

# A State-of-the-Art Review of Electrochemical Chloride Extraction for Concrete Structures

**Thamara Tofeti Lima**

iBMB (Institute of Building Materials, Concrete Constructions and Fire Safety), Division of Concrete Construction,  
TU Braunschweig, Braunschweig, Germany  
Email: [t.tofetilima@ibmb.tu-bs.de](mailto:t.tofetilima@ibmb.tu-bs.de)

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## Abstract

Electrochemical chloride extraction is a promising technique for the rehabilitation of concrete structures under chloride induced corrosion. This study consists of an extensive literature review of this treatment including application cases. It is found that the rate of chlorides removed is affected by the total charge passed, whereas increasing charge in a range between 1500 to 2000 Ah/m<sup>2</sup> increases the amount of chlorides removed and this can be more effective by increasing current density instead of duration of treatment. Bound chlorides are extracted during treatment and, water works better than Ca(OH)<sub>2</sub> as an electrolyte, possibly due to modifications on the concrete pore structure. Moreover, ECE is not efficient in re-passivate structures but is efficient in its purpose of removing chlorides if treatment setup is well planned, which justifies the need for better international standards on the topic.

## Keywords

Chloride Induced Corrosion, Corrosion Rehabilitation, Electrochemical Chloride Extraction, Electrochemical Rehabilitation Methods, Steel Reinforced Concrete

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## 1. Introduction

Durability of concrete structures can be defined as its capacity to resist aggressive conditions from the environment, such as a chemical attack, weathering, abrasion, or any other externality that can be harmful to its quality and reduce the service life. The concerns about structural durability are found in the literature from early periods when Wig and Ferguson [1] pointed out that more than the disintegration of concrete itself, corrosion of reinforcing steel is the greatest harm for durability, in severe aggressive environments. Gjorv [2] affirmed that

the energy and resource consumption for the maintenance of concrete structures is producing a significant environmental burden and large quantities of waste. Therefore, the lack of measures focused on the durability problems does not represent only a technical and economical issue but also brings sustainability and ecological problems. Corrosion of steel has been considered the leading cause of failure for concrete structures considering that it is complicated to detect corrosion at the initial phase therefore when it is detected usually the structure is already severely damaged [3]. This is confirmed by different reviews, analyzing practical cases of premature deterioration of RC structures, and it was said that in 70% - 90% of the evaluated cases, corrosion was the dominant degradation mechanism. Knudsen *et al.* [4] estimated annual costs of \$5 billion for repair of corroded concrete structures in Western Europe. In the United States, a report produced by the Federal Highway Administration (FHWA) in 2002 estimated the direct costs associated with metallic corrosion in nearly every industry sector, from infrastructure and transportation to production and manufacturing and the results lead to a staggering \$276 billion—approximately 3.1% of the nation's Gross Domestic Product (GDP) [5]. The annual direct cost of corrosion in highway bridges alone is roughly \$8.3 billion, including maintenance, repair, replacement, and the cost of capital. Indirect costs, including traffic delays and lost productivity, may run 10 times that number. However, corrosion is more than an economic issue. In May 2000, in Concord, North Carolina, USA, more than 100 people were injured when steel strands corroded in a pre-stressed concrete pedestrian bridge and the structure collapsed onto the highway below.

Exposure of reinforced concrete to chloride ions is one of the main reasons for premature corrosion seeing that the intrusion of aggressive chloride ions from the external environment into reinforced concrete can lead to acidification and, if oxygen and moisture are available, it can sustain the corrosion reactions. Traditional techniques to repair corrosion in concrete structures consisted of removing the damaged area, clearing the rust of rebar, coating and covering it with less permeable concrete. This method was complex for being executed and sometimes not the most economical and sustainable option although it was temporarily efficient. Moreover, the biggest issue of traditional techniques consisted of not dealing with chemical attacks from the environment, such as ingress of chloride ions, therefore even after repair, the risk of corrosion was yet considerable. Therefore, electrochemical rehabilitation methods were developed to handle these limitations by mitigating corrosion through the passage of a direct current, which involves the migration of aggressive ions away from the steel rebar and alkaline ions from the concrete to the steel vicinity, restoring alkalinity of the environment. Among those, cathodic protection, realkalization and chloride extraction are the most explored and recently, in the US, the focus is given preferentially to chloride extraction due to its short-term characteristic compared to permanent treatments.

Many papers were presented on the last 50 years to explain mechanisms of

ECE and how to improve its efficiency, however innumerable questions remain unanswered. A wide range of results is presented on the efficiency of the treatment, for example. The percentage of extracted chlorides varies from as low as 30% for carbonated structures [6], which would be useless, to complete removal [7], which is almost impossible to be achieved at all depths of the concrete cover. The setup of ECE consists on the treatment arrangement, for example, the electrolyte and anode choices, the most appropriated current density and, some extra features that can be included to achieve better results. A variety of setup options is found as well including the usage of Na(OH), water, Ca(OH)<sub>2</sub> and Sodium Borate as electrolytes; titanium mesh, stainless steel, or carbon coats as anodes; and a total charge passed going from as low as 500 Ah/m<sup>2</sup> to as high as 4032 Ah/m<sup>2</sup>. There are a number of reports on the effectiveness of ECE method however, up to date it was not enough to establish an optimal system and more studies are needed to increase efficiency of treatment, which is the aim of this paper. Through a literature review, principles of electrochemical treatments are first introduced and standards and guidelines are discussed. Aiming to clarify some aspects of the treatment the focus will be: differences among standards and necessity of a unified code, influence of charge passed and electrolyte on chloride removal rate, post treatment evaluations concerning repassivation of structure and a minor issue on side effects of ECE on structural behavior.

