Extended Essay in Chemistry

Evaluation of concrete admixtures counteracting the chloride-induced corrosion of reinforcing steel embedded in concrete

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Abstract

As the subject of corrosion of reinforcing steel embedded in concrete is an important issue in modern engineering I decided that the research described in this essay will be aimed at this area. I became interested if there were any ways of delaying chloride – induced electrochemical corrosion. Hence my research question was formed:

Is it possible to alter the chloride ions concentration in aqueous solution and hence in concrete in order to delay the onset of the reinforcing steel corrosion?

I decided to investigate starch, lead (II) oxide and silver (I) nitrate (V) in terms of capability to decrease the chloride ions concentration in aqueous solution, concrete and delay the reinforcing steel corrosion. Answer to the research question was obtained by carrying out a research divided into 3 parts:

- Volumetric Titrations in aqueous solutions to determine the impact of the investigated substances on chloride ions concentration
- Making water extracts out of hardened cement mortar with different admixtures and determining the differences (if any) in chloride ions concentration
- Conducting electrochemical test determining the effectiveness of admixtures involving preparing cement mortar specimens with a steel bar and ponding them in sodium chloride solution while monitoring the corrosion potential with a half cell electrode awaiting its fall

Above methods helped me to find out that it is possible to alter the chloride concentration in aqueous solution and in cement mortar and hence delay the corrosion of reinforcing steel by using silver (I) nitrate (V) as the admixture. However it was also proved by this research that substance unable to decrease the concentration of chloride ions in the solution may act as corrosion delaying agent like in the example of starch. Lead (II) oxide was found to have no effect on the chloride ions concentration and time of corrosion start.

Word Count: 299
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1 Introduction

1.1 Introducing the topic

Concrete usually ensures excellent protection for the reinforcing steel. Highly alkaline environment in concrete causes the formation of a tightly adhering film which passivates the steel and therefore protects it from corrosion risk\(^1\). Also, the penetration of corrosion causing substances may be slowed down by high density and low permeability of concrete. These factors make corrosion of reinforcing steel unlike to happen.

However, though seemingly unlike, corrosion of reinforcing steel is one of the biggest problems of engineering nowadays. In recent years, this issue has been receiving more and more attention because of its presence in majority of concrete structures. Corrosion of reinforcing steel is very common occurrence in all type of reinforced concrete marine structures or other constructions exposed to chlorides.

Chloride ions are considered to be major cause of premature corrosion of steel reinforcement. This is a prominent issue for several reasons. Most obvious one is that corroded reinforcing steel is weaker and does not provide sufficient strengthening for concrete structures. Other reason is that the products of corrosion occupy greater volume that the reinforcing steel itself causing cracking of the concrete coating.

There are several ways of corrosion protection (frankly the best one is providing chloride – free environment). These involve changing the permeability or using various admixtures. Knowing that the chloride ions content in concrete is crucial to the matter of reinforcement corrosion I decided that it is worth investigating this topic. I thought that it may be useful to investigate the possibilities of altering the chloride ions content in concrete.

Therefore my research question reads as follows:

**Is it possible to alter the chloride ions concentration in aqueous solution and hence in concrete in order to delay the onset of the reinforcing steel corrosion?**

1.2 Predictions

Knowing that certainly there are ways to reduce chloride concentration in aqueous solution it should be possible to apply them in this case. It is suspected that the chemical reactions leading to fixing of chloride ions as sediment (or otherwise) will also take place in water-saturated concrete. Assuming that this is possible and chloride ions concentration in concrete can be decreased this way it should be also possible to delay the onset of the reinforcing steel corrosion this way.

Therefore it is predicted that using various substances as concrete admixtures aiming at decreasing the chloride ions concentration in concrete may prolong the time needed for steel depassivation and start of the corrosion.

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\(^1\) American Concrete Institute, 1997, *Corrosion of Metals in Concrete*. 1st edition, Farmington Hills: American Concrete Institute
1.3 Theoretical background

In this chapter explanations of the choice of substances for the investigation and all theoretical background will be given that will be used to support any conclusions drawn from the experiments.

1.3.1 Corrosion mechanism

It is believed that oxide film on the surface of metal is responsible for its passive state and corrosion protection. Chloride ions, as very small particles are able to penetrate this film through pores or otherwise and disperse it.

The process of steel corrosion is an electrochemical reaction. Any metal surface that undergoes corrosion is composed of cathodes and anodes connected through the body of the metal itself.

