Reuse Of Purified Effluent in The Fiber Line–Laboratory Results

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ABSTRACT

A closed mill system has been one of the main targets in kraft mill development. The ultimate target is to close the circuit so completely that the mill does not have any purge water and does not take any clean water to the process from the water reserves. The target of this work is to partially solve this problem by decreasing the usage of clean water in fiberline.

An experimental test was conducted to find out how the mill effluent can act as bleach plant raw water after secondary treatment. The effluent was collected from the secondary clarifier of a market pulp mill and used as dilution water so that the effluent was present in the A, D0, and D1 stage reactions. The pulps used were mill cooked and oxygen delignified eucalyptus and softwood pulps. The sequences were ECF sequences with or without the HexA removal stage.

According to the results, the secondary treated effluent is suitable wash water for bleaching. The secondary treatment removes the lignin from the effluent and the inorganic compounds and the color is inert in the bleaching reactions. Additionally, the purified effluent proved to be suitable with and without the A stage and for hardwood and softwood. The purified effluent does not cause any brightness ceiling and, when the Cl content is high, it increases the brightness development.

To simulate the circulation and hazardous process conditions, the Eop stage was conducted with a high carry-over from the D0 stage. The carry-over naturally decreases the brightness after the Eop stage, but the difference was the same when the D0 stage was conducted with deionized water or effluent. At the laboratory scale, there is no evidence of any negative effect of using effluent in the bleaching process.

By combining an excellent bleaching result and modern recovery with the Cl removal system, a more closed mill concept can be designed.

Keywords: kraft pulp mill, ECF-bleaching, closure, effluent

Introduction

Over the past 40 years, the water consumption and effluent volumes of the modern pulp mill have decreased dramatically. Several driving forces have been behind the decreased usage of water and increasing internal circulations in the mills. All reasons for a higher closure rate have not been directly environmental, but most of them have had a positive impact on the environment.

One of the key driving forces is increased production. In the past 40 years, the production of the mills has increased from 300-600 adt/d per unit up to 5,000 adt/d in a single production line. The absolute water intake of a mill producing 1 million adt/a is as much as that of a mill producing 100,000 adt/a in the case that its water consumption is only 10% of that of the old mill.

The reduction in the usage of water is important as the heating and cooling of water consume a significant amount of energy. The system closure and reduction of fresh water usage dramatically reduce the energy and heat consumption in the mills and have formed the key technology for making the pulp mill self-sufficient in energy. As a combination of secondary waste-water treatment and a typical modern energy balance, the mills with this kind of process solutions have represented the most modern and advanced technology and also provided a reference for the future mill design. However, in some areas the environmental pressure is extremely strong, like in highly populated areas of the world. In such areas, pulp mills have found specific solutions such as light ECF or TCF, or special enhanced water cleaning systems for waste waters.

Today the actual size of the mill and in many cases also the location of the mill in an area with a population of several million people using the same water reserves, create a demand for more sophisticated solutions for water management. The ultimate goal for pulp mills has been set – the zero effluent pulp mill – but any steps to reduce the water consumption and effluent volumes have been of great interest. The target, the zero effluent pulp mill cannot be achieved on a short term, because the mill's wood raw material and chemicals include water which causes a purge from the mill.

State-of-The-Art Mill Technology

For years, the closure of pulp mills has been stabilized to cover a situation in which the mill's cooking, brownstock systems and oxygen delignification have been connected to the recovery island to perform in a closed loop, whereas wood handling, bleaching and drying operate separately. The water from these areas has not had access to the recovery cycle, but these process departments cause the main purge out from the process. There has naturally been a limited connection from the first alkaline stage of bleaching to the brownstock system in ECF bleaching, or in the case where the first bleaching stages use oxygen-based chemicals as the main chemical.

In many areas, wood includes a significant amount of non-process elements, but the chlorine content is high especially in many eucalyptus areas. In these locations, the mills might utilize the chlorine removal system in the recovery cycle. This system has been installed because the chlorine has accumulated into the liquor cycle and made the modern recovery system uneconomical to operate. However, modern bleaching and fiberline technology has not made use of all advantages of this technology so far. Normally the bleaching and brownstock system water circuits have been totally separated from each other (Figure 1).

