Electrolytic Treatment with Aluminum Anodes for Reuse of Cooling Tower Water

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Abstract – The efficiency of electrolytic treatment in reducing the Langier Saturation Index (LSI) of the cooling water from a cooling tower of a textile industry was investigated in this study. A series of batch experiments using aluminum anodes were conducted with five different current densities (10, 15, 20, 25, and 30 A/m$^2$) and ten different electrolysis times (8, 16, 24, 32, 40, 48, 56, 64, 72 and 80 min). The use of 25 A/m$^2$ for at least 48 min electrolysis time yielded a satisfactory efficiency in reducing alkalinity (82% reduction), calcium hardness (88% reduction), total hardness (81% reduction) and total dissolved solids (64% reduction), while the pH was approximately stable with values ranging between 7.7 and 8.2. The LSI decreased from 1.85 to <0.4, indicating that the treated water became good enough to be reused in the cooling process.

Keyword: Electrochemical, Cooling Water, Langelier Saturation Index, Hardness, Water Reuse
1. Introduction

Industries use cooling water in various processes, for example, in power generating units, boilers, steel mills and paper mills. In addition, many larger buildings use cooling water in air conditioning systems. The water is used to exchange heat with hot fluid. After use, the water must be cooled in order to be reintroduced into the production processes. Typically, the water is pumped to the top of a cooling tower and flows down through plastic or wooden shells. While flowing down, the water transfers heat to an upward air flow, causing it to cool down typically from 40-60°C to 10-20°C. After a few cycles of operation, the cooling water requires extensive treatment due to pollution of the cooling water by air pollutants and microorganisms and an increase of salt concentrations arising from water loss by evaporation.

Three main factors are concerned in the reuse of cooling water: corrosion, scaling and microbial growth [1]. Low pH and high dissolved solids can enhance corrosion and shorten the life-span of the cooling system materials. Corrosion can be prevented by pH adjustment and alteration of dissolved solids concentration. Scale forms as a result of calcium and magnesium ion deposits on the units of a cooling system. This causes the formation of an insulating layer which negatively influences heat transport. Water loss by evaporation during a cooling process enhances scaling because salt concentrations in the water increase. Microbial growth in the cooling water system may occur because water and air normally contain bacteria. A bio film can also be formed which can clog pipes and heat exchanger units.

The three above-mentioned factors cannot be considered separately. For example, lower pH values can prevent scaling, but they increase metal corrosion. Therefore, an index that combines more than one factor has been introduced. Among the available indexes, the Langelier Saturation Index (LSI) is one of the most widely used indexes for estimating the scaling potential of cooling water. The LSI was derived from the theoretical concept of the degree of saturation of water with respect to calcium carbonate [2]. The LSI approximates the base 10 logarithm of the calcite saturation level. Water with an LSI of 1 is one pH unit above saturation. A negative LSI indicates that the water is not saturated, there is no potential to scale and the water will dissolve CaCO3. A positive LSI indicates that CaCO3 precipitation may occur and scale may form. A near zero LSI indicates a borderline scale potential, in which changes in temperature and evaporation can change the index [3].

In this study, the electrolytic method was selected to control the Langelier saturation index of cooling water from a textile industry. The electrolytic technique has been shown to effectively remove many components from water, for example, suspended solids [4-6], heavy metal [7-8], oil emulsions in water [9-10], complex organics [11], [12], [13] and bacteria, viruses and cysts [14]. In this study, the two operational parameters, current density and electrolysis time, were investigated. These parameters are effective for reducing Langelier saturation index and for controlling other water properties such as pH, alkalinity, calcium hardness, total hardness, total dissolved solids and conductivity. In addition, the technical and energy consumption requirements of the electrolytic process for treating cooling water were estimated.

2. Research methodology

2.1 Cooling water

The cooling water used in this study was obtained from a cooling tower of Luckytech Engineering (Thailand) Co. Ltd. This cooling water had been recycled through the cooling tower and become polluted with dissolved ions. The properties of the cooling water were: pH 8; conductivity μS/cm; alkalinity 390 mg/l as CaCO3; calcium hardness 947.50 mg/l Ca2+ as CaCO3; total hardness 1414 mg/l Ca2+ as CaCO3 and total dissolved solids 581 mg/l.

