ABSTRACT

A new system has been developed for removal of chloride contamination from kraft process liquors. The compact, skid-mounted system which utilizes ion exchange columns only 24 inches in height, is shown to be capable of removing 90-99% of the chloride from a wide variety of sources including dissolved ESP catch, oxidized white liquor, spent bleaching liquor, spent ion exchange demineralizer regenerants and caustic soda makeup. By removing chloride contamination, these liquors can be recycled to kraft recovery without causing a chloride buildup. By lowering the chloride content in kraft liquors, the sticky temperature of recovery boiler deposits can be significantly increased, which should lead to reduced pluggage and boiler down-time. Selectivity of the ion exchanger for chloride is extremely high and recovery of other chemicals such as sodium sulfate, sodium carbonate and sodium hydroxide is demonstrated to be typically 92-98%. Regeneration of sodium chloride from the resin is achieved with only water (ie. no chemicals), so that operating costs are negligible.

INTRODUCTION

Accumulation of chloride in the kraft recovery cycle is known to cause a number of problems. Chief among these is an increased tendency for recovery boiler plugging, although increased corrosion has also been attributed to elevated chloride levels. Many mills could significantly reduce down-time and reduce costs if an effective means of removing chloride could be incorporated into the mill.

As mills move towards increased levels of system closure, chloride levels will inevitably increase as natural purges due to liquor losses are reduced. Consequently, the number of mills needing chloride removal is expected to increase in the future.

RECOVERY BOILER PLUGGING

High levels of the non-process elements chloride and potassium in the kraft recovery cycle are known to accelerate recovery boiler plugging under some circumstances. The current levels in some mills require that boilers be shut down for water washing as frequently as every three months. Other mills avoid such non-scheduled shutdowns by increased soot blowing and thermal cycling.

The range of sticky temperatures of the flue dust in a recovery boiler is defined as that temperature where the amount of liquid in the material is high enough for the mixture to stick on a metal surface. Laboratory and mill measurements have shown that the sticky temperature range is reached when approximately 15%-70% of the mixture becomes molten\(^1\). Rapid plugging of the recovery boiler can occur if the flue gas temperature is between \(T_{15}\) and \(T_{70}\) in the generator bank.
As Fig. 1 shows, the chloride and potassium levels of the recovery boiler tube deposits have a significant effect on the sticky temperature, $T_{15}$. If the chloride level can be reduced below 5% mole fraction, the sticky temperature should significantly increase and a reduced tendency for boiler plugging may be experienced. For example, at 5% K, by reducing the chloride level from 5% to 1.5%, the sticky temperature would increase from about 620°C to 740°C. It is important to note that when the deposit chloride levels are low, potassium has very little effect on the sticky temperature.

As mills move towards higher levels of closure the current outlets for these elements are reduced. This will result in even higher chloride and potassium concentrations throughout the kraft recovery cycle. Computer simulations on specific mill cases have predicted that depending on the degree of closure, dust sticky temperature can decrease by as much as 100 °C, primarily due to increased levels of chloride. While a requirement for effective chloride removal technology clearly exists today for some mills, the need is destined to become more universal and more pressing in the future.

![Fig. 1. Effect of Chloride and Potassium on Deposit Sticky Temperature](image)

**RECOFLO ION EXCHANGE TECHNOLOGY**

Most mill personnel are familiar with the large ion exchange demineralizers which are employed for purification of recovery boiler feed water. These systems typically utilize ion exchange columns 8-16 feet (2.5-5 m) in height. Even though these columns are only partially filled with ion exchange resin, most of the resin is not actively being used for ion exchange all of the time. In fact, ion exchange only occurs in a very narrow exchange zone. The resin above the exchange zone is exhausted, while the resin below the exchange zone is still freshly regenerated. The exchange zone moves down the column as the service cycle proceeds. When it reaches the bottom of the column, ions begin to leak into the product water and the column is regenerated. This concept is illustrated in Fig. 2.

