec, and the device applied for these measurements has been described in [1]. After collecting encouraging experiences, especially in clarifying scenarios that were difficult to evaluate on the basis of the “traditional” test methods potential survey plus chloride and water content [2], it was a logical step to use them also for the assessment of ECE applications.

General explanations about ECE are given for instance in [3]. It has been observed from many projects, that much higher amounts of residual chloride than 0.4 %, related to the cement mass can be tolerated even in the rebar vicinity with proven elimination of corrosion activity. This information was received mainly by potential surveys that demonstrated significantly more positive values in the treated areas than before ECE and a low deviation from potentials in adjacent, chloride-free areas. Unfortunately such conditions cannot be found immediately after terminating ECE, where the strong cathodic polarization enforces instant-off potentials < -800 mV vs. CSE, and in the usually very wet concrete it

lasts some 3 to 6 months until equalized, stable moisture conditions allow a useful assessment of potential measurements.

For having a solid evaluation of the success of the treatment, respective measurement results must be available directly at its termination and not just many weeks after. The 3 case studies of this paper give good confidence in a promising approach.

2 Short descriptions of the enhanced corrosion measurements

For the enhanced electrochemical measurements a potentiostat/ galvanostat is needed, which is a standard testing device in electrochemistry [1]. In addition to the voltmeter and the reference electrode which are used for potential measurements on the reinforcement, it has a current source and a counter electrode for triggering changes to the working electrode/ reinforcement (fig. 1). The following electrochemical test methods have been applied at different stages of the ECE:

AC impedance: With this method it is possible to obtain the electrolyte resistance of the concrete in a 2-electrode setup at a frequency of ca. 1 kHz.

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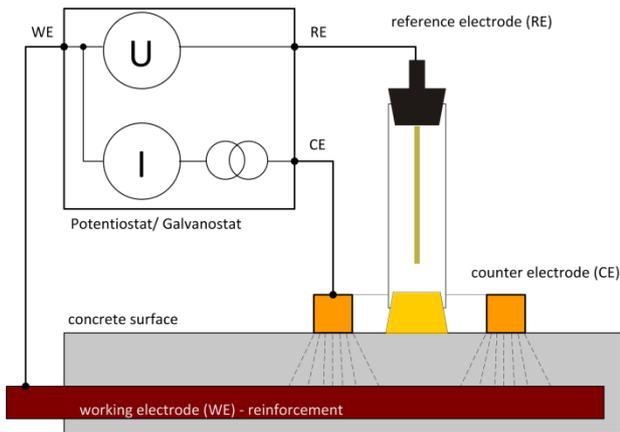


Fig. 1. Corrosion measurement setup with a potentiostat

Galvanostatic pulse measurement (GPM): Here, a small anodic constant current is applied via the counter electrode, and the forced shift of the potential at the working electrode is measured. The change of potential is to be divided into the IR drop, which equals the electrolyte resistance R_B , and the “true” polarization resistance R_p . Details of the application of this method on reinforced concrete structures can be read in [2], [4]. There exist various approaches for the measurement setup; here, the anodic pulse has been at $-100 \mu\text{A}$ over 60 s.

Linear polarization measurement (LPR): The potential is shifted slowly in a small range around the open circuit potential (OCP) (max. $\pm 20 \text{ mV}$ at ca. 0.5 mV/s scan rate). This is considered to exhibit a linear dependency between potential and current. The total polarization resistance R_p' (including electrolyte and polarization resistance) is the forced shift of potential divided by the resulting shift of current.

Tafel polarization measurement (TPM): In this method, a much wider potential shift is done, usually ca. $\pm 200 \text{ mV}$ around the open circuit potential. The measurement curve is displayed in a $\log I/E$ -graph, and at the two visible straight sections the so called Tafel slopes will be fitted. At their intersection with the OCP, the corrosion current I_{corr} at the corrosion potential can be determined. If no IR correction is done, the I_{corr} is by experience ca. 10 to 15% higher than the true value. More information about this method is available in [5] and [6]. For obtaining corrosion rates from the I_{corr} value, a related rebar area has to be assumed, which is very tricky in practical cases. The approach taken here considers the range between a minimum and a maximum area, referring either to a rebar length directly under the counter electrode ($l = 6 \text{ cm}$) or under an angle of 45° (which results at a cover of 3 cm in a rebar length of 12 cm), multiplied by the number of rebars, their perimeter and a surface factor of between 1.2 for the ribs and 2 for a surface additionally covered with corrosion pits.

