Non-Process Elements In Agro Based Black Liquors And Their Influence On Chemical Recovery Operations

Gupta Abha and Kulkarni A.G.

ABSTRACT

In last one decade, there have been significant developments in chemical recovery processes and equipments for improved safety and enhanced thermal & chemical recovery efficiencies. Recently, the R&D activities are focussed in the area of Non-Process Elements (NPE) and their role in Chemical recovery loop. Central Pulp and Paper Research Institute (CPPRI) initiated the studies on NPE's and the adverse effect of silica was well established. It was observed that agricultural residues are also rich in Potassium and Chlorides (K & Cl), which essentially come through soil, water and fertilisers and enter the chemical recovery loop through black liquor and build-up subsequently. Agro residues contain upto 2.5% Potassium and chlorides as compared to wood which contain Potassium in traces. It is experienced that calcium, silica and aluminium tend to form scales and deposits in evaporator boiler tubes. Potassium and chlorides when present lower the eutectic melting temperature and thus affect combustion. The laboratory investigations clearly reveal that the presence of potassium and chlorides have significant effect on initial sticky temperature and final smelting temperatures of the ash. Even 1% increase in K & Cl decreases the smelting temperature by 20-30°C. Slag samples analysed from some of the recovery installations show the presence of K & Cl in appreciable quantities and possibly their direct influence on smelting temperature and sublimation of sodium compounds.

This paper highlights the levels of NPE on black liquors from pulping of agro residues and their influence on combustion properties and subsequent problem in chemical recovery operations.

Central Pulp & Paper Research Institute,
P.O. Box - 174,
Saharanpur, U.P., 247001.

INTRODUCTION

Chemical recovery operations unlike pulping, bleaching and papermaking are more complex in nature. The various unit operations like black liquor evaporation, combustion, causticization, etc. are significantly influenced by the Non-Process Elements. Raw material, process water are the major sources of NPE's. and gradual erosion/corrosion of the various transporting systems are due to these NPE's. Silica is one of the Non-Process Elements (NPE) and the adverse effect of silica are well established (1,2,3). The recent investigations on the study of NPE's like Potassium and Chloride have come to certain conclusions that NPE's when present in appreciable quantities build-up significantly in the subsequent recovery cycles and adversely affect the chemical recovery operations, specifically the smelt and the slag formation. etc.

Central Pulp & Paper Research Institute has conducted extensive R&D work on characterisation of black liquors and their subsequent effect on the recovery operations. The agricultural residue black liquors, which contained significant amount of K&Cl were found to have adverse effect on the recovery processes involving low temperature operations like DARS and Copeland systems. The effect of chlorides was studied systemtically and the extensive sublimation was reported during the operation of the DARS process.

The mills, which are based on agro-residues are likely to have such problems and it is necesary to critically evaluate the source and the effect of the NPE's and possible methods to reduce the amount of NPE's in the recovery loop.

The smelting temperature is an important parameter and any changes in the smelting temperatures often lead to number of operational problems. Basic studies conducted clearly established the adverse effect of NPE's on smelting temperatures (4). When the input of NPE is significant, the build-up of NPE in recovery cycle is relatively very rapid and can cause severe damage to process equipments by way of plugging of flue gas passages through massive deposit build up

Due to lack of adequate information, often the requisite significance is not attached to NPE's. For instance, when a manufacturer designs a furnace, the heating surfaces will be sized so that the estimated sticky point is achieved in the superheater, where the spacing is adequate to prevent plugging of passages and sootblowers can be used to good effect. Most of the recovery installations have certain amount of overload which results in increased carry over of such NPE's.

MATERIAL AND METHODS :

TAPPI Standard Methods were followed for determination of Carbonates and Sulphates.

Chlorides Estimation: Standard Argentometric titrations were followed for chlorides estimation. However, depending on the estimation of chlorides in raw materials, black liquors or slag, the method was slightly modified so as to initially obtain a stable chloride salt, which does not get volatilised on ignition.