In the patented Recoflo process, the length of the column is reduced to just a little more than the length of the exchange zone. By utilizing other features such as fine mesh resins, the length of the exchange zone is reduced even more, allowing a further opportunity to reduce the length of the column. Typically in the Recoflo process, the column height can be reduced to as little as six inches for water demineralizer applications such as the one shown in Fig. 3, up to a maximum of 24 inches for concentrated chemical treatment applications. As a result of the short bed height, regenerations are required more frequently, but since there is a proportional decrease in the regeneration time, the short cycles are not disadvantageous. Despite the reduction in column height and cycle times, Recoflo demineralizer systems typically produce higher quality water than conventional ion exchange systems, with as little as 50% of the chemicals consumed in regeneration.
Even taking into account the efficient utilization of chemicals afforded by Recoflo, it still makes no economic sense to utilize a relatively expensive chemical such as sodium hydroxide to recover a less expensive chemical like sulfuric acid or sodium sulfate. In 1978 a Recoflo ion exchange system called the APU was commercialized for purification of waste acid that addressed this issue. The APU (acid purification unit) utilizes ion exchange resins which are capable of sorbing strong acids such as sulfuric acid, while excluding salts such as sodium sulfate. The unique feature of the APU process is that purified acid can be desorbed from the resin with merely water. No chemicals or significant energy is required to operate the APU process. It is therefore possible to economically purify waste acid solutions which previously were not worth recovering. Since its introduction, more than 500 APU’s have been installed in over forty countries, in a variety of different applications such as aluminum anodizing (sulfuric acid) and stainless steel pickling (nitric, hydrofluoric acid).

An alliance between PAPRICAN and the Prosep Technologies division of Eco-Tec was formed in 1993 to develop applications for this technology in the pulp and paper industry. A system developed by the Alliance called GAP (generator acid purification) for recovery of sulfuric acid and sodium sulfate from chlorine dioxide generator effluent was introduced in 1997.
THE SSU PROCESS

The Recoflo technology has recently been adapted into a new unit called an SSU (Salt Separation Unit) for separating different types of salts. The basic SSU process and equipment is the same as the APU, however the SSU employs a new type of sorption resin. The SSU resin is a special amphoteric ion exchange resin with both cation and anion exchange groups existing on each resin particle. In the ‘regenerated’ resin the anion and cation exchange groups neutralize each other, but are available to remove cations and anions from solution. This resin can therefore remove both anions and cations simultaneously in a single column. As with the APU, the SSU resin is regenerated with only water. The process is therefore very inexpensive to operate.

The SSU resin has unusual selectivities compared to conventional ion exchange resins. Although conventional anion exchange resins generally prefer multivalent ions such as sulfate and carbonate over monovalent ions such as chloride, the SSU resin has a very high selectivity for sodium chloride compared to other chemicals such as sodium sulfate and sodium carbonate. It also prefers chloride over hydroxide. As a result, the SSU can effectively remove sodium chloride from even concentrated alkaline solutions of competing salts of divalent anions.

The SSU resin is very stable and under normal conditions should have an operating life time of many years. APU resins, which are very similar in composition and operated under similar hydrodynamic conditions, have shown lifetimes of 5-10 years in much more arduous environments.

There are two basic steps in the SSU operating cycle as indicated in Fig. 4. During the upstroke step, the solution to be treated containing a mixture of sodium chloride and other chemicals, is introduced into the ion exchange resin column. Sodium chloride is picked up by the resin according to the reaction (1), where ‘R’ represents the ‘regenerated’ polymeric resin substrate. The purified, chloride free solution is collected from the top of the column.

\[
R \cdot R^- + NaCl \rightarrow R \cdot Cl^- \cdot Na^+ \tag{1}
\]

During the downstroke, water is passed counter-currently down through the column. The resin is regenerated by elution of the sodium chloride from the resin according to reaction (2). Waste sodium chloride solution is collected from the bottom of the column.

\[
R \cdot Cl^- \cdot Na^+ + H_2O \rightarrow R \cdot R^- + NaCl \tag{2}
\]

The system alternates automatically between the upstroke and downstroke approximately every five minutes.