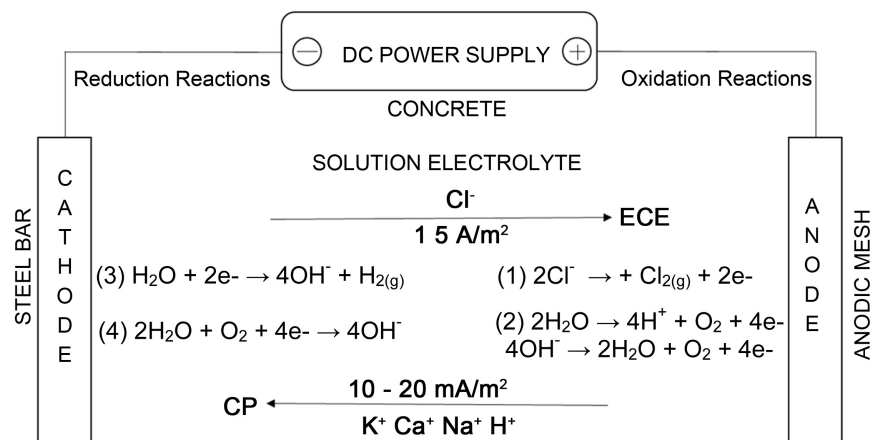
## 2. Mechanism of Electrochemical Treatments

Electrochemical treatments for concrete structures were developed from the 60's as a non-destructive option to combat concrete deterioration as preventive or rehabilitation methods mainly focused on the damage caused by corrosion of reinforcement. There are some options of electrochemical treatments classified according to the aim of treatment. The first electrochemical treatment to be largely applied was Cathodic Protection (CP), dating from 1959. On cathodic-protection, the external power supply provides the direct current to the embedded steel to polarize it into a more negative potential, less susceptible to corrosion progress. The current density applied during this process is usually limited to 10 - 20 mA/m<sup>2</sup> of reinforcement, requiring a permanent time of application usually considering lifespan of 15 - 25 years [8]. According to the guidelines, CP is more effective when applied to the structure as a preventive measure. According to Broomfield [9] [10], until 1994, there were more than one million square meters of cathodic protection applied in concrete structures in the United States and Canada and, probably, another million or more in the rest of the world. Later, dating from 70's, another technique called Electrochemical Chloride Extraction (ECE) was developed. ECE has a similar mechanism to CP but applying higher current densities, varying between 1 to 5 A/m<sup>2</sup>, which implies shorter periods of treatment varying from few weeks to months, aiming mainly the electrochemical migration of chloride ions away from the steel rebar. The total

amount of charge (current x time) applied for chloride extraction is about the same as cathodic protection would deliver over a period of about 10 years [11]. The chemical reactions involved on the process for electrochemical treatments are classified in two groups: 1). the reduction of corrosion products at the steel surface parallel to the migration of alkaline cations from hydration products, and, 2). the oxidation of some aggressive ions and release into the surface covered by the external anode, represented by Equations (1) to (4) pointed in **Figure 1**. The corrosion products are electrochemically reduced at the cathode represented by the steel rebar, in addition to the reaction represented by Equation (4), producing hydroxyl ions, increasing alkalinity of the vicinity. Hydrogen evolution occurs at the rebar due to the low potential induced by high current densities as it can be seen in Equation (3); hydrogen gas is evolved at  $-1170$  mV. The electrochemical reactions at the external anode are represented by Equations (1) and (2), and, include the evolution of chlorine gas and oxygen. However, the chlorine production can be avoided if the pH of electrolyte solution is kept alkaline or neutral, at least. It is possible to see as well by Equation (1) that oxygen is used at the beginning so that hydroxyl and chloride ions can move to the external anode through the pores of concrete. Therefore, the aggressive chloride ions are removed gradually as the treatments continue.

### 3. Standards and Guidelines

Currently the official standards for ECE are still under development in most parts of the world. The first institute to mention ECE for concrete structures was the Federal Highway Administration of the USA in 1970s, and the first trials were conducted in Ohio and Kansas [12]. The projects completed in North America followed guidelines developed by the Strategic Highway Research Program National Research Council, the document SHRP-S-347 [8], containing a detailed implementation guide of ECE in addition to some criteria introduced by clients requesting the repair. However, the American society is working on more



**Figure 1.** Schematic representation of main electrochemical treatments and chemical reactions involved.

focused discussions for producing an official specification since 1995 until nowadays. For the European side, the Danish standard DS/CEN/TS 14038-2 [13] was recently developed and is more widely accepted. Due to the lack of specifications but promising effect of ECE, a company named Norcure applied for a patent in 1988 [14], containing details on the setup of treatment to make it time and cost efficient. In 2022, a specific task group from the federation Internationale du B'eton wrote a chapter on better practices on chloride extraction/ desalination [15]. The fact that the technology for ECE is still considered new and underdeveloped in some countries, and, standards lack better information considering actual engineering applications, leads to some problems that remain uncovered and some will be further discussed.

Three major variables play an important role during the chloride removal process, the direct current, the electrolyte solution, the external anode, therefore the choice over them is of great importance, and guidelines suggest some options, different from each other. The variations on guidelines are summarized on **Table 1**. Concerning electrolytes, SHRP-S-347 indicates the usage of a Borate Buffered electrolyte to avoid alkali silica reaction (ASR) during the process, while the Danish Standard do not specify any solution, just mention that it should be alkaline, and, the Norcure patent suggests fresh water. These differences can be explained by the fact that the availability of reactive aggregates in USA is bigger than in Europe due to the geographical location and climate, thus the American guidelines tends to be more worried about ASR when performing ECE. On the other hand, Norcure is a patent from a private company, which means their main goal is the profit over treatment, which explains the choice for water, the cheapest electrolyte possible.

About the direct current, three values are usually defined by guidelines: maximum voltage, maximum current density and total charge passed. The limitations for voltage in the above mentioned guidelines is always around 40 to 50 V due to safety reasons, however this value is yet questionable because the risk of hydrogen evolution at such high voltage is considerably high. It is common to

**Table 1.** Summary of standards and guidelines currently available for ECE.

Reference	Electrolyte	Anode system	Current (A/m <sup>2</sup> )	Duration	Voltage	Total charge (A-hr/m <sup>2</sup> )
SHRP-S-347 USA	NaBo <sub>3</sub> LiBo <sub>3</sub>	Titanium mesh	1 - 2 A/m <sup>2</sup> of steel surface	10 to 50 days	50 V	600 to 1500 A-hr/m <sup>2</sup>
CEN/TS 14038-2 EUROPE	Any alkaline solution	Not specified	1 - 2 A/m <sup>2</sup> of steel surface	Variable	40 V	1000 to 2000 Ah/m <sup>2</sup>
Norcure	Fresh water	Metallic mesh	1 A/m <sup>2</sup> of concrete surface	28 to 56 days	40 V	800 to 1200 A-hr/m <sup>2</sup>

see in papers and reports that the voltage used is around maximum 20 V but for real structures trials, the values tend to be near 40 V considering that it is troublesome to control this value. For current density, the American and Danish standards suggest maximum of 5 A/m<sup>2</sup> of concrete surface, which is questionable as well due to the risk of bond strength reduction and alkali softening caused by high current densities already documented by some authors [16]. Norcure patent is more conservative about maximum current density (1 A/m<sup>2</sup>), which can be explained by the compromise of the private company of not damaging the structure and that if it happens profits can be reduced. Duration of treatment, which is directly related to current density and total charge passed, is informed to be around 50 days, however, this does not reflect a real engineering problem because it is unrealistic to think about completing treatment in less than 2 months.

