

Salt Removal From Pulp Mills

Douglas C. Pryke¹, Douglas W. Reeve², W. Howard Rapson³, Jerome A. Lukes⁴,
and Hoc Nghia Tran²

¹Douglas Reeve & Associates, Toronto, Ontario, Canada

²Douglas Reeve & Associates and Department of Chemical Engineering and Applied Chemistry, University of Toronto

³Department of Chemical Engineering and Applied Chemistry, University of Toronto

⁴Lukes Process Development Corp., Ogden, Utah, USA

ABSTRACT

Sodium chloride enters pulp mill chemical recovery cycles with wood, make-up chemicals and by recovery of bleach plant effluent. The accumulation of NaCl can be controlled, depending on the rate of input, by various means including normal recovery cycle losses, purging of NaCl enriched process streams, recovery boiler precipitator dust leaching, recovery boiler flue gas scrubbing and by various green liquor and white liquor evaporation processes.

Salt removal by white liquor evaporation has been practised since 1977 at the world's first closed cycle pulp mill at Great Lakes Forest Products Ltd. Thunder Bay, Ontario, where twenty-five tons per day of 99% pure sodium chloride is removed from the pulping chemical recovery cycle and is reused in the generation of bleaching chemicals.

INTRODUCTION

In the production of kraft pulp, wood chips are treated under high temperature (120°C) and high pressure with pulping chemicals, sodium hydroxide and sodium sulphide. After treatment, the spent pulping chemicals are separated from the wood fibre and recovered by counter-current washing. Approximately 50% of the wood constituents, (lignin, etc.) is removed in pulping and recovered with the spent pulping chemicals. The spent liquor, known as weak black liquor, is concentrated by evaporation from 15 to 65 wt% total dissolved solids and burned in a chemical recovery boiler. The organic compounds produce heat for steam generation and the inorganic compounds form a smelt in the bottom of the furnace. The smelt, consisting mainly of sodium carbonate and sodium sulphide with minor amounts of sodium sulphate, sodium chloride, and sodium hydroxide, is removed and dissolved in water to form "green liquor".

The green liquor is causticized with slaked lime, Ca(OH)₂, to convert sodium carbonate to sodium hydroxide solution, known as "white liquor", for pulping the wood chips. The calcium carbonate formed in this reaction is recovered, burned and converted back to calcium oxide in a lime kiln. The pulping chemical recovery cycle and lime cycle are shown schematically in Figure 1 (Whitney, 1968). Various make-up chemicals are used in the recovery cycle including sodium hydroxide, sodium

sulphate, sulphur, sodium carbonate, calcium carbonate and calcium oxide. Sodium sulphate is the most common make-up chemical.

Sodium chloride can enter the chemical recovery process in many different ways at different rates as summarized in Table 1. In locations where wood has been transported, stored or sorted in seawater, the sodium chloride input with the wood is typically 10 kg per air dry tonne and can reach as high as 27 kg per air dry tonne (Reeve, 1976). Minor amounts of NaCl can enter the chemical recovery cycle with the makeup sodium hydroxide, typically less than 0.5 kg per air dry tonne.

Bleaching chemicals (chlorine, chlorine dioxide, sodium hypochlorite and sodium hydroxide) give rise to sodium chloride in bleach plant effluent. When the effluent is partially recovered as is the practice in some mills in Scandinavia, or fully recovered as in the closed cycle mill, relatively large amounts of sodium chloride enter the chemical recovery cycle. Sodium chloride input can reach 110 kg per air dry tonne when full bleach plant effluent recovery is practised and chlorine dioxide substitution for chlorine in the first stage of bleaching is low.

