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INFLUENCE OF CEMENT TYPE ON THE EFFICIENCY OF ELECTROCHEMICAL CHLORIDE EXTRACTION

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ABSTRACT: The corrosion of steel in concrete due to chlorides is well established. Concrete structures are susceptible to chloride ions ingress when exposed to de-icing salts or seawater which pass through the cover zone to the embedded steel. Erosion of the passive layer leads to corrosion, a reduction in cross-sectional area, cracking and a loss of structural capacity.

Electrochemical Chloride Extraction (ECE) has been shown to reduce the chloride concentration in concrete. However, previous work has demonstrated that improper application of the electrical charge has led to adverse side effects such as loss of bond strength and cracking around the steel/concrete interface.

This paper presents the effect of a constant voltage and current density on three different cement types and the subsequent rate of chloride ion removal from the cover zone and deeper in the concrete. The findings show how appropriate electrical energy can lead to improved and efficient ECE treatments.

Keywords: Electrochemical Chloride Extraction, Cement, Reinforced Concrete, Current density, Voltage

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Brian Norton is the President of Dublin Institute of Technology. He is the author or co-author of over 400 papers principally in solar energy research including nearly 170 in major international learned journals He has supervised forty doctorates and serves as Editor-in-chief of Foundations and Trends in Renewable Energy, Associate Editor of Solar Energy - the premier international journal in the field and serves on four other editorial boards.

INTRODUCTION

The aim of this work is to investigate how the performance of Electrochemical Chloride Extraction is effected by different cement types. In order to speed up treatment, a slightly higher current than recommended was used. By analysing how different cement types respond to the treatment in terms of chloride concentration through the depth, a better understanding of the appropriate applied current for each cement type can be achieved.

Reinforced concrete is one of the most widely used materials in the world due to the availability of raw materials. Since concrete is permeable, it is susceptible to the penetration of dissolved chloride ions from the environment such as exposure to a marine environment, salty groundwaters or de-icing salts during cold spells. There are many ways that chloride ions can ingress into a reinforced concrete (RC) structure including capillary action, absorption, hydrostatic pressure and diffusion [1].

Chloride ions are considered to be the major cause of premature corrosion of reinforced concrete structures as they lead to a reduction in the cross-sectional area due to pitting. Chloride ions accumulate near the rebar until they reach a concentration that is sufficient to initiate corrosion (e.g. 0.2% to 1.5% by weight of cement [2]). Local disruption of the passive oxide film that protects the steel in a high alkaline environment may occur on the steel surface [3].

Until recently, rehabilitating concrete bridge decks and piers, subjected to corrosion or chloride ingress, involved the removal of affected damaged concrete and patching. However, this practice was found to lead to the introduction of new electrochemical cells between the new chloride-free concrete following the repair. In turn, these new cells accelerated corrosion often within a few years of the repair [4]. As steel corrosion is an electrochemical process, the most effective means to stop it are electrochemical techniques, such as chloride extraction (ECE) which protects the structure by removing the chloride ions in the vicinity of the reinforcement.

ECE is based on the principle that negatively charged chloride ions may be migrated toward a positive anode positioned on the surface of the concrete. The process turns the concrete and embedded reinforcement into an electrochemical cell, powered externally. The direct current power supply for the system is typically provided using diesel generators. Treatment times for ECE generally last around 6 to 8 weeks depending on the cement type and chloride levels.
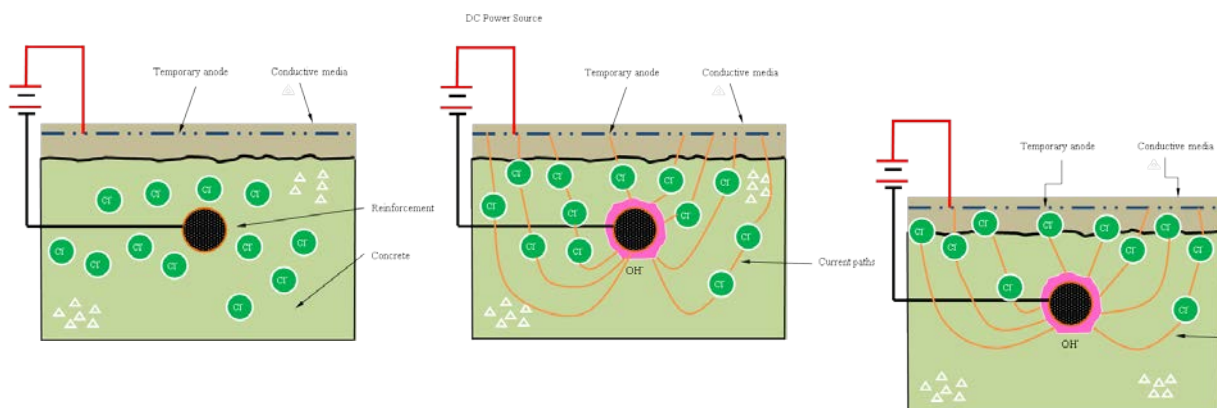
A schematic diagram of the typical migration of chloride ions in the concrete is shown in Figureure 1 below.