The most common way to reduce the water consumption in the mills has been to introduce a closed filtrate circulation in the bleaching. The bleach plant closure has been stabilized to a level of 10-13 m^3/adt of effluent from the bleaching /6/. A smaller figure than that is hard to reach and has a significant impact on the bleach chemical consumption and scaling tendency. A more thorough bleach plant closure requires investments in the internal cleaning system of the plant, such as in ultra filtration or membrane technology.

In modern bleaching technology and especially in hardwood bleaching, the use of chlorine containing chemicals has decreased dramatically during the past decade. The best hardwood plants charge less than 5 kg Cl/adt into bleaching and the Cl content in bleach plant filtrates and effluents has also been reduced dramatically over the years.

Washing R&D has revealed that the main chemical component in bleaching, which causes the brightness loss in each bleaching stage, is lignin. Because the lignin is removed from the fibers to the filtrates, it always exists at higher concentrations when the bleaching filtrate circulation has been closed. This phenomenon was clearly seen when the first D stage filtrate was circulated prior to the same stage. The impact of the other chemical components has been smaller. It has, in fact, been reported that the Cl content has a positive impact on the bleaching result and increases the brightness in the stage /1/, but when the lignin has been in the same liquid, its negative effect has been significant /3/. Therefore, the circulation has caused a brightness loss and increased the chemical consumption.

A misleading parameter in the water discussion has been the color. Lignin increases the color number of the filtrate, and in that way the color has been considered to be the reason for the harmful effects in the bleach plant /2/. However, on a mill scale there are several other chemical components that cause the color in the liquid, but these do not have the same impact on the operation of the bleaching stage as lignin. Basic studies have been conducted to treat the pulp mill effluents in several treatment steps to especially reduce the color in the filtrate and then reuse the water in the process, but the role of color was not defined. Water turbidity, metals, or many other components can also cause color but they have a minor or no impact on the bleaching reactions. Following the color as a key component has therefore been misleading.

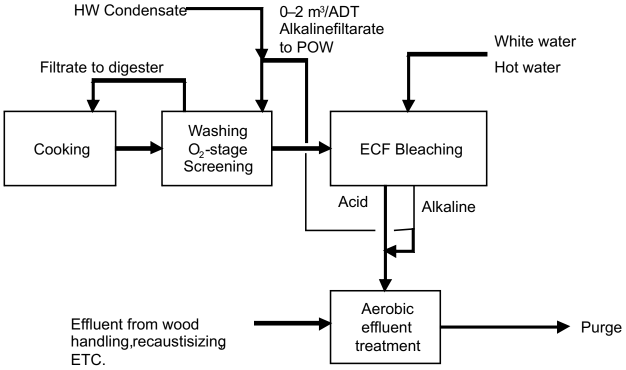

Figure 1. A state-of-the-art solution that separates bleaching and the brownstock system. A small stream from the alkaline stage to POW can exist.

A new solution

The color is not the key component in the effluent; instead the lignin content must be followed as a key parameter. In modern bleach plants, the mill effluent is treated in aerobic biological treatment processes. The key benefit of secondary treatment is that it is the most efficient process to reduce lignin and small molecular sugar content in the water. The key target of the lab trials was to define, how this kind of a liquid, with a low lignin concentration but with color, works in bleaching instead of clean hot water. A new solution is to use purified effluent as wash water in stages to minimize the use of clean hot water (Figure 2). Andritz has patents and several patent applications for this new technology.

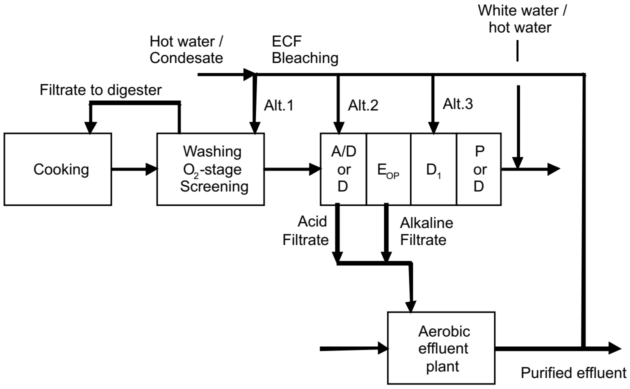

Figure 2. A new solution where the purified effluent is connected to the bleaching process. In alternative 1, the effluent is used in post oxygen washing whereas in Alt 2 and 3, the effluent is used in the A and D bleaching stages.

