

Removal of Chlorides From ESP ASH By Treating With Sulphuric Acid

Vadivel M¹., Umarani C²., Rajesh K.S³. & Eashwaran⁴

1. JKKM College of Technology, T.N. Palayam Post Gobi (T.N.)

2. Govt Arts College, Salem - 7

3. TCT Aqua Chemicals Pvt. Ltd., Chennai

4. SVCE, Chennai

ABSTRACT

The presence of 40% to 50% inorganic material in black liquor being fired to a recovery boiler forms a low melting temperature ash or smelt after combustion. As a result of burning black liquor, fly ash deposits on tube surfaces in the upper furnace. These deposits grow and eventually restrict flue gas flow if they are not occasionally removed from the tube surfaces by soot blowers. Massive deposit accumulation will lower the heat transfer efficiency of the boiler. Deposits can form a localized corrosive environment, possibly resulting in tube damage. Various methods have been proposed in the past to remove chloride and potassium from the liquor cycle which have been responsible for such deposits. The common practice is to purge precipitator dust, because it is enriched in both Cl and K. Chlorides can be removed by re-crystallization and by leaching precipitator dust. Increasing liquor sulfidity also helps remove chloride from the system. In this paper we experimentally evaluated the removal of chloride from the ESP ash by treating with sulphuric acid as HCl which can be collected and reused, unlike other methods which necessitate purging of chloride rich effluent.

KEY WORDS : Kraft Pulp Mill , Black liquor , Recovery Boiler, Chloride, Potassium, Removal Process, ESP Ash, ECF bleaching, TCF bleaching

Introduction

Chemical Recovery boiler has two unit operations one is burning of concentrated black liquor and steam production by utilizing the Black liquor calorific value 13000–15000 KJ/Kg, yields steam from Black liquor solids. As mill closure increases, so does the accumulation of non process elements (NPEs) in the Kraft recovery liquor cycle (1) especially with the conventional bleaching and ECF bleaching where as TCF bleaching does not. The main non-process elements of concern to a pulp mill and bleach plant are potassium and chlorides which are alkali soluble. Depending on the wood species and how they are transported to the mill, and the amount and type of makeup chemicals, Cl and K inputs may vary from 1.2 to 14 kg/adt as Cl, and from 0.7 to 4 kg/adt as K (2). Other non-process elements that are routinely found in bleach plants are magnesium, manganese, iron, strontium, and radium. Of these, the transition metals manganese and iron can have an impact on bleaching, and radium is invariably radioactive and can co-precipitate in barium sulfate scale, causing scale and salvage pipe to be radioactive. Most of these trace cations come to the pulp mill in the wood (3). All of the divalent metals are insoluble in strong alkaline conditions either as the carbonate (calcium, strontium, barium and iron (II)), the hydroxide (magnesium, manganese and iron (III)), the sulfate (barium and radium) or the sulfide (manganese and iron (II)). Since they all start out contained within the wood, the most likely location for them to precipitate is within the fiber wall or lumen. Evidence is that most of the calcium in brown stock pulp is calcium carbonate.(4), Black liquor is the fifth most important fuel in the world next to coal, oil, nature gas etc (4). Mill closure causes increased chloride and potassium concentrations in the Kraft liquor cycle can result in accelerated corrosion, boiler plugging and ring formation in the lime kiln. Typical mill

operation would have about 85% - 95% of the K load coming from the wood chips and about 60% - 70% of the Chloride load coming from both wood chips and water. The concentration of Cl and K in the Kraft recovery cycle varies from mill to mill, depending on the inputs the degree of mill closure and the liquor sulfidity. Mills with increased closure can build the Cl and K levels up to 4 - 12 times greater than mills which operate fairly open (5). Deposits are derived from two different sources,

- (1) Carryover. Smelt and/or partially burned black liquor particles physically entrained in flue gas.
- (2) Condensation. Fume or dust resulting from the condensation of compounds volatilized from the lower furnace.