The reaction taking place at the anode is oxidation of iron to ferrous ions:

\[ Fe \rightarrow Fe^{2+} + 2e^- \quad (A) \]

\[ E^o = -0.440 \, V \]

The reaction at the cathode is the formation of hydroxide ions:

\[ \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (B) \]

\[ E^o = 0.401 \, V \]

It is apparent that oxygen and water are essential for the reaction to carry on and its concentration in the environment in which the reaction is taking place is crucial to the rate at which the corrosion is progressing (there is excess of iron for the reaction at the anode). That is why in order to sustain the reaction of steel corrosion concrete must be subjected to cycles of wetting and drying in order to keep the oxygen and water supply.

Indication of the corrosion start is the decrease of the potential between reinforcing steel and half-cell electrode. The potential decreases because according to Nernst equation\(^4\) the concentration of reagents at the cathode and anode decreases.

1.3.2 Chloride – related reactions

- Well known reaction of precipitation of chloride ions is the reaction of two salts- silver (I) nitrate (V) and sodium chloride. This reaction was the first one chosen to be included in this research. Silver (I) nitrate (V) reacts with potassium chloride forming silver (I) chloride (precipitate) and sodium nitrate:

\[ AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3 \quad (C) \]

Silver (I) nitrate (V) was chosen for this research as it is the basic method of precipitation of chloride ions.

\(^2\) American Concrete Institute, 1997, *Corrosion of Metals in Concrete*. 1st edition, Farmington Hills: American Concrete Institute

\(^3\) American Concrete Institute, 1997, *Corrosion of Metals in Concrete*. 1st edition, Farmington Hills: American Concrete Institute

\(^4\) Nernst equation is provided in Appendix 7
While carrying out the literature survey I encountered an abstract of an article\(^5\) reporting the use of lead (II) oxide to decrease chloride ions concentration in concrete. As far as my knowledge is concerned lead (II) oxide is insoluble in water and incapable of undergoing any ionic reactions therefore I decided this is worth investigating.

Iodine test may be used to detect the presence of starch in the solution by creating a dark blue starch-iodine complex. As iodine is not well soluble it is dissolved in water in presence of potassium iodide. I\(_3^–\) ions are formed that are capable of slipping in to starch molecule creating starch complex. This inspired me of adapting this phenomenon in my research. As iodine lies in the same group as chlorine and presents very similar properties it should be possible to form complex of starch with chlorine instead of iodine and therefore reduce the content of free chloride ions the solution. I chose to investigate this as I once became interested in iodine clock reactions and was curious about starch complexes.

2. Method – outline of the procedures

In order to verify whether a given substance has an impact on the chloride ions concentration in concrete and therefore helps to delay the time when corrosion begins I designed 3 independent experiments.

2.1 Volumetric Titrations

One of them is checking if the reaction in aqueous solution causes the decrease of chloride concentration. This will help to estimate to what extent the free chloride ions concentration can be reduced. Mohr method will be used to determine this as I am used to using it.

2.2 Making water extracts out of hardened cement mortar

The next independent step is preparing samples of cement mortar containing every substance that is under investigation. These samples will be subjected to soaking with sodium chloride solution in such a way that the chloride ion content will be equal to 1% of the cement mass in the sample. The samples will be, after 2 weeks curing time, crushed to powder and water extracts from all of them will be prepared and chlorides – tested. This part of the experiment however may be accused of being the repetition of the previous one (involving tests in aqueous solutions), after all powdered samples are mixed with water and everything that is soluble will dissolve in water, therefore the reactions, even if did not occur in hardened cement mortar, will occur in aqueous medium. This experiment needs to be carried out to check whether cement mortar itself does not affect the chloride concentration and to measure the effectiveness of investigated admixtures.

2.3 Conducting electrochemical test determining the effectiveness of admixtures

Knowing whether given substance may cause the decrease in chloride ions content in concrete is still not enough to predict whether it will delay corrosion start or not. Therefore specimens containing steel bars and appropriate admixtures will be produced. After letting the cement mortar to harden these specimens will be subjected to cycles of wetting with sodium chloride solution and drying. Simultaneously the electric potential of each metal bar will be monitored while awaiting its fall – indicator of corrosion start. This will be measured using saturated calomel electrode. This test is supposed to verify whether a substance that proved some chloride ions content reducing abilities actually is able to cause the delay in the corrosion start and to what extent it can be delayed, or otherwise – this test may also be used to verify whether a substance that did not prove any chloride ions content reducing abilities in e.g. aqueous medium is actually capable of delaying the onset of reinforcing steel corrosion. Data gathered in this experiment will be subjected to comparison with appropriate models and publications in order to interpret them correctly and determine their validity.

