

**CHLORIDE AND POTASSIUM IN THE KRAFT RECOVERY CYCLE:
A PRACTICAL GUIDE**

Project F01706

Subtask: Closed Mill Salt Recovery—Electro Membrane Processing

Report 4

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

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By

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Chloride and Potassium in the Kraft Recovery Cycle: A Practical Guide

Report Number 4

Project F01706 Closed Mill Salt Recovery - Electro Membrane Processing

by

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Disclaimer

The contents of this report cannot be used as the sole basis for actual decisions on mill operation or investments. This report is a rough outline of existing knowledge and know-how. Each mill case has to be considered carefully and in more detail than can be covered here.

This report is based on published data and on IPST's own research and consulting work. Reference citations and discussion of the literature have been completely omitted for the sake of brevity. The author would like to acknowledge that this report would not have been possible without the outstanding work by many authors that is published in the open literature. To review references the reader is referred to prior detailed IPST Member reports on this project and to the final report that will be issued in Summer 1999. The author would also like to gratefully acknowledge the many enlightening conversations and discussions with colleagues at IPST.

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Purpose of this report

Chloride and potassium accumulation in the kraft pulping cycle is a growing problem for many pulp mills. Chloride and potassium accumulation often leads to significant increases in the frequency of shutdowns of the chemical recovery boiler due to plugging of the heat exchanger passages (sticky dust). Frequent recovery boiler shutdowns and washes not only cause loss of production, but can contribute significantly to recovery boiler corrosion.

Diagnosis of problems with potassium and chloride

Background

Potassium (K) enters the kraft process with the wood. Chloride (Cl) enters the pulping process with wood, replacement caustic, and with two possible recycle streams from the bleach plant: from the chlorine dioxide generators (depending on generator technology) and from counter-current washing or other bleach effluent recycle to the kraft chemical recovery operation.

Most significant chloride inputs in a conventional mill are the wood and diaphragm-grade caustic. Bleach effluent recycle that introduces a large amount of chloride is currently only rarely used. However, with a closure scheme such as Champion's BFRTM process (recycling of virtually all bleach plant effluent to chemical recovery), major amounts of chloride far exceeding all other inputs may have to be considered. This is a very rare occurrence in current U.S. mill practice.

Both chloride and potassium contribute to a lowering of the melting point of the fume particles produced in the recovery boiler. This causes particles to be softened and sticky at temperatures where they would normally be hard. Sticky particles can attach themselves to surfaces such as the heat exchange surfaces in the upper part of the recovery boiler. Eventually the gas passages may become partially or almost entirely plugged and this will require a shutdown and water wash.

Practical problems

Frequent boiler shutdowns due to plugging are a good indication that sticky dust caused by high chloride and potassium levels could be the problem. Some mills can

operate without any additional water washups of the recovery boiler beyond scheduled shutdowns. A water washup frequency of more than four per year (including scheduled shutdowns) is a possible indication that plugging may need to be handled by chloride/potassium control.

Samples from the recovery boiler electrostatic precipitator (ESP) dust and from the as-fired black liquor should be taken (with prudent compositing and repetitions), and chloride and potassium levels should be determined. Potassium is easily and cheaply determined by inductively coupled plasma spectrometry (ICP) or atomic absorption spectrometry (AAS), while chloride concentrations can be determined by titration or capillary electrophoresis (CIE). The chloride analysis is far more complex and error prone than the potassium analysis.

Chloride concentrations of 1 wt.% or less of chloride (not NaCl) of the as-fired black liquor solids would be a good value for trouble-free operation and should result in no plugging from sticky dust. Even at inland mills, concentrations as high as several wt.% can be found in some cases. Chloride concentrations in the dry recovery boiler ESP dust of about 1 wt.% (not NaCl) are considered quite good, but concentrations up to 10 wt.% can also be found. Concentrations of 1 wt.% of chloride in the dry ESP dust can be found at mills operating with intentional ESP dust purge to the sewer to control chloride.

How the practical problems come about

If the pulping operation is tightened (control and recycle of spills, minimizing of carryover from the pulping operation to the bleach plant) then a buildup of chloride and potassium can occur since both of these elements are very soluble in the kraft recovery liquor cycles. There is no natural purge point (such as grits or dregs for some metals) where potassium or chloride would precipitate and be removed from the process. Some chloride does leave the recovery boiler with the stack gas as hydrochloric acid (see discussion below). If inputs exceed outputs, buildup occurs. This buildup can be quite slow (order of months) due to the large holdup volume of the process.

