Electrochemical Generation of Hydrogen Peroxide
With In-Situ Brightening of Mechanical Pulp

by

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Abstract

Generation of hydrogen peroxide by electroreduction of oxygen on a slurry graphite cathode in an alkali medium was investigated to brighten mechanical pulp in-situ in the reactor. Four different reactors comprising both divided and undivided configurations were evaluated for peroxide generation and two of these were used for in-situ brightening experiments. Several different types of particulate graphite as the oxygen sparged slurry cathode and stainless steel, graphite and platinised titanium as anode materials were evaluated in different electrolytes for the generation of hydrogen peroxide, all of which contained the standard additives (MgSO$_4$, Na$_2$SiO$_3$ and DTPA) for peroxide brightening.

Diaphragms of three different materials were investigated for hydrogen peroxide production in a diaphragm reactor of 1.9 liters volume. Results from these experiments with a diaphragm sheathed stainless steel anode indicate the loss of hydrogen peroxide by oxidation on the anode due to the high permeability of diaphragm material.

Experiments in a divided membrane reactor without pulp show hydrogen peroxide concentrations of up to 0.025 M, comparable to the concentration of peroxide employed in conventional brightening of TMP could be obtained with a current efficiency of 20% at 2 Amps current with 500 ml UCAR 1 graphite of size -0.42 + 0.29 mm as cathode slurried in 500 ml 0.5 M Na$_2$SO$_4$ catholyte containing NaOH at 60°C and pH around 11.

The efforts to brighten pulp in the divided membrane reactor with UCAR 1 and pyrolytic graphite cathodes were hampered by the generation of graphite fines of less than five micron in size and subsequent graphite loading of fiber lumen. Consequently, the brightness of the in-situ brightened pulp declined to 32% ISO from an unbrightened value.
Abstract

of 47% ISO. Agitation imparted by the impeller to the graphite-pulp mixture appear to cause the generation of graphite fines and the consequent loss of brightness.

Hydrogen peroxide generation and in-situ brightening were investigated in an undivided reactor of 12.5 cm diameter incorporating a fritted SS sparger plate and a water cooled anode. Six different types of graphite as particulate cathode with platinised titanium or SS as anodes were evaluated for peroxide production. Oxygen was sparged through the cathode graphite bed and an impeller at 60 rpm was used to rake the graphite bed to achieve good oxygen transfer without disturbing the integrity of the bed. With the platinised titanium anode and pyrolytic graphite (-1.7 + 0.5 mm) cathode up to 0.043 M H$_2$O$_2$ was obtained at 2 Amps and 5.7 volts with 44% current efficiency in 1 M Na$_2$CO$_3$ at 60°C and pH 11.15 with an oxygen flow of 0.31 liters/min @ STP. Peroxide generation was not favored on the SS anode.

The effect of alkali darkening of TMP in in-situ brightening was investigated. The results indicate the undesirable alkali induced darkening could be avoided by the introduction of pulp into the reactor after sufficient peroxide is generated and present in the electrolyte. Consequently, TMP of 1% consistency in 1 M Na$_2$CO$_3$ was utilised for in-situ brightening with pyrolytic graphite cathode and platinised titanium anode in the undivided reactor and the pulp was introduced to the reactor after 60 minutes of run, when the peroxide concentration was 0.036 M. The electrolyte pH ranged from 11.15 to 10.7, the cell voltage and current were 6.9 volts and 2 amps respectively and oxygen flow was maintained at 0.31 liters/min @ STP. In this case brightness of the pulp increased from an initial value of 43% ISO to 47% ISO at the end of 150 minutes run while yellowness declined from 34% to 19%.
Abstract
The successful in-situ brightening was repeated twice and the brightness increased from 43% ISO to 53% ISO and yellowness declined from 34% to 21% consistently. Increasing the run duration from 150 to 240 minutes resulted in final pulp brightness of 53% ISO and yellowness of 23%.

Preliminary cost calculations indicate the relatively high cost of US$ 3800 to brighten a ton of TMP in-situ as compared to US$ 33 in conventional brightening. The cost of oxygen and Na$_2$CO$_3$ reflect 95% of the cost of in-situ brightening. The disparity between the cost of in-situ and conventional brightening could be significantly reduced by further investigation and redesigning the process to recover and recycle the oxygen and Na$_2$CO$_3$. 
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Nomenclature

$E^\circ$ : Standard electrode potential \hspace{1cm} Volts
F : Faraday number \hspace{1cm} Coulomb/equiv.
I : Current \hspace{1cm} kA
V : Potential \hspace{1cm} Volts
C : Concentration \hspace{1cm} Molarity
n : Electron stoichiometry of reaction
R : Production rate of hydrogen peroxide \hspace{1cm} kmole/sec.
Acknowledgement

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Chapter 1

Introduction

Under market pressures for environmentally friendly paper products and alternative ways of making existing ones, mechanical pulp brightening technology is evolving to meet industry needs. In this evolution, hydrogen peroxide is becoming the dominant chemical for mechanical pulp brightening in Canada.

Hydrogen peroxide is favored for brightening mechanical pulp to brightness values up to 80% ISO for use in high volume products such as newsprint and tissue. Brightening of mechanical pulp is a lignin retention process, maintaining the desired high yield. The ease of handling and application and the relatively non-toxic and innocuous nature of its reaction products in the brightening process make hydrogen peroxide a desirable, environmentally friendly, brightening agent.

Hydrogen peroxide is produced by the conventional process of auto oxidation of anthraquinols. The product is relatively stable and non volatile and releases only water and oxygen on decomposition. Hydrogen peroxide is shipped and stored in aqueous solutions of up to 70% concentration.

The objective of the following study is to examine the alternative method of generating hydrogen peroxide for in-situ pulp brightening through electroreduction of oxygen on a graphite slurry cathode in alkaline electrolytes. The generation of relatively expensive hydrogen peroxide from cheaper oxygen to brighten mechanical pulp in-situ may make the production of hydrogen peroxide by electroreduction of oxygen commercially attractive.
Chapter 2

Background and Literature Review.

2.1. Structure and Chemical Composition of Wood

Chemical Components in Wood

Wood is the most abundant source of papermaking fibers, and is virtually the only source utilized in North America. Fibers in their native state are embedded in a matrix of non-fibrous material. Wood primarily consists of three polymeric chemical components, cellulose, hemicellulose and lignin. The chemical composition of wood is given in Figure 2.1.(1)
Chapter 2. Background and Literature Review

Cellulose

Cellulose, a polysaccharide, is a high molecular weight stereo regular linear polymer. Cellulose is the major constituent of wood fiber walls. The fiber bundles it forms impart a high tensile strength to the wood. The polymeric linkages during cellulose synthesis are such that the chains form in an extended manner. The structure of cellulose is shown below in Figure 2.2.(1)

![Cellulose structure diagram](image)

Figure 2.2. Structure of Cellulose

Hemicellulose

Hemicellulose is a polymer composed of five different sugar monomers. They serve as
Chapter 2. Background and Literature Review

a supportive matrix for the cellulose microfibrils.

Lignin

Lignin is a highly-polymerized, amorphous and complex chemical substance that makes up about 28 percent of wood substance. It forms the middle lamella, the intercellular material which cements the fibers together and provides mechanical reinforcement for the tree. The chemistry of lignin is extremely complex and consists primarily of phenyl propane units linked together in three dimensions. The structure of lignin is indicated in the figure 2.3.(3)
Chapter 2. Background and Literature Review

Structure and Chemical Composition of Wood Fiber

Wood and fiber characteristics vary depending upon species, and genetics, tree age, climate, natural fluctuations in the environment and soil fertility. Woods are classified into two major groups, softwoods or conifers and hardwoods or broad-leafed trees.

Generally hardwoods contain a larger proportion of holocellulose and less lignin as compared to soft woods, but a greater percentage of extractives as indicated in Table 2.1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Hardwood %</th>
<th>Softwood %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>45-47</td>
<td>42-44</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>30-35</td>
<td>27-29</td>
</tr>
<tr>
<td>Lignin</td>
<td>20-24</td>
<td>28-31</td>
</tr>
<tr>
<td>Extractives</td>
<td>5-8</td>
<td>3-5</td>
</tr>
</tbody>
</table>

Table 2.1. Chemical Composition of Wood

Fiber Morphology

Fiber morphology of the wood is very important in brightening because it largely controls the extent and manner to which the brightening chemicals penetrate and diffuse through the wood. About 95 percent of the volume of the wood is occupied by fibers which are oriented in the vertical direction. The reminder is mostly horizontally aligned.
Chapter 2. Background and Literature Review

Ray tissue. In wood the lignin-rich middle lamella is the "cementing medium" that binds and holds individual fibers together. The compound middle lamella includes the very thin primary wall. The lignin content of this zone is 75 percent. We can think of the lignin as if it were concrete, and of the cellulose rich microfibrils as if they were steel rods in reinforced concrete. The secondary wall is composed of three separate layers, $S_1$, $S_2$ and $S_3$. About 80 percent of this region is holocellulose, and 20 percent is lignin. The hollow air space inside the fiber is called lumen and the greatest density difference on the microscopic level can be observed between the lumen, the void airspace of a fiber enclosed by the fiber walls and the fiber wall, made up of porous wood substance. On the average, softwood fibers are about 3.5 mm and hardwood fibers are about 1.5 mm in length and approximately 35 and 20 microns in diameter, respectively. Lumen diameter of the fiber varies with the species of the tree and ranges between approximately 3 to 10 microns.
Chapter 2. Background and Literature Review

2.2 Mechanical Pulping and Brightening

Mechanical processes in the pulp mill free the fibers from the lignin matrix and leave the fiber in a relative degree of purity depending on the end use. In mechanical pulping, cellulose fibers are removed from the wood matrix by thermal softening of lignin and micro-abrasion.

There are two basic types of mechanical pulping - stone groundwood in which fiber is removed from wood by pressing a log against a grindstone, and chip refining in which wood chips are broken into fibers on passing between rotating disks having bars on their surface. A summary of the key parameters of mechanical pulp is given in Table 2.2.
Chapter 2. Background and Literature Review

<table>
<thead>
<tr>
<th>General Parameters</th>
<th>Mechanical pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield fiber/wood</td>
<td>High 90-98%</td>
</tr>
<tr>
<td>Cellulose purity</td>
<td>Low - lignin remains</td>
</tr>
</tbody>
</table>
| End uses           | - Low quality  
|                    | - High volume  |

<table>
<thead>
<tr>
<th>Quality parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength</td>
<td>Low - fibers damaged</td>
</tr>
<tr>
<td>Bulk</td>
<td>High - few and less flexible fibers</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cost parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>Low - high yield</td>
</tr>
<tr>
<td>Capital</td>
<td>Low</td>
</tr>
<tr>
<td>Operating (chemicals, energy, etc)</td>
<td>Low - becoming lower with improved technology</td>
</tr>
</tbody>
</table>

Table 2.2. Characteristics of mechanical Pulp

Mechanical pulp brightness is mainly a function of the species and condition of the wood pulped. Generally only those species yielding pulp with an initial brightness value over 55% ISO are utilized for mechanical pulping.
The objectives of brightening can be summarised as below.

- To decolorize lignin and other extraneous components without solubilizing them
- To preserve yield commensurate with the above
- To alter pulp properties
- To make pulp suitable for the desired end use
- To do the least mechanical damage to the fibers
- To inhibit the formation of carbonyl groups
- To brighten at reasonable cost

Mechanical pulp brightening involves the utilisation of chemicals that selectively destroy and decolorize some of the chromophoric groups but do not dissolve lignin. This is a lignin retention process preserving high yield. Reductive agents such as sodium dithionite, sodium borohydride and oxidative agents such as hydrogen peroxide are commonly used for brightening mechanical pulp.

The brightening process is limited in many cases to achieving ISO brightness values between 70 and 80%. The brightening process is affected by the wood species. Softwoods and hardwoods respond differently to treatment. All species give different unbrightened brightness and respond differently to brightening depending on their natural color, their quality and their extractive content and type.

Although the brightness gains can be substantial, no known method of selective brightening produces a permanent effect; exposure to light and atmospheric oxygen causes the lignin to rapidly discolor, as can be readily observed with old newspapers(1).
Chapter 2. Background and Literature Review

2.3 Mechanical Pulp Brightening by Hydrogen Peroxide

Chemistry of Peroxide Brightening

There are a number of theories regarding the mechanism of the brightening of mechanical pulp with hydrogen peroxide. One of the most widely accepted involves the destruction of the orthoquinone chromophore structure in the lignin (4). Reactions occurring between the components of peroxide brightening liquors and the organic substrates are complex in view of the variable properties of pulps. Jones (17) indicated that the brightening effect was attributable to the reaction of peroxide with lignin and proposed that peroxide attacked lignin through a portion of the carbonyl groups in the molecular structure.

The reactivities of other components of brightening liquor with the substrate have not been systematically investigated. However, Martin (18) observed the development during groundwood brightening of a yellow color, which was more pronounced at high pH levels and was attributed to the reaction of groundwood with alkali. This appears to be due to the generation of chromophoric groups by the reaction of lignin with the oxygen, derived from decomposition of peroxide under the alkaline conditions of brightening. Since polysaccharides are white when rid of all contaminants, it could be assumed that the major brightening effect in the case of all pulps is the result of reactions between peroxide and lignin.

Yields on groundwood brightening with peroxide commonly lie in the range of 90-95%. This suggests that very little of the lignin is degraded to the point of solubilization.
Chapter 2. Background and Literature Review

Factors Affecting Brightness Response

Hydrogen peroxide is an effective lignin preserving oxidative brightening agent, improving the brightness of mechanical pulps without significant yield loss. The response of a mechanical or chemimechanical pulp to peroxide depends on a variety of factors, including wood species (hardwood or softwood), the condition of the wood (age and cleanliness), pulping processes (mechanical or chemimechanical), brightening conditions (peroxide charge, consistency, alkalinity and temperature) and the availability of transition metals.

As a consequence, it is virtually impossible to make generalizations about the relationship between peroxide charge and brightness increment without partially defining conditions.

Alkalinity of Hydrogen Peroxide Brightening

Hydrogen peroxide dissociates by Reaction 1 in alkaline solutions to form the perhydroxyl ion which is believed to be the active oxidizing and brightening agent in peroxide solutions(1).

\[ \text{H}_2\text{O}_2 \rightarrow \text{OOH}^- + \text{H}^+ \quad \text{Rxn 1} \]

\[ \text{pKa} = 11.67 \text{ at } 25^\circ\text{C} \]

This dissociation reaction is promoted by high pH levels generally produced by the addition of sodium hydroxide. At a pH of 10.5 less than 10% of the peroxide exists as the perhydroxyl ion(3). However, high pH levels also lead to the formation of new chromophores through alkali darkening and accelerate the decomposition reaction of
Chapter 2. Background and Literature Review

hydrogen peroxide to form water and oxygen by Reaction 2.

\[ \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \quad \text{Rxn 2} \]

An optimum pH therefore exists which may vary depending on additives, type of pulp, pulp consistency and peroxide concentration. At a constant peroxide concentration, an increase in the alkalinity level leads to a decrease in residual hydrogen peroxide concentration due to Reaction 2 and an increase in pulp brightness up to the optimum pH due to Reaction 1. Reaction 2 is catalyzed by the presence of certain metal ions such as iron, lead, manganese and copper which can come from the process water or from the pulp and wood fibers themselves\(^5\). These metals can also form highly colored complexes which decrease the pulp brightness.

Strunk\(^6\) reports that the initial alkali concentration of the peroxide brightening liquor should be high enough so that at the end of brightening it is approximately 10% of the original value. In the tower brightening of West Coast mechanical pulps, equal proportions (by weight) of sodium hydroxide and peroxide have been recommended for optimum brightening\(^7\). However, the optimum peroxide:alkali ratio is affected by several factors in addition to wood species and is best determined empirically for a given pulp on an individual basis\(^8\).

**Hydrogen Peroxide Stabilisation**

Heavy metal compounds of such elements as iron, manganese and copper catalyze the decomposition of hydrogen peroxide by reaction (2). This reaction wastes hydrogen
Chapter 2. Background and Literature Review

peroxide. The source of the undesired metals can include the wood, process water and equipment. Wood can frequently contain 100 ppm of manganese which is sufficient to cause serious decomposition of hydrogen peroxide in a brightening system(3).

DTPA

To stabilize the peroxide solutions, a chelating agent such as the sodium salt of DTPA (diethylene triamine penta acetic acid) can be added which will chelate the metal compounds, preventing them from functioning as catalysts in the decomposition of peroxide. The amount of required chelant depends on the metal concentration but generally about 0.25% by weight based on OD (oven dry) pulp is added to the solution prior to hydrogen peroxide addition(3). For maximum effectiveness, it has been recommended (9) that DTPA be added well in advance of peroxide to allow time for metal chelation to occur. Brightness increases of up to 3-4 points were obtained with implementation of a good washing stage with little carry over of dissolved substances and heavy metals (10).

Sodium Silicate

Sodium silicate is added as a source of alkali and as a buffering agent for hydrogen peroxide brightening liquors. It also acts as a stabilizer for hydrogen peroxide in the presence of heavy metals. It forms insoluble heavy metal silicates or adsorbs these metals in calcium and magnesium silicate flocs(6). The addition of silicate to peroxide solutions in concentrations ranging from 1 to 5% by weight on OD pulp also appears to increase the level of brightness. The mechanism of this function is not quite clear.
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Magnesium Sulfate

If mill water is not sufficiently hard, small amounts of magnesium sulfate may be added to brightening liquor. The magnesium acts as another stabilizer, presumably forming insoluble flocs to adsorb or coprecipitate heavy metal ions. Usually, about 0.05% weight-percent magnesium sulfate, based on OD pulp, is a sufficient amount.
Chapter 2. Background and Literature Review

2.4 Effect of operating Variables

For a given brightening operation in industry, the temperature, consistency, peroxide charge, alkalinity and retention time selected are empirically optimized, taking into consideration brightness requirements, other variables such as consistency and alkalinity, and specific operational constraints (16).

Improvements in brightness can be achieved by balancing retention time and temperature. The rate of brightening of mechanical pulp increases as the temperature increases. Too high a temperature is reflected in a loss in brightness response, which appears to be caused by peroxide decomposition. Similarly, excessive retention periods result in brightness reversion caused by alkali darkening in the presence of insufficient peroxide.