Quality of effluent

The COD content in treated effluent drop down to 200-400 mg/l level and it is significantly lower than in Acid or alkaline filtrate in two first bleaching stages and also lower than the evaporation condensate COD in many mills. The Effluent has high colour value, but in experimental part it is shown that effluent colour is not stabile feature in bleaching conditions but also colour has no influence to bleaching reactions at all. The presence of effluent has no influence to brightness development or final brightness, but it must also be considered how the effluent influences the process due to inorganic deposits. To understand the level of effluent concentrations, the numbers are compared to NPE content in typical fiber lines without effluent use.

The mill effluent is neutralized and the biological cleaning process removes the harmful lignin and partially metals from the liquid. The neutralization of the acid filtrate reduces many ions like calcium solubility and the participated ions are removed from process with sludge or partially participated in ETP basins (table1). The calcium content in effluent is fairly low.

Table 1. Effluent characteristics of the pulp in integrated mills

	COD	Color	Cl-	Ca	Mn	
Effluent	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	
1	182	380	190	110	0.068	
2	130	**	280	110	0.5	
3	430	**	30	140	*	No Bleaching
4	140	400	150	40	0.2	

* Not detected
** Not measured

Calcium´s role

The main source for NPE is wood and the difference between typically used raw materials is significant. However also raw water cause in some mills NPE's to process. Calcium is one of the most difficult NPE in process because it can enter to process in many ways and in many chemical compositions. For the wood the soil´s quality causes significant variation in chip NPE content but the debarking degree causes the biggest variation in calcium content (Table 2). 3-5 % bark in chips can double the calsium content in pulp and therefore debarking is critical /8/.

Table 2. Average NPE content of wood species used in pulp manufacturing

	Cl, Chlorides,	Al	Ca	Fe	K	Mg	P
Wood	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
SW	91	21	1511	34	540	390	92
Euca	332	119	1931	55	1689	450	188
Mixed HW	85	16	2035	39	1704	537	118
India HW	809	51	3903	97	3155	1001	414

Other origin for calcium is raw water. In some areas calcium content in water can be high and exceed the solubility level 0.14 g/l, but the solubility is also highly dependent on very small changes for example in pH and temperature. High calcium content in raw water is the case for example in the middle' part of USA. Calcium also exist in white liquor circulation and in ETP neutralization, so it is present all over the process, it is active chemical in chemical plant and for that reason it can not be avoided in pulping process.

Calcium is very complicated compound in fiber line and it has several chemical forms, which behave chemically differently. Therefore calcium behaviour in fiber line conditions is difficult to understand, but if the phenomena of the calcium solubility and its behaviour in fiber suspension is understood, it can be identified, why calcium problems exist in beginning of bleaching.

Calcium solubility is highly dependent on pH. Therefore in fiber line conditions calcium can be seen in high portions in acid conditions, but washable calcium content in alkaline conditions is low. In these conditions calcium is bound back to fibers and stays there due the ion exchange properties of fibers. In neutral range pH 6-8 the calcium solubility is about 50-200 mg/l. When the pH decreases, the solubility increases and can be several thousand mg/l and it is higher than calcium concentration in bleaching filtrates. Therefore calcium is released from fibers in acid conditions and it is washable only in low pH. That is why the calcium content in D0 stage is high and D0 washing is in key role to remove calcium from process.

Because calcium is bound to fibres in alkaline conditions, the brown stock washing process and efficiency have quite small influence to calcium carry over. The post oxygen washer outlet consistency has in practice no effect to calcium carry over as kg/adt. In beginning of bleaching in acid conditions, typically in D0-stage, calcium start to release from fibres and it is moving to free liquid. In an optimum process calcium is washed out from the process by minimizing the calcium concentration in pulp suspension and using efficient washing technology.