SALT REMOVAL

Sodium chloride accumulates in the chemical recovery cycle until the rate of removal equals the rate of input. For most mills, sodium chloride accumulation (high

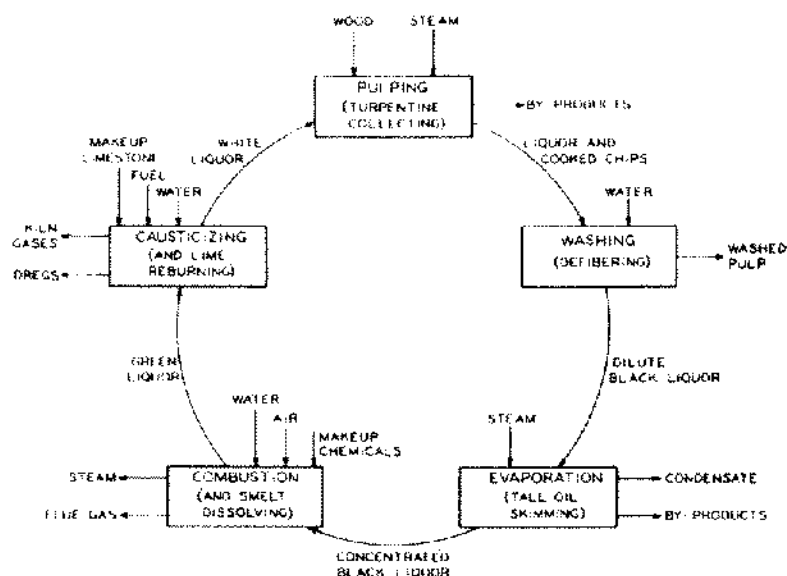


Figure 1. The Pulp Chemical Recovery Cycle.

TABLE 1

Potential Sources of Sodium Chloride in Pulp Mills	
Sodium Chloride Input	
Source	kg per air dry tonne
Make-up Chemicals	0.5
Wood (Sea borne)	10.0
Bleach Plant Effluent	10.0
E Stage Only	
Bleach Plant Effluent	60
D → CEDED Bleaching	
Bleach Plant Effluent	110
C _D EDED Bleaching	

NaCl concentration in the white liquor) has not been a problem. The NaCl is purged by the normal process liquor losses. As liquor is recovered and process losses are minimized, greater accumulation occurs. Typical salt concentrations in white liquor for most mills is less than 10 gpl.

A sodium chloride removal process must be employed in cases where accumulation of sodium chloride in the chemical recovery cycle cannot be controlled by normal process losses. Sodium chloride can be removed by leaching the dust electrostatically precipitated from the recovery boiler flue gas. In one such process, precipitator dust is leached with water and sulphuric acid is added to convert the sodium carbonate to sodium sulphate (Christie, 1979). The leach liquor is enriched with sodium chloride ($\text{NaCl}/\text{Na}_2\text{SO}_4$ weight ratio = 3) and is discarded thereby removing NaCl from the chemical recovery cycle. The amount of NaCl that can be removed with this process is limited by the concentration of NaCl in the precipi-

tator dust. At 35 gpl NaCl concentration in white liquor the maximum removable by this process is estimated to be 25 kg per air dry tonne. This process has been used by a west coast pulp mill achieving removal rates of 12.5 kg per air dry tonne. (Christie, 1979).

Removal of chloride as HCl, can also be achieved by scrubbing the recovery boiler flue gases. The process requires operation of the chemical recovery cycle at high sulphidity ($\text{Na}_2\text{S}/(\text{Na}_2\text{S} + \text{NaOH})$) in order to achieve maximum removal rates. Mill trials indicate that 5 kg per air dry tonne NaCl can be removed at 40% sulphidity (Warnqvist and Norrstrom, 1976). This process has been in operation in a mill in northern Sweden for several years.

Larger amounts of sodium chloride in the chemical recovery cycle can be removed by various green liquor and white liquor processes (Reeve, 1980, 1981, 1982; Lukes, 1979; Lukes and Shroeder, 1976). The processes involve manipulation of the $\text{NaOH}-\text{Na}_2\text{S}-\text{Na}_2\text{SO}_4-\text{Na}_2\text{CO}_3-\text{NaCl}-\text{H}_2\text{O}$ system to remove sodium chloride at a rate equal to the rate of input, thereby controlling the concentration of NaCl in the pulping liquor. The SRP process, a white liquor evaporation process for salt control, has been operating since 1977 in the first closed cycle pulp mill at Great Lakes Forest Products Ltd., Thunder Bay, Ontario, removing twenty-five tons per day NaCl (Pryke et al., 1983).