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6 Appropriate theory may be seen in Appendix 1
7 All chloride ions masses will be given in % of the cement mass in cement mortar
8 As described in 1.3.1
9 Results will be confronted with appropriate standards enabling correct interpretation
3. Experimental part

3.1 Volumetric Titrations - experiment

3.1.1 Preparing the set-up for the volumetric titrations

The procedure was carried out with the aid of the following apparatus:

- 20 cm³ pipette for reagents pouring and equipment calibration
- 50 cm³ scaled burette (tirant) ±0.1 g
- 100 cm³ conical flask (analyte)
- 100 cm³ scaled cylinder ±1 g
- 1000 cm³ volumetric flask
- scales ±0.01 g

The following reagents were used:
- silver (I) nitrate (V) AgNO₃ - 16.99 g
- potassium chromate (VI) K₂CrO₄ – 1 g
- sodium chloride NaCl - 5.85 g
- starch [C₆H₁₀O₅]ₙ, where n>300 – 1.62 g
- lead (II) oxide PbO – 2.23 g
- distilled water

0.1 M solution of sodium chloride was prepared by dissolving 5.85 g of sodium chloride in 0.5 dm³ of distilled water in 1000 cm³ volumetric flask and filling the flask with water up to the mark. Simultaneously, 0.1 M solution of silver (I) nitrate (V) was prepared by dissolving 16.99 g of silver (I) nitrate (V) crystals in 0.5 dm³ distilled water in 1000 cm³ volumetric flask and filling the flask with water up to the mark again. All laboratory glassware used for this was calibrated using 20 cm³ pipette (glassware of larger volume was calibrated using calibrated 100 cm³ cylinders).

I dosed each substance by adding 0.01 mol of it per every 0.02 mol of sodium chloride in the solution. As the solution of sodium chloride is 0.1 M total amount of lead (II) oxide needed in 1 dm³ solution would be 0.1 mol, hence 0.01 mol (2.23 g) was added to 0.2 dm³ of sodium chloride solution. The mixture was the blended thoroughly and filtrated. The same procedure was carried out with starch. Then all the solutions were tested using Mohr method.

3.1.2 Carrying out the titrations

As three substances are under investigation, only two were added to sodium chloride solution to reduce chloride ions concentration because adding silver (I) nitrate (V) to sodium chloride solution and then checking the amount of chloride ions in the solution using Mohr method (silver (I) nitrate (V) titration) was pointless. Therefore three solutions were made – sodium chloride aqueous solution, sodium chloride with lead (II) oxide solution and sodium chloride with starch solution.

First solution titrated with 0.1 M silver (I) nitrate (V) was 20 cm³ of 0.1 M sodium chloride. First titration was indicatory. Yellow, turbid witness was made by adding few sodium chloride crystals to

---

10 The smallest scale was taken for the error margin
orange-brown titrated solution so any discoloration of sodium chloride solution titrated with silver (I)
nitrate (V) was clearly noticeable through comparison with witness.

Then all other titrations were carried out. The solutions were titrated until slightly orange
discoloration appeared. Each type of solution was titrated six times to reduce any type of random
error. Also the parallax error was taken into consideration.

3.1.3 Volumetric Titrations – presentation of gathered data

Data from the titrations carried out are presented in Table 1.

<table>
<thead>
<tr>
<th>No. of titration</th>
<th>Volume of titrant used up in the titration [cm$^3$]±0.1cm$^3$</th>
<th>NaCl</th>
<th>NaCl+starch</th>
<th>NaCl+PbO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.3</td>
<td>20.0</td>
<td>19.6</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>19.9</td>
<td>20.2</td>
<td>20.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>20.0</td>
<td>20.1</td>
<td>19.9</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>20.1</td>
<td>19.9</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>19.7</td>
<td>19.8</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>20.0</td>
<td>20.0</td>
<td>20.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Data from titrations of sodium chloride solutions with silver (I) nitrate (V)

Precise volume of titrant used up should be 20cm$^3$, as both titrant and analyte were 0.1M solutions
and the volume of analyte was 20cm$^3$.