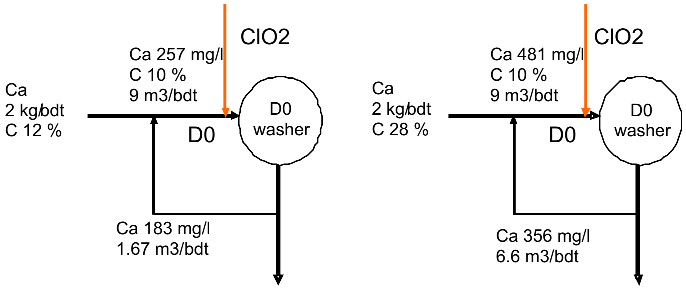

Figure 3 Calcium accumulation in the D0-stage. To the left, a conventional bleaching stage and, to the right, a typical solution in case of a reduced D0 effluent amount.

HexA removal technology also improves calcium removal and other NPE removal /9/. From Figure 3 it can be seen that there is significant difference in calsium concentration, if the D0 is diluted with D0 washer filtrate or washed with clean water. The calculation is done so that all calsium is washable in D0stage, but in real process some amount stays with pulp and causes problems in later stages. In this calculation example calcium content in pulp is 2 kg/adt, which is normal in most of the mills globally, but low where the wood debarking is a problem. If the calsium content increases to 4 kg/adt, the concentrations are two times higher. This calculation shows that the use of purified effluent with fairly low amount of calcium is attractive, because in low effluent process it can significantly help to clean the system from calsium.

Experimental

Experimental work was carried out to test how the pulp mill

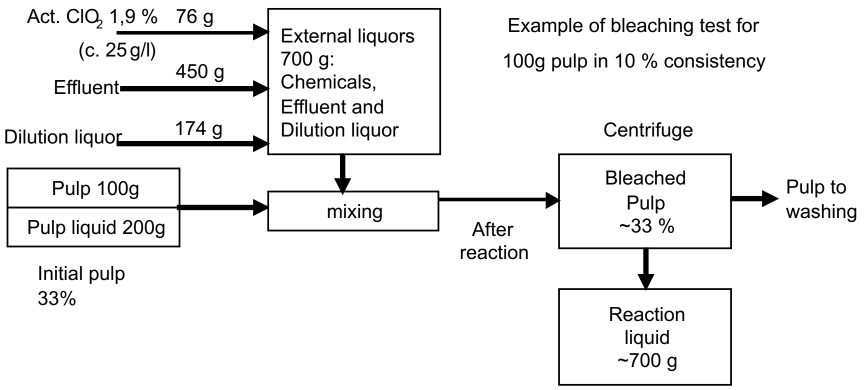

Figure 4. Schematic figure of a lab bleaching test. The example is for 100 g bleaching at 10% consistency.

Table 3. Three-stage bleaching tests with South American eucalyptus and effluent from a South American mill

	A/D-Ep-D	A/D-Ep-D	D-Ep-D	D-Ep-D
A-stage 120 min 90 °C c: 10%				
D-stage 30min 65 °C c:10%				
Dioution Liquor, D0	Clean Water	Effluent	Clean Water	Effluent
Effluent, m3/bdmt	-	4.5	-	4.5
ClO_2, % act. Cl	1.9	1.9	2.3	2.3
D0 Brightness	73.9	73.8	76	75.1
D0 kappa	4.2	5.1	5.2	5.6
EP-stage 75 min, 80 °C, 10%				
H_2O_2	0.4	0.4	0.4	0.4
EOP Brightness	84.7	85.2	85.9	85.9
EOP kappa	3.2	3.9	4.1	4.4
EOP viscocity	975	1000	1035	1025
D1-stage 150 min, 70 °C, 10%				
D1 ClO_2, % act. Cl	0.9	0.9	0.9	0.9
D1 Brightness, % (ISO)	89.5	89.5	90.1	89.9
D1 kappa	1.5	2	2	2.3
D1 Viscosity, ml/g	995	1005	1005	990

	Euca Effluent
COD, mg/l	290
AOX, mg/l	3.2
Chloride, mg/l	300

Table 4. A/D-EP-D-P bleaching trials with effluent and reference bleaching using the same chemical charge. The D0 stage charge is 5 kg (act. Cl)/adt.

