# A Systematic Approach of Controlling Water Soluble Scales in Modern Evaporator Plant

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In Kraft pulping process, the evaporators, which concentrate the weak black liquor from ~15% to 65-75% total solids for firing in the recovery boiler, routinely foul with inorganic and/or organic scale on heat transfer surfaces. This is a major problem in modern evaporator plant, resulting in lost capacity and lost time for scale removal.

In respose to industry need, the study, is conducted on evaporator performance to evaluate the nature and extent of evaporator fouling problems (particular on water soluble scales) and is recommended a strategy to minimize the problem. Particularly at higher concentration of black liquor.

## INTRODUCTION

Scaling and fouling of black liquor evaporator is a major problem in many pulp and paper mills. There are at least six compounds of groups of compounds in black liquor that contributes to fouling during evaporation,

1. Sodium compounds, ($Na_2CO_3$) and $Na_2SO_4$).

2. Calcium compounds ($CaCO_3$).

3. Aluminum and silica.

4. Cellulose fiber.

5. Black liquor soap.

6. Lignin.

Each of these has its own particular mechanism, and mainly depends on mill practice to avoid its effects. Sodium salts scaling is often referred to as "Burkeite" scaling and is the most common today's scaling issue for mills. Sodium salts scaling, sodium carbonate ($Na_2CO_3$) that results from incomplete causticizing of the green liquor, and sodium sulfate ($Na_2SO_4$) that results from incomplete reduction of sodium sulphate to sodium sulphide in the recovery boiler.

### Solubility behavior of $Na_2CO_3$ + $Na_2SO_4$ in black liquor

Fouling occurs when $Na_2SO_4$ and $Na_2CO_3$ precipitate from solution as illustrated [1] in Figure 1. The two critical solids points occur as the liquor solids content is raised. The Ist critical solids point occurs when the liquor becomes saturated with respect to $Na_2SO_4$ + $Na_2CO_3$ and burkeite starts to precipitate. At the 2nd critical solids point, $Na_2SO_4$ has been depleted and the solution becomes saturated with the remaining $Na_2SO_4$ and $Na_2CO_3$ precipitates along with any remaining burkeite. The steeper slope above the 2nd critical solids point indicates that the extra $Na_2CO_3$ precipitate at a significantly higher rate than the burkeite above the 2nd critical solids point. This increase in precipitation rate is an important characteristic of the 2nd critical solids point.

The observed evaporator fouling behavior can be described in terms of specific fouling regions that have been identified in figure 1. Fouling is "minimal" in region A. In reigon B, where burkeite is gradually precipitating; the fouling is "manageable". The fouling is "serious" in region C, a small solids change around the 2nd critical solids point, leads to the sudden increase in precipitation rate. Finally, above the 2nd critical solids point, the fouling behavior once again becomes "manageable" (region B) as the additional precipitate has had the opportunity to grow on existing crystals.

The relative composition of $Na_2SO_4$ and $Na_2CO_3$ in the black liquor determines the locations of the 1st and 2nd critical solids points. These can be moved as illustrated in figure 2. Addition of $Na_2SO_4$ to the system (e.g., makeup salt cake) will increase the 2nd critical solids point. This is a desirable effect. However, because of the extra salt in the system, the 1st critical solids point will decrease, which is not desirable. To prevent this decrease in 1st critical solids. Sulfate should be added after 1st point. Reducing the $Na_2CO_3$ content (e.g., by improving the causticizing conversion) will increase both critical solids points, which is desirable.

