

The electrochemical generation of ferric ions in cooling water as an alternative for ferric chloride dosing to effect flocculation

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Abstract

The research deals with the electrochemical dissolution of iron in cooling water as an alternative to ferric chloride dosing to effect flocculation. The generation of this anion-free flocculant has far-reaching implications in a cooling-water system. Its primary benefit is the elimination of chloride dosing into the system, chloride being an initiator of pitting corrosion, the most destructive and insidious form of corrosion. Alternating current was applied to the electrochemical reactor in order to curb the deleterious passivation of the electrodes, characteristic of direct current application. Through the manipulation of process variables several process phenomena were identified. Untreated cooling water proved to be an ideal electrolyte for the generation of the desired quantity of ferric ions. It was observed that dissolution in an alternating field is accompanied by the generation of heat in the electrolyte, which aids the precipitation of carbonate compounds in the clarifiers. It was also established that while the solution pH has very little effect on the process, the voltage applied to the electrodes and the flow rate of the cooling water through the reactor are significant in determining the extent of the dissolution process.

Nomenclature

- F - Faraday's constant (96487C)
I - electric current (A)
M - molecular mass of sacrificial electrode (55.85 g/mol)
n - number of anodes
t - time (s)
w - mass of sacrificial electrode dissolved (g)
z - number of electrons involved in the redox reaction

Introduction

Eskom has always been at the forefront of technology, committing itself to improving the control of water quality by accommodating technological advances in chemical treatment. The research of the electrochemical dissolution of a flocculating agent is no exception.

It was identified that Lethabo Power Station's cooling-water system is prone to pitting corrosion originating from the presence of high concentrations of chlorides in the circulating water. The root cause of this aggression is the introduction of chloride into the system via the dosing of the coagulant ferric chloride. This problem prompted the research into the substitution of ferric chloride with an anion-free flocculant while maintaining the coagulating properties of the cooling-water treatment.

It was decided to investigate the possibility of dissolving iron in cooling water for the production of this anion-free flocculant.

Literature and theory survey

In 1986 Ewald Heitz (Heitz and Kreysa, 1986) predicted that electrochemically based processes would be gaining increasing potential in order to meet the economic and social challenges

resulting from urgent demands for energy saving, low-grade material utilisation and environmental protection. Since then, industrial needs have evolved in such a way as to substantiate Heitz's prediction. Electrochemical dissolution caters for this philosophy in that it is a reagentless process using low-grade material for its sacrificial electrodes.

The history of electrochemical treatment of water dates back to the 19th century, with England and France reporting patents to treat a mixture of sewage and sea water (Marson, 1965). More recently from Europe, Vik et al. (1984) reported on the electrochemical treatment of Norwegian river waters using aluminium electrodes.

In the United States, electrolytic sludge treatment plants were operated as early as 1911 in Santa Monica, California and Oklahoma City, Oklahoma (Vik et al., 1984). In the Soviet Union electrochemically produced iron was first used at a power station in 1925. This research was reported by Strokach (1975) and subsequently a substantial amount of research in the Soviet Union came to light.

The principles of electrochemical dissolution are those associated with basic electrochemistry. An electric current imposed on an electrolytic cell with iron electrodes gives rise to an anodic and a cathodic reaction:



The decrease in the acidity and the continuous formation of hydroxide ions in the cathode space results in the subsequent formation of ferrous hydroxide:



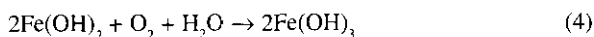
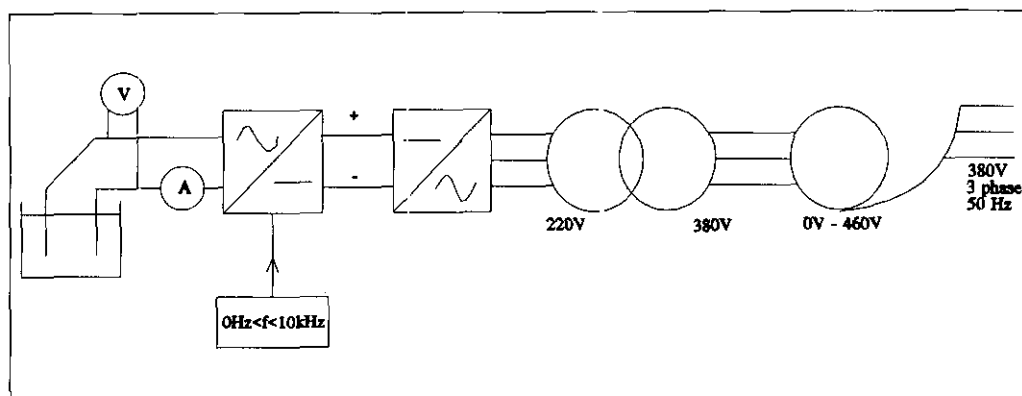
As the concentrated cooling water at Lethabo Power Station is saturated with oxygen, it is expected that the latter reacts with ferrous hydroxide, converting it to ferric hydroxide according to the following equation:

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Figure 1
Simple flow diagram of experimental unit



Theoretically, for direct current application, the dissolution of iron can be predicted using Faraday's law (Vik et al., 1984):

$$w = \frac{ItMn}{zF} \quad (5)$$

Ivanishvili et al. (1987) listed a number of advantages of the electrochemical treatment. These include:

- The absence of additional mineralisation of the water
- The simplicity of the technological scheme
- The possibility of automation
- The lower capital investment of equipment.

Despite citation of the obvious advantages of electrochemical dissolution, a literature survey of recent research also disclosed several shortcomings in this field of study. A major problem associated with the direct current electrochemical dissolution of steel electrodes is passivation of the anodes which reduces the efficiency of the process (Ivanishvili et al., 1987). This research presented a solution to this problem in the utilisation of an alternating current source with variable polarity and frequency. This switch in electrode polarity should increase the mobility of the dissolved species away from the electrode surface and thus prevent the accumulation of reaction products on the electrode surface. Few authors (Nikolaev, 1982; Bozin and Mikhailov, 1990) have investigated this phenomenon. The latter, however, demonstrated that the practical dissolution of the electrodes in an alternating field differs greatly from the theoretical prediction, as well as from the stationary field theory. For this reason, an empirical study of the process had to be performed to ascertain the extent of the electrochemical reaction. This study was performed on a bench scale using statistical methods of experimental design.

Experimental

The mechanism underlying electrochemical dissolution in an alternating field is not understood sufficiently well to allow an exact model to be postulated from theory. This makes it necessary to establish and optimise the response of the process empirically during its development. The first experimental phase dealt with the preliminary investigation conducted to establish whether the electrochemical generation of ferric ions is feasible in cooling water. This was followed by the optimisation of the process on a bench scale. The first step in this phase of experimentation was the identification of the process variables having a significant effect on the generation of ferric ions. The significant variables were

then manipulated according to statistical experimental designs in order to optimise the process in a bench-scale batch reactor. Results obtained from these experiments led to optimisation in a bench-scale plug-flow reactor.

The experimental units developed to perform the empirical study of the electrochemical dissolution process are discussed below.

The electrical equipment

The electrical equipment consisted of a 380V power supply, an on/off switch, a variable transformer, a 380V to 220V transformer, a rectifier, a function generator, an inverter and an electrochemical cell. A simple flow diagram of the system is shown in Fig. 1.

The complex electrical and electronic configuration was necessary to ensure flexibility of the system. The 380V power supply enabled the selection of a wide range of voltages for experimentation. The variable transformer enabled manipulation of the voltage. Through the function generator the system frequency was altered to the desired level improving the degree of freedom of the system operation. The inverter regulated the "alternating current" simulation and specific wave form.

Bench-scale batch reactor

The bench-scale batch electrochemical cell consisted of an 800 ml glass beaker. The sacrificial electrodes used were mild steel plates with submerged surfaces of dimensions 105 mm × 30 mm × 1 mm. The plates were held in position in the electrolyte by means of a specially designed electrode holder providing even spacing between the electrodes, and allowing freedom in the width of the spacing and the selection of the number of electrodes to be connected in parallel (Fig. 2).

