



**TOGETHER**  
*for a sustainable future*

## OCCASION

This publication has been made available to the public on the occasion of the 50<sup>th</sup> anniversary of the United Nations Industrial Development Organisation.



**TOGETHER**  
*for a sustainable future*

## DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as “developed”, “industrialized” and “developing” are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

## FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

## CONTACT

Please contact [publications@unido.org](mailto:publications@unido.org) for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at [www.unido.org](http://www.unido.org)

18908

RESTRICTED

**IMPROVEMENT OF AFYON PULP MILL, TURKEY**  
( UNIDO PROJECT-SI / TUR/88 / 805 )

**Final Report**  
on  
**Desilication of Black Liquor**

SUBMITTED TO  
**United Nations Industrial  
Development Organization (UNIDO), Vienna**

BY



**Central Pulp And Paper Research Institute**  
P.O. BOX NO. 174, SAHARANPUR - 247 001,  
UTTAR PRADESH (INDIA)

MARCH - 1991

ii, 78p.

tables  
graphs  
diagrams

**IMPROVEMENT OF AFYON PULP MILL, TURKEY**

**(UNIDO PROJECT - SI/TUR/88/805)**

**FINAL REPORT**

**ON**

**DESILICATION OF BLACK LIQUOR**

**submitted to**

**UNITED NATIONS INDUSTRIAL  
DEVELOPMENT ORGANIZATION (UNIDO), VIENNA**

**by**

**CENTRAL PULP & PAPER RESEARCH INSTITUTE  
P.O. BOX NO.174, SAHARANPUR-247 001,  
UTTAR PRADESH (INDIA)**

**MARCH - 1991**

30. Mrs. K. Singh

## TABLE OF CONTENTS

CONTENTS	FACE NO. (S)
Introduction	1
The SEKA Group	5
SEKA-Afyon Pulp Mill	5
Pulping	5
Chemical Recovery	6
Need for Desilication	6
Advantages from Desilication of Black Liquor	8
Desilication Methods	9
Methods Involving Precipitation of Silica by Cations	10
Methods Involving use of Acids/pH Reduction	10
Commercial Scale Implementation of SBR Technology and Operating Experience at HNL	13
Desilication Work at SEKA-Afyon	14
Laboratory Desilication Trials using Carbonation Arrangements for Carbonation	15
Materials and Methods	16
Results	16
Foaming Tendency	16
pH Reduction and Precipitation of Silica	17

<b>Silica Sludge</b>	<b>18</b>
<b>Desilication Using Semi Pilot Submerged Reactors</b>	
The Semi Pilot Plant Unit	19
Flue Gas Composition	20
Materials & Methods	21
Results	
Lignin Co-precipitation	21
Critical Precipitation pH	22
Continuous Trials	24
Filtration of Carbonated Liquor	24
Characterization of Sludge	25
Realkalization of Carbonated Liquor	26
Viscosity and Calorific Value of Original and Carbonated Liquor	27
<b>Proposed Desilication Plant for SEKA-Afyon Pulp Mill</b>	<b>28</b>
<b>On-Job Training</b>	<b>33</b>
<b>Conclusion</b>	<b>35</b>
<b>References</b>	<b>36</b>
Table 1 to 11	
Figures 1 to 7	
<b>Terms of Reference</b>	<b>Annex-I</b>
<b>Procedures of Testing of Black Liquor</b>	<b>Annex-II</b>
<b>Personnel met During Mission</b>	<b>Annex-III</b>
<b>Process variables likely to influence the desilication plant design</b>	<b>Annex-IV</b>

## **ABSTRACT**

Afyon mill is one of the eight Pulp & Paper mill complexes of SEKA group in Turkey producing chemical grade pulps, from wheat straw and lake reed. Wheat straw and reed are silica rich fibrous raw materials. Silica dissolved during the pulping operation has adverse effect and does not permit the smooth operation of chemical recovery section. Need for desilication at above pulp mill was recognised in 1987 and Central Pulp & Paper Research Institute (CPPRI), Saharanpur, India, with its experience for more than 10 years of research in the area of desilication was considered for carrying out desilication work at Afyon Pulp Mill and subsequently in 1990 UNIDO awarded a contract to CPPRI. Two scientists from CPPRI visited above pulp mill for a period of one month and carried out work on desilication of black liquors, using carbonation technique both on laboratory and semi-pilot scale. The results of desilication have been highly encouraging and studies have clearly indicated that it is possible to apply the desilication technology developed by CPPRI and implemented on commercial scale, at Hindustan Newsprint Limited, Kerala, India. The present report deals with the results and findings of work carried out by CPPRI scientists at the project site and home office and also the proposed flow sheet for desilication plant at SEKA Afyon pulp mill.

## **INTRODUCTION**

Silica is one of the major non-process elements in pulping and chemical recovery cycle and comes mainly from fibrous raw materials like reeds, bamboo, straws, bagasse etc. Presence of silica in black liquor poses several problems in chemical recovery section which are discussed in the following pages.

Afyon Pulp Mill in Turkey is facing problems due to silica in the black liquor. Recovery unit of the mill is not functioning smoothly. Despite the high purity of lime from rotary lime kiln, the mill is forced to dispose about 20,000 tonnes of lime mud, annually, due to presence of high silica in mud. The main advantages of removal of silica from black liquors are going to be smooth operation of chemical recovery units, with reduced down time and increased life of process equipments and possibility of reburning of lime mud for obtaining lime.

Efforts for removal of silica (desilication) from black liquors have been going around the world since last few decades. Desilication by carbonation and lime treatment are the two widely accepted methods (1). The lime treatment method could not become commercially attractive due to massive quantities of lime requirements and problems in sludge filtration. Research work was carried out on desilication by carbonation by various research groups in various parts of the world (2). The disadvantage of desilication by carbonation technique is co-precipitation of lignin, invariably, as the pH range of lignin and silica precipitation are very close to each other 9.5 to 10.2 (3). Thus selective precipitation of silica in carbonation becomes a crucial step of the desilication process. Extensive research and better understanding of the chemical aspects of co-precipitation of lignin precipitation enabled CPPRI to achieve a break-through in desilication technology during its UNIDO assisted Project on "Desilication of bamboo black liquor" (4). The stepwise carbonation in submersed bubble reactor (SBR), is the key step which facilitated in achieving selective precipitation of silica. Based on this process technology, a prototype mill size demonstration desilication plant became operational in May, 1989 at Hindustan Newsprint Limited, Kerala, India, and the results of one year trial runs are highly encouraging.

The objective of the desilication work at Afyon Pulp Mill, Turkey, is to investigate, whether it is possible to apply the carbonation technique developed by CPPRI for bamboo black liquors to straw black liquors produced at above pulp mill.

The work at SFKA - Afyon mill is thus divided into two parts:-

**Work at Project Site :**

- a) Laboratory studies on black liquor desilication using synthetic flue gas to optimise process parameters for desilication.
- b) To install a semi pilot plant unit using submerge bubble reactor technology and to conduct desilication experiments using the process parameters developed in the laboratory.
- c) To impart on-job training to the counterpart laboratory staff.

**Work at Home Office :**

- a) To analyse various samples, collected in the SFKA Afyon Pulp Mill during desilication experiments.
- b) Preparation of procedures for testing of black liquors and silica sludges.
- c) Preparation of initial concept of desilication plant for SFKA Afyon Mill and to prepare a flow-sheet of the proposed desilication plant.



Following team of scientists from CPPRI worked for the UNIDO Project in Turkey.

**Project Area**

**Home Office**

Dr.A.G. Kulkarni

(Team leader)

Dr. R.M. Mathur

Dr. Rajesh Pant, Director

Dr. A.G. Kulkarni

Dr. R.M. Mathur

Dr. S. Naithani

Mrs. Rita Tandon

During the course of desilication work at Afyon Pulp Mill, CPPRI team was joined by Mr. P. Rajasekhara, Consultant & Technical Adviser to UNIDO.

The CPPRI has to fulfil the obligation given in Annex-I. This report covers the results & findings of laboratory and semi pilot scale desilication work at Afyon Pulp Mill, on-job training given to personnel at Afyon Pulp Mill, supporting analytical work carried out at home office and the conceptual flow-sheet of proposed desilication plant for the SFEA Afyon Mill.

## **THE SEKA GROUP :**

The SEKA Group of mills are Government controlled pulp and paper mills in Turkey. The group has eight pulp and paper mills which produce various grades of papers from different raw materials. The SEKA group came into existence in the year 1936 when the total production was about 4000 tonnes/year, and went upto 367,271 tonnes/year in the year 1988. The present average per capita consumption of paper in Turkey is about 16.2 kg.

### **1. SEKA - AFYON PULP MILL :**

The SEKA - Afyon mill is the only mill among the group which utilizes wheat straw and lake reed to produce bleached chemical pulp. The ratio of wheat straw to reed is 70:30 and the annual production capacity is 50,000 tonnes of pulp.

#### **1.1 Pulping :**

Mixed pulping of wheat straw and reeds is carried out with 15% active alkali in Kanyr continuous digester. The average unbleached pulp production is 130 tonnes per day. The cooking bath ratio of 1:3:5 is maintained with a top temperature of 155°C. Unbleached pulp yield is about 45 per cent. The pulp washing is carried out on rotary drum washers. The chemical losses are about 4 kg/tonne of pulp. Weak black liquor generated has about 10% solids concentration. The unbleached pulp is bleached by conventional CEHH sequence to bring the final brightness to a level of 85% ISO.

## 1.2 Chemical Recovery :

The SEKA - Afyon is one of the few mills which has conventional chemical recovery based on black liquors entirely from non-woody fibrous raw material. The initial liquor about 10% solids is evaporated in LTV multiple effect evaporators having fire. The final concentration around 46% is achieved. Centrifugal pumps are used for circulation. Further concentration of the black liquor to around 55-58% is carried out in cascade type direct contact evaporators. The concentrated black liquor is then fired to the recovery boiler of Stra Muller make. This boiler is capable of handling 200 tonnes of black liquor solids per day. Auxilliary fuel required is 24 tonnes of furnace oil per day. Presently the furnace is operating with about 12-14 t of concentrated liquor and 1 m<sup>3</sup> of fuel oil per hour. The steam generated is around 1.5 tonnes tonne of black liquor solids which is very much on the lower side as compared to mills in Europe (based on softwoods) of black liquor solids. Lower steam output might be due to low concentration of black liquor fired. Presence of silica is one of the factors affecting the evaporator efficiency and as a result it might be difficult to achieve the desired concentration.

## 2. Need for Desilication :

Silica enters the black liquor stream through the raw material as both wheat straw and lake reed contain high proportion of silica as seen in Table-1. The silica dissolves in the cooking chemicals in the alkaline pulping process and subsequently poses problems in various stages of chemical recovery.

The material balance of silica in the chemical recovery loop is given in Table-4. The problems caused by silica in various sections are :-

### 2.1 Evaporators Performance :

It forms hard deposits on the evaporator tube walls which sometimes get blocked reducing the heat transfer for efficiency. This calls for frequent mechanical or chemical treatment. The analysis of evaporator scales is given in Table-5, which shows that silica is its major component. The scale formed due to silica adversely affect the heat transfer according to following equation :

$$R_s = \frac{\delta_s}{\lambda_s}$$

where  $R_s$  is heat transfer and  $\delta_s$  &  $\lambda_s$  are scale thickness and its heat conductivity.

### 2.2 Recovery Boiler - Life & Efficiency :

Silica when fired into the recovery boiler forms hard beehive like structures preventing heat transfer to the tube walls and also reducing the life of the equipment.

### 2.3 Causticization Stage :

During green liquor causticization, silica reacts with part of lime forming calcium silicate which is slow settling and adversely affects the white liquor clarification.

## 2.4 Lime Burning :

The lime mud containing silica cannot be reburnt due to high percentage of silicates which form rings on the walls of the lime kiln in presence of alkali. The lime mud generated is disposed off as land fill and as a consequence poses serious problems like:-

- High cost of transportation by lorries;
- Requirement of open land for lime disposal. It has been estimated that for an average production of 100 tonnes lime mud per day for a period of 10 years and with a disposable height of 4 meters, about 30 hectares of land will be needed for lime mud disposal.
- There are ample chances of contamination of ground water and surface water due to the presence of sodium in the lime mud. The lime mud contains about 2-3% sodium (Table-2) which is also disposed alongwith the lime mud.

## 3.0 ADVANTAGES FROM DESILICATION OF BLACK LIQUOR :

By going in for desilication, following advantages are going to be achieved :-

- i) Improved evaporator performance leading to increased steam economy and higher solids concentration,

- ii) Reduced down time and increased life of evaporator tanks.
- iv) Reduced down time and increased life of furnace and less chances of sport jaring.
- v) Improved performance of causticizers and reducing the load on causticizer.
- vi) Possibility of increasing the dryness of lime mud and subsequent reburning and recycling of lime mud.

### 3. DESILICATION METHODS :

Efforts for removal of silica from black liquor date back to the decade of 30's and a number of research workers, both in India and abroad have studied different desilication techniques. The desilication techniques can be divided into two categories :-

- (1) Involving precipitation of silica as insoluble silicates by treating with cations like  $Ca^{++}$  and  $Al^{+++}$ .
- (2) Involving lowering of pH by addition of acids which results in precipitation of silica as soluble silicates (SAG).

#### **4.1 Methods Involving Precipitation of Silica by Cations :**

Lime treatment for desilication was extensively studied by various research groups. This method, however, could not gain commercial significance, as massive quantities of lime was required and it has been reported that as high as 400-600% of calcium oxide on silica, is needed depending upon the method of treatment (1). Studies conducted at an Indian paper mill revealed that filtration of calcium silicate precipitate poses several problems (2). The studies conducted using bauxite ( $\text{Al}_2\text{O}_3$ ) also were not successful.