The precipitation rate above the 2nd critical solids point is higher than just below it. The 2nd critical solids point can be controlled by adjusting the $Na_2CO_3$ and /or $Na_2SO_4$ content of the liquor. The 2nd critical solids point also correlates with soluble-scale problems in falling-film evaporators.
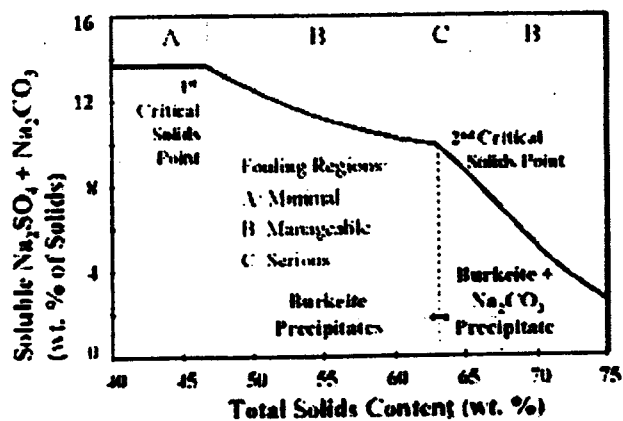
and NaOH.

Effective sodium is defined as.

- Effective sodium, g Na/L = Total sodium - $23(Na_2CO_3/53 + Na_2SO_4/71)$ ........................................1



Figure 1 : Solubility behavior of $Na_2SO_4$ + $Na_2CO_3$ in black liquor [1].



Figure 3 : Observed solubility of burkeite in black liquor (at $Na_2CO_3/Na_2SO_4$ ratio of 80:20) at six levels of effective sodium [13]
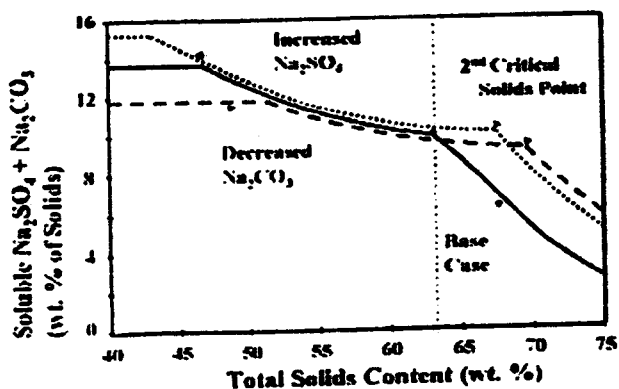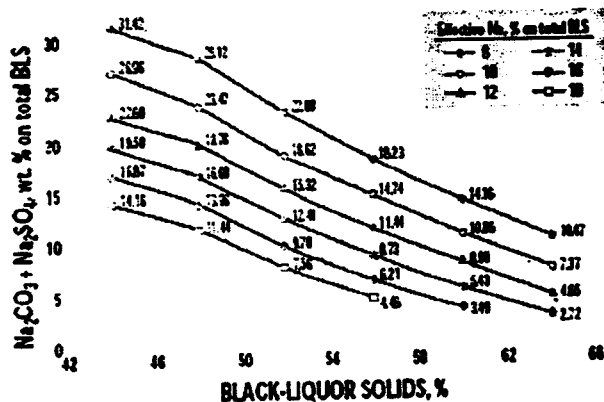


Figure 2 : Control of critical solids points by varying the black liquor chemistry [1].

The solubility of the $2Na_2SO_4$, $Na_2CO_3$ is independent of temperature in range of 100-140°C and is assumed to be unaffected by liquor organics. The major components affecting burkeite solubility are,

- Effective sodium

- $Na_2CO_3$ + $Na_2SO_4$ mass-concentration ratio

- Blank liquor solids content.