According to the statistical fractional factorial experimental design (Box and Behnken, 1960), a number of plates were fitted in the PVC holder, a selected distance from one another. The electrochemical cell was filled with 800 ml of cooling water. If the pH of the electrolyte needed to be adjusted, it was treated with carbon dioxide, the plates were connected in parallel to the inverter terminals, and the selected voltage was supplied to the cell. The experiment was executed for a pre-determined period of time, according to the experimental design. During this time, the dissolution process was observed and monitored.

Bench-scale plug-flow reactor

The experimental unit consisted of a tank for the storage of cooling water, a centrifugal pump, two rotameters, an electro-

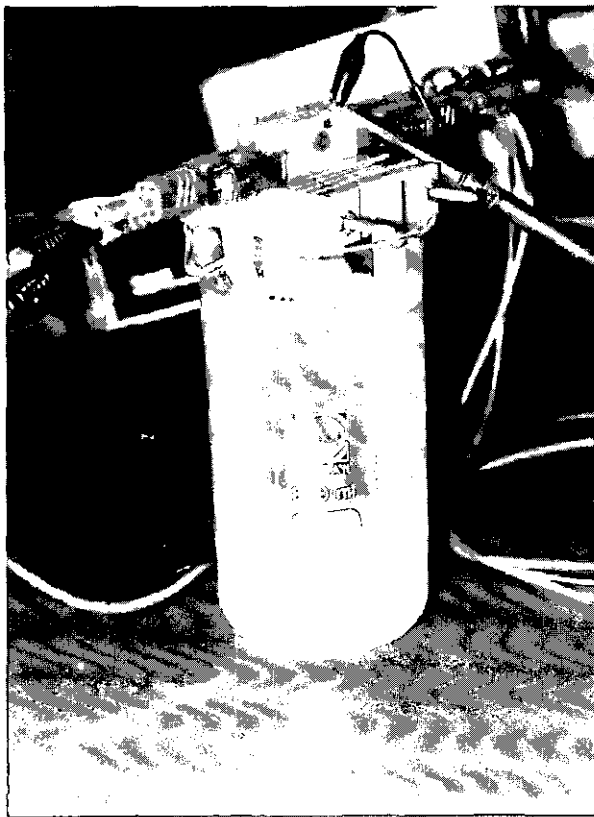


Figure 2
Bench-scale batch electrochemical cell



Figure 3
Bench-scale plug-flow electrochemical cell

chemical dissolution cell, and a clarifier. The reactor was a rectangular unit of dimensions 135 mm × 35 mm × 55 mm (Fig. 3). Four mild steel plates (70 mm × 100 mm × 1 mm) were slotted into the cell. These electrodes were connected in parallel to the power supply as previously described. In this phase of experimen-

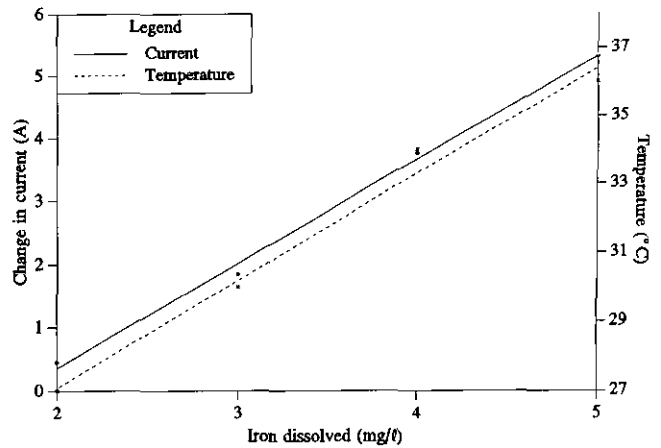


Figure 4
The relationship between the iron dissolved, change in current and temperature

tation, the number of electrodes was kept constant at four, the distance between the plates was fixed at 5 mm, the frequency was maintained at 50 Hz, and the cooling water pH was uncorrected. The voltage applied and the water flow rate were the only two variables manipulated.

