# DARS chemical recovery—Will it continue to be an alternative choice for small pulp mills ?

A.G. Kulkarni* and Rajesh Pant**

## ABSTRACT

More and more small scale paper mills have been built across the country and number is likely to increase in comming years. These units usually make mills' own pulping capacity based on non-wood fibers. With stringent legislation to pollution control and also increasing price of caustic soda these units have no other alternative except to choose a suitable chemical recovery system. Efforts to develop small scale chemical recovery system have been intensified particularly in China and India. In the last few decades number of technologies have emerged, but most of them have failed to live upto expectations, when tried on a commercial basis. Central Pulp and Paper Research Institute has been actively engaged in evaluating the compatibility of Direct Alkali Recovery System (DARS) for black liquors produced from non-woody fibrous raw materials.

Although lot of information is missing, only DARS has made headway among the emerging technologies, by going on a commercial scale of operation—one in Australia and another one in Denmark. Motivated by these two commercial scale installations CPPRI decided to extend the bench scale studies to batch scale pilot plant studies. The DARS pilot plant having capacity to handle 300 kg black liquor solids/hr, became operational in November-91, since then number of trials, on batch scale, have been carried out with black liquors from grasses, bagasse and rice straw and employing Indian haematite ore. The present paper high lights the experience of DARS technology in processing of non-woody black liquors.

## Introduction :

Today chemical recovery furnace and boiler technology represents more than 100 years of developments with last decades devoting primarily to scale-up of unit size, material selection for corrossion control, unit safty and total computer control. Although notable developments have taken place in conventional recovery system, the compatability of the system for small size mills based on non-woody raw materials like straw. grasses, etc. is still a big question mark. Chinese paper industry which.all at present,is recovering only 30% of the caustic soda employed. claims to have modified conventional chemical recovery, which can handle the type of black liquors produced from non-woody raw materials(1).In the lasttwo decades, number of new techologies have emerged either on bench scale or pilot scale. However these technologies are primarily aimed at replacement of kraft recovery boilers to overcome complexities of operation at and explosion hazards (2).

Among the new technologies, DARS process attracted the enterpreneurs, primarily due to simplicity and flexibility in operation (3.) Further, unlike, conventional furnaces, where it is difficult to reduce the scale of operation, DARS employing fluid bed reactor offers advantage of scaling down the operation (4). The basic principle of DARS was conceived in 1975

* Scientist & Head Chemical Recovary.

**Director

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

by Toyo Pulp Company, Japan and subsequently the process was extensively studied in Australia; which resulted in commissioning of first commerical plant in Tasmania(Australia)in1986. Followed by Australian unit another commercial unit with number of improvements was commissioned in Frederecia(Denmark), for a straw based mill. There is a scanty information on the status of these two commercial units. However according to latest information it appears that these two commercial installations are making preparation for rehabilitation. CPPRI. motivated by the success of pilot plant trials in Australia & Denmark and also commercialization of the process decided to investigate the adaptability of the system for processing of black liquors from grass, cereal straws and bagasse, The paper highlights the work carried out on pilot plant scale.

### Review of Emerging Technologies

The technologies which have emerged in the last two decades can be grouped into two catagories..

- Wet methods
- High temperature (Pyrolytic methods).

### Wet methods

Wet cracking, Wet oxidation are examples of wet processes, which do not require preevaporation of black liquor. Only the wet air oxidation (WAO) process was commercialized, initially for treatment of organic wastes and subsequently adapted for black liquor treatment. However the process did not live up to expectations as far as chemical recovery, primarily due to capital intensiveness. Wet cracking process was developed in China, and the process differes from WAO process as the cracking is performed in absence of air (5)

### Wet air oxidation

$$\underset{(12-14\%,\ \text{solids})}{\text{Black liquor}} + O_2 \xrightarrow[30\text{M. Pa.}]{320^\circ C} Na_2CO_3 + NaHCO_3 + O_2 + \text{Steam} + \text{Char}$$

### Wet Cracking :

$$\underset{\text{Black liquor}}{5-10\%\text{Solids}} + N_2 \xrightarrow[200\text{ atms}]{350^0 C} CO_2 + CH_4 + C_2H_6 + \text{char} + NaHCO_3$$

### High temperature Methods :

Unlike in wet process, where the organic residues ase partially decomposed and major part comming out as charpowder, the dry pyrolytic methods utilize the maximum calorific value for generation of heat energy. Conventional chemical recovery and Copeland fluid bed processes are two well established technologies

### Conventional Chemical Recovery :

Nearly 80–90% of the big mills :n the world employ this conventional chemical recovery system involving preevaporation, combustion and recausticization to generate NaOH and $Na_2S$. The process is generally accepted in wood/bamboo based mills. One of the major requirement of this recovery system is the minimum final solids concentration range of 58-65% which is difficult to achieve in straw based pulping liquors, due to high silica contents and unstable organic components. One of the major constraints of this conventional chemical recovery is the inability to scale down as combustion furnace and heat recovery operations being in one single integral unit (6).