Figure 1   Chloride ions migration in the concrete

A suitable conductive anode may be a stainless steel or a titanium mesh submerged in an electrolyte or a cement paste placed on the concrete surface. The positive terminal of the power supply is connected to the external anode and the negative terminal to the reinforcement (cathode), embedded within the concrete. Since the electrons are repelled from the negative terminal towards the reinforcement, the cathode becomes negative due to the electrons negative charge. The chloride ions being negative ions are therefore migrated towards the positive anode located at the surface of the concrete via the pore water solution.

This causes the concentration of chlorides inside the concrete located around the reinforcement to be reduced. The speed of the chloride removal is largely dependent on the magnitude of the applied current. The higher the current can be set, the more intensive the chloride movement will be. The treatment usually utilizes a current density of 1-5 A/m^2 and a potential difference of less than 41V for safety reasons [2].

The work here was carried out on concrete blocks containing embedded reinforcement with different cement types. The ECE treatment was measured by analysing concrete dust samples collected through the depth in the concrete to trace the movement over time.

LITERATURE REVIEW

The efficiency of ECE relies on the availability of free chlorides in the pore water solution. Chlorides are present in concrete in either a free or bound state. The free chloride ions exist in the pore water solution and the bound in the concrete mix (cement, aggregate, sand, add-mixtures). With continuous ECE treatment, the concentration of the free chlorides will decrease over time and the chloride extraction efficiency will also decrease. At the end of the treatment, only the bound chlorides remain in the concrete. [5] By switching-off the current, a balance between the free and bound chloride will take place in the concrete with the bound chlorides dissolving into the pore water solution until equilibrium is re-established [5/6].

Laboratory studies were carried out by Angst [7], in which a current-off treatment period was used on two concrete blocks with dimensions of 320 x 245 x 70 mm and w/c ratio of 0.5 and 0.6. The specimens were contaminated with chlorides sodium solution and steel reinforcement was embedded at an average depth of 50 mm. Sensors were embedded in the concrete at different depths to measure the free chloride content in the pore solution. The current density applied was 2 A/m^2 by the steel surface in a discontinuous manner, as shown in Table 1.

The results of this study, in terms of chloride concentrations are shown in Figure 2. The ECE treatment was most efficient in the early stage of the treatment and became inefficient over-time. Overall, both specimens showed a complete removal of the free chloride ions present in the pore solutions within a few days.

Table 1   Schedule of the ECE [7].