Potassium, Manganese and Magnesium: These elements extracted by acid treatment were analysed using Atomic Absorption Spectrophotometer. -AAS-680G.

Thermal Properties of Ash, Smelt and Slag/ boiler deposits: (5)

Quadruple Cone Test: For cone slumping tests powdered deposit samples/black liquor ash were formed in to a small cone as depicted in **Fig.-1.** The cone was heated slowly at a known heating rate and physical changes observed. The terms for physical changes are defined as follows-

(a) Sticky Temperature: The temperature at which the cone starts "sweating" due to the appearance of the liquid phase in the sample.

(b) Radical deformation Point/Smelt formation Temperature: The temperature at which the cone starts bending down, changing shape.

(c) Smelting Temperature: The temperature at which the cone is completely molten and retains none of its shape.

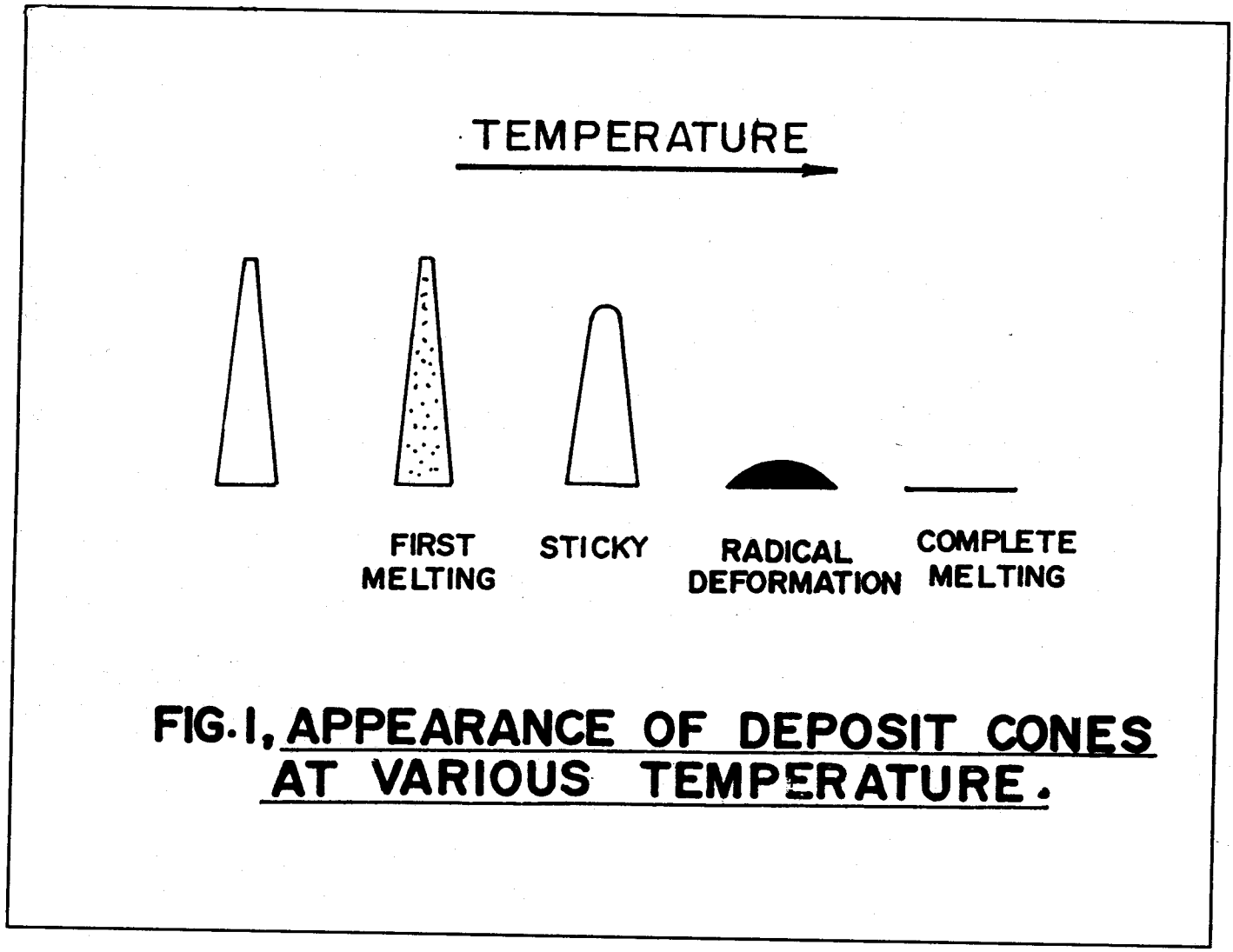

FIG. 1, APPEARANCE OF DEPOSIT CONES AT VARIOUS TEMPERATURE.

RESULTS AND DISCUSSION

Non-Process Elements (NPE) : These are elements other than those which are normally a part of pulping and recovery cycle (Na, S, C, H and O). The two major non-process elements appear to have influence on recovery boiler operation are Potassium and Chlorine as Chlorides. Potassium and chlorides do not really take part in the chemical recovery but any build-up of these is the dead load in the system. It is apparent from the studies that they are volatile at relatively lower temperatures and have adverse effect on ash melting temperatures.

NON-PROCESS ELEMENTS IN CELLULOSIC RAW MATERIALS

Table-1 shows the typical characteristic of Non-woody agricultural residues and the tropical hard-woods with respect to these NPE's. It is evident from the results that the quantum of NPE's varies significantly in different cellulosic raw materials. Agro residues are characterised by comparatively higher proportion of these NPE's.

Bagasse analysed was depithed bagasse and possibly during wet depithing operations, the K and Cl must have been leached out. The higher proportion of K & Cl in straws may be due to intake of these from the fertilisers and water.