#### **4.2 Methods involving use of Acids/pH Reduction :**

By lowering the pH of the black liquor, silicates are converted into insoluble polymeric anhydrides of silicic acid gel (SAG). The Figure-1 shows mechanism of silica precipitation. Two methods are generally employed for pH reduction :-

- a) Addition of mineral acids;
- b) By carbonation using  $\text{CO}_2$  gas.

Addition of mineral acids was not found to be suitable because of difficulties in controlling the threshold pH and as a consequence, a large amount of lignin is also co-precipitated with silica.

#### 4.2.1 Silica Precipitation by Carbonation :

Carbon dioxide is mildly acidic and therefore pH reduction using carbon dioxide is slow and controlled. Various methods were studied to carbonate the black liquor in order to find the most suitable method so as to have selective precipitation of silica without lignin precipitation.

#### 4.2.2 Carbonation by Direct Bubbling :

Carbon dioxide gas from compressed gas cylinders or from the recovery boiler was injected directly into the black liquor and pH was reduced gradually. Silica precipitation commences at a pH 10.2 to 10.3 but as the carbonation progress, lignin also starts co-precipitating due to over acidification in some pockets.

#### 4.2.3 Carbonation in Packed Bed Column :

Direct bubbling method suffers from the disadvantage that rate of gas-liquid mass transfer is very slow and it takes a long time for carbonation and on continuous operations size of equipment may be huge. Packed bed absorption columns are normally used for reactions involving gas-liquid transfer operations. Packing materials like intalox ceramic saddles, Raschig rings, Pall rings, Berl Saddle were used for black liquor carbonation in a packed bed column. It was possible to achieve desilication over 70% in packed bed columns where liquor is fed at the top and flue gas from bottom but again the sludge was rich in co-precipitated lignin. Heavy foaming and localised carbonation were responsible, in lignin precipitation. Deposits of silica



and lignin was also noted in the packing material. The rate of carbonation was very fast and it was not possible to carbonate uniformly.

#### **4.2.4 Carbonation in Submerge Bubble Reactor (SBR) - Concept and Reality :**

All the methods discussed above have one major disadvantage that massive lignin co-precipitation occurs along with silica which makes the filtration of silica sludge difficult and at the same time significant loss of heating value from black liquor. At this stage, the idea of Submerge Bubble Reactor (SBR) was conceived. A typical lay-out of SBR is illustrated in Figure-2. In this reactor, the liquor to be treated with gas is circulated through a pump in a tubular system. The CO<sub>2</sub> gas from the compressed gas cylinders or from the recovery boiler is injected at the upper limb of the tube. The liquid on its downward path sucks in the gas in the form of discrete bubbles. The shearing action of the flow works the gas bubbles in a kneading fashion continuously exposing new gas liquid interfaces. This results in slow reduction of pH. It was also noted that sludge obtained in this reactor is light coloured and can be washed to a white coloured silica. Table-6 shows the comparative account of two liquor carbonated on packed bed column and on SBR.

## **5. COMMERCIAL SCALE IMPLEMENTATION OF SUBMERSE BUBBLE REACTOR TECHNOLOGY AND OPERATING EXPERIENCE AT HINDUSTAN NEWSPRINT LIMITED**

The laboratory technique of desilication using SBR technology was scaled to design and construct a mill size prototype desilication plant capable of processing about 40 cubic meters of black liquor per hour. The plant was installed at Hindustan Newsprint Limited (HNL), Kerala, India. The plant became operational by May 1990.

The desilication plant at HNL has three submerse reactor tanks connected in series. The first reactor tank has two submerse reactor heads and other two have one submerse reactor head. The pH of the black liquor is reduced in the submerse reactor tanks from 12.0 to 10.0. The temperature of the reactor is 70-80°C, when the desired level of pH is achieved in the third tank, the liquor enters the hot retention tank, where the silica flocculation takes place. The liquor is then filtered on a horizontal belt-filter to separate the precipitated silica from the mother liquor.

### **Operating Experience of the Plant :**

The weak black liquor from the chemical pulp mill is fed to the desilication plant. The Table-7 records the observations made when flow of black liquor was maintained 10 and 20 m<sup>3</sup>/hr. The weak black liquor has almost the same physico-chemical properties i.e. pH 12.4-12.5 at 30°C. The total solids concentration is 15-17 % (w/w). Silica in black liquor is about 3-4 g/l. The carbonated liquors show a pH 10.0 with reduced alkali at less than 0.3 g/l. The sludge obtained in the two case is white in colour. The ash content is about 90% and above and

silica in ash is about 90%. In both the cases foaming in the submerse reactor tanks is moderate. Extent of desilication is about 80%. Heat loss in black liquor due to desilication is only marginal and black liquor obtained is 10% w/w. The results indicate that the plant efficiency is not affected with change in the quantity of black liquor to be carbonated and practically similar properties of carbonated black liquor and sludge are observed when volume of feed liquor is doubled from 10 m<sup>3</sup>/hr to 20 m<sup>3</sup>/hr.

## **6. DESILICATION WORK AT SEKA - A YON :**

### **6.1 Laboratory Desilication Trials using Carbonation :**

Laboratory desilication trials were conducted at the SEKA Ayan mill to establish the important process parameters like :

- Optimum pH level for maximum desilication, without precipitating lignin,
- pH at which lignin precipitation commences,
- Stability of lignin at various pH levels,
- Filterability of carbonated black liquor using a filter paper and a vacuum pump,
- Characteristics of carbonated liquor - change in RAA level, pH, total solids, specific gravity and silica removal,

- Characteristics of silica mud - physical appearance like colour, nature of the powder, lignin content, silica content, etc.

These properties were considered necessary to establish the suitability of desilication process and to lay down the process conditions for a semi-pilot desilication plant.

## 6.2 Arrangements for Carbonation :

Simple arrangements were made for laboratory carbonation studies. Synthetic flue gas was used for carbonation as a substitute for boiler flue gas. Carbon dioxide from the compressed gas cylinder and air from the mill compressed air supply line were blended to get a mixture containing 10-15% CO<sub>2</sub>. All carbonation studies were carried out at the liquor temperature 70°C was maintained by using a hot plate. Agitation was provided by a variable speed rigid shaft stirrer which simultaneously served the important purposes like :-

- Distribution of gas bubbles into the entire solution as the gas injection is at one point in the liquor. Quick distribution of the gas is necessary to avoid localised carbonation.
- Maintaining uniform temperature in the vessel.
- Assists particle to particle contact, once silica flocs start to precipitate.

- It also helps to subside foam which is generated in the earlier stages of gas liquid interaction.

The experimental set-up is illustrated in Figure-3.

### 6.3 Materials and Method :

Representative sample of fresh black liquor were collected from the Kamyr digester for each trial. About 1 litre sample of the liquor was first heated to 80°C, which was then carbonated using a steady, gentle flow of the synthetic flue gas. The CO<sub>2</sub> concentration in the synthetic flue gas was maintained at 10-12% to keep it on par with that of recovery boiler flue gas. The pH of the liquor was monitored and recorded continuously. During the initial stages of carbonation the pH remains steady due to high residual alkali level in the liquor. Once the excess alkali is neutralised then the pH drops steadily. Carbonated black liquor samples were collected at different pH levels for testing filtration properties and the extent of desilication. Original spent liquor and carbonated liquor were analysed according to TAPPI standard and silica was estimated according to CPPRI methods (Annex-2).

### 6.4 Results :

#### 6.4.1 Foaming Tendency :

Foam generation is noticed in the earlier stages of carbonation. The quantity of foam generated depends upon the initial liquor concentration. When the black liquor of low solids was carbonated, fragile, unstable foam was generated. When the

solids concentration of the liquor exceeded 15%, the foam generated was more stable. Increasing the rate of agitation helps to subside foam. Use of antifoam agent like kerocone also helped in effectively reducing the foaming tendency.

#### 6.4.2 pH Reduction and Precipitation of Silica :

pH was measured at a temperature of 30°C in order to protect the pH electrode. Silica precipitation commenced at a pH of 10.2. This was visually observed by taking a sample in a small glass beaker and swirling the liquor on the walls when gelatinous white deposit appeared on the wall of the beaker. However, in case of black liquors from pulping of the agricultural residues, hemicelluloses are also present in higher amounts, and they also appear like silica precipitate. The distinction between the two could be made by filtering the liquor.

The silica mud is readily filterable and washes clean off any occluded liquor. Silica cake, brittle in nature after dewatering, shows multiple cracks. When sludge is contaminated with large amount of hemicelluloses, it is difficult to filter and the cake formed is gelatinous, smooth with no cracked surface. The liquor samples were withdrawn at various pH levels to study the extent of desilyation and nature of silica mud, filterability of liquor. In silica precipitation was observed, pH was controlled carefully. The results of the laboratory trials are recorded in Table-8. The time required for carbonation was 80-85 minutes. The rate of gas flow was not measured as very low gas velocity was required, however, by knowing the rate of bubbling in water, a constant velocity was maintained. The analysis of original

liquor showed that the liquor possessed a high pH, sometimes more than 13.0. The total solids concentration was between 9-13% but normally was about 10%. The liquor also showed a high residual alkali concentration in the range of 8-12 gm/litre. Silica content, as determined on black liquor solids varied between 2.5-3.5%, depending upon the raw material composition. Due to high pH and residual alkali, it is expected that the lignin in black liquor are more stable due to the fact that enough alkali concentration is there to prevent lignin condensation and also sodium lignates are present which are more hydrophylic. This is expected to help in selective desilication of the black liquor. The Table-8 also depicts that carbonated liquor pH was normally 9.5-9.7, which is on the lower side as compared to that for bamboo and reeds (3). The R.A.A. of carbonated liquor was generally reduced below 1 g/l. The silica concentration was generally reduced below 1% (w/w) depending upon the end pH, e.g. when pH of carbonated liquor was 9.5, upto 76% desilication was achieved whereas only 55% silica was removed when the pH of carbonated liquor was 10.1.

In the laboratory desilication trials, sometimes there is a tendency of lignin co-precipitation due to local overcarbonation as the bubble size during direct bubbling is large. This causes problems in filtration and further carbonation had to be terminated due to poor filtration. The pH and amount of silica removal results indicate that good desilication is possible at pH 9.5 to 9.7.

#### 6.4.3 Silica Sludge :

Under the optimum desilication conditions, it is imperative that there is a high extent of desilication (80% and above) at the same time silica sludge should be free of organic impurities.

The analysis of sludge at various pH levels and in different experiments reveal that under optimum conditions of pH ( 9.7) the sludge is relatively free of organic matter and shows higher ash and silica content. A perusal of the Table-8 reveals that ash content of the sludge is upto 75%.

The laboratory trials clearly indicate that it is possible to achieve desilication over 70% in the pH range of 9.5 to 9.7 (measured at 30°) at an optimum temperature of 80°C. The desilication was equally good for black liquor solids range of 10-16% w/w.

## **7. DESILICATION USING SEMI-PILOT SUBMERSE REACTORS :**

Two stage glass submerse reactors for spent liquor carbonation was used in CPPRI for desilication trials. As the glass submerse columns and accessories could not be taken to Turkey from India, it was decided to construct semi pilot reactor at Afyon mill.

### **7.1 The Semi-Pilot Plant Unit :**

The semi-pilot plant consisted of two reactor columns made of mild steel, each 1.6 meters in length and having an internal diameter of 15 cms. The detailed pilot plant set up is shown in Figure-4. Each column had a volume of 26 litres. Four glass



windows, two on the upper and two on the lower end of the glass column were provided. The windows were opposite to each other so that visual observation on size of the bubbles, gas flow, liquor flow and foam could be made. The liquor was fed to the reactors through a vertical delivery system using a pump in each of the reactors. The axial pumps were driven by 2800 RPM motor, each capable of pumping 45-47 litres of spent liquors per minute. The gas injection port assembly was designed in such a fashion so as to assist the gas suction and to affect the roughing of gas interaction. The injection port had 4 nozzles - two fixed opposite to each other tangentially at an angle of 30°. The nozzles had 0.8 and 1.0 mm openings. Arrangements were also provided for transfer of liquor from the 2nd reactor to the first reactor tank and from the foam tank to the first reactor tank so as to carry out continuous desilication trials.

## 7.2 Flue Gas Composition :

Initial experiments were conducted on the semi-pilot submerse unit using synthetic flue gas, i.e. mixture of carbon dioxide from the compressed gas cylinders and air. The composition of flue gas was maintained as close to that of plant recovery boiler flue gas as far as possible. Gas analyses were carried out for all the trials using Orset apparatus. CO<sub>2</sub> content in the synthetic flue gas was maintained between 10-12%. After the arrangements were made to tap the recovery boiler flue gas, it was possible to use the actual flue gas for all further trials. The carbon dioxide content in the flue gas was found to be between 11.0 to 14.6% but for one trial it was only 5%. Several trials were taken on the semi pilot desilication plant.

### 7.3 Materials and Methods :

Black liquor from pulping of straw and reed in the Kanyr digester is stored in a storage tank. The semi-pilot plant unit was fitted with a fresh black liquor line to obtain fresh hot black liquor. Flue gas from the flue gas stack of the recovery boiler, is used. The analysis of spent liquor and carbonated liquor was carried out as per TAPPI standard T-625 and analysis of sludge and silica determination was carried as per methods of CPPRI given in Annex-2. Time taken for carbonation was about 4 hrs, when 80 litres of the black liquor was carbonated in single column. When both columns were employed the time required for carbonation was about 3.5 hours. The flow of flue gas into the reactors through the gas injection port was maintained by regulation through rotameters. A gas flow of 40 litres per minute was maintained to have a steady carbonation. While using synthetic flue gas, a gas blender was used. The air and carbon dioxide were introduced from the bottom of rugged metal cylinder closed at both ends with both the gases entering through tangentially placed nozzles. The outlets were provided at the top and the gas flows were regulated by rotameter. The arrangement ensured proper mixing of the gases and constant homogenous flow was provided.