### Copeland Fluid bed technology.

Copeland fluid bed process employs direct incineration of black liquors of about 45–50% solids concentration. Under controlled temperature, organic matter is decomposed and inorganic matter, mostly $Na_2CO_3$. appear as palletts, from which the NaOH is regenerated by recausticization. The process is flexible in operation as boiler and furnace are not integrated.

### Modified Conventional Chemical Recovery :

Shanghai paper company has now come up with modified conventional chemical recovery system. The major changes incorporated are

- Black liquor spraying through vortex spray nozzle,
- Concentration of B L. is 50—52%.
- Increased distance between hearth and spray point.
- High temperature of primary & secondary air (250°C).

These changes have facilitated to burn the black liquor at 50% concentration. Nevertheless the chemical recovery & thermal efficienc and economic viabili ty aspects are not clear.

### Gasification Processes.

Other chemical recovery technologies have emerged in the last decades. These technologies are based on gasification (7). Basically two tapes of gasifications are carried out—direct gasification at high temperature and indirect gasification relatively at lower temperature. The products of gasification are usually inorganic salts and producer gas ($CO + H_2$) and methane. The **Chemrec process** developed by M/s Chemrec AB, & marketed by M/s Kamyr is based on plasma (direct) gasification. The process is claimed to be economically viable for mills having capacity 30,000—50,000 tpa.

### MTCI Indirect Gasification.

Gasification by thermo chemical conversion reactor (TCCR), based on pulse combustion technique is the recent development and the process is flexible. As claimed by Venkatraman, (8) the system can process black liquor with concentration as low as 35%. The process also claims to give producer gas having higher heating values.

Demonstration plants are being built in India&USA. Esvin technology, Madras, is planning to build a demonstration pilot plant of 500 kg/hr capacity, at Shashesayee paper and Board Ltd, Erode. In USA, MTCI is building a demoplant of 2 0 tph capacity for a Weyerhauser mill. Although no details are available on compatibility of the process for non-wood black liquors, the demoplant of SPB, should throw ligh' on this technology.

### Results Of R & D work On Dars Process Carried Out At CPPRI

CPPRI initiated studies on DARS/Ferrite process in 1983. Extensive laboratory work was carried out on various process parameters. However it was not possible to generate important data on static state bench experiments and the need for pilot scale was felt seriously. In the meanwhile UNIDO came to assist in *this project. It took* almost 4 years to negotiate and reach an agreement to obtain process know-how and pilot plant equipments. Pilot plant equipments were received from DarCell A/s Denmark, a company having experience in DARS technology and also in setting up a commercial scale plant at Frederecia Cellulose A/S Denmark. The CPPRI p lot plant was errected and became operational in November, 1991. Since then number of trails have been carried out and results are highlighted below.

### Discussion :

### Conceptual theory of the process :

The process involves combustion of black liquor together with $Fe_2O_3$ at 850°C. The product sodium ferrite when leached with hot water, NaOH is generated

**Combustion**

$$\text{Black liquor} \xrightarrow{\text{Heat}} Na_2CO_3 + CO_2$$

$$Na_2CO_3 + Fe_2O_3 \xrightarrow{850°C} \underset{\text{Sod. Ferrite}}{Na_2Fe_2O_4} + CO_2$$

**Leaching**

$$Na_2Fe_2O_4 + H_2O \longrightarrow 2NaOH + Fe_2O_3$$

Thus the process of combustion and auto-causticization are accomplished in single step and a single reaction vessel. The sodium carbonate and $Fe_2O_3$ reaction take place in solid-solid phase. Here the temperature is critical and should be more than 850°C. In the event of drop in temperature the $Na_2CO_3$ does not react, instead becomes molten mass leading to sintering and loss of fluidization. The conceptual theory of DARS process is well illustrated in Fig. 1.

