

Removal of Non - Process Elements in Chemical Recovery- A Review of Technologies

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ABSTRACT

Pulp mills have tightened their liquor cycle to improve the spill control and decrease the chemical losses. Closing up the liquor cycle has resulted in build-up of non process elements (NPE), such as potassium and chloride in the pulping and chemical recovery cycle. Majority of the mills in India, which are using wood as their main raw material are faced with the problem of severe build-up of these NPE. Chloride & Potassium enter the liquor cycle through wood, process water and chemicals. Depending on the quality of wood, degree of recycling of liquor streams and process technologies applied, these NPE's may cause severe production related problems in the chemical recovery. Due to their high volatile nature at high temperature 'Cl' and 'K' compounds (Na Cl and KCl) vaporize from recovery boiler char bed and becomes enriched in electro static precipitator ash. These non-process elements, despite their small quantities in black liquor can drastically lower the melting temperature of ash deposits leading to severe fouling of heat transfer areas of recovery boiler thereby adversely affecting the thermal efficiency. The Wood & Pulp Research Centre at Harihar Polyfibers initiated the research work on review of available technologies for removal of non-process elements in chemical recovery cycle and laboratory investigation on various techniques, which have potential application in reducing the build-up of non-process elements. The present paper highlights the problems associated with build-up of non-process elements in chemical recovery cycle and the status of established technologies and also findings of laboratory scale studies on removal of non-process elements at Wood & Pulp Research Centre, employing the cooling and evaporative crystallizations. The paper discusses about various commercially available technologies like- leaching of ESP ash, evaporative crystallization, cooling crystallization, and Ion exchange for removal of potassium and chloride from the ESP ash and relevance of these technologies to mills in India and also the case studies involving the impact of removal of potassium and chloride on the performance of chemical recovery boilers.

Introduction

Chemical recovery system is an integral part of pulp and paper units and the efficiency of chemical recovery plays an important role in economics. Efficiency of chemical recovery units in terms of thermal efficiency, energy recovery and conversion of thermal energy to electrical energy, has tremendous impact on over all economics of pulp production. With increased closing of chemical recovery and pulping cycles and with increasing chemical recovery efficiencies, there is a build up of non process elements such as potassium, chloride, calcium, SiO₂ etc. Major source of entry of these non-process elements is through process inputs such as wood, bark from wood, water, lime, salt cake etc, and wood along with wood bark contributing the maximum of NPE levels. Since there is no purging point for these non-process elements (NPE) there is a continuous build up of these in

the closed loop of chemical recovery cycle.

Due to their high volatile nature, these NPE, particularly chlorides (NaCl and KCl) which vaporize from recovery furnace char bed and become enriched in the electrostatic precipitator ash. Therefore efforts to remove "Cl" and "K" from recovery cycle have been directed at ESP ash.

Levels of Potassium and Chlorides in Pulp and Paper Mills

The build-up of NPE is a common problem in almost all the Pulp & Paper Mills throughout the world including majority of the integrated Pulp & Paper Mills in India also. Level of 'K' & Chloride in some of these pulp and paper mills is given below:

Table - 1
Levels of 'K' & 'Cl' in Indian Pulp & Paper Mills

| Mill. No. | K% | | Cl% | |
|-----------|-------|-------|-------|------|
| | K | KCl | Cl | NaCl |
| 1 | NA | NA | 2.75 | 4.5 |
| 2 | 4.25 | 8.22 | 13.15 | 21.5 |
| 3 | 11.35 | 21.19 | 5.18 | 8.32 |
| 4 | NA | NA | 5.51 | 9.0 |
| 5 | 3.24 | 6.65 | 7.84 | 12.6 |
| 6 | 10.7 | 19.98 | 4.74 | 7.61 |

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Results indicate that these mills had very significant concentration of 'K' and 'Cl' in the ESP ash due to continuous build-up of these elements in closed loop of chemical recovery cycle.

Review of Technologies on commercial scale, for removal of “Cl” and “K” from ESP Ash

All the commercially available Cl and K removal processes to treat the ESP ash from recovery boiler fall into four main categories i) Leaching ii) evaporation crystallization iii)freeze/cooling crystallization and iv)ion exchange.