### 7.4 Results :

#### 7.4.1 Lignin Co-precipitation :

The precipitation point for silica and lignin lie in close proximity and slight deviation from the critical silica precipitation pH may result in lignin precipitation. The experiment on laboratory as well as pilot plant scale have indicated that when black liquor solids increase beyond 18-20%, there are

more chances of lignin co-precipitation. It has also been found that relatively stable lignins are present in spent liquors which have higher residual alkali as compared to the ones with low or no residual alkali. It is also experienced that once the lignin precipitates, filtration of carbonated liquor becomes impossible, and even repeated washing with warm water also does not help in improvement of filtrability or colour of the precipitate. Keeping this in view, the pH reduction was closely monitored in every 10 minutes.

#### 7.4.2 Critical Precipitation pH :

The desilication trials were started with a spent liquor pH exceeding 12.5 in all the cases. Initially, the pH reduction was slow due to very high residual alkali. The first appearance of the precipitate was observed at a pH about 10.4. This precipitate was very fine and almost nothing was retained on filter paper when this liquor was filtered. The larger flocs are observed as the pH dropped to 10.0 and below. On filtration the liquor was readily filtrable, leaving behind light coloured silica mud which was easily washable with warm water. The adhered spent liquor was easily washed off with cold water. It was observed that with the mixed spent liquor of wheat straw and reed the pH for 80% desilication lies in the range 9.8-9.6. Figure-5 shows the pH reduction with progressive carbonation. It was observed that when the initial pH was high, the reduction in pH was rather slow. The curves distinctively, show that the initial pH reduction was relatively faster than pH reduction in the range 9.5-10.5. The initial reduction is faster due to neutralization of NaOH and later reduction slow due to neutralization of organic acid salts. Thus the length of period of carbonation is purely dependent on chemical nature of black

liquors. As the temperature during carbonation was varying between 60-80°C, the pH measurements were performed at constant temperature of 30°.

The results of desilication in semi pilot plant scale are given in Table-9. Weak black liquor had solids concentration in the range of 7-10% with residual alkali ranging from 3-7 g/l as  $\text{Na}_2\text{O}$ . Carbonated black liquors had pH range from 9.7 to 10.2, with active alkali reduced to less than 1 g/l. There was a reduction in solids concentration after carbonation presumably due to some steam condensate leaking into black liquor as the black liquor tank was heated with a steam coil. The degree of desilication varied from 67-98%. Here the main objective was to see that by repeated trials whether it would be possible to get easily filterable silica or not. Results clearly indicate that it is possible to obtain easily filterable silica with 98% desilication efficiency. Experiment-7 shows desilication of semi-concentrated liquor (SCHL). It was difficult to desilicate SCHL as there was a co-precipitated solids from which resulted in liquor co-precipitation.

The silica sludge obtained from various trials were analysed and were found to contain high percentage of ash and silica. The ash content was 70-91% and silica was 67-87% which indicates that there was minimal precipitation of liquor and other carbohydrates along with silica.

### 7.5 Continuous Trials :

The desilication trials carried out on single and double column showed that effective desilication can be carried out using the submerge bubble reactor.

In continuous trials, initially, black liquor was carbonated to desired pH level of 9.6 in two column. When the entire liquor had attained this level of pH, fresh liquor was added at the rate of about 1.6 litre/minute to the first tank. When carbonated in two reactor liquors was drawn at the same rate as the fresh liquor input. Rate of spent liquor flow into the reactors was so monitored that the overflow obtained from the second reactor or finally carbonated liquor, pH remained the same for all the samples collected over a length of period of time. The trial was continued for about 90 minutes and pH of the overflow was maintained constant at a level of 9.8. The entire system was therefore brought in an equilibrium state. Steady gas flow of about 50 lit/minutes and fresh black liquor flow of 1.6 litres/minute was maintained. The carbonated liquor was filtered. It gave easily filtrable silica mud and had similar characteristics to that of the batch scale sample.

### 7.6 Filtration of Carbonated Liquor :

The efficiency of desilication depends much upon the filtrability of the carbonated liquor. The liquor separated should be free from any precipitated silica and at the same time silica sludge should be easily washable and should also be free from any precipitated lignins and other organics.

In laboratory scale experiments lignin co-precipitation slowed down the filtration rate. The cause of lignin precipitation was attributable to the possibilities of localized carbonation and increased liquor concentration during heating to maintain a constant temperature of 80°C during carbonation.

In the semi-pilot plant experiments employing submerge bubble reactor technique for carbonation, improved rates of filtration was noted. In plant trial No.5 where CO<sub>2</sub> and air mixture was used the carbonated liquor had filtration rate of 36.8 litre/m<sup>2</sup>/min. In another trial with mixed liquor a high filtration rate as high as 132.8 litre/m<sup>2</sup>/min, was observed. In the plant trial No.9 when two stage continuous carbonation was carried out, the liquor at pH 9.8 had a filtration rate of 47.4 litre/m<sup>2</sup>/min. In the trial No.7 flue gas was used for carbonation and still a gentle carbonation was effected, and a rate of filtration of 133/m<sup>2</sup>/min was observed at pH of 9.9.

These results clearly indicate that in semi-pilot plant, due to gentle carbonation, there was very little or no lignin co-precipitation. When the sludge was free from lignins the porosity was high and therefore filtration was rapid.

### 7.7 Characterisation of Sludge :

The results of analysis of sludge samples (Table-10) indicate that black liquor occluded in the silica mud was effectively washed by warm water as indicated by reduction in values of loss on ignition after washing of silica sludge. The lignin content in washed sludge ranges from less than 0.2 to 2%. However, carbohydrate fraction in the sludge was on higher side and washed

silica mud had about 5-8 per cent carbohydrates. This might be attributed to the presence of pith and possibly some hemicelluloses which are present in excessive quantities in agricultural residues black liquors. The loss of sodium along with washed sludge was not very substantial. The washed sludge had silica content over 80% on sludge dry solids. The silica sludge from semi-pilot desilication plant had white appearance after washing. It was light and bulky. The semi-pilot plant scale trials gave silica sludges having low lignin and sodium contents and rich in silica. The washed sludge obtained at Afyon, with the exception of higher carbohydrate, had chemical composition almost similar to bamboo silica sludge obtained at desilication plant at Hindustan Newsprint Limited, Kerala, India.

#### 7.8 Re-alkalization of Carbonated Liquor :

It is important from the view point of rheological properties of the carbonated black liquor that a minimum amount of alkali level need to be maintained so that there is no abnormal rise in viscosity of the liquor during concentration and also the precipitation of black liquor solids due to colloidal instability does not occur at a relatively low total solids content.

It was noted that in almost all the experiments, after carbonation the residual alkali level of spent liquors dropped down to less than 1 gpl. From the past experience on several spent liquors, it is known that at least 5-6 gpl of alkali is needed for maintaining low viscosity in the liquors. It is therefore imperative that caustic should be added to the spent liquor to

bring the residual alkali level to the required limit. The laboratory experiments reveal that (Table-11) a minimum of 5 gpl of NaOH should be added to the carbonated spent liquor to bring the residual alkali to about 5 gpl, and further addition of NaOH was not beneficial.

#### 7.9 Viscosity and Calorific Value of Original and Carbonated Liquors :

Viscosity is an important parameter which governs the final concentration of the spent liquor and also the pumping of the liquor into the recovery boiler. Therefore monitoring of viscosity is very essential. Upon carbonation, the pH of the liquor drops which can adversely affect the viscosity. To overcome this problem a step called realkalization is introduced wherein alkali is added to the black liquor to restore the viscosity to almost the same level as in the case of original liquor. To get an idea of the viscosities of carbonated and the original black liquor viscosity were measured using Rheo Viscometer. This viscometer measures viscosity in terms of resistance offered to falling ball in the black liquor sample. The viscosity curves shown in Figure 6, indicate that the carbonated and desilicated black liquor when brought to original pH (around 12) showed viscosity almost comparable to that of original liquor.

During carbonation due to reduction in pH some amount of lignin-carbohydrate complexes precipitate along with silica. Thus some portion of organic matter going along with silica sludge may result in reduced calorific value of carbonated and desilicated liquor. In order to find out the changes in



calorific value, tests were performed. Calorific value of the original and carbonated liquor were determined using Bomb Calorimeter. The original sample had a calorific value of 2992 cal/gm and the treated liquor 2798 calories/gm. The reduction in calorific value, although is significant, cannot be attributed to only organic matter lost with the sludge, but could also be due to some reactions taking place during carbonation and more studies to understand this would be essential.

## **8. PROPOSED DESILICATION PLANT FOR SEKA-AFYON PULP MILL :**

The semi pilot plant scale experiments at Afyon confirm that the submerge bubble reactor carbonation technique is ideal and can be successfully used in desilication of wheat straw and reed black liquors. Based on the semi pilot plant results at Afyon and experience of the desilication plant at BNL, India, the conceptual desilication plant is shown in Figure-7.

### **8.1 Quantity of Black Liquor :**

On an average the mill is producing about 1200-1400 m<sup>3</sup> day of black liquor with about 8-10% solids content. For development of desilication flow sheet about 1500 m<sup>3</sup> day of black liquor is taken. The pH of the black liquor varies between 12-13 (at 30° C and the residual alkali lies between 3.5-7.5 g/l as Na<sub>2</sub>O.

## 8.2 Flue Gas:

The experiments conducted on carbonation of black liquor have revealed that upto 30% CO<sub>2</sub> in flue gas it is not difficult to control the end pH. The flue gas containing CO<sub>2</sub> content upto 30% is ideal for carbonation. Lower CO<sub>2</sub> content in flue gas may require higher gas flow and large size equipment. Foam problem may also be more when flue gas of low CO<sub>2</sub> content is used as more gas will be required. Afyon mill has two sources of flue gas, namely the lime kiln flue gas and recovery boiler flue gas.

**Lime Kiln Flue Gas:** Lime kiln is already operational at the Afyon mill. The average CO<sub>2</sub> content of lime kiln flue gas is around 20% and 5% O<sub>2</sub> and fluctuations in CO<sub>2</sub> concentration are lower as compared to recovery boiler flue gas. It is recommended to use flue gas from lime kiln due to high and steady concentration of CO<sub>2</sub>.

**Recovery Boiler Flue Gas:** At the Afyon Mill it was found that CO<sub>2</sub> content of the flue gas lies between 5-14%. On an average the CO<sub>2</sub> concentration lies at about 10%. At this concentration about 2000 m<sup>3</sup>/hr. of flue gas at 1100 m.bar pressure will be required.

### **8.3 Gas Liquor Transfer Rate :**

Based on the earlier experience, it was found that on an average there is about 60% absorption of  $\text{CO}_2$  from the flue gas during carbonation to bring down the pH from 13.0 to 9.7. The total quantity of  $\text{CO}_2$  required for carbonating 1500  $\text{m}^3$  day of black liquor is 4.95 tonnes.

### **8.4 Blower :**

The blower for supplying the flue gas into the reactor will be required to have a capacity of 2000  $\text{m}^3$ /hr of flue gas at 1200 m.bar when drawn from recovery boiler and 1000  $\text{m}^3$ /hr. at 1400 m.bar pressure when drawn from lime kiln.

### **8.5 Stepwise Carbonation in SBR Tanks :-**

Three steps of carbonation of black liquor will be required to bring the pH from original 12.5 to about 9.7. Each stage will comprise of a submerse reactor tank fixed with two reactors. The pumps required to pump the liquor into the reactor should be of centrifugal type and axial flow with low head capable of circulating about 1500  $\text{m}^3$ /hr. at about 400 rpm. The flue gas is to be injected into the liquor in the circulation loop through specially designed injectors or gas delivery head. The reactor may be about 7 meter high and 'U' shaped. The flue gas enters through the injection head at right angles of the flow of black liquor. Black liquor on its downward path sucks the flue gas.

The proposed capacity of submerse reactor tanks would be about 160 m<sup>3</sup>. The construction can be mild steel type and with insulation.

The three submerse reactor tanks are to be connected in series and overflow from one tank enters the other. When pH is reduced to required level in SR-1, the overflow is taken to the SR-2 and finally to the SR-III and making the process continuous by adding the fresh black liquor equivalent to the black liquor taken out from the last tank.

#### 8.6 Foam Tank :

Foam generated in the submerse reactor tanks is carried over to the foam tank by a common foam line. A tank of about 15 m<sup>3</sup> fitted with a slow agitator will be sufficient for the breaking of the foam. The foam converted into liquor is taken back to SRT-1.

#### 8.7 Hot Retention Tank :

When the pH of the carbonated liquor is reduced to the desired level in SR-3, there is normally drop in temperature. Higher temperature is essential for obtaining better flocs of silica. The liquor enters the hot retention tank. Under hot conditions and mild agitation the precipitated silica molecules are allowed to grow by particle to particle contact. Optimum time for build up of silica flocs is around 1 hour. A hot retention tank of a capacity of about 60 m<sup>3</sup> is required.

### **8.8 Horizontal Belt Filter :**

Different types of equipments are available for solid-liquid separation operation. In the recent days, belt filters have become more common for filtering solids having fine particles. The DELKOR horizontal belt filter's performance at HNL has been very satisfactory. So in the proposed Afyon desilication plant, belt filter is recommended. The filter consists of a rubber transporter belt moving horizontally on HDPE gland strips. The belt supports the fabric which is the filtering medium. Grooves on the transporter belt convey the filtrate to the centrally located holes and from there to the vacuum box located below the belt. From the vacuum box the filtrate air mixture goes to filtrate receiver-cum-air separator. Partitions in the vacuum box and filtrate receiver enable the mother filtrate and wash filtrates to be separated. In the receiver the air is separated and goes to the vacuum pump. The filtrate flows down through the droplegs to the respective seal tanks. This system provides for three stage counter current washing of the silica residues on the fabric. The hot black liquor can be fed to one end of the belt through a feed distributor and as the belt moves, cake is washed by wash filtrates and finally by hot fresh water at the discharge end.