**Mathematical model to predict first critical solid point**

The mathematical equation [3] helped to predict BLS from a known $Na_2CO_3$ + $Na_2SO_4$ weight % on solids and known level of effective sodium. Both values are obtained from a WL analysis of $Na_2CO_3$. $Na_2SO_4$, $Na_2S$
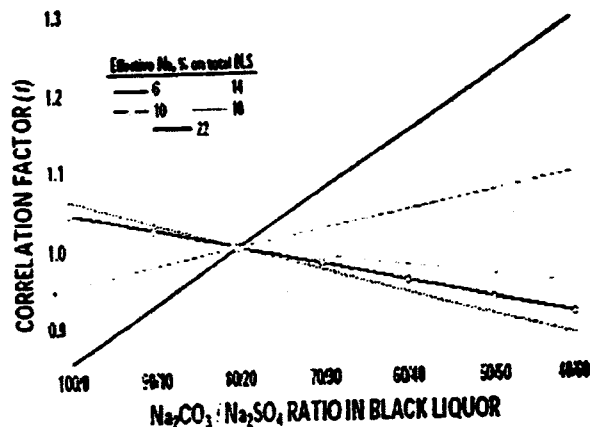


Figure 4 : Correction factor for determine solubility of burkeite in black (relative to $Na_2CO_3/Na_2SO_4$ ratio of 80:20) at five level of effective sodium [3]

The general solubility relationship at $Na_2CO_3/Na_2SO_4$ ratio of 80:20, from data developed by T.M. Grace is,

- BLS = 85.47 − 1.47Z - 0.95W ................................2

The correction factors for the other $Na_2CO_3/Na_2SO_4$ ratio of 80:20 from data developed by T.M. Grace is,

- $f=r(5*10^{-5}x^2 − 7.7*10^{-4}x − 2*10^{-5})−(1.013*10^{-3}x^2 + 0.01568x + 0.9993)$ ..........................3

The relations are referred to the following data developed by T. M Grace (13),

Finally; the critical BLS - the black liquor solids content where burkeit precipitation will begin-is calculated from following equation using the correction factor (eq., 3) and liquor solids content (eq., 2),

*   Critical BLS, % = [f(BLS/100)]/{1-(1-f)(BLS/100)]}..............4

Where,

Z - Effective sodium, % on total BLS

W - $Na_2CO_3$ + $Na_2SO_4$, % wt on total BLS

BLS - Black liquor solids, %

x = [(effective sodium, %* BLS, %)/(100 − BLS, %)].

f − Correction factor

r − Precent $Na_2SO_4$ from ratio of $Na_2CO_3/Na_2SO_4$.

## Possible improvement by controlling water soluble scale - A mill case study

The evaporation of WBL from 18%TS to 67%TS is taken care by 7 effects FFFF evaporator, with the steam economy of 5.98. The first effect is subdivided in to three bodies out of which two are working and one is available for cleaning with WBL and process condensate. Similarly, the second effect is subdivided in to two bodies out of which one is working and other is available for cleaning. The change over of bodies takes place after each 5 hours of running. The body change over sequence is given in Appendix-1.

The system is supplied by manufacturer for 8 hrs running cycle, due to the problem of scaling; the running hours came down to 5 hrs. The analysis is carried to find out the nature of scale formation. The samples of scale had been collected during the washing period of the effects; the results are given in Table (1).

**Table 1 : Analysis of Scales from 2nd effect of Multi Effect Evaporator**

| Particulars | 1st Hour of washing | 4th hour of washing |
|---|---|---|
| Calcium (as $CaCO_3$)% by Wt | 1.2 | 0.68 |
| Magnesium (as $MgCO_3$) % by Wt | 0.46 | 0.09 |
| Sodium sulphate (as such) % by Wt | 8.71 | 1.3034 |
| Acid insoluble % by Wt | 3.08 | 2.06 |
| Silica % by Wt | 2.07 | - |
| Loss of ignition % by Wt | 35.31 | 31.28 |

The discussion with referred to above table; it is found that natures of scales are water soluble. Where the hard scales due to $CaCO_3$ is less in percentage compared to