Results and discussion

Feasibility study

The preliminary investigation revealed that cooling water is ideally suited as an electrolyte due to its high conductivity. No reagents are added to facilitate the process thereby ensuring zero addition of contaminants. It was also proven that ferric ions are generated in the cooling water at the desired rate and above, i.e. in excess of 5 mg/kg.

The feasibility study revealed that increases in the process variables, number of electrodes, voltage applied and duration of experiment have favourable effects on the dissolution rate. The results confirmed the relationship between the electrical current flow and the iron generated as described by Faraday's law. The experiments also shed light on the exothermic nature of the reaction, an important characteristic of the electrochemical process. These relationships are represented in Fig. 4.

Variable significance test

Having confirmed the potential of the electrochemical process, the study progressed to the optimisation phase. In order to simplify the experimental design, a test was first performed to discriminate between significant and insignificant process variables. Six variables and their influence on the electrochemical process were investigated. Out of those, four were identified as having a significant effect on the electrochemical generation of ferric ions by means of a variable significance test. These were the number of electrodes, voltage applied, duration of experiment, and initial cooling water pH. These were manipu-

TABLE 1 CENTRAL COMPOSITE DESIGN I VARIABLES AND THE IR LEVELS							
Variables	Axis	Levels					Dimensional units
		-2	-1	0	1	2	
Voltage applied	x	5	10	15	20	25	V
Number of electrodes	y	2	4	6	8	10	-
where z = iron dissolved (mg/kg)							
TABLE 2 CENTRAL COMPOSITE DESIGN II VARIABLES AND THEIR LEVELS							
Variables	Axis	Levels					Dimensional units
		-2	-1	0	1	2	
pH of electrolyte	x	5	6	7	8	9	-
Duration of reaction	y	1	2	3	4	5	min
where z = iron dissolved (mg/kg)							

$$z = 3.292 + 2.938x + 3.896y + 1.617x^2 + 1.469xy + 1.555y^2 \quad z = 7.208 + 1.063x - 1.021y - 0.8672x^2 - 0.4063xy - 0.3672y^2$$

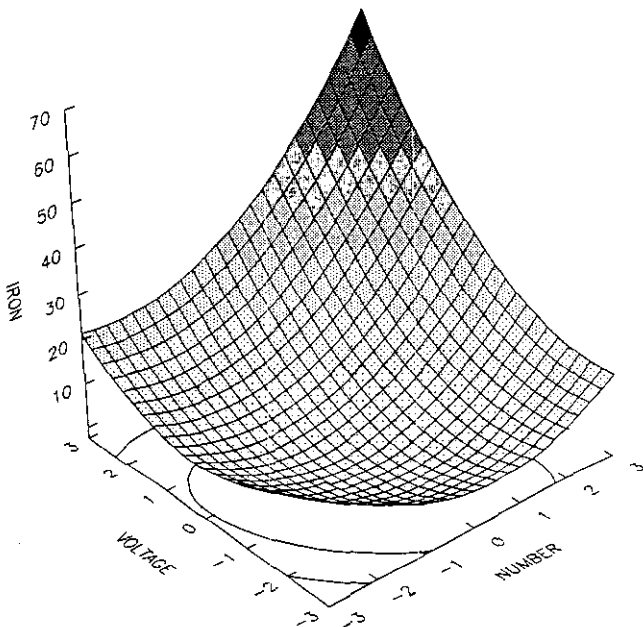


Figure 5

Three-dimensional response surface of dissolved iron over the variables, number of electrodes and voltage