Literature Review

Two technologies for removing chloride and potassium from ESP Ash is very familiar. One is an evaporator/crystallizer based process, while the other uses ion exchange. The evaporator/crystallizer process is effective for both chloride and potassium removal (90%), whereas the ion exchange process is more efficient at chloride removal (95%) and less selective in removing potassium (5-10%). The latter is more effective at salt cake recovery (95%) compared to the former (80%). The best suited technology depends on the requirements of each mill which will vary. The commercially available processes include: (6)

- **Leaching:** Kvaerner, Andritz
- **Evaporation/Crystallization:** Andritz, HPD, Eka Chemicals
- **Freeze crystallization:** by Mitsubishi
- **Ion exchange:** Eco-Tec and Paprican

The first three processes take advantage of differences in solubility between the various salts, primarily alkali sulfates (Na_2SO_4 and K_2SO_4) and alkali chlorides (NaCl and KCl), while the ion exchange process uses a proprietary resin which selectively adsorbs NaCl . All of the processes remove the Cl and K in a purge stream, and return the more purified alkali sulfate to the recovery liquor cycle. From the literature sources we can find the Effect of chloride on carryover deposit by TSTK (Sticky temperature temperature above which the material becomes sticky because it contains 15 to 20% liquid phase. TSTK or T15) and TRD (Radical deformation temperature temperature above which the material contains about 70% liquid phase and is so fluid that it can run off due to its own weight (also referred to as slagging temperature). TRD or T70. (7)

Figure: 1

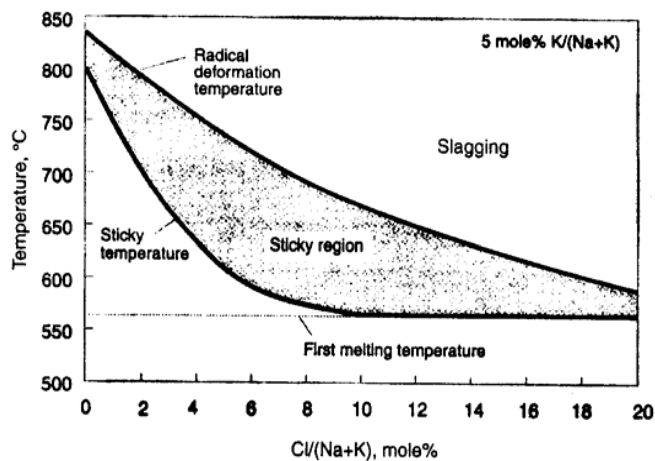
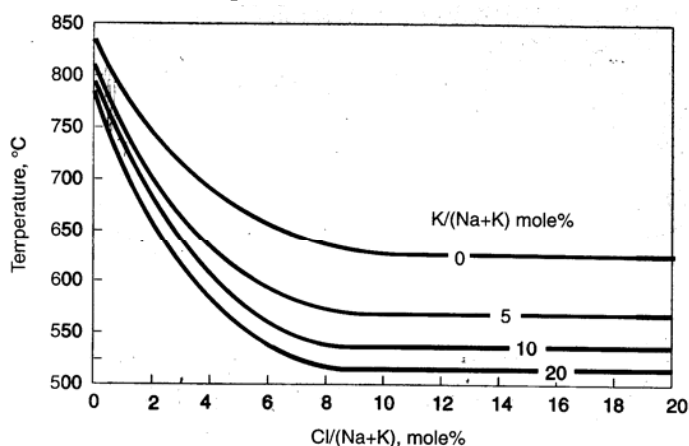


Figure 2 . Effect of Cl on the deposit TSTK for a range of potassium mole ratios



Chloride has been found to lower both the sticky deposit and the radical deformation temperatures of recovery boiler fireside deposits. The effect of increasing potassium concentrations is similar to chloride, but not as pronounced. Potassium works together with chloride to decrease the sticky deposit temperature and the radical deformation temperature. At low chloride concentrations, potassium has very little effect on sticky deposit temperature. On the other hand, when the chloride mole % $\text{Cl}/(\text{Na}+\text{K})$ exceeds 10%, potassium has a significant effect on lowering the sticky temperature. The enrichment is usually defined as the ratio of the content in the dust to the content in the virgin black liquor.