**Table 2 : White liquor Analysis**

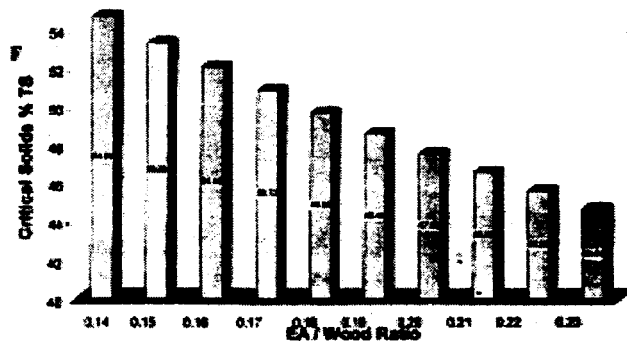| White Liquor Analysis (as $Na_2O$) | | |
|---|---|---|
| NaOH | : | 68 gpl |
| $Na_2S$ | : | 21gpl |
| $Na_2CO_3$ | : | 17 gpl |
| $Na_2SO_4$ | : | 2.3gpl |
| Active Alkali | : | 89 gpl |
| Sulphidity | : | 23.59% |
| TTA | : | 106 gpl |
| Causticizing Efficiency | : | 80% |



**Figure 5 :** Critical solids % TS Vs EA/Wood Ratio
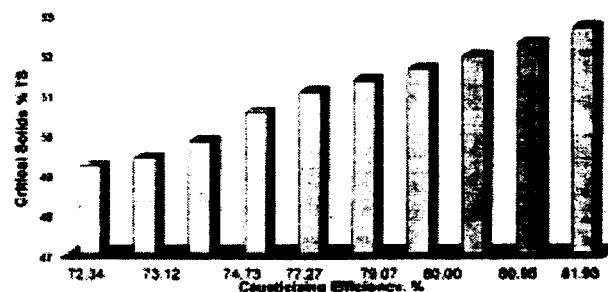


**Figure 6 :** Causticizing Efficiency, % Vs Critical solids % TS

water soluble scales. The system behavior at beginning of each cycle is observed (i.e. after each boil outs) and compared with behavior after periodic cleaning (i.e. once in two months pressurized water cleaning), the deviation is less. So study is carried on controlling the water soluble scales.

The first critical solid point of black liquor evaporation of present system using the white liquor analysis in Table (2) is calculated and results are shown with effect of variation in causticizing efficiency and EA/Wood ratio on critical black liquor solids, in figure (5,6). And assuming the brown stock yield to be steady of 46%.

The solubility of sodium salts from black liquor is also predicted using white liquor analysis in Table (2), the
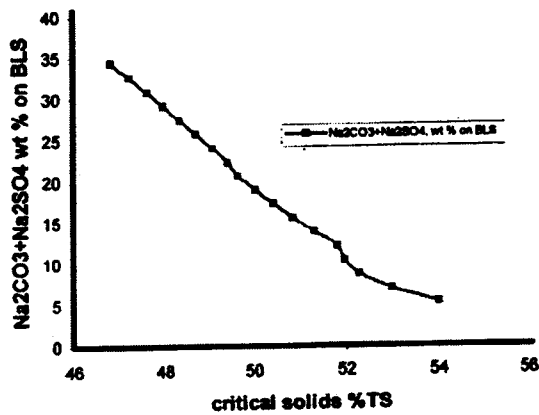
**Figure 7** :Results of solubility level of burkeite in black liquor evaporation



**Figure 8** : Effect of $Na_2SO_4\%$ wt on black solids and its effect on solubility level of burkeite in black liquor evaporation.
Based on the predicted results shown in Figure(7,8), the conclusion drawn as,

results are shown in figure (7,8).

Figure (5) shows predicted relationship between critical solids and the EA/ wood ratio. The EA / wood ratio is a pulping parameter driven on bases of pulp quality not on black liquor evaporation. The present EA/ wood ratio is 0.165, the burkeite begins to precipitate at 50% BLS. At particular case EA/ wood ratio of 0.2, the burkeite begins to precipitate at about 2.62% weight on BLS, lower than the present condition.

