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Considerations regarding the polarity reversal in electrochemically generated hypochlorite

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The effect of reversing the polarity of the applied voltage on the electrochemically generated active chlorine concentration was studied for various operating parameters such as applied current densities, initial brine concentration, polarity reversal periods. The electrochemical reactor consists of an undivided cell chlorinator, provided with two platinised platinum electrodes. The polarity reversal device is based on a multipin relay device which is triggered by a commercially available timer. In order to quantify the effect of the polarity reversal on the active chlorine concentration, one has proposed an amplification factor, K, taken as the ratio between the active chlorine concentration when polarity reversal is applied and the active chlorine concentration when no polarity reversal is applied, having the significance of an indication criterion regarding the effectiveness of the polarity reversal onto the active chlorine generation process. It was found that, with few exceptions, applying the polarity reversal procedure has a beneficial effect on the electrochemically generated hypochlorite.

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Keywords: Active chlorine; Polarity reversal; Platinum electrodes

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1. Introduction

Chlorination is one of the most common methods used for water disinfection as it destroys pathogens present in drinking water [1-4] and it also reacts with several compounds present in water [5-9]. One of the advantages of using chlorine compounds is that any reduction of their concentration is diagnosed in short time [10]. In the last years, many studies have focused on replacing conventional chlorination due to the fact that during the conventional chlorination some controversial unwanted disinfection by-products (DBPs) are formed [10-20]. An alternative to the conventional (chemical) chlorination of water is electrochemical disinfection. Electrochemical methods have been used previously for wastewater treatment. One mentions the removal of heavy metals from industrial wastewater [21]. The electrochemical disinfection consists in an electrochemical generation of hypochlorous acid starting from a chloride based solution, normally brine [22]. Moreover, during the electrochemical disinfection little or no harmful compounds are generated. The effectiveness of the active chlorine obtained during electrochemical disinfection depends on a series of physical and chemical characteristic parameters such as *p*H, current density, temperature, contact time, turbidity, the presence or the absence of interfering substances [23], electrode material, electrodes surface area ratio and distance between electrodes [24].

In the electrochemical disinfection, the main reaction is the electrolysis of water: hydrogen is produced at the cathode and oxygen at the anode, whereas the anodic production of hypochlorite is a side reaction at the anode [22, 25, 26, 27]. In the region near the cathode surface the *p*H increases while near the anode surface the *p*H decreases due to the evolution of oxygen [25].

$$2H_2O+2e^- \rightarrow H_2+2OH^- \quad (1)$$

$$2H_2O \rightarrow O_2+4H^++4e^- \quad (2)$$

The hypochlorous acid/hypochlorite is generated at the anode in a side reaction to oxygen evolution. Firstly, chlorine is produced at the anode by primary oxidation of chloride to chlorine. Chlorine hydrolyses rapidly in water and hypochlorous acid (HClO) is formed. Hypochlorous acid can dissociate to form hypochlorite anion and H^+. The equilibrium is *p*H-dependent [22, 26, 27]. The disinfecting action of hypochlorous acid is given by release of atomic oxygen [22].

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (3)$$

$$Cl_2+H_2O \rightarrow HClO + HCl \quad (4)$$

$$HClO \rightarrow ClO^- + H^+ \quad (5)$$

$$ClO^- \rightarrow O + Cl^- \quad (6)$$

In addition to the main reactions, in the electrolytic cell take place side reactions that reduce the amount of hypochlorite generated [27].

$$6OCl^-+3H_2O \rightarrow 2ClO_3^- + 6H^+ + 4Cl^- + 1.5O_2 + 6e^- \quad (7)$$

$$ClO^- + H_2O \rightarrow 2H^+ + Cl^- + O_2 + 2e^- \quad (8)$$

$$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \quad (9)$$

$$2HOCl + OCl^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \quad (10)$$

When one uses untreated hard water, due to the increase of pH at the cathode, during water electrolysis, a thin film of calcareous deposits is formed [22, 25, 26, 28]. This film is mainly made of $CaCO_3$ and $Mg(OH)_2$ [25, 26]. Several cleaning methods have been studied. These include ultrasonication [28], continuously rotating brushes or vanes [22], the imposition of a current pulse [22], the use of a cathode which consists of an elastically deformable electrically conductive body [28], the use of fluidized spherical particles with higher density which move throughout the reactor leading to the mechanical cleaning of the electrode [28], polarity reversal [25, 26, 28]. Among these methods, polarity reversal is efficient in long time use as the other methods do not totally prevent scaling [22, 28].