### **8.9 Realkalization Tank :**

The filtrate at low pH (9.7) has to be realkalized with fresh caustic to increase the pH and residual alkali before pumping to the evaporators. The dosage of alkali is pre determined and the addition is necessary to prevent high black liquor viscosities and also to avoid lignin precipitation during concentration.

## **9. ON-JOB TRAINING :**

Training of mill personnel and laboratory staff was one of the obligations in terms of reference. Although the laboratory staff was well versed with some of the analytical procedures used for black liquors but methodology was not based on any standard testing methods. Laboratory staff was trained in following areas during the course of desilication work.

### **a) Method of Carbonation :**

Various steps involved in carbonation of weak black liquor, monitoring of the pH, control of gas flow, visual observation on onset of desilication, filtration of the silica sludge and its washings were demonstrated on both laboratory and semi-pilot scale trials.

### **b) Analysis of Black Liquors :**

For the desilication experiments, some properties like residual alkali, pH, silica content, lignin content etc. are very important tests and need to be performed with greatest precision and accuracy.

#### **i) Residual Alkali :**

Estimation of residual alkali (RAA) in black liquor is very important and need to be determined carefully. Laboratory staff at Afyon were following a method which usually give very high values of RAA. The laboratory staff was given standard procedures for estimation of RAA which is

based on TAPPI standard method. A demonstration on performance of the test was also given. The detailed procedure is given in Annexure-II.

**ii) Silica :**

For estimation of silica, the laboratory staff at Afyon mill were following a different method and normally results on lower side were obtained. A standard TAPPI procedure was explained and demonstrated to the laboratory staff how to perform this test.

**iii) Lignin Estimation :**

Demonstration of method for estimation of lignin in black liquor, washings and silica sludge was given. This is an essential test for estimation of organic matter coprecipitated with silica. The laboratory had a spectrophotometer - Spectronic 20, but the laboratory staff did not know the method for estimating lignin using this instrument. Detailed procedure was given to the users (Annex-2).

**iv) Other Properties :**

Accurate measurement of pH, monitoring of pH during carbonation, preparation of synthetic flue gas, determination of carbonated liquor filtration rates, settling time of silica sludge etc. were demonstrated to the lab staff.

## 9.1 Literature :

Useful literature concerning desilication including reprints from periodicals and journals, CPPRI publications and reports relating to desilication and testing methods were given to the laboratory staff in order to enable them to understand various physical and chemical aspects of desilication process.

## 10. CONCLUSION :

1. Laboratory experiments and semi-pilot scale trials clearly indicate that it is possible to achieve desilication upto 80%, in a pH range of 9.5-9.7 for the black liquor at SFKA-Afyon Pulp Mill.
2. Higher temperature of 70°C and above facilitate better filtration.
3. Carbonation of black liquors with solids concentration more than 20% is not efficient and results in substantial lignin co-precipitation.
4. Silica sludge obtained under optimum carbonation was easily filtrable and had relatively lower proportion of lignin and other organic matter.
5. The desilicated black liquor is stable and possess viscosity almost comparable with untreated liquor.
6. The semi-pilot scale trials using the gas from recovery boiler stack proves, beyond doubt that the technology implemented at Hindustan Newsprint Mills, Kerala, India is very much valid for application in Afyon Mill and the



desilication technology developed for bamboo black liquor in India can also be employed for desilication of straw black liquor.

7. The conceptual flowsheet developed for desilication of about 1500 m<sup>3</sup> of black liquor per day, for Afyon Pulp Mill should facilitate in design and development of production units.

#### REFERENCES :

1. Panda, A; "Removal of Silica from Recovery System of Alkalines Pulp Mills", Indian Pulp & Paper, 12(6):1962.
2. Bleir, P; "UNIDO/SIDA Desilication - Facts and Basic Principles", International Seminar on Desilication - Cochin, India, (Dec., 1989).
3. Naithani, S; Jain, R.K; Kulkarni, A.G. and Panda, A; "Silica Sludge Composition and Filtration Characteristics", International Seminar on Desilication - Cochin, India, (Dec.1989).
4. Kulkarni, A.G; Mathur, R.M; Naithani, S; Roy, T.K. and Pant, R; "Supporting Research Work on Desilication of Black Liquor", CPPRI, Report No.22, Jan., 1987.

**TABLE - 2**  
**PROXIMATE CHEMICAL ANALYSIS**

<b>Properties</b>	<b>Wheat straw (Afyon)</b>	<b>Lake Reed (Afyon)</b>
Alcohol Benzene Solubility, % w/w	8.4	4.4
Ash,% w/w	5.3	4.0
Silica,% w/w	4.0	3.9
Hot Water Solubility,% w/w	10.3	6.6
1% NaOH Solubility,% w/w	39.2	39.0
Lignin,% w/w	15.3	22.6
Pentosans,% w/w	21.1	18.8

**TABLE -2**  
**ANALYSIS OF LIME**  
**(Afyon Mill)**

<b>Properties</b>	<b>Values</b>
Loss on ignition, % w/w	14.90
Available lime index, % w/w	74.4
Silica, % w/w	0.3
Ash, % w/w	85.1

**TABLE -3**  
**ANALYSIS OF LIME MUD**  
**(Afyon Mill)**

<b>Properties</b>	<b>Values</b>
Calcium, % w/w (as Cao)	35.5
Sodium, % w/w	5.5
Loss on ignition, % w/w	33.0
Silica, % w/w	11.8
R <sub>2</sub> O <sub>3</sub> , % w/w	1.4

**TABLE-4**  
**SILICA BALANCE**

Particulars	Silica in B.L. gms.	Silica going into evapora- tors, gms.	Silica in lime Sludge, gms.	Silica load %
No Desilication	4.43	0.88	4.34	98
After 70% Desilication	1.329	0.026	1.303	29
After 80% Desilication	0.89	0.018	0.872	19.8
After 90% Desilication	0.443	0.009	0.434	9.8

**TABLE -5**  
**ANALYSIS OF MULTIPLE EFFECT EVAPORATOR SCALE DEPOSITS**

<b>Properties</b>	<b>Values</b>
Ash, % w/w	84.97
Loss on ignition, % w/w	15.03
Hot water insolubles, % w/w	96.80
Silica, % w/w	58.49
Calcium, % w/w	11.09
Sodium, % w/w	0.52
Mixed Oxides, % w/w	2.61
Undetermined, % w/w	12.26

TABLE-6

## BLACK LIQUOR DESILICATION IN PACKED BED AND SBR

Particulars	Packed Bed Column		Submerse Bubble Reactor	
<b><u>Initial Liquor</u></b>				
pH/30°C	12.1	11.8	12.1	12.3
Total solids, %, w/w	12.3	13.8	15.0	12.0
Silica, g/l	5.0	6.1	6.0	7.5
Residual Active Alkali, g/l	5.9	6.4	- -	- -
<b><u>Desilicated Liquor</u></b>				
pH/30°C	10.2	9.9	10.4	10.3
Total solids, %, w/w	11.9	12.1	- -	- -
Silica, g/l	0.9	0.8	1.4	1.0
Residual Active Alkali, g/l	0.4	Nil		
<b><u>Sludge</u></b>				
Filtration, min/500 ml.	10.0	No filtration	Good	Good
Loss on ignition at 700°C, %, w/w	15.0	18.0	1.6	3.3
Silica, %, w/w	75	75	- -	- -
Desilication, %	82.0	87.0	77.0	87.0

TABLE-7  
DESILICATION IN SBR ON MILL SCALE

Particulars	Flow Rate 10 m <sup>3</sup> /hr.	Flow Rate 18 m <sup>3</sup> /hr
<b><u>Feed Black Liquor</u></b>		
pH/30°C	12.5	12.4
o Tw	20.0	16.5
Total solids, %, w/w	17.3	15.0
Residual Active Alkali, g/l as Na <sub>2</sub> O	6.14	6.07
Silica, %, w/w on solids	2.06	2.36
Calorific value, Cal/g.	3110	3510
<b><u>Carbonated Black Liquor</u></b>		
pH/30°C	10.1	10.0
o Tw	19.0	15.5
Residual Active Alkali, g/l as Na <sub>2</sub> O	0.25	0.31
Silica, %, w/w	0.4	0.45
Calorific value, Cal/gm.	2940	3190
<b><u>Sludge</u></b>		
Color (washed sludge)	White	White
Moisture	74.0	77.5
SiO <sub>2</sub> on OD sludge	84.02	87.6
Desiccation, %	77.0	80.93

TABLE-8.  
RESULTS OF LABORATORY TRIALS

Test No.	Carbonation Conditions		Original Liquor				Carbonated Liquor				Silica Sludge		Desilication
	Time min.	Temp. °C	pH 30°C	T.S. %w/w	RAA* g/l	Silica %w/w	pH 30°C	T.S. %w/w	RAA* g/l	Silica %w/w	Ash %w/w	Silica %w/w	Silica removal %
1	80	80	11.5	10.3	7.75	2.46	9.5	14.2	4.03	0.82	40.7	-	67
2	85	80	12.7	9.7	8.52	2.90	9.7	9.7	0.62	1.37	56.9	52	67
3.	-	80	13.5	13.6	17.67	1.59	10.1	10.0	0.62	0.71	40.1	27.7	55
4.	-	80	13.2	10.4	5.27	2.12	9.5	11.2	0.62	0.50	73.0	60.2	76
5.	80	80	13.0	16.2	11.47	3.04	9.7	15.5	2.17	0.83	46.9	93.1	73

\*RAA - Residual active alkali as Na<sub>2</sub>O

\*\* Two stage desilication carbonation followed by lime treatment.



Table 9

**RESULTS OF SEMI-PILOT PLANT DESILICATION**

Trial No.	Carbonation Conditions		Initial Liquor				Treated Liquor				Sludge	Desilication	
	Time	Temp.	pH	Solids	RAA* (g/l as Na <sub>2</sub> O)	Silica	pH	Solids	RAA* (g/l as Na <sub>2</sub> O)	Silica	Ash	Silica	Silica removal
	min	°C	30°C	%w/w		%w/w	30°C	%w/w		%w/w	%w/w	%w/w	%
1.	190	60	11.4	8.3	3.41	4.10	9.70	5.5	0.62	0.70	74.6	68.6	82.7
2.	-	82	11.8	7.3	4.03	3.91	9.80	7.3	0.62	0.71	76.4	71.4	81.8
3.	100	80	11.6	7.6	3.72	4.12	9.70	7.8	0.62	1.50	75.9	70.8	63.6
4.	125	82	11.8	9.7	5.0	3.87	9.90	9.7	0.30	1.36	70.1	67.1	64.9
5.	100	82	11.8	26.9	22.30	3.78	10.19	19.4	1.24	0.05	59.8	56.5	98.6
6.	205	75	13.0	8.6	7.44	3.75	10.15	9.1	0.31	0.17	91.1	87.5	95.5

\*RAA - Residual Active Alkali.

**TABLE 10**  
**ANALYSIS OF SILICA SLUDGE SAMPLE**

Plant Trial No.	Loss on Ignition % w/w	Silica % w/w	Lignin % w/w	Carbo- hydrate % w/w	Sodium % w/w	COD mg/l
1 (unwashed)	26.0	65.8	11.4	11.4	-	29.3
2 (unwashed)	35.0	27.7	17.5	13.5	6.94	40.8
4 (unwashed)	39.0	46.4	30.3	11.5	12.1	58.2
5 (washed)	7.8	81.0	2.0	7.0	NIL	10.4
6 (unwashed)	39.1	53	24.0	7.4	1.65	44.6
7 (unwashed)	31.2	55.2	10.2	18.3	27.5	34.7
7 (washed)	9.1	82.5	0.9	4.6	NIL	6.2
8 (unwashed)	45.6	42.8	31.4	19.7	0.4	68.5
9 (washed)	10.5	85.3	0.16	6.3	0.1	6.9

**TABLE-JJ**

**REALKALIZATION STUDIES**

**Carbonated Liquor - Straw : Reed = (70:30)  
Desilicated to pH 9.8 (82°C)**

<b>Set No.</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Spent Liquor*, ml	50	50	50	50
NaOH added, g/l as Na <sub>2</sub> O	3.0	5.0	7.0	10.0
Expected R.A.A., g/l	3.02	4.62	7.22	8.62
Actual R.A.A. as Na <sub>2</sub> O, g/l	3.72	5.27	6.36	8.99
pH at 30°C	11.2	12.1	12.3	12.5

\* Carbonated & Filtered black liquor was used and had initial R.A.A. - 0.62 g/l.