### The Pilot Plant :

The pilot plant essentially designed for batch scale operation and consists of two main sections—Fluid bed reactor for combustion and a counter current column for leaching of sodium ferrite. The technical specification of the pilot plant are given below.

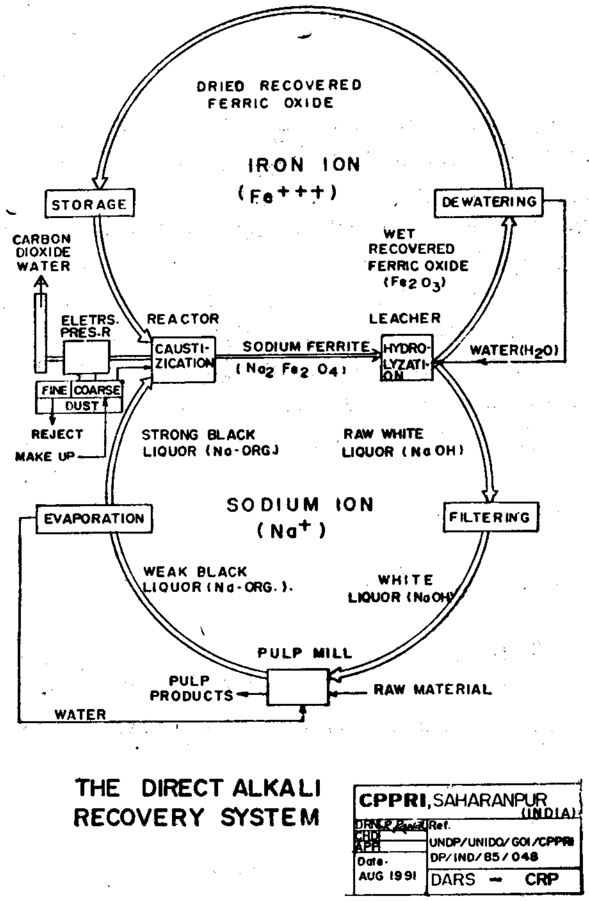



FIG. 1

**Reactor :**

| | |
|---|---|
| Strong black liquor firing (46%) | —(00kg/hr |
| Approximate energy | —1 MW |
| Size of bed | —1000mm |
| Operating temperature | —850—1000°C |
| Bed volume (100% load) | —0.63m³ |

**Leacher :**

| | |
|---|---|
| Sodium ferrite feeding | —150kg/hr |
| White liquor (WL) | —200kg/hr |
| Concentration of WL, | —150—200kg/m³ |
| Process water at 90°C | —300kg/hr |
| Transport water (at ambient temp.) | —1200kg/hr |

The reactor and leacher are illustrated in Figures 2 and 3.

**Operation :**

Based on the amount of black liquor to be fired, the bed material (haematite ore) was fed into reactor. The amount of bed material depends on purity of iron ore, higher the purity lesser will be the dead load. The bed materia lis initially wind sieved by fluidizing