During the reversal of polarity, the former cathode acts as an anode and the calcareous deposits are removed due to the acidic anodic pH [22, 25]. The scale is removed according to the following reactions [25]:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \quad (11)$$

$$Mg(OH)_2 + 2H^+ \rightarrow Mg^{2+} + 2H_2O \quad (12)$$

The calcareous deposits that are further distant from the anode surface cannot adhere and are removed from the system by the water flow. Shortly after the polarity reversal, one may observe an outgassing effect near the former cathode due to the formation of CO_2 [25].

The main disadvantage of polarity reversal is that it reduces electrode lifetime [22, 25, 28] and affects the activity of electrode materials in active chlorine generation [25, 28]. Having considered that, and taken into account that in other electrolysis processes the most stable inert electrodes are platinum electrodes [22, 27], we have considered these types of electrodes as a first choice for our electrochemical reactor.

It has been also reported that the application of a polarity reversal procedure in conjunction to platinum electrodes leads to a rise of active chlorine rate due to the change in the platinum surface during the time the electrode was acting as a cathode [25]. When the electrode acts as an anode, a thin film of platinum oxide is formed. After the polarity reversal, this thin film is reduced to platinum metal, which has higher activity with respect to chlorine production comparing to the platinum oxide surface [25].

The aim of this paper is to present the effect of polarity reversal on electrochemically generated active chlorine. The active chlorine species were generated by electrolysis of NaCl solutions using platinised platinum electrodes in an undivided cell. Moreover, one has also investigated the effect of polarity reversal frequency on the efficiency of chlorine production.

2. Experimental procedure

The sodium chloride solutions used during the experiments were prepared using analytical grade sodium chloride supplied by Chimopar S.A. Bucharest and distilled water.

The experiments were performed using a two platinised platinum electrodes reactor. Each electrode was of rectangular shape and had a total area of 1.3 cm^2. The electrodes were platinised before the beginning of the experiments using a base solution containing hexachloroplatinic acid (3.5%) and lead acetate (0.005%). The platinisation was performed by reversing the electrodes polarity every 30 s for 5 minutes at a current density of 300 $A \cdot m^{-2}$. Prior to the platinisation the electrodes were cleaned by immersion in aqua regia and distilled water. As recommended by Zoski [29], the electrodes were kept in distilled water for 24 h for the purpose of coated surface stabilisation.

The electrolysis of sodium chloride solutions was performed in an undivided cell manufactured from a ClearWater Chlorinator provided by Aqualux by adding the platinised platinum electrodes at the bottom of the cell in order to ensure that it can stand the aggressive attack of oxygen and chlorine.

In order to reverse the polarity accurately for the above said cell during the electrolysis process, an electronic switch was employed. This was made using an electronic timer (CD4541, Complet Star Service, Bucharest) used in connection with two relays (5 A/250 V), see Fig. 1-3. The electronic switch is able to reverse the polarity, user selectable, from 10 seconds up to 15 minutes. Moreover, the switch is acting as a bistable system, allowing more than one polarity switch (e.g. if the time base is established at 2 minutes and the total electrolysis time is 10 minutes, then 4 automatic polarity reversals occur). Tables 1, 2 and 3 show the components of the electronic timer [30].

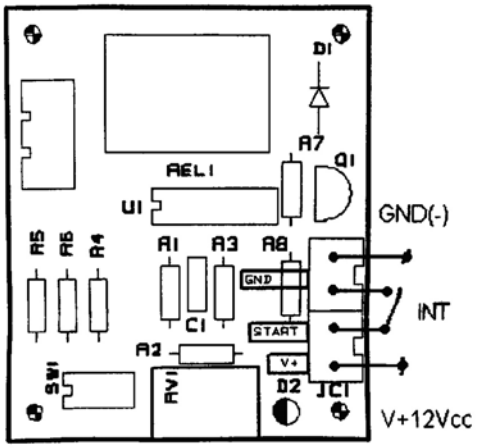

Fig. 1. The printed circuit board layout of the CD4541 electronic timer [30].