3 Project cases and results

In this case study, 3 different ECE applications are presented, where data of enhanced corrosion measurements were available from dust sampling

locations before, directly after and mostly also some weeks or months after terminating the ECE. All numeric results are summarized in table 1 at the end of this paper, along with the graphical presentation of the electrochemical data in dependency on the chloride content in rebar vicinity.

Hollow box girder floor slab: This is a typical, very beneficial application field for ECE, as chloride has penetrated into the mainly dry concrete of the floor slab from leaking drainage pipes that are meant to remove surface water from the bridge deck. Along with the repair of the drainage system, ECE can remove the chloride smoothly and without restricting the use of the bridge. Multi-stage applications, which might be necessary in case of deep chloride ingress and low concrete cover, usually do not cause technological or administrative conflicts. With the eliminated origin of chloride ingress, the corrosion protection in a floor slab can be restored by ECE durably, and no other, long-term or additional steps are required.



Fig. 2. ECE electrode layout on the box girder floor slab

As long as tendon ducts do not have large defects, ECE can be applied safely also in pre-stressed, post-tensioned slabs (Faraday Cage). This has been the case in the project introduced here; furthermore some small areas of delaminated concrete were present; in one of them a test location has been specified and surveyed.



Fig. 3. Floor slab area after removing the ECE electrodes and while running the first corrosion measurements

All test locations have been surveyed with dust sampling, OCP and impedance measurements, GPM, LPR and TPM before ECE, directly after removing the electrodes and 3 months later. As can be seen in table 1, the chloride values in the rebar vicinity did not get reduced dramatically during the one-stage, 7-week application, but a very high amount of chloride has been analysed from the re-usable electrodes – ca. 100 g/m². The data obtained from the one test location in a delaminated area (yellow marked) did not deviate much from the other 3 locations, so the ECE seems to have worked there in a similar performance than on the other, undamaged areas.

Track bed of a subway: In a subway station considerable amounts of chloride and rebars showing pitting corrosion have been found in the track bed area. The source of the chlorides remained unclear; one assumption was that it came from acidic cleaning agents which had been used over many years on the tiles of the adjacent wall.



Fig. 4. ECE in the track bed of a subway under traffic

After a corrosion diagnosis and extensive testing of the ECE equipment for its feasibility under these special circumstances (no influence of the running equipment on the automated train control, and that the electrodes and cables remain safely in their position also at full speed of passing trains), the application was run as designed in up to 3 stages of 6 weeks each per sub-area and intermissions of also 6 weeks between the applications.



Fig. 5. View of the ECE electrodes and their fixing to the rails

The resulting data are also to be found in table 1. The amount of removed chloride was in the same range as on the box girder floor slab (100 g/m²), but the initial chloride contents as well as the amount of impressed charge were much higher. The end chloride level was at 3 of the 4 shown test locations very low, but in one (ref 3) 1.67 % residual chloride was analysed. The R_B , R_p and I_{corr} values are on a similar “good” level as in the other test locations.

Wall section of a highway tunnel: It was a special issue of this ECE application that it ran as part of a major repair project in the tunnel. This way, there was a strict schedule limiting the time of application and the accessibility of the wall section during the application. Furthermore, the power supply of the ECE was connected to the temporary power supply of the construction site, which caused frequent shut-downs during the first of two parts/ areas and required many site visits to replace fuses and to reboot the process. During the second part, high-capacity UPS devices were added that could filter voltage peaks and compensate short power interruptions even for the DC power supplies. In the first part, only 3.5 of possible 6.5 weeks operation time could be achieved, but in the second part the ECE worked during the available 6.5 weeks without interruptions.



Fig. 6. ECE electrodes on the tunnel wall



Fig. 7. ECE control centre and power supply

The ECE was applied as a one-stage treatment to wall areas at the tunnel entrance with high local chloride contents and relatively low concrete cover (ca. 30 – 40 mm, regularly > 60 mm). The general repair concept included a surface protection that prevents further chloride ingress.

Again, all data of the tunnel wall application can be seen in table 1. Its first part worked just 3.5 weeks net, and low amounts of removed chloride and impressed charge resulted from this. In test location ref 2 some reduction from the initial 5.35 % chloride content can be seen, but 3.7 % remained in an analysis 2 months after the scheduled termination of the treatment. Unlike ref 1 and 3, the corrosion measurement data of ref 2 showed no significant changes towards passivity. The open circuit potential was found to be rather positive, similar to the test locations ref 1 and 3.

