研 究 報 文

紫外線によるクラフトパルプの光漂白

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Photochemical Bleaching of Kraft Pulp by UV Radiation

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Abstract

Potential of ultraviolet (UV) radiation as a bleaching method for kraft pulps were investigated. Some conditions that improve bleaching efficiency based on a consumption of electricity were revealed. It was shown that photochemical bleaching efficiency was significantly improved by hot acid pretreatment that is often adopted in ECF bleaching sequence of hardwood pulp. It is thought that removal of iron ion from the pulp by hot acid treatment before UV irradiation contributes to better brightness enhancement by UV.

Simultaneous treatment by UV and ozone, which is a well-known system in water treatment area as advanced oxidation processes, was revealed to be highly effective method for photochemical bleaching. It is suspected that hydroxyl radicals are generated in UV/ozone treatment, and that they react with carbohydrates as well as lignin, resulting in considerable damage to fiber. However, this UV/ozone treatment did not seem to have a detrimental effect on strength of the pulp. When mill bleached hardwood pulp was treated by UV with ozone, brightness was enhanced from 86 to 91% while tensile strength of the treated pulp was almost the same as that of untreated one.

Although the efficiency needs to be improved further and more thorough understanding of the reaction mechanisms of photochemical bleaching is required, it is suggested that photochemical process has a possibility to be adopted as a certain part of industrial total chlorine free (TCF) bleaching sequence.

Keywords : photochemical bleaching, UV, hot acid treatment, ozone, advanced oxidation processes, hydroxyl radical

分類 : K₁ パルプの漂白一般, K₀ その他, F₁KP 製造一般 (アルカリパルプ含む)

1. はじめに

クラフトパルプの漂白プロセスは、旧来の塩素や二酸化塩素を主体としたものから塩素を使用しない ECF 法への転換が進んだ。これに伴い有機塩素化合物やクロロホルムの発存量・排出量の大幅な削減を達成できたものの、二酸化塩素による ECF 漂白ではクロレートの排出量が増加傾向にあることも報告されている¹⁾。

こうしたことから、二酸化塩素を使用しない漂白法が将

来像としては理想的であると考えられるが、近年の漂白工程で一般に用いられている、酸素、過酸化水素、オゾンといった、酸素系漂白剤のみを用いて二酸化塩素を全く使用せずに完成漂白パルプを得るのは、技術的には可能であるが漂白効率の面で問題がある。従って、二酸化塩素を使用しない漂白プロセスの実現には、新たな漂白要素技術の開発が必要と考えられる。

新たな漂白手段としては酵素、酸化触媒、過酢酸などを用いた報告例が知られているが²⁻⁴⁾、我々は次世代の漂白要

素技術のひとつの可能性として、紫外線（以下 UV）を用いた光技術に着目した。UV は可視光線と比較して強いエネルギーを有しており、酸化力を持つ。また薬物の残留や副生成物の発生がないといった特徴があり、殺菌や有機物分解を目的とした用排水処理の分野での適用例が増えている。UV が単独で用いられることもあるが、オゾンや過酸化水素などの酸化剤を併用し、高い酸化還元電位を有する非常に反応性の高いヒドロキシルラジカルを発生させて有機物を酸化分解させることができる。こうした方法は促進酸化処理（AOPs: advanced oxidation processes）と呼ばれ、注目を集めている⁵⁾。

近年では綿布の漂白に光技術を応用した例も見られる。綿布の漂白工程では多くの場合、塩素系漂白剤を用いた長時間の高温処理がされているが、光技術を用いて省エネルギー・ハロゲンフリーの低環境負荷漂白プロセスを開発したという報告がある⁶⁾。ところがこうした光技術のパルプ漂白への応用については、UV 照射による光反応でクラフトパルプの漂白、脱リグニンが起きるという報告例^{7,8)}はあるものの、いずれも漂白効率が非常に悪い。