The overall concentration of dissolved chlorine in water was identified as active chlorine, defined as the sum of the three possible species (Cl_2, HClO and ClO^-). The active chlorine content was determined using the iodometric titration method, carried out in accordance with the procedure presented in details in [31]. The titration was performed using a Solarus digital burette supplied by Hirschmann, Germany.

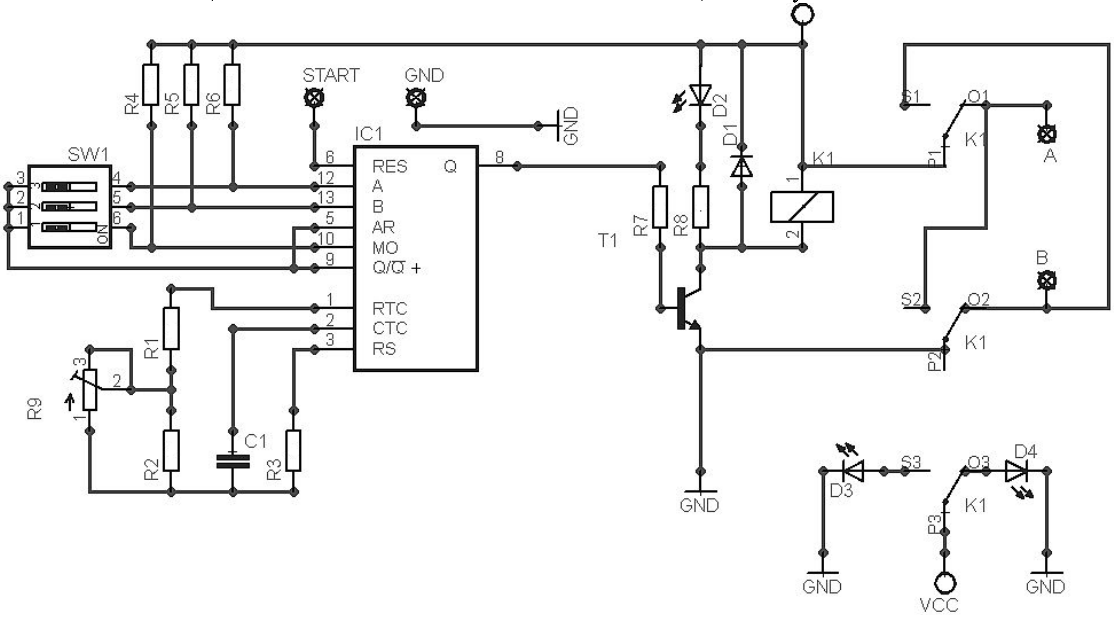

Fig. 2. Depiction of the electronic scheme of CD4541 timer adapted using a basic timer scheme [30]