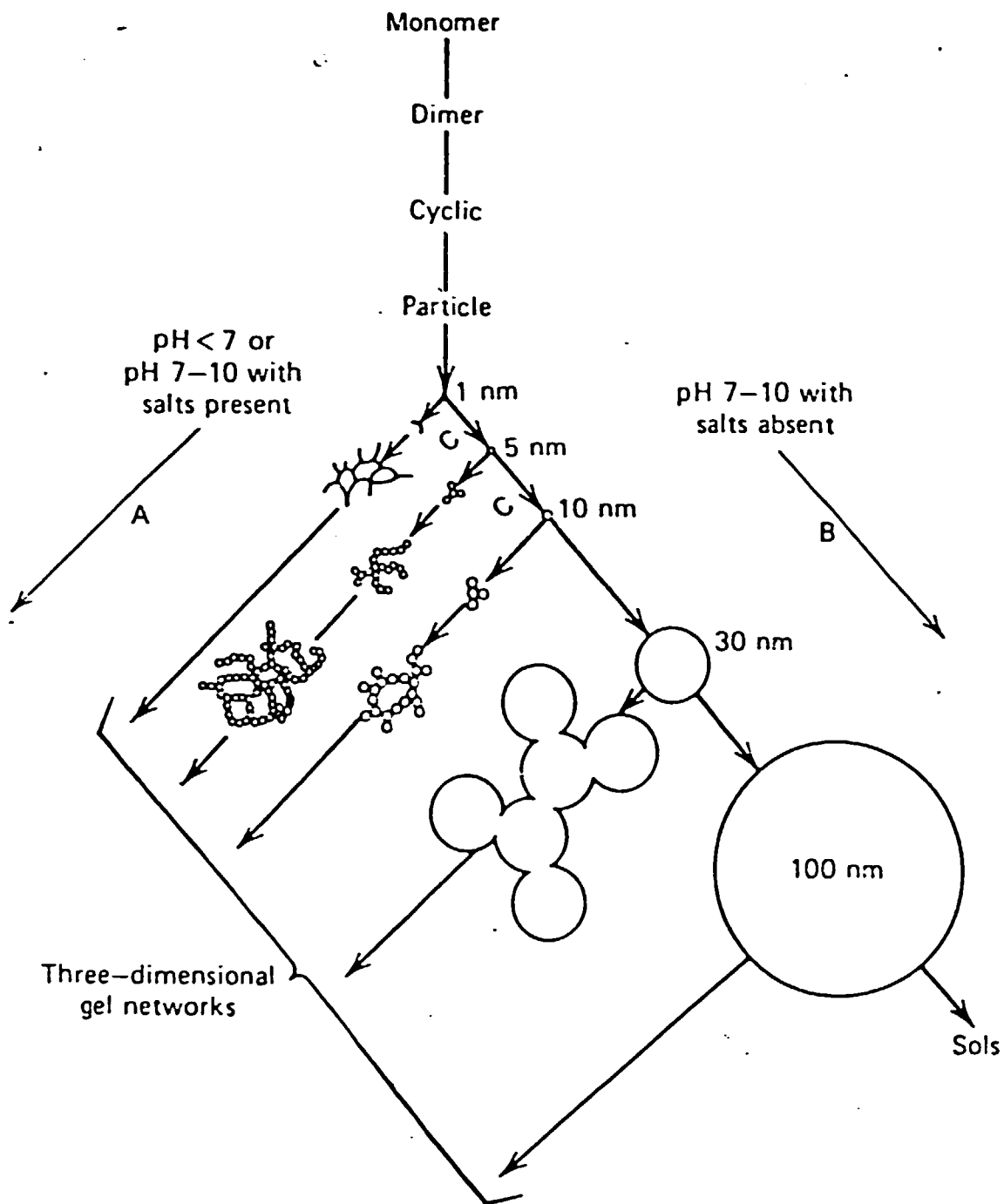
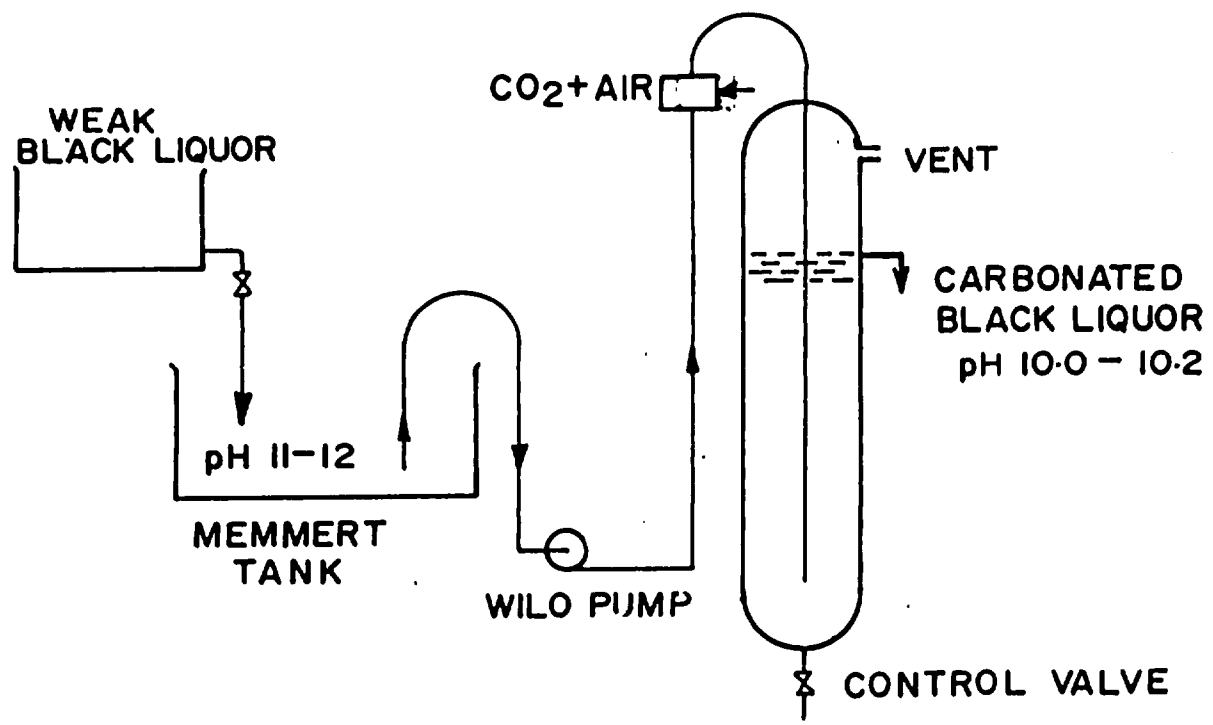
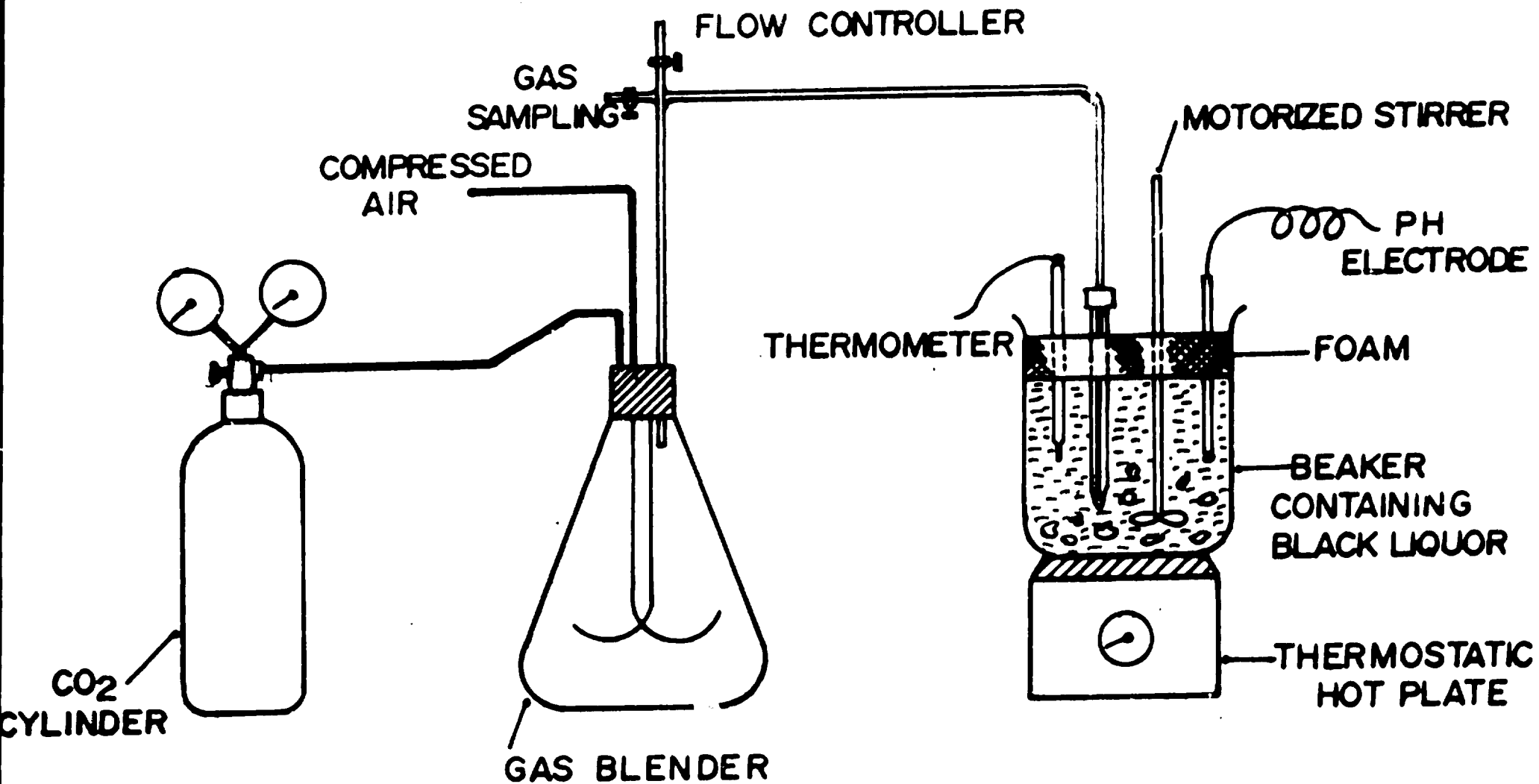


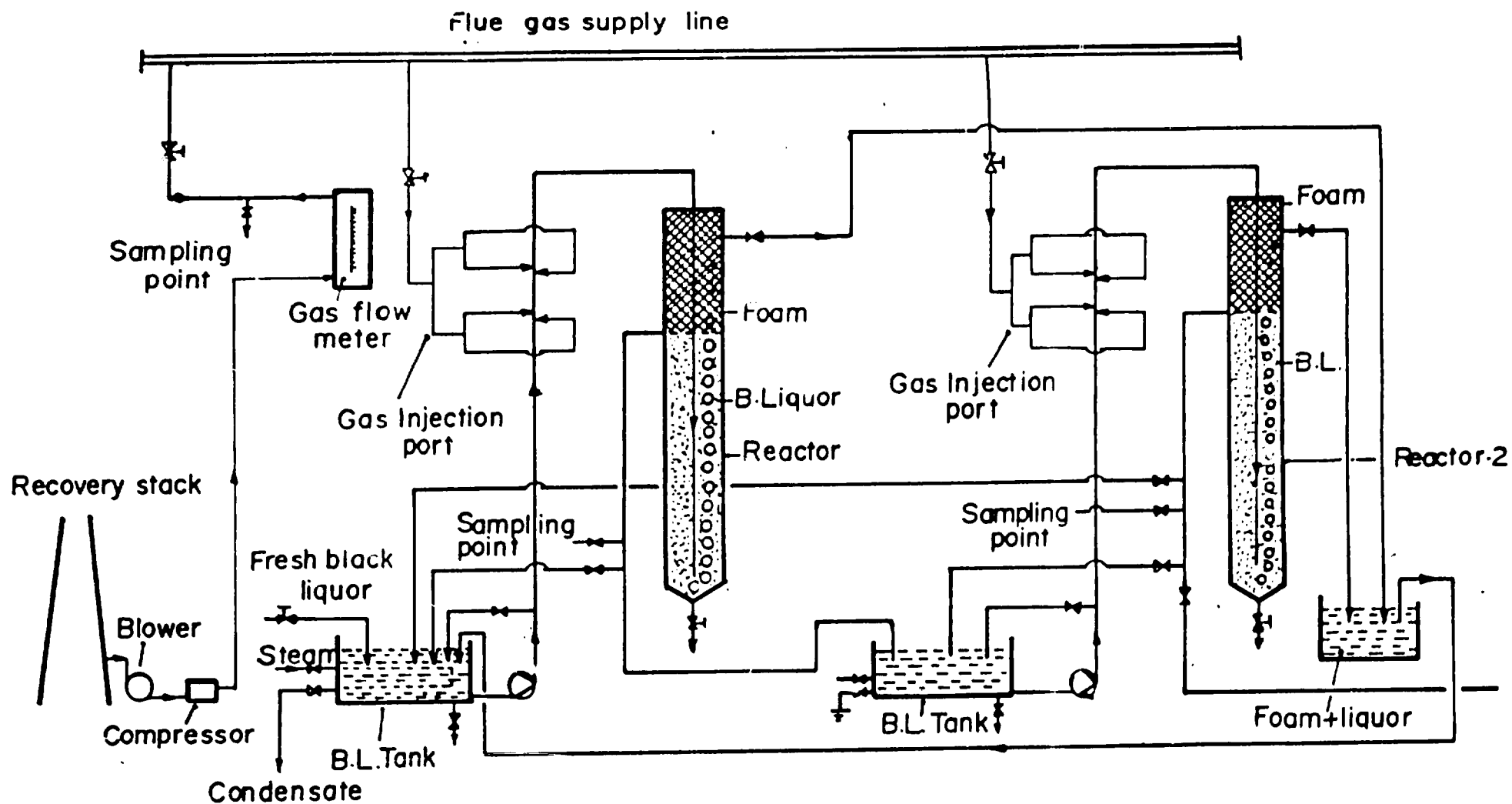
FIG. 1 MECHANISM OF SILICA PRECIPITATION