Black Liquor Characteristics and its Role on Chemical Recovery Operations:

Black liquor is one of the highest ash containing fuel and the quality of the black liquor has tremendous effect on Chemical Recovery operations.

TABLE-1					
NON-PROCESS ELEMENTS IN VARIOUS CELLULOSIC RAW MATERIALS					
Particulars	**Bagasse**	**Wheat Straw**	**Rice Straw**	**Sabai grass**	**Tropical Hardwoods**
Ash, % w/w	2.3	9.5	18	8.5	0.3
Silica, % w/w as SiO_2	1.8	5.8	11	6.5	0.2
Potassium, % w/w as K	0.2	1.8	2.0	1.5	Tr.
Chlorides, % w/w as Cl	0.02	0.88	0.94	0.3	0.05

Tr. - Traces

Over the years, lot of developments have taken place in Chemical recovery installations for wood based paper industry. China and India have now developed and installed Chemical Recovery System. The efficiencies of Non-wood based particularly agro based chemical recovery systems are not as high as wood based. The primary reason is the nature of raw material and its effect on the resultant black liquor generated with varying nature and proportions of inorganic and organic components. These components ultimately influence the evaporation and combustion in the Chemical Recovery operations.. **Table-2** gives the typical composition of non-wood and wood black liquors.

Number of articles have been published highlighting and handling the problem of black liquors in chemical recovery systems and the role of various organic and inorganic (Process) components on black liquor thermal and rhelogical behaviour during evaporation and combustion, (6, 7) but few articles published have dealt with the impact of NPE's on recovery operations.

NON-PROCESS ELEMENTS IN BLACK LIQUORS

Table-3 shows the evaluation of various black liquors for the NPE's. The results show that the spent liquors from non-woody raw materials contain significant amounts of NPE's in terms of Potassium, Chloride and Silica, which mainly find their entry through the raw material and process water. With the advent of desilication technology, the problems due to silica can be successfully tackled. Therefore build up of other NPE's and the way to reduce their build-up are matter of concern.