SALT REMOVAL BY WHITE LIQUOR EVAPORATION

Salt removal by white liquor evaporation is a two-stage process, as shown in Figure 2. In the first stage, white liquor at 11 wt% active alkali ($\text{NaOH} + \text{Na}_2\text{S}$) and ap-

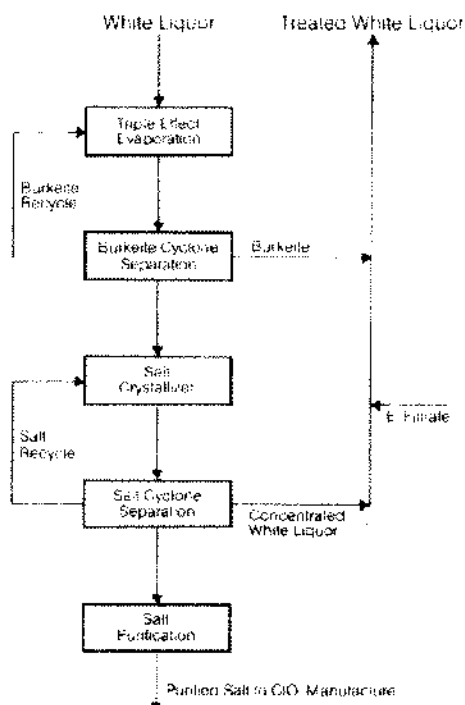


Figure 2. The Salt Recovery Process.

proximately 20–30 gpl NaCl is concentrated in a forced-circulation triple-effect evaporator to approximately 28 wt% active alkali, approaching salt saturation. The sodium carbonate that was not converted to sodium hydroxide in the recausticizing process of the chemical recovery cycle and the sodium sulphate that was not reduced to sodium sulphide in the chemical recovery boiler crystallize as anhydrous sodium carbonate and the

double salt, burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$). The first stage crystals are removed from the concentrated liquor.

In the second stage of the process, the liquor is further concentrated to 36 wt% active alkali ($\text{NaOH} + \text{Na}_2\text{S}$), and cooled from 120°C to 75°C in an evaporator crystallizer, crystallizing sodium chloride and small amounts of burkeite and sodium carbonate. The crude salt is separated from the concentrated liquor and leached with water in a 3-stage countercurrent decantation circuit. The salt is finally washed on a horizontal belt filter. The concentrated liquor, low in sodium chloride, is diluted to normal pulping liquor concentration with caustic extraction stage effluent from the bleach plant. The pulping liquor leaving the salt recovery plant contains 12–18 gpl NaCl.

After washing and filtration, the salt enters a gravel bed lixator to produce saturated brine. The brine is clarified to remove suspended organic and inorganic solids, treated with a small amount of sodium hypochlorite, sand filtered and then reused in the generation of the bleaching chemical, chlorine dioxide.

Operating Experience

The SRP process at Great Lakes Forest Products Ltd. started up in early 1977. In the original design, gravity thickeners and bottom feed rotary drum filters were used for separation of burkeite in the first stage and crude salt in the second stage. The burkeite crystal size was highly variable, as shown by the different settling rates in Figure 3 (Pryke et al., 1983). Operation of the gravity thickener and particularly the bottom feed filter was extremely difficult when the crystals were large and fast settling. The thickener would plug and the crystals would settle in the vat of the filter preventing cake formation. Similar diffi-