Effect of chloride and potassium content on recovery boiler fouling

Tran, Barham and Reeve have reported that mills with low chloride in the as-fired black liquor dry solids, less than 1.6 $\text{Cl}/(\text{Na}+\text{K})$ mole %, or 0.5 wt % chlorides, have an insignificant amount of plugging caused by potassium. Composition of dust from recovery boiler furnace ESP ash varies much depending on liquor properties and firing conditions including the heat load of the super heaters and especially of the concentration of the potassium and chloride in the firing black liquor In Table 1 is the range of major components in ESP ash presented

Typical composition range of ESP ash

Component	Wt %	Compound	% Wt
Na	28 - 35	Na_2SO_4	65 -90
SO_4	45 - 65	Na_2CO_3	9 - 27
CO_3	5 - 15	NaCl	2 -10
K	2 - 10	K_2O_4 KCl	5-10
Cl	1 - 5		

Chloride removal processes:

Leaching

Leaching is proposed and developed by Kvaerner and Andritz. The ESP dust is dissolved in warm water (around 90°C) at a controlled ash-to-water ratio to make near-saturated solution: 1.2-1.6 kg ash/kg water. The higher solubility of NaCl and KCl than Na_2SO_4 keeps chlorides in solution while Na_2SO_4 precipitates. The solid/liquid separation step consists of either a centrifuge or a filter. Advantages: simple and cheap; disadvantages: low removal and recovery efficiency. [8] [9]

Evaporation/Crystallization

It is commercialized by Andritz and HPD, the dust is completely dissolved in excess water, about 0.4 kg ash/kg water. Single or multiple vacuum evaporators are used depending on the heat source. Normally secondary heat from the evaporators is used. The condensate is used to dissolve ash. Na_2SO_4 crystals are separated in a filter or a centrifuge and have a water content of about 15-25%. Advantages: Good removal and recovery efficiency, crystals are larger than precipitated Na_2SO_4 ; disadvantages: more complicated and expensive set-up.

Freeze Crystallization

Mitsubishi has developed this technology which is based on the precipitation of $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ that occurs below 20°C . These crystals are huge and easily separated from NaCl and KCl . To recover as much Na as possible, sulphuric acid can be added in order to transform Na_2CO_3 into Na_2SO_4 . Most modern mills, however, have a sulphur surplus and additional sulphur is not desired. Advantages being easy separation and fairly good Chloride removal. Disadvantages include expense, requires large amounts of electricity, possibly gives an extra water-load on the evaporators. [10]

Ion Exchange

This method is developed by Eco-Tec and Paprican. The dust is dissolved in water and filtered before entered into an ion exchange column. An amphoteric resin with high selectivity for NaCl is used. The resin contains cation as well as anion exchange groups. The two steps of the method are adsorption, where Na⁺ and Cl⁻ are attached to the resin and warm water elution, or desorption, where the NaCl-rich solution is washed out and the resin is regenerated. Advantages: very good chloride removal, low capital and maintenance cost, minimal space needed; disadvantages: poor potassium removal, extra evaporation need since the purified salt cake has very low solids content, plugging of the resin in the harsh pulp mill environment. [11]

Shortcomings Of The Above Processes

All the above processes mentioned are no doubt commercially established and proven methods for chloride and potassium removal from ESP ash. But considering the fate of the removed chlorides, they have to be purged out to the effluent. With more and more stress on the paper mills for zero liquid discharge, the mills can't afford to drain the chlorides which will lead to increase in total dissolved solids. Considering the environmental aspect all the processes fail to offer an eco friendly approach. Taking into account the levels of chlorides circulating as dead load, purging the same into the effluent stream or disposal considerations otherwise makes it alarming. Thus there is a need for an alternative approach for the chloride removal problem.