3 Discussion

Generally, the data obtained from the enhanced corrosion measurements appear to be plausible and fit into expected schemes: $R_p' > LPR \geq R_p'$, GPM, as fig 8 shows (at least in the interesting range of resistances up to 3,000 Ohm). The I_{corr} values fit quite well in an exponential relationship with the R_B values from AC impedance and the R_p values from GPM (figs 9 and 10).

It should be mentioned that these data have been taken on very different structures at different stages of the ECE, which were tested under widely varying conditions. In another relation, the electrochemical data are displayed versus the respective chloride content in rebar vicinity (figs 11 to 13).

In fig 11 it can be seen that due to the partly intensive wetting and strong cathodic polarization, extremely negative potentials were measured. Apparently these influences did not affect the other measurements (AC impedance, GPM, LPR, TPM), which is an indicator for the feasibility of these measurements under conditions that won't allow a useful interpretation of potential measurement data or where varying moisture conditions make the potential assessment very difficult.

The fit of the R_B and R_p data over the chloride values is not that excellent as over the I_{corr} values, very likely because the dust sampling has a larger "spread by coincidence" and does not match exactly to the test location of the measurement cell.

Figs 14 and 15 show the dependency of the assumed corrosion rates on the chloride contents, and this refers to the conversion of the obtained, absolute I_{corr} values into specific corrosion rates according to the remarks made in the introduction of the TPM. One has to be aware of the uncertainties of that step, but with the suggested corridor between estimated minimum and maximum rebar areas the true corrosion rate should be covered reasonably.