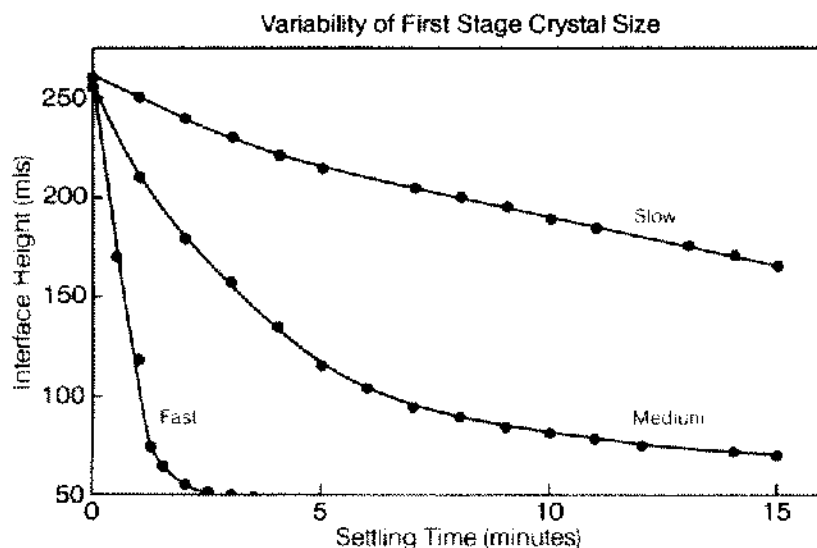


Figure 3. Variability of the First Stage Crystal Settling Rates.

culties were experienced in the salt system. The variability of the crystal size is not well understood but is postulated to be caused by traces of organic compounds in the feed white liquor acting as agglomerating agents during crystallization.

These operating problems were overcome when cyclone separation systems, as shown in Figure 4, replaced the gravity thickeners and filters. The systems have operated trouble-free for over two years, substantially improving the salt removal efficiency and plant availability and reliability.

The SRP plant availability is 85%. Water washing and acid-cleaning to maintain high heat transfer coefficients account for 40% of the SRP downtime. In the first effect heat exchanger, sodium carbonate and burkeite deposit on the liquor side of the tubes and the walls of the evaporator. The wall salt builds up and if not removed it falls and plugs tubes. A wall washing system is employed to prevent salt plugging.

The rate of deposition in the heat exchanger of first effect is highly variable. To minimize fouling rates, 50% of the burkeite is recycled to the first effect to increase the recirculating crystal slurry density.

In the second effect, calcium carbonate deposits on the heat transfer surfaces. These deposits sometimes respond to water washing and are easily removed by acid washing. Iron sulphide deposits slowly on the heat transfer surface of the third effect and is also removed easily by acid washing. The crystallizer heater does not foul but is prone to salt plugging. A wall washing system has been installed to minimize wall salting.

Salt Quality

Twenty-five tons per day NaCl is removed from the closed cycle mill by the SRP process. The salt is typically 99% NaCl and in crystal size distribution compares favorably with commercially available evaporator fine salt. A typical analysis of the salt can be found in Table 2. The salt is highly coloured, light orange to medium brown, due to the presence of trace organic contaminants. The main contaminants, totalling less than 1% are typically: sodium carbonate 0.4%; sodium sulphate 0.2%; active alkali (NaOH + Na₂S) 0.08%.

Calcium, magnesium and iron are present in concen-

TABLE 2
SRP Salt Quality

Composition	
<i>Major Components</i>	
Moisture	5 %
NaCl	99 % dry basis
Na ₂ CO ₃	0.4% dry basis
Na ₂ SO ₄	0.2% dry basis
Total S as Na ₂ SO ₄	0.4% dry basis
Active Alkali (NaOH + Na ₂ S)	0.1% dry basis
<i>Minor Components</i>	
Ca	< 50 ppm
Mg	< 50 ppm
Fe	< 50 ppm
Soluble Organic Material	300 ppm total organic carbon on salt
Insolubles (20% brine)	100 ppm on salt