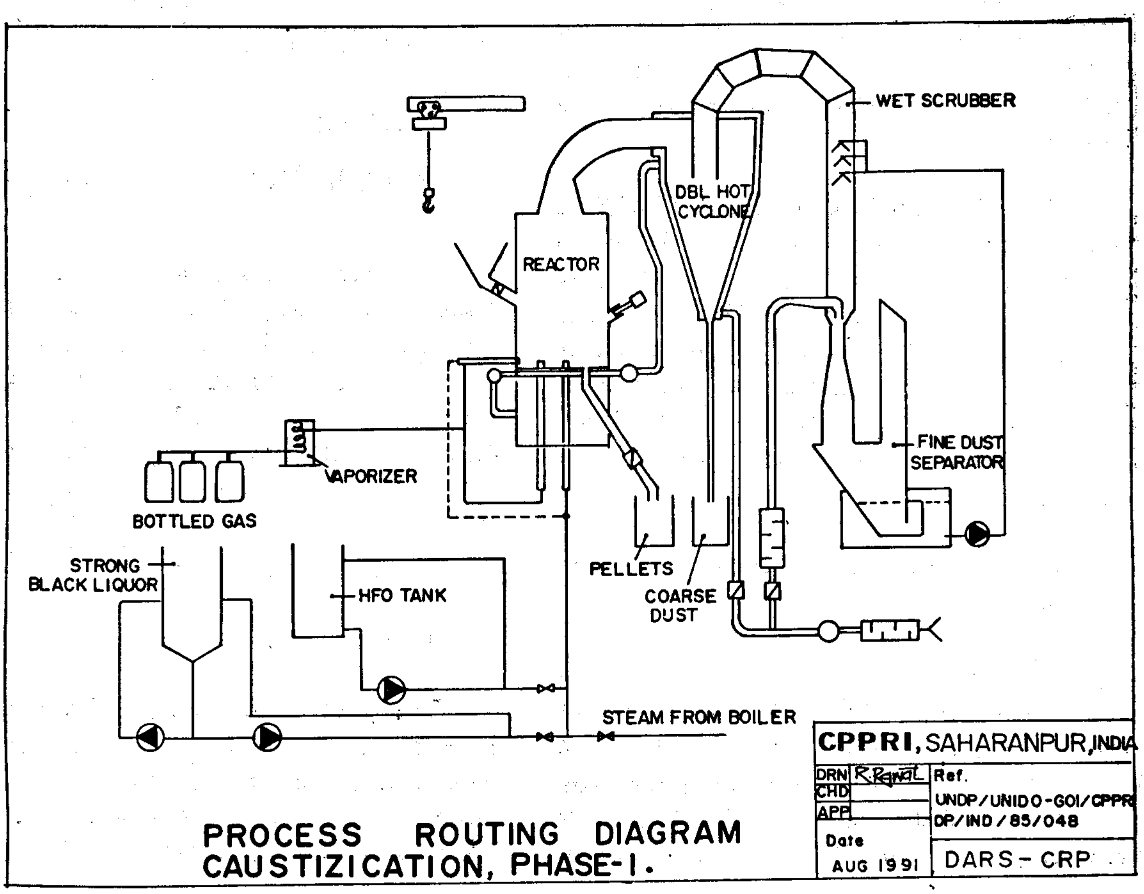



FIG. 2

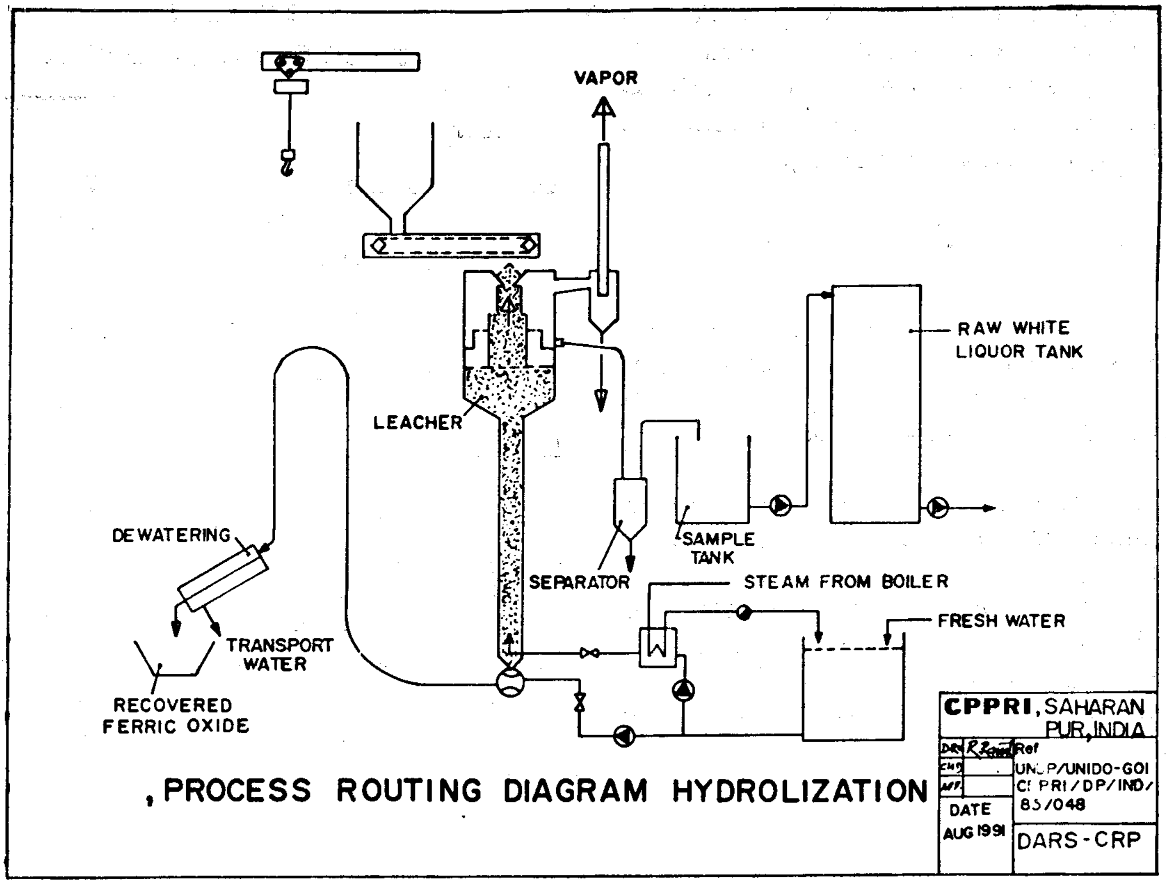



FIG.—3

without heating to remove undesirable dust. After wind sieving, the bed was heated by LPG till temperature of 700°C is attained. Temperature was raised to 850—900°C employing furnace oil. After having attained desired temperature black liquor was sprayed. At this temperature reaction between $Na_2CO_3$, released from black liquor combustion, and $Fe_2O_3$ takes place to form brownish sodium ferrite. Black liquor was sprayed through a special nozzle. The flow of black liquor was so adjusted so that a self sustained combustion was achieved. The excess air is controlled through an oxygen analyser. It was always ensured that there is no de-fluidization and temperature of the bed not lessthan 850°C. This situation will lead to clinker formation. The temperature safty is taken care-off by an inter locking arrangement, as the temperature falls below 850°C, the BL gun automatically closes. When the black liquor was completely fired the fluidization at 850°C was continued for 10—15 minutes. The ferrite formed was cooled to 300°C & then taken out.

The sodium ferrite was screened, to remove small clinkers. The screened ferrite was transfered to hopper of the leacher. The leacher column was filled completely with hot water from a heat exchanger and then feeding of sodium