Scaling in Multiple Effect Black Liquor Evaporators

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Introduction

Spent liquor from Brown Stock washers at 12–16% total solids is sent to Soda Recovery Section for recovery of pulping chemicals. This liquor is concentrated to 60–65% solids before incineration in a recovery furnace. In case of recovery units equipped with direct contact evaporator, the liquor is evaporated in multiple effect evaporators, to 40–45% total solids and then to 60–65% total solids in direct contact evaporators. However in case of other designs where direct contact evaporators are not used, the spent liquor must be concentrated to about 60% total solids in multiple effect evaporators (M. E. E.). Spent liquor from soft woods does not pose significant problem in M.E.E. and could be concentrated without difficulty to 60% total solids. In our country main raw-materials are bamboo, hardwoods, grasses and agricultural residues. It is difficult to concentrate the black liquor from these raw-materials to about 60% solids in M.E.E. only as most of the evaporator units in the country are based on the designs suitable for handling black liquor from softwoods. This is due to high silica content in black liquor from bamboo and polymerisation of solubilized material in the case of hardwoods, due to which the formation of the scales inside the evaporator tubes is enhanced. The heat transfer characteristics of black liquor from hardwoods are also unfavourable. As a result, the capacity of evaporator section is noticeably reduced, and with increasing use of hardwoods in many mills, this has turned out to be a major bottleneck of production.

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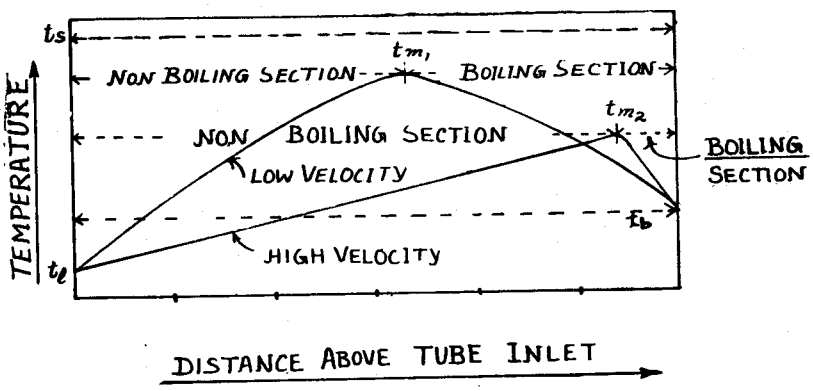
2. Mechanism of Heat Transfer in Evaporators :

Most of the mills in the country are equipped with long tube vertical (LTV) evaporator for concentration of black liquor. Mechanism of heat transfer in long tube vertical evaporators is quite complicated. The liquid enters the tubes at the bottom and during its course of travel upwards it is heated by the steam or vapours outside the tube. Somewhere between inlet and outlet, depending upon the pressure and velocity of entering liquid, the boiling starts and part of liquid is converted to vapours. Since the volume occupied by the vapour is considerably larger, the velocities of the liquid–vapour mixture are considerably higher than the velocity of liquid entering. Hence a tube could be considered as consisting of two sections namely boiling and nonboiling, the line of demarcation being fictitious and arbitrary.

Temperature profile of the liquor with reference to distance from inlet of the tube has been shown in Fig. 1. It can be seen that at higher inlet velocity, the liquid starts boiling towards the end of the tube while at lower velocity the transition from non-boiling to boiling takes place somewhere in the middle.



t_s = Steam Temperature
t_l = Liquid inlet temperature
t_b = Boiling temperature of black liquor corresponding to vapour space pressure

Fig. 1. Temperature profile of liquid in a long tube vertial evaporator.

3. Formation of Scales

Some of the salts with an inverted solubility curve are considered to be mainly responsible for tube side scaling in the evaporators. Calcium Sulphate, anhydrous Sodium Sulphate, Sodium Carbonate monohydrate etc. are well known in this category and their solubility decreases with the increase in temperature. Since the temperature of liquor at the tube wall is highest, the salts with an inverted solubility curve tend to precipitate out at the tube walls. Lower liquor velocities near the tube wall compared to the bulk of liquid, facilitate the deposition of solids at the wall.

The scale formation on the outer side of tubes is generally known as fouling. It is the deposit of some substances other than the condensate on the vapour side of the tube. The scale formation and fouling both are responsible for reduction in the heat transfer coefficients as their existence means insertion of an additional resistance in the path of heat transfer. This additional resistance results in lowering the total heat transferred and the evaporation capacity of the unit. The temperature profile in case of an evaporator tube, handling black liquor and having scales on both the sides of the metal, is shown in Fig. 2. It can be observed that presence of the scales is responsible for large temperature drops. An attempt to maintain the same capacity by increasing the temperature of the steam results in lower steam economy, because of lower latent heat of steam at higher temperature. The heat losses are also more at higher temperatnre.