The Table below clearly indicates that during pulping, major portion of K and Cl elutriate in the black liquors from the raw material. The concern due to K and Cl is due to two reasons-

(i) Neither is naturally purged from the cycle and they can build up to relatively high quantities, when the input is significant. (10).

(ii) They are comparatively volatile in the furnace, lower the melting points of smelt, at times without complete burn outs of organics.

The effect of these NPE's on thermal properties in terms of sticky temperature and ash smelting temperatures are presented in **Table-4.**

From the data presented in Table-3 & 4, it is now quite clear that three raw materials viz. Wheat and Rice straws and Sabai containing higher proportion of chlorides and Potassium have lower smelting temperatures.

ROLE OF NPE'S ON SLAG/DEPOSIT FORMATIONS

The above findings of CPPRI are in concommitance with the findings of Tran, Reeve et al (11) who have shown that these NPE's significantly drop down the ash melting temperatures and substantially attribute towards deposit formations. The detailed studies carried on the slag/deposit samples received from two wood based mills are shown in **Table-5.** In mill-I, where the black liquor is rich in K and Cl shows to have frequent deposit formations with lower ash fusion temperatures in

TABLE-2

TYPICAL COMPARISON BETWEEN WOOD AND NON-WOOD. AGRO BLACK LIQUORS

Particulars	Agro Residue Black Liquors	Wood Black Liquors
Organics, % w/w	68-72	65-70
Lignin, % w/w	35	40
Lignin-Carbohydrate Complexes, % w/w	10-25	2-4
Hemicelluloses, % w/w	10-25	1-2
Organic Acids, % w/w	10-15	15-20
Inorganics, % w/w	28-32	30-35
Process Elements:		
Total Alkali, % w/w as Na_2O	20-24	23-27
Non-Process Elements:		
Ash, % w/w	2-15	0.1-1.2
Silica, % w/w as SiO_2	1-8	0.05-0.3
Potassium, % w/w as K	0.2-5	Tr.
Chlorides, % w/w as Cl	0.1-2.0	Tr.-0.5
Viscosity, mPaS at 90°C and at 50 % Solids	200-600	50-70
Combustion Behaviour:		
Temp. of Ignition, °C	600-750	600-65

Tr. - Traces

TABLE-3

BLACK LIQUOR EVALUATION FOR INORGANIC PROCESS & NON-PROCESS ELEMENTS

Particulars	Bagasse	Black Liquors Wheat Straw	Rice Straw	Sabai	Woods
pH at 30°C	10.6	10.9	8.3	10.1	12.9
Process Elements:					
Total Alkali, % w/w as NaOH	27.0	25.8	16.0	23.0	32.0
Sulphur, % w/w as S	Tr.	Tr.	Tr.	Tr.	1.95
	<----------Soda Pulping----------> Kraft				
Non-Process Elements:					
Silica, % w/w as SiO_2	1.7	2.0	1.8	3.0	0.3
Potassium, % w/w as K	0.38	3.1	3.7	2.4	0.8
Chlorides, % w/w as Cl	Tr.	1.5	1.95	0.7	0.4

Tr. - Traces

TABLE-4

EFFECT OF NPE'S ON THERMAL PROPERTIES OF BLACK LIQUORS

Property	Bagasse	Black Liquors Wheat Straw	Rice Straw	Sabai	Woods
Sticky Temp., °C	806	744	709	720	753
Smelting Temp., °C	825	760	728	770	790

TABLE-5

CHEMICAL CHARACTERISTICS OF SLAG/BOILER DEPOSITS

Particulars	MILL - I Slag Sample	MILL - II Slag Sample
Inorganics		
Calcium, %w/w as Ca	0.01	0.01
Magnesium, %w/w as Mg	0.01	0.01
Manganese, %w/w as Mn	0.002	0.001
Iron, %w/w as Fe	0.02	0.03
Potassium, %w/w as K	12.2	6.81
Chlorides, %w/w as Cl (-)	4.73	0.91
Sulphates, %w/w as SO_4 (-2)	54.3	51.6
Thermal Properties :		
Sticky Temperature, °C	650	755
Smelt formation Temp., °C	685	780
Smelting Temperature, °C	745	810

terms of sticky temperature and also Smelt formation and smelting temperatures.

