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A new electrochemical technique for bleaching cellulose pulp

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A study of electrochemical bleaching of cellulose pulp was carried out in an electrolyte cell composed of a horizontal graphite anode and a parallel stainless screen steel cathode, using NaCl as electrolyte. Variables studied were: current density, sodium chloride concentration, pulp concentration, pH and temperature. The rate of bleaching was found to increase with increasing current density, salt concentration and temperature. The rate of bleaching was found to decrease with increasing pH and pulp concentration. Energy consumption ranged from 0.1 kWh kg^{-1} (pulp) to 1.75 kWh kg^{-1} (pulp), depending on current density and degree of bleaching. The quality of electrochemically bleached pulp was found to compare favourably with that of chemically bleached pulp.

1. Introduction

Cellulose pulp required for the manufacture of paper and rayon is obtained from wood or agricultural residues (e.g. rice, straw and bagasse) by removing non-cellulose materials (mainly lignin). Lignin removal is carried out in two processes [1–3], the first process is known as cooking and consists of reacting wood with sodium hydroxide and sodium sulphide (kraft process) or sodium sulphite (sulphite process) under high pressure and temperature. The second process is known as bleaching and involves the removal of residual lignin by the sequence chlorination – alkali extraction – hypochlorite bleaching in three steps.

Lignin is a polymerized product derived from a building unit R–C–C–C in which R is the 4 hydroxy-3-methoxyphenyl group. The main possibilities of reactions between lignin and chlorine water are the addition of chlorine to double bonds, substitution of a hydrogen atom of the benzene nuclei with chlorine and oxidation of both lignin and the chlorolignin formed. With hypochlorite, lignin and/or chlorolignin is oxidized to water soluble products [1–3]. Pulp mills usually buy the required chlorine from chlorine distribution centres in the liquid form under high pressure at a high cost, partly because of the transportation and storage expenses. The object of the present work is to explore the possibility of carrying out the process of bleaching electrochemically in one stage (*in situ* bleaching) with a view to reducing the cost of the bleaching process and also eliminating the hazards involved in Cl_2 transportation and handling. In addition, the approach would eliminate the dependence of pulp mills on Cl_2 producers by installing an electrochemical bleacher in the pulp mill, thus avoiding work interruption due to strikes or shutdowns of chlorine plants.

To this end, pulp slurry was bleached in an electrolytic cell composed of a horizontal graphite anode placed at the bottom of the cell and a horizontal stainless steel screen cathode placed above the anode. The pulp slurry occupied the cell volume above the cathode. In this way, the possible increase in ohmic drop due to the presence of pulp suspension between the two electrodes was avoided. The stirring effect of the cathodic H_2 and anodic Cl_2 bubbles served to keep the pulp suspended in the solution and prevented its sedimentation on the cell electrodes.

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2. Experimental technique

Unbleached kraft soft wood pulp of brightness 25.6% GE was provided by Irving Pulp and Paper Ltd. (New Brunswick, Canada). The pulp was bleached in a cylindrical plexyglass cell having a diameter of 11 cm and a height of 24 cm (Fig. 1). A graphite disc anode of 11 cm diameter was placed at the cell bottom, and a horizontal stainless steel screen cathode was placed at a distance of 2 cm above the anode. Pulp slurry was prepared outside the cell by mixing sodium chloride, water and the pulp under continuous stirring to break up pulp flocks and disperse them in the electrolyte. The pH of the pulp slurry was adjusted by addition of sodium hydroxide solution. Two dm^3 of pulp slurry were used in each run, electrolysis was conducted for a time ranging from 15 to 180 minutes. After each run pulp brightness was measured by a brightness tester (Elrepho – by Carl Zeiss) which involves a photoelectric reflectance photometer. Also, after each run pulp viscosity was measured using a capillary viscometer (pulp sample is dissolved in cupriethylinediamine solution at a concentration of 0.5%), to make sure that no serious cellulose degradation had taken place, temperature inside the cell was controlled by placing the cell in a thermostated water bath.

The electrical circuit used consisted of a 6 V d.c. power supply with a voltage regulator connected in series with a multi-range ammeter and the cell. A voltmeter was connected in parallel with the cell to measure the cell voltage.