UV 光源に関する技術の進展は、エネルギー効率の向上、光源の形状や得られる UV 波長の多様化など近年めざましいものがある。したがって光源を含めた反応条件の最適化により、効率の良いクラフトパルプの光漂白方法を開発できる可能性は充分にあると考えられる。また光漂白技術を開発するにあたり、これを現行のクラフトパルプ漂白プロセスにどう組み合わせていくのかも重要であるが、そのような視点からのアプローチは既往の報告には皆無である。

そこで本報告では、光漂白の効率を飛躍的に高めるために、有効で現実性のある反応助剤や反応条件、また前処理方法について広葉樹クラフトパルプを中心に検討した。さらに促進酸化処理のクラフトパルプ漂白への適用についても検討した。

2. 実 験

実験には工場で生産された酸素脱リグニン後パルプ、完成漂白パルプを使用した。

助剤の光漂白促進効果の検討に際しては、プラスチックバッグに針葉樹酸素脱リグニン後パルプ由来の手抄きシー

ト（ISO 白度 37.6%）と助剤（0.15 g/10 mL 水）を入れ、出力 16 W、主波長 254 nm の低圧水銀ランプ（㈱日本フォトサイエンス）で 2 時間照射後に、水洗して ISO 白度を測定した。なおこの実験では広葉樹パルプを用いた場合に UV 照射に伴いシートが形態を保持できなくなる例があったため、針葉樹パルプを使用した。

パルプの UV 照射処理に関するその他の実験では、2 L のメスシリンダーに 0.25% のパルプスラリーを満たしてスターラーで攪拌し、この中心に UV 光源を配置して UV を照射した。UV 光源としては、前述の出力 16 W で主波長 254 nm の低圧水銀ランプの他に、出力 20 W で主波長 310 nm、或いは出力 40 W で主波長 360 nm の低圧水銀ランプ（共に PHILIPS 社）を使用した。

パルプの加温酸処理を行う場合、標準条件としては硫酸で pH 3.0 に調整し、濃度を 10% としてプラスチックバッグに入れ、オートクレーブで 90℃、3 時間の処理を行った。処理後のパルプを濾紙で吸引ろ過後、孔径 20 μm のメンブレンフィルターでさらにろ過して得た濾液を硝酸で酸性にし、ICP 発光分光分析装置で金属イオンの定量を行った。

オゾンと UV による促進酸化処理の検討では、市販のオゾン発生装置を使用し、前述のメスシリンダーを用いたパルプスラリーへの UV 照射実験でオゾンガスをメスシリンダーの底部に吹き込んだ。この時の発生オゾンは 300 ppm、300 mg/h である。

パルプの ISO 白度は JIS P 8148、カップー価は JIS P 8211、濾水度は定法に従い測定した。叩解は PFI ミルを用いて行い、濾水度と比引張り強さを測定した（JIS P 8121・JIS P 8113）。

3. 結果と考察

3.1 光漂白の基本条件

本報告で用いた添加助剤と、UV 照射の有無で 2 時間処理後の ISO 白度を表 1 に示す。

薬品単体での白度向上が最も大きかったのは水素化ホウ素ナトリウムであり、2 時間の処理で ISO 白度は 13.9 ポイント向上した。UV 照射による白度向上を最も促進した薬品は過炭酸ナトリウムであり、2 時間処理後の ISO

Table 1 Improvement of the photochemical bleaching performance by additives, using softwood pulp after O₂ delignification.

Additives	ISO brightness (%) after 2 h treatment			Price ⁹⁾ Ratio, to NaOH price
	(A) Without UV radiation	(B) With UV radiation	(B-A)	
—	37.6	41.7	4.1	0
NaBH ₄	51.5	66.9	15.4	300
H ₂ O ₂ · Na ₂ CO ₃	44.4	65.6	21.2	6
NaOH	39.6	56.7	17.1	1
H ₂ O ₂	42.6	56.7	14.1	2~3
(C ₂ H ₅) ₂ NH	38.0	52.7	14.7	20

Fig. 1 Relationship between UV light source (main wavelength, electricity consumption), pH of hardwood pulp suspension, and ISO brightness after 2 hour UV treatment. The pulp suspension was 2 L, 0.25%.

