State-of-the-art Studies of Chemical Changes in the Non-Fibrous Pulping Black Liquors During Storage

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ABSTRACT

In this research emphasis have been made on the problems encountered by storage of the straw based kraft black liquors. There is considerable decrease in pH of the black liquor with aging in the storage tanks. Active, effective and total alkali contents also decrease with time. These changes add various problems in further treatment of this aged black liquor. In fact black liquor is stored at high temperatures, normally at 80-90°C. At this temperature degradation of the organic components of the black liquor occurs. Normally carboxylic acids are formed from organic components degradation, which further degrade into carbon dioxide and sulfur dioxide. These gases neutralize available alkali contents within the black liquor and express their effect in reduction of pH. This black liquor is unfit for the set-parameters of the evaporators and hence causes problems in its treatment and recovery.

Key words:

Kraft pulping, thermal aging, degradation, available alkali and effective alkali.

INTRODUCTION

The production of chemical pulp for paper manufacture chiefly uses wood as raw material. However about 10% of the chemical pulp produced worldwide is using non-wood raw materials. Rice and wheat straw are most available raw materials in the paper and pulp industry of South Asia. For the cooking of the non-wood raw materials sodium hydroxide alone is required as an active chemical, so the major part of chemical pulp production for these raw materials is utilizing the soda process [1]. So the most of the pulp and paper mills utilizing these raw materials use soda process for pulping.

Non-fibrous pulping is being applied on the non-fibrous raw materials (wheat and rice straw). The pulping chemical is only sodium hydroxide but the efficiency is enhanced by thermal and mechanical action. Kraft is very fast pulping process, which produces pulp in least time of processing even in one hour from feeding of pulp. Most of the kraft plants are working for wood based raw materials and all of the past research work relates to these specific raw materials. Though most of the workers had worked and determined methods for the treatment of these black liquors. But a little work has been done on the straw based liquors from kraft pulping processes [2].

Packages is currently treating CTMP effluent in its effluent treatment plant to convert it into environmental friendly waste. Future prospective of this effluent seems to be fed into chemical recovery plant. Presently chemical recovery is running sulfite pulping waste and will offer some different pros and cons after this effluent will be fed for recovery. Purpose of this research is to develop chemical treatment of this black liquor in order to make the effluent environment friendly and to recover fiber contents.

The black liquor obtained from the pulping process is brownish black in color and is obtained from multiple type sources. Major sources of the effluent at this plant include screw drainers, pulp washers, dewatering press, back water from washing filter, Vickery screen drain, straw washing etc. Nature and composition of the black liquor from this process is different from that of chemical pulping processes like soda or kraft pulping. Effluents from a mechanical pulp mill are toxic and if not treated before entering into a stream, will be fatal to aquatic life [3-4]. About 60 to 90% toxicity comes from the acid extracts in the wood, predominantly resin acids and unsaturated fatty acids. Neutral components such as pimarol, juvabione and diterpene alcohols represent 25 to 30%of the total toxicity in the effluent. The primary factor governing effluent pollution from a pulping mill is type of raw material used [5].

Material and Methods

All the research work was carried out by following standard test methods given in reference # 6 and 7. All the solutions, glass ware and instruments used were according to reference # 8.

RESULTS AND DISCUSSION

In order to draw comprehensive relation of black liquor aging with various properties some determinations have been made. Aging effect during storage of the black liquor depends upon the chemical composition of the black liquor. Hence chemical composition and aging depend upon the chemical nature of the black liquor. Relations have been derived with chemical composition, nature and aging/storage of the black liquor. This unique approach determines the evaluation and solution to the various problems encountered by this black liquor when fed to the chemical recovery plant after storage.

Total Alkalies

Sum of all the alkaline contents (hydroxides, carbonates, bicarbonates and sulfides) determine total alkali contents of the black liquor. There is considerable decrease in total alkali contents of the black liquor with time. This effect is greater in first 50 hours of storage and then no effect is found in its further storage. The reduction in total alkaline contents is due the neutralization of the alkalies with the acid contents generated from the degradation of the organic components. Settling also causes a decrease in solid contents in the supernatant portion of

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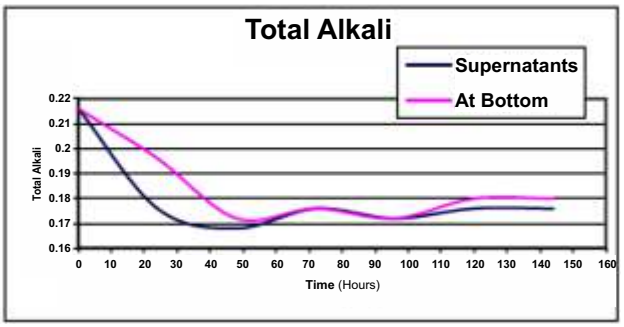

Fig 01: Effect of aging on total alkalies of the black liquors.