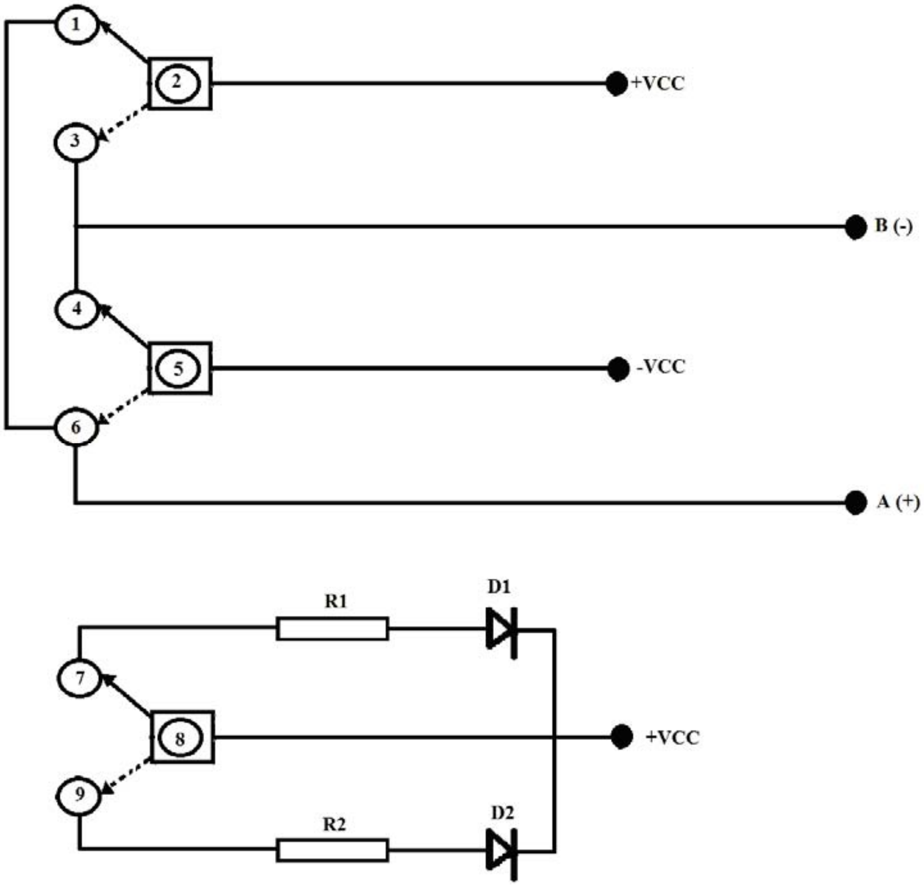

Fig. 3. A depiction of the relays connecting scheme of the polarity reversal device

Table 1. The components of the electronic CD4541 timer [30].

Name of the component	Type/value
C1	1 μF
D1	R4007
D2	LED
IC1	CD4541BE
Q1	BC177
REL1	12 V
R1	10 kΩ
R2	10 MΩ
R3	220 kΩ
R4, R5, R6	4.7 kΩ
R7	120 Ω
R8	1.2 kΩ
R9	Variable resistor
SWI	SW DIP-3

Table 2. Electronic components used for the construction of the polarity reversal device.

Component	Type/value
2, 5, 8	RGI TGL 200-3796 relays
R1, R2	Resistors, 52 Ω
D1, D2	Diodes, 1N4007
+VCC, -VCC	Relays input voltage

Table 3. The state of contacts for the polarity reversal device.

Contacts									Voltage output
1	2	3	4	5	6	7	8	9	
NC	C	NO	NC	C	NO	NC	C	NO	A (+) B (-)
NO	C	NC	NO	C	NC	NO	C	NC	A (-) B (+)

NC = normally closed, NO = normally open, C = connecting point, A, B, final voltage output terminals

The active chlorine species were electrogenerated using the electrolysis of sodium chloride using a square experimental matrix made of 4 current densities (500, 1000, 3000 and 5000 $A\cdot m^{-2}$) and four concentrations, namely 0.1, 0.5, 1 and 2 $mole\cdot L^{-1}$, conducted in closed reactor. In addition, each experimental run was divided in two parts. The first one, related to the electrolysis of the sodium chloride solution of a previously established concentration was conducted with no polarity reversal. The second part was an identical replication of each set of above said experiments, the only difference being that in this case one has used the polarity reversal at electrodes using a time base of 1, 2, 3, 4, 5 and 10 min.

The total electrolysis time, regardless of polarity reversal or not was 20 min. At the end of each experiment, one has determined the active chlorine content of the resulting solution.

The timer depicted in Figures 2 and 3 provides a programmable operational timing with a duration starting from 0,3 seconds up to 10 minutes, the period being split into 4 zones, namely from 0,3 to 3 s, 1 s to 10s, 10 s to 90 s, 60 s to 600 s, the particular range being chosen by a combination of switches belonging to the dip-switch SW1 (Fig. 2) and the fine tuning by the adjustment of the variable resistor R9. The timer was operated as an astable device having a filling factor of 0.5.

By coupling this timer with the polarity reversal device depicted in Fig. 3, one is now able to obtain a series of alternating periods of anodic and cathodic polarization at terminal A and B.