ferrite was started. When the column was completely filled the transport water was started and collection of white liquor in a tank was begun. The basic principle of leaching is that the white liquor is formed at the top of leacher, when solid ferrite comes in contact with hot process water. The high density NaOH moves downward and process water upward. The white liquor formed at the launder portion of leacher overflows. The leached ferrite (recovered $Fe_2O_3$),moves downward and then is carried by the transport water through an ejector. The reactor and leacher units are provided with adequate instrumentation to monitor, various process parameters like airflow, differential pressure, windbox pressure, black liquor flow, etc. The temperature in reactor bed is measured at four points. Fluegas temperature and excess air as oxygen is also monitored. Typical operating conditions are given in Table 1. A typical fluidbed operation is illustated in Fig. 4. Recovered ferric oxide comming with transport water through an ejector was taken on screen for drainage of water. The recovered $Fe_2O_3$ is recycled after drying.

**Results And Discussion :**

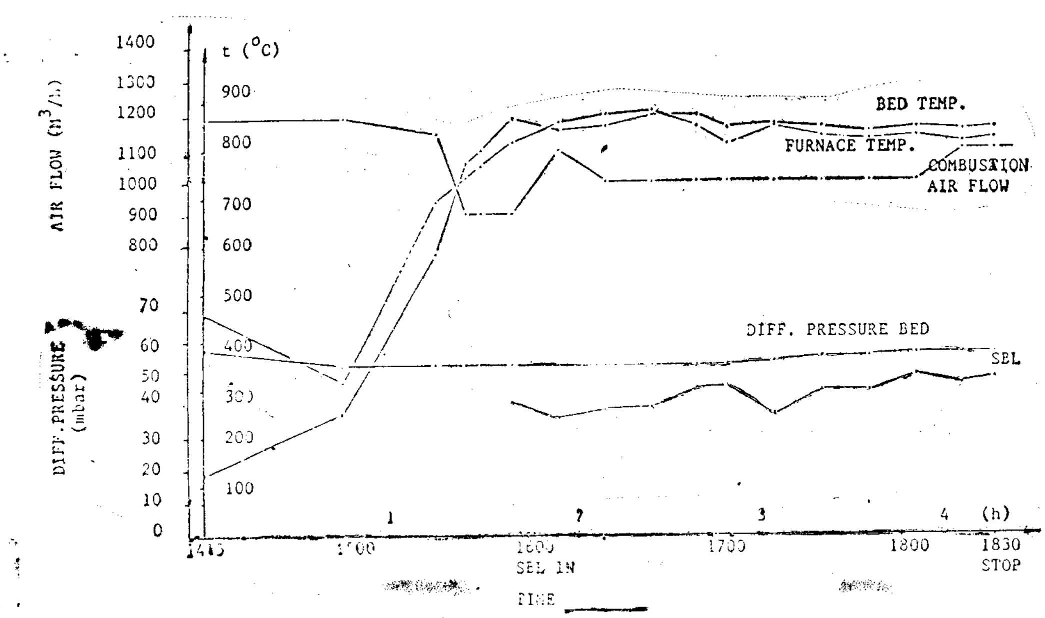
Trials are carried out with grass black liquor and bagasse black liquor using Indian haematite ore. The properties of concentrated black liquors and haematite ores are given in Table—2 and 3.