**FIG.2, THE SUBMERSE BUBBLE REACTOR FOR BLACK LIQUOR CARBONATION**

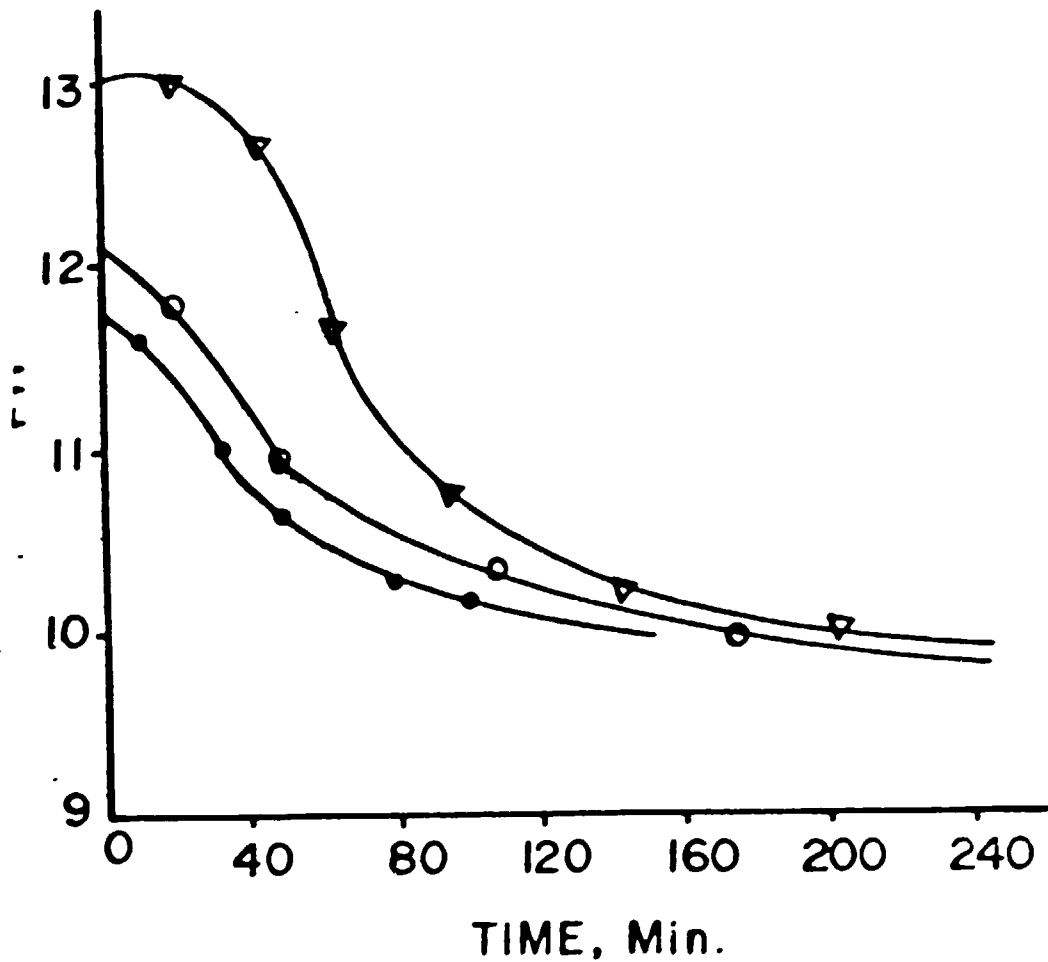


**FIG.3, EXPERIMENTAL SET-UP FOR CARBONATION ON LABORATORY SCALE.**



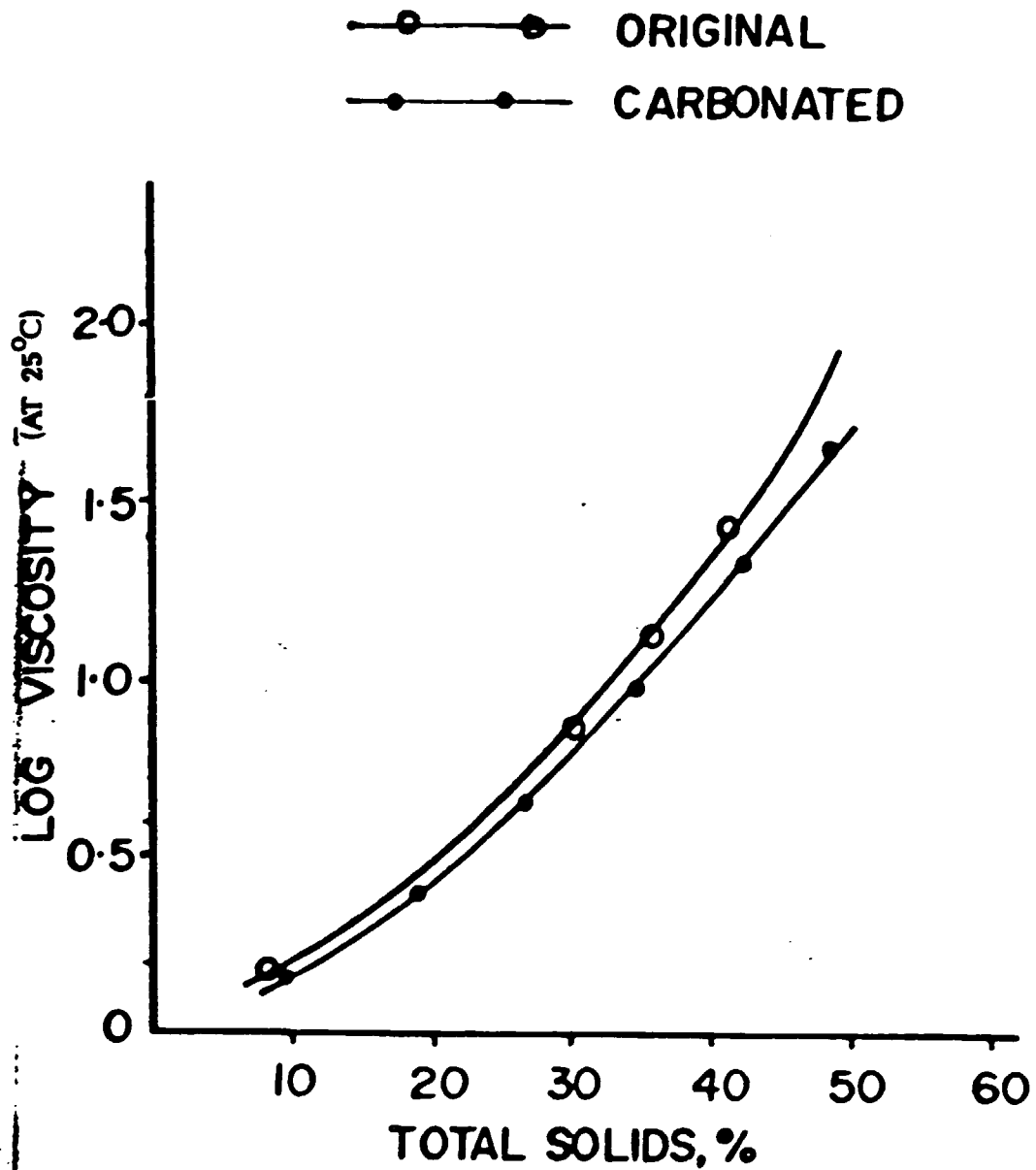
**FIG. 4, EXPERIMENTAL SET-UP OF TWO STAGE SEMI-PILOT PLANT FOR DESILICATION OF BLACK LIQUOR.**

- TRIAL No.6, (Air+CO<sub>2</sub> 33 lt/min.)
- ▼—▼ TRIAL No.7, (Flue gas 44 lt/min)
- TRIAL No.9, (Flue gas 50 lt/min)

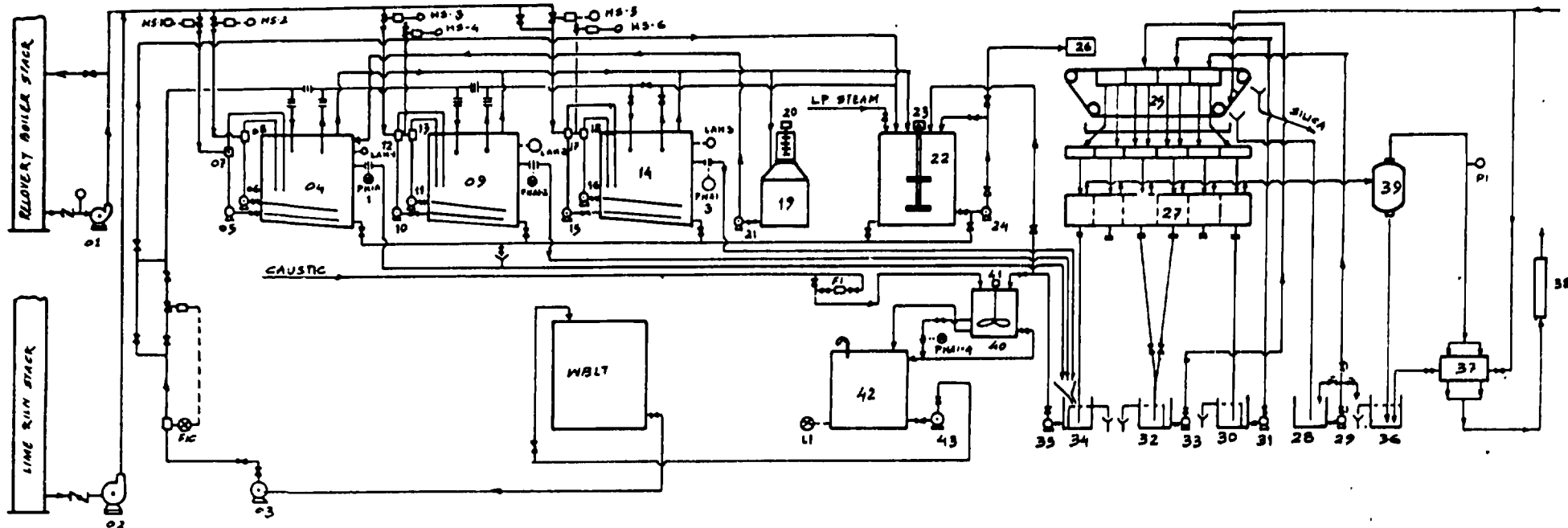


**FIG.5, RATE OF CARBONATION  
V/s PH**





**FIG.6, VISCOSITY CURVES OF ORIGINAL AND CABONATED BLACK LIQUOR**



01	FLUE GAS BLOWER (RECOMBENT)	13	REACTOR-2 FOR SR2	25	DELKOR FILTER ASSLY.	36	SEAL TANK FOR MOISTURE TRAP.
02	FLUE GAS BLOWER (LIME KILN)	14	S.R. TANK-3	26	FILTER DIST HEAD BOX	37	VACUUM PUMP
03	B.L. TRANSFER PUMP 1	15	CIRCULATION PUMP 1 FOR SR3	27	FILTRATE RECEIVER	38	VACUUM EXHAUST SILENCER
04	S.R. TANK 1	16	CIRCULATION PUMP 2 FOR SR3	28	FRESH WASH WATER TANK	39	MOISTURE TRAP
05	CIRCULATION PUMP-1 FOR SR1	17	REACTOR-1 FOR SR-3	29	FRESH WASH WATER PUMP	40	MIXING TANK
06	CIRCULATION PUMP-2 FOR SR1	18	REACTOR-2 FOR SR3	30	SEAL TANK FOR WASH FILTRATE 1	41	MIXING TANK AGITATOR
07	REACTOR-1 FOR SR1	19	FOAM TANK	31	FILTRATE TRANSFER PUMP-1	42	HIGH PH. B.L. STORAGE TANK
08	REACTOR-2 FOR SR1	20	FOAM BREAKER	32	SEAL TANK FOR WASH FILTRATE 2	43	B.L. TRANSFER PUMP-4
09	S.R. TANK-2	21	B.L. TRANSFER PUMP-2	33	FILTRATE TRANSFER PUMP-2		
10	CIRCULATION PUMP 1 FOR SR2	22	HOT RETENTION TANK	34	SEAL TANK FOR MOTHER FILTRATE		
11	CIRCULATION PUMP 2 FOR SR2	23	H.R. TANK AGITATOR	35	MOTHER FILTRATE TRANSFER PUMP		
12	REACTOR 1 FOR SR2	24	B.L. TRANSFER PUMP 3				

FIG. 7

**C P P R I, SAHARANPUR**

Drawn	Sgn	Date	Subject. SCHEMATIC LAYOUT OF PROPOSED DESILICATION PLANT FOR SEKA AFYON PULP MILL.	
Checked	R	19.1.91	SCALE: NTS	MAT.
Appd				REV
Ref.			Org. no	DE3/7/A2
HNL/4-11/A2/005				0

TERMS OF REFERENCE

1. Project Title: Improvement of the Afyon Pulp/Paper Mill
2. Objectives: To produce more high-quality pulps from indigenous raw materials like straw/reeds at lower costs.
3. Obligations:

A team from a consulting company having experiences in non-wood black liquor recovery comprising a high-level inorganic chemist and a design engineer will

  - visit the mill and carry out tests and determine how to precipitate silicic acid by carbonation and pH control;
  - carry out on-the-job training for the laboratory staff in desilication;
  - develop a concept and a first flow-sheet for a desilication production unit;
  - develop a first flow-sheet for a desilication production unit at their home-office.
4. Background:

Afyon pulp mill is one of the 8 pulp and paper mill complexes of "SEKA" Group in Turkey. It went into operation in 1978. The mill has been designed to produce 50.000 tons of bleached pulp per year - using the indigenous raw materials wheat straw and reed.

Initially, the mill could not run under stable conditions due to several drawbacks in its design and operational practices. However, most of these problems have been solved in the course of past years and the mill is now in its stream-line operation and heading towards optimum production.

One of the serious deficiencies that the mill is facing is the presence of a high percentage of silica (approximately 6 %) in black liquor, carried through pulping of straw and reed. It is causing a major set-back in all the stages of operation of chemical recovery system. The efficiency of chemical recovery has been limited to around 80 % besides high consumption of steam in the process and lower steam generation per ton of solids burnt in the recovery furnace.

One of the important factors is that the entire quantity of lime sludge (calcium carbonate) produced to the extent of approximately 15.000 tons per year on an optimum production level, is being disposed off as land-filling, since this product cannot be reburnt to recover lime due to the presence of silicate salts. In fact, the Afyon

Mill is fully equipped with a lime kiln for continuous operation.

As the present set-up of operation is substantially adding to the cost of production in several aspects, it is imperative that a serious consideration should be given to implement a full scale black liquor desilication plant prior to processing the liquor in Afyon Pulp Mill.

The mill management has requested UNIDO to assist in carrying out preliminary tests for desilication of black liquor, either in laboratory scale or in pilot plant scale before a final decision is made for full-scale implementation for regular plant operation.