When the timer and the power supply (+VCC and –VCC) are linked to the polarity reversal device, in the initial phase, the positive polarisation goes through pin 1 and 2 towards the output A (see Fig. 3) and from here to the platinum electrode 1, while –VCC is fed through pin 4 and 5 and reaches the output B and the platinum electrode 2. As a result, the electrode 1 becomes anodically polarised, while the electrode 2 is cathodically polarised. The contacts 7 and 8 are closed, playing the role of indicating the presence of direct polarisation, determining the LED D1, Fig. 3 to indicate a positive polarisation at the output A and a negative polarisation at the output B.

When the timer depicted in Fig. 1 reaches the prescribed timing period, the relay REL 1 from figure 2 is triggered, connecting contacts 2 and 3 and at the same time contacts 5 and 6, and 8 and 9 determining now the output A and the platinum electrode 1 to be subjected to a negative polarisation, –VCC while the output B and the platinum electrode 2 are now positively polarised, +VCC. As a result, the electrode 1 becomes anodically polarised, while the electrode 2 is cathodically polarised. As now the contacts 8 and 9 are closed, the LED D2 lights indicating a positive polarisation at the output B and negative polarisation at the output A.

When the astable circuit depicted in Fig. 2 completes its timing period, the relay REL 1 is reverted back to the original position determining also the circuit shown in Fig. 3 to go back to the initial position, pin 1 and 2 towards the output A (see Fig. 3), pin 4 and 5 to output B and pins 7 and 8 to the LED D1 so that A becomes positive and B becomes negative. The process takes place repeatedly until the electrolysis time is reached (e.g. for an electrolysis time of 20 minutes, a polarity reversal period of 1min, the process is repeated 19 times).

The contact 11 and 13 play the role of indicating the presence of direct polarisation, so when A is positive and B is negative, the LED is green and when A is negative and B is positive, the LED is red.

3. Results and discussion

The concentration of active chlorine generated during the experiments carried out for all concentrations, the current densities specified above and the relative error of the triggering period of the polarity reversal device are presented in Tables 4 and 5.

Table 4. The concentration of active chlorine generated during the experiments.

Current density, i, $A \cdot m^{-2}$	Initial brine conc. C_{NaCl}, $mole \cdot L^{-1}$	Active chlorine concentration, C x 10^3 $g \cdot L^{-1}$						
		No polarity reversal	Polarity reversal period					
			1 min.	2 min.	3 min.	4 min.	5 min.	10 min.
500	0.1	5.396	6.106	7.810	7.526	9.940	8.520	4.118
	0.5	7.526	9.940	12.496	11.360	13.348	13.916	11.786
	1.0	11.076	13.490	12.212	16.330	13.064	14.200	10.792
	2.0	12.212	11.644	11.786	15.336	14.910	16.046	13.064
1000	0.1	5.964	8.804	11.644	10.508	10.934	9.514	5.396
	0.5	14.910	21.442	24.992	23.146	23.714	23.714	21.868
	1.0	24.708	26.838	23.998	29.252	22.152	24.566	24.282
	2.0	24.140	22.294	24.708	24.708	25.134	27.122	21.016
3000	0.1	15.194	21.158	22.862	23.146	21.158	19.738	19.028
	0.5	44.304	85.768	65.462	68.160	61.344	65.888	58.078
	1.0	57.226	71.994	73.840	72.704	68.160	67.876	70.716
	2.0	67.166	67.166	77.532	70.432	68.870	69.580	65.462
5000	0.1	25.844	42.884	38.198	34.648	33.938	35.642	24.424
	0.5	71.852	90.596	108.630	99.542	83.212	100.110	90.028
	1.0	91.448	114.168	114.026	113.458	111.044	118.286	107.920
	2.0	92.726	97.128	111.754	116.298	75.544	78.384	88.040

Table 5. The relative error (ε_r) of the triggering period of the polarity reversal device

Polarity reversal period	1 min	2 min	3 min	4 min	5 min	10 min
Real time, s	62	122	176	239	301	603
Triggering time, s	60	120	180	240	300	600
ε_r, %	3.23	1.64	2.27	0.42	0.33	0.50