To define the efficiency of chloride removal post treatment evaluation methods are proposed by the guidelines including most often half-cell potential, macrocell current measurements and visual inspection notations. However, it is important to notice that results provided by the post treatment evaluation can be misjudged by the lack of accuracy. For example, considering half-cell potential, depending on the time that the measurement is executed, the structure is still polarized, therefore high values that would indicate corrosion can be found, while that is not actually the case. Furthermore, authors have already suggested that even though ECE cannot fully repassivate the embedded steel, if the chloride content is reduced to a certain level, the risk of corrosion is reduced, making the half-cell potential measurements inconclusive. On the other hand, accessing the proportion of chloride removed from concrete, through the extraction of core samples and chloride profiling, can be really useful, but it should not be the only indicator. For example, the American guidelines suggest that ECE can extract around 50% of chlorides from bulk concrete, which is true, but if the profile is unknown, it is impossible to know the location of residual chlorides in concrete, which means that they can still emigrate or can be between the reinforcing bars, which does not represent a risk. Thus, it is recommended to use the chloride removal rate considering profile, remembering that is not necessary complete extraction for the treatment to be efficient. If necessary, structural behaviour might be also verified to check compressive strength and bond strength reductions.

#### **4. Application of ECE**

Chloride extraction is being extensively applied to real structures worldwide from the 90's. As reported by the US Department of Transportation [17] until 1999, 12,314 m<sup>2</sup> of concrete bridge structures were treated using ECE, including decks, columns, walls and slabs, suffering from chloride induced corrosion mostly due to the extensive use of de-icing salts. In more developed countries, usually parts of world that started using reinforced concrete as structural materi-

al since earlier periods, rehabilitation techniques, like electrochemical treatments, are more commonly seen. Application cases were reported later from countries in Europe and Japan following the Norcure process guidelines, and in 1996, China began the first ECE tests [18]. Notwithstanding, for some particular developed countries, ECE is not very popular on-site because they believe from practical experience and site investigations that a concrete with high quality (concrete cover of minimum 40 mm, >40 MPa compressive strength, ordinary Portland cement as binder) is still the main method to avoid corrosion. On the other side, for under-developed countries, it is generally accepted that such quality for concrete, as well as correct site placement, presents practical difficulties that cannot always be avoided, due to high costs, yet they usually prefer another method to avoid corrosion, such as galvanization, better than thinking about expensive and complex rehabilitation methods.

Reviewing the literature available on ECE reveals that on the same application case it is possible to occur really low and high chloride removal rates due to difficulties on the installation of treatment. Problems that can occur include: the concrete resistance on site is too high and decreases efficiency of current passed; the anode does not cover the total concrete area to be treated, causing different removal at the same structural component; or the electrolyte is led to acidification if it is not daily monitored increasing chlorine gas evolution. Moreover, due to lack of planning after treatment, it can be useless, such as in case of the Campus Loop Bridge repair, in Albany, New York. On this case, after treatment was applied the structure was not repaired for cracks, thus, as time passed, remigration of chloride ions summed up to the ingress of more chloride ions from the environment and, dissipation of hydroxyl, made the perfect scenario for corrosion to start again. On the other hand, in some other cases, companies reported that although the chloride content after treatment was still above the threshold present on standards and guidelines for causing corrosion, signs of passivation and visual signs of corrosion repair could be perceived, which is considered enough for the efficiency of treatment [16].

Even though ECE has been used extensively in other countries, not only USA, there are not many reports about case studies for structures on the literature. One challenge of evaluating and reviewing application cases of ECE is that as a new technique, the long-term measurements are still on going, what slow the process of publishing reports. One of the most recent applications of ECE was conducted in Zhanjiang, a southern city in China. The results measured on field pointed to the reduction of chloride ions after ECE and the relationship between total electricity quantity and residue chlorides on the structure. After two months the current potential of the steel rebar was measured at different places of the testing beam and it showed that the potential was reduced after ECE. The electrical potential after treatment was higher than 150 mV for all points tested, which implicates that the risk of corrosion was lower than 10%, confirming that ECE mitigated the corrosion state of embedded steel and recovered

the structure [19].

## 5. Efficiency of ECE

### 5.1. Chloride Removal Rate

Various conditions can affect the chloride removal rate during ECE, including voltage, current density, electrolyte solution type, anode materials, concrete mix design and geometry of reinforcement. Most part of research papers choose only a few factors to be studied in normal conditions considering that the relationship between influencing factors and the order of significance among them is still unknown. On this line, this literature review gathered data from a significant number of papers which can be seen in **Table 2** that contains as well some application cases specifically in USA, due to the amount of details on reports available for the public access. Following, in each specific case, some factors are kept constant and the relevant one is modified, in order to identify the influence of treatment setup on chloride removal. It is meaningful to note that cases compared on this paper will mainly refer to the electrical current quantity in terms of charge passed instead of current density, because on this way it is possible to align different current densities that applied for different durations, delivered the same amounts of charge in Ah/m<sup>2</sup>.

#### 5.1.1. Influence of Charge Passed on Chloride Removal

It is a plausible affirmation that increasing the charge passed during ECE can increase the chloride removal because the stronger is the force acting on the ions, the greater is the migration speed of them, based on the concept of local current strength [56]. An analysis of the data compelled in **Table 2** is given in **Figure 2(a)** and **Figure 2(b)**, confirming that an increase in the charge passed is accompanied by an increase in the chloride removal rate. However, it is possible to see as well that the removal rate increases just until a certain level, around 70% to 80% in most part of the cases, independent of how high it is the charge used. After a certain point an increase in charge passed does not increase the removal rate, thus it is plausible to state that part of the chlorides present in concrete cannot be extracted by any circumstance under the electrochemical removal irrespective of the initial dosage level, which will be discussed in further details on the next section. Another visible trend is that for higher initial contamination levels same removal rates can be achieved at lower current densities, Cheang *et al.* stated confirming what, because higher initial chloride contents implicate higher free chloride proportions [57].