Language of the  
Final Report:

English

Number of Copies  
to be supplied:

10 copies

Date of Delivery  
of Final Report:

One month after completion of mission

Debriefing:

Upon completion of mission, one day debriefing in UNIDO Headquarters foreseen.

## PROCEDURES FOR TESTING OF BLACK LIQUOR PROPERTIES

The laboratory evaluation of black liquors for their chemical, physico-chemical and thermal properties can provide information on their behaviour during the evaporation and combustion operations in the mills. A better understanding of these processes may also indicate ways in which the special problems encountered by the mills from various raw materials can be handled.

### 1. SAMPLING OF BLACK LIQUORS

1.1 **Sample Collection :-** It must be always ensured that the sample collected from laboratory or mill cooks is representative of the entire black liquor generated. If any fibrous material is present in the sample, it must be removed by filtration. Sample collected should be such that it completely fills the bottle. This ensures that all air is excluded and avoids oxidative processes.

1.2 **Sample Storage :-** The filtered sample should be stored in stoppered, narrow mouthed plastic bottles, preferably at a temperature of around 4°C and away from light.

The measurement of various physical and chemical properties should be made as soon as possible after the collection of the sample. Chemical analyses of the black liquor and the determination of residual active alkali, sodium sulphide and pH must be made within 48 hours.

## CHEMICAL ANALYSIS FOR BLACK LIQUOR

### TOTAL SOLIDS

1) For weak black liquor :- 10 ml of weak black liquor is taken in 3 inch diameter porcelain or platinum dish and weighed accurately and immediately and then placed in oven maintained at  $105 \pm 3^\circ\text{C}$  for 24 hrs. Cool in desiccator to room temperature and weigh to nearest 5 mg.

$$\% \text{ total solids} = \frac{\text{residue wt.}}{\text{sample wt.}} \times 100$$

ii) For concentrated black liquors :

Dilute the sample by weighing a portion of concentrated black liquors to the nearest 0.05 g transferring it into weighed 500 ml volumetric flask. Dilute upto mark and again weigh to nearest 0.5 g.

Total solids for this diluted sample is then determined as for weak liquors :

Calculations :

I. Dilution ratio =  $\frac{\text{Weight of diluted sample}}{\text{Weight of original sample}}$

II. % Solids (diluted) =  $\frac{\text{Weight of dried solids}}{\text{Weight of diluted specimen}} \times 100$

III. % Solids (Original) = % solids (diluted) x dilution ratio

Apparatus :

Weighing bottles with ground glass stoppered with 50 mm diameter and 30 mm weight.

**Experiment Procedure :-** Pure quartz sand is taken as inert material for experiments . Place about 25-30 g of inert material in the weighing bottle and heat the bottle and cap in the oven at 105° C to constant weight. Cool in desiccator and weigh to nearest 0.0005 g. By means of pipette transfer enough specimen to weighing bottle to ensure 1-3 g of dry solids (for weak liquors 5-10 g as such specimen is required, for concentrated and diluted as in method I 2-5 g of sp. is required). Cap the bottle and weigh to nearest 0.0005 g add 10 20 ml. water to specimen if it contains over 30% solids. Place the weighing bottle in oven cap-off and heat for minimum of 6 hr. Remove and cool in desiccator and weigh repeat this heating procedure at 1 hr interval until the weight loss is less than 0.1% per hr. (.001 to .003 g loss per hr). Make triplicate determinations. Calculation are as in method II.

### SUSPENDED SOLIDS

Take at least 2 sets of previously weighed centrifuge tubes. Take 50 ml of well shaken black liquor in each tube and centrifuge them for about 20 minutes. Take out the supernatant black liquor and given single washing with distilled water. Dry the tubes at 105°C, and take the OD wt.

#### Calculations

Wt. of OD empty tube	= X gms
Wt. of OD residue in tube	= Y gms
Wt. of residue	= Y - X gms.

Suspended solids, g/l	= $\frac{Y-X}{\text{ml. of the sample taken}} \times 1000$
-----------------------	--

### RESIDUAL ACTIVE ALKALI :

Pipette 25 ml of B.L. into 500 ml of volumetric flask containing about 100 ml of water and allow the pipet to drain for its calibration period. Add 20 ml of 0.5 N  $\text{BaCl}_2$ , stir, and allow to settle until partially clear. Dilute the contents of flask to mark, mix well and allow to settle until about 200 ml of clear liquid stands above the precipitate. Pipette 100 ml of the supernatant liquid to a 250 ml beaker equipped with a mechanical or magnetic stirrers and titrate immediately with 0.1 N HCl to a pH of about 3.5. Follow the course of titration potentiometrically on the pH range of a pH meter using saturated calomel-general purpose glass electrode pair. Add the titrant in increments of fixed volume, record the pH value after each addition and plot the data on the linear coordinates with -- as the ordinate and milliequivalents of HCl as the abscissa. Connect the plotted points in a smooth curve. Obtain the milliequivalents of acid corresponding to the end point by projecting the inflection point near pH 7.0 to the abscissa.

#### Calculation :

$$\text{R.A.A. g/l as NaOH} = \frac{\text{milliequivalent of acid} \times 1 \times 40}{\text{ml of B.L. taken}}$$



## TOTAL ALKALI

Add 10 ml. of black liquor sample to a beaker containing 100 ml. of water. Immerse the electrodes of the conductance bridge in the solution, stir continuously with a mechanical or a magnetic stirrer and obtain initial bridge reading. For most black liquors a 1 cm spacing of electrodes discs will be suitable. Add 1N HCl in fixed increments of volume and take a reading after each addition, keeping the temperature constant. Continue the titration until the change in the bridge reading remains constant for five or six additions of titrant. Plot the data on linear coordinates with reciprocal ohms as ordinate and milliequivalents of acid as abscissa. The curve obtained will usually resemble a V with the apex flattened or broadly rounded to locate the end point. Extrapolate the arms of the V in a straight line until the extrapolated segments intersect. The point of intersection projected on the abscissa will give the milliequivalents of acid corresponding to the end point.

### Calculations :

$$\text{Total alkali g/l, as Na}_2\text{O} = \frac{\text{milliequivalents of acid} \times 1 \text{N} \times 31}{\text{ml of B.L. taken}}$$

## SULPHATED ASH AND ORGANIC MATTER

**Procedure :** In a platinum crucible 2-3 gms exactly weighed residue/solids obtained from B.L. evaporation is taken and starting with a cold muffle furnace, the residue is heated until the organic material is mostly, but not completely destroyed. The residue, then, is cooled moistened with water, a drop of methyl orange & concentrated  $H_2SO_4$  is added till the indicator colour turned pink. The contents in crucible, first dried on steam bath and then in muffle furnace at  $600^\circ C$  till the residue turns white - colourless. Then the residue is cooled in desiccator and weighed. After weighing, again the residue is moistened and a drop of methyl orange is added to see whether residual  $H_2SO_4$  is left or not. If pink colour develops - indicating the presence of residual  $H_2SO_4$  - repeat the above procedure until acid is destroyed completely. The residue is arbitrarily assumed to be pure  $Na_2SO_4$ .

### Calculations :

The percents of E.L. residue turned to  $Na_2SO_4$  - expressed as NaOH gives the inorganic matter present. the rest i.e. (100-inorganics) gives the organics.

Wt. of B.L. residue : 3.3443 g

Wt. of  $Na_2SO_4$  : 1.7504 g

Inorganics i.e. sulfated ash, as NaOH (as % of total solids)

$$= \frac{\text{Sulfated ash residues} \times 40}{\text{Total solid residue} \times 71} \times 100$$

$$= \frac{\text{Sulfated ash residue}}{\text{Total solid residue}} \times 56.5 = \frac{1.75 \times 56.4}{3.3443} = 29.4$$

$$\text{Organic matter, \%} = 100 - 29.4 = 70.6$$

## DETERMINATION OF SILICA BY COLORIMETRIC METHOD

**Principle :** Ammonium molybdate at a pH 1.2 reacts and produces molybdosilicic acid. The yellow colour developed corresponds to reactive silica present in the sample. This molybdosilicic acid is reduced to heteropoly blue by amino naphthol sulfonic acid which increases sensitivity of the method.

**Interference :**  $PO_4$ , tannin, Fe in large conc., colour, turbidity and sulfide are potential sources of interference. Interference caused by  $PO_4$  and tannin can be eliminated by addition of oxalic acid. The interference due to colour and turbidity can be compensated by using an appropriate blank.

### Apparatus :

1. Colorimeter for use at 690 m $\mu$  providing 1 cm light path.
2. Nessler's tubes, cap. 100 ml.

### Reagents :

1. HCl : 1+1
2. Ammonium molybdate reagent: Dissolve 10 g amm. molybdate and dilute to 100 ml. Adjust pH to 7-8 and store in polythene bottle.
3. Oxalic acid solution : Dissolve 10 g  $H_2C_2O_4 \cdot 2 H_2O$  and dilute to 100 ml. Store in polythene bottle.
4. Stock silica solution : Dissolve 4.73 g  $Na_2SiO_3 \cdot 9 H_2O$  in recently boiled cooled distilled water and dilute to 900 ml. Estimate silica conc. gravimetrically and dilute accordingly to have 1000  $\mu g/l$   $SiO_2$ .
5. Standard  $SiO_2$  : Dilute 10 ml stock  $SiO_2$  soln. to 1000 ml with boiled cooled distilled water. 1 ml = 10  $\mu g$   $SiO_2$ . Store silica solutions in plastic bottle.

6. Reducing reagent : Dissolve 500 mg 1-amino, 2-napthtol, 4-sulfonic acid and 1 g  $\text{Na}_2\text{SO}_3$  in 50 ml water. Add this to a solution of 30 g  $\text{NaHSO}_3$  in 150 ml water. Filter through Whatmann paper No.42 and store in a plastic bottle.

**Procedure :**

1. Take suitable vol. of filtered sample in nessler tube. If sample is turbid or coloured prepare approximate blank as follows :

To the identical aliquot add 1 ml 1+1 HCl followed by 1.5 ml oxalic acid. Do not add ammonium molybdate or reducing agent. Dilute to 100 ml.

2. Add 1 ml 1+1 HCl followed by 2 ml ammonium molybdate. Allow to stand for 5-10 min.

3. Add 1.5 ml oxalic acid to the samples and mix well.

4. Add 2 ml reducing agent and dilute to 100 ml. Measure the colour at 690 m $\mu$  after 10 min. using 1 cm path.

5. In case of clear sample prepare blank substituting sample by water and processing through all above steps from 1 to 4.

6. Prepare a standard curve using standard silica solution covering 0.0 to 240  $\mu\text{g SiO}_2$ .

7. Calculate the conc. from standard graph and express as  $\text{SiO}_2$  mg/l.

## DETERMINATION OF SILICA BY GRAVIMETRIC METHOD

The following procedure, or a modification described by Bethge may be applied to dried solid or liquid spent liquor. The essence of the method is the destruction and removal of all organic matter and the oxidation of all inorganic material, including sulfur, to its highest valence by digesting it with  $\text{HNO}_3$  and  $\text{HClO}_4$ . The result of the digestion is a clear solution containing all the inorganic constituents of the original liquor with the exception of silica, which is dehydrated and precipitated.

Pipet 10 ml of the black liquor into a 100 ml Kjeldahl flask, allowing the pipet to drain for its calibration period for the black liquor. Rinse down the neck of the flask with 10 to 15 ml of distilled water. Next add 15 ml of conc.  $\text{HNO}_3$  and 5 ml of conc. (70%)  $\text{HClO}_4$  in that order.

**Warning :** To prevent an explosion be sure to have the nitric acid present before adding the perchloric acid.

Place the flask on a steam bath situated in a hood. If the solution being digested suddenly darkens when the main part of the excess  $\text{HNO}_3$  has boiled off, stop the digestion immediately and add more  $\text{HNO}_3$  (5 ml) before continuing the digestion.

**Note :** A sudden darkening almost always indicates insufficient nitric acid and until the worker is familiar with the procedure, an excess of the recommended quantity of nitric acid should be used.

When the oxidation reaction has subsided, as indicated by the absence of red-brown nitrogen dioxide fumes, remove the flask from the steam bath and heat over a burner with low to moderate heat until the oxidation is complete, as evidenced by a colorless solution and

dense white perchloric acid fumes. Allow the solution to cool, then add 5 ml of conc. HCl, and heat again until the perchloric acid fumes appear. Allow the solution to cool to room temperature and add about 50 ml of warm distilled water to dissolve all the salts. If it is desired to determine the silica, it is better to carry out the digestion in a platinum vessel.

**Silica :** Filter off the silica on a small filter paper of medium porosity and wash with 1:99 HCl. Collect the filtrate and washings in a platinum evaporating dish. Evaporate the filtrate and washings to near dryness on a steam bath and add 2 to 3 ml of conc. HCl. Add enough hot distilled water to dissolve all the salts and again filter off the silica on the filter used previously. Wash the residue thoroughly with cold 1:99 HCl and catch the filtrate and washings in a 250 ml beaker. Remove any silica adhering to the evaporating dish by wiping with a small piece of filter paper, using the stirring rod, and place the bits of paper in the filter. Reserve the filtrate and washings for determination of iron and aluminium.

Place the filter with its bits of paper in a tared platinum crucible with cover. Dry the filter paper and smoke it off at low heat with the cover placed at an angle on the crucible. When the paper has been charred and smoking almost ceases, increase the heat to at least 1000° C and heat at this temperature for onehalf hour or more. Place in a desiccator with the crucible lid in place and cool to room temperature. Weigh, remembering that dehydrated silica is hygroscopic, reheat, and weigh again to make sure that it is at constant weight.