Fig. 2 Effect of hot acid pretreatment and temperature on the efficiency of photochemical bleaching for hardwood. The pulp suspension was 2 L, 0.25% and temperature is the value at the beginning of photochemical treatment.

白色度は UV 照射の有無で 21.2 ポイントの違いを示した。

これら 2 つの薬品を助剤として用いることで UV 照射により得られる ISO 白色度を最大限に高くできることが分かったが、いずれも高価な薬品であり、薬品価格とのバランスで UV 照射による漂白の助剤として最も優れていたのは水酸化ナトリウムであると考えられた。

そこで助剤を水酸化ナトリウムとし、主波長の異なる低圧水銀ランプを用いて、UV 処理時の pH と 2 時間の UV 照射後の到達 ISO 白色度について調べた (図 1)。ランプの消費電力の違いを考慮すると、最も漂白効率が高い条件は主波長 254 nm, pH が 11.5 であると考えられた。

3.2 加温酸処理が光漂白性に及ぼす効果・処理温度の影響

酸素脱リグニン後広葉樹パルプを pH 11.5 にて主波長 254 nm の低圧水銀ランプで UV 照射処理した。図 2 に示すように、UV の照射に伴い経時的に白色度が上昇し、8

Fig. 3 Relationship between kappa number and ISO brightness for UV treated hardwood pulp with and without hot acid pretreatment.

時間程度の UV 照射 (積算照射量: 26 kW/kg-pulp) で白色度が 80% となった。これに対して、同じ酸素脱リグニン後パルプを加温酸処理した後に同様の条件で UV 照射した場合には、漂白効率が大幅に上昇し、5 時間程度の UV 照射 (積算照射量 16 kW/kg-pulp) で白色度 80% が得られた。

なお上記の加温酸処理後のパルプを用いて、初期のスラリー温度を 5°C、或いは 70°C として 2 時間の UV 照射処理を行った所、到達白色度はいずれの場合も初期のスラリー温度を 25°C とした場合を下回った。一般に光反応には熱依存性がなく、一方で低圧水銀ランプは通常 25°C 付近で UV 出力が最大になることはこの結果を支持していると考えられる。光処理はそれ自体がクリーンな漂白方法であるが、更に加熱に要するエネルギーが不要であることは注目に値する。

この実験において、銅価と ISO 白色度には図 3 に示すように高い相関があった。未晒パルプ中のリグニンが光反応により、主にフェノール性芳香環からのカルボン酸の生成や β -O-4 結合の開裂を経て低分子化するとの報告¹⁰⁾があり、本実験においても、同様の反応が起きている可能性が考えられる。

加温酸処理はパルプ中のヘキサセウロン酸 (以下 HexA) の加水分解や金属イオンの溶出に作用し、漂白薬品の無効な消費、分解やスケールの抑制、完成パルプの色戻りの減少などの効果が得られることが知られている。ここでは HexA と金属イオンのどちらが光漂白の効率に影響するのかを推定するために、以下の実験を行った。

まず、加温酸処理において温度や pH を変え、またキレート剤 (エチレンジアミン四酢酸ナトリウム) を対パルプ 0.05% 添加することで銅価や金属イオンの含有量が異なるパルプを調製して光漂白への影響を調べた。その結果、加温酸処理後の銅価と UV 処理後の白色度には明確な相関は見られなかったが (図 4)、加温酸処理後のパルプの濾液中の鉄イオン濃度、すなわち加温酸処理によりパルプから溶出した鉄イオンの量と UV 処理後の白色

Fig. 4 Relationship between kappa number after hot acid pretreatment (before UV treatment) and ISO brightness after 2 h UV treatment for hardwood pulp.