The black liquor had concentration range around 50% and there was not much deviation in calorific value. Indian haematite ore was mine crushed while the Denish ore was pelletized one. However CPPRI had found that there are some ores in India which have $Fe_2O_3$ contents as high as 96%. The influence of imprtant process variables is discussed in subsequent sections.

TABLE—1

Typical Operating Conditions

| | | |
|---|---|---|
| **Reactor** | | |
| Ore Charged, kgs | 700 | — 900 |
| Black liquor, kgs (52%) | 400 | — 800 |
| Operating temp°C | 870 | — 900 |
| Auxilliary fuel,% | 15 | — 30 |
| Air flow, $m^3$(400 mbar) | 1500 | —2000 |
| Retention time, Hrs | 1 | — 00 |
| Dust formed,% | 15 | — 25 |
| **Leacher** | | |
| Sodium ferrite charge, kgs (Hopper) | 600 | —1000 |
| Process water, temp°C | 80 | — 90 |
| Solids flow, kgs/hr | 150 | — 180 |
| Transport water $m^3$/hr | 1000 | —1200 |
| Maximum NaOH conc. g/1 | 91 | — 210 |
| Causticity,% | 82 | — 97 |
| Sodium Recovery,% | 52 | — 88 |




CURVES SHOWING THE OPERATING CONDITIONS OF REACTOR IN DARS PROCESS

FIG. 4 : CURVES SHOWING THE OPERATING CONDITIONS OF REACTOR IN DARS PROCESS

TABLE—2

Properties of Black Liquors

| Particulars | Grass B.L. | Bagasse B.L. | Rice straw B.L. |
|---|---|---|---|
| Total solids,% w/w | 39.7 | 51.4 | 47.6 |
| RAA,g/l as NaOH | 2.6 | 2.0 | 1.2 |
| $SiO_2$, % | 3.8 | 2.0 | 3.8 |
| Calorific value, cal/g | 3040 | 3000 | 3100 |
| Total 'Na', % | 20.9 | 2.0 | 14.1 |
| Potassium % | 2 2 | 1.9 | 2.0 |

TABLE—3

Properties of Haematite Ores Used

| | INDIAN | DANISH |
|---|---|---|
| **1. Physical Properties** | | |
| Source | Mine crushed | Palletised |
| Density | 2.3 | 1.3 |
| Dust (less than 0.15mm) | 5 | 12 |
| Porosity | Less | More |
| Average grain size, mm | 1.4 | 0.9 |
| **2. Caemical composition** | | |
| $Fe_2O_3$, % | 57.2 | 56.0 |
| $SiO_2$, % | 3.6 | 4.1 |
| **3. Operational Parameters required.** | | |
| Fluidization air, $m^3/hr$ | 2000 | 1500 |
| Differential pressure, ($\triangle P$) m.bar | 70 | 50 |
| Heating period to attain temp of +850°C, min. | 200 | 165 |

The results of the various trials are given in Table-4. Ore was always maintained in excess compared to 'Na'. The optimum excess is about 50%. This excess is maintained to avoid lower molar ratio of Fe :Na. It is observed that the total recoverable sodium was more than 70% in most of the trials. The auxilliary fuel requirement was maximum in the heating-up period and was almost neglegible when black liquor attained sustained combustion. Table-5 shows results of the composition of white liquors produced in different trials. It is evident that white liquors produced had high concentrations with causticity more than 85% in most of the cases. The strength of the composite white liquor was lower due to dilutions taking place in the initial start-up and end-up operations, which can be avoided in a continuously operating plant.