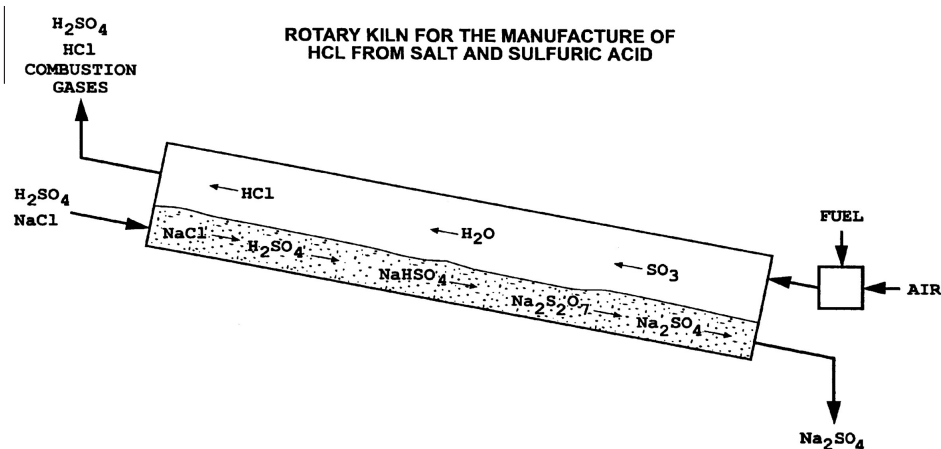
Our Proposed Alternative Approach

The proposed method is based on a simple fundamental chemistry principle which is adopted for detecting the presence of chlorides using concentrated Sulphuric acid, where in the chlorides are converted to Hydrogen chloride which detected by fuming in presence of ammonium hydroxide.

The ESP ash when treated with calculated quantity of Con Sulphuric acid and roasted to required temperature, results in conversion of chloride to hydrogen chloride which can be dissolved in water and comfortably used.

Materials And Methods

Process Equipment Design

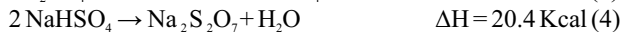
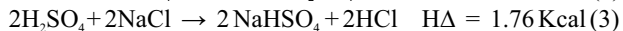
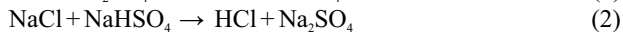


Chloride and sulphate estimations were performed as per standard test methods.

Results And Discussion

The Chemistry Behind The Reaction of NaCl with Consulphuric Acid

A complete Knowledge of the chemical reaction engineering and Thermodynamics is absolutely necessary to design the process equipment . The actual reaction which takes place in this method is



Equation 1, 3 is same proceeds at about 150 °c . Equation 4 takes place at about 240 to 250 °c , Endothermic . The decomposition of Sodim pyrosulfate to Sodium sulfate by Eq 5 proceeds at close to 460 °c . Equation 6 is to be studied extensively.

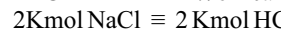
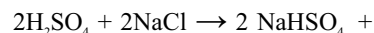
The conversion process will require an arrangement like a rotary lime kiln, operating at maximum outlet temperature of about 600 deg C, which is sufficient for conversion of chlorides to HCl with con Sulphuric acid.

COMPOSITION OF ESP ASH

Compound	ESP ash composition in %
Chloride as NaCl	29.57
Sulfate as Na2SO4	64.83
Potassium K	5.60

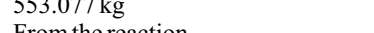
Mass Balance

For 29.57 % Chloride as NaCl and 98 % H₂SO₄ to produce 100 Kg HCl . Assume the conversion is 92 %



$$\text{Actual Amount of NaCl required} = 117 \times 100 / 73 \times 0.2957 \times 0.98 = 553.077 \text{ kg}$$

$$\text{From the reaction}$$



$$\text{Actual Amount of H}_2\text{SO}_4 \text{ required} = 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

$$= 98/73[100/0.2957 \times 0.98] = 463.261 \text{ kg}$$

Lab studies:

For lab based estimation, 50.2 gm of sulphuric acid and 100 gm of ESP ash were mixed in a 1:2 molar ratio. The mixture was then heated in china dish at different temperatures and then the HCl evolved was dissolved in water. The ESP ash after treatment was tested for sulphate and chlorides. The results obtained at different temperature are obtained as below

Compound	Temp C	Cake		pH		Na ₂ CO ₃ Consumption
		Sulfate %	Chloride %	Before neutralising	After neutralising	
Original ESP Ash		76.0	29.0			
Ash +H ₂ SO ₄	150	89.0	11.0	1.0	7.5	2.2
Ash +H ₂ SO ₄	480	99.7	0.20	1.1	7.5	1.1

Since the salt obtained after acid treatment had some free acid, it had to be neutralized so that it can be used back in the process.