Fig. 5 Relationship between iron ion concentration of filtrate after hot acid pretreatment (before UV treatment) and ISO brightness after 2 h UV treatment for hardwood pulp.

度には正の相関が認められた (図5)。

また, HexA をほとんど含有していない針葉樹の酸素脱リグニン後パルプでも, 加温酸処理で光漂白の効率が向上することが判った (図6)。

光漂白の効率を高めるには鉄イオンの除去が非常に重要であることが示唆された。

3.3 UV とオゾンの促進酸化処理による漂白

加温酸処理済みの広葉樹パルプスラリーに UV 照射および/またはオゾン曝気処理を 2 時間行い, ISO 白色度を比較した (図7)。白色度の向上は UV 照射単独の処理では約 13 ポイント, オゾン曝気のみでは約 6 ポイントに留まったのに対して, UV 照射とオゾン曝気を同時に行うと約 26 ポイントに達した。UV 照射/オゾン曝気処理で白色度が 80% に到達するのに必要な UV の積算照射量は約 7.6 kW/kg-pulp であり, 酸素脱リグニン後のパルプを UV 照射のみで処理する場合よりも約 70% 少なくなった (表2)。

Fig. 6 Effect of hot acid pretreatment on the efficiency of photochemical bleaching, for softwood. The pulp suspension was 2 L, 0.25% and temperature at the beginning of photochemical treatment was 25°C.

Fig. 7 Effect of simultaneous treatment by UV and ozone on the efficiency of photochemical bleaching for hardwood.

以上のように, UV 照射処理のみでクラフトパルプの漂白を行うのは現状では非常に困難であるが, ECF 漂白の 1 工程として用いられる加温酸処理と組み合わせることや, 更にオゾンと UV の併用による促進酸化処理を行うなど, 様々な要素技術を応用することで光漂白の効率を飛躍的に高められると考えられた。

UV/オゾンなどの促進酸化処理で発生するヒドロキシルラジカルはリグニンの分解反応だけでなくセルロースの解重合も引き起こし, リグニンに対する反応性がセルロースに対する反応性の 5~6 倍程度と言われている¹¹⁾, 促進酸化処理によるパルプ強度への影響が予想される。そこで UV/オゾン処理のパルプ強度への影響を, 濾水度と手抄きシートの比引張り強さの関係で評価した (図8)。ここでは ISO 白色度 86% の完成漂白パルプを UV/オゾン処理に供し, ISO 白色度 91% のパルプを得たが, 比引張り強さの低下は認められなかった。本実験でのヒドロキシルラジカルの発生量は定量できていないが, ヒドロキシルラジカ

Table 2 Effect of pretreatment and photochemical treatment for hardwood pulp, on the consumption of electricity required for UV radiation.

Treated pulp	Photochemical treatment	Consumption of electricity* required to 80% ISO brightness (kWh/kg-pulp)
After O ₂ delignification	UV	26
After hot acid	UV	16
After hot acid	UV+O ₃	7.6

*Only for UV radiaion

Fig. 8 Influence of advanced oxidation process by UV and ozone on the tensile index of handsheets derived from mill bleached hardwood pulp (LBKP).

ルを積極的に発生させても条件次第では実際にパルプ強度に影響しない可能性を示しており、興味深い。

漂白に要するエネルギーは現行のECF漂白と比較して、なお大幅に過大であるが、加温酸処理との組み合わせや効果的な助剤との併用により、光漂白の効率を飛躍的に高められることが分かった。しかしながら本報告は非常に低濃度のパルプスラリーを用いた検討結果である。また光漂白の詳細なメカニズムについて解明する必要がある、開発を進めていく上で多くの課題がある。

今後は更なる光漂白条件の最適化、既存の漂白技術との組み合わせについての検討を進めると共に、上記の課題についても取り組み漂白効率の限界を見極めたい。また、UV技術は近年非常に進歩の速い分野であり、今後も多様な光源の実用化や、エネルギー変換効率の向上などが期待できる。こうした進歩にも注目しながら検討を進めていきたい。