	Clean A/d-stage	**A/d-stage with effluent**	
A/d-stage 240+10 min, 90+85 °C			
Effluent, m3/adt	-	4.5	4.5
H_2SO_4, %	0.52	0.55	0.55
Final pH	3.2	3.4	3.4
ClO_2, % act. Cl	0.45	0.45	0.45
EP-stage 90 min, 85 °C			
NaOH, %	0.88	0.88	0.88
H_2O_2, %	0.56	0.56	0.56
Brightness, %	**76.3**	**76**	**76**
D-stage 90 min, 70 °C			
ClO_2, %, act. Cl	1.33	1.33	1.33
Brightness, %	**87**	**87.2**	**87.2**
P-stage 90 min, 85 °C			
H_2O_2, %	0.18	0.18	0.54
H_2O_2, % consumed	0.18	0.12	0.3
NaOH, %	0.7	0.7	0.7
Brightness, % (ISO)	**89.8**	**90.7**	**91.7**
Total			
ClO_2, kg act. Cl/adt	17	17	17
H_2O_2, kg/adt	7	7	11 (8.6 consumed)

Effluent test: 4.5 m3/adt effluent added to A/d-stage

	Euca effluent
COD, mg/l	140
Chloride, mg/l	150
Color, mg/l (Pt color)	400

secondary treated effluent influences ECF bleaching especially in terms of D stage reactions. All effluents and pulps were collected from Scandinavian and South American mills and the criteria was that the effluents had to be from a market pulp mill and not be mixed with paper mill waters and chemicals. Mill cooked and oxygen delignified eucalyptus pulp from South America were used. The key issue was the pulp bleaching properties, but some properties of the effluents were also measured. Effluent treatment plants represent well-operating aerobic and modern water handling systems. The test liquid was collected after the secondary clarifier and was held in cold storage before the bleaching test. Effluent properties are presented under the each bleaching table.

To maintain the comparability, all cases of the bleaching performance were compared with a similar reference bleaching that had a similar chemical charge, temperature, and bleaching conditions. In that respect each bleaching stage can be compared against a reference bleaching and then the whole sequence can be compared against a clean sequence carried out with deionized water or a sequence with effluent. The reference case is always conducted in a laboratory and bleaching was conducted using laboratory- demineralized water at exactly the same bleaching conditions and chemical charges.

All analyses have been performed according to ISO standard analyses.

The pulp was centrifuged to 30-35% consistency and diluted to bleaching conditions using treated effluent. Most of the bleaching was done in polyethylene bags, but the softwood tests were carried out in a CRC mixer. The pulp preparation was always the same in the parallel bleaching tests (Figure 4).

A/D-Eop-D and D-Eop-D Sequence For Eucalyptus

The tested pulp was washed and oxygen delignified eucalyptus from a South American mill and the tested effluent was taken after the secondary clarifier from a mill where the total bleach plant effluent is below 15 m^3/adt and the mill's total effluent below 25 m^3/adt. The conventional three-stage sequences A/D-EOP-D and D-EOP-D were compared. Initial pulp kappa was 11.7, brightness 61.9% (ISO), and viscosity 1080 ml/g. Results from the bleaching tests are shown in Table 3. In the A/D and D stages, 4.5 m3/adt of effluent was used. The EP and D1 stages were diluted with demineralized water.

The bleaching result with effluent and in the reference case is similar. The small differences in brightness values are below the method accuracy.

In the next trial, the target was to test the sensitiveness of the A/D-EP-D-P sequence and optimize the D stage chlorine dioxide charge. This optimization has a future target to reduce the first D stage chemical charge so much that the option to use purified effluent in brownstock washing is more feasible (Table 4). Initial kappa of the pulp was 11.3 and brightness 57.8% (ISO).

The trials show that the pulp can reach a very low chemical consumption not only when the effluent is charged in the A/D stage, but also to the second D stage. It can be noted that the final brightness is higher with effluent than with clean water which shows that the effluent has a small benefit in brightness development in the sequence. The effect can be explained with a higher Cl content in the effluent, but because the effluent does not include lignin, the full benefit of the chloride concentration can be seen. The pulp reached the 91.7% (ISO) brightness easily which shows that the effluent in the A/D or the D1 stage does not cause a brightness ceiling and can be considered in the effluent usage also in case the mill is planning to run 92% (ISO) brightness.

Scandinavian softwood pulp was also tested in the short D-Eop-D sequence, the mill reference sequence being the three-stage sequence /5, 7/. The effluent in bleaching process works similar way with SW as with HW. In these tests 10 m3/adt effluent was used in sequence. The results were similar with HW.