Carefully moisten the contents of the crucible with about 2 ml of water, adding it from a pipette inserted beneath the cover. Add 4 or 5 drops of 1:2 H<sub>2</sub>SO<sub>4</sub> and then add carefully about 5 ml of conc. HF measured from a polyethylene graduated cylinder. Place the crucible in a hood and heat gently to evaporate off the HF without

boiling the liquid. Increase the heat to fume off the  $H_2SO_4$ . When the contents of the crucible are nearly dry, gradually increase the heat to at least  $1000^\circ C$  and bring the crucible to constant weight as before. The loss in weight represents the grams of  $SiO_2$  in the 10 ml specimen.

**Calculations ;**

$$\% \text{ of silica} = \frac{\text{gms of } SiO_2}{\text{gms. of B.L. solids}} \times 100$$

### Estimation of Lignin:

Lignin an important organic constituent of the spent liquor is normally measured at 280 nm in the ultraviolet region. the UV spectra of the lignin shows peak maxima at 205 nm and a flattened shoulder at about 230 nm which is due to the presence of polyphenols in the spent liquor. Experiments carried out at CPPRI laboratories have shown that lignin can also be measured at 465 nm in the visible region, which is a selective wavelength for color generating groups. It is found that values at 280 nm and 465 nm are almost identical. Since there was no UV spectrophotometer available at Afyon Mills, all the lignin measurements were carried out at 465 nm in the visible region. The details of the procedures is discussed below.

Procedure: About 2 ml of the spent liquor to be analysed was diluted to 100 ml in a volumetric flask. Absorbance of the above solution after proper dilution was measured at 465 nm. Lignin percent was calculated as follows taking absorptivity of  $88 \text{ lg}^{-1} \text{ cm}^{-1}$  for lignin.

$$\text{Organics (as lignin) \%} = \frac{\text{absorbance at 465 nm} \times 40.54 \times 100}{88 \times C}$$

(where C = wt. of the sample dissolved/lit.).



## PREPARING BLACK LIQUORS OF DIFFERENT CONCENTRATIONS

Black liquors from laboratory cooks have 16% to 22% solids contents. The liquor is concentrated in a rotary vacuum flash evaporator under a vacuum of  $0.6 \text{ kg/cm}^2$ . For black liquors which froth badly the vacuum is reduced to  $0.5 \text{ kg/cm}^2$ . The rotary vacuum flask is heated in an electrically heated oil bath maintained at 96-99°C.

Solids concentrations of 35%, 45%, 50% and 55% are usually prepared. A 500 g sample of weak black liquor is placed in the flask and heating continued until the amount of water removed has given a black liquor with a solids content of about 35%. A sample is withdrawn for viscosity measurements and solids estimation. Evaporation of the black liquor remaining in the flask is continued, after weighing the flask contents, for the next concentration. The procedures are repeated to give the other concentrations.

All concentrations should be prepared on the same day. If this is not possible it is essential that the last three concentrations be made on the first day.

## MEASUREMENT OF VISCOSITY

Viscometers usually measure either the drag or torque produced by the movement of an element through the fluid or the resistance to flow. Rotational type viscometers measure the torque resulting from the rotation of a spindle inside the sample chamber. Capillary type measure the pressure drop which occurs when a constant flow of fluid takes place through a capillary tube of specified diameter and length.

The rotational type is the more suitable for measuring the viscosity of black liquors. It uses a much larger sample than the capillary type thus giving a better representation of the black liquor. If material precipitates during the concentration of the black liquor this will tend to block the capillary type viscometer and will give erroneous results.

This laboratory uses a Brookfield Synchroelectric rotational type viscometer (RVT model). It is provided with seven spindles and has eight operating speeds. The minimum range of measurement is from 0-100 cps and the maximum 0-8,000,000 cps. By using an ultra-low adapter (UL) a minimum range of 0-10 cps can be used. The instrument normally uses a sample of 500 ml but the fitting of a small sample adapter (SC4-21/13) permits viscosity measurements to be made using a sample of only 8 ml over the 50-100,000 cps range.

Viscosity measurements are made at a temperature of  $80 \pm 0.05^\circ\text{C}$  using an Ultrathermostat (MLW) for temperature control. Any variations in temperature will effect the viscosity values. The dial reading on the viscometer must remain constant while making the reading. The black liquor fed into the chamber is heated to  $80^\circ\text{C}$  to avoid any hysteresis effects on viscosity due to heating or cooling.

The sample collected for the solids estimation is diluted to an appropriate volume and 10 ml taken for the determination of total solids.

The logarithm of the viscosity values of the black liquors at the various concentrations is plotted and the viscosity values at the desired concentrations (usually 35%, 45%, 50%, 55%) are obtained from viscosity curves.

## FOAM INDEX

Foaming character of black liquors varies for different black liquors. Different black liquors show different foaming tendency. Foaming index can be determined by following method:-

### Method:

The method is very simple. Vacuum is created in the vessel containing black liquor by aspirator which pushes inside the vessel and creates foam.

### Apparatus:

Graduated glass vessel, Aspirator, hot water bath or thermostat, glass tubes.

### Procedure:

The apparatus is set up as shown in Figure. Apparatus consists of graduated vessel of the type shown in figure (700 ml capacity) in which 10 ml of black liquor sample is taken. The capacity of aspirator is about 500 ml capacity with stop cock at the bottom. The rate of process water in the aspirator is to be adjusted to 500 ml/30 sec.

When the temperature of black liquor becomes the required temperature using thermostat the system is checked for leaking and then the stop cock of aspirator is opened to empty it by 500 ml water in 30 seconds. After 30 seconds or after emptying the 500 ml process water, stop cock is closed. Due to the formation of vacuum in the graduated vessel-A connected to aspirator - air comes through T, which produces foam in black liquor. After 30 seconds, the volume of the foam is found out and at the same time the volume of the black liquor converted into the foam is calculated by the difference in black liquor level before and after the experiment and can be carried out at different temperatures. Each time fresh black liquor is taken for the experiment to avoid creidation effect.

**Calculations:**

With the above results, the foam index or foam number F and the foam coefficient  $K_f$  can be found out as follows:-

Foam index gives the percents of black liquor changing into foam thus,

$$F = \frac{V_1}{V} \times 100$$

Where,  $V_1$  = Volume of black liquor converted into foam

$V$  = Volume of black liquor taken for experiment, i.e. 10 ml

Foam coefficient  $K_f$  shows how many times the foam volume is greater or lesser the volume taken for analysis. Hence,

$$K_f = \frac{V_f}{V}$$

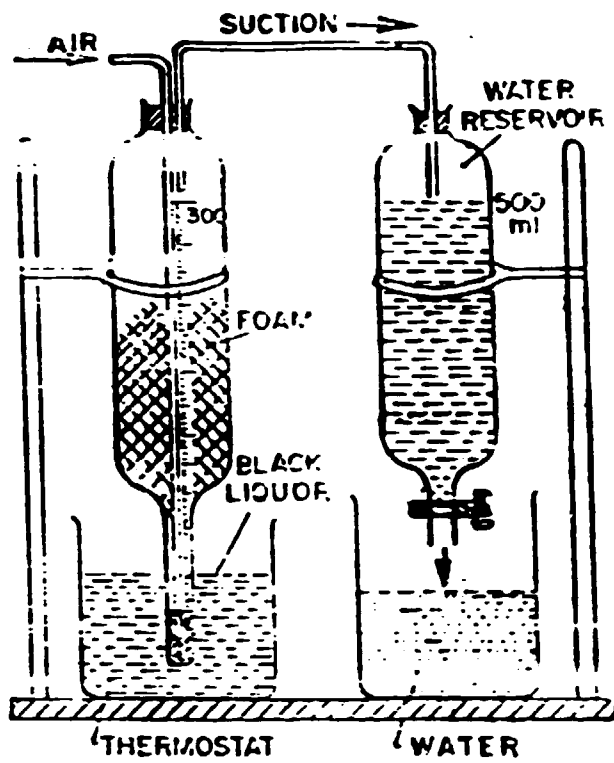
Where,  $V_f$  = Volume of foam.

A typical black liquor sample gave the following results:-

$V$	- Volume of B.L. taken for experiment	: 10.0 ml
$V_1$	- Volume of B.L. converted into foam	: 0.5 ml
$V_f$	- Volume of foam	: 150 ml

$$\text{Foam number } F = \frac{0.5 \times 100}{10} = 5$$

$$\text{Foam coefficient } K_f = \frac{150}{10} = 15$$



**FIG. 1—APPARATUS FOR MEASURING FOAM INDEX**

LIST OF MEMBERS MET DURING THE MISSION IN TURKEY

**A. Directors and Senior Members of SEKA General Management:**

Mr. Sabahattin Yellinpapa	General Manager of SEKA group
Mr. Ismet Genc	Deputy General Manager Technical
Ms. Ferhan Taptic	Director of Mill Operations
Mr. Sazai Sarisoy	Senior Engineer Mill Operations
Mr. Haluk Iber	Engineer Mill Operations.

**B. Senior Counterpart staff and Senior Members of SEKA Mill Management:**

Mr. Isik Anlipak	Mill Manager
Mr. Husamettin Sari	Assistant Mill Manager Technical
Mr. Yahya Sekerci	Chief of Production
Mr. Mehmet Makam	Chief Chemist Laboratory
Mr. Muhteram Kar	Engineer Laboratory
Mr. Ramazan Camuzoglu	Chief of Pulp Production

**C. UNIDO Officials:**

Dr. Kamal Hussein	Country Director, UNIDO, Turkey
Mr. P. Rajasekhara	Pulp & Paper Consultant, UNIDO

PROCESS VARIABLES LIKELY TO INFLUENCE THE DESILICATION PLANT DESIGN:**Process control systems:**

Some process control equipments need to be employed for on-line measurements of various important process parameters, to run the desilication plant efficiently. pH the controlling parameter for selective precipitation of silica requires accurate and continuous monitoring. Hence on-line monitoring of pH becomes essential. Although desilication plant at present has a provision for on-line pH measurements, but the problem of silica adhering to the glass membrane occurs quite often giving erroneous pH values. Proper maintenance of the electrodes need to be accomplished by giving hot water flushing or dipping the electrodes in acidic solutions periodically.

**Performance of electrostatic precipitator :**

The performance of ESP has a marked influence on the efficiency of desilication plant. In case of ESP failure the particulate carryover in the flue gas ranges from 15-50ng/m<sup>3</sup> of flue gas. The solids in flue gas will increase the inorganic content of the black liquor thereby lowering the heating value of the liquor.

Variation in Black liquor composition and its influence on desilication operation :**Effect of Alkali concentration:**

Wheat straw and rice, in particular contain high amounts of silica. The dissolution of silica depends on the cooking process and pulping conditions employed. Variation in



pulping conditions would alter the chemical composition of the resultant liquor. Cooking with low alkali (6-8% of NaOH) will produce a liquor with low amounts of lignin and silica, due to reduced alkalinity the pH will be on lower side. Although CO<sub>2</sub> requirement for such liquors will be less but to achieve the precipitation point for silica would be difficult due to lignin co-precipitation at lower pH values. However in case of low kappa number pulp the liquor produced will have higher silica and lignin contents, besides higher initial pH. CO<sub>2</sub> requirement for such liquors will be on higher side. Due to higher initial pH, the silica precipitation would be easier and purity of sludge obtained will be better. It is experienced that precipitation point for silica in non-woody raw materials lies between 9.5 to 9.8. Hence the liquor with high initial pH and active alkali will be easier to process for selective precipitation of silica. The chances of lignin co-precipitation in such cases is always minimized due to its stability.

#### **Effect of lignin stability :**

Agricultural residues are characterised by low lignin content compared to wood and bark. Lignin in spent liquor is colloidal in nature and its stability is dependent on the pH of the black liquor, the salt concentration in the liquor and the molecular size of the lignin macromolecules. Observations made from experiments reveal that lignins from straw are quite stable

even at lower pH values as compared to bamboo. Only 7.4% of total lignin gets precipitated at pH level of 6.0 in case of straws, whereas 40% of total lignin gets precipitated at a pH level of 8.0 in case of bamboo liquor. Thus the stability of lignin in black liquors, becomes one of the important factors determining the nature of silica sludge obtained after carbonation.

## EFFECT OF CO<sub>2</sub> CONCENTRATION ON FLUE GAS REQUIREMENT

Black liquor quantity = 1400 m<sup>3</sup>/day

Blower Capacity = 2000 m<sup>3</sup>/hr.

Residual active alkali g/l as  
Na<sub>2</sub>O in black liquor = 3.5 g/l

Total Residual active alkali, in kgs = 204kgs/hr.

When the CO<sub>2</sub> concentration is 5% (Recovery Boiler)

Total CO<sub>2</sub> in flue gas = 100 m<sup>3</sup>/hr or 200kg/hr.

Total CO<sub>2</sub> required to  
neutralize 204 kg of Na<sub>2</sub>O = 145 kg/hr

Flue gas required = 1450m<sup>3</sup>/hr

Taking 60% Gas liquor transfer rates.

Total flue gas required will be = 2030 m<sup>3</sup>/hr.

When the CO<sub>2</sub> concentration is 14% (Recovery Boiler)

Total CO<sub>2</sub> in flue gas = 280 m<sup>3</sup>/hr or 560kg/hr

Total CO<sub>2</sub> required to  
neutralize 204 kg of Na<sub>2</sub>O = 145 kg/hr

Flue gas required = 518 m<sup>3</sup>/hr

Taking 60% gas liquor transfer rates.

Total flue gas required will be = 725 m<sup>3</sup>/hr.

When the CO<sub>2</sub> Concentration is 18% (Line Film).

Total CO<sub>2</sub> in flue gas = 360 m<sup>3</sup>/hr or 720 kgs/hr.

Total CO<sub>2</sub> required to  
neutralize 204kg of Na<sub>2</sub>O = 145 kg/hr.

Flue gas required = 403 m<sup>3</sup>/hr.

Taking 60% Gas liquor transfer rates

Total flue gas required will be = 564 m<sup>3</sup>/hr.

Thus increasing the CO<sub>2</sub> concentration in flue gas is beneficial from the view point of four problems associated with high flue gas intakes.