Brightening chemical efficiency increases as the pulp consistency increases, probably due to the increase in concentration of brightening chemicals in the reduced volume of the aqueous phase (14). The brightening liquor must be sufficiently alkaline to maintain an adequate concentration of perhydroxyl ions but not so alkaline as to cause excessive peroxide decomposition.

Temperature

Industrial brightening reactions usually proceed in the 40-70°C range. As temperatures move into the 80°C plus range, there frequently can be a penalty in brightening efficiency as the decomposition of hydrogen peroxide into water and oxygen is accelerated by higher temperatures (6).
Chapter 2. Background and Literature Review

At high temperatures, the amount of alkali present also becomes critical. High concentrations of alkali will also accelerate the decomposition of hydrogen peroxide. If the total alkali is high, rapid decomposition of peroxide occurs; if the total alkali is too low, the brightening reaction slows markedly. Studies usually indicate that, as the brightening temperature increases, the amount of alkali required for optimum brightening response will decrease.

Pulp Consistency

Although hydrogen peroxide can be used to brighten pulp of all consistencies, most commercial installations brighten pulps with consistencies in the medium consistency (10% to 15%) or low consistency (3% to 6%) range. Medium consistency pulp can be used for brightness gain of up to 12 points. For brightness increases above 12 points, high consistency pulp is generally required. These need shorter retention time and lower chemical dosage, but the equipment costs are higher. The consistency used will depend on the balance between capital cost and the cost of chemicals.

Peroxide Charge

A suitable balance between peroxide and free alkali should be maintained in brightening systems. The brightness of pulp after brightening increases as the amount of peroxide applied is increased, but the incremental gains diminish to a point where further increases in peroxide charge can not be economically justified. The levelling off effect in brightness becomes apparent especially at charges greater than 1% peroxide by weight on OD pulp. Economic considerations thus limit peroxide charges in most commercial
Chapter 2. Background and Literature Review

operations to the range of 1-2% peroxide by weight on OD pulp, with brightness gains amounting to 10-15 points.

Alkalinity and Peroxide Stability

If insufficient alkali is present, the pH may fall to the point where brightening ceases. Alternatively, if the alkali concentration is too high, oxygen may be released through peroxide decomposition. The oxygen from peroxide decomposition, in conjunction with the alkali may react with the lignin, generating new chromophores. The alkalinity of brightening liquor is provided by caustic soda and sodium silicate.

Reichert and Pete (15) recommended that the total alkali calculated as NaOH should fall between the limits of 1.2 to 1.9% by weight based on OD pulp. The higher alkalinity was said to be preferable for brightening at low consistency and low temperature, whereas the lower alkalinity was preferable at higher consistencies and temperatures.

Retention Time

Industrial brightening reactions usually utilise retention periods of 1-5 hours. The amount of brightening that occurs is greatest in the early stages of the brightening process when the concentration of chemicals is high and the brightness of the pulp is low (7).

Mixing

Good mixing is a critical requirement for effective brightening. Mill experience and
laboratory studies have shown that improved mixing reduces chemical consumption and leads to a more uniform product (11). However, good mixing remains difficult to achieve and even the measurement and characterization of mixing are difficult tasks (12). When mixing is not uniform, some regions of pulp receive chemical in excess of that required, some of which is consumed in less desirable reactions. Other regions receive insufficient chemical and are not adequately brightened. The net effect is that additional chemical is required to attain a desired degree of brightening, and a pulp of less than optimal strength is produced (13).

Stabilization of Brightness

After the completion of the brightening process, the stock should be stabilized by reducing the pH to the 5 to 6 range. This prevents alkali darkening and loss of brightness when the residual hydrogen peroxide disappears. The pH can be reduced with either sulfuric acid or sulfur dioxide. When sulfur dioxide is used, the residual hydrogen peroxide is also destroyed according to reaction 3.

\[ \text{H}_2\text{O}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \]  

Rxn 3

When sulfuric acid is used to adjust the pH, the residual peroxide remains in the stock. These small amounts of peroxide do not interfere with subsequent paper-making operations.
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Fiber Properties

Resin removal is important in brightened TMP for tissue and absorbency products. Effective peroxide treatment of pulp will reduce the resin and fatty acid content from >1% to less than 0.3%. Peroxide brightening increases fiber flexibility, improving tensile index by about 25%. The fiber to fiber bonding is increased, reducing the amount of dust during the tissue manufacturing and converting operations. Peroxide brightened pulp can be stored several months without causing disintegration problems.
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2.5 Electrochemical Production of Hydrogen Peroxide

A simple electrochemical system comprises two electrodes and an electrolyte. The electrode at which an electron producing reaction occurs is the anode and the electrode at which an electron consuming reaction occurs is the cathode. The rate of an electrochemical reaction is dependent on the electrode material, reactant concentration, electrode potential and temperature.

Current efficiency of an electrochemical process can be calculated by equation (1) given below.

\[ CE = \frac{nFR}{I} \quad (1) \]

Where

- \( n \) = Electron stoichiometry for desired reaction
- \( F \) = Faraday number (96480 Coulombs/equivalent)
- \( R \) = Production rate of desired product (kmole/s)
- \( I \) = Total current (kAmp)

Electrode materials should be chosen carefully with electrocatalytic properties to promote the desired electrode reactions and suppress the undesirable secondary reactions. The electrode material is chosen taking into consideration the electronic conductivity, chemical stability and electrocatalytic properties.

The electrocatalytic properties of the electrode material are important in the large, energy...
Chapter 2. Background and Literature Review

intensive electrolytic processes where the cost of power is a dominant factor in determining process economics. In the electrolytic production of fine chemicals, the electrocatalytic properties of the electrode determine the selectivity of the process and consequently the process economics because of the high cost of starting materials and the cost of removing undesirable side products from the product stream.

Cathode materials should be chosen carefully taking into consideration the electrocatalytic properties favoring the desired process. Electroreduction of oxygen to hydrogen peroxide is favored on graphite cathode (28). The superficial current density for an electrocatalytic reaction can be increased by increasing the surface area of the electrocatalyst. Three-dimensional electrodes present an electro-active surface in the direction of the current. Three-dimensional electrodes are used to obtain increased space-time yield of electrochemical reactors. The increased space-time yield is however, limited due to excessive ohmic losses within the electrode and electrolyte. These ohmic losses create variations in the local electrode-electrolyte potential difference, which is the driving force for the electrochemical reaction. This results in non-uniform reaction-rate distribution and less than full utilization of the internal surface area of the electrode (19). The effectiveness of the three-dimensional electrode is influenced by the effective conductivities of the solid matrix and the electrolytic solution. Either very low or very high conductivity of the electrode matrix relative to the conductivity of the solution creates a non-uniform reaction rate distribution, reducing the effectiveness of the electrode (20). Utilization of the internal surface area of the electrode can be increased by minimizing the ohmic influence on the effectiveness of the electrode.

Free space for electrical current flow is increased by increasing the porosity of the
Chapter 2. Background and Literature Review

electrode. This increases the volumetric fraction leading to a decrease in the effective conductivity of the electrode matrix. Good matrix conductivity, high internal surface area and high porosity are some of the basic requirements for design of an effective three-dimensional electrode (21). Supporting electrolytes which carry current but do not engage in electrode reactions are employed, if necessary, to increase the conductivity of the electrolyte. The conductivity of electrolyte solutions increases with increasing temperature.

The overall rate of the industrial electrochemical processes is often under mass transfer control because the electrode material is chosen for fast electrode kinetics. The transport of the reactants and products between the electrode surface and the bulk electrolyte becomes important and has a critical impact on the process efficiency. Factors such as reactant concentration, mixing and the electrochemical reactor configuration influence mass transport in electrochemical processes.

Industrial processes require high mass transfer rates to minimize capital investments and large electrode surfaces to achieve high production rates. Three-dimensional electrodes with multiphase flow are employed to achieve these objectives in commercial operations. Multiflow occurs in electrochemical processes either due to the nature of the electrochemistry of the process or due to the deliberate introduction of a phase in a process.

Production of hydrogen peroxide by electroreduction of oxygen in which the electroactive species is a gas and benzene electrooxidation in aqueous sulfuric acid in which the electroactive species is a sparingly soluble liquid are some of the examples where the
Chapter 2. Background and Literature Review

multi-phase flow occurs due to a natural consequence of the electrochemistry of the process. In some processes, the second phase (gas or immiscible liquid) is not electrochemically reactive and is not a necessity for the electrochemistry of the process but is deliberately introduced to enhance the transport of the reactive species or to purge out the undesirable gas evolution.

Most of the two phase mass transfer studies conducted in fixed beds are not applicable to porous electrodes and electrolyte solutions. First, these studies were performed for particle sizes greater than 2 mm (22) but porous electrodes typically consist of particles less than 1 mm. Secondly, the bubble size in electrolyte solutions could be markedly different from that in non-electrolytes. For example, the oxygen bubbles formed in 0.2 M sodium sulfate solution were finer in size when compared to those formed under identical conditions in distilled water (23). However, in the case of porous electrodes the packing size and the liquid flow rate are more important factors in determining the bubble size. The electrolyte can also have an impact on the bubble coalescence behavior. The intimate interaction between bubble swarms and electrified solid surfaces in three dimensional electrochemical systems differentiate it from the non-electrochemical ones. Therefore, specific studies are required in the case of electrochemical systems.

The overall gas-solid mass transfer in the electrochemical reduction of oxygen on graphite in the production of hydrogen peroxide usually occurs in two major steps. The transfer of the reactive gas at the gas(bubble)-liquid interface proceeds followed by the liquid(solubilized reactive gas)-solid mass transfer. The (inside the bubble) mass transfer is usually negligible when compared to the other two resistances mentioned above (22,23).
Chapter 2. Background and Literature Review

Rapid mass transfer is achieved by the flow of bubble swarm over large packings, generating turbulent behavior. Flow over smaller packings generates essentially laminar behavior and the bubbles flow through restricted channels. The mass transfer, in this case is due to the disruption of the boundary layer which facilitates replenishment of dissolved reactants (24).

Mass transfer in three phase (S/L/G) fluidized bed electrodes has not been studied extensively. Generally higher mass transfer rates can be achieved in fixed bed electrodes than in fluidized bed electrodes because of the higher allowable velocities.

In the proposed system, oxygen transfer in the electrolyte is facilitated by sparging oxygen through the cathode graphite - electrolyte slurry. The cathode bed is raked by an impeller to achieve good oxygen transfer and consequently to enhance the production of hydrogen peroxide by electroreduction of oxygen on the graphite particulates. The oxygen flow rate and the impeller rpm are controlled so that the integrity of the cathode graphite particulate bed is not compromised and the conductivity of the bed is not affected.

The established methods for producing hydrogen peroxide are the hydrolysis of peroxydisulfuric acid formed by the electrooxidation of concentrated sulfate solution, now an obsolete process and the autooxidation of anthraquinone. The electrolytic process requires that the electrolyte be continuously purified and also has very high capital and power requirements. Thus it cannot economically compete with the anthraquinone oxidation process (25,28). Consequently, research has continued to find a more economic way to produce hydrogen peroxide on-site.
Chapter 2. Background and Literature Review

One such method is the electrochemical reduction of oxygen in alkaline solutions. This method was studied by Oloman et al in electrolysers with fixed and fluidized beds of graphite particles (26,27). The electrochemical reactions of interest in the present study are the cathode reactions below (Reactions 4,5).

Cathode: \( \text{O}_2 + \text{H}_2\text{O} + 2e \rightarrow \text{HO}_2^- + \text{OH}^- \) \( E_\circ = -0.076 \text{ V SHE} \) Rxn 4

Undesired: \( \text{HO}_2^- + \text{H}_2\text{O} + 2e \rightarrow 3\text{OH}^- \) \( E_\circ = +0.878 \text{ V SHE} \) Rxn 5

Major anode reaction: \( \text{O}_2 + 2\text{H}_2\text{O} + 4e \leftrightarrow 4\text{OH}^- \) \( E_\circ = +0.401 \text{ V SHE} \) Rxn 6

Undesired: \( \text{O}_2 + \text{H}_2\text{O} + 2e \leftrightarrow \text{HO}_2^- + \text{OH}^- \) \( E_\circ = +0.15 \text{ V SHE} \) Rxn 7

The undesired reaction on the anode, Reaction 7, which wastes the peroxide generated is suppressed by utilising a separator such as a diaphragm or a cation membrane. The separator prevents the transport of peroxide ions leading to their destruction on the anode. Transport across the separator takes place by diffusion and migration.

Hydrogen peroxide can also be generated by the electro-oxidation of carbonates on a platinised titanium anode. The principal reaction on the anode is given below.

Anode: \( \text{C}_2\text{O}_6^{2-} + 2e \leftrightarrow 2\text{CO}_3^{2-} \) \( E_\circ = +2 \text{ V SHE} \) Rxn 8

Secondary: \( 2\text{H}_2\text{O} + \text{O}_2 + 4e \leftrightarrow 4\text{OH}^- \) \( E_\circ = +0.4 \text{ V SHE} \) Rxn 9

At room or higher temperatures, the percarbonate produced by Reaction 8 hydrolyses to form bicarbonate and hydrogen peroxide as follows:
Chapter 2. Background and Literature Review

\[ \text{C}_2\text{O}_6 + 2\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{O}_2 \] 
Rxn 10

Hydrogen peroxide generation can be enhanced by combining electrochemical reduction of oxygen on the cathode represented by Reaction 4 and electro-oxidation of carbonate to percarbonate on the anode followed by hydrolysis to peroxide given by Reactions 8 and 10. Hydrogen peroxide is produced simultaneously on the cathode and the anode. Such a system involves sparging oxygen through a three dimensional graphite cathode in an electrolyte such as sodium carbonate incorporating a water cooled platinised titanium anode.

Reactions 5 and 7 represent loss mechanisms which waste peroxide leading to reduced efficiencies. Catalyzed decomposition of peroxide may also occur by Reactions 11 and 12.

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \] 
Rxn 11

\[ 2\text{HO}_2^- \rightarrow 2\text{OH}^- + \text{O}_2 \] 
Rxn 12

Reactions 11 and 12 can be catalyzed by the presence of metal ions and is suppressed by the addition of chelating agents such as DTPA. Reduction of oxygen to perhydroxyl ion occurs readily on carbon and graphite in alkaline solution and the reaction product is an alkaline solution of hydrogen peroxide (29). Wood pulp brightening with hydrogen peroxide is usually done under alkaline conditions, employing caustic soda to maintain the pulp pH around 10 to 11. Electroreduction of oxygen in aqueous sodium hydroxide thus appears as an interesting prospect for the generation of peroxide brightening solutions.
Chapter 2. Background and Literature Review

2.6. In-situ Brightening of TMP

In-situ electrochemical oxidative brightening of mechanical pulp involves the speculative concept of generation of hydrogen peroxide which reacts with the pulp in the electrochemical reactor. The only previous work mentioned in literature is that of Brouillette. Brouillette et al. (30) evaluated the possibility of in situ hydrogen peroxide brightening of mechanical pulp by the cathodic reduction of oxygen bubbling through the alkaline pulp solution. TMP of 1% consistency and brightness 59% ISO was used in in-situ brightening experiments in an electrochemical reactor employing graphite plate cathode and a mesh platinized titanium anode. TMP was mixed with water, anthraquinone, MgSO₄, Na₂SiO₃ and DTPA before being introduced into the reactor. Sodium hydroxide or sulfuric acid was used to adjust the pH and the brightening time varied from 1 to 5 hours. Different process temperatures ranging from 15 to 70°C and pH values 2, 7 and 11 were investigated. It was reported hydrogen peroxide was generated but not in sufficient quantity to brighten pulp. To increase the peroxide production, the anode material was changed to nickel and a larger surface of cathode was employed. Sodium tetraborate was added to increase the conductivity of the solution and a maximum residual peroxide concentration of 0.4 % was reported. No significant change in peroxide production was reported at 15, 35 and 50°C except at 70°C the residual peroxide concentration decreased to 0.03 wt %. No brightness gain was obtained in these investigations.

Electrochemical synthesis and accumulation of hydrogen peroxide is favored at pH values > 11 and at low temperatures, < 40°C. Mechanical pulp brightening requires moderate pH, between 10.5 to 11 to avoid alkali darkening and decomposition of hydrogen
Chapter 2. Background and Literature Review

peroxide to water and oxygen by Reaction 2. Moderate pH also facilitates oxidative
brightening of mechanical pulp by the dissociation of hydrogen peroxide to form
perhydroxyl ions by Reaction 1. High process temperatures, ranging between 60 to 80°C
are required in mechanical pulp brightening to achieve faster reaction rates.

The process conditions favoring the generation of peroxide, high pH and low temperature
are balanced against the conditions required for pulp brightening, moderate pH and high
temperature. In the proposed in-situ brightening process, a balance is struck by choosing
a pH of 11 to 11.15 at 60°C to suppress the undesirable decomposition of hydrogen
peroxide, yet allowing brightening of TMP.
Chapter 3.

Proposed Research Objectives

The proposed work involves generation of hydrogen peroxide by Reaction 4 and brightening of mechanical pulp in-situ on a slurry cathode in an alkali environment. No previous work has been done on in-situ hydrogen peroxide brightening of mechanical pulp by electroreduction of oxygen employing a graphite slurry electrode. Hydrogen peroxide generation by simultaneous reduction of oxygen on a cathode and electro-oxidation of carbonate on an anode in an alkali environment will also be investigated. Several different types of graphite cathode, anodes, separators, catholytes and anolytes at various operating conditions and reactor configurations will be evaluated for peroxide generation.

The benefit of such a system would include the generation of relatively expensive hydrogen peroxide from oxygen in-situ in the reactor in an alkali environment suitable for mechanical pulp brightening. The proposed system may integrate and compact the two different processes of generation of hydrogen peroxide and mechanical pulp brightening into a single operation.

The work described in the following chapters investigates the possibility of generating hydrogen peroxide in-situ to brighten mechanical pulp.
Chapter 4.

Experimental Apparatus and Procedure

Hydrogen peroxide generation and in-situ brightening were investigated in four different reactor configurations, namely a divided diaphragm reactor, a divided membrane tank reactor, a divided membrane reactor and an undivided reactor with water cooled platinised titanium anode.

4.1 Diaphragm Reactor

The reactor consisted of a cylindrical stainless steel cylindrical vessel of 120 mm ID and 170 mm height and is shown in Figure 4.1 and schematic diagram of the experimental arrangement is given in Figure 4.2. Anode and cathode were separated by fabric diaphragm sheathed over the anode. The purpose of the diaphragm is to suppress the transport of \( \text{HO}_2^- \) to the anode and its destruction by Reaction 7. The cathode was 500 ml of graphite particles slurried into the catholyte.