Discussion

The activated sludge plant is sufficient to purify the effluent so that it can be used in the beach plant instead of clean water. The maximum effluent charge in the tests was 10 m^3/adt with a positive or a neutral impact on pulp bleachability or pulp quality. The purified effluent can be utilized both in HW and SW fiber lines. Because the various D0-stage carry over up to 40% in the Eop-stage did not cause any negative impacts on the bleaching, existing bleach plants can utilize purified effluent. As reported, the Cl content seems to improve the D-stage efficiency; thus this benefit can also be considered, when this technology is utilized.

In HW bleaching, no difference was shown by the typical short three-stage sequences whether or not purified effluent was used in the first bleaching stage. The chemical consumption was reasonable and the pulp reached the 90% (ISO) brightness easily. The purified effluent amount was significant and the mill from where the effluent was collected represents a state-of-the-art eucalyptus mill with purified effluent concentrations.

The A/D-Eop-D-P sequence with a low ClO_2 charge shows that the effluent in the D stage does not have any influence even when the chemical charge is reduced to a minimum. The purified effluent usage is not sensitive to the chemical charge and the chemicals are used effectively also with low charges. As a single result, 17 kg act. Cl/adt for 90% ISO brightness pulp is excellent and when it is implemented on a mill scale, it reduces the environmental impact of the mill. However, the low ClO_2 charge is beneficial, as the target is maximum usage of purified effluent also prior to bleaching (in POW). The low Cl concentration of the purified effluent decreases the Cl input to the recovery cycle. As a consequence, the operational cost of the salt removal system will be reasonable.

The purified effluent usage is not limited to HW fiber line, but SW line can also utilize it as bleach plant raw water. The bleachability and properties of the pulp were the same or better and no negative impacts were observed.

All effluents have a significant brown color. The color parameter did not have any correlation with the bleaching reactions, brightness, or bleaching results, but the color was an inert component during bleaching. When the liquid properties are suitable for bleaching, the color parameter has no correlation with the bleaching result.

Secondary treatment is a sufficient method for removing the lignin, and its cleaning effect for untreated effluent is enough for being used in bleaching. This unlocks the new technology and shows that mills with secondary treatment have all the necessary process departments to close their bleaching water circulation and decrease their raw water usage. Existing modern mill´s equipment and processes are sufficient to operate with purified effluents.

In all tests, the purified effluent was used in the D0 stage where its usage is the most beneficial. An industrial solution could be to use the purified effluent in dilution prior to that stage and reduce the use of raw water, but the opportunity to use effluent so that it is partially recovered in the brownstock process is also very attractive. This naturally requires a chlorine removal process in the recovery system, but the technology is already in use with several mills and needed because of the high Cl content of the wood raw material.

All conclusions are based on laboratory work and analysis, but the results are so promising that if mills are interested in reducing especially their raw water usage, this technology is very attractive. Mill water usage is the main benefit. The mills can reduce their water intake to bleaching and brownstock washing to allow them to be located in places where the water resources are limited. If the filtrate connections are made so that the purified effluent is partially taken to the recovery cycle, then the COD load is also reduced.

The purified effluent calcium content is fairly low compared to many mills calcium concentration at the beginning of bleaching. The use of fairly low calsium content liquid in bleaching and this way removing the highest contaminated streams, there is change to improve the plant´s runability.

Conclusions

- Biological effluent treatment provides a sufficient method for producing water for the bleach plant.
- Biological treatment removes the lignin from the effluent and the rest of the liquid has no impact on the bleaching reactions. Color as a single parameter is meaningless among the bleach plant water criteria.
- The purified effluent has a positive or neutral impact on the pulp bleaching result.
- In some mills purified effluent usage can clean the process by reducing the NPE content in water circulations
- Andritz has several patents and patent applications for this technology.

These results show several technological advances that can be considered and which have a comprehensive influence on the mill specification:

- By combining salt removal technology and purified effluent usage in the fiber line, water circulations of bleach plant and brownstock system can be connected.
- By using purified effluent in the bleach plant, the mill's raw water intake can be significantly reduced.
- By using purified effluent in brownstock washing, the mill's COD emission is reduced.
- By utilizing the existing process and equipment, the purified effluent usage can be implemented in existing mills.

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