One has defined an amplification factor, K, as the ratio between the active chlorine concentration when polarity reversal is applied, C_{PR}, and the active chlorine concentration when no polarity reversal is applied, C_0.

$$K = \frac{C_{PR}}{C_0}\text{, dimensionless} \qquad (13)$$

The significance of this factor is that of an indication criterion regarding the effectiveness of the polarity reversal conditions (if K < 1, the polarity reversal contributes negatively towards the generation of active chlorine, if K = 1, the polarity reversal procedure has no impact whatsoever towards the generation of active chlorine and if K>1, then the polarity reversal has a beneficial effect on the process of generating the active chlorine).

The behaviour of K as a function of current density is depicted in Figs. 4-9.

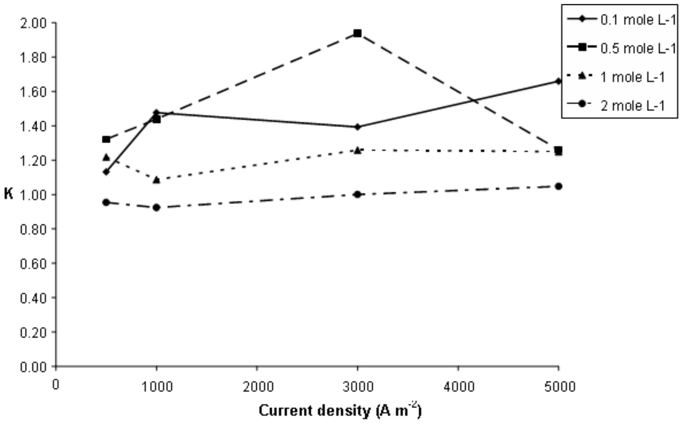

Fig. 4. The dependence of K on the applied current density for a polarity reversal period of 1 minute

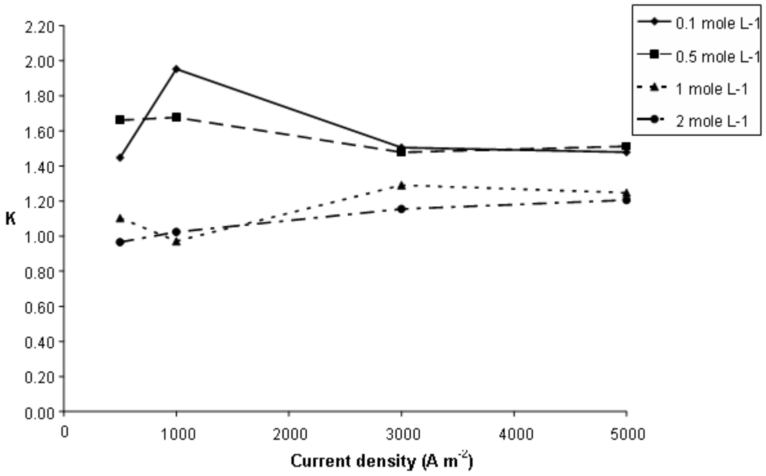

Fig. 5. The dependence of K on the applied current density for a polarity reversal period of 2 minutes.

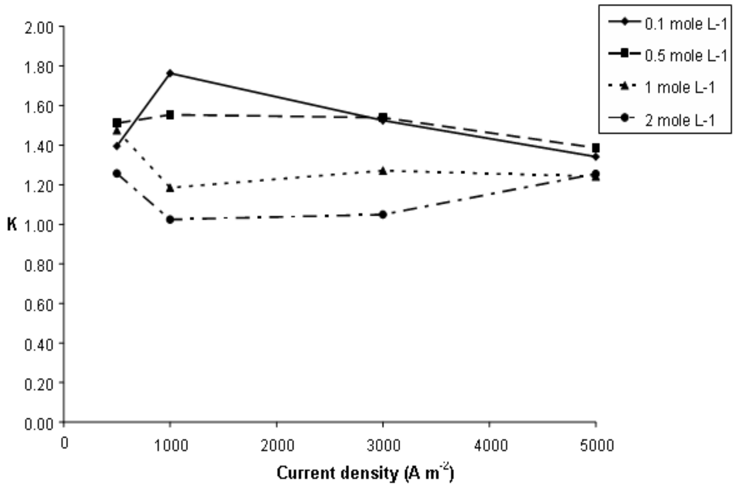

Fig. 6. The dependence of K on the applied current density for a polarity reversal period of 3 minutes.