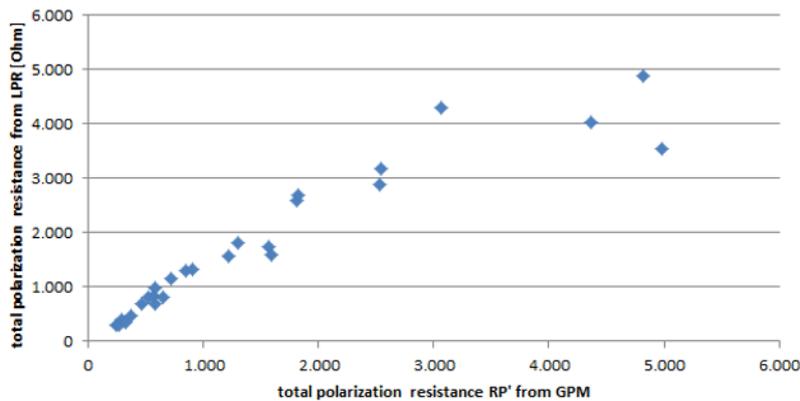


Fig. 8. Total polarization resistances R_p' from LPR versus R_p' from GPM

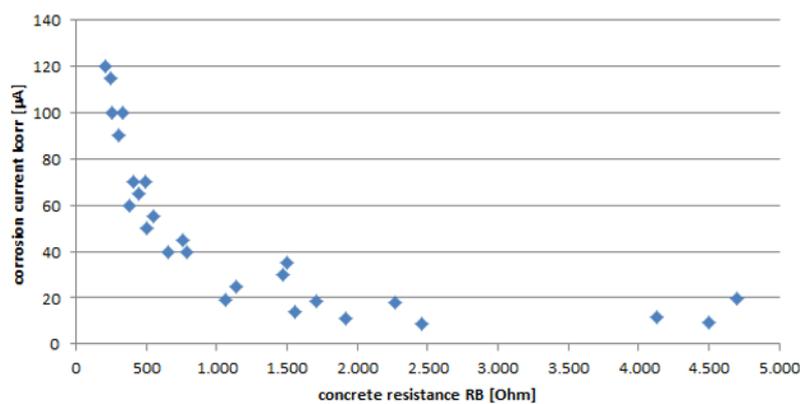


Fig. 9. Corrosion currents I_{corr} versus electrolyte resistances R_B

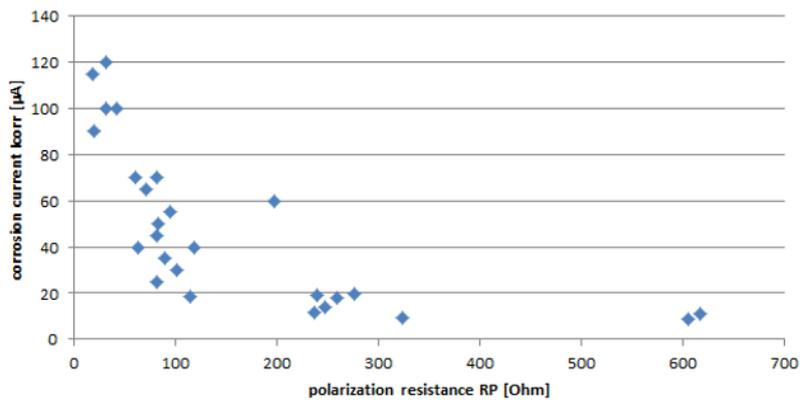


Fig. 10. Corrosion currents I_{corr} versus polarization resistances R_p

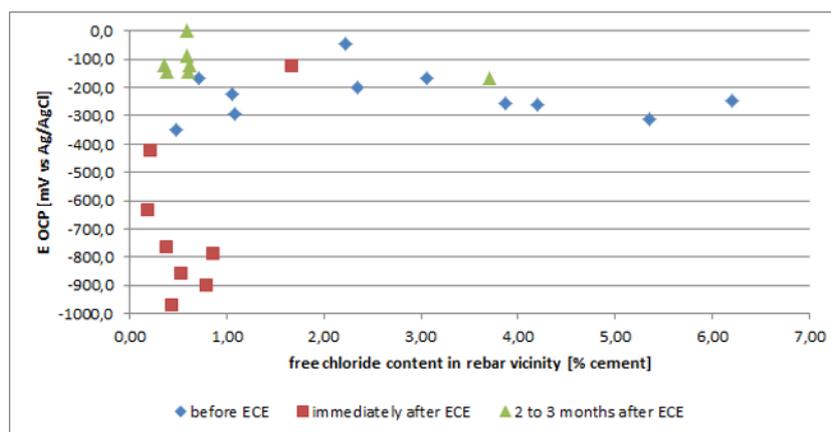


Fig. 11. Open circuit potentials versus chloride content in rebar vicinity at different stages of ECE

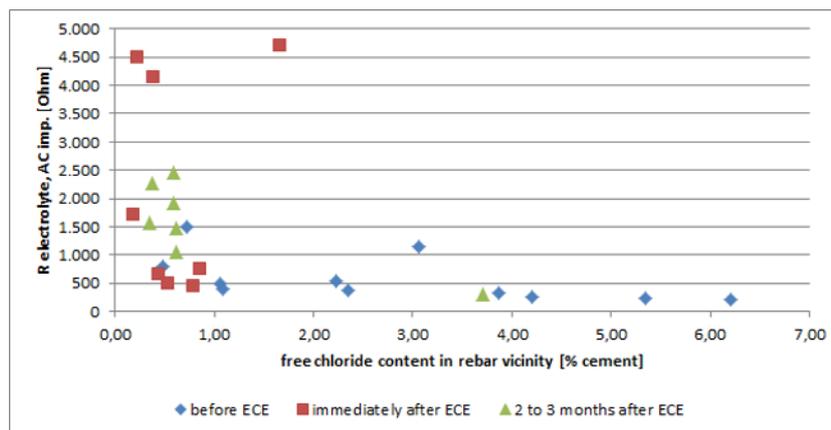


Fig. 12. Electrolyte resistances versus chloride content in rebar vicinity at different stages of ECE

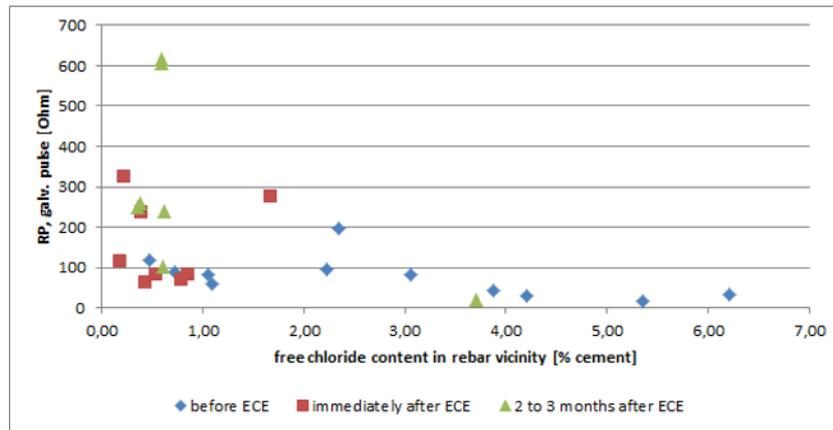


Fig. 13. Polarization resistances versus chloride content in rebar vicinity at different stages of ECE