Hydrogen peroxide generation was investigated employing UCAR 1 low strength graphite particles of size \(-0.42 + 2.9 \) mm as the cathode. Trials were also conducted by employing slurried nickel particles of size 0.5 mm diameter as cathode. Different materials such as an 0.5 cm outer diameter tube of stainless steel, 1 cm diameter graphite rod and platinised titanium of size 7 cm length, 1 cm wide and 0.5 cm thick were evaluated as anodes. Three different types of diaphragm material, polypropylene, polyester and polyester screen were also evaluated for hydrogen peroxide generation. The diaphragm covered anode was immersed in 100 ml of water containing 5-8 drops of
Makon NF-12 surfactant for ten minutes before being used in the reactor. The surfactant was used to wet the diaphragm, making it permeable for the transport of ions.

Oxygen was supplied to the catholyte by a glass sparger connected by Teflon tubing to the oxygen cylinder. A Xantrex XT-14-4 DC power supply system was used for supplying current. Current was fed to the cathode through electrical contact between slurried graphite particles and the inner surface of the stainless steel container by a crocodile clip attached to the top rim of the stainless steel container. A variable speed motor with a polyethylene sheathed three blade stirrer provided the mixing during the experiments. The temperature of the system was regulated by placing the reactor in a constant temperature bath. The pH of the catholyte was monitored continuously during the experiments.
Chapter 4. Experimental Apparatus and Procedure

Figure 4.2. Schematic Diagram of the Experimental Set-up for Diaphragm Reactor

Chapter 4. Experimental Apparatus and Procedure

4.2 Membrane Tank Reactor

A plexiglass membrane tank reactor was constructed to investigate hydrogen peroxide generation in a divided cell. The membrane tank functioned as the anode chamber and consisted of a cylindrical plexiglass tube of 5 cm inner diameter and 14 cm in length with 0.5 cm circular holes distributed evenly on the surface to cover an area of 100 cm$^2$. The bottom end of the tube was sealed and the tank was attached to the plexiglass cover plate of the reactor. The cathode chamber was provided by a cylindrical stainless container of 120 mm diameter and 170 mm height. The two chambers of the reactor were separated by a cation membrane (Nafion 214) attached on to the outer surface of the anode tank. 1 cm outer diameter stainless tube was used as anode and 500 ml of UCAR low strength type graphite particles of size -0.42 + 0.29 mm slurried into the catholyte provided the cathode. DC current, oxygen sparging and mixing were provided during the experiment. The membrane tank reactor is shown in Figure 4.3.

Figure 4.3. Representation of Membrane Tank Reactor
Chapter 4. Experimental Apparatus and Procedure

4.3 Divided Membrane Reactor

The divided membrane reactor used for hydrogen peroxide generation and in-situ brightening runs is shown in Figure 4.4

![Figure 4.4. Representation of Divided Membrane Reactor](image)

The reactor consisted of a cylindrical stainless steel vessel of 17 cm diameter and height divided into anode and cathode chambers. The inner surface of the reactor was coated with PTFE to prevent metal ion contamination. The two chambers were separated by a cation membrane (Nafion 214) supported by two perforated plexiglass plates. An 0.5 cm outer diameter stainless tube of length 7 cm was the anode and 500 ml of graphite particles of four different types, sizes and shapes slurried into the catholyte were employed as cathodes. A curved 20 mesh stainless steel screen of area 205 cm² to fit the
Chapter 4. Experimental Apparatus and Procedure

contour of the catholyte chamber provided the electrical contact for the graphite particles. An area of 115 cm$^2$ of the stainless screen was in electrical contact with the graphite slurried into catholyte. A graphite plate of 5 mm thick and an area of 153 cm$^2$ with 106 cm$^2$ in contact with the graphite slurried into catholyte was also evaluated as cathode contact. Oxygen was supplied to the catholyte at a rate of 4.88 liters/min @ STP by a glass sparger connected by Teflon tubing to the oxygen cylinder.

Xantrex XT-15-4 DC power supply system was used for supplying current. A variable speed motor with a three blade stirrer provided the mixing during the experiments. The temperature of the system was regulated by placing the reactor in a constant temperature bath. The pH of the catholyte was monitored continuously during the experiments. A schematic diagram of the experimental set up is given in Figure 4.5.

![Schematic Diagram of the Experimental Set-up for Divided Membrane Reactor](image)

Figure 4.5. Schematic Diagram of the Experimental Set-up for Divided Membrane Reactor

4.4 Undivided Reactor with Water Cooled Anode

Hydrogen Peroxide generation and in-situ brightening were investigated in an undivided stainless steel reactor incorporating a bottom welded SS sparger plate to facilitate better distribution of oxygen through the electrolyte. The reactor and the water cooled anode are shown in Figure 4.6.

Figure 4.6. Representation of Undivided Reactor
Chapter 4. Experimental Apparatus and Procedure

The reactor consisted of a stainless steel sparger plate sandwiched between two flanged cylindrical stainless steel vessel sections of 12.5 cm inner diameter bolted together. The inner surface of the top cylinder measuring 16.5 cm in height was coated with Kynar® to prevent metal ion contamination. This cylindrical section accommodated the electrolyte, mixer and anode assembly and was bolted to the bottom cylinder. Oxygen was supplied to the lower chamber by a 6.4 mm diameter Teflon tubing attached to the oxygen cylinder. The oxygen bubbled up through the sparger plate sandwiched between the upper and lower cylindrical compartments into the upper section containing the electrolyte. A rotameter and needle valve system was used to adjust the flow of oxygen through sparger the plate into the cathode graphite bed.

The oxygen distribution system consisted of a 10 cm diameter fritted stainless steel sparger plate of thickness 5 mm welded centrally into a circular stainless steel disc of 15.5 cm diameter and 5 mm thickness. Neoprene gaskets of 3 mm thickness were placed above and below the stainless steel disc and the gasket-disc assembly was placed in between the upper and lower cylinders. The two cylindrical sections with the oxygen sparger plate assembly sandwiched in between were bolted together by means of eight evenly spaced 1/4" bolt and nut fixtures.

A water cooled anode was incorporated in the reactor system to increase the over potential of Reaction 8, increasing the percarbonate and subsequently peroxide yield. A 1/4" OD platinised titanium tube cooled by water flowing in the inside was employed as U-anode. Platinum was chosen for its electrocatalytic properties favoring the production of percarbonate by electro-oxidation of carbonate by Reaction 8.
Chapter 4. Experimental Apparatus and Procedure

The U shaped water cooled anode consisted of a length of 63.5 cm titanium tube of 1/4" diameter, cooled by internal flow of tap water at about 15°C. A section of the titanium tubing measuring 15.5 cm in length connecting the two prongs of the U tube which were arranged 4.5 cm apart was coated with a 5 micron thick coating of platinum. The platinised titanium section of the U tube provided the electroactive surface and was in contact with the electrolyte. Peroxide production was investigated by exposing 7.5 cm² and 15 cm² of the electroactive surface to the electrolyte. The anode was positioned in the electrolyte as desired by fittings and was connected to cold water supply.

Current was supplied to the slurried graphite cathode through electrical contact between stainless steel sparger plate and the graphite slurry. Xantrex XT-15-4 DC power supply system provided current to the sparger plate assembly through a crocodile clip snapped on to a 1 cm in length and 1.5 cm in width stainless steel tab welded to the sparger plate assembly.

The cathode consisted of a bed of 500 ml of graphite particles placed in the upper section. 500 ml of electrolyte was added to the cathode graphite particles. The oxygen flow rate was adjusted to avoid disturbing and fluidizing the cathode graphite bed leading to undesirable contact with anode and short circuit. The oxygen flow was maintained at an empirically found rate of 0.31 liters/min @ STP to achieve good sparging of oxygen through the cathode graphite particle bed. At this flow rate the graphite particle bed was not disturbed and the undesirable contact between the graphite particles and the anode was avoided.

The graphite particle bed in the electrolyte was raked at 60 rpm by an impeller to
Chapter 4. Experimental Apparatus and Procedure

facilitate oxygen transfer and to promote better contact with the electrolyte. The plexiglass impeller consisted of four blades, each 5 cm in length, 2 cm deep and 0.3 cm thick, arranged perpendicular to each other and attached on to a 2 cm diameter plexiglass rod. The plexiglass impeller was attached by a sleeve to the 1 cm diameter drive shaft of a Servodyne mixer head. Impeller rpm was controlled by a Servodyne mixer controller.

The process temperature was maintained at 60°C by placing the reactor in a constant temperature water bath. The pH of the catholyte was monitored continuously during the experiments. A schematic diagram of the experimental set up is given in Figure 4.7.

![Schematic Diagram of the Experimental Set-up for undivided Reactor](image)

Figure 4.7. Schematic Diagram of the Experimental Set-up for undivided Reactor

Chapter 4. Experimental Apparatus and Procedure

4.5 Preparation of Chemicals and Pulp

Generation of hydrogen peroxide and attempts to brighten mechanical pulp in-situ were conducted in an alkali environment. Sodium hydroxide and sodium silicate provided the alkali environment and were obtained from BDH Chemicals. Sodium sulphate was used as the supporting electrolyte in the cathode chamber and was purchased from BDH Chemicals. DTPA, purchased from Fisher Scientific as 40% solution of the sodium salt was used as the chelant. Magnesium sulfate obtained from BDH Chemical was used as the peroxide stabiliser.

The other chemicals used such as sulfuric acid, nitric acid, sodium carbonate, hydrogen peroxide 30% solution, sodium cyanide and disodium tetraborate were purchased from BDH Chemicals. Potassium permanganate and Ferroin used in the titration analysis to determine the concentration of hydrogen peroxide in the catholyte (see Appendix A) were obtained from Fisher Chemicals as 1 N solutions. Makon NF-12 surfactant manufactured by Stepan Chemicals was used in experiments employing the diaphragm reactor. All chemicals were reagent grade and were used without further purification.

All solutions were prepared using distilled water, A solution of 0.5 M sodium sulfate was used as supporting electrolyte, 0.052 M disodium tetraborate as buffer in the catholyte was also evaluated and 40% DTPA was added as the chelant to achieve a concentration of $8.67 \times 10^{-4}$ M. Solutions of 0.1 M magnesium sulfate and 1 M sodium silicate were added to the catholyte to attain concentrations of $5.68 \times 10^{-4}$ M and $0.336$ M respectively. Solutions of sodium hydroxide, 2 M and 4 M in strength were used, when needed, to raise the pH of catholyte to around 11.
Chapter 4. Experimental Apparatus and Procedure

Several different types of particulate graphites were evaluated as cathodes for peroxide production. The different types of particles and their size ranges are listed in Table 4.1 below.

<table>
<thead>
<tr>
<th>Type</th>
<th>particle size (mm)</th>
<th>volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCAR 1 (low strength)</td>
<td>-1.651 + 1.18</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>-1.18 + 0.5</td>
<td>130</td>
</tr>
<tr>
<td>UCAR 1 (low strength)</td>
<td>-0.42 + 0.29</td>
<td>500</td>
</tr>
<tr>
<td>UCAR 1 (low strength)</td>
<td>&lt; 0.5</td>
<td>500</td>
</tr>
<tr>
<td>Ultracarbon</td>
<td>-1.651 + 1.18</td>
<td>368</td>
</tr>
<tr>
<td></td>
<td>-1.18 + 0.5</td>
<td>132</td>
</tr>
<tr>
<td>Pyrolytic carbon</td>
<td>-1.0 + 0.5</td>
<td>423</td>
</tr>
<tr>
<td></td>
<td>-1.7 + 1.0</td>
<td>77</td>
</tr>
<tr>
<td>Sigradur-G</td>
<td>-1.0 + 0.5</td>
<td>500</td>
</tr>
</tbody>
</table>

Table 4.1 List of Various Types of Graphite Particles Investigated for Hydrogen Peroxide Generation and their Size Ranges

The Pyrolytic and Sigradur-G type of graphites were obtained from St. Jude Medical Inc, St. Paul, MN and The Electrosynthesis Co Inc, NY respectively. Nickel particles of size -0.5 + 0.25 mm and 99% purity, obtained from Sheritt Gordon, Alta were also evaluated as a particulate cathode. Graphite particles were cleaned by immersing in 10%
Chapter 4. Experimental Apparatus and Procedure

HCl at 60° C for two hours followed by thorough washing with water.

DTPA pre-washed TMP with moisture contents of 70 and 77% obtained from Howe Sound Pulp and Paper Limited, comprising 70% spruce, pine & fir and 30% hembal* species was used in the brightening runs. For runs involving in-situ brightening, 5 gms of oven dry pulp was added to the 500 ml catholyte containing 500 ml of graphite particles to attain a pulp consistency of 1%. The pulp sample was prepared by weighing 5.00 ± 0.01 gms OD pulp equivalent from the sealed bag in the refrigerator. This was mixed into a suspension and added to the catholyte in the reactor.

* Hemlock/Balsam
Chapter 4. Experimental Apparatus and Procedure

4.6 Hydrogen Peroxide Generation and TMP Brightening

Hydrogen peroxide generation trials were conducted with several different anolytes and catholytes. Anolytes of 2 M sodium hydroxide or 1 M sodium carbonate and catholytes of 0.5 M sodium sulfate, 1 M sodium carbonate or 0.5 M sodium sulfate buffered with 0.052 M disodium tetra borate were investigated. The reactor was placed in the constant temperature bath and runs were conducted at 25°C and 60°C. The slurry was sparged with oxygen at atmospheric pressure, mixed homogeneously and subjected to the desired current for the reaction duration. Samples of the electrolyte were analyzed for hydrogen peroxide concentration at regular interval as detailed in Appendix B.

In-situ brightening was attempted by introducing 1% consistency TMP into the reactor at 60°C and following the procedure for the generation of hydrogen peroxide. After reaction, the pH of the electrolyte containing graphite particles and pulp was adjusted to around 5.5 to 6 by the addition of sulfuric acid and the mixture removed from the reactor. The pulp-graphite slurry was allowed to settle and form separate layers. This was achieved in 15 to 20 minutes and the pulp layer was carefully siphoned out with a 5 mm diameter Teflon tube. Distilled water was added and the procedure repeated till the entire pulp was recovered. The oven dry weight of the recovered pulp indicated a yield of 97-99%.

The pulp was washed and dewatered in the standard handsheet maker. A handsheet was made as per CPPA standard C.5 (31) and the brightness of the sheet was measured as per CPPA standard E.1 (32).
Experimental Results and Discussion

In these experiments the pH, temperature (11.2, 60°C) and additives were chosen to match the conditions of conventional peroxide brightening. The choice of electrode materials and separators was based on their availability and the experience of the project supervisor (Prof. Oloman). Other variables such as the current, oxygen sparge rate, mixing, bed volume, cathode feeder configuration and age of graphite particles were explored by trial and error. The pulp consistency was set at 1% to give enough pulp for one handsheet and for ease of mixing in the reactor volume of 1 liter.

5.1 Hydrogen Peroxide Generation in Diaphragm Reactor

Hydrogen peroxide generation was investigated in a stainless steel reactor with different diaphragms as separators. The diaphragm was wound over the exposed area of anode. Experiments were performed with three different diaphragms and as many different anodes.

Polypropylene Diaphragm

Hydrogen peroxide generation employing a polypropylene woven diaphragm and anodes of 1/4" and 1/8" outer diameter stainless tubes and 1/2" graphite rod was evaluated in Runs 8 to 18. A volume of 500 ml of UCAR 1 graphite particles of size -0.42 + 0.29 mm was used as cathode. The effect of catholyte pH at the beginning of the run on the peroxide concentration obtained was investigated by conducting runs with initial pH
Chapter 5. Experimental Results and Discussion

ranging from 11.12 to 13 utilizing 0.5 M Na$_2$SO$_4$ as supporting electrolyte. The runs were conducted at 25°C for 60 minutes with 2 amp current. Electrolyte samples were analyzed for hydrogen peroxide concentration at 15 minute intervals. Maximum peroxide concentration of 0.002 M was obtained employing a 1/4" ss anode at an initial pH of 11.23. The detailed results are given in Table C.1.

Electroreduction of oxygen occurs on the cathode by Reaction 4 with the generation of 2OH$^-$ ions. Oxidation of OH$^-$ ions proceed on the anode by Reaction 6 and involve the consumption of 4OH$^-$ ions producing O$_2$ and H$_2$O. Ignoring undesirable Reactions 5 and 7, the pH of the system will decrease as the reaction proceeds due to the nett consumption of 2OH$^-$ ions in the process.

Lack of significant amounts of hydrogen peroxide in the electrolyte on analysis and a declining electrolyte pH as the reaction proceeds suggest the possible oxidation of HO$_2^-$ ions on anode by the undesirable Reaction 7 to O$_2$ and H$_2$O. The oxidation reaction is fast and most perhydroxyl ion reaching the anode is probably destroyed by Reaction 7.

The polypropylene diaphragm, probably was not effective in suppressing this undesirable reaction that wastes hydrogen peroxide. The high permeability of polypropylene diaphragm indicates it can not be employed effectively in this environment. Decomposition of hydrogen peroxide is catalyzed by metal ions by Reaction 2. The lack of hydrogen peroxide on analysis also indicates the possibility of metal ion contamination of the electrolyte from the dissolution of the SS anode and subsequent catalyzed decomposition of any peroxide produced.
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The electrolyte was buffered with 0.052 M disodium tetraborate and experiments were conducted with 1/4" od ss tube and 1/2" diameter graphite rod as anodes to investigate the impact on hydrogen peroxide production. No hydrogen peroxide was generated and the results indicate the buffering of electrolyte pH does not have any significant effect on peroxide evolution under these conditions.

A set of runs was conducted without diaphragm to evaluate the effect of diaphragm on pH progression. The results of Runs 19 to 24 are given in Table C.2.

A new diaphragm was used on the three types of anodes and a set of experiments was conducted at the same conditions as in Runs 19 to 24 to investigate the effect of repeated use of diaphragms. The results indicate hydrogen peroxide production with the new diaphragm remained the same as those with the old diaphragm.

Polyester Diaphragm

Several runs were conducted with a new diaphragm of woven polyester material to study the impact on hydrogen peroxide production. Anodes of stainless steel and graphite were employed at an initial pH 12.5 and 11.2. The results of Runs 25 to 30 are given in Table C.3.