An increasing in the amount of electric charges passed during ECE treatment seems to be beneficial for chloride removal just until a certain level, that seems to be around 1500 to 2000 Ah/m<sup>2</sup> according to graph on **Figure 2**. A rise of the total charge passed can be achieved by either increasing the current density of treatment or increasing the period of application. Hassanein *et al.* [58] argued that as period of treatment is extended the concentration of chloride ions of the



**Table 2.** Data collected organized author, setup of treatment and removal rate.

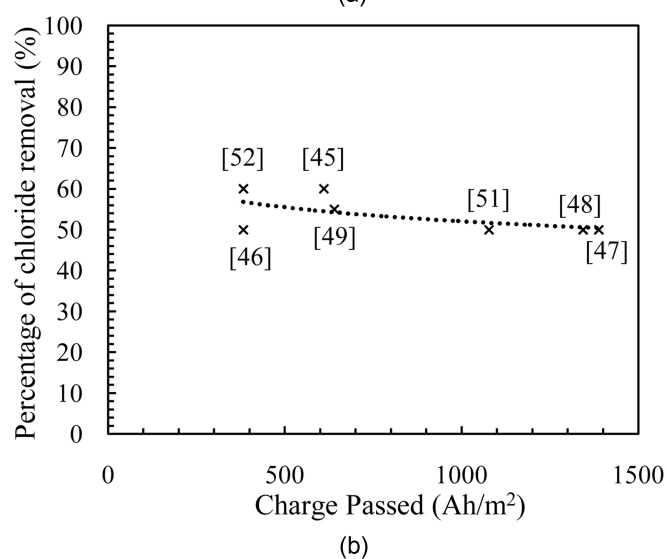
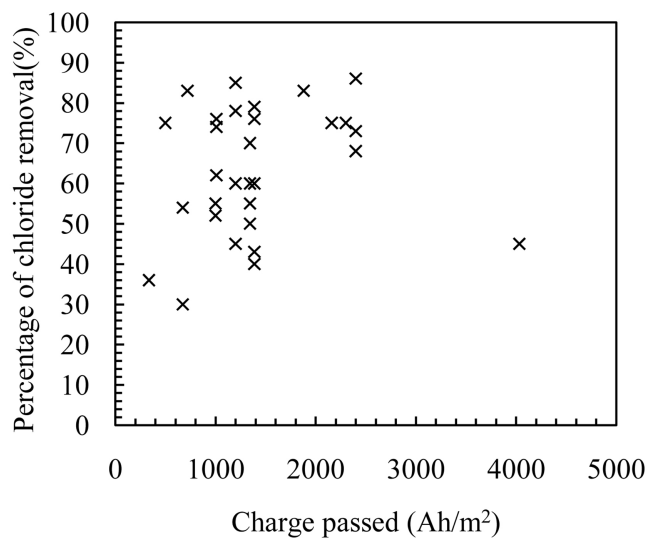
Author	Anode	Electrolyte	Initial Cl <sup>-</sup> content	Current density (A/m <sup>2*</sup> )	Duration (weeks)	Charge Passed (Ah/m <sup>2</sup> )	Removal rate (%)	Ref
Arya <i>et al.</i>	TM	NaOH	4	1.0	12	2000	67	E [20]
			3	1.0	12	2000	59	
			2	1.0	12	2000	36	
			1.87	1.0	12	2000	50	
			1.87	0.75	8	600	45	
Ihekwaba	TM	Na <sub>3</sub> BO <sub>3</sub>	3	3.0	8	4032	45	E [16]
		Na <sub>3</sub> BO <sub>3</sub>	1.7	1.0	8	1344	55	
Buenfeld and Broomfield	TM	Water	1.5	0.75	4	500	75	E [21]
Otero <i>et al.</i>	TM	Ca(OH) <sub>2</sub>	3	1.0	4	672	54	E [22]
Sharp <i>et al.</i>	TM	Ca(OH) <sub>2</sub>	3	1.0	7	1200	60	E [23]
Polder <i>et al.</i>	TM	Water	3	4.0	3	2300	75	E [24]
Chang	TM	Ca(OH) <sub>2</sub>	3	1.88	6	1880	83	E [25]
Sieglwart <i>et al.</i>	TM	Water	2	5.0	6 days	1388	79	E [26]
Orellan <i>et al.</i>	TM	Ca(OH) <sub>2</sub>	3	1.0	7	1200	45	E [27]
Hosseini and Khaloo	TM	Ca(OH) <sub>2</sub>	2	1.0	8	1344	60	E [28]
			1.5		8	1344	50	
Sanchez <i>et al.</i>	TM	Water	3	5.0	8	1388	43	E [29]
Miranda <i>et al.</i>	SS	Ca(OH) <sub>2</sub>	3	1.0	12 days	1200	85	E [30]
Sanchez <i>et al.</i>	TM	Water	3	5.0	6	1388	76	E [31]
Climent <i>et al.</i>	TM	Water	0.5	5.0	12 days	1388	40	E [32]
							60	
Swamy and McHugh	TM	Ca(OH) <sub>2</sub>	2.4	1.0	12 days	1344	70	E [33]
Fajardo <i>et al.</i>	TM	Water	4.6	1.0	~13	2160	75	E [34]
Miranda <i>et al.</i>	TM	Ca(OH) <sub>2</sub>	3	1.2	6	1200	78	E [35]
Elsener and Angst	SS	Water	1.5	0.63	8	860	69	E [36]
Abdelaziz <i>et al.</i>	SS	Water	3	1.0	4	672	30	E [37]
		Ca(OH) <sub>2</sub>	5		2	336	36	
Canon <i>et al.</i>	TM	Water	1.5	5.0		1000	79	E [38]
Qiao <i>et al.</i>	SS	Ca(OH) <sub>2</sub>	3	1.0		720	83	E [39]
Yodsujai <i>et al.</i>	SS	NaOH	5	1.5	4	1008	62	E [40]
		KOH					74	
		Ca(OH) <sub>2</sub>					76	

