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Hybrid Treatment of Black Liquor to Control Scaling in Paper Industry

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Abstract

Wood-based raw materials have always been favorable for pulp making purposes. Non-wood raw materials like wheat straw, bagasse, river grass, rice straw, etc. are although abundantly available but globally their use has been discouraged due to presence of silica. Wood is preferable due to absence of silica in it. Silica causes serious problems in the chemical recovery process as it causes scaling of heat transfer surfaces. This phenomenon reduces the plant production capacity and causes black liquor wastage, which is environmentally and economically undesirable. Black liquor is the by-product obtained from cooking process at the pulp washing stage. The best way to treat black liquor is to process it through chemical recovery plant where it is first evaporated and then burned. In this research article, a number of experiments were carried out by using different conditions of temperature and residence time. Encouraging results were obtained and compared with other available techniques.

Key Words: Scale Removal, Evaporators, Black Liquor, Silica

1. Introduction

The pulping of wheat straw as a raw material has always been a challenge due to its adverse environmental impacts and inherent presence of silica. Despite the abundance and economy of using wheat and similar straws, the process of its pulping generates wash liquid called "Black Liquor", which is environmentally very hazardous. The best way to treat black liquor is to process it through chemical recovery plant, which involves three stages; evaporation, combustion and chemical conversion.

Since, gradual scale formation in the tubes of liquor evaporators seriously impedes heat transfer and creates a capacity bottleneck in the process within duration of 1 – 2 months. Because of this, phenomenon all the available black liquor cannot be treated and the Chemical Oxygen Demand (COD) of wastewater increases due to partial liquor wastage. Therefore, evaporator required frequent cleaning that is caused by high silica and short fiber content of cellulose material.

2. Literature Review

Scale formation occurs to some extent in all types of evaporators, but it is of particular importance when the feed mixture contains a dissolved material that has an inverted solubility. For a material of this type, the solubility is least near the heat transfer surface where the temperature is greatest, enhancing the likelihood of forming a scale on surface [1]. Like any aqueous solution, the boiling point of the black liquor increases with increasing solids content. The boiling point rise (relative to water) is about $3^{o}C$ at 33% solids [2].

These characteristics make the long tube vertical (LTV) evaporators especially susceptible to serious problems when operated close to the critical solids content. If the solubility limit is exceeded, scale may form at rapid rate and begin to plug tubes. As little as fifteen to thirty minute operations beyond the solubility limit may be enough to initiate tube plugging. Once a tube becomes plugged, it cannot be cleaned out by a water boil out, even though the scale is fully water soluble, because the wash water will not be able to penetrate the plugged tube. Scale removing techniques includes a wide variety from physical cleaning to advanced chemical treatment. A careful list of methods include, cleaning with boiling water, mechanical cleaning with scrapers or high pressure water (600-1000 bar) and chemical cleaning by various acids and derived compounds [3][4][5][6].

According to Kirk and Othmer [7], stainless steel and high nickel alloy scales are tightly adherent and difficult to remove with the acids used for plain steel, although either of the following is effective;

1) Hot 10% sulfuric acid containing 1 – 2% sodium thiosulfate or hydrosulfite, or
2) 2% hydrofluoric acid with 6 – 8% ferric chloride

Moderate and light scale is removed with 20% nitric acid containing 2 – 4% hydrofluoric acid. Nitric acid is a widely used pickling agent and does not affect the stainless character of steel; in fact these steels are passivated in nitric acid of greater than 20% concentration. Hydrofluoric acid may be used as an activator or as a first treatment to remove scale, but it tends to pit the metal and is not recommended.

Similarly, silica scales are difficult to remove. Although there are some indications that the scaling problem becomes worse at high residual alkali concentrations, reducing the residual alkali could aggravate other scaling problems. According to Kulkarni et al [8], on a non-wood plant fiber pulping, the silica scale removal may be accomplished by boiling for two hours in a solution of sodium acid sulfate at 20% concentration. This operation is followed by mechanical cleaning to remove the scale that was loosened by chemical cleaning. According to Bruce Der et al [9], the standard procedure for removing silica scale is to circulate a 20% solution of sodium hydrosulfate through the tubes maintaining a maximum temperature of 72^{o}C. It may be necessary to circulate the solution for three to four hours and then remove the acid, applying steam to the outside of the tubes to dehydrate the surface jelly that forms. After this is done, the acid must be recirculated for approximately two hours. According to D. K. Misra [10], caustic soda is recommended for use. It involves caustic soda boiling for 4-6 hours in a week; this may permit the evaporator unit to operate continuously for three weeks before it warrants a shutdown for general cleaning and maintenance. When high free alkali is maintained in the black liquor cycle, de-scaling operation is comparatively easy. Pokhrel, D. and T. Viraraghqvan [11] presented an excellent review for paper waste generated in paper industry and its treatment methods. Huang et al [12, 13] developed method to decrease the cooking time and formation of pulp without black liquor. They found that addition of caustic potash not only reduces the quantity of ammonia, it significantly reduces the cooking time. The effect of heat flux and bubble formation due to the surfactants present, in black liquor was studied by Tohasson, M. et al [14] in a falling film evaporator. They observed that the bubble significantly decrease the rate of heat transfer which that decrease evaporation. Additionally they found that rate of heat transfer decreases by increasing heat flux. Chandra, R. et al [15] investigated the effect of different nutritional and environmental factors for decolourization of black liquor and found that the developed bacterial consortium can cause decolourization up to 85%.