**Influence of process variables :**

**Bed material :**

Quality of bed material, the haematite ore, which also acts as auto-causticizing agent, is very important. We have used two types of ores-pellettized and mine crushed. The only disadvantage with pelletized ore was its inability to with stand heavy abbrasion, which resulted into considerable dust, (25%). The dust formation was relatively low in Indian ore. Amount of dust formed for Indian ore is given in Table-3. It is evident from results in Table-6 that dust formation is in the initial stage and not during combustion. The dust formation should be as minimum as possible to avoid chemical losses.

**Grain size :**

The grain size of haematite ore, particularly the mine crushed one, was found to be an important parameter influencing the sodium binding capacity and subsequent recovery during leaching. Results in Table-7 clearly show that with reduction in grain size the chemically bound Na and recovery of sodium was on higher side.

**Density of ore :**

The density of bed material was another important variable. Higher density of mine crushed ore required higher fluidization air, which might influence the thermal efficiency.

TABLE—4

Results Of Pilot Plant Trials

| Batch No. | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Reactor :** | | | | | | | | | | | |
| Ore, kgs, | 950 | 990 | 760 | 756 | 770 | 617 | AIR | 858 | 809 | FLUIDI- | 761 |
| Black liquor (52%,kgs) | 810 | 868 | 531 | 631 | 476 | 316 | DISTRI- | 449 | 444 | ZATION | 384 |
| Total sodium, kgs(a) | 111 | 119 | 88 | 87 | 85 | 65 | BUTOR | 88 | 85 | FAILURE | 149 |
| **Leacher :** | | | | | | | | | | | |
| Sodium ferrite, kgs | 1000 | 900 | 744 | 555 | 758 | 538 | PLATE | 721 | 603 | AND | 627 |
| Total $Na_2O$, kgs | 68 | 92 | 60 | 61 | 66 | 51 | DIS- | 71 | 64 | TRIAL | 65 |
| Total $Na_2O$, in white liquor, kgs | ND | 61 | 32 | 29 | 41 | 33 | PLACED | 42 | 39 | WAS | 37 |
| Recovered $Fe_2O_3$,kgs, | — | 776 | 617 | 463 | 650 | 474 | | 700 | 574 | TERMI-NATED | 600 |
| Total recoverable $Na_2O$,%(b) | — | 82 | 73 | 77 | 85 | 77 | | 88 | 81 | | 52 |
| Dust formed,% | 32 | 16 | 18 | 24 | 20 | 16 | | 15 | — | | 19 |
| Auxilliary fuel,%** | — | 18 | 26 | 15 | 46 | 35 | | 26 | 50 | | 37 |

TABLE—5

Composition of white Liquors Produced in the Pilot Plant

| Batch No. | Total alkali g/l as $Na_2O$ | NaOH g/l, $Na_2O$ | Maximum conc as $Na_2O$,g/l | $Na_2CO_3$ as $Na_2O$, g/l | Causti—city, % | Silica as g/l $SiO_2$, |
|---|---|---|---|---|---|---|
| 2 | 110 | 83 | 210 | 27 | 75 | 1.9 |
| 4 | 50.5 | 50.4 | 173 | 10 | 87.1 | 2.8 |
| 5 | 55.5 | 53.0 | 108 | 2.5 | 95.5 | 1.8 |
| 6 | 63.6 | 55.5 | 130 | 8.1 | 87.2 | 3.1 |
| 7 | 45.0 | 37.2 | 118 | 7.8 | 82.0 | 1.9 |
| 8 | 45.6 | 50.2 | 106 | 4.4 | 92.1 | 2.8 |
| 9 | 54.6 | 50 2 | 93 | 5.9 | 87.6 | 2 0 |
| 10 | Fluidization stopped due to falling of refractory line in furnace. | | | | | |
| 11 | 35.0 | 32.2 | 91 | 2.8 | 92.0 | 2.0 |
| 12 | 56 0 | 53.5 | 110 | 2.50 | 95.5 | 2.4 |
| 13 | Grid plate displaced. | | | | | |
| 14 | 53.3 | 51.7 | 100 | 1.6 | 97.0 | 2.6 |

TABLE-6

Dust Formation in Fluidized Bed Reactor

| STAGE | PERCENTAGE OF BED MATERIAL |
|---|---|
| Wind sieving < 100°C | 4 |
| Wind sieving 100-850°C | 7 |
| Total wind sieved | 11 |
| Cyclone dust (firing) | 6 |
| Total dust | 17 |
| Bed ash | 83 |