2.2 Experimental apparatus and procedure

The electrochemical system used in this study was of bench-scale. The system consisted of a DC power supply, a power control and measurement units, an electrochemical reactor and a magnetic heater and stirrer. The experimental setup is shown in Fig.1. The electrochemical reactor was a 2-L beaker with a set of five pairs of electrodes made of aluminum with a total area of 1047 cm². The electrodes were connected vertically with a gap of 8 mm between them. The electrodes were connected to the DC power supply in monopolar and in parallel mode and the electrochemical reactor was operated in batch and galvanostatic mode.

![Figure 1: Set-up of the electrochemical system 1: Electrodes 2: Magnetic Bar Stirrer 3: Magnetic Stirrer Controller 4: Ammeter 5: D.C Power Supply 6: Voltmeter 7: 2-L Beaker](image-url)

Before and at the end of each run, the electrodes were washed thoroughly with water, dipped in HCl solution (5% v/v) for at least 15 min and rinsed again with tap water. Typical runs were conducted at 298 K. During the runs, the reactor unit was stirred at
150 rpm by a magnetic stirrer (IKA, C-MAG HS, Germany). The experiments were carried out in a batch mode with a liquid sample of 1.8 L. Five different current densities were applied (10, 15, 20, 25, and 30 A/m²). For each current density, electrolysis times of 8, 16, 24, 32, 40, 48, 56, 64, 72 and 80 min were used. After the specified electrolysis time, the system was stirred at 50 rpm for 20 min and was allowed to stand at room temperature for 20 min and the supernatant was collected for the analysis of water properties.

2.3 Analytical method

The following properties of water were examined: pH, conductivity, alkalinity, calcium hardness, total hardness and total dissolved solids (TDS). Alkalinity was measured according to the Standard Methods (American Public Health Association, 1998). pH was measured by a pH meter (Schott, Lab 850, Germany) and conductivity by a conductivity meter (Milwaukee, EC59, Italy). TDS was also measured by the conductivity meter. The TDS values corresponded fairly well with the TDS values measured by the Standard Methods. Calcium and magnesium ions concentration was analyzed by ICP spectroscopy (Optima 2000DV, Perkin). Each measurement was performed three times. LSI was calculated according to eqn. (1) [1], [15]

\[
LSI = \text{pH} - \text{pH}_s \quad (1)
\]

where pH is the measured water pH and pH\text{\textit{s}} is the pH at saturation in calcium carbonate defined as:

\[
\text{pH}_s = (9.3 + A + B) - (C + D) \quad (2)
\]

where \(A = (\log_{10}[\text{TDS}] - 1)/10\) \quad (3)

\(B = -13.2\log_{10}(C+273) + 34.55\) \quad (4)

\(C = \log_{10}[\text{Ca}^{2+} \text{ as CaCO}_3] - 0.4\) \quad (5)

\(D = \log_{10}[\text{alkalinity as CaCO}_3]\) \quad (6)

3. Results and Discussion

3.1 Effect of current density and electrolysis time on pH

Fig. 2 shows the evolution of pH values during the electrolytic treatment. The pH was approximately stable with values ranging between 7.7 and 8.2. It has previously been reported that an electrocoagulation process exhibits some buffering capacity because of the balance between the production and the consumption of OH [16]. A study on the removal of turbidity from a solution of silica gel by electrocoagulation [17] reported a similar finding that when the initial pH of the silica gel solution was slightly above 7, the pH hardly changed.

The forms of Al-species present in a solution are dependent on the solution pH. For the pH ranges in this study, the Al\textsuperscript{3+} and OH\textsuperscript{-} ions generated by the electrodes react to form various monomeric species such as Al(OH)\textsuperscript{3+}, Al(OH)\textsuperscript{2+} and polymeric species such as Al\textsubscript{4}(OH)\textsubscript{10}\textsuperscript{3+}, Al\textsubscript{3}(OH)\textsubscript{6}\textsuperscript{4+}, Al\textsubscript{2}(OH)\textsubscript{3}\textsuperscript{5+} that finally transform into insoluble amorphous Al(OH)\textsubscript{3} through complex polymerization and precipitation [18].