## Continued

Martinez <i>et al.</i>	TM	Water	5	N/A**	N/A	2400	73	E [41] [42]
			2.5				68	
			2				86	
Shan <i>et al.</i>	TM	Ca(OH) <sub>2</sub>	2	N/A**		1000	52	E [43]
Xia <i>et al.</i>	SS	Ca(OH) <sub>2</sub>	3	1.0	2	1344	60	E [44]
Tissier <i>et al.</i>	TM	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	0.9	1.0	8	1344	90	E [45]
Lin <i>et al.</i>	MPC-CFRP	Ca(OH) <sub>2</sub>	1.8	1.0	4	1344	50	E [46]
				2.0			62	
				3.0			75	
Hao <i>et al.</i>	MPC-CFRP	Ca(OH) <sub>2</sub>	1.8	3.0	4	2016	60	E [47]
de Almeida Souza <i>et al.</i>	SS	Ca(OH) <sub>2</sub>	0.9	1.0	8	1344	80 84	E [48]
Bennet and Schue	SS	Water	N/A***	1.0	8	610	60	IS [14]
Clemena and Jackson	TM	Water	N/A***	1.0	10 - 11	249 - 382	44	IS [49]
Whitmore	TM	Water	N/A***	0.7 - 1.0	6 - 8	1388	50	IS [50]
Jacobsen <i>et al.</i>	TM	Ca(OH) <sub>2</sub>	N/A***	1.0	8	1344	52	IS [51]
FHWA	TM	Na <sub>3</sub> Bo <sub>3</sub>	N/A***	0.7	9	640	55	IS [52]
FHWA	TM	Na <sub>3</sub> Bo <sub>3</sub>	N/A***	1.1 - 3.2	2 - 3	800 - 930		IS [53]
FHWA	SS	Li <sub>3</sub> Bo <sub>3</sub>	N/A***	0.7 - 0.9	8	741 - 1077	40	IS [54]
FHWA	SS	Ca(OH) <sub>2</sub>	N/A***	0.3 - 0.45	10 - 11	382	50	IS [55]

\*Current density measured by A/m<sup>2</sup> of concrete surface, \*\*Constant voltage and not constant current density, \*\*\*For real structures usually there is no fixed determination of initial chloride content because it is variable (Abbreviations: TM: Titanium mesh, SS: Stainless Steel, E: Experimental, IS: In site).

pore solution decreases and so the proportion of current due to migration of these ions, which is already one explanation for a not linear relationship among increasing charge passed and chloride removal. Some authors [59] affirm that the magnitude of current density has a more significant effect on removing chlorides and increasing the pH of the pore solution near the rebar due to the increase in the local current strength as it was mentioned earlier on this topic. Increasing just time of treatment does not allow redistribution of chlorides, therefore the concentration of free chlorides decreases to low levels and then it stop, which is the idea that based intermittent electrochemical chloride extraction. Moreover, although opting for increasing current density instead of treatment time seems to be more efficient it is of concern the side effects included when a high current density is used, such as loss of bond strength, which is not totally proved yet. In addition, using high current density on field is a dangerous option for the workers involved on the process due to the possibility of short circuit.



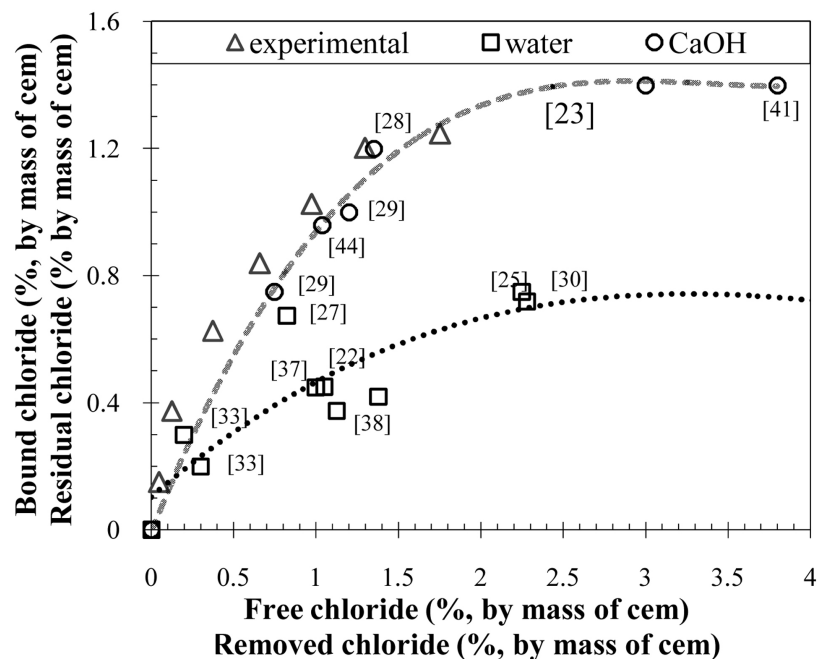
**Figure 2.** Influence of charge passed on the chloride removal rate for (a) experimental cases and (b) in site structures. \*Due to the amount of cases, reference numbers are not added as labels for each data on the experimental cases, aiming to provide a clearer view of the figure. For more details in each case, refer to **Table 2**.

### 5.1.2. Influence of Different Electrolytes and Chloride Types on Chloride Removal

For instance, it is from common knowledge that chlorides are present in concrete as free and bound chlorides, which can be divided into physically and chemically bound. Glass *et al.* [60] classified the chloride ions taking into consideration mainly the mobility level, leading to four types of chloride ions—free, bound, loosely bound and strongly bound. Still according to Glass *et al.* the “loosely bound chlorides” are called this way because they can be easily extracted from C-S-H gel, by physical adsorption. An increased temperature for example could already accelerate the thermal vibration of absorbents, breaking the weak

physical binding, generating more free chlorides, turning that these ions are bound but still mobile [61]. The movement of physically bound chloride is affected as well by the surrounding molecules and increases with increasing distance from the surface of hydration product [62]. Seeing in this way, Pargar *et al.* [63] says that physically bound chlorides can be considered as free chloride ions but with low activity. Therefore, the term bound chlorides refers to the chemically bound chlorides, which cannot be extracted under physical changes of the environment.