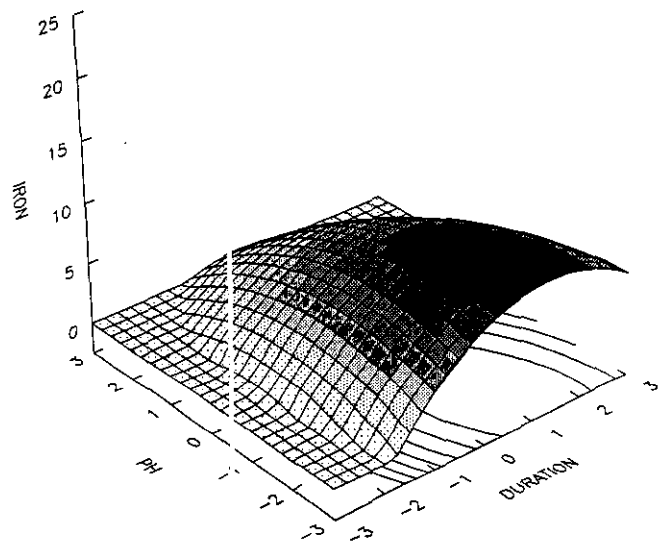


Figure 6

Three-dimensional response surface of dissolved iron over the variables, duration and pH

lated in the optimisation of the process whereas the insignificant parameters, distance between electrodes and frequency, remained constant in the next phase of experimentation.

Optimisation phase

The optimisation phase was divided into two sections: experimentation in a batch reactor and experimentation in a plug-flow reactor.

The significant process variables were manipulated simulta-

neously to determine their combined effects on the generation of iron. A central composite experimental design was used to generate and analyse the response.

Two objectives were to be achieved in this phase of experimentation. A mathematical model was to be fitted to the experimental results to describe the response surface in the defined range and ultimately predict the extent of iron dissolution under any conditions within the limits of the design. The response tendencies with regard to certain variable combinations were to be identified for better understanding of the mechanism and

TABLE 3 CENTRAL COMPOSITE DESIGN III VARIABLES AND THEIR LEVELS							
Variables	Axis	Levels					Dimensional units
		-√2	-1	0	1	√2	
Flow rate	x	0.2	0.3	0.5	0.7	0.8	l/min
Voltage applied	y	6	9	17	25	28	V
where z = iron dissolved (mg/kg)							

further refining of the process.

Batch reactor experiments were conducted with the process variables at various levels as depicted in Tables 1 and 2. Manipulation of these variables according to the experimental design revealed process responses which are represented in three-dimensional graphs in Figs. 5 and 6.

The increments on the x- and y-axes of these two graphs represent the levels given in Tables 1 and 2 respectively, while the z-axis shows the extent of iron dissolution in mg/kg. The second-order models depicting the generation of ferric ions in terms of process variables are given above each graph.

The response surfaces clearly show that an increase in the dissolution of iron is obtained with an increase in the dimensions of the variables, number of electrodes, voltage applied and duration of experiment. This favourable response is substantiated by the fact that an increase in electrode surface area and an increase in applied potential promote the conductivity of the electrochemical cell and thus dissolution. It was also observed that this rate decreased after a certain period of time (Fig. 6). This phenomenon is explained by the accumulation of reaction products between the electrodes of the batch reactor. It is therefore recommended to operate the system continuously in order to combat this problem. The effect of pH on the electrochemical process was found to be too insignificant to consider pretreating the cooling water with carbon dioxide.

Knowledge acquired from this experimental work was used as the basis for further experimentation in a plug-flow reactor. The variables, voltage applied and cooling-water flow rate were manipulated at the levels represented in Table 3.

A statistical interpretation of the results revealed that the maximum dissolution of iron is obtained using a combination of high voltage and low flow rate (Fig. 7). The second-order model depicted above the plot describes and predicts the process response in terms of changes in the process variables.

The high correlation coefficient (92.57%) demonstrates the fitting relationship between the calculated response and the experimental response. The error factor (7.43%) is most likely due to uncontrollable variables such as environmental conditions and the human factor.

The effect of high voltage on the dissolution of ferric ions has already been related to Faraday's law in the feasibility study. The higher the voltage applied or equivalently current flowing through the cell, the higher the electrochemical dissolution rate.