From the table it can be seen that both starch and lead (II) oxide did not affect the concentration of
chloride ions in the solution as the results do not vary at all. Though it was noticeable from the
appearance of the solution containing lead (II) oxide that not all of the lead (II) oxide was consumed
it was not expected that the reaction will not occur at all.

Starch did not provide expected results either. The outcome of this experiment implies that starch
complex with chloride ions mentioned in chapter 1.3.2 was unable to form.

Small disparities in the results, as in all titrations, may have been caused by random errors like
overlooking the color change.

3.2 Making water extracts out of hardened cement mortar - experiment

3.2.1 Preparing the set-up for making water extracts out of hardened cement mortar

The procedure was carried out with the help of the following apparatus:

- scales ±0.01g
- 200cm$^3$ plastic cups
- grinder
- 10cm$^3$ pipette ±0.1g

The following reactants were used:
- silver (I) nitrate (V) $\text{AgNO}_3$ – 0.584g * 3
- sodium chloride NaCl – 0.122g * 12
- starch $[\text{C}_6\text{H}_{10}\text{O}_5]_n$, where $n>300$ – 0.557g * 3
- lead (II) oxide PbO – 0.767g * 3
- dry component of cement mortar – 70g * 12
- distilled water

There were 4 series of 3 samples made. 3 series contained different admixture, one did not contain any admixture. Each sample contained 70 grams of dry component, 9.8 grams of water and admixture that fit the later dosage of chloride ions that was equal to 1% of the cement mass in the sample. Let silver (I) nitrate (V) dosing be an example:

1m$^3$ of mortar – 1965kg

1965kg of mortar – 300kg of cement

300kg of cement – 3kg of Cl$^-$ ions (1% of cement mass)

0.0798 kg of mortar (sample mass) – 0.122g of Cl$^-$ ions

0.122 : 35.5 = 0.00344 mol Cl$^-$ ions = 0.00344 mol Ag$^+$ ions

0.00344 * 169.8 = 0.584g AgNO$_3$

This way lead (II) oxide and starch dose was calculated. Each admixture was first mixed with dry component and then water was added. Because of the fact that all samples were destined for crushing, storing them in glass vessels was inappropriate idea as the vessels would have to be destroyed in order to take the samples out. That is why plastic cups were used.

After all samples hardened they were soaked with 3ml of such sodium chloride solution that these 3ml contained exactly the amount of chloride ions equal to 1% of cement mass in the sample. This was done this way:

1965kg of mortar – 300kg of cement

300kg of cement – 3kg of Cl$^-$ ions (1% of cement mass)

0.0798 kg of mortar (sample mass) – 0.122g of Cl$^-$ ions

0.122g of Cl$^-$ ions – ~3g of aqueous solution

0.122 : 35.5 = 0.00344 mol Cl$^-$ ions = 0.00344 mol Na$^+$ ions

0.00344 mol Na$^+$ ions = 0.0791g

---

11 [mass] * X denotes that given mass will be used in making X samples
13 Proportions taken from the package instructions
14 It was estimated that samples are sure to absorb this amount of liquid
The solution was poured on top of every sample allowing it to absorb all liquid. After being soaked, the samples were left for a period of time to allow the chlorides to penetrate them thoroughly and all necessary reactions take place.

3.2.2 Making water extracts and measuring chloride ions concentration

After that all the samples were grinded to powder and aqueous extracts were made. Each powdered sample was added to amount of water equal ten times its mass. In each solution pH was measured and it turned out that average pH was 12.5, which was predictable as concrete is highly alkaline. This disabled the use of Mohr method on these water solutions. Though attempts were made to apply this method in this case the yellow analyte solution, after adding some titrant turned to green-black color making the observation of appearing of red-brown Ag_2CrO_4 impossible. That is why a decision was made to obtain a commercial chloride test kit. The kit contained of dimethylacetamide, nitric acid, titrant – mercury (II) nitrate plastic 20ml beaker and burette. All reagents except for titrant (that was provided in normal plastic vessels) were provided in little containers that enabled pouring them drop wise. In order to carry out a titration, solution under investigation was poured up to the mark of 5ml in the plastic beaker. Then 2 drops of dimethylacetamide was added and the solution was stirred. Red color appeared. After adding two drops of nitric acid the solution changed its color from red to bright yellow. Then the solution was titrated using mercury (II) nitrate until violet color appeared. The scale on the pipette was given in [mg/l].