For a long period, it was thought that free chlorides mean water soluble and mobile ones, while the bound would count for immobile ions. However, this hypothesis was proved to be partially wrong as investigations about chloride binding raised up. Elsener and Angst [36] and Tritthart *et al.* [64] pointed that during the chloride removal process, sometimes the total amount of chlorides removed overcome the total amount of free chlorides, which clearly means that part of bound chlorides can be removed under the electrical field, contradicting the previous idea. In order to investigate details of the chloride removal and still relate it to different electrolytes, **Figure 3** shows a graph combining data about the chloride binding capacity and chloride removal under ECE. The binding capacity curves were obtained experimentally through chloride profiling generating the Langmuir and Freundlich isotherms, while data obtained by the literature review were organized in terms of residual and removed chlorides considering different electrolytes, water and  $\text{Ca}(\text{OH})_2$ , used during ECE.



**Figure 3.** Quantification of residual and removed chlorides in terms of different electrolytes using results obtained by the literature review compared to values obtained experimentally in this study for bound and free chlorides in terms of the chloride binding curve.

According to the curves obtained, it can be seen that using calcium hydroxide, the chloride extraction follows a similar trend to what is expected by the chloride binding capacity, being the amount of bound and residual chlorides in concrete pretty similar. Withal, for water it is seen that the amount of residual chlorides is lower than the amount of bound chlorides on the isotherms, which proves that definitely part of these bound chlorides are being extracted during treatment, which follows the hypothesis about extraction of bound chlorides. It is important to highlight that the removal of bound chlorides must accompany on the same proportion a release into free because it is mostly impossible that these chloride molecules just migrated through concrete pores due to limitations of pore size and connectivity. This difference among electrolytes on the possibility of reducing the maximum of residual chlorides can hypothetically be explained by the precipitation of  $\text{Ca}(\text{OH})_2$  in the concrete pores that would reduce mobility of chloride ions, which does not happen when water is used. The precipitation of certain ions on the concrete pores is proved from the late 80's when electro-deposition method was developed in Japan as a crack-repair treatment, where a direct current is provided between the reinforcing steel bar and an anode placed on the concrete surface, system which is pretty similar to the one used for chloride removal [65].

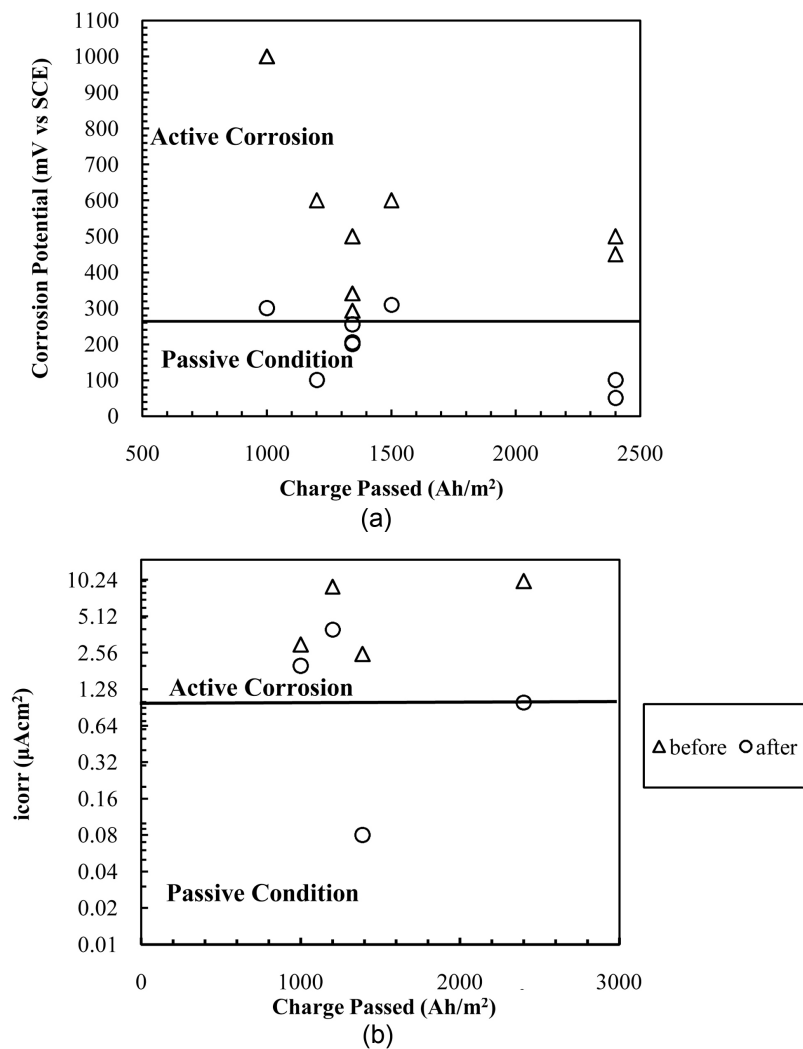
## 5.2. Post Treatment Evaluation

The progress and efficiency of ECE applied for concrete structures can be monitored by different approaches. The first and most common way is to check the chloride content on the concrete body before and after treatment, through chloride profiling, and compare the final result with the CTL (chloride threshold level). Using just this measure implies some limitations because the CTL is still under discussion and there is no total agreement about a unique value; on structures with nonhomogeneous chloride distribution making a comparison of values before and after treatment is complicated; and drilling the concrete to get samples for profiling would cause some damage as it is a destructive method. Another method would be checking the chloride content on the confined electrolyte however this is a plausible option more for laboratory tests, seeing that according to several reports about application of ECE for on-site structures electrolyte tanks are not generally used. In addition, Martinez *et al.* [42] added that the quantification of chlorides removed during treatment does not indicate precise information on the structure passivation, therefore other procedures are needed to confirm whether treatment was efficient or not on interrupting corrosion process.