Figure (6) shows predicted relationship between critical solids and the causticizing efficiency. The relation is predicted at present EA/ wood ratio of 0.165. The present causticizing efficiency is 80%. At particular case of 77% causticizing efficiency, the burkeite begins to precipitate at about 0.51% lower than present condition.

• At critical solids point of 49-52% the fall of $Na_2CO_3$ + $Na_2SO_4\%$ wt on BL is higher than 47-49% solids point.

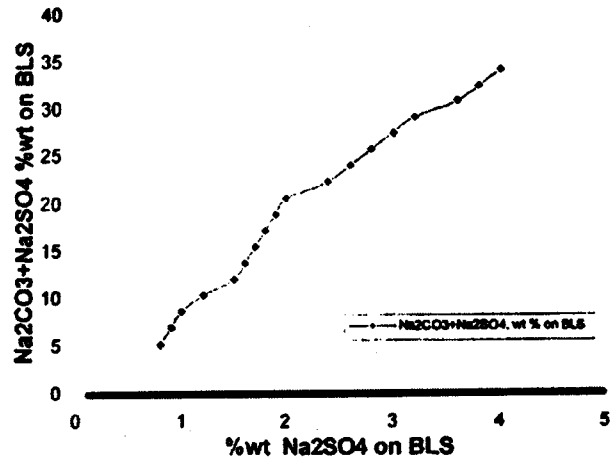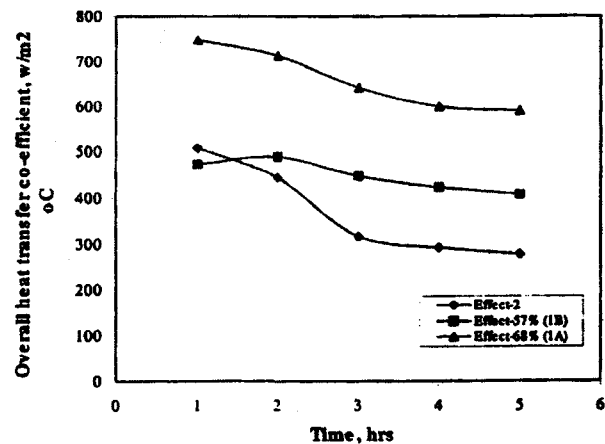• Where the settlement rate of Burkeite is higher at critical solids point of 49 to 52% is predicted.



**Figure 9** : Overall heat transfer co-efficient for the present 5hrs running cycle, w/m2deg.C

**Table 3** : Composition of $Na_2CO_3$ and $Na_2SO_4$ in concentrated black liquor from effect 1& 2

| Particulars | | Effect-2 | | | Effect-1 | | |
|---|---|---|---|---|---|---|---|
| Time in hrs | | 1 | 2 | 3 | 1 | 2 | 3 |
| Solids, %TS | In | 40.13 | 40.31 | 42.77 | 49.48 | 48.83 | 50.65 |
| | Out | 49.48 | 48.83 | 50.65 | 66.30 | 64.20 | 63.00 |
| $Na_2CO_3$, % wt | In | 20.54 | 21.81 | 18.08 | 18.96 | 16.55 | 15.78 |
| on BLS | Out | 18.95 | 16.56 | 15.78 | 11.73 | 11.38 | 14.96 |
| $Na_2SO_4$, % wt | In | 6.35 | 7.05 | 5.75 | 6.35 | 3.17 | 3.81 |
| on BLS | Out | 6.11 | 3.17 | 3.81 | 3.57 | 2.62 | 2.31 |
| $Na_2CO_3$/ | In | 3.36 | 3.09 | 3.14 | 2.99 | 5.22 | 4.14 |
| $Na_2SO_4$, % wt on BLS | Out | 2.98 | 5.22 | 4.14 | 3.29 | 4.43 | 6.48 |

The samples of black liquor, feed to 2nd, feed to 1st effect, and feed to HBL tank is collected from the time of body change over to next change over time. At the same, the performance of the body is noted; the system behavior is shown in figure 9. The $Na_2CO_3$ and $Na_2SO_4$ are tested from the collected samples, to know the rate of precipitation of sodium salts from the black liquor. The results are such,

Based on analysis shown in Table 3 & Figure 9, the following conclusion drawn as,

- The samples concentration levels are in the range of predicted critical solids points.