The lack of hydrogen peroxide on analysis indicates the polyester diaphragm is ineffective in preventing the oxidation of $\text{HO}_2^-$ ions on anode, and the possibility of metal ion catalyzed decomposition of any hydrogen peroxide produced by the dissolution of SS anode.
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Polyester Screen Diaphragm

Runs 25 to 30 were repeated with a different diaphragm of polyester screen to study the effect on hydrogen peroxide evolution. The results are given in Table C.4. The polyester screen was ineffective and no hydrogen peroxide was detected on analysis of the electrolyte.

The effect of surfactant on hydrogen peroxide production with woven polypropylene and polyester and polyester screen was studied in Runs 37 to 44 by conducting a series of runs with half a drop of Makon NF-12 surfactant as a wetting agent for the diaphragm in the catholyte. The anode was subjected to surfactant treatment as before. A 5 mm × 2 mm platinised titanium anode of length 10 cm was also evaluated in these runs. All the runs were conducted with an initial pH of 11.2 at 25°C employing 0.5 M Na₂SO₄ containing 0.004 M NaOH as supporting electrolyte with 2 amps current. The detailed results are given in Table C.5.

No hydrogen peroxide was produced in this series of experiments and the addition of half a drop of surfactant to the catholyte had no positive effect on the production of hydrogen peroxide.

Results from Run 1 to 44 indicate the polypropylene diaphragm gives the best performance. The polyester diaphragms appear to have high permeability for H₂O₂ ions leading to their undesirable oxidation on the anode by Reaction 7.

The effect of type of graphite particles on hydrogen peroxide production was evaluated.
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by conducting a series of runs with new graphite particles of the same size and type as used in Runs 1 to 44. Results from Run 45 to 49 indicating the impact of replacing the old batch of graphite with a new one of the same type and size are given in Table C.6.

No significant difference in hydrogen peroxide production was observed on replacing the old graphite particles with new ones of the same type UCAR graphite.

Runs 50 to 52 were conducted to investigate the hydrogen peroxide decomposition on the introduction of current into the system. 30% hydrogen peroxide solution was used to achieve an initial concentration of approximately 10 mM of peroxide in the catholyte. Mixing and oxygen sparging were turned on and no current was supplied to the electrodes. Hydrogen peroxide concentration in the catholyte was determined by analysis every fifteen minutes over a duration of one hour. The experiment was repeated with a current of two amperes through the system. The results are given in Table 5.1 and 5.2.
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Conditions

Electrolyte: 500 ml of 0.5 M Na$_2$SO$_4$ + 0.004 M NaOH
Anode: Platinised titanium
Diaphragm: Polypropylene
Graphite: 500 ml of UCAR graphite of size -0.42 + 0.29 mm
DTPA dosage: 2.168 \times 10^{-4} M
Temperature: 25°C
Duration of run: 60 minutes
Current: 2 amps
H$_2$O$_2$ analysis interval: 15 minutes

No current

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<thead>
<tr>
<th>Time (min)</th>
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<th>30</th>
<th>45</th>
<th>60</th>
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<tr>
<td>H$_2$O$_2$ (M)</td>
<td>0.0093</td>
<td>0.0083</td>
<td>0.0043</td>
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<td>0.0017</td>
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</table>

Table 5.1. Effect of Absence of Current on Decomposition of Hydrogen Peroxide

2 amp current

<table>
<thead>
<tr>
<th>Time (min)</th>
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<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$ (M)</td>
<td>0.0127</td>
<td>0.0039</td>
<td>0.0012</td>
<td>0.001</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

Table 5.2. Effect of Current on Decomposition of Hydrogen Peroxide

This indicates loss of hydrogen peroxide by undesirable Reactions 5 and 7 occurs on the introduction of current through the system.
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5.2 Hydrogen Peroxide Generation in Membrane Tank Reactor

Problems were encountered in attaching the cation membrane over the anolyte tank. The alkali attacked the adhesive leading to anolyte leakage. Several different adhesives were tried but the membrane could not be attached to the membrane tank successfully without leaks. Experiments could not be conducted with the membrane tank reactor.
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5.3. Hydrogen Peroxide Generation in Divided Membrane Reactor

Different anolytes and catholytes as well as various types of graphite particles were evaluated for hydrogen peroxide generation in the divided SS reactor with Nafion 214 cation membrane. In-situ brightening of TMP was also attempted in this reactor.

UCAR 1 Graphite of Size -0.42 + 0.29 mm

Runs were conducted with 500 ml of UCAR 1 low strength graphite particles as cathode and 1/4" od SS tube as anode. The experiments were conducted at 25°C for 60 minutes with 2 amps current. A solution of 0.052 M di sodium tetra borate was also evaluated as catholyte pH buffer. The catholytes and anolytes investigated in Run 56 to 63 are given in Table 5.3.
### Chapter 5. Experimental Results and Discussion

<table>
<thead>
<tr>
<th>Catholyte</th>
<th>Anolyte</th>
</tr>
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<tbody>
<tr>
<td>0.5 M Na₂SO₄ + 0.004 M NaOH</td>
<td>1 M Na₂CO₃</td>
</tr>
<tr>
<td>Buffered 0.5 M Na₂SO₄ + 0.1 M NaOH</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>2 M NaOH</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>0.5 M Na₂SO₄ + 0.004 M NaOH</td>
<td>&quot;</td>
</tr>
<tr>
<td>Buffered 0.5 M Na₂SO₄ + 0.1 M NaOH</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

**Table 5.3. Catholytes and Anolytes Evaluated for Peroxide Generation**

A concentration of $2.2 \times 10^{-4}$ M DTPA was present in the catholyte. A maximum peroxide concentration of 0.01 M was obtained in Runs 60 and 63 employing 0.5 M Na₂SO₄ and buffered 0.5 M Na₂SO₄ as catholyte respectively and 2 M NaOH as anolyte with SS screen as cathode contact. The detailed results are given in Table C.7.

Runs 57 to 63 were repeated in Runs 64 to 72 with graphite plate as cathode contact to investigate the impact on peroxide production. A reduction in hydrogen peroxide concentration was observed on catholyte analysis with the graphite plate contact. Anolyte samples were analyzed for hydrogen peroxide periodically at an interval of 30 minutes in several runs to investigate the effectiveness of the membrane in suppressing the
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Transport and subsequent oxidation of $\text{HO}_2^-$ ions on anode by undesirable Reaction 7. No hydrogen peroxide was detected on the analysis of anolyte while it was present in the catholyte indicating effective functioning of the membrane.

Transport and oxidation of $\text{OH}^-$ and $\text{HO}_2^-$ ions on the anode is essentially eliminated by the cation specific membrane and this reflects in the increasing pH values of catholyte over the duration of run.

Effect of Chelating agents and Stabilisers

$\text{MgSO}_4$ and sodium silicate were added to the catholyte as stabilisers in addition to DTPA as chelating agent to investigate the impact on hydrogen peroxide production. $\text{MgSO}_4$, $\text{Na}_2\text{SiO}_3$ and DTPA concentrations in the catholyte were maintained at $5.68 \times 10^{-4}$ M, $3.36 \times 10^{-2}$ M and $8.67 \times 10^{-4}$ M respectively as indicated by Strunk (6). Runs were performed employing SS screen and graphite plate as cathode contacts and UCAR 1 graphite particles of size $-0.42 + 0.29$ mm size, used in the previous runs as cathode. A solution of 1 M NaOH was used, if necessary, to adjust the initial pH of catholyte to around 11 and runs were conducted at both 25°C and 60°C.

A maximum peroxide concentration of 0.019 M was detected in Run 75 with SS screen cathode contact at 25°C employing 0.5 M $\text{Na}_2\text{SO}_4$ as catholyte and 2 M NaOH as anolyte. The peroxide concentration of 0.019 M achieved in Run 75 is close to the conventional TMP brightening concentration of 0.03 M. The detailed results of these runs are given in Table C.8. Peroxide concentration increased approximately ten fold, from 0.002 M in Run 73 to 0.02 M on replacing 1 M Na$_2$CO$_3$ in Run 73 with 2 M
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NaOH in Run 75 as anolyte.

Run 75 that produced the highest concentration of 0.019 M H\textsubscript{2}O\textsubscript{2} with an initial pH of 11.22 was repeated in Run 77 at an initial pH of 10.25 to study the impact of low initial pH. As can be seen from Table C.8, no difference in final H\textsubscript{2}O\textsubscript{2} concentration or in pH change over the duration of the run was observed.

Effect of Graphite Plate Cathode Contact

Runs 73 to 77 employing 0.5 M Na\textsubscript{2}SO\textsubscript{4} and 0.5 M Na\textsubscript{2}SO\textsubscript{4} containing a buffer of 0.052 M di sodium tetraborate as catholytes and 1 M Na\textsubscript{2}CO\textsubscript{3} and 2 M NaOH as anolytes were repeated in Runs 78 to 82 with graphite plate as cathode contact to investigate the impact on peroxide synthesis. Concentration of H\textsubscript{2}O\textsubscript{2} decreased on employing a graphite plate as cathode contact. Peroxide concentration of 0.019 M, the maximum concentration obtained at 25°C in Run 75 utilising 0.5 M Na\textsubscript{2}SO\textsubscript{4} as the catholyte and 2 M NaOH as the anolyte employing SS screen contact decreased to 0.0084 M in Run 80 on replacing the SS screen with graphite sheet as cathode contact. The detailed results are shown in Table C.9.

Effect of Temperature

Runs were conducted at 25, 60 and 80°C with SS screen as cathode contact to examine the impact of temperature on peroxide production. In addition to 0.5 M Na\textsubscript{2}SO\textsubscript{4}, with and without buffer, 1 M Na\textsubscript{2}CO\textsubscript{3} was also evaluated as a catholyte. A solution of 2 M NaOH was utilised as anolyte in these runs.
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Peroxide concentration of 0.019 M obtained in Run 75 increased to 0.022 in Run 84 on increasing the process temperature from 25°C to 60°C with all the other conditions remaining the same. The temperature was further increased to 80°C in Run 86 and the peroxide concentration was found to decrease dramatically from 0.025 M to 0.007 M. The decrease in peroxide concentration on increasing the process temperature to 80°C suggests the acceleration of decomposition of peroxide by Reactions 8 and 9 and/or the decreased solubility of oxygen in the catholyte.

Peroxide concentration of 0.025 M was detected in Run 88 utilising 1 M Na₂CO₃ containing 0.06 M NaOH as the catholyte at 60°C at the end of 105 minutes run. Run 88 was repeated at 25°C in Run 89 to study the impact of temperature. Run 89 yielded a concentration of 0.025 M at 25°C, the same as obtained in Run 88 at 60°C. The detailed results of these runs are given in Table C.10.

When the temperature was reduced to 25°C, pH increased rapidly and reached a value of 12.13 from an initial value of 11 after 60 minutes. In Run 88, at 60°C, pH progression was less rapid and from 11.12, comparable to the initial pH in Run 89, increased to 11.65, lower than the final pH reached in Run 89 after a much longer duration of 105 minutes as opposed to 60 minutes in Run 89.

A peroxide concentration of 0.013 M H₂O₂ was obtained after 30 minutes at a pH of 11.54. The decrease in peroxide concentration from 0.025 M in Run 88 to 0.013 M in Run 89 and the accompanying rapid increase in pH suggest the loss of HO₂⁻ ions on the cathode by the undesirable Reaction 5 leading to the formation of 3OH⁻ ions. The accelerated production of OH⁻ ions by the destruction of HO₂⁻ ions appears to reflect in
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the rapid increase in pH of the catholyte. The detailed results are given in Table C.15.

Effect of Catholyte Composition

Cathlytes of 0.5 M Na$_2$SO$_4$ + 0.01 M NaOH, 1 M Na$_2$CO$_3$ + 0.06 M Na$_2$CO$_3$ and 0.5 M Na$_2$SO$_4$ + 0.052 M disodium tetraborate + 0.16 M NaOH were utilised at 60°C in Runs 84, 85 and 88 respectively. A solution of 2 M NaOH was used as anolyte and peroxide concentrations of 0.022 M, 0.018 M and 0.025 M were obtained in Runs 84, 85 and 88 respectively.

The peroxide generation was not affected by the catholyte composition. Concentration of peroxide and the progression of catholyte pH against time for Runs 84, 85 and 88 are given in Figure 5.1 and 5.2 respectively.

![Figure 5.1. Hydrogen Peroxide Concentration vs Time](image-url)
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Figure 5.2. Catholyte pH vs Time

Current Efficiency

Current efficiencies for hydrogen peroxide in Runs 84, 85, 87 and 88, generating $\text{H}_2\text{O}_2$ concentrations amongst the highest achieved, are presented in Table C.11-C.14
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respectively. Figure 5.3 shows the current efficiencies for Run 84, 85 and 88 against time.

![Figure 5.3. C.E vs Time](image)

Effect of Anolyte, Increased Current and Cathode Contact Area

Run 88, which yielded the maximum concentration of 0.025 M peroxide with 1 M Na$_2$CO$_3$ as the catholyte and 2 M NaOH as the anolyte was repeated in Run 92 by replacing the anolyte with 1 M Na$_2$CO$_3$. The pH increased from 11.12 at the beginning of Run 92 to 11.57 at the end of 60 minutes, yielding a H$_2$O$_2$ concentration of 0.013 M. Table C.16 shows the results of Run 92.

Run 88 was repeated again with maximum current possible with the DC power unit, 4.19
amps in Run 93. The pH increased from an initial value of 11.1 at the beginning of the run to 11.62 at the end of 60 minutes run. A concentration of 0.014 M H$_2$O$_2$ was detected at the end of 60 minutes. The pH increased more rapidly on increasing the current from 2 amps to a maximum of 4.19 amps. The pH increased from 11.10 to 11.62 in Run 93, comparable to the initial and final pH values in Run 88, but in 60 minutes as opposed to 105 minutes in Run 88.

As the current density is increased, the overvoltage increases, resulting in a lower cathode potential. As the cathode becomes more negative, the rate of undesirable Reaction 5 will possibly increase leading to the destruction of peroxide by reduction on the cathode. Table C.17 presents the detailed results of Run 93.

A new stainless steel cathode contact of area 4.56 $\times$ 10$^{-3}$ m$^2$, representing 25% of the cathode contact area used up to Run 93 was fabricated. Stainless steel screen of 20 mesh size was used to construct the cathode contact. Run 84 was repeated in Run 95 using the new stainless steel cathode contact to evaluate the impact of cathode contact area on H$_2$O$_2$ production.

The pH increased from 11.15 to 11.65 at the end of 90 minutes run yielding H$_2$O$_2$ concentration of 0.011 M. Cell voltage increased from 3.6 V in Run 88 to 5.5 V on reducing the cathode contact area by 75%. Concentration of H$_2$O$_2$ fell from 0.025 M in Run 88 to 0.011 M on decreasing the cathode contact area by 75%, from 18.2 $\times$ 10$^{-3}$ m$^2$ to 4.56 $\times$ 10$^{-3}$ m$^2$ in Run 95. The reduced contact area may lead to less than ideal current distribution reflecting in decreased H$_2$O$_2$ concentration. The results of Run 95 are given in Table C.18.
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Effect of Various Types of Graphite Material

Several types of graphite particles were evaluated as cathodes for \( \text{H}_2\text{O}_2 \) production in Runs 96 through 112 in addition to UCAR 1 low strength material used till Run 90. Nickel particles as the slurry cathode were also investigated in Run 109. The different types of particles and their size ranges are listed in Table 4.1.

The results of the runs evaluating the impact of the different types of graphite on \( \text{H}_2\text{O}_2 \) production are given in Table C.19. The concentration of hydrogen peroxide obtained with various types of graphite materials and Ni particles under the constant conditions given in Table C.19 is shown in Figure 5.4.

![Peroxide Generation with Various Types of Graphite](image)

**Figure 5.4. Effect of Various Cathode Graphite Materials on the Generation of Hydrogen Peroxide**
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5.4 In-situ Brightening of TMP in the Divided Membrane Reactor

After the evaluation of various types of graphite particles, in-situ brightening at 1% TMP was attempted in Run 103. Pyrolytic carbon was tried in this run due to its high strength and consequently the possibility of minimising graphite fines being formed by vigorous agitation.

After 90 minutes of run, attempts were made to separate the pulp from the graphite by repeated washing and siphoning the pulp fiber layer. The fiber suspension appeared dark and a large quantity of graphite fines was noticed in the solution. On separating the pulp fibers, it was noticed the fibers were dark in color and repeated washings did little to remove the discoloration. The brightness of the handsheet declined from 45% ISO for the unbrightened TMP to 30% ISO after in-situ brightening. The results are given in Table C.20.

Effect of Brightening Chemicals

Runs 104 and 105 were conducted to better understand the possibility of graphite loading of fiber lumen and the impact, if any, of brightening chemicals on the size of graphite fines produced. The catholyte, at the end of the run was analyzed to determine the size range of graphite fines produced. No pulp was used in Run 104 and no brightening chemicals nor pulp was used in Run 105. The conditions are given in Table 5.4.
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<table>
<thead>
<tr>
<th>Conditions</th>
<th>Run 104</th>
<th>Run 105</th>
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<tr>
<td>Pulp</td>
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</tr>
<tr>
<td>Anode</td>
<td>1/4&quot; ss tube</td>
<td>1/4&quot; ss tube</td>
</tr>
<tr>
<td>Cathode</td>
<td>pyrolytic carbon</td>
<td>pyrolytic carbon</td>
</tr>
<tr>
<td>O₂ sparging</td>
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<td>on</td>
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</table>

Table 5.4. Conditions to Evaluate the Effect of Brightening Chemicals on the Generation of Graphite Fines.
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The graphite was separated from the catholyte at the end of run and a sample volume of 100 ml each of the solution containing graphite fines from Run 104 and 105 was filtered through several successively small pore size filter papers. The solution was first put through 30 micron mesh filter cloth and the filtrate was filtered through 14 micron and 5 micron filter papers in a Millipore filter. A filtrate sample from each stage of filtration was examined under a microscope for graphite fines.

Graphite fines were detected in filtrate samples from 30 micron, 14 micron and 5 micron filter stages. The lumen in the pulp fiber measures approximately 10 to 20 micron in diameter and this indicates the possibility of graphite loading of lumen in Run 103. The presence of brightening chemicals in the catholyte appear to have little impact on the generation of graphite fines up to 5 micron in diameter.