4. ま と め

紫外線によるクラフトパルプの光 (UV) 漂白について

検討し、以下の知見を得た。

- ① NaOHを助剤として、パルプスラリーにUVを照射することで漂白が可能であった。
- ② 前処理として加温酸処理が有効であり、光漂白効率が向上した。この理由として、パルプ中の鉄イオンが光漂白のメカニズムに関与していることが示唆された。
- ③ UV照射とオゾン曝気を同時に行う促進酸化処理も、光漂白の効率向上に非常に有効であった。加温酸処理と促進酸化処理を利用することで、酸素脱リグニンパルプをUVで単独処理する場合と比較して電力消費量を約70%削減できた。
- ④ 促進酸化処理によってヒドロキシルラジカルの発生が予想されるが、実機完成パルプをUV/オゾン処理して得られたパルプでは強度の明確な低下は認められなかった。

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1. Introduction

The bleaching process of kraft pulp has been converted from one conventionally using chlorine and chlorine dioxide to ECF that does not use chlorine. This conversion has greatly reduced the production of organo-chlorine compounds and chloroform, and lowered their emission from mills. On the other hand, ECF bleaching that uses chlorine dioxide has increased the emission of chlorates¹⁾.

So, bleaching processes that do not depend on chlorine dioxide are thought to be idealistic in the future. Though bleaching processes which use such oxygen-oriented chemicals as oxygen, hydrogen peroxide and ozone without depending on chlorine dioxide are technically feasible, they have some problems in bleaching efficiency. We believe that new elemental technologies have to be developed for bleaching processes that do not need chlorine dioxide.

There are reports on using enzymes, oxidative catalysts and peracetic acid as new materials²⁻⁴⁾. We have been interested in ultra-violet light (abbreviated as UV) as one of potential elemental technologies. UV has a strong level of energy compared with visible light and a strong oxidative power. It does not generate any residuals and by-products from itself. The number of its applications in water and effluent treatment is increasing. It can be used as a sole technology, and moreover when it is used with other oxidative chemicals like ozone and hydrogen peroxide, it produces a hydroxyl radical, which has a high redox potential and is very reactive, and decomposes organic compounds. This method is attracting attention as advanced oxidation processes (AOPs)⁵⁾.

There are reports using UV radiation on the bleaching of cotton cloth. One paper claimed that a process using UV radiation reduced energy consumption, was free from halogen and was pro-environmental against conventional bleaching processes relying on chlorine compounds⁶⁾. Regarding its application on pulp bleaching, there are several papers reporting that UV radiation could bleach and delignify kraft pulp^{7,8)}. Their efficiencies of bleaching, however, were very low.

The technology on UV light has been developed re-

markably. Its energy efficiency has been improved, and various kinds of light sources and a wide range of UV wavelength have been available. It is probable that the efficiency of photochemical bleaching of kraft pulp could be developed by optimizing reaction conditions including light source selection. What's more, it is important that the process should be applicable to bleaching processes now being in use. However, no paper has been studied with this kind of approach yet.

In order to improve the efficiency of photochemical bleaching in a drastic level, we investigated additives that were effective and feasible, reaction conditions and pre-treatments in hardwood kraft pulp bleaching. We also studied applying advanced oxidation, which used oxidation reaction under UV radiation simultaneously, to kraft pulp bleaching.

2. Experiment

Pulp samples are one after oxygen delignification and one after fully bleached. They were produced in mill operation.

When the effect of additives on photochemical bleaching was investigated, softwood pulp after oxygen delignification was used instead of hardwood pulp. Hand sheets made from the softwood pulp (37.6% ISO brightness) and an additive (0.15 g/10 mL water) was sealed in a plastic bag, and was radiated by a low pressure mercury lamp whose output power was 16 W and whose main wavelength was 254 nm (made by Photoscience Japan Corp.) for 2 hours. Then, the hand sheets were washed and their ISO brightness was measured. The reason why hardwood pulp was not used in the experiment was that its hand sheets could not keep their sheet form in some cases.