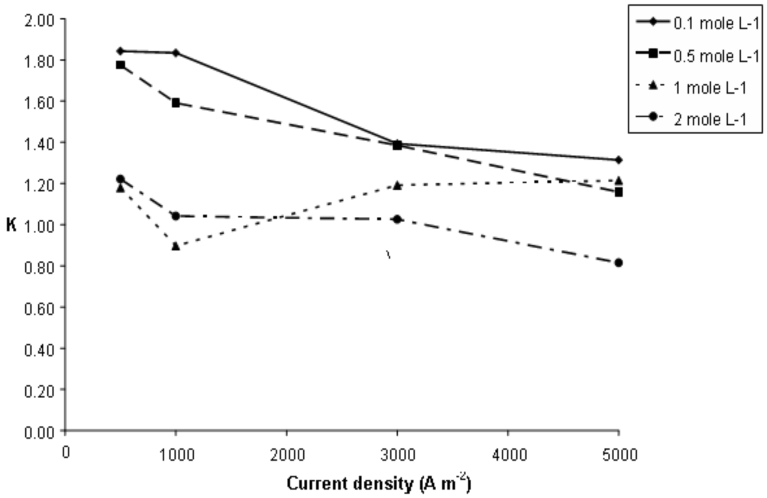

Fig. 7. The dependence of K on the applied current density for a polarity reversal period of 4 minutes.

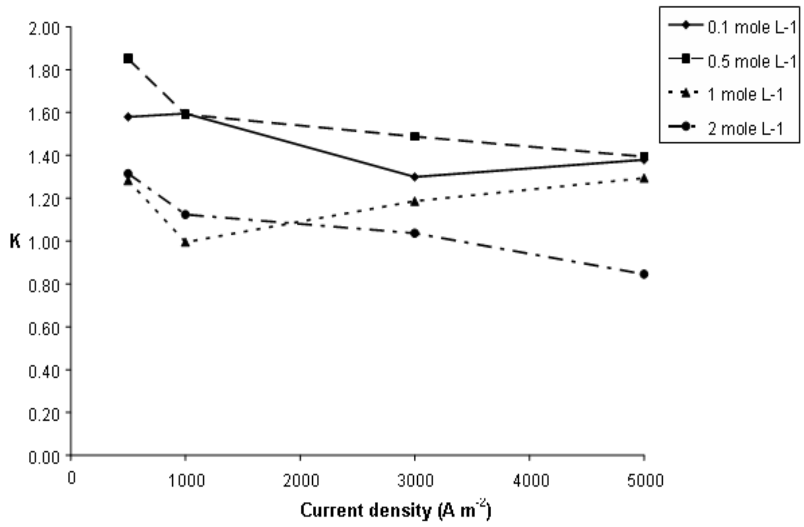

Fig. 8. The dependence of K on the applied current density for a polarity reversal period of 5 minutes.

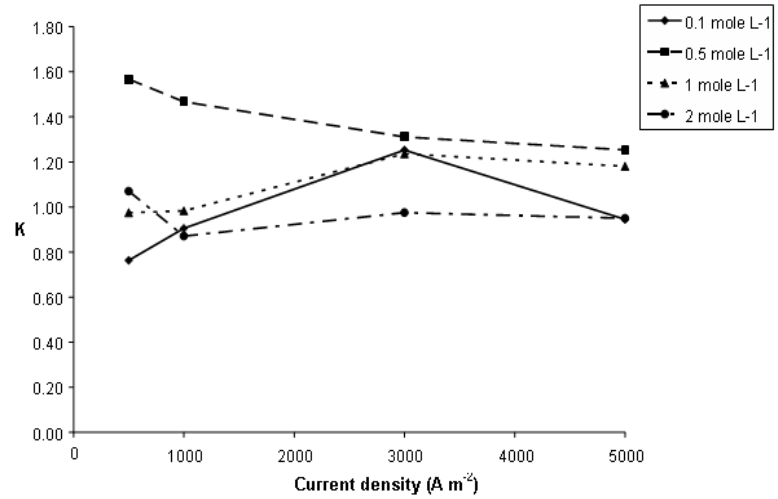

Fig. 9. The dependence of K on the applied current density for a polarity reversal period of 10 minutes.