3.2.3 Making water extracts out of hardened cement mortar - presentation of gathered data

Data obtained from this experiment are presented in Table 2. It is clearly visible that once again starch and lead (II) oxide failed completely in decreasing chloride ions concentration in cement mortar samples. The results coming form samples containing starch and lead (II) oxide are exactly the same as those from control sample. The only admixture that worked was silver (I) nitrate (V) – amount of chloride ions in these samples is more than four times lower than in other samples. Although it was not expected that there will be any chloride ions left, because each admixture was dosed in such a way that it is capable of fixing all chloride ions, while in silver (I) nitrate (V) sample there is 30mg/l of chloride ions left.

<table>
<thead>
<tr>
<th>No. of sample</th>
<th>Concentration of chloride ions in tested solutions [mg/l] ±1mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm(^{17}) Control</td>
</tr>
<tr>
<td>1</td>
<td>128</td>
</tr>
<tr>
<td>2</td>
<td>128</td>
</tr>
<tr>
<td>3</td>
<td>128</td>
</tr>
</tbody>
</table>

Table 2. Data from measuring the amount of chloride ions in water extracts from powdered samples

\(^{15}\) Explanation of this is provided in Appendix 1
\(^{16}\) Aquamerck 11106 Chloride test by Merck
\(^{17}\) For further data presentation – cm indicates cement mortar, inh indicates corrosion inhibitor
Above data can be recalculated so mass of chloride ions in each solution may be obtained. Let Control sample be an example:

\[
\begin{align*}
128 \text{ mg} \cdot \text{l}^{-1} &- 1 \text{l} \\
\times \text{ mg} \cdot \text{l}^{-1} &- 0.798 \text{l} \\
\times &- 102 \text{mg} = 0.102 \text{g}
\end{align*}
\]

This is represented by Table 3.

From the data below it is visible that the mass of chloride ions is not equal to the initial mass of chloride ions that was placed in each sample. The disparity is not huge, though noticeable (0.102 - 0.122=0.02). The surprise is that though silver (I) nitrate (V) was added in amount equal to amount of chloride ions in the sample and theoretically the mass of chloride ions in water extract from powdered sample should be 0g, it is equal to 0.024g.

<table>
<thead>
<tr>
<th>No. of sample</th>
<th>Mass of chloride ions [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cm Control</td>
</tr>
<tr>
<td>1</td>
<td>0.102</td>
</tr>
<tr>
<td>2</td>
<td>0.102</td>
</tr>
<tr>
<td>3</td>
<td>0.102</td>
</tr>
</tbody>
</table>

Table 3. Data from measuring the amount of chloride ions in water extracts from powdered samples

3.3 Conducting electrochemical test determining the effectiveness of admixtures - experiment

3.3.1 Preparing the set-up for conducting electrochemical test determining the effectiveness of admixtures

Simulation of real diffusion of Cl⁻ ions through concrete towards reinforcing steel was made. After unsuccessful trials with other type of specimen design, proper one has been developed as shown on Picture 1. There were 5 series of 3 specimens made as listed in Table 4.

Picture 1. Design of the sample (not in scale)

---

18 Further description is provided in Appendix 4
<table>
<thead>
<tr>
<th>Type of specimen</th>
<th>added admixture</th>
<th>dosage of admixture[^g]</th>
<th>purpose of specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONTROLcm/1</td>
<td>-</td>
<td>-</td>
<td>comparison</td>
</tr>
<tr>
<td>CONTROLcm/2</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CONTROLcm/3</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>cm+AgNO₃/1</td>
<td>AgNO₃</td>
<td>5.04 per 779g of cement mortar</td>
<td>evaluation</td>
</tr>
<tr>
<td>cm+AgNO₃/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cm+AgNO₃/3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cm+PbO/1</td>
<td>PbO</td>
<td>6.61 per 779g of cement mortar</td>
<td>evaluation</td>
</tr>
<tr>
<td>cm+PbO/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cm+PbO/3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cm+STARCH/1</td>
<td>starch</td>
<td>4.80 per 779g of cement mortar</td>
<td>evaluation</td>
</tr>
<tr>
<td>cm+STARCH/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cm+STARCH/3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cm+INH/1</td>
<td>commercial corrosion inhibitor</td>
<td>6.00 per 779g of cement mortar</td>
<td>comparison</td>
</tr>
<tr>
<td>cm+INH/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cm+INH/3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Types of specimens used in electrochemical corrosion test