3. Experimental Procedure

The representative samples were collected very carefully from an operating recovery plant. The collected samples were tested in laboratory and following results were obtained.

Test	**Observation (on dry basis)**
Water insoluble matter	93%
Ash at 900^{o}C	89.8%
Silica and Silicate in Ash	94%
Iron Oxide (Fe_2O_3)	0.06%
Sodium Sulfate	0.07%
Total Sodium as Na^+	3%

The analysis shows that the scale mainly consists of inorganic matter (90%), which is in turn dominated by the presence of silica (94%). Total sodium almost makes up the rest of inorganic matter (3%) along with other minor species.

After detailed literature review, following chemicals were selected for lab studies:

1) Nitric Acid
2) Sulfuric Acid
3) Sodium hydrogen sulfate solution
4) Sodium Hydroxide Solution
5) Phosphoric Acid Solution
6) Sulfamic Acid solution with inhibitor.
7) In order to apply a pH shock, the scale was first treated with sodium hydroxide solution and then with nitric acid.

The judgment of scale softening or dissolution was rather challenging because it is more of a qualitative aspect and no proper distinction or verdict criteria prevails. So the following measurement scale was established to record the effect of each chemical recipe on the "scale."

0	1	2	3	4	5
No Effect	Very Slight Softening	Slight Softening	Moderate Softening	Significant Softening	Partial Dissolution

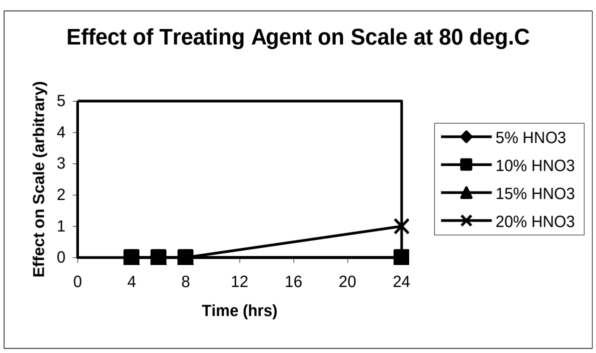
It should be noted that partial dissolution was the maximum extent of effectiveness because it would be the optimum (from feasibility point of view) considering minimum time and minimum chemical addition. The objective was to soften the scale enough so that the surface tension between the tube and scale could be lowered in order to remove scale.

Same methodology was adopted for each of the above chemical recipes. Some scale chips (more or less identical in size/shape) weighing in the range of 20-30 grams was immersed in 100ml chemicals and observations were taken at periodic intervals. The softening was checked by gently tapping the scale chips with glass rods to see if the disintegrate, using a mechanical arm to ensure equal tapping pressures.

4. Results and Discussion

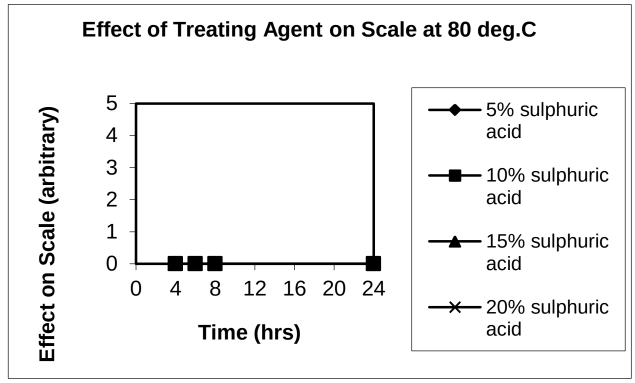
Recipe 1: Nitric Acid

Upon immersion in nitric acid solution at different concentration (5%, 10%, 15% and 20%) no scale was dissolved or even softened. Increasing the temperature had some effect.



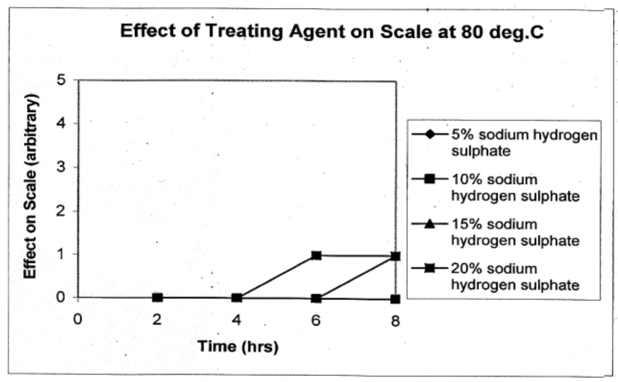
Recipe 2: Sulfuric Acid

Various concentrations (5%, 10%, 15% and 20%) of sulfuric acid were not effective in dissolving or softening the scale. Increasing the temperature has no effect s as well.