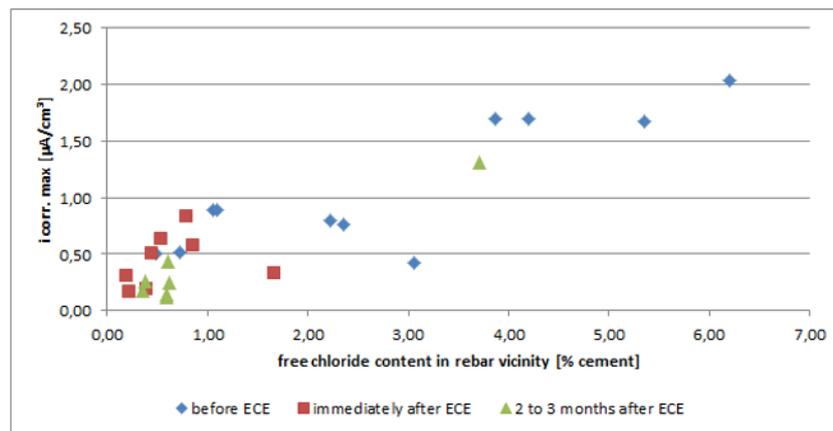


Fig. 14. Assumed maximum corrosion rates versus chloride content in rebar vicinity at different stages of ECE

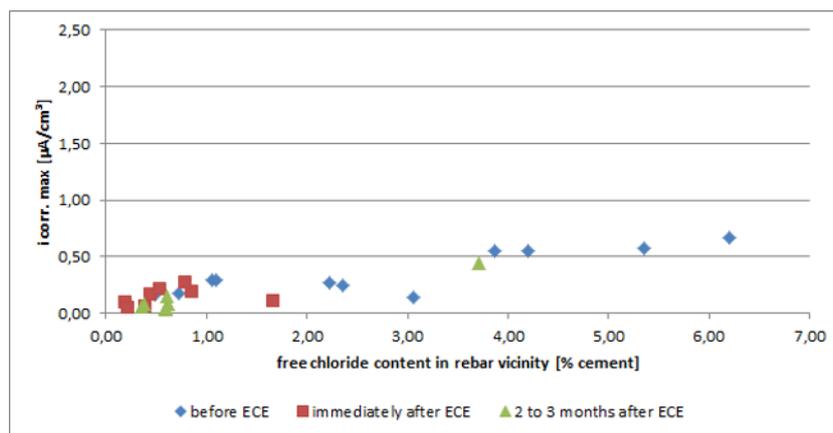


Fig. 15. Assumed minimum corrosion rates versus chloride content in rebar vicinity at different stages of ECE

In figs 16 and 17, the minimum and maximum i_{corr} values are displayed against the respective R_B and R_P values. The 4 regression lines have a good fit to the data points ($R^2 > 0.8$), so it is possible to extract some limit values for R_B and R_P that may characterize passive behaviour. As passive corrosion rates, 0.1 or $0.2 \mu A/cm^2$ are commonly considered. In [7] these two values are assigned to the type of measurement cell; without a guard ring $0.2 \mu A/cm^2$ is suggested, which has been the case for the measurements discussed here. Table 2 summarizes the results:

Table 2. Limit R_B and R_P values for passive condition

$i_{passive}$ $\mu A/cm^2$	R_B Ohm			R_P Ohm		
	min	max	avg	min	max	avg
0.20	700	2,800	1,750	90	340	215
0.10	1,700	6,000	3,850	200	700	450

With these average R_B and R_P limit values and the average i_{corr} values, the evaluation of the measurement results of table 1 is made in table 3. There, an extended assessment scheme is used with limit values, partly

specified by experience, which classify the data into “good”, “intermediate” and “poor”. The ECE results of the 3 project cases can now be discussed as follows:

Hollow box girder floor slab: Despite that in 3 of 4 test locations the target chloride content of 0.4 % cement mass in rebar vicinity could not be met according to CEN TS 14038-2 and the impressed charges were rather low (between 300 and 650 Ah/m²), the electrochemical data indicated that passive conditions were achieved for the polarization resistance and the corrosion rate.