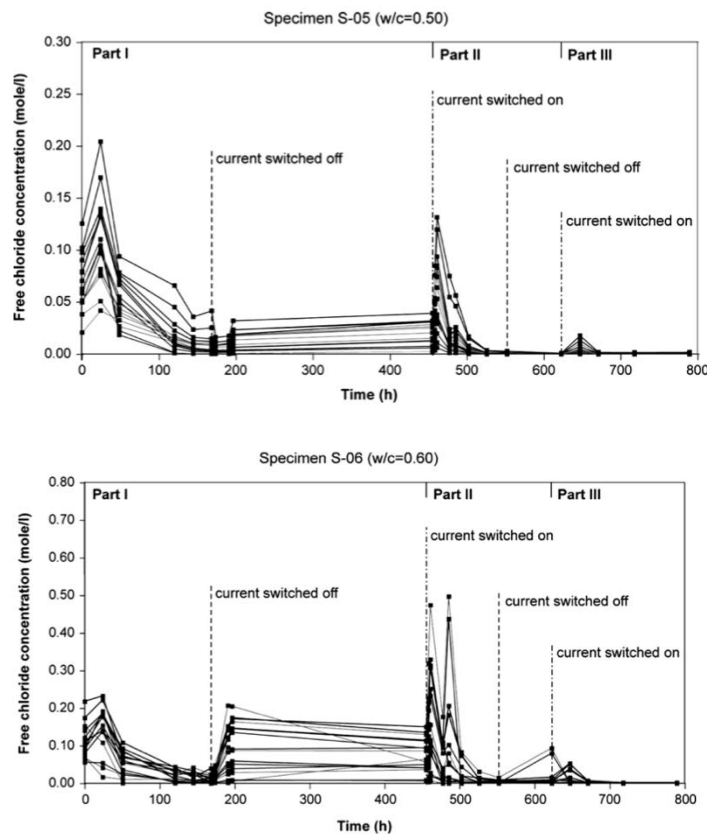| Period	Duration (days)
Phase I – On	7
Phase II – Off	12
Phase III – On	4
Phase IV – Off	3
Phase V – On	7

Figure 2   Change in free chloride content in concrete structure with time [7]

As seen in Figure 2, due to the complete elimination of free chlorides, the release of bound chlorides into the pore solution occurred in the first few days of the current-off period, and the equilibrium between the bound and free chloride was re-established, followed by a gradual decrease during the current-off period.

The results show that by switching the current off for a period it allows the chloride extraction to be more effective by promoting the release of the bound chlorides than continuous application of the electric current field.

In work carried out by Elsener [6] a field study was performed on the durability of ECE in Switzerland. The ECE process was applied as a rehabilitation method on an abutment of an underpass under a highway that had been exposed to deicing salt. The cover depths of the concrete varied between 25mm and 35mm, and the concrete quality reported as good [6]. A titanium mesh anode was used during the treatment and the process was applied using a voltage of 36 - 40V in two stages; a continuous current of 0.3 to 0.75A/m^2 by concrete surface was applied for 60 days [9]. An intermittent current was applied six months later to treat the areas with high chloride concentrations (more than 1% of the cement weight) with current densities of 1 to 0.7A/m^2 for 60 days. The intermittent current was applied for two weeks on followed by one week-off [2, 6].

After 6-8 weeks, it was found that 50% of the total chloride contents were extracted in each stage of the treatment and the intermitted ECE treatment was found to be more effective in areas with high chloride contents [2, 6]. It was concluded that the current-off treatment was

more beneficial than the continuous current treatment, due to its ability to rebalance the chloride ions [6].

EXPERIMENTAL WORK

Preparation of Specimens

Specimens S1, S2 and S3 were cast with Ordinary Portland Cement (CEM I), CEMII with 30% Pulverised Fuel and CEM II only respectively. In order to achieve sufficient chloride concentration and ensure an even distribution, a NaCl solution of 2.2 % (by cement weight) was added during mixing. The mix proportions of the concretes cast are presented in Table 2 and a description of each specimen in Table 3. Each specimen was covered with a 50% cement:sand mix.

Table 2   Concrete compositions in kg/m^3

Mix ID	CEM I	CEM II	PFA	Water	W/C	FA	CA	
							10mm	20mm
S1	524.8	-	-	224.9	0.43	586.8	521.4	521.4
S2	-	367.3	157.4	224.9	0.43	586.8	521.4	521.4
S3	-	524.8	-	224.9	0.43	586.8	521.4	521.4

- FA – Fine Aggregate, CA – Coarse Aggregate, PFA – Pulverised Fuel Ash

Table 3   Description of specimens

Mix ID	Description
S1	CEMI cement only
S2	70 % CEMII cement and 30% PFA
S3	CEMII cement only

Figure 3 shows a schematic of the specimens and the depths at which dust samples were taken. In each specimen, a 10mm diameter bar was cast into the concrete at a depth of 50mm. The samples were mixed in the laboratory using a concrete mixer and were cast in the molds, shown in Figure 4. The fresh concrete was vibrated on a vibrating table to remove trapped air. They were then stored for 24h after which they were de-molded and stored in a curing tank for one month until testing

Setup of Electrochemical Chloride Treatment

A titanium mesh was placed on the surface of the specimens (Figure 5a) and covered with a cementitious material (Figure 5b), to serve as the electrolyte. A direct current (DC) power source was used to power the treatment (Figure 6).