To study the impact of initial pH of the catholyte on the size distribution of graphite fines generated during the course of the experiment, Run 107 was conducted without pulp at Run 105 conditions indicated in Table 5.4 but with an initial pH of 11.23. A concentration of 0.007 M H$_2$O$_2$ was obtained at the end of 30 minutes run with a final pH of 11.52. On analysis, the size distribution of graphite fines generated closely paralleled to that observed in Run 104 and 105.

Run 84 employing UCAR 1 graphite, which generated the maximum concentration of 0.023 M H$_2$O$_2$ was repeated in Run 108 with 1% consistency pulp. A significant quantity of graphite fines was observed in the pulp-graphite suspension. The pulp fibers were separated by repeated washing, settling and siphoning. The brightness was found to have decreased from 45 % ISO to 34 % ISO and on analysis of the pulp fibers under
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microscope, graphite loading of the lumen was observed.

A final concentration of 0.023 M H₂O₂ was detected at a pH of 11.6 in Run 84, under the same conditions but with no pulp. On the introduction of 1% consistency TMP, at a comparable pH, the H₂O₂ concentration on analysis declined to 0.014 M at the end of Run 108. This is probably due to the consumption of H₂O₂ in the pulp brightening reactions. The detailed results are given in Table C.21.

Effect of Intensity of Impeller Agitation

The impact of vigorous mixing on the generation of graphite fines and on oxygen transfer were evaluated in Run 112-116 utilising Sigradur-G graphite as the slurry cathode. The intensity of mixing was varied and the catholyte samples were analyzed for the size range of the graphite fines generated.

Run 112 was conducted employing 0.5 M Na₂SO₄ as catholyte and 2 M NaOH as anolyte with vigorous mixing provided by impeller. The temperature was maintained at 60°C and 2 amps current was used for 120 minutes. Pulp was not introduced and the detailed results are given in Table C.22.

Runs were conducted by reducing the impeller rpm first by 25 % and then by 37 % over Run 112 to understand the effect of impeller rpm on the generation of graphite fines. The no load impeller drive motor shaft rpm was 5600 in Run 112. The detailed results of Runs 113 and 114 are given in Tables C.23 and C.24 respectively.
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Graphite fines of size less than 5 micron were detected in catholyte samples from Runs 112 to 114 on filtration through several filter papers of progressively small pore sizes. Reduction of impeller rpm and the resulting shear appears to have little impact in eliminating the generation of graphite fines of size < 5 microns. The peroxide concentration declined from 0.011 M in Run 112 to 0.008 M in Run 114 on reducing the impeller rpm. Run 114 was repeated in Run 115 with 1% consistency TMP in the catholyte. The brightness decreased from 45% ISO for unbrightened pulp to 33% ISO after in-situ brightening. Run 115 results are given in Table C.25.

A new Pyrex glass sparger was employed in Run 116 to achieve better sparging of oxygen and Run 115 was repeated. No change in H$_2$O$_2$ concentration over Run 115 was observed on employing the new gas sparger and a decline in the brightness of the hand sheet similar to Run 115 was noticed. The results of Run 116 are presented in Table C.26.

The brightness loss could be due to either alkali darkening or graphite loading of fiber lumen. Run 118 was conducted to isolate the factor primarily responsible for loss of brightness. TMP of 1% consistency was introduced into Sigradur-G graphite-distilled water slurry and was subjected to oxygen purging and mixing for 120 minutes.

Brightness decreased from 45% ISO to 33% ISO after being subjected to vigorous mixing with Sigradur-G graphite. Since no chemicals were employed in Run 118, the brightness loss indicates graphite loading of fiber lumen.
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5.5 Hydrogen Peroxide Generation in Undivided Reactor with Water Cooled Anode

Hydrogen peroxide generation was evaluated in the reactor with different types of graphite particles. Platinised titanium and stainless steel were evaluated as anodes. The impact of increasing the anode area was also investigated. Runs were also conducted to study the effect of several different surfactants on peroxide production with Sigradur-G graphite.

Effect of Type of Graphite on Hydrogen Peroxide Generation

In Runs 120 to 145 several types of graphite cathode material such as UCAR 1, Pyrolytic and Sigradur-G were evaluated for peroxide generation. The size range of these graphites is given in Table 4.1.

UCAR 1 Graphite of Size -0.42 + 0.29 mm

Runs 120 to 123 were conducted to study the generation of peroxide with 500 ml UCAR 1 graphite particles employing 1 M Na\textsubscript{2}CO\textsubscript{3} as electrolyte at 60°C. MgSO\textsubscript{4}, Na\textsubscript{2}SiO\textsubscript{3} and DTPA concentrations were maintained at 5.68 × 10\textsuperscript{-4} M, 3.36 × 10\textsuperscript{-2} M and 8.67 × 10\textsuperscript{-4} M respectively in the electrolyte. NaOH was added to the electrolyte, when needed to adjust the initial pH of the electrolyte to 11.15.

An area of 7.6 cm\textsuperscript{2} of the water cooled platinised titanium anode was in contact with the electrolyte. Silicon glue was used to cover the rest of the platinised titanium tubing
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surface to shield it from contact with electrolyte. The impeller rpm was maintained at 60. Electrolyte samples were analyzed for hydrogen peroxide at regular intervals of 15 minutes.

Run 120 was conducted at 2 amp current with oxygen flow set at 2.2 liters/min @ STP. Expansion of the graphite particle cathode bed was observed at this oxygen flow rate. Less than 0.001 M peroxide was detected at the end of 45 minutes run. The oxygen flow rate appeared high enough to disturb and break the graphite particle bed. The particles swirling in the electrolyte came in to contact with the anode resulting in short circuit and decreased peroxide production. Run 120 was repeated in Run 121 at 4 amperes current and no peroxide was detected at the end of 45 minutes run.

In Run 122, the oxygen flow was reduced to 0.31 liters/min @ STP and Run 120 was repeated. A peroxide concentration of 0.025 M was detected at the end of 75 minutes run. The pH of the electrolyte decreased from 11.14 to 11.05. Run 122 was repeated to check the results and the same peroxide generation profile seen in Run 122 was obtained. Detailed results of Run 122 are given in Table C.27.

Pyrolytic Graphite

Run 120 was repeated in Run 124 with pyrolytic graphite to investigate the impact of graphite material on hydrogen peroxide generation. Hydrogen peroxide generation increased on replacing UCAR 1 graphite with pyrolytic graphite and at the end of 75 minutes run, 0.041 M peroxide was obtained. The pH of the electrolyte declined from 11.15 at the beginning to 11.08 at the end of 75 minutes run. The 0.041 M peroxide
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obtained in this run is approximately twice the concentration of hydrogen peroxide required in conventional brightening of TMP. The detailed results are given in Table C.28.

Sigradur-G Graphite

Sigradur-G graphite was evaluated for peroxide generation in Run 129 with platinised titanium anode at 60°C with an initial pH of 11.15. Conditions were maintained as in Run 120. A peroxide concentration of 0.005 M was obtained at the end of 45 minutes run and the pH declined from 11.15 to 11.

It was observed that Sigradur-G graphite floats at the surface of the electrolyte as a thick floc, coming into contact with anode. Throughout Run 129 continuous contact of this floating graphite floc with the anode was observed reflecting in decreased efficiency. The integrity of the cathode bed could not be maintained with Sigradur-G graphite.

UCAR 1 Graphite of Size < 0.5 mm

Run 120 was repeated in Run 130 with UCAR 1 graphite. 0.007 M peroxide was obtained at the end of 60 minutes run and the pH declined from 11.15 to 11.11.

Effect of Water Cooled SS Anode

A water cooled SS anode of the same dimension as the platinised titanium anode used before was evaluated for peroxide production in Runs 125 to 128 and in Run 131. The
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anode area in contact with the electrolyte in these experiments was the same as in those
with platinised titanium electrode, the contact area being 7.6 cm².

Run 124 yielding 0.041 M peroxide employing pyrolytic graphite and platinised titanium
anode was repeated in Run 125. The final peroxide concentration declined to 0.030 M
on replacing the platinised titanium anode with stainless steel one. The pH of the
electrolyte decreased from 11.15 to 11.05 at the end of 75 minutes run, similar to the
trend observed in Run 124. Cell voltage was 4.2 volts as compared to 5.8 volts obtained
in Run 124 with platinised titanium electrode.

Run 123 utilising UCAR 1 graphite yielding 0.022 M peroxide was repeated in Run 126
with stainless steel electrode. No peroxide was detected at the end of 45 minutes run. A
pale green color was noticed in the electrolyte indicating the presence of metal ions, the
possible source being the dissolving stainless steel anode.

Run 129 and 130 producing 0.005 M and 0.007 M peroxide employing Sigradur-G and
UCAR 1 graphites respectively were repeated in Run 127 and 131. No peroxide was
obtained at the end of 60 minutes run and a green color electrolyte indicating
contamination by metal ions was observed.

Peroxide formation was not favored on the SS anode and the peroxide yield declined on
replacing the platinised titanium anode with stainless steel. Metal ion contamination by
dissolving SS anode observed in Runs 126-127 and 131 by the presence of green color
in the electrolyte resulted in catalyzed decomposition of generated peroxide by Reactions
11 and 12. The percarbonate formation by Reaction 8 was not favored on the SS anode
Chapter 5. Experimental Results and Discussion

due to the lack of high enough oxygen overvoltage.

Effect of Increased Current

Run 124 and 125 yielding 0.041 and 0.030 M peroxide utilising platinised titanium and stainless steel anodes were repeated in Run 132 and 128 respectively with 4 Amps current instead of 2 Amps. No Peroxide was detected at the end of 45 minutes run. A dark brown color was noticed in the electrolyte at the end of run, possibly the product of some undesirable reaction triggered by the increased current density.

Effect of Increased Anode Area

In Runs 134 to 137 the area of the platinised titanium anode exposed to the electrolyte was doubled from 7.5 cm² used in Runs up to 133 to 15 cm² by removing the silicon glue covering the anode surface. In Run 134 pyrolytic graphite with 4 amps current was used and after 15 minutes of run the catholyte turned brown in color indicating the products of some unknown and undesirable reactions. The color of the electrolyte was similar to the one observed in Run 132 with 4 amps current and 7.5 cm² anode area exposed to the electrolyte.

Run 134 was repeated in Run 135 with 2 amps current resulting in the electrolyte turning brown in color. Sigradur-G and UCAR 1 graphite of size < 0.5 mm were evaluated in Runs 136 and 137 at 2 amps current with an area of 15 cm² of the platinised titanium anode in contact with the electrolyte. Run 136 could not be completed because of the floating of the cathode Sigradur-G graphite in the electrolyte that brings it into contact
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with the anode surface. No peroxide was obtained in Run 137 employing UCAR 1 graphite particles of less than 0.5 mm in size. It was observed that the very fine size of the graphite particles caused the graphite bed to expand on the introduction of oxygen and mixing. The graphite particles ceased to exist in the form of bed and the circulating graphite was in continuous contact with the anode.

The anode area was reduced from 15 cm$^2$ to 7.5 cm$^2$ by applying silicon glue and Run 124 producing 0.04 M peroxide was repeated in Run 138. No peroxide was detected and the electrolyte turned brown in color at the end of 45 minutes run.

Runs 139 and 140 were conducted to better understand the factors responsible for the undesirable brown color in the electrolyte. The brown color could be the product of attrition of graphite particles induced by mixing and oxygen sparging, generating fines or due to the current triggering undesirable reactions.

In Run 139, a slurry of 500 ml pyrolytic graphite and 500 ml distilled water was subjected to mixing and oxygen purging for 120 minutes. No current nor brightening chemicals were employed. The water remained clear and no graphite fines were observed at the end of run.

Run 140 was conducted by subjecting a mixture of 500 ml 1 M Na$_2$CO$_3$ and 500 ml pyrolytic graphite to mixing and oxygen sparging as used in the previous runs. Brightening chemicals were utilised and the initial pH was adjusted to 11.15 but no current was used. A clear electrolyte was obtained at the end of 120 minutes.
Chapter 5. Experimental Results and Discussion

Runs 139 and 140 demonstrate that the brown color observed in the electrolyte is a product of undesirable reactions activated by the current. The brown color was observed in the electrolyte in the experiments subsequent to Run 132, where the current was increased to 4 amps from 2 amps used prior to Run 132. It appears irreversible changes in the graphite characteristics were caused by the increased current in Run 132. The reactor was dismantled and cleaned thoroughly with distilled water to remove traces of any contaminants that might have been carried over subsequent to Run 132. A fresh batch of pyrolytic graphite of the same size used before was utilised in Run 141 employing the platinised titanium anode at Run 124 conditions given in Table C.28.

No peroxide was obtained at the end of 60 minutes run and a dark coffee color was observed in the electrolyte. This color was noticed in Run 99 in the divided membrane reactor with pyrolytic graphite prior to cleaning the graphite with HCl and subsequent cleaning eliminated this undesirable color. Run 141 was repeated in Run 142 after acid cleaning the graphite.

A peroxide concentration of 0.018 M peroxide was obtained at the end of 75 minutes run at a cell voltage of 6.5 volts and the coffee color observed in the electrolyte in Run 141 disappeared. The electrolyte pH decreased from 11.15 to 10.95 at the end of run. Run 142 was repeated in Run 144 and at the end of 105 minutes run 0.027 M peroxide was obtained with the pH of the electrolyte decreasing from 11.15 to 10.9 at the end of run.

Effect of Surfactants on Sigradur-G Graphite

Several types of surfactants were evaluated with Sigradur-G graphite for their efficacy
**Chapter 5. Experimental Results and Discussion**

in suppressing the formation and floating of Sigradur-G graphite flocs in the electrolyte. The floating flocs of graphite come into contact with anode resulting in decreased efficiency in the generation of peroxide. The different types of surfactants is given in Table 5.5.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>133</td>
<td>Makon NF-12</td>
</tr>
<tr>
<td>147</td>
<td>Fluorad 3M</td>
</tr>
<tr>
<td>148</td>
<td>Dow Corning 194</td>
</tr>
<tr>
<td>149</td>
<td>Dow Corning 472 Glycol Polysilox</td>
</tr>
<tr>
<td>150</td>
<td>Merpol-ultra low foam</td>
</tr>
<tr>
<td>151</td>
<td>Petro-UIP-ultra low foam</td>
</tr>
</tbody>
</table>

Table 5.5. Surfactants Evaluated with Sigradur-G Graphite

Merpol and Dow Corning 472 surfactants performed very well in suppressing the formation and floating of Sigradur-G flocs. However, peroxide generation declined steeply on the introduction of surfactants in the electrolyte. Peroxide concentration of less than 0.001 M was obtained in Runs 133 and 147 to 151. It appears the surfactant coating on the surface of the graphite particles impedes oxygen transfer between the cathode graphite surface and the bulk electrolyte. Performance of Sigradur-G graphite with various surfactants was evaluated because the superior physical strength of Sigradur-G graphite makes it less prone to the production of fines, a very desirable feature in in-situ brightening of TMP.
Chapter 5. Experimental Results and Discussion

5.6 In-Situ Brightening of TMP in the Undivided Reactor

In Run 146 in-situ brightening of TMP was attempted with 1 % consistency pulp. An electrolyte of 1 M Na$_2$CO$_3$ was used with pyrolytic graphite. A platinised titanium water cooled anode was utilised and the brightening was carried out at 60°C for 120 minutes with 2 amps current. The brightness of the in-situ brightened TMP declined to 26 % ISO from 43 % ISO for unbrightened handsheet made from the same batch of TMP. The detailed results are given in Table C.30. The unbrightened and in-situ brightened TMP is shown in Figure 5.5.

Run 146

26% ISO Brightness

16% ISO Yellowness

Unbrightened TMP

43% ISO Brightness

34% ISO Yellowness

Figure 5.5. Representation of Unbrightened and In-situ Brightened TMP
Chapter 5. Experimental Results and Discussion

The pyrolytic graphite subsequent to its use with various surfactants in Runs 147 to 151 was cleaned thoroughly by keeping it under running water with agitation by mixer for 16 hours to rid it of traces of surfactants. The pyrolytic graphite was then washed with distilled water and evaluated for peroxide generation in Run 152. A peroxide concentration of 0.026 M was obtained at the end of 120 minutes run at 60°C with 2 amps current.

TMP of 1 % consistency was used for in-situ brightening in Run 153 with the pyrolytic graphite. Peroxide generation increased and 0.043 M peroxide was detected at the end of 180 minutes run. The brightness and the yellowness of the pulp declined from 43 to 30% ISO and 34 to 16% respectively in Run 153. The detailed results are given in Table C.31.

Run 153 was repeated in Run 154 without current to investigate the effect of alkali darkening of TMP in the absence of hydrogen peroxide. At the end of 180 minutes run the brightness declined to 27% ISO, a loss of 16 points of brightness due to alkali darkening.

Run 154 was repeated in Run 155 without pyrolytic graphite to evaluate if the graphite produced fines leading to the loss of brightness gain observed in Run 154. Loss of brightness gain similar to obtained in Run 154 was noticed indicating the role of alkali darkening in the loss of brightness.

The concentration of peroxide required to brighten TMP, around 0.02 M, was achieved at approximately 60 minutes of in-situ brightening in Run 153. During this interval of
Chapter 5. Experimental Results and Discussion

time, the undesirable effects of alkali darkening overwhelm the desirable effects of peroxide brightening resulting in irreversible darkening of the pulp. A peroxide concentration of 0.043 M was realised in Run 153, which was approximately twice the concentration of peroxide used in conventional brightening of TMP.

The high concentration of 0.043 M peroxide could not be harnessed to drive in-situ brightening to achieve brightness gain due to the irreversible alkali darkening of pulp during the initial period of the run when less than sufficient peroxide was present in the electrolyte to overcome the undesirable effects of alkali.

In-situ brightening was attempted in Run 156 with 500 ml of pyrolytic graphite in 300 ml of 1.667 M Na\textsubscript{2}CO\textsubscript{3} as electrolyte containing 0.23 M NaOH. TMP equivalent to 5 grams by OD weight (12 gms wet pulp) was mixed into 200 ml of water and introduced into the reactor after 60 minutes of run to avoid alkali darkening. The addition of the 200 ml pulp-water mixture to the 300 ml electrolyte achieved a consistency of 1% TMP in 500 ml of 1 M Na\textsubscript{2}CO\textsubscript{3} + 0.14 M NaOH electrolyte. The temperature was maintained at 60°C and 2 amps current was used. A peroxide concentration of 0.036 M was present after 60 minutes of run at the time the pulp was introduced into the reactor.