3. Results and discussion

To gain an insight into the nature of the reactions involved in electrochemical bleaching and how different variables affect the process, the cell reactions must be defined [4–6]. These are generally considered to be:

Anode reactions:

(1) $6\mathrm{Cl}^- \rightarrow 3\mathrm{Cl}_2(\mathrm{aq}) + 6\mathrm{e}$

(2) $6\mathrm{ClO}^- + 3\mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{ClO}_3^- + 4\mathrm{Cl}^- + 6\mathrm{H}^+ + 3/2\ \mathrm{O}_2 + 6\mathrm{e}$

Solution reactions:

(3) $3\mathrm{Cl}_2(\mathrm{aq}) + 3\mathrm{H}_2\mathrm{O} \rightleftharpoons 3\mathrm{HClO} + 3\mathrm{Cl}^- + 3\mathrm{H}^+$

(4) $\mathrm{HClO} \rightleftharpoons \mathrm{ClO}^- + \mathrm{H}^+$

(5) $\mathrm{ClO}^- + 2\mathrm{HClO} \rightarrow \mathrm{ClO}_3^- + 2\mathrm{Cl}^- + 2\mathrm{H}^+$

Cathodic reaction:

$6\mathrm{H}^+ + 6\mathrm{e} \rightarrow 3\mathrm{H}_2$

As shown by the above equations, the first anode reaction is discharge of Cl^- to form dissolved Cl_2, which undergoes hydrolysis to form hypochlorous acid. Ionization of hypochlorous acid gives hypochlorite ion in equilibrium with the acid. Reactions of hypochlorite ion and hypochlorous acid gives chlorate ion in solution. Discharge of hypochlorite anodically gives chlorate and oxygen. The extent of chlorate formation through reaction (2) depends on pH, electrode material and concentration of hypochlorite; for a given electrode material and current density, the formation of chlorate through reaction (2) is favoured in slightly alkaline solution. In slightly acid solution reactions (3) and (4) predominate and may lead to the formation of ClO_3^- through reaction (5) when the concentration of hypochlorite and hypochlorous acid concentration becomes sufficiently high.

Under the present conditions where chlorine, hypochlorous acid, hypochlorite and chlorate exist in the solution, it seems that electrochemical bleaching takes place by chlorination of lignin simultaneously with oxidation of lignin. Lignin oxidation takes place mainly by HClO and ClO^-, the rate of oxidation of lignin with ClO_3^- is known to be too slow [1]. Figure 2 shows that the rate of electrochemical bleaching increases with current density owing to the increase of Cl_2, HClO, ClO^- concentrations in the cell solution.

Increasing sodium chloride concentration increases the rate of bleaching, Fig. 3. This may be attributed to the fact that increasing sodium chloride concentration increases the concentration of chlorine through:

(i) the increase of current efficiency of chlorine formation at the anode,

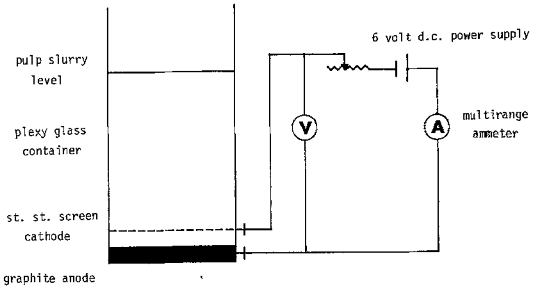

Fig. 1. Experimental set-up.

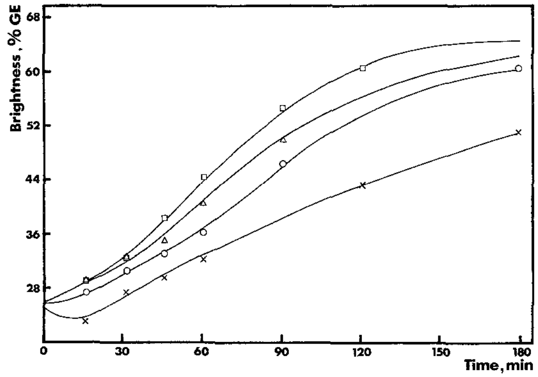

Fig. 2. Brightness versus time at different current densities (A cm^{-2}); □, 0.08; △, 0.06; ○, 0.04; ×, 0.02; pH = 7.3, C_{NaCl} = 3.5%, temperature = 303 K, pulp consistency = 2%, and initial brightness = 24.6.