First three processes have taken the advantage of difference in solubility between various salts primarily alkali sulfates (Na_2SO_4 and K_2SO_4) and alkali chloride (NaCl & KCl) while ion exchange process uses ion selective resin which selectively absorb NaCl . All these processes remove the 'Cl' and “K” in purge stream (ESP ash) and return the purified alkali sulfate to recovery liquor cycle. In solution of mixed salts (Na_2CO_3 , NaCl , Na_2SO_3 , K_2SO_4 and KCl) the presence of NaCl dramatically decreases the solubility of Na_2SO_4 , due to common ion effect, which allows more NaCl to be dissolved from slurry of ESP ash without dissolving Na_2SO_4 or allows more Na_2S_4 to be recrystallized from ESP ash solution without recrystallizing the NaCl .

Generally “K” removal is more complicated than “Cl” removal because of different forms of potassium such as K_2SO_4 , $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ (glaserite) which hinders the removal of potassium in both leaching and evaporation crystallization. In such situation most effective solution may be to simply

purge ESP ash, until the 'K' concentration decreases

Leaching:

Leaching takes advantage of the high solubility of NaCl and KCl , compared to the relatively less soluble Na_2SO_4 , especially in NaCl -saturated solution. The leaching process consists of two main unit operations. In the first stage, precipitator ash is combined with water (and recycled leachate) to form a slurry or paste. The amount of water/leachate used must be carefully controlled to promote the dissolution of chloride and potassium salts without dissolving sodium sulfate. A typical leaching system developed by Kvaerner is illustrated of fig-1.

A higher temperature also improves the selectivity of the process, as more Cl salts and less sulfate salts dissolve in the system. After mixing in a stirred tank, the slurry passes to the separation stage, typically a filter or centrifuge. The solids (primarily sulfate) are returned to the Kraft liquor cycle, while the leachate (rich in Cl and K) is recycled back to the first step. A portion of the leachate is purged from the system as the means of Cl and K removal.

The solid-liquid separation is achieved by means of a centrifuge. The first unit was started-up at the Aracruz mill in Brazil in 2002. The Cl and K removal efficiency was reported to be about 70%, with 80% recovery of Na and 85% recovery of Sulphate.

Evaporative crystallization:

Evaporation/crystallization processes also take advantage of the relatively low solubility of Na_2SO_4 , as compared to the NaCl and KCl , but in the opposite manner to leaching. The precipitator dust is first dissolved in water (or recycled process condensate); the

solution is then evaporated. Because of its lower solubility, Na_2SO_4 crystallizes first. The presence of Cl ions helps to decrease the solubility of Na_2SO_4 further. The purified Na_2SO_4 is filtered and returned as a solid to the liquor cycle. Most of the mother liquor (rich in Cl and K) is returned to the crystallizer, but a small portion is sewered to purge the Cl and K.

There are three evaporation/crystallization processes available commercially: i) HPD CRP “Chloride Removal Process”, ii) Andritz ARC “Ash Re-Crystallization” process, and iii) Eka Chemicals PDR “Precipitator Dust Recovery”. The design has been updated considerably since its first installation in 1995, designed for the Champion BFR “Bleach Filtrate Recycle” project in Canton, FL. The evaporator operates under vacuum with an external reboiler. Single- and multi-effect systems are now in use, depending upon the quantity of ash being processed and the integration of the CRP into the black liquor evaporator train. Instead of the original salt cake filter, the CRP now uses an internal wash column for solid-liquid separation. A typical evaporative crystallization technology is given below in Figure No. 2

There are six CRPs operating worldwide: 3 in North America, 2 in South America and 1 in Australia. Published data from the Canton installation shows a chloride removal efficiency of 95% and 80% sulfate recovery. The Eka Chemicals' PDR process is also a re-circulating evaporator-crystallizer, operating under vacuum with an external reboiler. The PDR has not yet been commercialized, but laboratory and