### Measurement of $E_{\text{corr}}$ and $I_{\text{corr}}$

The procedure for measuring half-cell potentials includes a connection made between the reinforcement and an external reference electrode such as copper, copper sulphate, CSE and SCE and then potential readings are taken on the con-

crete surface. Elsener [66] performed a detailed analysis on the validity of half-cell potential measurements on assessing repair of corroded concrete structures and stated that it is not correct to rely in a fixed value to define if passivation was achieved because many factors can influence that condition. Moreover, the above mentioned author affirms that after ECE process is finalized, very negative potentials of rebars are measured because of strong polarization induced by treatment, therefore meaningful potential readings must be taken only after a certain period, usually from one to three months after current is switched off. By doing so, the half-cell potential measurements can provide direct indicators of rebars passive condition, notwithstanding due to the many factors that can affect half-cell potential reading, the interpretation of results must be made carefully because different potential values indicate corrosion of rebars on different structures. **Figure 4(a)** shows data collected by some papers that measured



**Figure 4.** Corrosion values at each given charge passed before and after treatment for data from different authors, in terms of (a) Corrosion potential and (b) Corrosion current density.

the electrical potential of structures after application of ECE for a comparison basis. It can be seen that in most of the cases ECE brings the structure to a more passive condition, and by increasing charge passed by treatment, more passive values are achieved, however still not enough to reach the passive zone in some situations. Stoop and Polder [62] confirmed that ECE is an effective mean of bringing potentials to more passive zone and that treated specimens retained their positive values one year after treatment was finished. However, this interpretation must include also the chance of misjudgements of the potential readings when they are presented as the only post-treatment evaluation.

Regarding corrosion rate ( $I_{\text{corr}}$ ) measurements, there are not many papers containing data about it after ECE and some authors affirm that results of corrosion rate can contradict results from electric potential.  $I_{\text{corr}}$  ( $\mu\text{A}/\text{cm}^2$ ) values are calculated through the measure of linear polarization resistance (LPR), half-cell potential ( $E_{\text{corr}}$ ) and electrical resistance of concrete ( $R_e$ ). Green *et al.* [67] and Abdelaziz *et al.* [37] studied the effects of ECE on reducing the corrosion rate and confirmed that as for half-cell potential, assessment of the short-term efficiency of ECE on the corrosion rate of corroded reinforcement is preferable to be carried out after ECE is off, about 3 to 4 weeks, because that is when the corrosion rate is reduced significantly. In addition, both authors agree that corrosion rate can be significantly reduced. **Figure 4(b)** includes data from few papers that measured the corrosion rate change after treatment, and it confirms what was stated by other authors, values are reduced after treatment however not enough to achieve the passive condition. Miranda *et al.* [35] affirmed that not even the complete removal of chlorides guarantees the repassivation of corroded rebars, and much less when the chlorides removal is partial, which is most often the case, concluding that ECE can be considered an effective prevention method for early corrosion, but not as rehabilitation method for structures already highly deteriorated. The authors affirmed in addition that long-term efficiency of ECE on the corrosion rate of reinforcement after halting ECE treatment was improved by increasing charge passed during treatment and by using water as an electrolyte, following same trend for charge passed as it was found in this literature review for half-cell potential values. One possible explanation found on the literature for the benefits perceived on increasing charge passed is that it can minimize the concentration ratio of  $\text{Cl}^-/\text{OH}^-$ , which, in turn, would keep the passive state of reinforcing steel for long periods.

## 6. Side Effects on the Structural Behaviour after ECE

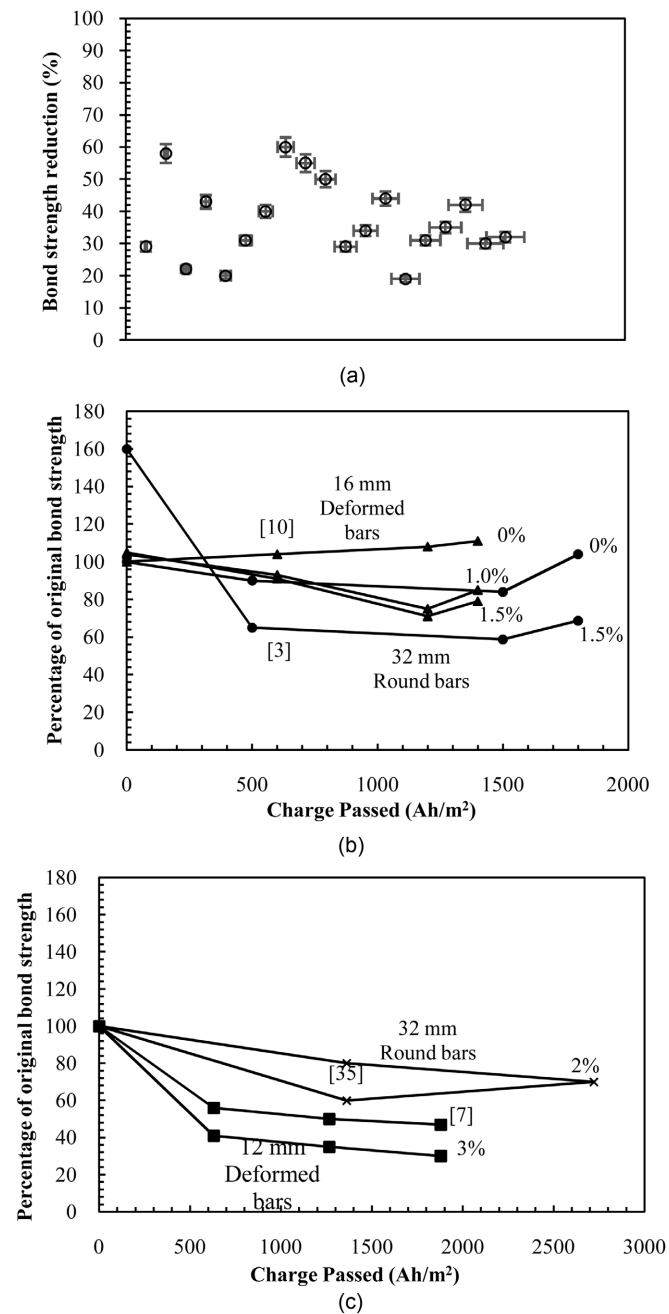
Historically, there are concerns about the effects of ECE on concrete properties, especially on the structural behaviour, which comprises mainly the mechanical properties. For example, Ihekwaba *et al.* [68] examined the effect of structural requirements and geometric shape of concrete columns under ECE. They concluded that geometrically curved structures reinforced with longitudinal steel and spiral ties have better chloride extraction than in structures with planar sur-

faces. Later, Zhang and Gong [69] studied the seismic behaviour of reinforced concrete columns after ECE treatment and agreed with previous works that ECE treatment had no significant effect on the concrete compressive strength. However, it was commonly argued that the treatment may affect bond strength negatively, decreasing adhesion between the concrete matrix and the steel bar [70].