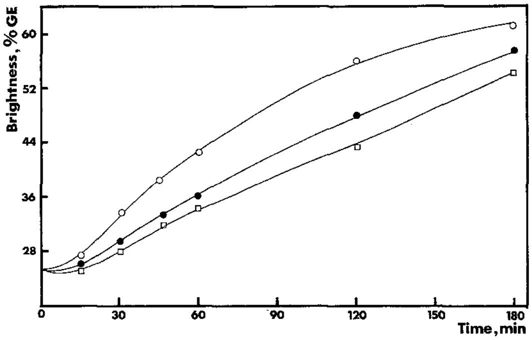

Fig. 4. Brightness versus time at different temperatures; ○, 313 K; ●, 303 K; □, 293 K, pH = 7.5, C_{NaCl} = 2.5%, pulp consistency = 2%, I = 0.04 A cm^{-2} and initial brightness = 24.6.

(ii) increase of sodium chloride concentration suppresses chlorine hydrolysis thus increasing the concentration of unhydrolysed chlorine in solution according to the reaction $3Cl_2(aq) + 3H_2O \rightleftharpoons 3HClO + 3Cl^- + 3H^+$.

Unhydrolysed chlorine reacts with lignin by substitution and addition, producing water soluble chlorolignins and easily oxidizable chlorolignins. Delignification by chlorination is known to be faster than delignification by hypochlorite oxidation [1–3].

Figure 4 shows that the rate of bleaching increases with increasing cell temperature; this finding is in agreement with the effect of temperature on chemical bleaching [1, 2]. Increase of temperature not only increases the rate of reactions of chlorine and hypochlorite with

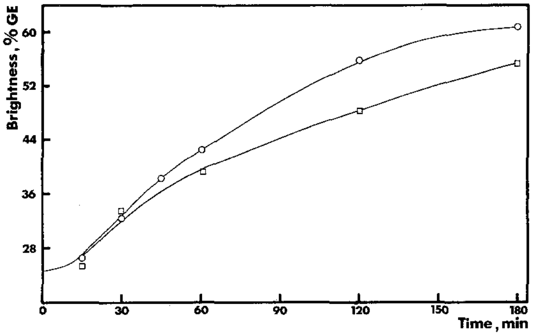

Fig. 5. Brightness versus time at different pH, ○, 7.5; □, 11.0, C_{NaCl} = 2.5%, temperature = 313 K, pulp consistency = 2%, I = 0.04 A cm^{-2} and initial brightness = 24.6.

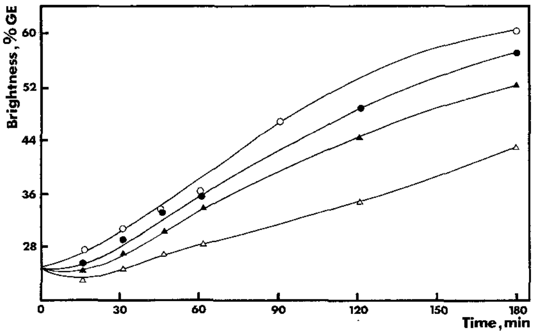

Fig. 3. Brightness versus time for different salt concentrations; ○, 3.5%; ●, 2.5%; ▲, 1.5%; △, 0.75%; pH = 7.3, temperature = 303 K, pulp consistency = 2%, I = 0.04 A cm^{-2} and initial brightness = 24.6.

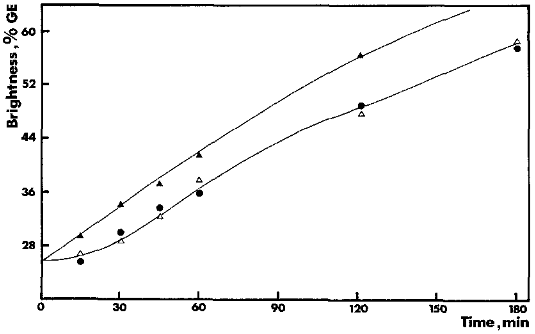

Fig. 6. Brightness versus time for different pulp consistencies: ▲, 1%, ●, 2%, △, 3%; pH = 7.4, C_{NaCl} = 2.5%, temperature = 303 K, I = 0.04 A cm^{-2} and initial brightness = 24.6.