As one can see, the effect of the polarity reversal determines, in most cases, an increase in the active chlorine content of the solution.

As for its magnitude, an increase in the polarity reversal frequency leads to a decrease in the active chlorine content, even though it will remain higher in most cases comparing to the absence of the polarity reversal procedure.

The largest increase in active chlorine generation, more than 90% comparing to the case where no polarity reversal is applied (K=1.93) was obtained for an initial brine concentration of 0.5 mole$\cdot$L^{-1}, a polarity reversal period of 1 min and at a current density of 3000 A$\cdot$m^{-2}.

However, one may notice that in some circumstances, at a concentration of 2 mole$\cdot$L^{-1}, concentration rarely used in most practical applications, the amplification factor K decreases marginally below 1. This may be explained by the increased density and viscosity of the electrolyte solution, affecting negatively the mobility of the electrochemically generated reaction products.

When 0.1 mole$\cdot$L^{-1} NaCl solution was used, the polarity reversal frequency had the largest influence when a polarity reversal period of 1 min was applied (an increase from 10% to 60%) and the least favourable effect in the case of a polarity reversal period of 4 min (an increase from 10% to 20%, with the exception of the applied current density of 1000 A$\cdot$m^{-2} when the amplification factor is less than 1 (K=0.89) see figure 7).

The results obtained in the case of 2 mole$\cdot$L^{-1} NaCl solution are similar to those obtained when using a 1 mole$\cdot$L^{-1} NaCl solution, the only difference being that the case when the polarity is reversed at 10 min, the active chlorine content of the resulting solution being significantly different from the case with no polarity reversal is applied.

The differences obtained here, compared to data reported in [22], [25] and [26] where lower active chlorine concentrations were found when polarity reversal was applied, may be explained if one takes into account that in this particular case the brine solutions were prepared using distilled water. Unlike the hard water, distilled water does not contain calcium and magnesium ions and hence there are no carbonate deposition processes which may lead to electrode fouling. Moreover, the advantage of using platinum electrodes electrochemically plated with a layer of black platinum, ensure, besides the increased activity due to the black platinum layer, the necessary protection versus the anodic dissolution process as the platinum electrodes are not prone to any anodic attack.

4. Conclusions

As a result of the investigation carried out to determine the effect of reversing the polarity of the applied voltage on the electrochemically generated active chlorine concentration it was found that, with few exception, it enhances the active chlorine generation process, the largest increase being more than 90% when a polarity reversal period of 1 min and at a current density of 3000 $A \cdot m^{-2}$ were used to electrolyse a brine solution of 0.5 $mole \cdot L^{-1}$, comparing to the case where no polarity reversal is applied.

The use of identical platinised platinum electrodes for anode and cathode proved to have some advantages compared to the use of other types of anodic soluble electrodes, the platinum electrodes being stable and inert to anodic dissolution processes, so that no electrode damage will during the polarity reversal procedure. Moreover, covering the electrodes with a black platinum layer allows for a better chlorine evolution and hence a better active chlorine generation process.

One has also proposed a dimensionless amplification factor, K, taken as the ratio between the active chlorine concentration when polarity reversal is applied and the active chlorine concentration when no polarity reversal is applied which may be useful for an easier understanding and to quantify better the effect of the polarity reversal on the active chlorine concentration. Its significance is that of a practical indication criterion showing if the polarity reversal procedure has a beneficial or a detrimental effect towards the generation of active chlorine (if $K < 1$, the polarity reversal contributes negatively towards the generation of active chlorine, if $K = 1$, the polarity reversal procedure has no impact whatsoever and if $K > 1$, then the polarity reversal has a beneficial effect).

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