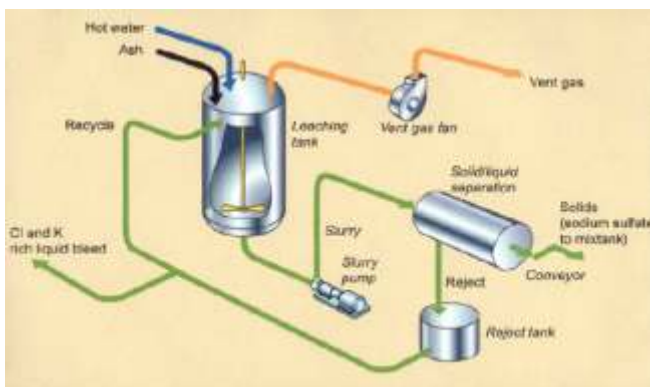


Figure -1
Kvaerner Ash Leaching System

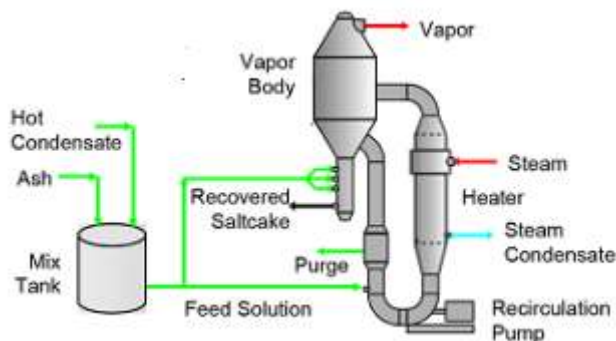


Figure 2
HPD-Evaporation Crystallization

pilot-scale testing indicates a chloride and potassium removal efficiency of 90%, with 80% recovery of sulfate and carbonate.

Cooling crystallization:

Freeze crystallization relies on the dramatic decrease in solubility of sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) at low operating temperatures. Below about 30°C , Na_2SO_4 suddenly precipitates as large $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals, leaving Cl and K in solution. The two phases can then be separated, with the purified sodium sulfate crystals returned to the Kraft liquor cycle, and the solution purged to remove Cl and K. A typical cooling crystallization technology developed and commercialized by Mitsubishi Power System is shown in Figure 3. The

precipitator ash is mixed with sufficient amount of water to dissolve the chloride and potassium salts, along with a portion of the sodium sulfate. Acid may be added to improve sodium recovery, as described previously. The slurry is then transferred to a precipitation tank, where ice is added to decrease the temperature to 15°C , causing Na_2SO_4 in solution to recrystallize as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The slurry is then decanted to separate and recover the decahydrate crystals, along with any undissolved Na_2SO_4 , while the decanted liquor is purged. The removal efficiency was reported to be 90% for Cl and 75% for K with 70% sodium recovery.

The impact of removal of Potassium and Chlorine from ESP ash is illustrated below in Figure -4