Comparison of Chloride Removal With Other Process

Components	Crysatallization	Membrane Separation	Ion Exchange	Proposed Chemical Method
Chloride Removal%	98.0 -99.0	94.0 -96.0	96.0-98.0	99.00 -99.98
Sulphate %	85.0- 88.0	96.0-98.0	98.0-99.0	99.00 -99.45

As a generalization guide for the evaluation of chloride removal, a concentration of chloride of less than 1.5% by weight in ash with a low potassium concentration may provide the desired one-year of continuous recovery boiler operation without interruption for cleaning. Chloride has also been removed by evaporating of white liquor to recrystallize sodium chloride (10) and by leaching precipitator dust and disposing of the chloride-rich leach liquor. Increasing liquor sulfidity also helps remove chloride from the system. Here high sulfur input to the recovery boiler results in high SO₂ concentration in the flue gas. This leads to the formation of HCl vapor, which purges Cl from the system via the recovery boiler stack.

In practice some safety margin for the maximum allowed temperatures has to be reserved. Generally the following maximum chloride and potassium concentrations are recommended

Hence to maintain a low chloride concentration at the same time convert chlorides into useful product viz HCl, the proposed con Sulphuric acid treatment method is promising.

Recommended maximum weight for % Cl and K

Steam Temp C	Virgin Black liquor Cl%	Virgin Black liquor K%	ESP Cl%	ESP Cl%
< 480	0.5	1.5-3.0	2.5	4-7
< 500	0.2-0.3	1-2	1.0-1.5	2.5-5.0
> 500	0.15	1-2	1.0-1.5	2.5-5.0

Future work

In this work experiments have been done in laboratory scale. Future work should include looking into the solubility of typical ESP dust, in equilibrium tests and also process equipment design. Materials for designing should be based on the chemical and physical nature of the process inputs.

Acknowledgement

The authors sincerely thank to Research Guide, Co authors and the support of Correspondent and Principal of JKK Munirajah College of Technology, Gobi for the valuable guidance on submission of this Article in IPPTA seminar -2012

References

1. A. Mark Minday et al., An Over view of various strategies for balancing salt cake, chloride and potassium levels an ECF kraft mill., Presented at the TAPPI Minimum Effluent Symposium, San Fransisco, Oct.23-24, 1997. P.01.
2. Tran, H.N., Barham, D., and Reeve, D.W., "Chloride and Potassium in the Kraft Chemical Recovery Cycle", Pulp & Paper Canada 91(5) : 55-62 (1990).
3. Järvinen, R.; Välttilä, R. A Practical Method for Studying NPes in a Kraft Mill. Int. Chemical Recovery Conf. Tampa FL, June 1998; TAPPI Press: Atlanta. GA, 1998; 107-116.
4. Hartler, N., and Libert, J., "The behaviour of certain inorganic ions in the wood/white liquor system", Svensk Papperstidning, 76(12): 454-457(1973).
5. Reeve . D.W., "The Kraft Recovery Cycle "Tappi Kraft Recovery Operation Short course, Tappi Press 2002
6. Ulrica Johansson ., Different Methods for the Purge of Chlorides and Potassium from Electrostatic Precipitator Dust in the Kraft Mill ., Department of Chemical Engineering, Lund Institute of Technology, February 2005
7. Tran, H.N., "Kraft Recovery Boilers Chapter 9, Upper Furnace Deposition and Plugging," edited by T.N. Adams, TAPPI Press, pp. 247-282 (1997).
8. M.Eriksson, Process Engineer, Kvaerner Power AB, Göteborg 2005
9. Heikki Jaakkola, Director of Evaporation Technology, Andritz Oy, Helsingfors, Finland 2004
10. C.J.Brown, A.Russer, M.Paleologou, R.Thompson, N.Jemaa, Chloride Removal from Kraft Liquors Using Ion Exchange Technology, TAPPI Environmental Conference, Vancouver, Canada 1998
11. Yoshihisa Arakawa, Deputy General Manager, Boiler Engineering dep. Mitsubishi Heavy Industries Ltd, Yokohama, Japan 2004
12. Borg, A., Teder, A., Warnquist, B., "Inside a Kraft Recovery Furnace - Studies on the origins of sulphur and sodium emission", Tappi, 57 (1) 126-129 (1974).
13. H.Tran, Fouling of tube surfaces in kraft recovery boilers, Toronto, Canada 2004.