3.2 Effect of current density and electrolysis time on alkalinity

Alkalinity is associated with the presence of the hydroxides [OH\textsuperscript{-}], carbonates [CO\textsubscript{3}\textsuperscript{2-}] and bicarbonates [HCO\textsubscript{3}\textsuperscript{-}] of elements such as calcium, magnesium, sodium, potassium and ammonia. Fig. 3 shows the alkalinity as a function of current density and electrolysis time. A sharp decrease of alkalinity from 390 mg/l as CaCO\textsubscript{3} to the range of 130 could be observed in 24 min for the current density of 30 A/m\textsuperscript{2}, 32 min for 25 and 20 A/m\textsuperscript{2} and 40 min for 15 and 10 A/m\textsuperscript{2}. For longer electrolysis times, the alkalinity continued to decrease but at a slower rate and became relatively stable at the range of 70 mg/l as CaCO\textsubscript{3}. The maximum alkalinity reduction was approximately 82% for every applied current density. The experimental data showed that the electrolysis time had a more pronounced effect than current density in reducing alkalinity.
3.3 Effect of current density and electrolysis time on calcium hardness and total hardness

Fig. 4 shows the calcium hardness as a function of current density and electrolysis time. The calcium hardness steadily dropped with increasing electrolysis time and became relatively constant. The relationship between the current density and the reduction of calcium hardness was not straightforward. The highest decline of calcium hardness was obtained with a current density of 20 A/m² and the reduction became flat at 48 min electrolysis time. The next highest decline was obtained with 15 A/m² for at least 56 min electrolysis time. The current densities of 10 and 30 A/m² gave the lowest reduction in calcium hardness. The experimental data showed that the calcium hardness reduction depended on the level of the current density.

Total hardness is the sum of calcium and magnesium hardness. Fig. 5 shows the total hardness as a function of current density and electrolysis time. The effects of current density and electrolysis time on total hardness were similar to those on calcium hardness. The lowest calcium and total hardness was 111 and 124 mg/l Ca²⁺ as CaCO₃, corresponding to 88 and 91 % reduction respectively.

During an electrolytic process using aluminum anodes, the reactions at anode and cathode are as follows:

Anode:
$$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \quad (7)$$

Cathode:
$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (8)$$

The generated hydroxide ions react with the bicarbonate (HCO₃⁻) to increase the concentration of carbonate (CO₃²⁻) through the following reactions:

$$\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (9)$$

The added hydroxide basically takes away the hydrogen ions (H⁺) from the bicarbonate ions to convert them to carbonate. The carbonic acid/bicarbonate/carbonate balance is such that it is biased heavily towards carbonate. According to the solubility equation for calcium carbonate,

$$[\text{Ca}^{2+}][\text{CO}_3^{2-}] \leq K_{sp} = 2.8 \times 10^{-9} \text{ at } 25^\circ\text{C} \quad (10)$$

If the product between the concentration of calcium and carbonate ions is greater than 2.8×10⁻⁹, which is a very small number, calcium carbonate will precipitate out of solution until either the calcium concentration or the carbonate concentration is low enough to satisfy this equation. The precipitation was evidenced by an observation of a milky white haze which has been previously reported to be comprised of calcium carbonate [19] :

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3(s) \quad (11)$$

As the result, the clear water that remained had both a lower alkalinity and lower hardness than the initial cooling water. Magnesium carbonate is about 100 times more soluble than calcium carbonate and therefore it is likely that the magnesium was precipitated as magnesium hydroxide which is a factor of approximately 100 time less soluble than calcium carbonate [20].
3.4 Effect of current density and electrolysis time on total dissolved solids and conductivity

The electrical conductivity is a measure of the ability of a solution to conduct an electrical current. The conductivity depends on both the concentration of ions and TDS concentration. Therefore, the conductivity is used as a surrogate measure of TDS concentration. The relationship between the conductivity and TDS concentration used in this study is as follows:

\[
TDS (\text{mg/l}) = 0.52 \times \text{Conductivity (} \mu \text{S/cm)} - 12.34 \quad (12)
\]

The mechanism for TDS removal by electrolytic treatment is mainly adsorption. The generated \(\text{Al}^{3+}\) ions undergo spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides. These hydroxides/polyhydroxides/polyhydroxymetallic compounds have strong affinity with the dissolved molecules. Fig. 6 shows the TDS concentration as a function of current density and electrolysis time. The TDS reduction was not strongly dependent on current density, but was dependent more on electrolysis time. The TDS steadily dropped with increasing electrolysis time and became relatively constant during 40-56 min electrolysis time. With a reduction of TDS of approximately 64%, the TDS reduction was the lowest of all of the pollutants studied in these experiments.