Fig. 4. SSU Operating Cycle
The SSU is physically very similar to an APU. The main component is a resin column typically 24 inches (60 cm) in height. Scale-up is accomplished by increasing the diameter of the bed. The size of the system required depends on the flow rate of the stream to be treated and its chloride content. A typical unit equipped with a 54 inch (137 cm) diameter resin column is illustrated in Fig. 5. Larger units, up to nine feet (270 cm) in diameter have been built. The very compact size allows these units to be completely factory assembled. Space requirements for installation in the mill are minimal and because they are pre-tested prior to shipment, commissioning can usually be accomplished in just a few days.

Fig. 5. Typical SSU Equipment

**PRECIPITATOR DUST PURIFICATION**

A survey of 17 mills, performed by Tran and co-workers\(^8\) revealed that the enrichment ratio for Cl is highest in the ESP dust compared to other pulp mill streams. This is, therefore, a logical place from which to attempt removal of chloride. A precipitator dust purification (PDP) system utilizing the SSU is shown in Fig. 6.

![Precipitator Dust Purification System](image)

Fig. 6. Precipitator Dust Purification System
The dust is first dissolved in warm (i.e. 40-60°C) water to produce a nearly saturated sodium sulfate/sodium carbonate solution (28%0 containing chloride impurities. A small portion of the dust is insoluble in water, however. This insoluble material largely comprises oxides of multi-valent metals such as iron, calcium, manganese and zinc. NMR and IR analysis also indicates the presence of low concentrations of hydrocarbons. The concentration of the resulting suspended material is typically several hundred parts per million. In cases where a direct contact black liquor evaporator is employed, the ESP dust may contain a significant amount of partially combusted material, resulting in abnormally high suspended solids concentrations. This should be treated as a special case, in view of the low numbers of direct contact evaporators still in operation. The results of an X-ray fluorescent metal analysis of a typical dust are shown in Table I.

### Table I: Typical ESP Dust Metal Analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>26.3%</td>
</tr>
<tr>
<td>K</td>
<td>3.18%</td>
</tr>
<tr>
<td>Ca</td>
<td>0.05%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0273%</td>
</tr>
<tr>
<td>Fe</td>
<td>0.1%</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0068%</td>
</tr>
</tbody>
</table>

The suspended solids must be removed prior to ion exchange treatment since any suspended material will tend to clog the ion exchange resin bed. Various types of filtration systems were evaluated for this purpose including pressure filter presses and rotary drum vacuum filters. A type of pressure filter called a pulse filter similar to that commonly employed for filtering white liquor in many kraft mills was finally selected (see Fig. 7).

![Fig. 7: Pulse Filter Operating Cycle](image)

After the dust is dissolved in water, it is pumped to the pulse filter. This filter utilizes polypropylene ‘socks’ as a filter media. The socks are suspended vertically from a tube sheet inside a pressure vessel. Clear liquid passes through the socks and is collected in a chamber located immediately above the tube sheet. Filtrate overflows from this chamber to the SSU feed tank. Solids accumulate on the surface of the socks as a thin filter cake and the pressure gradually increases as the cycle proceeds. When the differential pressure across the socks reaches a predetermined level, the inlet flow is stopped and filtrate is allowed to drain by gravity from the upper chamber back through the socks, thereby dislodging the cake from the surface of the socks. The relatively large cake solids settle to the bottom of the filter vessel, where they thicken to a concentration of about 10-20% solids. Periodically, sludge containing non-process elements (NPE’s) is withdrawn from the bottom of the filter and either purged from the system or bypassed around the SSU to the sulfate product tank, before recycle back to the recovery cycle. A back-pulse occurs on the pulse filter every 5-10 minutes and lasts about 15 seconds.

A particle size distribution for the suspended solids contained in the dissolved dust collected from three different mills is shown in Fig. 8. Note that the effective size (i.e. 10% smaller) ranges from about 12 µm to 22 µm. Fig. 9 shows
the particle count of the liquor produced from Mill #1’s dust as well as the filtrate from the pulse filter. It can be seen that the filter is extremely efficient in removing suspended solids from the liquor. The turbidity of the filtrate is consistently less than 0.1 NTU’s and chemical analysis indicates virtually complete removal of the metals listed in Table I.