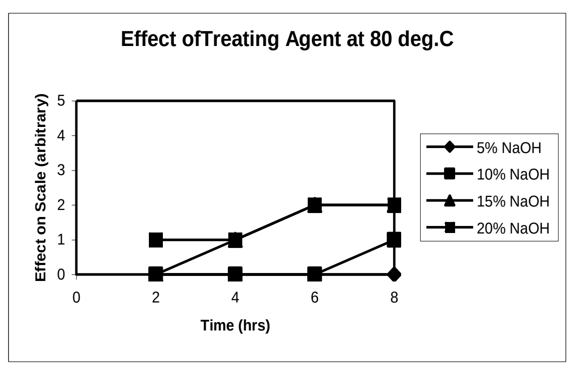
Recipe 3: Sodium hydrogen sulfate

Sodium bisulfate solution at 5%, 10%, 15% and 20% concentration neither dissolved nor softened the scale sample at room temperature. At higher temperature, some softening was observed.



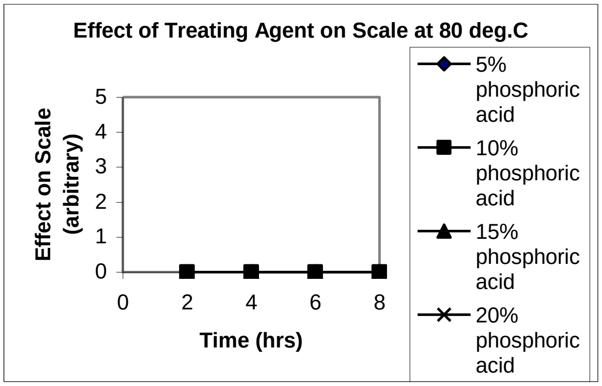
Recipe 4: Sodium Hydroxide

Sodium hydroxide solution at 5%, 10%, 15% and 20% concentrations have no noticeable effect on scale dissolution or softening at room temperature. However, it softened the scale when kept at 80^{o}C for 8 hours.



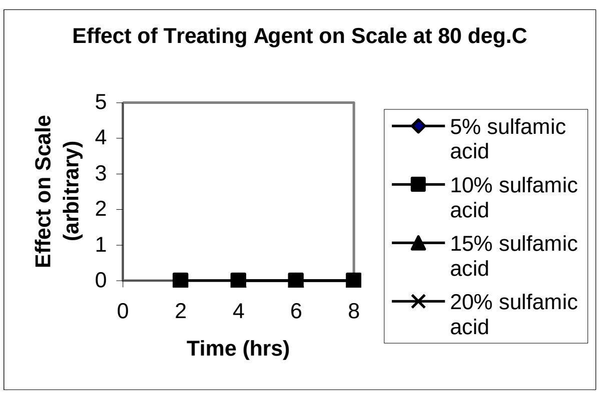
Recipe 5: Phosporic Acid

Various concentrations (5%, 10%, 15% and 20%) of phosphoric acid were not effective in dissolving or softening the scale. Increasing the temperature has no effect s as well.



Recipe 6: Sulfamic Acid

Various concentrations (5%, 10%, 15% and 20%) of sulfamic acid were not proved effective in dissolving or softening the scale. Increasing the temperature has no effect s as well.

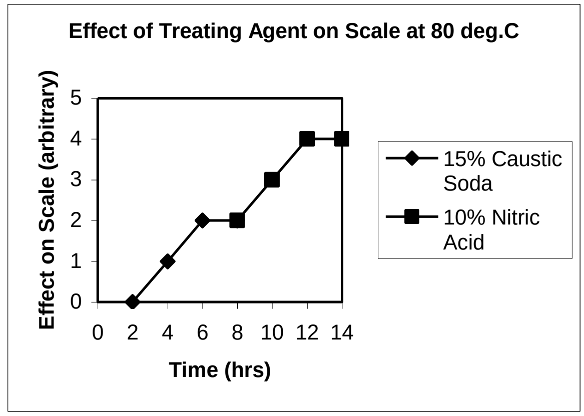


Recipe 7: Sodium Hydroxide+Nitric Acid

The scale was first treated with NaOH at 15% concentration at 80°C for up to 8 hours. After thorough washing of scale chips with water, they were immersed in HNO_3 of 10% concentration at 80°C for up to 8 hours. This combination was found effective. Moreover, this combination of chemicals is safe fro stainless steel.

5. Conclusion

From above studies, it can be concluded that a combination of sodium hydroxide and nitric acid is



most effective with respect to scale softening and removal. Adding to the prospect is that both chemicals are harmless to stainless steel and safety / handling aspects are not critical as with other washing chemicals like Hydrofluoric Acid.

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