Precautions were taken to ensure that the only possibility for the chloride ions to reach the steel is to diffuse through 8mm mortar cover. Top of each specimen was impregnated with molten wax to prevent contact of sodium chloride solution with the metal bar sticking out of the top of each specimen and additionally metal bars were insulated with insulating tape[^19]. These specimens were placed in vessels that were flooded up to the mark indicating 3cm section of metal bar inside the specimen (185cm³ of water) for twenty four hours in order to soak them and establish aqueous medium necessary for measurements using an half-cell electrode.

### 3.3.2 Making measurements using a half-cell electrode

After soaking with water, all specimens were weighted to determine the amount of water absorbed and check whether there were any differences in permeability among the specimens. Water was then displaced with 6% sodium chloride solution and electric potential of each bar was measured using saturated calomel electrode and a voltmeter according to the standard[^20]. All measurements taken by calomel electrode were recalculated to Cu|CuSO₄ values[^21]. The potential was measured once a day. The conditions during the experiment were constant – 20 centigrade’s and 1atm pressure.

After each measurement specimens were taken out of the sodium chloride solution for overnight drying. In the morning, ponding began once again. The experiment was continued until all metal bars in the specimens were depassivated which was the indication of corrosion onset. Depassivation of reinforcing steel was indicated by the rapid fall of electric potential between metal bar and the half-cell electrode.

[^19]: Explanation of this is provided in Appendix 3
[^21]: That is because the model of interpretation was provided according to Cu|CuSO₄. Recalculation approach is provided in Appendix 2
3.3.3 Conducting electrochemical test determining the effectiveness of admixtures - presentation of gathered data

First data gathered were the masses of water saturated specimens after first day of ponding. As not all specimens were of equal mass (which resulted from construction method) percentage absorbance among each group was calculated and presented in Table 5 to give more reliable information about how much water was absorbed relatively to mass of the specimen.

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<tr>
<th>Group of specimens</th>
<th>Measured mass of water absorbed ±0.5 [g]</th>
<th>Measured mass of saturated specimens ±0.5 [g]</th>
<th>Calculated water absorption capacity of dry specimens (=100*(1)/((2)-(1))) [%]</th>
<th>Percentage error of calculated absorption capacity of dry specimens [%]</th>
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<td>301</td>
<td>8.27</td>
<td>±2.53</td>
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</table>

Table 5. Average water absorption of groups of specimens

Data from Table 4 are plotted on Graph 1.

Water absorption capacity of samples in each group [%]

Graph 1. Percentage absorption capacity in each group

It may be seen that the results are very convergent meaning that the specimens are comparable in terms of permeability. This is an important information as it simplifies the interpretation of data appearing below.
After displacing water with aqueous solution of sodium chloride potential between the SCE and the steel bar was recorded using a voltmeter. Data collected are presented in Table 7.

Data from Table 7 were recalculated to form Table 6 showing readings according to Cu|CuSO₄ half-cell electrode. Additionally readings that imply that corrosion has already started on given bar are highlighted in red and rounded.

The situation described in the Table 6 may be more readable when plotted on Graph 2.

It is possible to see apparent trends on the Graph 2. It can be noticed that in every single group of specimens the electric potential decreases approximately simultaneously (the lines of one color are not far apart each other) which confirms the authenticity of measurements.

First species to decrease their electric potential were control specimen and lead (II) oxide specimen. First species after the control specimen and lead (II) oxide specimen where the decrease of the potential was detected was silver (I) nitrate (V) specimen. Starting with the highest potential recorded among all specimens it gradually decreased, to drop rapidly in days 5-7 from the beginning of the experiment (note: active corrosion was detected in days 6-9 – red fields in the Table 6 and appropriate range on the Graph2). Active corrosion was detected in the majority of silver (I) nitrate (V) specimens (2 out of 3) in 3 and 4 days respectively after the decrease of the potential of last of lead (II) oxide specimens, though there was one silver (I) nitrate (V) specimen in which the corrosion was detected 1 day after the last of lead (II) oxide specimens. Last species was starch. Active corrosion was detected in specimens containing starch approximately at the same time as in the specimens containing corrosion inhibitor – 14 days after the start of the experiment in best 2 specimens of these 2 species and 11 and 12 days after the start of the experiment in worst specimens in corrosion inhibitor and starch groups respectively.