Results also confirm the findings that Potassium and Chlorides salts are more volatile than sodium salts. For instance, it is reported that the K/Na ratio in the fly ash is 1.5-3 times that in black liquor and the ratio of Cl/Na in fly ash to Cl/Na in smelt ranges from 3-4 (8).

CHEMICAL ASPECTS OF SLAG/DEPOSIT FORMATIONS

The deposits are proposed to be formed by two clearly different mechanisms-the impaction of molten or partialy molten **carryover particles** entrained in the flue gas and the **condensation** of the vapours. The carryover deposits are prominently Na_2CO_3 and/or Na_2SO_4 with some NaOH. The condensation deposits are depleted in Na_2CO_3 contain little or no NaOH and are enriched in Chlorides and Potassium. **Figure-2** proposes the pathways for deposit formation in superheater kraft recovery boiler. The condensation and carryover mechanism act alone or in combination depending on the temperature of the flue gas and the superheater tube surface (9).

LEACHING OF NON-PROCESS ELEMENTS FROM AGRICULTURAL RESIDUES

Looking into the adverse effects of these NPE's, it is apprehended that the agro residue black liquors containing higher proportions of these NPE's are more likely to face such problems in their recovery installations. Preliminary studies conducted have shown that it is possible to leach out some of these salts. More studies are being carried out in these directions and different approaches of water and mild alkali pretreatment of raw material are being adopted.

CONCLUSIONS

Presence of higher proportions of NPE's in agro residue black liquors is a concern and there is a need to evaluate critically the performance of the recovery installations based on such agricultural residues. The lowering of smelting temperatures and the sublimation of the Sodium compounds is attributed to higher proportion of K and Chlorides. The Potassium and Chlorides when present in quantities beyond 1% is undesirable. In view of the adverse effects of these NPE's, there is a need for finding out appropriate techniques for leaching out these and to generate black liquors almost free from NPE's. More studies are required in this direction.

ACKNOWLEDGEMENTS

Authors express their sincere thanks to Dr. B.P. Thapliyal, Mr. A.K. Dixit and Mrs. Anuradha Dhusia, Scientists, CPPRI for their contribution in this work.

REFERENCES

1. A.G. Kulkarni, R. Pant & A. Panda. Proceedings of the International Seminar and Workshop on Desilication. Organised Jointly by UNIDO, SIDA, CPPRI and HNL. India. 1989.

2. A. Panda. Proceedings of the International Seminar and Workshop on Desilication. Organised Jointly by UNIDO, SIDA, CPPRI and HNL. India. 1989.