Fig. 8. ESP Dust Liquor Suspended Solids Particle Size Distribution

Fig. 9. Pulse Filter Feed and Filtrate (Mill #1)
The filtrate collected from the pulse filter is fed to the SSU. Sodium chloride is taken up by the resin and a purified sodium sulfate/carbonate solution is withdrawn from the top of the bed and collected in the sulfate product tank (see Fig. 6). In the downstroke, warm water is pumped into the top of the bed eluting sodium chloride from the resin. A portion of the chloride waste collected from the bottom of the bed is recycled back to the dissolving tank to dissolve more dust and the remainder is purged from the system.

The mass balance for a PDP system for a typical mill, based upon laboratory pilot plant results, is shown in Table II. Note that the system removes as much as 97% of the chloride while recovering up to 99% of the sulfate and carbonate values. This compares very favorably with results recently reported on evaporative crystallizer systems which show only 80% sulfate recovery and 90% chloride removal.

The SSU does not show any selectivity for potassium, although as discussed above, this should not prove to be an issue for most mills. Potassium removal for an inland mill would typically be about 5% - 10%, while for coastal mills with higher chloride levels, the potassium removal would increase to about 10% - 15%. Recent computerized mill simulations for a mill with varying degrees of system closure indicated that the modest potassium removal provided with this system will be adequate.

### Table II - Precipitator Dust Purification System Mass Balance

<table>
<thead>
<tr>
<th>Flow (L/h)</th>
<th>[Na] (g/L)</th>
<th>[K] (g/L)</th>
<th>[SO₄] (g/L)</th>
<th>[CO₃] (g/L)</th>
<th>[Cl] (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>15,948</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product</td>
<td>10,750</td>
<td>111.4</td>
<td>24.6</td>
<td>172.0</td>
<td>24.4</td>
</tr>
<tr>
<td>Waste</td>
<td>6,557</td>
<td>11.0</td>
<td>2.1</td>
<td>2.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Removal</td>
<td>5.7%</td>
<td>5%</td>
<td>1%</td>
<td>0.5%</td>
<td>97%</td>
</tr>
</tbody>
</table>

While the SSU itself does not consume any significant amounts of energy for its operation, recycle of the purified salt cake solution will impose an additional evaporation load on the black liquor evaporators. To determine the impact of this load a typical mill is assumed to process 1,750 kg of black liquor solids (BLS) per tonne of pulp. Approximately 5% - 6% of this material, 96 kg-BLS/tonne-pulp, is captured as ESP dust and processed by the PDP system. The purified salt cake solution recycled for recovery is 28% w/w and therefore the total additional evaporation required is roughly 235 kg-water per tonne of pulp. Some mills will be able to ‘squeeze’ out this much extra capacity from the existing evaporators. There are often many modifications possible to debottleneck evaporators at moderate cost. Other cases it will be necessary to upgrade the evaporator train. In many mills it will not be necessary to purify 100% of the ESP catch to lower the chloride to the desired target level. Treating less dust will reduce the evaporation load proportionately.

To avoid any precipitation or scaling, the point at which this solution is introduced must be carefully selected. In a typical multiple-effect evaporator, the weak black liquor is concentrated to 50% BLS which is then brought up to firing strength, 70%, in a concentrator. Generally, the multi-effect evaporators are limited to 50% BLS due to the solubility limits of sodium sulfate and carbonate which are thought to precipitate out as burkeite, 2Na₂SO₄·Na₂CO₃. As Fig. 10 shows, the critical BLS level at which burkeite precipitates is a function of the sodium sulfate content as well as total black liquor solids (BLS). Combining the purified salt cake with a typical weak black liquor increases the sodium sulfate content from about 3% for a typical Canadian kraft mill to 8% - 10% which reduces the critical BLS solids concentration to 44.5 - 46.5%. Thus returning the entire PDP product to the multi-effect evaporators under these conditions could result in scaling. To avoid this problem, a portion of the purified salt cake solution should be fed to the concentrator which has been designed to allow for the crystallization of burkeite.
Under these conditions, a mill with a single stage concentrator integrated with a six effect evaporator (steam economy = 4.8 kg water/kg-steam) is estimated to require 57 kg/adt or 3.3% more steam when processing the PDP product assuming 100% of the ESP catch is treated.