In other experiments, pulp slurry of 0.25% was poured in a 2 L measuring cylinder, and was agitated by a stirrer. The UV lamp was located at the center and emitted radiation. As low pressure lamp sources, two other lamps, beside one described before, were used. They were one whose output power was 20 W and whose main wavelength was 310 nm and one whose output power was 40 W and whose main wavelength was 360 nm. Both lamps were made by Philips Electronics Japan, Ltd.

In case of the hot acid pretreatment, pulp slurry, of which consistency was 10%, was adjusted to pH 3.0 by sulfuric acid and was sealed in a plastic bag. Then, it was heated at 90°C for 3 hours in an autoclave. After the reaction, the pulp slurry was sucked through filter paper, and then was filtered through a membrane filter whose pore size was 20 nm. The filtrate was acidified by nitric acid. Metal ions in the filtrate were quantitatively measured by ICP atomic emission spectrometry.

In case of the advanced oxidation with ozone and UV, an ozone generator commercially available was used. Ozone gas was injected into the pulp slurry under UV radiation at the bottom of the measuring cylinder. The ozone gas consistency was 300 ppm and its production rate 300 mg/h.

ISO brightness of the pulp was measured by JIS P 8148, and kappa number of the pulp was measured by JIS P 8211. Freeness of the pulp was determined by usual method. Refining was done by PFI mill. Freeness and tensile factor of the resulting pulp were measured (JIS P 8121, JIS P 8113)

3. Result and discussion

3.1 Basic condition for photochemical bleaching

The effects of additives with and without UV radiation on ISO brightness were summarized in Table 1. Without the radiation, sodium tetrahydroborate showed the best improvement in brightness, and the gain was 13.9 points by ISO brightness. Under the radiation, sodium percarbonate gave the best improvement and the gain was 21.2 points by ISO brightness.

Though these two chemicals proved to be effective as an additive under UV radiation, they are very expensive. From cost performance evaluation, sodium hydroxide seemed to be the best.

Consequently, sodium hydroxide was selected as an additive. Then, the effect of two-hour radiation on brightness was studied with different low pressure mercury lamps under different pHs. Taking into account the difference in power consumption, the best condition was with the main wavelength of 254 nm at the pH of 11.5 (Fig. 1).

3.2 The effect of hot acid pretreatment on photochemical bleaching and the effect of temperature

Hardwood pulp after oxygen delignification was radiated with a low pressure mercury lamp whose main wavelength was 254 nm at the pH of 11.5. As in Fig. 2, the pulp brightness increased along with radiation time, and was 80% in 8 hours (accumulated radiation amount : 26 kW/kg-pulp). When the same pulp was pretreated with hot acid and then underwent the same treatment, a great improvement was observed. The brightness reached 80% in five-hour radiation (accumulated radiation amount : 16

kW/kg-pulp).

The same hot-acid treated pulp was radiated at two different initial temperatures, 5°C and 70°C, for 2 hours. The final brightness in both cases was less than that of the treatment whose initial slurry temperature was 25°C. Photochemical reaction is not dependent on temperature in general. The fact that the output power of low pressure mercury lamp is at its maximum around 25°C corresponds to the result and supports the independence of slurry temperature. Photochemical bleaching is a clean process in itself, and is deserved to be noticed for not requiring additional heat-up energy.

In this series of experiment, a strong relationship between the kappa number and the ISO brightness was observed as shown in Fig. 3. There is a report saying that lignin in unbleached pulp was decomposed to lower molecule compounds under photochemical reaction by generating carboxylic acids from phenol aromatic ring or by cleavage of β -O-4 bonding. It is probable that the same reactions occurred.