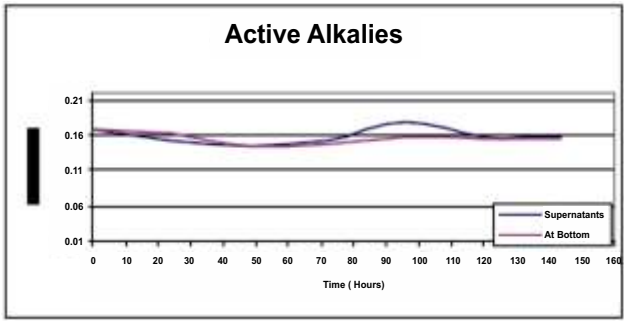

Fig 02: Effect of aging on active alkali contents of the black liquors.

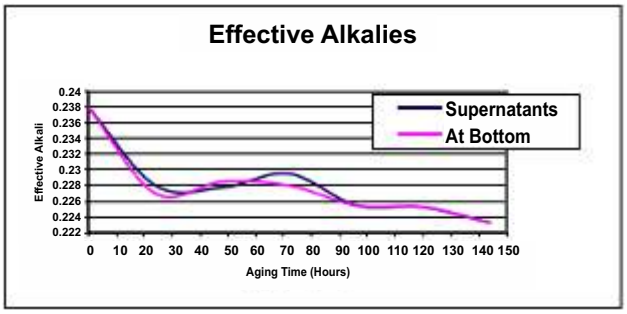

Fig 03: Effect of aging on effective alkali contents of the black liquors.

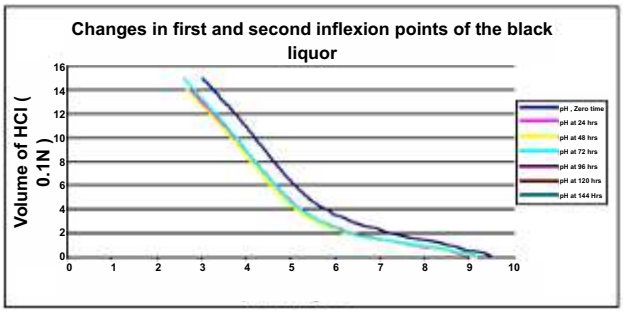

Fig 04: changes in the pH of the black liquor with aging.

the black liquor. The degradation along with black liquor dry solid contents (sodium and sulphate) settle down and causes reduction in total alkalies. Effect of aging on the total alkali contents of the black liquor is described in figure 01.

Another important factor that contributes in reduction of total alkalies is degradation of the hemicelluloses and lignin contents into their respective carboxylic acids. The production of acid contents is verified by reduction in the pH to a certain level. After 4 5 days the degradation rate of the lignolytic and cellulosic contents decreases and total alkali contents become stable between 0.17 0.18 % of the total dry solid contents of the black liquor.

Active Alkalies

Total concentration of alkaline constituents, except carbonates, as determined by titration of a sample of the liquor with strong acid is termed as active alkalies. In practice, active alkali is considered to be the sum of the concentrations of hydroxyl and hydrosulphide ions, including hydroxyl ions formed by the hydrolysis of sulphides. Minor decrease in active alkalies has been observed in the black liquor with aging.

Fluctuations in the active alkali contents are observed due to interferences in the settling and degradation processes. This effect is observed only in first 50 - 60 hours of storage and after that no change was observed. In fact there is rapid settling of the calcium and magnesium carbonates from the black liquor, which is responsible for the decrease in total alkalies. But there is scarcely any change in hydroxide and hydrosulphide ions and hence no considerable change in the active alkali contents of the black liquor has been found. Hydroxides are non-settle able portion of the black liquor hence the trend in consumptions of (Fig 02) active alkali contents in both settled and supernatants show no differences.

Effective Alkalies

The concentration of strongly alkaline constituents determined by titration of a sample of the liquor with strong acids with the first inflexion point is termed as effective alkali. In practice this is considered to be the concentration of hydroxyl ions including those formed form sulphides by hydrolysis. There is decrease in effective alkaline contents of the black liquor with time. The change in more pronounced in first 20 - 30 hours and then there is little decrease with further aging. Change in effective alkalies is due to gradual removal of alkaline contents from the liquor by settling of inorganic components (Fig 03) and neutralization with carboxylic acids formed by thermal degradation of the organic components. The removal of inorganic components causes reduction in pH and hence consequently lowering of affective alkalies.

pH variations

pH variations of the black liquor with continuous aging at high temperatures is measure of the changes occurring in the black liquor. Fig 04 has been derived form the first inflexion point of the titration curve. Both of the curves show the changes in first inflexion point of the titration curve (with HCl). There is trend of shifting towards right in the successive inflexion curves. This determines net changes in the pH in both contents (settled and supernatants) of the black liquor. Relative decrease in the pH is due to the degradation of organic components of the black liquor into organic acids, which neutralizes the alkaline contents and results into decrease of the pH and ultimately shifting of the first inflexion point towards right.