**OTHER APPLICATIONS**

While the most effective way to remove chloride from the liquor cycle is to treat the ESP dust, under some circumstances it may be advantageous to remove chloride from other locations in the mill. For example if a significant portion of the bleach plant effluent is recycled to recovery, treating only ESP dust may not be sufficient to reduce the concentration of chloride to the desired level. Several other liquors have been successfully evaluated as candidates for chloride removal using the SSU technology. These include:

- caustic soda makeup
- oxidized white liquor
- demineralizer effluent
- spent scrubber liquor

**Caustic Soda Makeup**

A significant amount of the chloride input to many mills is the diaphragm cell grade caustic soda that is used for chemical makeup. In one study, chloride input from caustic was 0.27 kg/adt or 14.4% of the total chloride input to a softwood kraft mill. In other inland mills, chloride from caustic makeup ranged from 4-56% of the total, depending on the degree of closure practised and the chloride content of the wood. While use of rayon grade caustic with low chloride levels would avoid this problem, the supply of this material is limited and commands a premium of about $15/ton NaOH.

While the SSU resin is not stable in 50% NaOH, it is stable in lower concentrations and excellent results have been obtained in producing a purified NaOH at concentration of about 10%. In many mills caustic soda is diluted to this concentration prior to storage and ultimate use, so that dilution is not a problem. If fact, in such cases this approach may be preferable to treatment of precipitator dust, in that there is no increased load on the evaporators. In addition, filtration is not an issue.

Typical laboratory pilot plant results for caustic purification are shown in Table III.
**Table III: Caustic Soda Purification**

<table>
<thead>
<tr>
<th></th>
<th>relative flow</th>
<th>[NaOH] (g/L)</th>
<th>[Cl] (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>feed</td>
<td>1</td>
<td>143</td>
<td>1.65</td>
</tr>
<tr>
<td>product</td>
<td>1.13</td>
<td>130</td>
<td>0.13</td>
</tr>
<tr>
<td>waste</td>
<td>1</td>
<td>1.0</td>
<td>1.68</td>
</tr>
<tr>
<td>recovery</td>
<td></td>
<td>91.7%</td>
<td>0.7%</td>
</tr>
<tr>
<td>mass balance</td>
<td></td>
<td>3.1%</td>
<td>4.2%</td>
</tr>
</tbody>
</table>

**Oxidized White Liquor**

A logical stream to consider for chloride removal is white liquor. Unfortunately it has been found that sulfide contained in white liquor has an adverse effect on the SSU resin. There are applications in the mill which employ oxidized white liquor (OWL) which can be successfully treated, however. It should be noted that the white liquor must be fully oxidized before treatment with the SSU. That is to say, that the sulfide ions must be oxidized all the way through the thiosulfate intermediate to sulfate.

During oxygen delignification, caustic solutions are employed to solubilize the lignin that has reacted with oxygen. The effluent from the oxygen delignification stage is usually recycled back to recovery. To avoid the use of purchased NaOH and to maintain the mill’s Na/S balance, OWL is often used as an alkali source for the delignification process.

OWL can similarly be used in place of purchased caustic for the alkaline extraction stage (E-stage) following chlorine dioxide bleaching. This is necessary to maintain the Na/S balance where the E-stage filtrate is recycled to recovery.

Laboratory pilot plant experiments have been conducted on synthetic solutions to demonstrate the feasibility of removing chloride from fully oxidized white liquor. Typical results are shown in Table IV. After oxidation of the white liquor and removal of the chloride with the SSU, the purified OWL can then be used for its intended purpose.