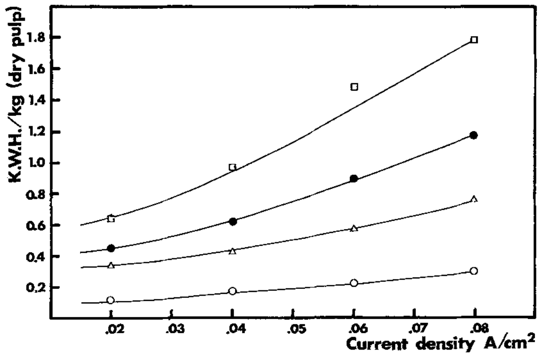

Fig. 7. Power consumption versus current density for different degrees of bleaching; □, 60; ●, 50; △, 40; ○, 30.

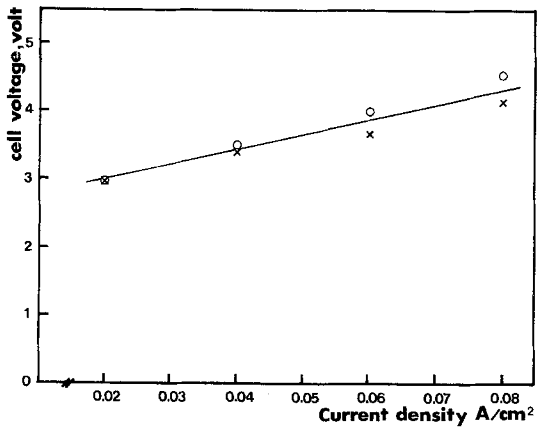

Fig. 8. Cell voltage versus current density; ○, with pulp; X, without pulp. $C_{NaCl} = 2.5\%$, pulp consistency = 2%, and temperature = 303 K.

lignin, but also increases the rate of diffusion of chlorolignin and oxidized lignin out of the cellulose fibres.

Figure 5 shows a comparison between the rate of bleaching in almost neutral solution and an alkaline solution; the rate of bleaching in the neutral solution is higher than the alkaline solution. This is attributed to the fact that chlorine concentration diminishes with increasing alkalinity as it becomes converted to hypochlorite, which oxidized lignin at a rate lower than chlorine [1–3]. However, it was found through viscosity measurement of the bleached pulp that the stability of cellulose decreases with decreasing pH because of degradation.

Figure 6 shows that the rate of bleaching for

Table 1. Comparison between chemical bleached and electrochemically bleached pulp

	Chemical Bleaching		*Electrochemical Bleaching*
Conditions	1st stage (chlorination)	pH: 2 Active Cl_2: 6% on pulp pulp consist: 3% temperature 288 K	pH: 11.1 I: 40 mA cm^{-2} NaCl Conc: 2.5% pulp consist: 2% temperature 313 K
	2nd stage (extraction)	pH: 11 NaOH: 2% on pulp pulp consist: 10% temperature 323 K	
	3rd stage (Hypochlorite)	pH: 12 active Cl_2: 1.5% on pulp pulp consist: 10% temperature 303 K	
time required to produce 60% bright (min)	255		180
Viscosity* of produced pulp ($\times 10^{-2}$ Nsm^{-2})	24		21

* 0.5 $Cu(En)_2$ capillary viscosities, initial pulp viscosity = 26×10^{-2} Nsm^{-2}.

1% pulp consistency is higher than that of 2% and 3% pulp consistency; it seems that increasing pulp consistency tends to lower the rate of diffusion of chlorine and hypochlorite to the fibres and lower the rate of diffusion of lignin breakdown products from the fibres. Also, increasing pulp concentration decreases the concentration of Cl_2, ClO^-, and HClO at a given current density with a consequent decrease in the rate of bleaching.

Figure 7 shows that the power consumption for different degrees of brightness ranges from 0.1 kWh kg^{-1} of pulp to 1.75 kWh kg^{-1}, depending on the current density and degree of brightness. The cell voltage corresponding to different current densities used in calculating power consumption is shown in Fig. 8.

In conclusion, the present study has proven that electrochemical bleaching is technically viable and produces a bleached pulp which competes in quality with that produced by the traditional three stage chemical method, as shown in Table 1. However, to judge the economic feasibility of the electrochemical method, much work remains to be done to refine the method beyond the present exploratory study using a pilot plant cell.

Acknowledgement

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