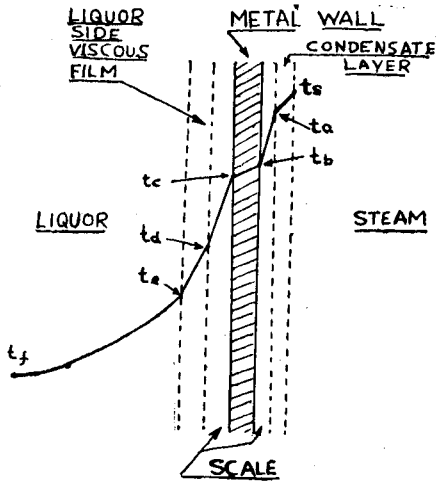


Fig. 2. Effect of scale formation on temperature gradient.

4. Nature of Scale

The nature of scale varies from mill to mill or even in the same mill, depending upon the cellulosic raw materials, pulping conditions, make up chemicals, lime quality, design of equipment and operating conditions in pulp and recovery sections. The analysis of typical scales from some mills in India and abroad are shown in Table–1.

4.1. Sodium Sulphate Scale

This scale may be found in high density effects of black liquor evaporators when sodium sulphate concentration in black liquor is high (5–6% on solid basis). This may be a result of poor reduction efficiency of recovery furnace. This

Table-1. Typical analysis of Scale from Black Liquor Multiple Effect Evaporators.

	MILL 'A'			MILL 'B'[1]	MILL 'C'	MILL 'D'[2]		
	I effect	II effect	Heat Exchanger	Bamboo Liquor	Prehydrolysis Kraft liquor	I effect	II effect	III effect
Loss on Ignition, %	18.5	25.0	6.3	15.5	20	—	—	—
SiO_2, %	35.0	33.0	46.8	53.8	46	35	7	8
R_2O_3, %	10.0	10.5	11.6	17.0	2	29	5	6
Total Alkali as Na_2O,%	3.1	2.9	2.6	—	—	—	—	—
Chlorides, %	1.9	2.3	1.8	—	—	—	—	—
Sulphate, %	1.1	0.5	1.3	1.1	—	20	2	2
Ca as CaO	—	—	—	12.6	32	6	78	75
Undetermined	—	—	—	—	—	10	8	9

scale does not pose significent problems in removal as it is soluble in water and can be mostly removed by water boiling.

4.2. **Calcium Carbonate Scale**

Lime with low CaO content and in-efficient white liquor clarification system are responsible for this type of scale. It can be removed by mechanical cleaning or by boiling with an inhibited acid solution such as hydrochloric acid or phosphoric acid.

4.3. **Silicate Scale**

It is hard, glassy and almost transparent in appearance. It consists of various sodium aluminium silicates. Silica is invariably present in the liquor entering with raw material or make up chemicals etc. and presence of alumina in the system is mainly the controlling factor in formation of this type of scale. This is difficult to remove by mechanical means, but circulation of 15% solution of $NaHSO_4$ through the tubes for 10–24 hrs. at 70–75°C, dehydrates the scale, making it fluffy and removable easily by mechanical means. Sometimes 'Thermal Shock' to the tubes helps in cracking such scale[3] The tubes are heated by steam and then filled with cold water after closing the steam valve. The water is then drained. Repeated thermal shocks may loosen the scale and it may go out with the cold water being drained. However thermal shocks may loosen the tubes from tube-sheets, and the tubes may have to be re-expanded after this treatment. Such type of scale is not so frequent now as the alumina refractory of recovery furnace has almost universally been replaced by chrome refractory.

4.4. **Char Scale**

Polymerisation of certain organic materials present in the black liquor may take place in presence of caustic soda and temperatures prevailing in the evaporators. This results in deposition of gummy, rubbery, black material on the inside of tubular surface. The formation of this type of scale is belieeved to be dependent mainly upon the temperature and concentration of a particular black liquor. Occurrence of this type of scale can be reduced by maintaining higher liquid velocities and by periodically blasting steam through the tubes.

4.5. **Soap Scale**

Resinous compounds present in the wood react with caustic soda during alkaline pulping, to form resinous soaps. This soap should be removed at an intermediate stage, otherwise it may form gummy coating in finishing effects. This scale is easily removable by water boil outs. Installation of a soap skimming tank for removal of soap at about 25-28% total solids, may reduce the formation of this type of scale.

4.6. **Combination of Fiber and Scales** :

Fiber alone, generally can not foul an evaporator but in combination with above mentioned scales it may be responsible for serious loss in evaporator capacity. It can be prevented by allowing the black liquor to be screened through 70–80 mesh, before being fed to the evaporator.

4.7. **Sulphide Scales**

The most common deposits outside tubes are iron sulphide and other corrosion products. This scale can be easily removed by circulation of caustic soda solution (250–300 gpl) on the vapour side for 20–24 hrs at 70°C. After caustic circulation the element should be flushed with water repeatedly to loosen and remove the scale. This type of scale can be prevented by continuous introduction of amines, or 10% caustic soda solution in the vapour stream[4] The use of tubes plated with chromium from outside, or stainless steel tubes is most effective to eliminate such scale but the proposition is no doubt very costly.

Considering above factors, it is desirable to design multiple effect evaporator units to concentrate black Liquor from hardwoods, bamboo etc. to 40–45% total solids. The concentration may be raised further to 60–65% total solids in direct contract evaporator or forced circulation finisher effects.

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