Organic to Inorganic Ratio

There is substantial increase in organic to inorganic ratio of the black liquor with time. Most of the silicates and fibrous cellulosic contents settle down, which raises the organic components ratio by 16 % (initial value 30 % and final value 46% on OD basis) and inorganic components settle and ultimately become lowered in the black liquor by 16 % (initial value 70% and final value 54 % on OD basis), (Tab 01).

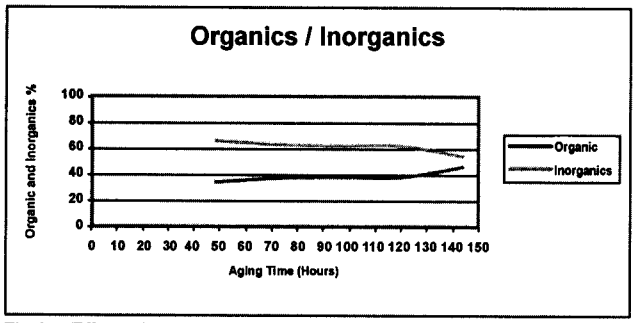

Fig 05: Effect of aging on organic to inorganic ratio of the black liquors.

Tab 01; Organic to inorganic components ratio in the black liquor with time (hrs).

Hours	Organics %	Inorganics %	Organic to inorganic ratio
0	30	70	0.43
24	33	67	0.49
48	34	66	0.52
72	37	63	0.59
96	38	62	0.61
120	38	62	0.61
144	46	54	0.85

The increase in organic to inorganic ratio from 0.64 to 0.85 is due to preferable removal of inorganic components from the liquor (Fig 05). The inorganic components settle down with time while the organic components remain in the bulk of liquor and form sludge in the bottom of the tank. As a result relative increases in the organic and conversely decreases in the inorganic components occurs.

The high alkalinity is largely responsible for solubilizing the various organic constituents. If the pH is reduced, various organic constituents will precipitate, beginning with the components with low pKa values (e.g. the phenolics) and eventually those with higher pKa values (e.g. the carboxylic acids). Thus, the soluble component would vary as pH is reduced. Consequently, if the pH is adjusted in order to perform certain tests, the nature and composition of the test material will necessarily change.

The inorganic constituents in black liquor are derived by the cooking liquor which is used in pulping, and are comprised of sodium hydroxide (NaOH), sodium sulfide (Na_2S), sodium carbonate (Na_2C0_3), sodium sulfate (Na_2SO_4), sodium thiosulfate, (Na_2SO_4) & and sodium chloride (NaCl). Collectively, inorganic salts constitute between 18 and 25% of the solids in black liquor.

CONCLUSION

The storage of black liquor causes increase of organic components and lowering of inorganic components due to settling of inorganics with time. The organic components are more volatile and the storage may possibly cause decaying of organic components into even more volatile compounds like CH_3SH, CH_3SCH_3, H_2S, SO_2etc. and are responsible for sulfur contents reductions. During evaporation of this black liquor these gases evolve from the liquor with greater quantity and consequently ejectors are unable to handle & maintain required vacuum from the given steam pressure. These changes in the black liquor have been confirmed by the active, effective and total alkali determinations with aging.

Proposed Solutions

Following solutions are proposed to eliminate the problem of vacuum production in the evaporators.

1) Fresh liquor should be used in the evaporators because it has low organic to inorganic ratio.

2) Low volume of the liquor should be fed into evaporators to get same efficiency.

3) High pressure of steam should be used to create vacuum in order to get same efficiency with the same volume of black liquor.

4) Third ejector which is used at start up can be used continuously to attain the required vacuum if WBL residence time increases more than 2 days in storage.

Applications

Our current research provides useful information about the storage/aging of the black liquor and its impacts on the chemical recovery process.

REFERENCES

1. Mackie, D. M. and Taylor, J. S., Pulp Paper Can. 89(2):T64 (1988).

2. Richardson, J. D., Appita 49(1):27 (1996).

3. Lindholm, C. -A., Paperi ja Puu 61(3):141 (1979).

4. Beatson, R., Heitner, C., Atack, D., J. Pulp Paper Sci. 10(1):J12 (1984).

5. Adler, E., Lindgren, B. O., Saedén, U., Svensk Papperstid. 55(7):245 (1952).

6. "Analysis of soda and sulfate black liquor" Tappi 2002. T 625 cm-85.

7. "Total, active and effective alkali" Scandinavian Pulp, Paper and board testing committee; SCAN 30:85, accepted April 1985.

8. Tappi T 610, " Preparation of indicators and standard solutions". Tappi Test Method 2002.