After 150 minutes of run, pulp brightness increased to 47% ISO from the initial value of 43% ISO, a brightness gain of 4% ISO. The detailed results are given in Table C.32.

Results from in-situ peroxide generation Runs 124 and 142 indicate the graphite cathode exhibits changing electrocatalytic properties for peroxide generation and degradation to form fines depending on the number of times of its prior utilisation. It may be that
Chapter 5. Experimental Results and Discussion

repeated use of the graphite particles expose successive fresh layers of the electroactive surface resulting in varying performances at identical conditions. A comparison of Runs 124 and 142 is given in Table C.33.

Run 156 was repeated twice in Runs 157 and 158 to verify the results achieved. TMP pulp of 1% consistency was used and brightening conditions and the run duration were maintained as in Run 156. A handsheet of 53% ISO was obtained after 150 minutes in Runs 157 and 158. Brightness of the in-situ brightened TMP increased by 10% ISO from the initial value of 43% ISO. The yellowness declined from 34% for the unbrightened TMP to 21% after in-situ brightening. The detailed results of Run 157 are given in Table C.34.

In Run 159, the run duration was increased to 240 minutes to investigate the impact on the brightness gain realised in Runs 157 and 158. TMP of 1% consistency was used in Run 159 and the brightening conditions were maintained as in run 156. The brightness of the TMP increased to 53% ISO at the end of 240 minutes run from the initial value of 43% ISO. The yellowness decreased from 34% for the unbrightened TMP to 23% for the in-situ brightened pulp.

Results indicate no additional brightness gain beyond the 10% ISO realised in Runs 157 and 158 was obtained on increasing the run duration by 90 minutes in Run 159. The detailed results of Run 159 are given in Table C.35.
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A representation of unbrightened and in-situ brightened TMP in Run 157 is shown in Figure 5.6.

Figure 5.6. Representation of Unbrightened and In-situ Brightened TMP
Chapter 5. Experimental Results and Discussion

Chapter 6

General Discussion

The proposed in-situ brightening of TMP involved the generation of hydrogen peroxide in stainless steel reactors, both divided and undivided configurations employing graphite particles as a slurry cathode. The hydrogen peroxide generation was evaluated in four different reactors. In-situ brightening of TMP was investigated in the divided stainless steel reactor with a cation membrane and in the undivided stainless steel reactor incorporating a water cooled platinised titanium anode.

A maximum hydrogen peroxide concentration of 0.025 M was achieved in the divided stainless reactor employing UCAR 1 graphite particles of size -0.42 + 0.29 mm at 60°C and 2 amps current, achieving a current efficiency of 20% for peroxide production. Several different types of graphite particles of various size ranges were evaluated.

The experiments indicated the size and type of graphite slurry electrode had significant impact on the concentration of hydrogen peroxide and current efficiency achieved. Several different catholytes and anolytes were also employed in conducting the experiments and the results showed the peroxide production and the pH progression were influenced by the composition of electrolytes. The peroxide generation declined on replacing the stainless steel cathode contact with a graphite one, possibly due to an increased contact resistance with the slurry.

The peroxide production increased on increasing the DTPA concentration and by the
Chapter 5. Experimental Results and Discussion

introduction of MgSO₄ and Na₂SiO₃ as peroxide stabilisers. Peroxide concentration increased on increasing the temperature from 25°C to 60°C. The concentration of peroxide obtained decreased approximately by a factor of ten on increasing the process temperature to from 60°C to 80°C indicating the acceleration of undesirable decomposition of peroxide prevailing over the electrode kinetics favoring peroxide formation at 80°C and/or the effect of decreased oxygen solubility. Reduction of cathode contact area resulted in decreased peroxide production indicating poor current distribution.

In-situ brightening of mechanical pulp was attempted in the membrane reactor employing various graphite slurry electrodes. Attempts to brighten TMP in-situ were compromised by the generation of graphite fines induced by the vigorous mixing employed to promote good oxygen transfer. Results indicated the generation of graphite fines of < 5 micron size even at the minimum possible impeller rpm. Loss of brightness of the TMP was observed in the in-situ brightening experiments due to the production of graphite fines and their subsequent undesirable loading into the fiber lumen. Experiments conducted to investigate the impact of the intensity of agitation by impeller on the generation of peroxide indicate the peroxide production declined on reducing the impeller rpm indicating the effect on oxygen transfer in the catholyte. The results indicated the need to balance the impeller rpm to achieve good oxygen transfer without the associated undesirable generation of graphite fines.

A concentration of 0.041 M peroxide, approximately twice the concentration of peroxide employed in conventional brightening of TMP, was obtained in the new undivided reactor incorporating a SS sparger plate. An electrolyte of 1 M Na₂CO₃ was used at 60°C with
Chapter 6. General Discussion

water cooled platinised titanium anode. Peroxide concentration increased due to its production on the graphite cathode by electroreduction of oxygen and by the hydrolysis of percarbonate formed on the anode. Experiments conducted with a SS water cooled anode resulted in metal ion contamination of the electrolyte from the dissolving anode.

Results from the in-situ generation of peroxide with pyrolytic graphite indicate the peroxide concentration achieved was influenced by the age of the graphite. Repeated use of the same graphite possibly resulted in changes to the electroactive surface. This was shown by the varying yield of peroxide with the same type of graphite of different age. The results also indicate friability of the graphite leading to fines production is influenced by the age of graphite and the fines component decreases as the number of times of graphite use increases.

Results from the experiments conducted with UCAR 1, Sigradur-G and pyrolytic graphite indicate the peroxide production is influenced by the type of particulate graphite cathode. A steep fall in peroxide production was observed on replacing pyrolytic graphite with UCAR 1 type. Experimental results with Sigradur-G graphite indicate loss of integrity of the cathode bed due to the surface properties of the graphite resulting in decreased efficiency. Several types of surfactants were evaluated to alter the surface properties to maintain the integrity of the bed and the results indicate the surfactants impede oxygen transfer in the process, jeopardising peroxide production.

Oxygen flow was empirically optimized taking in to consideration the integrity of the particulate graphite bed. Results indicate at too high a flow rate, the particulate graphite ceases to exist as a bed resulting in loss of conductivity and the consequent decline in
Chapter 6. General Discussion

yield of peroxide.

Experiments were conducted to evaluate the effect of alkali darkening of TMP in in-situ brightening during initial stages of the run when very little or no peroxide was present. The results indicate the occurrence of darkening of pulp which could not be reversed by the subsequent presence of a very high concentration of peroxide.

The TMP was successfully brightened in-situ when the mixing was adjusted to disperse oxygen without degrading the graphite and an initial concentration of peroxide was present to counter the alkali darkening. These conditions gave a brightness increase up to 10% ISO with a yellowness drop up to 15% after a 90 minutes brightening run with initial peroxide concentration of about 0.03 M. Doubling the brightening time to 180 minutes gave no further brightness gain, may be due to the interacting effects of pH and peroxide concentration on alkali darkening and chromophore oxidation in the longer brightening runs.
Chapter 7

Conclusions and Recommendations

Conclusions

TMP of 1% consistency was successfully brightened in-situ to 53% ISO brightness, achieving a brightness gain of 10% ISO. In-situ brightening of TMP represents an interesting integration of the two separate processes, namely generation of hydrogen peroxide and the conventional brightening of TMP into a single procedure.

Preliminary cost calculations indicate an operating cost of in-situ brightening approximately US$ 3850 per ton of OD TMP, reflecting the cost of 1 M Na₂CO₃ as electrolyte, 9300 cubic meters of oxygen and 6000 Kw.hrs of power per ton of pulp. When compared to the cost of conventional brightening of TMP with peroxide at US$ 33 per ton of OD TMP, the cost of in-situ brightening appears unrealistically high.

The economics indicate the cost of Na₂CO₃ and oxygen comprise 95% of the cost of in-situ brightening. The cost of in-situ brightening could be brought down to about US$ 180 by incorporating a system to recycle the electrolyte and the oxygen that is vented in the existing system.
Chapter 7. Conclusions and Recommendations

Recommendations

The following recommendations are suggested for future work in in-situ brightening of TMP.

1. Further investigation of the effect of factors such as pulp consistency, graphite age, size and type, oxygen flow, agitation, depth of particulate graphite bed, temperature, current, pH, concentration of Na$_2$CO$_3$, etc.

2. Design of a system to recover and recycle the electrolyte and the oxygen to achieve cost efficiency.

3. Design of a mechanical separation system based on centrifuge to separate the brightened pulp and the graphite.

4. Incorporation of a method to measure concentrations of hydrogen peroxide in-situ would be helpful in on-line monitoring and measurement.

5. Studies to search for a possible new electro-catalyst for oxygen reduction to peroxide which does not produce fines that contaminate the pulp.
Bibliography.


Bibliography


Bibliography


Appendix A

Current Efficiency of Hydrogen Peroxide Generation, Run 84

Hydrogen peroxide is generated on a graphite cathode via Reaction 4.

\[
\text{O}_2 + \text{H}_2\text{O} + 2e \rightarrow \text{HO}_2^- + \text{OH}^- \quad \text{Rxn 4}
\]

Average current efficiency of the process over a particular time is calculated from

\[
\text{Current efficiency} = \frac{nFR}{I} \quad \text{(1)}
\]

Where

- \(n\) = Electron stoichiometry for Reaction 4
- \(F\) = Faraday number (96480 coulombs/equivalent)
- \(R\) = Production rate of hydrogen peroxide (kmole/s)
- \(I\) = Total current (kAmp)

At 2 A current, after 15 minutes of Run 84, hydrogen peroxide concentration in 500 ml catholyte is 0.0059 M.

Electron stoichiometry for Reaction 4 = 2

H\textsubscript{2}O\textsubscript{2} Generation rate at the end of 15 min. = \((0.0059/2)\) mole / \((15 \times 60) \times 10^3\)

= \(3.28 \times 10^{-9}\) kmoles/sec

Current Efficiency = \(2 \times 96480 \times 3.28 \times 10^{-9} / (2 \times 10^{-3}) = 0.32\)
Appendices

Appendix B. Hydrogen Peroxide Titration Calculation

Hydrogen peroxide reacts with permanganate by Reaction 10.

\[ 2\text{MnO}_4^- + 5\text{H}_2\text{O}_2 + 6\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{O}_2 + 8\text{H}_2\text{O} \quad \text{Rxn 10} \]

A 5 ml sample of catholyte was collected for peroxide analysis using a pipette with the tip covered by fine filter cloth material mesh to exclude graphite and pulp in the sample. The 5 ml sample was analyzed for the hydrogen peroxide as per standard procedure (33).

The analysis was carried out in the absence of pulp and graphite. The 5 ml sample solution was added to 200 ml of 0.5 M ice-cold sulfuric acid in a 250 ml standard flask. Two drops of Ferroin was added to the solution as indicator and the sample was titrated against 0.01 N KMnO₄.

Hydrogen peroxide concentration was determined from the quantity of KMnO₄ consumed, where 1 ml of 0.01 N KMnO₄ titrated corresponds to a sample concentration of 0.001 M H₂O₂. In Run 88 after 105 minutes, 25.2 ml of 0.01 N KMnO₄ was consumed, on titration, by a 5 ml sample of the catholyte.

Hydrogen peroxide concentration in the catholyte = 25.2 ml × 0.001 M = 0.0252 M
Appendices

Appendix C. Experimental Results

Table C.1. Effect of Polypropylene Diaphragm on the Generation of Hydrogen Peroxide

Conditions

Electrolyte: 500 ml 0.5 M Na₂SO₄ + 0.004 M NaOH
DTPA dosage: 2.168 × 10⁻⁴ M
Cathode: -0.42 + 0.29 mm size UCAR 1 graphite
Temperature: 25°C
Oxygen flow: 4.88 liters/min @ STP
Duration of run: 60 minutes
Current: 2 amps
H₂O₂ analysis interval: 15 minutes

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<th>Final H₂O₂ conc’n (M)</th>
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<tr>
<td>8-9</td>
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Appendix C. Experimental Results

Table C.2. Effect of Diaphragm on pH Progression

Conditions Runs 19-24

Diaphragm: Polypropylene
Electrolyte: 0.5 M Na₂SO₄ + 0.004 M NaOH
DTPA dosage: 2.168 × 10⁻⁴ M
Cathode: -0.42 + 0.29 mm size UCAR 1 graphite
Temperature: 25°C
Oxygen flow: 4.88 liters/min @ STP
Duration of run: 60 minutes
Current: 2 amps

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<th>Without diaphragm</th>
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</tr>
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<td>7.92</td>
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<tr>
<td>1/2&quot; dia graphite</td>
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<td>8.10</td>
</tr>
</tbody>
</table>
### Appendix C. Experimental Results

Table C.3. Effect of Polyester Diaphragm on the Generation of Hydrogen Peroxide

#### Conditions

- Electrolyte: 500 ml 0.5 M Na$_2$SO$_4$ + 0.004 M NaOH
- DTPA dosage: 2.168 × 10$^{-4}$ M
- Cathode: -0.42 + 0.29 mm size UCAR 1 graphite
- Temperature: 25°C
- Oxygen flow: 4.88 liters/min @ STP
- Duration of run: 60 minutes
- Current: 2 amps
- H$_2$O$_2$ analysis interval: 15 min

<table>
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<tr>
<th>Run#</th>
<th>Anode</th>
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<th>H$_2$O$_2$ conc’n (M)</th>
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</tr>
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</table>
Appendix C. Experimental Results

Table C.4. Effect of Polyester Screen Diaphragm on the Generation of Hydrogen Peroxide

**Conditions**

Electrolyte: 500 ml 0.5 M Na₂SO₄ + 0.004 M NaOH  
DTPA dosage: 2.168 × 10⁻⁴ M  
Cathode: -0.42 + 0.29 mm size UCAR 1 graphite  
Temperature: 25°C  
Oxygen flow: 4.88 liters/min @ STP  
Duration of run: 60 minutes  
Current: 2 amps  
H₂O₂ analysis interval: 15 min

<table>
<thead>
<tr>
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<th>pH</th>
<th>Final H₂O₂ conc’n (M)</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>start</td>
<td>end</td>
</tr>
<tr>
<td>31</td>
<td>1/4&quot; od ss</td>
<td>12.51</td>
<td>12.10</td>
</tr>
<tr>
<td>32</td>
<td>1/8&quot; od ss</td>
<td>12.5</td>
<td>12.05</td>
</tr>
<tr>
<td>33</td>
<td>1/2&quot; dia graphite</td>
<td>12.51</td>
<td>10.20</td>
</tr>
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<td>1/2&quot; dia graphite</td>
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<td>6.40</td>
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<td>36</td>
<td>1/8&quot; od ss</td>
<td>11.21</td>
<td>9.05</td>
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</tbody>
</table>
Appendix C. Experimental Results

Table C.5. Effect of Hydrogen Peroxide Generation with 0.01% Surfactant in the Electrolyte

Conditions

Electrolyte: 500 ml 0.5 M Na₂SO₄ + 0.004 M NaOH
DTPA dosage: $2.168 \times 10^{-4}$ M
Cathode: -0.42 + 0.29 mm size UCAR 1 graphite
Surfactant: 0.01% in catholyte
Temperature: 25°C
Oxygen flow: 4.88 liters/min @ STP
Duration of run: 60 minutes
Current: 2 amps
H₂O₂ analysis interval: 15 min

<table>
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<tr>
<th>Run#</th>
<th>Anode</th>
<th>pH</th>
<th>H₂O₂ conc’n (M)</th>
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<td>end</td>
</tr>
<tr>
<td>37</td>
<td>1/4&quot; od ss, polypropylene diaphragm</td>
<td>11.25</td>
<td>7.95</td>
</tr>
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<td>38</td>
<td>1/2&quot; dia graphite, polypropylene diaphragm</td>
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<td>7.04</td>
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<td>39</td>
<td>1/4&quot; od ss, polyester diaphragm</td>
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<td>8.05</td>
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<td>40</td>
<td>1/4&quot; od ss, PTFE diaphragm</td>
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<td>9.10</td>
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<tr>
<td>43</td>
<td>Pt, polypropylene diaphragm</td>
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<td>10.90</td>
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<tr>
<td>36</td>
<td>1/8&quot; od ss</td>
<td>11.21</td>
<td>9.05</td>
</tr>
</tbody>
</table>
Appendix C. Experimental Results

Table C.6. Effect of New Batch of UCAR 1 graphite on the Generation of Hydrogen Peroxide

Conditions

Electrolyte*: (i) 500 ml 0.5 M Na₂SO₄ + 0.004 M NaOH
(ii) 500 ml 0.5 M Na₂SO₄ + 0.052 M di sodium tetraborate + 0.1 M NaOH
Diaphragm: Polypropylene
Cathode: -0.42 + 0.29 mm size UCAR 1 graphite
DTPA dosage: 2.168 × 10⁻⁴ M
Size of Pt-Ti anode: 7 cm length × 1 cm width × 0.5 cm thick
Buffer: 0.052 M di sodium tetraborate
Temperature: 25°C
Oxygen flow: 4.88 liters/min @ STP
Duration of run: 60 minutes
Current: 2 amps
H₂O₂ analysis interval: 15 min

<table>
<thead>
<tr>
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<th>Anode</th>
<th>pH</th>
<th>Final H₂O₂ conc’n (M)</th>
<th>Final C.E (%)</th>
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</thead>
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<td></td>
<td>start</td>
<td>end</td>
</tr>
<tr>
<td>45</td>
<td>(i)</td>
<td>1/4&quot; od ss</td>
<td>11.20</td>
<td>7.62</td>
<td>0</td>
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<tr>
<td>46</td>
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<td>1/4&quot; od ss</td>
<td>11.22</td>
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<td>0</td>
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<tr>
<td>47</td>
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<td>Pt-Ti</td>
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<td>10.46</td>
<td>0</td>
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<tr>
<td>48</td>
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<td>Pt-Ti</td>
<td>11.21</td>
<td>10.95</td>
<td>0</td>
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</table>
**Appendix C. Experimental Results**

Table C.7. Hydrogen Peroxide Generation in Divided Membrane Reactor

**Conditions**

Catholyte*: (i) 500 ml 0.5 M Na$_2$SO$_4$ + 0.004 M NaOH
(ii) 500 ml 0.5 M Na$_2$SO$_4$ + 0.052 M di sodium tetraborate + 0.1 M NaOH
DTPA dosage: $2.168 \times 10^{-4}$ M