Ihekwaba *et al.* [16] affirmed that ECE significantly reduces bond strength depending on the applied current density and initial contamination. Specimens with lower initial contamination level presented greater percentages of loss in bond strength, as well as the specimens treated at higher current density. The loss in bond strength was based on untreated control specimens and appeared to be more harmful when the electrochemical treatment is based on current densities over than  $1 \text{ A/m}^2$  of concrete surface. Buenfeld and Broomfield [21] contradicted that results by saying that most part of studies affirming that ECE reduces bond strength focused on unrealistically high current densities like 4 or  $5 \text{ A/m}^2$  or measured bond after treatment in comparison to corroded untreated specimens, which is not of concern considering that was the corrosion process that increased bond on these specimens, therefore, the reductions would just bring values to normal range for no chloride contaminated concrete specimens. Cheng *et al.* [71], on the same line, studied in which way ECE affects the evolution of porosity in concrete structure. They observed a decrease in porosity with treatment time close to the cathode and anode regions of the concrete, and highlighted that taking the evolution of porosity into account led to a better accuracy in ECE treatment evaluation.

**Figure 5(a)** shows a dispersion graph gathering data from different papers concerning bond strength reduction after treatment. According to the graph, there is always a reduction in bond due to chloride extraction and it seems to be in the range of 30% to 60% in most part of the cases. Considering the observations made by Buenfeld and Broomfield about conditions for better comparison, these data were separated in two other graphs. **Figure 5(b)** contains cases comparing loss of bond related to control specimens meaning not corroded. For this case, 100% corresponds to the bond strength value obtained for specimens that were not initially contaminated with chloride ions. Therefore, contaminated specimens undergoing corrosion showed values higher than 100%, showing the increase on bond caused by the corrosion process. Meanwhile, **Figure 5(c)** contain cases comparing to corroded but not treated specimens, whereas 100% corresponds simply to the bond strength value obtained before treatment, using as a reference the corroded specimen value. For these references, the bond strength values of non-contaminated specimens were not available, therefore any change on bond is only compared to specimens already undergoing corrosion. For both cases, it was taken into account the differences on size and shape of the bars as well. It is possible to notice that when comparing with corroded specimens, deformed bars experience greater reduction on bond compared to round bars, 60% and 20% respectively, however, when comparing with control specimens the





**Figure 5.** Bond strength changes due to ECE in terms of: (a) general cases to give an overview of the scenario, (b) values calculated taking into reference the original bond strength of specimens that were not chloride contaminated and therefore not corroded, (c) values calculated taking into reference the original bond strength of specimens already contaminated\*. \*On this view, 100% corresponds to the bond strength value obtained for specimens that were not initially contaminated with chloride ions. Therefore, contaminated specimens undergoing corrosion showed values higher than 100%, showing the increase on bond caused by the corrosion process. \*\*For this case, 100% corresponds simply to the bond strength value obtained before treatment, using as a reference the corroded specimen value. For these references, the bond strength values of non-contaminated specimens were not available, therefore any change on bond is only comparing to specimens already undergoing corrosion.

reduction perceived in the end for both cases is similar, around 25%, which supports the idea that ECE reduces bond due to the mitigation of corrosion. Greater reduction is perceived for that cases on deformed bars because corrosion products probably helped on filling voids and summed to the irregular shape of the bar, lead to a great increase of adhesion between steel and concrete before treatment. When there was no corrosion happening, reduction of bond was smaller, but still noticeable. Therefore, when applying ECE on real structures, a reduction in bond strength might always be taken in account, although in some cases with minor effects, safety issues must appear in cases where big diameter deformed bars were used on the structure design.

## 7. Conclusions

This literature review gathered data from a significant number of papers containing as well some application cases, in order to identify the influence of treatment setup on chloride removal, post treatment evaluation results and side effects on structural behaviour. The following conclusions were made through the manuscript:

1). An increase in the amount of electric charge passed during ECE is beneficial for chloride removal just until a certain level, which seems to be around 1500 to 2000 Ah/m<sup>2</sup>. To increase charge passed to these levels, increasing current density appears to be more efficient than increasing the duration of treatment, however, an extreme raise in current density, to 5 A/m<sup>2</sup>, did not show much difference from lower values, therefore, there is probably a limitation, such as for charge passed.

2). Concerning the usage of electrolytes on chloride removal, it was seen that using calcium hydroxide, the chloride extraction followed a similar trend to what is expected by the chloride binding capacity, the amount of bound and residual chlorides in concrete is pretty similar. This is explained by the precipitation of Ca(OH)<sub>2</sub> in the concrete pores that would reduce mobility of chloride ions, which does not happen when water is used.

3). The progress and efficiency of ECE applied for concrete structures can be monitored not only by the chloride removal rate but also by measuring corrosion electrical potential (half-cell potential) or corrosion rate, determined by linear polarization resistance method. It could be concluded that ECE does not guarantee the repassivation of corroded rebars and is better placed as an effective prevention method for early corrosion, but not as a rehabilitation method for structures already highly deteriorated. Furthermore, to achieve better results for post treatment evaluation is highly recommended to analyse all the factors combined: chloride removal rate,  $E_{corr}$  and  $I_{corr}$ .

4). This review pointed out that there is always a reduction in bond strength due to chloride extraction and it seems to be in the range of 30% to 60% in most parts of the cases. Compared with corroded specimens, deformed bars experienced a greater reduction in bond compared to round bars, 60% and 20% re-

spectively, however, when comparing with control specimens, the reduction perceived in the end for both cases was similar, around 25%. The greater reduction occurred for deformed bars because corrosion products probably helped on filling voids, leading to a great increase in adhesion between steel and concrete before treatment. Thus, it was concluded that for applying ECE on real structures, a reduction in bond strength might always be taken into account. In addition, safety issues must appear in cases where big diameter deformed bars were used on the structure design.

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## Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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