- The ratio of $Na_2CO_3$ to $Na_2SO_4$ feed to 2nd effect is 3.5. It is on higher side.

Figure 11 : Predicted Overall heat transfer co-efficient for 8 hours operating cycle.

- The sodium salts precipitation is higher in mid hours of 2nd effect and in beginning hours of 1st effect. (i.e.),

  In effect 2- $Na_2CO_3$ is 5.25% wt on BLS and $Na_2SO_4$ is 3.88% wt on BLS

  In effect 1-$Na_2CO_3$ is 7.23% wt on BLS and $Na_2SO_4$ is 2.78% wt on BLS.

- Reason of burkeite formation is due to,

  - Lower causticizing efficiency

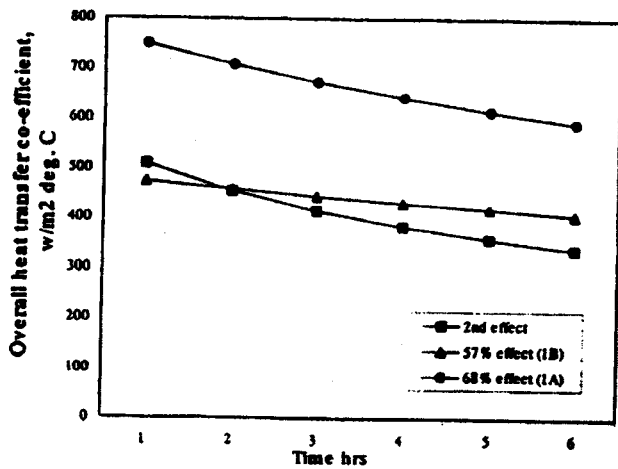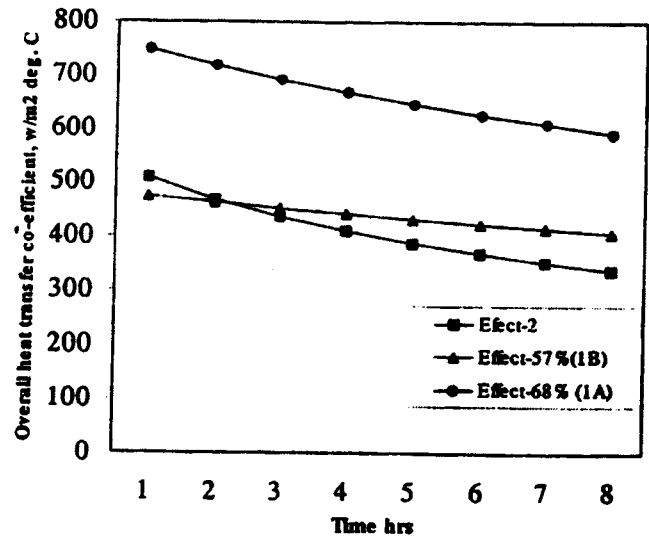  - Higher $Na_2SO_4$ in black liquor composition.

Figure 10 : Predicted Overall heat transfer co-efficient for 6 hours operating cycle.

- The system overall heat transfer co-efficient fall with respect to precipitation rate of sodium salts from black liquor evaporation is uniform.