Hot acid pretreatment is known for hydrolyzing hexenuronic acid (abbreviated as HexA) and dissolving metallic ions from pulp. These actions give several benefits in bleaching such as saving bleaching chemical consumption, preventing scale problems of equipment and improving brightness reversion of bleached pulp. Which of the two, HexA or metal ions, was influential on photochemical bleaching was our next subject.

We prepared several kinds of pulp which had different kappa numbers and metallic ion contents by varying conditions of hot acid pretreatment such as temperature, pH and addition of chelating agent (disodium ethylenediaminetetraacetate : 0.05% on pulp). There was not a definite relationship between the kappa number after the pretreatment and the brightness after the UV treatment as in Fig. 4. There was, however, a positive relationship between the ferric ion content in the filtrate, which was the amount of ferric ion dissolved from pulp by the hot acid pretreatment, and the brightness after the UV treatment (Fig. 5).

Softwood pulp after oxygen delignification, that had few HexA in it, was also improved in the efficiency of photochemical bleaching by the hot acid pretreatment (Fig. 6).

It was suggested that removing ferric ion was very significant in improving the efficiency in photochemical bleaching.

3.3 Synergistic effect by UV and ozone on photochemical bleaching (advanced oxidation)

Hardwood pulp slurry after hot acid pretreatment was radiated with UV along with and without ozone injection for 2 hours. The result is in Fig. 7. The UV radiation alone improved brightness by about 13 points. The ozone treat-

ment alone did by about 6 points. With the UV and the ozone, the improvement was about 26 points. The total UV radiation amount required for 80% brightness under the UV and the ozone was about 7.6 kW/kg-pulp, which meant the saving of 70% of the energy required by the UV radiation alone (Table 2).

In summary, it is very difficult to bleach kraft pulp only by UV radiation. However, it was possible to improve bleaching efficiency drastically by applying other elemental technologies like using hot acid pretreatment in sequence, which was common in ECF bleaching, and using UV radiation and ozone in joint.

Advanced oxidation, one of which is UV/ozone combination, generates hydroxyl radical that decomposes not only lignin but also cellulose. Its reaction to lignin is only 5–6 times faster than to cellulose¹¹⁾. It is afraid that advanced oxidation may affect pulp strength. We evaluated the effect by studying a relationship between freeness of the pulp and tensile strength of hand sheets from the pulp (Fig. 8). Full bleached pulp whose brightness was 86% ISO was treated under UV and ozone to the brightness of 91% ISO. There was not observed any loss in tensile index. Though we did not determine the amount of hydroxyl radical in the test, it was probable that even conditions which generate hydroxyl radical might not affect pulp strength.

Though the energy required in our experiment was still far larger than that of conventional ECF bleaching, it was found that using hot acid pretreatment in sequence and selecting suitable additives improved the efficiency of photochemical bleaching drastically. There are still problems to be solved, as our pulp slurry was of very low consistency and the mechanism of photochemical bleaching has to be clarified. We will investigate optimizing bleaching conditions and using in joint other bleaching technologies. We will also study how high the efficiency can be. Technology relating UV is advancing very rapidly, and we will be able to make the best of developments in light sources and energy conversion in our further study.

4. Conclusion

Followings were concluded on photochemical bleaching of kraft pulp using UV radiation.

- ① Pulp slurry could be bleached by UV radiation with sodium hydroxide as an additive.
- ② The hot acid pretreatment was very effective and improved the efficiency. The fact suggests that ferric ion in the pulp was influential on bleaching mechanism.
- ③ The advanced oxidation which meant applying UV radiation and ozone injection simultaneously was very effective in improving the efficiency of photochemical bleaching. By jointing the hot acid pretreatment with the advanced oxidation, the power consumption for bleaching oxygen-delignified pulp was saved by 70%, compared with that by UV radiation alone.
- ④ It was presumed that hydroxyl radical would be generated by the advanced oxidation. However, when full bleached pulp commercially available was treated with UV/ozone, there was not observed any strength loss in the pulp.

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