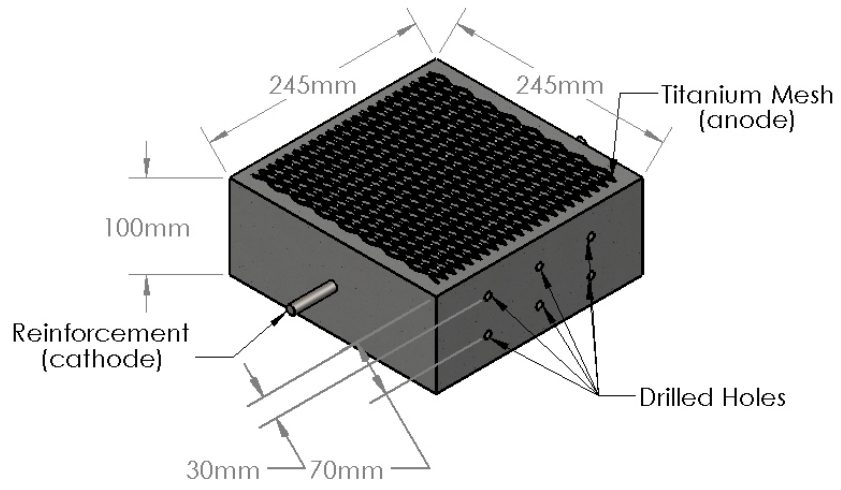Figure 3   Schematic of the concrete slab cast

Figure 4   Specimens cast into molds
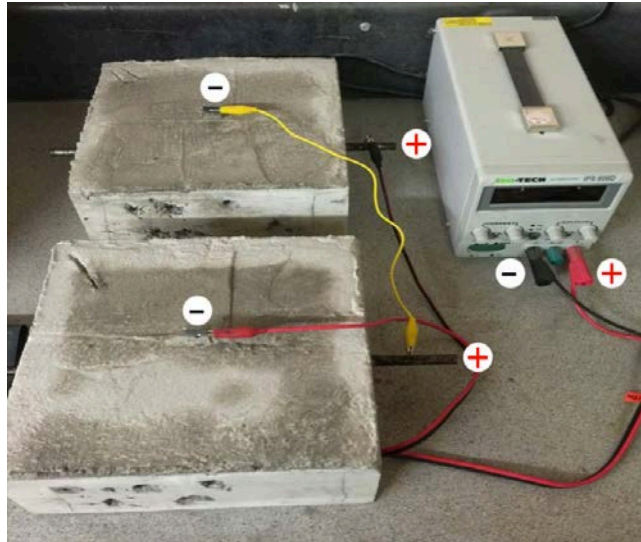

(a)   (b)

Figure 5   (a) Titanium mesh on surface of concrete (b) Cementious media placed over mesh

Figure 6   DC power supply connected to steel and titanium mesh

ECE began with the application of a D.C. current, in which the anode and the embedded steel in the concrete were connected to the two terminals of a DC power supply: the positive terminal was connected to the titanium mesh and the negative terminal was connected to the embedded steel. The specimens were connected in series to a DC supplier to regulate the current. The sides of each specimen was painted to ensure chlorides only moved vertically upwards.

Applying ECE Treatment

The current density used in this work depended on the voltage used and the concrete resistivity. A constant voltage of 30V was maintained, and the current densities were an average of $4.5A/m^2$ by steel surface for four weeks corresponding to charge densities of 2600 and $3300Ah/m^2$. The specimens were kept moist by pouring water onto the concrete's surface every four to five days.

Based on previous work in this area, the periods of current application were interrupted by switching-off the treatment to release the bound chlorides. The current was applied in cycles of 14 days on followed by two days off, as shown in Table 4.

Table 4   Schedule of ECE

Period	Duration (days)
Phase I – On	14
Phase II – Off	2
Phase III – On	12

Chloride concentration profiles were obtained from concrete samples collected from the test specimens before and during the ECE application. Holes were drilled at depths of 30mm and 70mm using an 8mm drill bit. The powdered dust samples were analysed using

potentiometric titration using a silver nitrate solution in accordance with (AASHTO T 260-97, 2005).