Cathode: 500 ml UCAR 1 graphite particles of size -0.42 + 0.29 mm
Anode: 1/4" od SS tube
Cathode contact: SS screen of area 115 cm$^2$
Buffer: 0.052 M di sodium tetraborate
Temperature: 25°C
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP
Duration of run: 60 minutes
H$_2$O$_2$ analysis interval: 15 min

<table>
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<tr>
<th>Run #</th>
<th>Catholyte*</th>
<th>Anolyte</th>
<th>pH</th>
<th>Final H$_2$O$_2$ conc'n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
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<td>end</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>(i)</td>
<td>1 M Na$_2$CO$_3$</td>
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<td>12.34</td>
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<td>11.25</td>
<td>12.29</td>
<td>0.006</td>
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<tr>
<td>58</td>
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<td>2 M NaOH</td>
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<td>12.29</td>
<td>0.006</td>
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<tr>
<td>59</td>
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<td>12.20</td>
<td>0.005</td>
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<td>11.98</td>
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<tr>
<td>61</td>
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<td>&quot;</td>
<td>11.23</td>
<td>12.19</td>
<td>0.004</td>
</tr>
<tr>
<td>62</td>
<td>(i)</td>
<td>&quot;</td>
<td>10.25</td>
<td>12.24</td>
<td>0.006</td>
</tr>
<tr>
<td>63</td>
<td>(ii)</td>
<td>&quot;</td>
<td>9.31</td>
<td>11.78</td>
<td>0.01</td>
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</tbody>
</table>
Appendix C. Experimental Results

Table C.8. Effect of Chelants and Stabilisers on Hydrogen Peroxide Generation

Conditions

Catholyte*: (i) 500 ml 0.5 M Na₂SO₄ + 0.002 M NaOH
(ii) 500 ml 0.5 M Na₂SO₄ + 0.052 M di sodium tetraborate + 0.1 M NaOH
DTPA in catholyte: $8.67 \times 10^4$ M
MgSO₄ in catholyte: $5.68 \times 10^4$ M
Na₂SiO₃ in catholyte: $3.36 \times 10^2$ M
Cathode: 500 ml UCAR 1 graphite particles of size -0.42 + 0.29 mm
Anode: 1/4" od SS tube
Cathode contact: SS screen of area 115 cm²
Buffer: 0.052 M di sodium tetraborate
Temperature: 25°C
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP
Duration of run: 60 minutes
H₂O₂ analysis interval: 15 min

<table>
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<tr>
<th>Run #</th>
<th>Catholyte*</th>
<th>Anolyte</th>
<th>pH</th>
<th>Final H₂O₂ conc'n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td>start</td>
<td>end</td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>(i)</td>
<td>1 M Na₂CO₃</td>
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<td>12.24</td>
<td>0.002</td>
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<td>&quot;</td>
<td>11.20</td>
<td>12.14</td>
<td>0.017</td>
</tr>
<tr>
<td>75</td>
<td>(i)</td>
<td>2 M NaOH</td>
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<td>12.19</td>
<td>0.019</td>
</tr>
<tr>
<td>76</td>
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<td>&quot;</td>
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<td>12.17</td>
<td>0.016</td>
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<td>77</td>
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<td>&quot;</td>
<td>10.25</td>
<td>12.22</td>
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</tbody>
</table>
Appendix C. Experimental Results

Table C.9. Effect of Graphite Plate Cathode Contact on Hydrogen Peroxide Generation

Conditions

Catholyte*: (i) 500 ml 0.5 M Na₂SO₄ + 0.002 M NaOH  
(ii) 500 ml 0.5 M Na₂SO₄ + 0.052 M di sodium tetraborate + 0.1 M NaOH  
DTPA in catholyte: $8.67 \times 10^{-4}$ M  
MgSO₄ in catholyte: $5.68 \times 10^{-4}$ M  
Na₂SiO₃ in catholyte: $3.36 \times 10^{-2}$ M  
Cathode: 500 ml UCAR 1 graphite particles of size -0.42 + 0.29 mm  
Anode: 1/4" od SS tube  
Cathode contact: graphite sheet of area 106 cm²  
Buffer: 0.052 M di sodium tetraborate  
Temperature: 25°C  
Current: 2 amps  
Oxygen flow: 4.88 liters/min @ STP  
Duration of run: 60 minutes  
H₂O₂ analysis interval: 15 min

<table>
<thead>
<tr>
<th>Run#</th>
<th>Catholyte*</th>
<th>Anolyte</th>
<th>pH</th>
<th>Final H₂O₂ conc'n (M)</th>
<th>C.E (%)</th>
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<td></td>
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</tr>
<tr>
<td>78</td>
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<td>1 M Na₂CO₃</td>
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<td>12.18</td>
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<tr>
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<td>11.20</td>
<td>12.14</td>
<td>0.013</td>
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<tr>
<td>80</td>
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<td>12.18</td>
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<td>10.00</td>
<td>11.97</td>
<td>0.011</td>
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</tbody>
</table>
Appendix C. Experimental Results

Table C.10. Effect of Increase of Process Temperature on Hydrogen Peroxide Generation

Conditions

Catholyte*: (i) 500 ml 0.5 M Na₂SO₄ + 0.01 M NaOH
   (ii) 500 ml 0.5 M Na₂SO₄ + 0.052 M di sodium tetraborate + 0.16 M NaOH
   (iii) 500 ml 0.5 M Na₂CO₃ + 0.06 M NaOH
DTPA in catholyte: 8.67 x 10⁻⁴ M
MgSO₄ in catholyte: 5.68 x 10⁻⁴ M
Na₂SiO₃ in catholyte: 3.36 x 10⁻² M
Cathode: 500 ml UCAR 1 graphite particles of size -0.42 + 0.29 mm
Anode: 1/4" od SS tube
Cathode contact: SS screen of area 115 cm²
Buffer: 0.052 M di sodium tetraborate
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP
H₂O₂ analysis interval: 15 min

<table>
<thead>
<tr>
<th>Run #</th>
<th>Catholyte*</th>
<th>Anolyte</th>
<th>pH start</th>
<th>pH end</th>
<th>Time (min)</th>
<th>Temp (°C)</th>
<th>H₂O₂ conc’n (M)</th>
<th>C.E (%)</th>
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</thead>
<tbody>
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<td>2 M NaOH</td>
<td>11.15</td>
<td>11.63</td>
<td>105</td>
<td>60</td>
<td>0.022</td>
<td>17</td>
</tr>
<tr>
<td>85</td>
<td>(ii)</td>
<td>&quot;</td>
<td>11.20</td>
<td>11.65</td>
<td>90</td>
<td>60</td>
<td>0.018</td>
<td>16</td>
</tr>
<tr>
<td>86</td>
<td>(i)</td>
<td>2 M NaOH</td>
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<td>11.20</td>
<td>105</td>
<td>80</td>
<td>0.007</td>
<td>5</td>
</tr>
<tr>
<td>87</td>
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<td>11.15</td>
<td>11.63</td>
<td>120</td>
<td>60</td>
<td>0.020</td>
<td>13</td>
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<tr>
<td>88</td>
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<td>89</td>
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<td>60</td>
<td>0.017</td>
<td>23</td>
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</table>
Appendix C. Experimental Results

Table C.11. Current Efficiency of Hydrogen Peroxide Generation, Run 84

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>( \text{H}_2\text{O}_2 ) conc’n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.15</td>
<td>3.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>11.19</td>
<td>3.3</td>
<td>0.006</td>
<td>32</td>
</tr>
<tr>
<td>30</td>
<td>11.20</td>
<td>3.2</td>
<td>0.010</td>
<td>27</td>
</tr>
<tr>
<td>45</td>
<td>11.23</td>
<td>3.1</td>
<td>0.014</td>
<td>24</td>
</tr>
<tr>
<td>60</td>
<td>11.26</td>
<td>3.1</td>
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<td>22</td>
</tr>
<tr>
<td>75</td>
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<td>3.0</td>
<td>0.019</td>
<td>21</td>
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Table C.12. Current Efficiency of Hydrogen Peroxide Generation, Run 85

<table>
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<th>pH</th>
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<th>( \text{H}_2\text{O}_2 ) conc’n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
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<td>0</td>
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<td>0</td>
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<td>3.5</td>
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<td>27</td>
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<td>45</td>
<td>11.36</td>
<td>3.5</td>
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<td>23</td>
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<td>60</td>
<td>11.53</td>
<td>3.4</td>
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<td>21</td>
</tr>
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<td>75</td>
<td>11.61</td>
<td>3.2</td>
<td>0.018</td>
<td>19</td>
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<tr>
<td>90</td>
<td>11.65</td>
<td>3.2</td>
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<td>16</td>
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</table>
Appendix C. Experimental Results

Table C.13. Current Efficiency of Hydrogen Peroxide Generation, Run 87

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
<th>C.E (%)</th>
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<td>27</td>
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<td>23</td>
</tr>
<tr>
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<td>3.2</td>
<td>0.014</td>
<td>19</td>
</tr>
<tr>
<td>75</td>
<td>11.54</td>
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<td>0.016</td>
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<td>0.019</td>
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<tr>
<td>120</td>
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<td>0.020</td>
<td>13</td>
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Table C.14. Current Efficiency of Hydrogen Peroxide Generation, Run 88

<table>
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<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
<th>C.E (%)</th>
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<td>11.38</td>
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<td>45</td>
<td>11.46</td>
<td>3.1</td>
<td>0.016</td>
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</tr>
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<td>11.50</td>
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<td>3.1</td>
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<tr>
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<td>11.61</td>
<td>3.1</td>
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<td>105</td>
<td>11.65</td>
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<td>19</td>
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</table>
Appendix C. Experimental Results

Table C.15. Effect of Reduced Process Temperature on Hydrogen Peroxide Generation

Conditions Run 89

**Anolyte**: 2 M NaOH  
**Catholyte**: 1 M Na₂CO₃ + 0.06 M NaOH  
DTPA in catholyte: 8.67 × 10⁻⁴ M  
MgSO₄ in catholyte: 5.68 × 10⁻⁴ M  
Na₂SiO₃ in catholyte: 3.36 × 10⁻² M  
Cathode: 500 ml UCAR 1 graphite particles of size -0.42 + 0.29 mm  
Anode: 1/4" od SS tube  
Cathode contact: SS screen of area 115 cm²  
Temperature: 25°C  
Current: 2 amps  
Oxygen flow: 4.88 liters/min @ STP  
H₂O₂ analysis interval: 15 min

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
<th>C.E (%)</th>
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</thead>
<tbody>
<tr>
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<td>0</td>
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<td>30</td>
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<td>4.4</td>
<td>0.025</td>
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</table>
Appendix C. Experimental Results

Table C.16. Effect of Different Anolyte on Hydrogen Peroxide Generation

Conditions Run 92

Anolyte: 1 M Na₂CO₃
Catholyte: 1 M Na₂CO₃ + 0.06 M NaOH
DTPA in catholyte: 8.67 \times 10⁴ M
MgSO₄ in catholyte: 5.68 \times 10⁴ M
Na₂SiO₃ in catholyte: 3.36 \times 10⁻² M
Cathode: 500 ml UCAR 1 graphite particles of size -0.42 + 0.29 mm
Anode: 1/4" od SS tube
Cathode contact: SS screen of area 115 cm²
Temperature: 60°C
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP
H₂O₂ analysis interval: 15 min

<table>
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<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
<th>C.E (%)</th>
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<tr>
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<td>11.12</td>
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<td>0</td>
<td>0</td>
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<td>15</td>
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<td>3.8</td>
<td>0.006</td>
<td>32</td>
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<td>30</td>
<td>11.45</td>
<td>3.8</td>
<td>0.008</td>
<td>21</td>
</tr>
<tr>
<td>45</td>
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<td>3.8</td>
<td>0.011</td>
<td>20</td>
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<td>11.57</td>
<td>3.8</td>
<td>0.013</td>
<td>17</td>
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</tbody>
</table>
### Appendix C. Experimental Results

Table C.17. Effect of Increased Current on Hydrogen Peroxide Generation

**Conditions Run 93**

- **Anolyte**: 2 M NaOH
- **Catholyte**: 1 M Na$_2$CO$_3$ + 0.06 M NaOH
- DTPA in catholyte: $8.67 \times 10^{-4}$ M
- MgSO$_4$ in catholyte: $5.68 \times 10^{-4}$ M
- Na$_2$SiO$_3$ in catholyte: $3.36 \times 10^{-2}$ M
- **Cathode**: 500 ml UCAR 1 graphite particles of size -0.42 + 0.29 mm
- **Anode**: 1/4" od SS tube
- **Cathode contact**: SS screen of area 115 cm$^2$
- **Temperature**: 60°C
- **Current**: 4.2 amps
- **Oxygen flow**: 4.88 liters/min @ STP
- H$_2$O$_2$ analysis interval: 15 min

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H$_2$O$_2$ conc’n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
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<td>43</td>
</tr>
<tr>
<td>30</td>
<td>11.50</td>
<td>4.6</td>
<td>0.011</td>
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<td>45</td>
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<td>4.6</td>
<td>0.012</td>
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<td>60</td>
<td>11.62</td>
<td>4.5</td>
<td>0.014</td>
<td>19</td>
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</tbody>
</table>
Appendix C. Experimental Results

Table C.18. Effect of Reduced Cathode Contact Area on Hydrogen Peroxide Generation

Conditions Run 95

Anolyte: 2M NaOH
Catholyte: 0.5 M Na$_2$SO$_4$ + 0.01 M NaOH
DTPA in catholyte: $8.67 \times 10^{-4}$ M
MgSO$_4$ in catholyte: $5.68 \times 10^{-4}$ M
Na$_2$SiO$_3$ in catholyte: $3.36 \times 10^{-2}$ M
Cathode: 500 ml UCAR 1 graphite particles of size -0.42 + 0.29 mm
Anode: 1/4" od SS tube
Cathode contact: SS screen of area 115 cm$^2$
Temperature: 60°C
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP
H$_2$O$_2$ analysis interval: 15 min

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<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H$_2$O$_2$ conc’n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
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<td>0</td>
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<td>5.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>11.15</td>
<td>5.3</td>
<td>0.005</td>
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<td>30</td>
<td>11.42</td>
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<td>45</td>
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<td>5.1</td>
<td>0.009</td>
<td>16</td>
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<td>60</td>
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<td>5.0</td>
<td>0.010</td>
<td>14</td>
</tr>
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<td>75</td>
<td>11.56</td>
<td>4.9</td>
<td>0.011</td>
<td>12</td>
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<td>90</td>
<td>11.65</td>
<td>4.8</td>
<td>0.011</td>
<td>10</td>
</tr>
</tbody>
</table>
Appendix C. Experimental Results

Table C.19. Effect of Various Types of Graphite Particles on Hydrogen Peroxide Generation

**Conditions**

Anolyte: 2 M NaOH  
Catholyte: 500 ml 0.5 M Na₂SO₄ + 0.01 M NaOH  
DTPA in catholyte: \(8.67 \times 10^{-4}\) M  
MgSO₄ in catholyte: \(5.68 \times 10^{-4}\) M  
Na₂SiO₃ in catholyte: \(3.36 \times 10^{-2}\) M  
Anode: 1/4" od SS tube  
Cathode contact: SS screen of area 115 cm²  
Temperature: 60°C  
Current: 2 amps  
Oxygen flow: 4.88 liters/min @ STP  
H₂O₂ analysis interval: 15 min

<table>
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<tr>
<th>Run #</th>
<th>graphite</th>
<th>Time (min)</th>
<th>pH</th>
<th>H₂O₂ conc’n (M)</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>start</td>
<td>end</td>
<td></td>
</tr>
<tr>
<td>96</td>
<td>Ultra carbon</td>
<td>75</td>
<td>11.16</td>
<td>11.70</td>
<td>0.021</td>
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<tr>
<td>97</td>
<td>UCAR 1 -1.651 + 0.5 mm</td>
<td>90</td>
<td>11.15</td>
<td>11.23</td>
<td>0.006</td>
</tr>
<tr>
<td>98</td>
<td></td>
<td>75</td>
<td>11.17</td>
<td>11.54</td>
<td>0.008</td>
</tr>
<tr>
<td>99</td>
<td>Pyrolytic carbon (without acid wash)</td>
<td>105</td>
<td>11.15</td>
<td>11.63</td>
<td>0.012</td>
</tr>
<tr>
<td>100</td>
<td>UCAR 1, &lt; 0.5 mm</td>
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<td>11.14</td>
<td>11.52</td>
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<tr>
<td>102</td>
<td>Pyrolytic carbon (acid cleaned)</td>
<td>120</td>
<td>11.15</td>
<td>11.54</td>
<td>0.01</td>
</tr>
<tr>
<td>109</td>
<td>Ni</td>
<td>75</td>
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<td>11.15</td>
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<tr>
<td>112</td>
<td>Sigradur-G</td>
<td>120</td>
<td>11.15</td>
<td>11.43</td>
<td>0.011</td>
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</tbody>
</table>
Appendix C. Experimental Results

Table C.20. In-situ Brightening of TMP with Pyrolytic Graphite

Conditions Run 103

Pulp: 1% consistency TMP
Cathode: 500 ml pyrolytic carbon
Anode: 1/4" od SS tube
Anolyte: 1000 ml 2 M NaOH
Catholyte: 500 ml 0.5 M Na$_2$SO$_4$ + 0.01 M NaOH
DTPA in catholyte: 8.67 x 10$^{-4}$ M
MgSO$_4$ in catholyte: 5.68 x 10$^{-4}$ M
Na$_2$SiO$_3$ in catholyte: 3.36 x 10$^{-2}$ M
Cathode contact: SS screen of area 115 cm$^2$
Temperature: 60°C
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP
H$_2$O$_2$ analysis interval: 30 min

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<th>Time (min)</th>
<th>pH</th>
<th>Volt (V)</th>
<th>H$_2$O$_2$ conc'n (M)</th>
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</thead>
<tbody>
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<td>3.9</td>
<td>0.001</td>
</tr>
<tr>
<td>30</td>
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<td>0.004</td>
</tr>
<tr>
<td>60</td>
<td>11.26</td>
<td>3.7</td>
<td>0.011</td>
</tr>
<tr>
<td>90</td>
<td>11.45</td>
<td>3.6</td>
<td>0.011</td>
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<th>Handsheet</th>
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<th>Yellowness %</th>
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</tr>
<tr>
<td>brightened</td>
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<td>53</td>
</tr>
</tbody>
</table>
Appendix C. Experimental Results