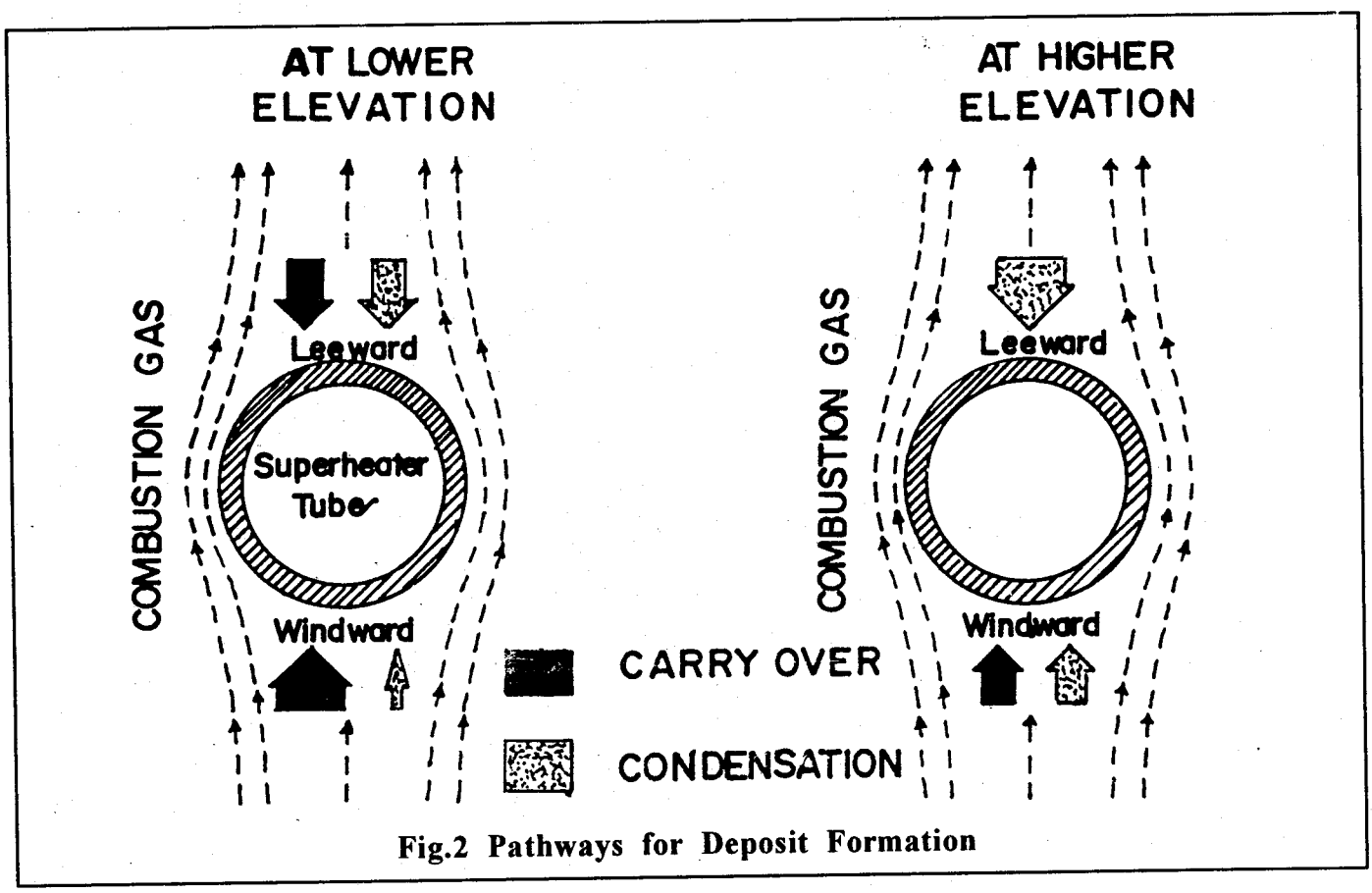

Fig.2 Pathways for Deposit Formation

3. Rita Tandon, Abha Gupta, A.G. Kulkarni and A. Panda. Proceedings of the International Seminar and Workshop on Desilication. Organised Jointly by UNIDO, SIDA, CPPRI and HNL, India. 1989.

4. R.M. Mathur, B.P. Thapliyal, Rita Tandon and A.G. Kulkarni, Proceedings of the 9th Symposium on Thermal Analysis, Bambolim, Goa, 1993.

5. H Tran. TAPPI Kraft Recovery Operations. 1990.

6. R.K. Jain, Abha Gupta, A.K. Dixit, Anuradha Dhusia. Workshop on Energy Efficiency Agenda for Pulp and Paper Industry. April'97. New Delhi.

7. A.G. Kulkarni, R.M. Mathur & A. Panda. Wood and Pulping Chemistry. 1989. p 485. Raleigh.

8. Gerald Hough, Recovery Operations in Alkaline Pulping Processes, TAPPI Press, p 116, 1991.

9. H.N. Tran, D.W. Reeve. Pulp and Paper Canada. 84:1 (1983).