3.5 The reduction of the Langelier Saturation Index by electrolytic treatment

LSI was calculated according to eqn.(1)-eqn.(6) with the use of an ambient temperature of 25°C (298 K). Fig. 7 demonstrates the reduction of LSI as a function of current density and electrolysis time. The reduction of LSI depended strongly on both current density and electrolysis time. The highest decline of LSI was obtained with the current density of 25 A/m². Using 48 min electrolysis time with this current density, LSI reached a value less than 0.40. A further increase in electrolysis time to 80 min resulted in a steady decrease of LSI to 0.08. The drop of LSI from 1.85 to near zero indicated that the quality of the cooling water was significantly improved and the treated cooling water had a low potential for scaling. In order to evaluate whether the cooling water is good enough to be reintroduced into the cooling process, the LSI of the treated cooling water was compared with that of the make-up water currently used by the industry. The properties of the make-up water were as follow: pH 7.6; conductivity 203 \(\mu\)S/cm; alkalinity 66 mg/l as CaCO₃; calcium hardness 50 mg/l Ca²⁺ as CaCO₃; total hardness 80 mg/l Ca²⁺ as CaCO₃. The LSI of the make-up water was calculated according to eqn. (1)-eqn.(6) and eqn. (12) with a temperature of 25°C and was found to be -0.57. When compared with the treated cooling water, the make-up water had no potential to scale but was relatively corrosive.

3.6 Technical and economic assessments of the electrochemical process for treating cooling water

Fig. 8 shows the electrical energy consumption as a function of current density and electrolysis time. A linear relationship between electrical energy consumption and electrolysis time was obtained as can be expected from Faraday’s law:

\[
\text{Electrical energy} = VIt \quad (13)
\]

where electrical energy is in Joule, voltage \(V\) is in volts, current \(I\) is in amperes (DC) and time \(t\) in seconds.

At a fixed electrolysis time, the electrical energy increased with increasing current density and reached the highest at 9.8 kWh/m³. With the use of 25 A/m² for 48 min and 80 min electrolysis time, yielding LSI of 0.4 and 0.08, the electrical energy consumption was 4.4 and 6.4 kWh/m³, respectively. Considering the cost of electricity at 2 baht/kWh (1 USD ~ 30 baht), the cost of water treatment by the electrochemical unit was 8.8-12.8 baht/m³. In a normal situation, fresh water was available for a small to medium-size industry at 16.45 baht/m³ and for a large-size industry at 21.50 baht/m³. Therefore, the cost of electrical energy for the electrolytic treatment can be competitive with the cost of fresh water.
Even with the satisfactory performance both in treating the cooling tower to desired properties and the competitive energy cost, the electrolytic treatment may still be unsuitable for practical use due to two main disadvantages. First, a significant amount of aluminum anodes are dissolved into the water and need to be regularly replaced. This leads to high maintenance costs. Secondly, an impermeable oxide film may be formed on the aluminum cathode leading to loss of efficiency [21]. Further research work to overcome these drawbacks is being conducted in our laboratory.

4. Conclusion

Electrolytic water treatment with aluminum anodes was used to treat the cooling water from a cooling tower of a textile industry. The use of 25 A/m² for at least 48 min electrolysis time yielded a satisfactory efficiency in reducing alkalinity (82% reduction), calcium hardness (88% reduction), total hardness (81% reduction) and total dissolved solids (64% reduction) and resulted in an LSI decrease from 1.85 to <0.4. With the use of 25 A/m² for 48 min and 80 min electrolysis times, the LSI was reduced from 0.4 to 0.08, and the electrical energy consumption was 4.4 and 6.4 kWh/m³, respectively. The cost of the electrical energy consumption in the electrolytic treatment has been shown to be competitive with the cost of fresh water. However, research work to overcome the high consumption of aluminum anode and the drop of electrode efficiency due to an impermeable oxide film is required before the electrolytic treatment can be regarded as a practical method.

5. Acknowledgements

The authors are grateful to Thailand Research Fund (TRF-Master Research Grant, Grant No. MRG-W1535E094) for financial support and scholarship to R. Rungyavaninee. We wish to thank Square Cooling Tower Co., Ltd. for supplying technical data and Luckytex (Thailand) Co. Ltd. for supplying the cooling water samples. Special thanks to Dr. Elvin Moore for his suggestions and critical reading of this manuscript.

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