Table C.21. In-Situ Brightening of TMP with UCAR 1 Graphite

Conditions Run 108

Pulp: 1% consistency TMP
Cathode: 500 ml UCAR graphite of size -0.42 + 0.29 mm
Anode: 1/4" od SS tube
Cathode contact: SS of area 115 cm²
Anolyte: 1000 ml 2 M NaOH
Catholyte: 500 ml 0.5 M Na₂SO₄ + 0.01 M NaOH
DTPA in catholyte: 8.67 × 10⁻⁴ M
MgSO₄ in catholyte: 5.68 × 10⁻⁴ M
Na₂SiO₃ in catholyte: 3.36 × 10⁻² M
Temperature: 60°C
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP

<table>
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<tr>
<th>Parameter</th>
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<th>30 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>11.17</td>
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<td>11.6</td>
</tr>
<tr>
<td>H₂O₂ Conc’n (M)</td>
<td>0</td>
<td>0.011</td>
<td>0.013</td>
</tr>
<tr>
<td>C.E (%)</td>
<td>0</td>
<td>64</td>
<td>13.7</td>
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<th>Yellowness %</th>
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<td>32</td>
</tr>
<tr>
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<td>40</td>
</tr>
</tbody>
</table>
Appendix C. Experimental Results

Table C.22. Effect of High Intensity of Impeller Agitation on the Generation of Hydrogen Peroxide

Conditions Run 112

Cathode: 500 ml Sigradur-G graphite
Anode: 1/4" od SS tube
Cathode contact: SS screen of area 115 cm²
Anolyte: 1000 ml 2 M NaOH
Catholyte: 500 ml 0.5 M Na₂SO₄ + 0.01 M NaOH
DTPA in catholyte: 8.67 $\times$ 10⁻⁴ M
MgSO₄ in catholyte: 5.68 $\times$ 10⁻⁴ M
Na₂SiO₃ in catholyte: 3.36 $\times$ 10⁻⁹ M
No load impeller speed: 5600 rpm
Temperature: 60°C
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.15</td>
<td>3.9</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>11.23</td>
<td>3.5</td>
<td>0.004</td>
</tr>
<tr>
<td>60</td>
<td>11.26</td>
<td>3.5</td>
<td>0.006</td>
</tr>
<tr>
<td>90</td>
<td>11.32</td>
<td>3.3</td>
<td>0.009</td>
</tr>
<tr>
<td>120</td>
<td>11.43</td>
<td>3.2</td>
<td>0.011</td>
</tr>
</tbody>
</table>
Appendix C. Experimental Results

Table C.23. Effect of Reduced Impeller Speed on the Generation of Hydrogen Peroxide
Impeller Speed reduced by 25 % over Run 112

Conditions Run 113

Cathode: 500 ml Sigradur-G graphite
Anode: 1/4" od SS tube
Cathode contact: SS screen of area 115 cm²
Anolyte: 1000 ml 2 M NaOH
Catholyte: 500 ml 0.5 M Na₂SO₄ + 0.01 M NaOH
DTPA in catholyte: 8.67 × 10⁻⁴ M
MgSO₄ in catholyte: 5.68 × 10⁻⁴ M
Na₂SiO₃ in catholyte: 3.36 × 10⁻⁹ M
No load impeller speed: 4200 rpm
Temperature: 60°C
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP

<table>
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<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
</tr>
</thead>
<tbody>
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<td>4</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>11.27</td>
<td>3.7</td>
<td>0.004</td>
</tr>
<tr>
<td>60</td>
<td>11.28</td>
<td>3.5</td>
<td>0.007</td>
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<td>11.31</td>
<td>3.4</td>
<td>0.009</td>
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<tr>
<td>120</td>
<td>11.35</td>
<td>3.2</td>
<td>0.009</td>
</tr>
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</table>
Appendix C. Experimental Results

Table C.24. Effect of Reduced Impeller Speed on the Generation of Hydrogen Peroxide

Run 114 Impeller Speed reduced by 37 % over Run 112

Conditions Run 114

Cathode: 500 ml Sigradur-G graphite
Anode: 1/4" od SS tube
Cathode contact: SS screen of area 115 cm²
Anolyte: 1000 ml 2 M NaOH
Catholyte: 500 ml 0.5 M Na₂SO₄ + 0.01 M NaOH
DTPA in catholyte: 8.67 × 10⁻⁴ M
MgSO₄ in catholyte: 5.68 × 10⁻⁴ M
Na₂SiO₃ in catholyte: 3.36 × 10⁻⁹ M
No load impeller speed: 3528 rpm
Temperature: 60°C
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP

<table>
<thead>
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<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc'n (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.15</td>
<td>4.4</td>
<td>0</td>
</tr>
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<td>30</td>
<td>11.24</td>
<td>4.1</td>
<td>0.002</td>
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<td>60</td>
<td>11.30</td>
<td>3.8</td>
<td>0.006</td>
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<tr>
<td>90</td>
<td>11.56</td>
<td>3.6</td>
<td>0.008</td>
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</table>
Appendix C. Experimental Results

Table C.25. In-situ Brightening of TMP with Sigradur-G Graphite at Reduced Impeller Speed

Conditions Run 115

TMP: 1% consistency
Cathode: 500 ml Sigradur-G graphite
Anode: 1/4" od SS tube
Cathode contact: SS screen of area 115 cm²
Anolyte: 1000 ml 2 M NaOH
Catholyte: 500 ml 0.5 M Na₂SO₄ + 0.01 M NaOH
DTPA in catholyte: $8.67 \times 10^{-4}$ M
MgSO₄ in catholyte: $5.68 \times 10^{-4}$ M
Na₂SiO₃ in catholyte: $3.36 \times 10^{-9}$ M
No load impeller speed: 3500 rpm
Temperature: 60°C
Current: 2 amps
Oxygen flow: 4.88 liters/min @ STP

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
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<td>0.004</td>
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<tr>
<td>60</td>
<td>11.32</td>
<td>3.8</td>
<td>0.004</td>
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<td>90</td>
<td>11.40</td>
<td>3.6</td>
<td>0.005</td>
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<td>120</td>
<td>11.50</td>
<td>3.6</td>
<td>0.006</td>
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<tr>
<td>brightened</td>
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<td>39</td>
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</tbody>
</table>
Appendix C. Experimental Results

Table C.26. Effect of Improved Oxygen Sparging on In-situ Brightening of TMP

Conditions Run 116

TMP: 1% consistency  
Cathode: 500 ml Sigradur-G graphite  
Anode: 1/4" od SS tube  
Cathode contact: SS screen of area 115 cm²  
Anolyte: 1000 ml 2 M NaOH  
Catholyte: 500 ml 0.5 M Na₂SO₄ + 0.01 M NaOH  
DTPA in catholyte: $8.67 \times 10^{-4}$ M  
MgSO₄ in catholyte: $5.68 \times 10^{-4}$ M  
Na₂SiO₃ in catholyte: $3.36 \times 10^{-9}$ M  
No load impeller speed: 3500 rpm  
Temperature: 60°C  
Current: 2 amps  
Oxygen flow: 4.88 liters/min @ STP

<table>
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<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
</tr>
</thead>
<tbody>
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<td>0.004</td>
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<td>60</td>
<td>11.25</td>
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<td>0.005</td>
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<td>3.4</td>
<td>0.006</td>
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</tr>
<tr>
<td>brightened</td>
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<td>37</td>
</tr>
</tbody>
</table>

113
Appendix C. Experimental Results

Table C.27. Hydrogen Peroxide Generation in Undivided Reactor with UCAR 1 Graphite

Conditions Run 122

Cathode: 500 ml UCAR 1 graphite of size -0.42 + 0.29 mm
Anode: water cooled platinised titanium U tube
Area of anode in contact with electrolyte: 7.5 cm$^2$
Electrolyte: 500 ml 1 M Na$_2$CO$_3$ + 0.14 M NaOH
DTPA in catholyte: 8.67 $\times$ 10$^4$ M
MgSO$_4$ in catholyte: 5.68 $\times$ 10$^4$ M
Na$_2$SiO$_3$ in catholyte: 3.36 $\times$ 10$^9$ M
Temperature: 60°C
Current: 2 amps
Impeller rpm: 60
Oxygen flow: 0.31 liters/min @ STP

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H$_2$O$_2$ conc'n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.14</td>
<td>5.9</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>5.9</td>
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<td>75</td>
<td>11.05</td>
<td>5.9</td>
<td>0.025</td>
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</table>
Appendix C. Experimental Results

Table C.28. Hydrogen Peroxide Generation in Undivided Reactor with Pyrolytic Graphite

Conditions Run 124

Cathode: 500 ml pyrolytic graphite
Anode: water cooled platinised titanium U tube
Area of anode in contact with electrolyte: 7.5 cm²
Electrolyte: 500 ml 1 M Na₂CO₃ + 0.14 M NaOH
DTPA in catholyte: 8.67 × 10⁻⁴ M
MgSO₄ in catholyte: 5.68 × 10⁻⁴ M
Na₂SiO₃ in catholyte: 3.36 × 10⁻⁹ M
Temperature: 60°C
Current: 2 amps
Impeller rpm: 60
Oxygen flow: 0.31 liters/min @ STP

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc'n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5.7</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>5.8</td>
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</table>
Appendix C. Experimental Results

Table C.29. Hydrogen Peroxide Generation in Undivided Reactor with Water Cooled Anode

**Conditions** Run 125

Cathode: 500 ml pyrolytic graphite
Anode: water cooled stainless steel U tube
Area of anode in contact with electrolyte: 7.5 cm²
Electrolyte: 500 ml 1 M Na₂CO₃ + 0.14 M NaOH
DTPA in catholyte: $8.67 \times 10^{-4}$ M
MgSO₄ in catholyte: $5.68 \times 10^{-4}$ M
Na₂SiO₃ in catholyte: $3.36 \times 10^{-9}$ M
Temperature: 60°C
Current: 2 amps
Impeller rpm: 60
Oxygen flow: 0.31 liters/min @ STP

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
</tr>
</thead>
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<tr>
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<td>4.1</td>
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<td>4.2</td>
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<tr>
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</tbody>
</table>
Appendix C. Experimental Results

Table C.30. In-situ Brightening of TMP in Undivided Reactor with Pyrolytic Graphite

**Conditions**  Run 146

Pulp: 1% consistency TMP  
Cathode: 500 ml pyrolytic graphite  
Anode: water cooled platinised titanium U tube  
Area of anode in contact with electrolyte: 7.5 cm²  
Electrolyte: 500 ml 1 M Na₂CO₃ + 0.15 M NaOH  
DTPA in catholyte: 8.67 × 10⁻⁴ M  
MgSO₄ in catholyte: 5.68 × 10⁻⁴ M  
Na₂SiO₃ in catholyte: 3.36 × 10⁻⁹ M  
Temperature: 60°C  
Current: 2 amps  
Impeller rpm: 60  
Oxygen flow: 0.31 liters/min @ STP

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
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<th>Yellowness %</th>
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<td>26</td>
<td>16</td>
</tr>
</tbody>
</table>
Appendix C. Experimental Results

Table C.31. In-situ Brightening of TMP in Undivided Reactor with Pyrolytic Graphite

Conditions Run 153

Pulp: 1% consistency TMP
Cathode: 500 ml pyrolytic graphite
Anode: water cooled platinised titanium U tube
Area of anode in contact with electrolyte: 7.5 cm²
Electrolyte: 500 ml 1 M Na₂CO₃ + 0.14 M NaOH
DTPA in catholyte: 8.67 × 10⁻⁴ M
MgSO₄ in catholyte: 5.68 × 10⁻⁴ M
Na₂SiO₃ in catholyte: 3.36 × 10⁻⁹ M
Temperature: 60°C
Current: 2 amps
Impeller rpm: 60
Oxygen flow: 0.31 liters/min @ STP

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
<th>H₂O₂ conc’n (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<tr>
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</table>
Appendix C. Experimental Results

Table C.32. In-situ Brightening of TMP in Undivided Reactor with Pyrolytic Graphite

Conditions Run 156

Pulp: 1% consistency TMP  
Addition of pulp: after 60 minutes of run  
Volume of pulp-water mixture: 200 ml  
Cathode: 500 ml pyrolytic graphite  
Anode: water cooled platinised titanium U tube  
Area of anode in contact with electrolyte: 7.5 cm²  
Electrolyte, after the addition of pulp: 500 ml 1 M Na₂CO₃ + 0.14 M NaOH  
DTPA in catholyte: 8.67 × 10⁻⁴ M  
MgSO₄ in catholyte: 5.68 × 10⁻⁴ M  
Na₂SiO₃ in catholyte: 3.36 × 10⁻⁹ M  
Temperature: 60°C  
Current: 2 amps  
Impeller rpm: 60  
Oxygen flow: 0.31 liters/min @ STP

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>0</td>
<td>0</td>
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<th>Yellowness %</th>
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<tr>
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<td>47</td>
<td>19</td>
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</tbody>
</table>
Appendix C. Experimental Results

Table C.33. Effect of Age of Graphite on Peroxide Generation

Conditions

Cathode: 500 ml pyrolytic graphite
Anode: water cooled platinised titanium U tube
Area of anode in contact with electrolyte: 7.5 cm²
Electrolyte: 500 ml 1 M Na₂CO₃ + 0.1 M NaOH
DTPA in catholyte: $8.67 \times 10^4$ M
MgSO₄ in catholyte: $5.68 \times 10^4$ M
Na₂SiO₃ in catholyte: $3.36 \times 10^9$ M
Temperature: 60°C
Current: 2 amps
Impeller rpm: 60
Oxygen flow: 0.31 liters/min @ STP

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Run 124</th>
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<th>Run 142</th>
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</thead>
<tbody>
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</tr>
<tr>
<td>voltage(v)</td>
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<td>5.9</td>
<td>5.9</td>
<td>6.5</td>
</tr>
<tr>
<td>peroxide (M)</td>
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<td>0.041</td>
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</table>
Appendix C. Experimental Results

Table C.34. In-situ Brightening of TMP in Undivided Reactor with Pyrolytic Graphite

Conditions  Run 157

Pulp: 1% consistency TMP
Addition of pulp: after 60 minutes of run
Volume of pulp-water mixture: 200 ml
Cathode: 500 ml pyrolytic graphite
Anode: water cooled platinised titanium U tube
Area of anode in contact with electrolyte: 7.5 cm²
Electrolyte, after
the addition of pulp: 500 ml 1 M Na₂CO₃ + 0.14 M NaOH
DTPA in catholyte: 8.67 × 10⁻⁴ M
MgSO₄ in catholyte: 5.68 × 10⁻⁴ M
Na₂SiO₃ in catholyte: 3.36 × 10⁻⁹ M
Temperature: 60°C
Current: 2 amps
Impeller rpm: 60
Oxygen flow: 0.31 liters/min @ STP

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>11.06</td>
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<td>0.030</td>
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<td>150</td>
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<td>9.5</td>
<td>0.018</td>
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<thead>
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<th>Handsheet</th>
<th>Brightness % ISO</th>
<th>Yellowness %</th>
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</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>brightened</td>
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</tbody>
</table>
Appendix C. Experimental Results

Table C.35. In-situ Brightening of TMP in Undivided Reactor with Pyrolytic Graphite

Conditions Run 159

Pulp: 1% consistency TMP
Addition of pulp: after 60 minutes of run
Volume of pulp-water mixture: 200 ml
Cathode: 500 ml pyrolytic graphite
Anode: water cooled platinised titanium U tube
Area of anode in contact with electrolyte: 7.5 cm²
Electrolyte, after
the addition of pulp: 500 ml 1 M Na₂CO₃ + 0.14 M NaOH
DTPA in catholyte: $8.67 \times 10^4$ M
MgSO₄ in catholyte: $5.68 \times 10^4$ M
Na₂SiO₃ in catholyte: $3.36 \times 10^9$ M
Temperature: 60°C
Current: 2 amps
Impeller rpm: 60
Oxygen flow: 0.31 liters/min @ STP

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
<th>Voltage (V)</th>
<th>H₂O₂ conc’n (M)</th>
<th>C.E (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.17</td>
<td>8.0</td>
<td>0</td>
<td>0</td>
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<td>60</td>
<td>10.98</td>
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<td>240</td>
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<td>0.008</td>
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<table>
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<th>Yellowness %</th>
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<tbody>
<tr>
<td>unbrightened</td>
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<td>34</td>
</tr>
<tr>
<td>brightened</td>
<td>53</td>
<td>23</td>
</tr>
</tbody>
</table>
Glossary

Brightness: Reflectivity of paper sample using light of specified wave length (457nm), commonly used an index of brightness.

Cellulose: Material that forms the solid framework or cell walls of all plants. It is the fibrous substance that remains after the non-fibrous portions, such as lignin, have been removed from the pulp during the cooking and bleaching operations.

Chromophore: A covalently unsaturated group responsible for electronic absorption.

Consistency: The concentration of fiber in a pulp suspension expressed as the weight percentage of pulp in a pulp and water mixture.

CPPA: Canadian Pulp and Paper Association

Current density: Current / electrode area

Current efficiency: Actual rate of desired reaction / rate of desired reaction in stoichiometric equivalence with total current.

Divided reactor: Reactor divided by ionically conductive separators into two chambers holding anolyte and catholyte separately.

DTPA: Diethylenetriaminepentaacetic acid.

Extractive: Substance in wood, not an integral part of the cellular structure, that can be dissolved out by a solvent that does not react chemically with wood components.

Fiber: An elongated, tapering, thick walled cellular unit which is the structural component of woody plants.

Handsheet: A sheet made by depositing the fiber from a suspension of fiber and water on a laboratory sheet mold, followed by pressing and drying under carefully standardized conditions.

Hemicellulose: Short-chain polysaccharides having a DP of 15 or less.

Holocellulose: Total carbohydrate content of fibers.

Lignin: Natural binding constituent of the cells of wood. It is removed along with other
Appendix C. Experimental Results

organic materials during the pulping and bleaching stages.

**Mechanical pulp**: Pulp produced by reducing wooden logs and chips into their fiber components by the use of mechanical energy.

**Middle lamella**: Lignin-rich cementing layer between cell walls in plants.

**SHE**: Standard hydrogen electrode

**Stone groundwood**: Process in which fibers are loosened and peeled out from wooden logs by pressing against grindstones.

**Superficial current density**: Current density based on the area of the separator or the projected area of the electrode

**TAPPI**: Technical Association of Pulp and Paper Industry

**TMP**: Thermomechanical pulp, produced from pre-steamed wood chips by passing them into a refiner.