TABLE-7

Effect of Particle Size on Extraction of Sodium

| GRAIN SIZE | SODIUM % As $Na_2O$ | SODIUM RECOVERED % As $Na_2O$ | $SiO_2$ % |
|---|---|---|---|
| | Whole sample | | |
| 71.18 mm. 1.6 | 11.6 | 54.3 | 1.8 |
| 1.18 mm. | 10 5 | 37.7 | 1.6 |
| 0.60 mm. | 14.6 | 50.7 | 2.0 |
| 0.43 mm. | 19.8 | 70.8 | 3.1 |

### Influence of 'Na' to 'Fe' Molar ratio :

Although in laboratory the reaction can be quantitatively effected with stoichiometric ratio, but in plant operation always excess 'Fe' is maintained to avoid smelting of $Na_2CO_3$, leading to formation of clinkers. Usually excess iron between 50-100% is maintained.

$$\text{Excess iron} = \frac{\text{Moles } Fe_2O_3 - 1}{\text{Moles } Na_2O} \times 100$$

### Influence of sodium & silica build-up :

It was evident that the mine crushed ore, unlike the porous palletized ore has limited binding capacity. Further the binding capacity of the recycled ore was influenced by 'Na' & 'Si' build-up. The results in Table—8 *clearly* indicate that in the first cycle there was a significant build-up of 'Na' and $SiO_2$'. However the build-up was reduced in subsequent cycles. The silica and sodium bound physically calls for more make-up ore in the reactor.

TABLE-8

Sodium & Silica Build-up During Recycling of Ore

| | ORE A** | | | ORE B** | |
|---|---|---|---|---|---|
| | 1st | 2nd | 3rd | 1st | 2nd |
| Sodium as $Na_2O$*, % | 6.3 | 8.1 | 8.4 | 7.8 | 8.2 |
| Silica as $SiO_2$, | 3.5 | 6.3 | 8.4 | 6.3 | 9.8 |

* Initial ores showed no sodium content.

** Recovered $Fe_2O_3$ (ores) recycled in subsequent cycles.

### Leaching of sodium ferrite :

There was a remarkable difference in leaching parameters for the sodium ferrite obtained from mine crushed ore and the one obtained from palletized ore. The former required higher retention time in leaching column (feed rate 1.5 lit/min) while the later required lower retention time (2.5 lit/min). Mine crushed ore may require leaching columns designed for sufficient retention time.

### Observation :

The batch scale pilot plant trials have been successful in terms of assessing the compatibility of the process for non-wood black liquors. It was observed that the operation was safe and flexible. Black liquor combustion at 50% solids concentration was self sustained. However for obtaining more engineering parameters, the data from a continuously operating plant should be more realistic under steady-state operation. Further the process has to be demonstrated to industry in continuous operation over a length of period.

### Risks and Rewards :

New technology always involves a certain degree of risk. Some of the emerged technologies have failed to live upto the expectations on commercial scale primarily due to excessive complexity, unit operations with extreme requirement and incompatibility between stages. DARS minimizes these risks, particularly in context of small pulp mills. Nevertheless following factors should determine the viability of the process.

— Productive capacity of mill should meet minimum economic limit of system chosen.

— Technical feasibility

— Magnitude of pollution

## Conclusions :

- The pilot plant trials have certainly proved the advantages of DARS process and its compatibility to non-wood black liquors.
- Pilot plant results are only indicative figures and for design purpose a continuously operating plant should give more realistic results.
- DARS is not only the technology for small pulp mills, but it is one of the alternatives to conventional recovery system.

## Acknowledgement

Authors express their sincere thanks to Shri V.K. Mohindru & his operation crew, Dr. R M. Mathur and his analytical team for their services in DARS pilot plant trials. Thanks are due to Miss Sudha Jain who assisted in preparation of this typescript.

## Literature Cited :

1. Chang Zou Pei, *Souvenir UNIDO/CPPRI Workshop, New Delhi*, P-44, Sept. 1991.
2. Kelleher, E G. *Tappi* 68 (12) : 17 (1985).
3. Covey, G.H. *Pape trade Journal* (5) : 51(1985).
4. Fellegi J, *Souvenir UNIDO/CPPRI Workshop* P-50 Sept, 1991
5. Long, Tan, *Pulp and Paper Internation* June, P-59 (1986)
6. Blaur N.P., *Tappi* 73 (2) : 65 (1991)
7. Empie, J.H., *Tappi* 73 (5) : (1991)
8. Venkatraman. T.S., *International Conference on Nonwood Fiber Pulping & Papermaking*. Procceding vol. II p-943, April, 1992 (Shanghai, P.R. China).