This trend may be represented by the Graph 3 showing total number of days needed for depassivation of metal bar in each specimen. Time needed for depassivation was understood as the time needed for the corrosion to be detected during the next measurement (denoted by white fields in Table 6).

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22 Table 7 is provided in the Appendix 6
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Table 6. Recalculated readings from potentials measurements
Graph 2. Readings from potential measurements
Graph 3. Time needed for depassivation of metal bars

Graph 4. Average time needed for depassivation of metal rods in specimens in each group [days]
4. Conclusions

My research proved that it is possible to decrease chloride ions concentration in concrete and delay the onset of reinforcing steel corrosion. The results clearly indicate that silver (I) nitrate (V) and starch proved to be corrosion delaying agents. Though from the point of view of the research question and method used only silver (I) nitrate (V) was capable of acting as chloride ions concentration decreasing agent both in aqueous solution and in hardened cement mortar and therefore of delaying corrosion.

Though starch proved to be even better corrosion delaying agent (2 times better in terms of time needed for depassivation of steel – Graph 4) it did not provide any satisfying results in experiments described in 2.1 and 2.2 which may be seen in Tables 1, 2 and 3. In chapter 1.3.2 argumentation was given why starch should be suitable for use in this research. Apparently conditions on 2.1 and 2.2 were unsuitable for mentioned complex to form. Hypothetically it was too unstable to form in solution subjected to constant stirring or otherwise – it may have formed but this way of complexing chloride ions did not fix them as non-reactive particles (e.g. as precipitate) which still enabled them to undergo chemical reactions. This may explain why starch did not appear to decrease chloride ions concentration in aqueous solution, while it worked efficiently as agent stopping the migration of chloride ions by forming complexes in experiment 2.3. In the light of the research question and devised method starch appears to be ineffective as an agent decreasing the chloride ions concentration in aqueous solution but when it comes to delaying the corrosion it proved to be as effective as commercial corrosion inhibitor and 4 times better than control specimen (in terms of time needed for depassivation).

First two experiments (2.1 and 2.2) clearly proved, that lead (II) oxide have no effect on chloride concentration in aqueous solution which was expected from the reasons highlighted in 1.3.2. From Tables 1, 2 and 3 it is clearly visible that results of testing solutions containing lead (II) oxide are identical with control solution containing pure sodium chloride. In Graph 2 and Table 5 however it may be noticed that specimens containing lead (II) oxide appear to be depassivated slightly smaller than control specimens. 1 day difference however is too little to assess whether it was random occurrence or factual action of lead (II) oxide. Bearing in mind these conclusions and the research question lead (II) oxide is considered to be incapable of decreasing chloride ions concentration in aqueous solution and in concrete leading to delay in onset of reinforcing steel corrosion.

The research also revealed that concrete itself may act as chloride concentration decreasing agent which was discovered in experiment described in 2.2. After recalculating the data obtained from the experiment it was noticed that mass of chloride ions detected after making aqueous extract is not equal to the amount of chloride ions that soaked into the sample (the difference is 0.02g). This would be probably said to be systematic error of equipment but convergence of data is denying it therefore it is suspected to be caused by chemical properties of concrete itself, though this cannot be said for sure without carrying additional research on this topic.

The same experiment also proved that silver (I) nitrate’s (V) action on chloride ions was limited to some extent. This may result from the fact that there were other ions in the solution than Cl⁻ and other silver (I) compounds must have formed therefore silver (I) nitrate (V) was not that effective as it was supposed to be.

To conclude it can be said that from the conducted research it appears that it is possible to alter the chloride concentration in aqueous solution and in concrete and hence to delay the corrosion of reinforcing steel by using silver (I) nitrate (V) as the concrete admixture. However it was also proved by this research that substance unable to decrease the concentration of chloride ions in the solution
may act as corrosion delaying agent like in the example of starch. Lead (II) oxide was found to have no effect on the chloride ions concentration and time of corrosion start.

5. Evaluation
From Table 4 (the only table containing processed data) it is apparent that the errors in the experiment were insignificant. This is also confirmed by convergence of results.