RESULTS

Cube Tests

Results from the cube tests are shown in Figure 7. Average 7, 28 and 56 day compressive strengths of 47.4 N/mm^2, 57.18 N/mm^2 and 58.03 N/mm^2 were achieved.
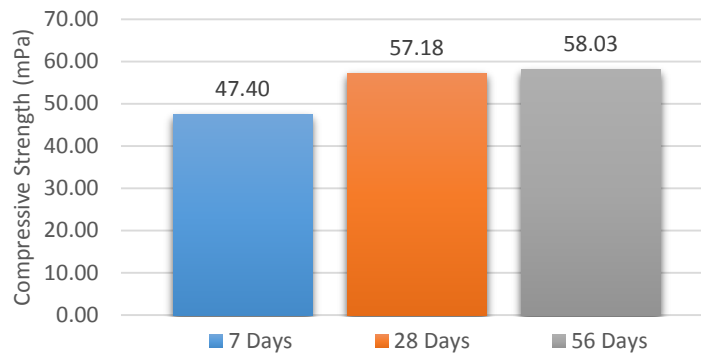

Figure 7   Concrete Cube Test Results N/mm^2

Chloride concentration

As may be seen in Figure 8, chloride extraction is influenced by the concrete type. For instance, the variation in chloride content with time shows that the removal was faster with S1, with a reduction of 45% achieved at 21 days as opposed to 28 days in S3. The average was computed by comparing the reduction in concentration with the initial chloride content in each specimen.
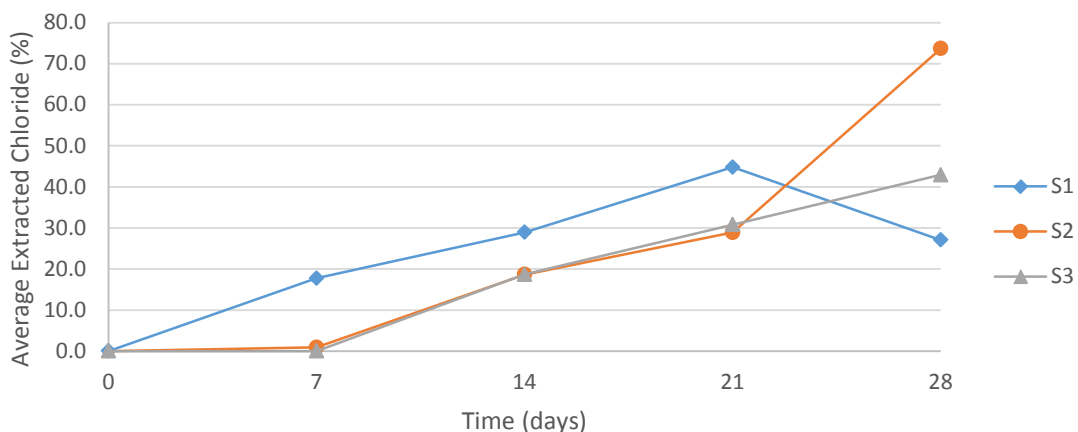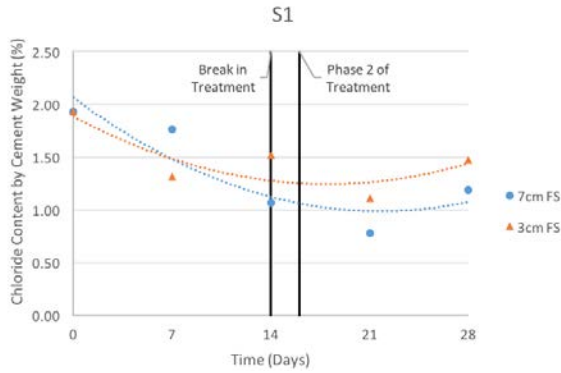

Figure 8   Average extracted chlorides in specimens during ECE treatment.