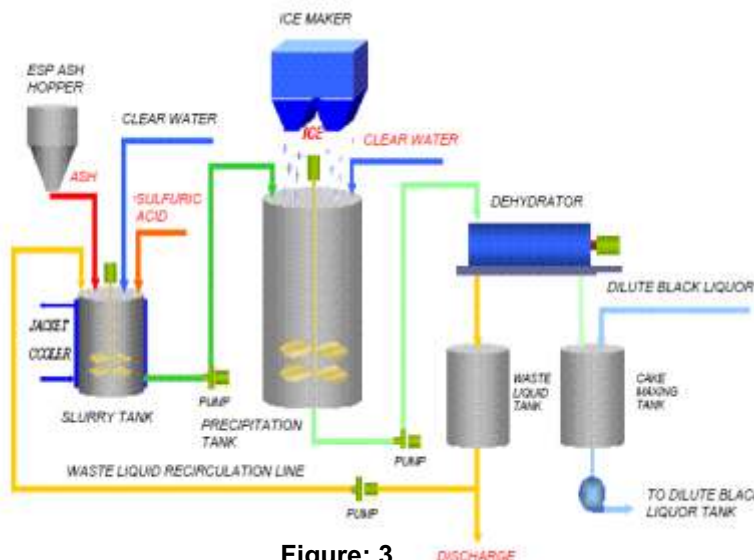


Figure: 3
Mitsubishi Freeze Crystallization Process

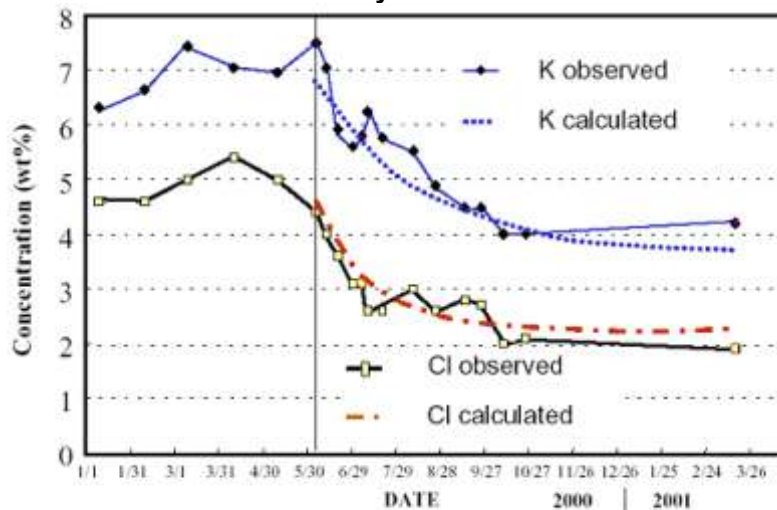


Figure - 4
Potassium and Chloride Concentrations in Recovery Boiler ESP Ash Before and After Potassium and Chloride Removal System installed at Oji Paper Kasugai Mill

Ion exchange:

Specialized ion exchange resins are commercially available which contain both cation- and anion-exchange groups on each particle, and so can remove both ions simultaneously. Because chloride ions are the only monovalent anions in the precipitator duct mixture, these resins will preferentially adsorb sodium chloride over sodium sulfate and carbonate. Using this resin, an ion exchange treatment system known as PDP (Precipitator Dust Purification) has been developed by Eco-Tec and Paprican. A process schematic is shown in Figure. Due to the sensitivity of the resin, the precipitator dust solution must be filtered beforehand, to minimize resin fouling. Regeneration is easily achieved with water. The PDP system has not been commercialized, although a pilot plant unit is in operation at Paprican's laboratory. Chloride removal is reported to be 97%, with minimal losses of sodium, sulfate, and carbonate (6%, 1%, and 0.5% respectively). However, because the sodium concentration exceeds that of potassium by many orders of magnitude, potassium removal is low, on the order of only 5%. An ion exchange system is therefore better-suited to a situation where chloride removal is significantly more important than potassium removal. One difference between the ion exchange process and other processes is that the purified sodium sulfate is returned to the Kraft liquor cycle in the form of solution, and not as a crystal or slurry, which may have impact on dilution of black liquor.

Impact of Non Process Elements

The present day chemical recovery installations are having very high chemical recovery efficiency and the system is completely closed and the build up of potassium and chloride is very fast. As a consequence the system becomes enriched with potassium and chloride. During combustion stage because of the low melting points of these potassium and chlorides which are primarily in the form of KCl and NaCl tend to evaporate and deposit in the upper regions of the chemical recovery boilers. Even small amount of potassium and chloride can tremendously influence the sticky temperature of the smelt causing serious plugging of the economizer and super heater zones of the boiler. It is clear from Figure -6 that the increasing

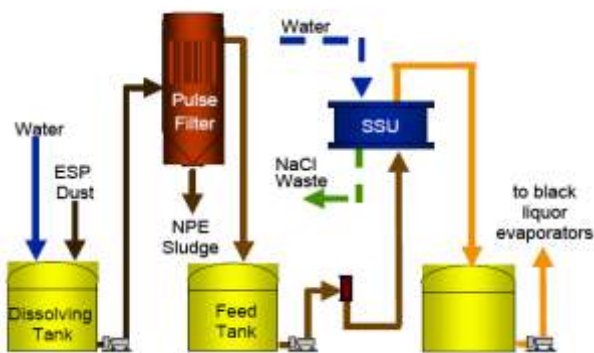


Figure -5
Eco-Tec PDP Ion Exchange System
(SSU = Salt Separation Unit)