In this project, all data were measured before, directly after and 3 months after the ECE, and a similar development of the electrochemical data can be seen in all test locations: directly after the ECE the electrolyte resistances R_B are at least in the same range as before, the polarization resistances R_P have partly dropped, while the I_{corr} values have remained or dropped slightly under apparent critical measurement conditions (between 6 and 15 % water content). The data obtained 3 months later indicate that this can already be interpreted as signs of a successful treatment as then all corrosion rates dropped by 65 to 80 % and were found in the passive range. The R_B and R_P values were also measured at levels indicating passivity according to table 2.

Track bed of a subway: In 3 of the 4 test locations (ref 1, 2, 4) the target chloride was reached, and due to the multi-stage treatments, the impressed charge was well above 1,000 Ah/m². The R_B , R_P and i_{corr} values of ref 2 were not in the specified range of passivity yet, but the respective OCP certainly indicated cathodic polarization, so the corrosion behaviour could be expected to be in the safe passive range in the near future. Ref 3 exhibits still a high residual chloride (after > 6 % of initial chloride content), but surprising positive OCP along with sufficiently high R_B and R_P values. Considering the experiences from the box girder floor slab case, sound passivity can be expected also here within the next months.

Wall section of a highway tunnel: The data of this ECE application in table 1 show the effect of the insufficient treatment time on the results: in ref 1 and 2 only little charge could be impressed (the vertical arrangement of the electrodes cannot support good conditions for wetting the concrete even with an implemented water supply). Consequently, the water content remained rather low, and especially in ref 2 more than 3.7 % chloride remained in the rebar vicinity. However, some effect of corrosion protection seemed to be achieved, as the potentials were at a quite positive level and did not show considerable differences between the test locations. Because of the time restrictions on this site it was decided to provide additional corrosion protection by discrete zinc anodes in the areas of initially very negative potentials.

4 Conclusions

The use of enhanced corrosion measurements for the instant evaluation of the success of an ECE treatment seems feasible and can support the usual evaluation by chloride content determination and impressed charge

quite well, especially if the target chloride values could not be met.

The observed similar increase of R_B and R_P along with the substantial drop of corrosion currents and of the assumed corrosion rates during 3 months after should be verified in future projects. If there is systematic, reliable development, this knowledge can be used for the extrapolation of the corrosion data and also for determining a suitable, early end point of treatment.

However, it is not advised to run an ECE under a tight schedule, especially if the conditions are difficult (chloride behind outer rebar layer, low concrete cover, chance of technical problems). If the targets of the ECE treatment are not met for any reason and there is no opportunity for repeated treatments, the ECE cannot be successful, which is not a disadvantage of the technology but the consequence of an improper design.

5 References

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Table 1: Results of the enhanced corrosion measurements in comparison to the other process data of all 3 project cases

project	ref	stage	cover mm	chl. max % cement	chl. rebar % cement	water rebar % concrete	chl. removed g/m ²	charge Ah.m ² .rebar	weeks	cycles	E _{OCP} mV vs SE	R _B Ohm	R _p .GPM Ohm	R _p .LPR Ohm	I _{corr} µA	i _{corr} .max µA/cm ²	i _{corr} .min µA/cm ²	
box girder floor slab	1	before ECE	19	2,35	2,35	2,96	98	665	7,0	1	-197,7	382	198	580	696	60	0,25	
		after ECE																
		ECE + 3m																
	2	before ECE	20	1,05	1,05	3,46	98	665	7,0	1	-225,3	490	82	572	848	70	0,29	
		after ECE																
		ECE + 3m																
3	before ECE	35	1,05	0,48	3,32	98	505	7,0	1	-346,9	790	118	908	1321	40	0,17		
	after ECE																	
	ECE + 3m																	
4	before ECE	36	1,86	1,09	3,75	98	302	7,0	1	-293,0	407	61	468	689	70	0,29		
	after ECE																	
	ECE + 3m																	
trackbed	1	before ECE	38	3,87	3,87	3,97	67	1,215	13,0	2	-257,0	327	42	369	475	100	1,70	0,55
		after ECE																
	2	before ECE	40	4,20	4,20	4,37	103	1,950	16,0	3	-261,0	258	31	289	410	100	1,70	0,55
		after ECE																
	3	before ECE	42	6,21	6,21	5,17	103	1,525	16,0	3	-635,0	1,710	114	1,824	2,690	18	0,31	0,10
		after ECE																
4	before ECE	44	5,78	3,06	4,09	103	1,423	16,0	3	-248,0	205	32	237	300	120	2,04	0,66	
	after ECE																	
tunnel wall	1	before ECE	38	1,56	0,72	1,62	37	219	3,5	1	-168,0	1,140	81	1,201	1,577	25	0,43	0,14
		ECE + 2m																
	2	before ECE	33	5,35	5,35	2,85	37	131	3,5	1	-423,0	4,500	324	4,824	4,882	10	0,16	0,05
		ECE + 2m																
	3	before ECE	39	2,82	2,23	n.a.	101	441	6,5	1	-165,0	303	20	323	348	90	1,31	0,45
		ECE + 2m																