Table 4 : Improvement in performance of MEE by controlling the water soluble scales

| Particulars | Performance value for existing process | New performance values by retrofitting | Remarks |
| --- | --- | --- | --- |
| $Na_2CO_3$ / $Na_2SO_4$ % wt on BLS. at beginning of cycle | 3.36 (Enter to 2nd effect) | 2.84 (By addition of spent acid from $ClO_2$ plant and sodium sulphate as make up) | Decreasing in deposition rate of sodium salt led to increasing in running hours. |
| Operation time of evaporation per cycle | 5 hours | 6 to 8 hours | Increasing in running hours -decreasing in down time and evaporation cost of condensate. |
| Time to attain product liquor after change over of body | 1.25 hrs/day | 0.75 to 1 hrs/day | Decreasing in down time. increasing in product liquor production. |

** Mill is adding 10 TPD as make up salts before firing a $Na_2SO_4$. Instread of adding there, adding in system of evaporation to control soluble scales.

## Recommended practice

The most important process in keeping the heating surfaces clean by controlling the crystallization of sodium salts in black liquor. Recommendations to control soluble scale deposition,

- Maintaining low levels of $Na_2CO_3$ and $Na_2SO_4$ in the black liquor at 5% and 15% wt on BLS.

- Maintaining the $Na_2CO_3$ to $Na_2SO_4$ ratio less than three.

Control by addition of recycled chemical streams, e.g., makeup sulfate stream such as salt cake, spent acid from $ClO_2$ palnt. Even fly ash from SRB can be added. By controlling the crystallization of black liquor, compared to present evaporation cycle time of 5 hours it get improves to 6 to 8 hours cycle time. The present and recommended cycle time of evaporation details are given in Appendix - 1.

The system overall heat transfer values are predicted by using straight line equation [5], $1/U^2 = a\theta b + d$, where a and d are constants for any given operation and U is the overall heat transfer co-efficient at any operating time $\theta b$, for possible improvement in running hours of system to 6 and 8 hrs. Assumption made during the prediction is by considering the present beharvior of system. The predicted overall heat transfer co-efficient of the system at 6hrs and 8hrs running cycle is shown in figure (10,11).

The present parameters and anticipated parameters after implementing the proposal are listed in the table below.

The net savings possible by implementation of this recommendation

## CONCLUSIONS

Sodium salt scaling of black liquor evaporation is an ongoing problem for many pulp and paper mills. From the available data on scaling clearly identifies the solids content of liquor where precipitation can begin. This help to control the point of precipitation of sodium salts from black liquor. The outcome of the recommendation helps the mill to improve its system availability.

## REFERENCES

1. Wolfgang Schmidi, "Evaporator Fouling: How IPST's evaporator performance audits can help mills", IPST.

2. Wayne Adams, "A crystal growth system effectively reduces evaporator scaling, while providing the flexibility for future liquor chemistry changes", Kellogg brown and Root engineering, Houston, Texas.

3. Mark A. Rosier, "Model to predict the precipitation of burkeite in the multiple effect evaporator and techniques for controlling scaling", Tappi Journal, April, 1997.

4. Terry N. Adams, "Sodium salt scaling in black liquor evaporators and concentrators", Tappi Journal, June, 2001.

5. Max S. Peters, "Plant design and economics for chemical engineering", McGraw Hill Book Company, New York, 1958.

Table 5 : Energy saving cost by increasing the system availabiligy of evaporation system of black liquor

| Particulars | Cycle time of 5hrs | Cycle time of 6hrs | Cycle time of 8hrs |
|---|---|---|---|
| Wash Process condensate addition in WBL tank, m3/day | 250 | 200 | 150 |
| Steam requirement to evaporate this water from WBL, TPD | 41.12 | 32.89 | 24.67 |
| Equivalent cost of thermal energy, Rs. Lakh per annum | 41 | 32.5 | 24.4 |
| Time to attain the product liquor after change over of body, Hrs/day | 1.25 | 1 | 0.75 |
| Equivalent cost of down time in term of steam generation in boiler, Rs. Lakh per annum | 99 | 79.20 | 59.40 |
| Total cost per annum, Rs Lakh | 140 | 111.70 | 83.80 |
| Net saving possible per annum, Rs. Lakh | Base | 27.95 | 55.89 |