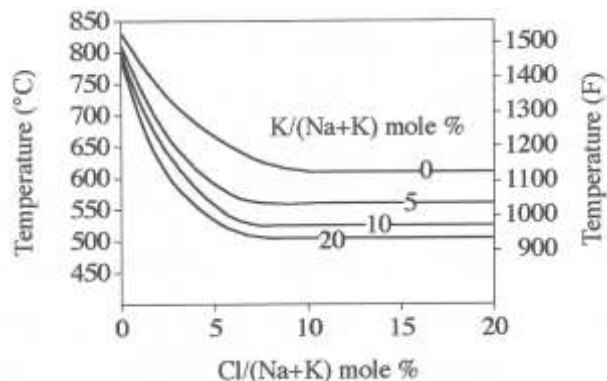


Figure-6
Effect of Chloride and Potassium on
deposit sticky temperature

percentage of Chloride & Potassium in the Black Liquor there is a decrease in the Sticky temperature which is one of the reason for reducing the smelt temperature & evaporation of potassium chloride & sodium chloride from the char bed.

form hard and more deposits. Due to these deposit formation there is a significant drop in the thermal efficiency which results in reduced steam temperature and also affect boiler runnability.

Laboratory Studies on Cooling Crystallization:

Slurry of ESP dust is mixed with minimum amount of water to form slurry at 30-40°C to dissolve Cl and K salts. H₂SO₄ is added so that most of the carbonates contained in ESP ash is

Table-2 shows the chemical composition of scale sample collected from the flue gas passage indicates significant proportion of K as K₂SO₄. The scale sample also contained high proportion of Na₂SO₄ & Na₂CO₃. Although the Na₂SO₄ & Na₂CO₃ are not in the ratios of burkeite but high concentration of K & Na₂SO₄ give indication of forming hard deposit presumably composed of burkeite & glasserite type double salts.

Table -2
Chemical composition of
scale sample obtained in
flue gas passage

| COMPONENTS | % w/w |
|---------------------------------|-------|
| Na ₂ CO ₃ | 32.5 |
| Na ₂ SO ₄ | 40.8 |
| NaOH | 2.5 |
| NaCl | 0.9 |
| K ₂ SO ₄ | 8.7 |
| Na | 29.6 |

To confirm the nature of deposits we carried out the synthetic mixture of Na₂SO₄ & Na₂CO₃ including the formation of Burkeite type double salts, drying of those double salts clearly indicate when Na₂SO₄ & Na₂CO₃ is present in the Burkeite form tend to

Figure 7
Laboratory scheme for Cooling Crystallization

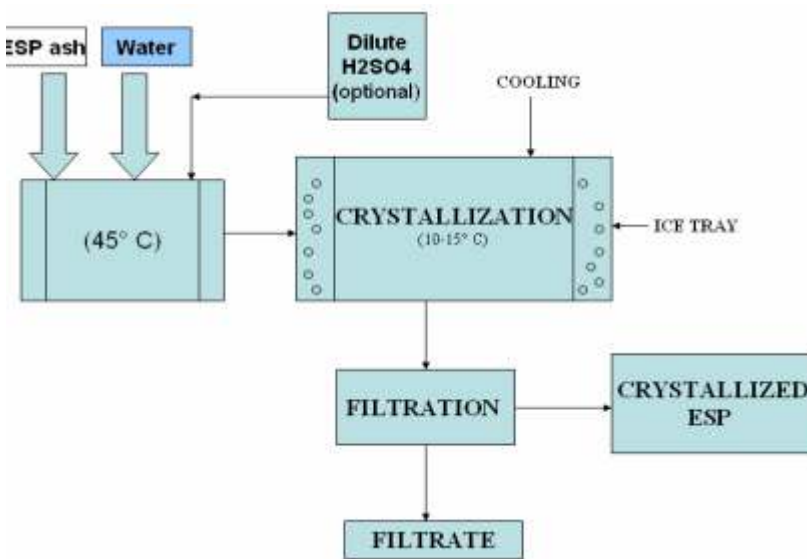


Table -3
Cooling crystallization trials

| Expt no | METHOD | Cl removal % | K removal % | Na recovery % |
|---|--|--------------|-------------|---------------|
| <i>By cooling crystallization technique</i> | | | | |
| 1 | (ESP:Water) 1:1.9, cooling to 15°C | 62 | 53 | 55 |
| 2 | (ESP:Water) 1:1.9 + 5ml of 4N H ₂ SO ₄ , cooling to 15°C | 81 | 46 | 68 |
| 3 | (ESP:Water) 1:1.7 + 5ml of 4N H ₂ SO ₄ , cooling to 15°C | 80 | 50 | 83 |

converted into sulphates. The slurry is cooled to below 20°C (but not below 10 °C) at which solubility of sodium sulphate is low and this makes it possible to precipitate, separate and recover sodium sulphate. Thus crystals formed can be separated by filtration. The Laboratory scheme for cooling crystallization is given in **Figure-7**.