high (> 1.0 .. 10.0 µA/cm²)
 moderate to low (> 0.2 .. 1.0 µA/cm²)
 passive (< 0.2 µA/cm²)

classification of corrosion current densities
 measurement cell without guarding

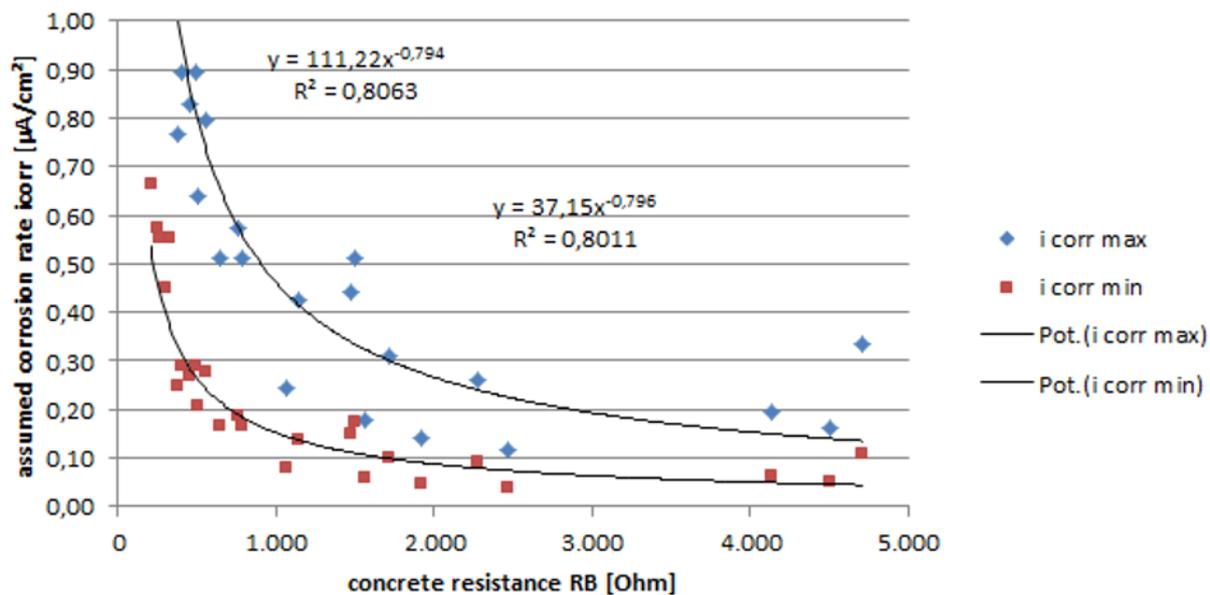


Fig. 16. Regression curves of the assumed maximum and minimum corrosion rates versus the concrete resistances