Measures for chloride control

Due to the large holdup of the liquor cycles, it can take weeks or months for buildup to occur, and for control measures to have an effect. The concentrations must be tracked over months. Tracking at one point in the process (white liquor, black liquor, etc.) is sufficient because of the closed cycle and interrelated nature of chemical recovery operations.

Changes in operation

It should be mentioned that an increased purge of chloride could theoretically be achieved through the recovery boiler stack gas as gaseous hydrochloric acid. This requires relatively low temperatures in the boiler to achieve the desired chemistry in the boiler. However, due to regulations on the composition of the stack gas (particularly the limitations on sulfur dioxide content) it is not likely that this purge is significant or could be made significant in current mill operations. Low sulfur dioxide requires increased temperatures in the boiler, which largely defeats the option of a chloride purge as hydrochloric acid in the stack gas.

Once the problem has been diagnosed to be in the area of chloride and potassium buildup, there are several simple measures that can be taken to reduce the chloride and potassium levels in mills.

1. Purchase membrane-grade caustic

Membrane-grade caustic is made using highly selective ion exchange membranes instead of the older diaphragm technology. This leads to much lower chloride levels in the caustic and lower chloride inputs to the mill. The reduction in chloride input to the mill (considering wood and caustic as inputs, but no bleach effluent recycle to recovery) may be 20-50% with membrane-grade caustic compared to diaphragm grade caustic. This chloride reduction comes at the expense of increased operating costs, but with no capital expense.

2. Purge electrostatic precipitator dust

The idea is to purge chloride and potassium from the point in the process where both elements are most enriched, due to the chemistry and physics in the recovery boiler.

This point is the ESP dust (several fold enrichment of chloride and potassium relative to other points in the recovery cycle). Operating costs are incurred to replace the saltcake portion of the discarded dust. If a mill also experiences high sulfidities, a dust purge may be additionally useful as a sulfur purge. A purge of 10-20% of the generated dust may be a good starting point. This can be done continuously, or in a periodic (for example, weekly or biweekly) fashion. Dust could be slurried up and discharged to the sewer. If a wet-bottom precipitator is used, a portion of the precipitator can be run on water, and the slurry can be discharged.

3. Check recycling streams from the chlorine dioxide generators for chloride content

Recycling streams can be a significant chloride source, as well as a cause for rising sulfidity. Reductions in chloride carryover from chlorine dioxide generation to recovery can be achieved by ensuring that the separation steps in the generator are well functioning, but capital will be needed to switch to a generation process without effluent generation. If capital expense is to be avoided, chloride can be purged with the ESP dust (see 2.).

At least one of the above measures 1. through 3. should be maintained for a few months while monitoring chloride levels in the ESP dust and the black liquor. This time is needed due to the long dead times caused by the large volumes of liquors in the recovery cycle. If the chloride concentrations recede, and boiler washes become less frequent, the above strategy can be maintained, or improved by purging more dust. If effluent conductivity limitations are a problem, purging of dust may not be a feasible solution.

Selective chloride removal technologies

In most mills, the above measures will help or suffice to control the chloride/potassium buildup. If low-chloride caustic does not improve the situation, and if dust cannot be purged due to effluent conductivity limits or other reasons, selective chloride removal techniques should be considered. If chloride-containing bleach effluent is recycled, or if another significant additional chloride input exists (for example, for coastal mills floating logs on sea water, or salt in the groundwater supply), dust purging

may cause high operating costs (due to the large amount of dust that needs to be purged) which may justify capital expense for selective separation of chloride from the dust.

Available technologies for selective chloride purging concentrate on removing chloride from the electrostatic precipitator dust of the recovery boiler. This is done since the chloride concentration is advantageously high in the dust compared to other points in the process. One technology is commercial with at least two full-scale implementations. The two other technologies have either been piloted or extensively tested. A fourth technology is for processing green liquor. This is under investigation in IPST's laboratories.

1. The Salt Removal Process (SRPTM) marketed by U.S. Filter/HPD

This process works by dissolving the ESP dust in water, and then removing the water in an evaporative crystallizer. The sodium sulfate in the dissolved dust (the major component) then crystallizes out in a pure form (potassium does not crystallize with the sulfate) and is filtered out. This solid sodium sulfate with minor amounts of entrained and bound water can then be recycled to the black liquor. A concentrated sodium and potassium chloride brine is purged. Installations are operating at Champion's Canton, NC and former Union Camp's Eastover, SC, mills.