Results and discussions

Number of lab scale trials were conducted and summary of results are given in the **Table-3**

When the resulting aqueous solution is cooled below 20°C by indirect cooling using ice, the degree of super saturation of the solution can be enhanced to promote the precipitation of coarse crystals. The crystals so precipitated have such a large grain size that they can subsequently be separated and recovered with ease. It was also observed that the residence time of holding the slurry at 15° C for a longer time, the crystals formation was more. Laboratory scale cooling crystalline studies clearly indicate that it was easy to remove chloride than potassium. By removing Sodium Chloride and Potassium from ESP ash, the concentrations of Chloride & Potassium present in the chemical recovery system can be reduced as a result, the operation period (boiler runnability) can be extended at the same time the steam consumed for the purposes of soot blowing to remove the ash adhering to the heat transfers surfaces can decrease remarkably.

Laboratory Studies on Evaporator Crystallization

Laboratory flash evaporator comprising of rotating flask connected to cooling condenser and a flask for receiving the condensate was used for evaporative crystallization. The saturated solution of ESP ash is taken in a rotating flask and water is evaporated till crystallization starts.

After ascertaining maximum crystallization of sodium sulphate, the evaporation is terminated and filtered on a suction flask using filter paper. The crystallized ESP and filtrates were analyzed.

The laboratory evaporative crystallization study has shown that it is possible to remove nearly 90% Chloride and 70% Potassium. For enhancing the salt recovery there is a need for

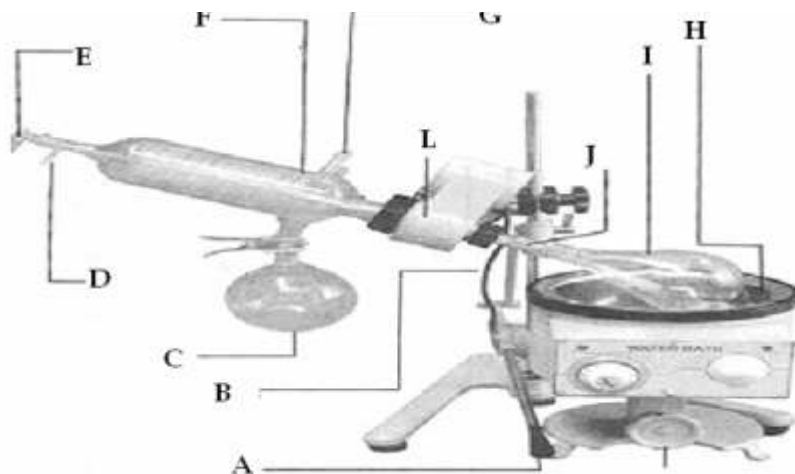


Figure -8
Rotary Vacuum Flash Evaporator

Table: 4

Evaporative crystallization trials for removal of NPE from ESP ash

| PARTICULARS | 1st CRYSTALLIZED ESP |
|---------------------------------------|-------------------------|
| Chloride % | 0.29 |
| Potassium % | 2.56 |
| Sodium % | 19.37 |
| Na₂CO₃ % | 0.795 |
| Na₂SO₄ % | 60.07 |
| Chloride removal % | 90.03 |
| Potassium removal % | 66.77 |
| Sodium recovery % | 70.23 |

recycling the mother filtrate after recovery of sodium Sulphate crystals.

Conclusions:

1. The evaluations of available technology clearly indicate that the crystallization technology has many advantages, compared to Ion exchange and Leaching techniques.
2. Among the evaporation or cooling crystallization there is need for critical evaluation of these for 'K' and 'Cl' removal efficiency and salt recovery and the size of the plant for which these technologies are economically viable.

3. Laboratory studies on cooling and evaporation crystallization showed significant reduction in 'K' and 'Cl' from ESP ash.

4. Looking into the present trend in extent chemical recovery technology, the NPE removal from ESP ash should form an integral part of Chemical Recovery.

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