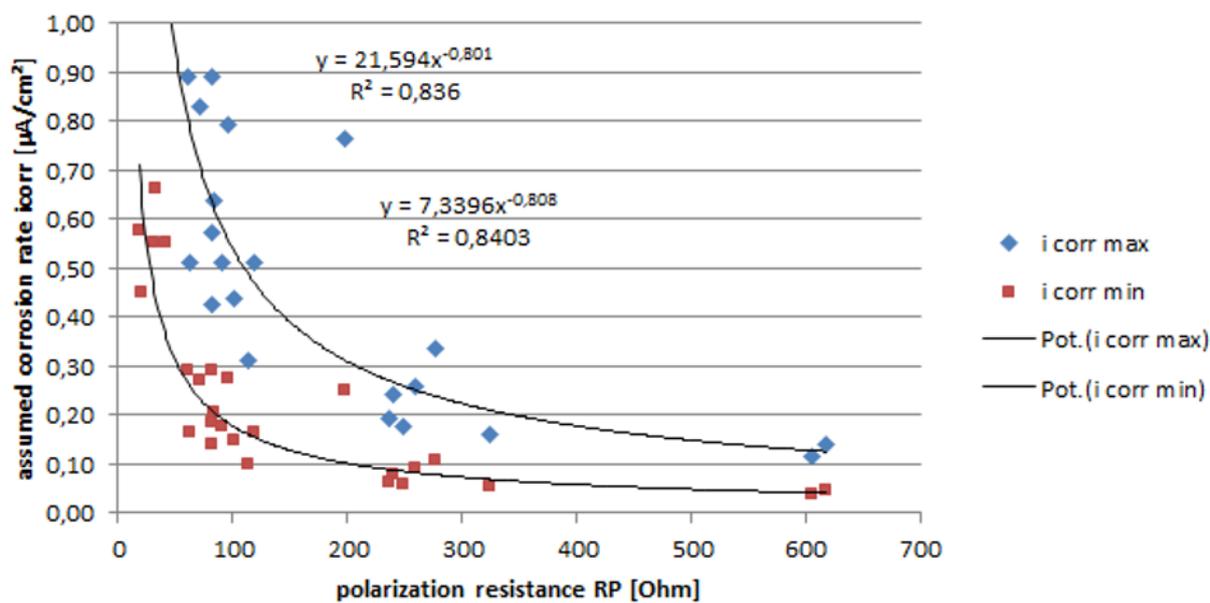


Fig. 17. Regression curves of the assumed maximum and minimum corrosion rates versus the polarization resistances

Table 3. Evaluated data of the measurements after ECE

project	ref	stage	chl. rebar % cement	water rebar % concrete	charge Ah/m ² rebar	E _{ocp} mV vs SE	R _B Ohm	R _B increase	R _p Ohm	R _p increase	i _{corr, avg} µA/cm ²	I _{corr} reduction	I _{corr} end to 3 m
box girder floor slab	1	after ECE	0,86	12,44	665	-790,7	760	199%	82	41%	0,38	-2,5%	
		ECE + 3m	0,59	1,68		-87,5	2.460	644%	606	306%	0,08	-85%	-80%
	2	after ECE	0,79	15,34	665	-898,6	450	92%	71	87%	0,55	-7%	
		ECE + 3m	0,62	4,15		-122,3	1.060	216%	239	291%	0,16	-73%	-71%
	3	after ECE	0,44	6,45	505	-970,9	650	82%	63	53%	0,34	0%	
		ECE + 3m	0,35	3,72		-120,0	1.560	197%	248	210%	0,12	-65%	-65%
track bed	4	after ECE	0,54	6,17	302	-857,9	500	123%	83	136%	0,42	-29%	
		ECE + 3m	0,59	4,34		0,0	1.920	472%	617	1011%	0,09	-84%	-78%
	1	after ECE	0,39	4,31	1.215	-765,0	4.134	1264%	237	564%	0,13	-89%	
	2	after ECE	0,19	4,20	1.950	-635,0	1.710	663%	114	368%	0,21	-82%	
tunnel wall	3	after ECE	1,67	4,88	1.525	-127,0	4.702	2294%	277	866%	0,22	-84%	
		after ECE	0,22	5,14	1.423	-423,0	4.500	395%	324	400%	0,11	-62%	
	1	ECE + 2m	0,61	2,92	219	-145,0	1.470	98%	101	112%	0,30	-14%	
	2	ECE + 2m	3,71	3,01	131	-165,0	303	121%	20	111%	0,88	-22%	
	3	ECE + 2m	0,38	n.a.	441	-145,0	2.270	413%	259	273%	0,18	-67%	

good/ suitable
 intermediate
 poor/ insufficient

< 0,4
 0,4 .. 1,0
 > 1,0
 < 3,5
 3,5 .. 4,5
 > 4,5
 > 600
 400 .. 600
 < 400
 > -200
 -200 ... -300
 < -300
 > 1750
 1750 .. 1000
 < 1000
 > 215
 215 .. 100
 < 100
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 0,2 .. 1,0
 > 1,0