**Table IV - Purification of Oxidized White Liquor**

<table>
<thead>
<tr>
<th>rel. flow</th>
<th>NaOH (g/L)</th>
<th>Cl (g/L)</th>
<th>SO(_4) (g/L)</th>
<th>CO(_3) (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>feed</td>
<td>1</td>
<td>95.6</td>
<td>15.07</td>
<td>51.8</td>
</tr>
<tr>
<td>waste</td>
<td>1.14</td>
<td>4.4</td>
<td>12.58</td>
<td>2.45</td>
</tr>
<tr>
<td>product</td>
<td>1.14</td>
<td>82.4</td>
<td>.47</td>
<td>42.35</td>
</tr>
<tr>
<td>recovery</td>
<td>99%</td>
<td>4%</td>
<td>93%</td>
<td>101%</td>
</tr>
<tr>
<td>mass bal</td>
<td>3.8%</td>
<td>-1.0%</td>
<td>-1.2%</td>
<td>5.3%</td>
</tr>
</tbody>
</table>

**Demineralizer Effluent**

As discussed above, most mills employ ion exchange demineralizers for purification of recovery boiler makeup water. Appreciable quantities of caustic soda are used to regenerate the anion exchange beds. The spent regenerant contains primarily sodium sulfate, sodium carbonate, sodium chloride and residual sodium hydroxide. The SSU can be used to removed sodium chloride from this liquor. It can then be used as a source of chemical makeup in the recovery cycle.

A spent anion regenerant sample was obtained from a mill and treated with the lab pilot plant. The results are shown in Table V. Although sulfate and carbonate were not analyzed, it is expected that recovery rates would be similar to that for NaOH.
Table V - Purification of Spent Demineralizer Regenerant

<table>
<thead>
<tr>
<th></th>
<th>[NaOH] (g/L)</th>
<th>[Cl] (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>feed</td>
<td>27.8</td>
<td>0.749</td>
</tr>
<tr>
<td>waste</td>
<td>2</td>
<td>1.25</td>
</tr>
<tr>
<td>product</td>
<td>27.2</td>
<td>0.126</td>
</tr>
<tr>
<td>recovery</td>
<td>96%</td>
<td>15%</td>
</tr>
</tbody>
</table>

Spent Scrubber Liquor

White liquor is frequently used for scrubbing residual bleaching chemicals from bleach plant exhausts. The presence of sulfide improves the efficiency of the scrubber since it chemically reduces oxidizers such as chlorine and chlorine dioxide. When the sulfide content or alkalinity have become exhausted, the liquor must be replaced with fresh white liquor. The spent liquor will have a very similar composition to oxidized white liquor, but at somewhat higher chloride and lower alkalinity.

The spent scrubber liquor still contains appreciable soda values and could be recycled to recovery once the chloride has been removed. A typical mill may produce 5-10 gallons per minute (1.1-2.2 m³/h) of spent scrubber liquor from the bleach plant, containing 35 g/L of NaOH. The value of the caustic soda contained in this solution would be about $200,000 U.S. per year.

Although this application has not yet been tested, it would appear to be an ideal candidate for purification with the SSU technology.

Caustic soda solutions are also used to scrub recovery boiler flue gas in some mills to remove HCl. The resulting NaOH/NaCl solution could be purified with an SSU and used for kraft chemical makeup.

CONCLUSION

A new system for removal of chloride from kraft liquors has been developed. The process is based upon a novel ion exchange/sorption process that was developed almost twenty years ago for purification of waste acid. It is possible to remove more than 90% of the chloride from a wide variety of different chemical solutions while recovering more than 90% of the valuable components. A key feature of this process is that sodium chloride is eluted from the resin with merely water.

Although the optimum application of this process is treatment of electrostatic precipitator dust, the process can also be used to remove chloride from other chloride bearing streams, such as caustic soda makeup, oxidized white liquor, demineralizer regenerants and spent scrubber liquor.

An important issue in implementation of this technology is the water balance of the mill. If the system is used to purify electrostatic precipitator dust, the water that is used to dissolve the dust must be evaporated. In addition to the increased evaporation load, provision must be made to deal with the increased possibility of scaling in the evaporators due to the higher sulfate content of the black liquor.

High chloride concentrations in black liquor are known to promote recovery boiler plugging. Although a few mills presently require frequent shutdowns for boiler cleaning due to high chlorides, it is expected that this problem will become more widespread as mills attempt to ‘close-up’ and reduce liquor losses that provide natural outlets for chloride contamination.
REFERENCES