Properly stated and sharply focused helped me to devise appropriate method which enabled me to collect valuable data. Low error boundaries ensured that even if somehow processed, the data are quite accurate. The fact that the data gathered are convergent proves their reliability. Though I had no impact on systematic errors, random errors were reduced by increasing number of trials in each experiment. I took care to avoid error such as parallax error.

Naturally there are things that can be changed to improve the results. These include using more accurate equipment to reduce systematic errors e.g. scales scaled to 0.001 instead to 0.01.
6 Bibliography

Books

Standards

Publications
- American Concrete Institute, 1997, *Corrosion of Metals in Concrete*. 1st edition, Farmington Hills: American Concrete Institute, p.2-5
7 Appendices

Appendix 1

Mohr method

This is a method used to determine the molar amount of chloride ions from titration of chloride containing solution with silver (I) nitrate (V) in the presence of potassium chromate (VI). During the titration insoluble precipitate (silver (I) chloride) is formed in amount equal to amount of chloride ions in the solution:

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow \quad (D)$$

The excess of silver (I) ions forms red-brown precipitate with chromate (VI) ions which is an indication that D reaction has gone to completion and all chloride ions has been precipitated:

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4 \downarrow$$

However this method is appropriate for solutions of pH range 6-10.5 because:

- In acidic solutions (pH<6) hydrogen ions join chromate ions:
  $$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$
- In basic solutions (pH>10.5) precipitation of Ag₂O occurs:
  $$2Ag^+ + 2OH^- \rightarrow Ag_2O + H_2O$$

making the appearance of Ag₂CrO₄ indicating the end of titration impossible.

Appendix 2

Saturated calomel electrode has been assigned the potential of +241mV vs. standard hydrogen electrode (meaning that 100mV measured by SCE is equal to 341mV measured by SHE) and -59mV vs. Cu|CuSO₄ electrode.

Appendix 3

Pilot survey was made in order to find out about the process of measuring the electric potential between the metal bar and the half-cell electrode. Metal bar was placed in hardening cement mortar in a 30ml glass. Then glass was removed and specimen was placed in sodium chloride solution. Potential was measured until its fall was recorded.

It was observed that sodium chloride crystals crystallized on top of the specimen and were in direct contact with steel bar. Therefore decision was made to insulate the steel bar with insulating tape and cover the top of specimens with molten wax to disable capillary sucking of sodium chloride solution to the top of each specimen.

Appendix 4

Firstly, square specimens were produced in frameworks from MDF fibreboard as shown on Picture 5. This type of construction was extremely time consuming and I discovered that after demolding the
framework the hardened cement mortar was not compacted properly as shown on Picture 7. This made me reinvent the method of constructing specimens

**Appendix 5**

Here is the gallery from carrying out the research.

![Initial testing of chlorides absorption capability of selected readymix cement mortar in May 2009](image-url)

*Picture 2 Initial testing of chlorides absorption capability of selected readymix cement mortar in May 2009*
Grinding hardened mortar samples to make water extracts for evaluation the content of Cl- ions.

Titrating extracts using Merck kit.
000704 -036

Picture 5. Designed formwork constructed of MDF fibreboard. Steel bars fixed in place waiting for casting mortar.

Picture 6. My first specimen just after casting.
Picture 7. Damaged specimen revealed insufficient compacting of the mortar despite of vibrations applied. Serious caverns were found between the bars. It definitely forced me to give up this type of formwork and specimen. Another weeks are lost...

Picture 8. Reinforcing bars prepared for new miniature specimens
Picture 9. Stacked elements of specimen formwork

Picture 10. Multiformwork just after casting - marked types of specimens visible
Picture 11. Specimen top closeup.

Picture 12. SCE and digital multimeter used for corrosion potential measurements.
Picture 13. SCE used for measurements.

Picture 14. Drying specimens
## Appendix 6

**Corrosion Potentials** [mV] ±1 of all samples in time  
- source values as measured against reference Saturated Calomel Electrode

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Table 7. Raw data obtained from potential measurements
Appendix 7

\[ E = E^0 + \frac{RT}{zF} \ln \left( \frac{[\text{ox}]}{[\text{red}]} \right) \]

R – gaseous constant equal to 8.314 J·K\(^{-1}\) mol\(^{-1}\)

T – temperature in Kelvins

z – amount of electrons exchanged in half-cell reaction

F – Faraday constant equal to 96485 C·mol\(^{-1}\)

[\text{red}] – concentration of reduced species

[\text{ox}] – concentration of oxidized species