The unfavourable effect of high solution flow rates on the dissolution rate is explained as follows. It is important to maintain a certain transfer rate of the reaction product away from the electrodes, in order to favour the rate of dissolution and prevent passivation of the electrodes. However, this transfer rate should still maintain the concentration gradient, the necessary driving force for mass transfer species during the reaction. If the flow rate

$$z = 6.75 + 4.173x - 3.173y + 0.9377x^2 - 0.25xy + 0.4376y^2$$

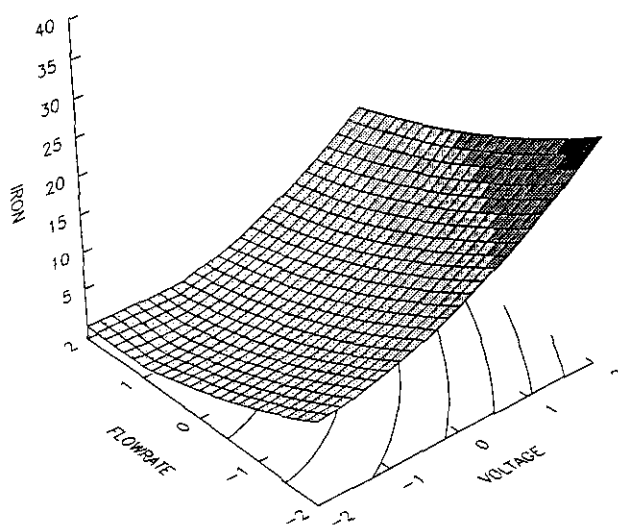


Figure 7

Three-dimensional response surface of dissolved iron over the variables, voltage and flow rate

is too high the concentration gradient is smaller and the process is therefore limited. An increase in solution flow rate also reduces the residence time in the plug-flow reactor. A shorter exposure to the electrodes means a smaller dissolution rate.

The statistical extrapolation and interpretation of the data pointed out that the process variable, voltage, is more significant than changes in the solution flow rate within a specified range. The maximum generation of iron within this designated range is therefore 28 mg/kg.

Conclusions

Having confirmed the potential of the electrochemical process, the study concentrated on the optimisation of the dissolution of ferric ions. The process variables electrode spacing, number of electrodes, initial cooling water pH, duration of reaction, solution flow rate, system frequency and applied voltage were manipulated to optimise the generation of iron on a bench scale. Based on the process responses observed the following deductions were made. Ideally the geometric shape of the electrochemical reactor should be such that the electrode spacing is as small and as even as permissible. The surface area of the electrodes per unit cell

volume should be large to ensure maximum dissolution. The natural pH of the cooling water is adequate for the production of ferric ions; carbon dioxide injection is therefore not justified. To prevent the accumulation of the passivating reaction product on the electrode surface with reaction time, the process should be executed in a flow reactor. The flow rate of the cooling water should be regulated so that sufficient product is removed from the electrodes while maintaining a concentration gradient. Changes in the system frequency have a negligible effect on the process so that industrial frequency can be used. Ultimately the voltage should be controlled to obtain the desired quantity of dissolved iron in the cooling water.

The use of alternating current in the electrochemical dissolution of iron in cooling water has several advantages over the use of direct current. Dissolution in an alternating field is accompanied by the generation of heat in the electrolyte. This increase in temperature aids the precipitation of carbonate compounds and the settling of floc particles in the cooling-water treatment process. The application of alternating current also implies a continuous change in the polarity of the electrodes, which helps to curb passivation of the electrodes.

Electrochemical dissolution in an alternating field is however associated with considerable energy expenditures. High current densities are required to dissolve relatively low concentrations of iron, which impairs the economic indices of the operation of the system. This disadvantage should be further investigated.

Electrochemically generated ferric ions offer a viable alternative to ferric chloride as coagulants by eliminating the addition of pollutant anions into the system. This concept of zero addition of chloride ions implies that the corrosion potential of the

cooling-water system is reduced, thereby increasing the life of major plant components such as condensers.

Acknowledgements

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