Another observation was the lower amount of chlorides extracted during the first three weeks from S2 and S3. After 7 days, the rate of extraction appears to be similar for all cement types between 7 and 21 days. At four weeks, a significant removal of chlorides (approximately 74%), was observed from S2. However, S3 maintained its extraction rate but slowed in the

Figure 9   Chloride content in S1 during ECE treatment

Figure 10   Chloride content in S2 during ECE treatment

final week. It can be concluded that CEM II with PFA will allow better removal when compared with CEM II alone. The chloride concentrations at 30mm and 70mm from the surface (FS) are plotted against time in Figures 9 to 11 with the average of all specimens shown in Figure 12.
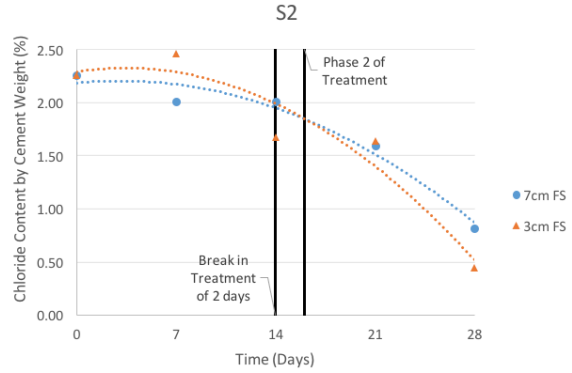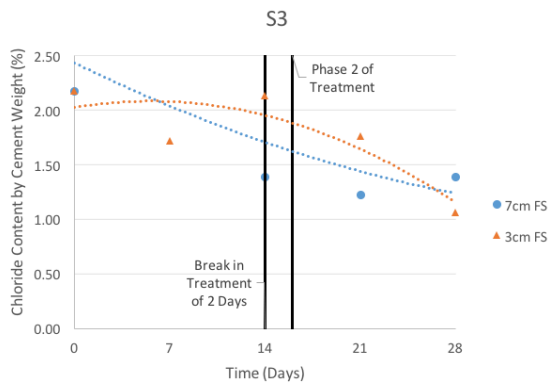

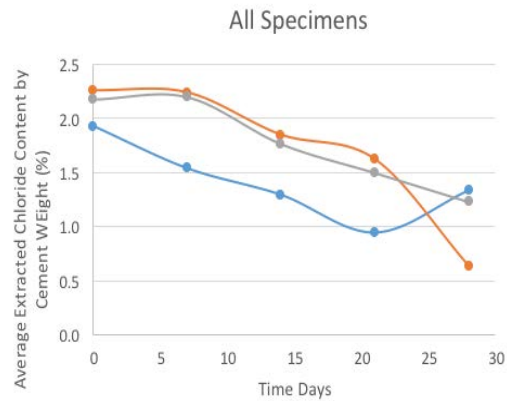Figure 11   Chloride content in S3 during ECE

Figure 12   Average Chloride content in S1/2/3 during ECE

As may be seen in S1 (Figure 9), the chloride concentrations at 30mm FS drop after 7 days. The concentration at 70mm FS is reduced significantly initially indicating that increased extraction rates are occurring. In S2 (Figure 10), the break in treatment appears to have had a positive effect on the ability to extract chlorides from the concrete. After the break, the slope of the line increases dramatically at each location. Elsener [7], showed that a break in treatment allows the bound chlorides to be dissolved into the pore solution which may explain the increase in concentrations at 28 days for S1. Following a slow start, S3 showed the most consistent extraction rate while not appearing to benefit from the break in treatment. It appears that the break in treatment has a positive effect on the CEM II with PFA.

CONCLUSION

In light of the results of this research, the following conclusions have been drawn:

1. The efficiency of the ECE treatment increases with permeability. If the concrete surface remained saturated during the ECE process, a significant amount of chlorides could be

removed.

2. A stable current density of 4.5 A/m^2 by steel surface with 30V makes the duration of the ECE treatment shorter, and it can be the optimal choice for treating concrete with normal reinforcing to avoid negative impacts on the reinforced concrete.

3. A current density of 4.5A/m^2 can be used in the CEMI concrete type in order to extract as much as 40% of chloride ions content in the concrete. While CEMII required longer time to extract the same rate.

4. A higher efficiency of the ECE treatment with the CEMI concrete type than with the CEMII and cement fly ash concrete types.

5. The cement fly ash has higher capacities to bind chlorides than the CEMI and CEMII. Therefore, the PFA cement replacement required a longer time to extract a significant amount of the chloride.

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