This process requires construction of an evaporative crystallizer and auxiliary equipment (filters etc.). The inherent economy of scale for a crystallizer makes the process suitable for purging very large amounts of chloride. At the Canton mill, for example, virtually all the dust from the boiler is dissolved and treated since so much chloride has to be removed due to bleach effluent recycling. Changes in operations (see above) should first be carefully evaluated before investing the significant capital needed.

2. Chloride removal by electrodialysis (piloted at IPST)

This process has been piloted at an IPST member mill. ESP dust is dissolved and the chloride is selectively removed from the solution using an electrodialysis membrane system. Selectivity for potassium over sodium is not as good as in the SRPTM process above. The process has been piloted for 700 hours in a kraft mill without any problems. No filtration or pre-treatment of the ESP solution was applied.

The main difference between the SRPTM process above and electro dialysis is that the sodium sulfate to be recycled to recovery is in the form of an up-to-25 wt.% solution, not as solid filtered crystals. The water in this solution must be evaporated when recycling the chemicals into the black liquor.

If concentrator capacity for evaporation on the order of 50,000 gallons of water per day is available, a 1000-ton-per-day kraft pulping operation can install the electro dialysis process for less than \$1,000,000 in capital (1000 kg of chloride purged per day). If a payback is obtained since sodium sulfate is recycled and not discarded (compared to purging whole dust), this payback is less than one year. If the mill already suffers from high sulfidity, whole dust purging may not be burdened with an operating cost penalty, and the payback will be less advantageous.

3. The Precipitator Dust Purification System (PDP)

In this system, marketed by Eco Tec Inc., Pickering, Canada, dust is dissolved and pumped through a fixed bed polymer resin. This packed resin bed is made of very small resin particles and is operated in a revolving cartridge system with small cartridges used for a short time (5-10 minutes) and regenerated in a rather fast frequency. The system is used at Champion's Canton, NC, mill to remove metals from an acidic bleach plant recycle stream. Extensive pre-filtration including a sand bed was needed at Canton, since the process can only operate on an absolutely particle-free feed, due to the tightly packed fixed resin bed.

The resin absorbs sodium chloride selectively, while it is not selective for potassium. The sodium chloride is then purged with water from the resin during the regeneration cycle.

No pilot-scale long-term data using PDP on dissolved ESP dust is available in the published literature or in the manufacturer's literature. The need for a complete feed cleanup to achieve a particle-free feed to this chloride removal system would probably incur extensive operating costs. The need for constant maintenance on the pre-filtration system may be even more of a problem in mill operation.

4. Ion exchange of green liquor (under development at IPST)

An ion exchange process to remove potassium and chloride from green liquor is currently being explored at the Institute of Paper Science and Technology. Commercial anion and cation exchange resins are used. It is an advantage that ion exchange systems for water treatment (boiler water, removing hardness from feed water) are quite familiar in most mills. The hardware and resins are readily available and proven. The proprietary operational details for the ion exchange system are crucial for selective chloride and potassium removal without detrimental effects on liquor composition.

This new process would be the only alternative to selectively remove both potassium and chloride without the need to evaporate significant amounts of water as in all processes where ESP dust has to be slurried to relatively low concentrations (electrodialysis, SRPTM, PDP) before removing chloride.

Conclusions

Mills that have a plugging problem in the recovery boiler should measure chloride levels in the black liquor. If the levels are high (more than 1wt.% of as fired dry solids as a rule of thumb), membrane-grade caustic should be used for several months. Simultaneously, some ESP dust may be dumped. This should reduce chloride levels measurably. Concentrations will have to be tracked on the order of months to see effects due to large liquor holdup volumes. If the reduction is not sufficient, more dust can be dumped.

Selective removal techniques requiring significant capital investment are available both for large amounts of chloride (>> 1000 kg chloride/day, U.S. Filter/HPD's SRPTM) and for moderate amounts of chloride (~1000 kg chloride/day, electrodialysis as piloted by IPST).

A new low-cost selective chloride and potassium removal technique based on commercial ion exchange resins and proven ion exchange process technology is under investigation at IPST.

Consultation on this issue is available from IPST. Please contact Peter Pfromm, 404-894-5305, pcter.pfromm@ipst.edu.