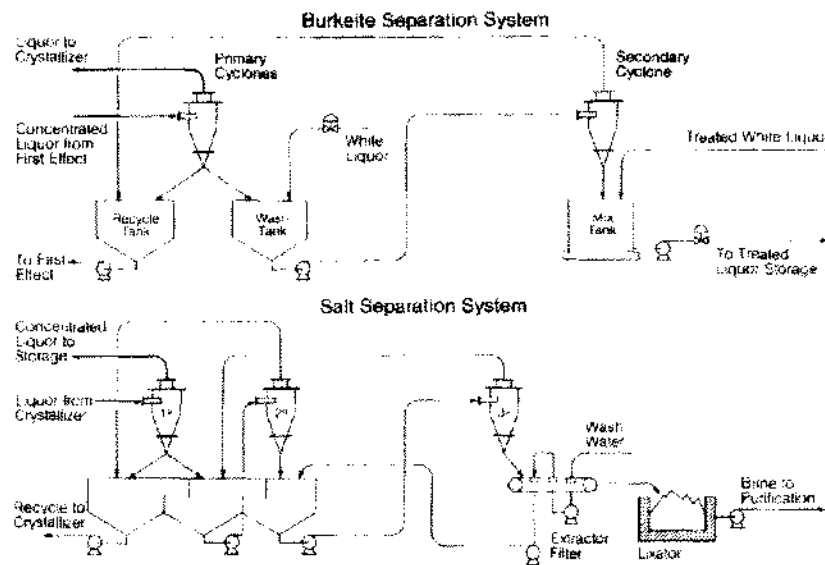


Figure 4. Burkeite and Salt Separation Systems.

trations less than fifty parts per million. Nickel, manganese, copper, and zinc concentrations are less than 1 ppm. Brine formed from SRP salt has 100 ppm suspended solids: calcium as calcium carbonate; iron as iron sulfide; and some insoluble organic material.

Soluble organic material, typically 300 ppm on salt expressed as total organic carbon, imparts a yellow colour to the brine. The soluble and insoluble organic compounds most likely originate from the bleach plant filtrate used to form white liquor. The bleach plant filtrate contains soluble organic material. The salt is reused in the manufacture of the bleaching chemical, chlorine dioxide.

SUMMARY

Sodium chloride can enter the pulping chemical recovery cycle in many ways. The accumulation and steady state concentration of NaCl in the liquor cycle can be controlled by several removal processes.

For relatively low input rate, up to 15 kg per air dry tonne, the accumulation of sodium chloride and steady state NaCl concentration in the chemical recovery cycle can be controlled by normal losses, by precipitator dust leaching, or by flue gas scrubbing.

For relatively large input rates, as in the case of the closed cycle mill, white liquor and green liquor evaporation process can remove NaCl and control its accumulation.

The first commercial application of a white liquor process for salt removal has been successfully removing 25 tons per day of NaCl, which is about 30 kg/ADt, for over six years at the closed cycle pulp mill of Great Lakes Forest Products Ltd. in Thunder Bay, Ontario. Early operating problems and corrosion have been overcome with successful process and equipment modifications.

The salt removed by the SRP process is 99% pure and

is reused in the manufacture of the bleaching chemical chlorine dioxide.

REFERENCES

- Christie, R. D. 1979. Salt Removal Experience in MacMillan Bloedel Limited, presented at the CPPA-TAPPI International Pulp Bleaching Conference, Toronto, Ontario, June 11-14.
- Lukes, J. A. 1975. Removal of Sodium Chloride from Pulp Mill Operation, U.S. Patent 3909344. Sept. 30.
- Lukes, J. A. and R. P. Shroeder. 1976. Sodium Chloride Removal in Pulp Mill Systems, U.S. Patent 3,945,880. March 23.
- Pryke, D. C., D. W. Reeve, J. A. Lukes, D. A. Donovan, G. Valiquette and E. M. Yemchuk. 1983. Chemical Recovery in the Closed Cycle Mill, Part II: The Salt Recovery Process, *Pulp and Paper Canada*, v. 84, no. 2, pp. T46-T49.
- Reeve, D. W. 1982. Removal of Dissolved Salts from Sulphide Liquors, Canadian Patent 1058358. July 17.
- Reeve, D. W. 1981. Modified System for Recovery of Sodium Chloride from White Liquor, Canadian Patent 1102055. June 2.
- Reeve, D. W. 1980. Pulp Mill Process with Sodium Chloride Removal, Canadian Patent 1072262. February 26.
- Reeve, D. W. 1976. The Effluent-Free Bleached Kraft Pulp Mill—Part VII: Sodium Chloride in Alkaline Pulping and Chemical Recovery, *Pulp and Paper Canada*, v. 77, no. 8, pp. T136-T143.
- Warnqvist, B. and H. Norrstrom. 1976. Chlorides in the Kraft Recovery System, Part 1: Chlorides in the Recovery Boiler, and a Mechanism for Chloride Removal, presented at the CPPA-TAPPI International Pulp Bleaching Conference, Chicago Illinois, May 2-6.
- Whitney, R. P., ed. 1968. Chemical Recovery in Alkaline Pulping Processes, TAPPI Monograph 32.