

Direct Alkali Recovery System (Dars)-The New 'State-Of-The-Art' System—A Review

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ABSTRACT

In this paper is presented a comprehensive review of the published literature on the Direct Alkali Recovery systems (DARS) also known as the Ferrite Process. How the concept of DARS first emerged out, the Chemistry and Technology of DARS Process; the development of DARS Process and the scope for application of DARS Process to Indian Paper industry are examined in this review article.

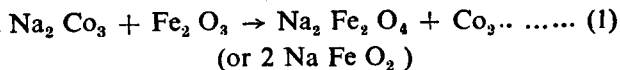
The Direct alkali Recovery system (DARS) is a process of Recovering sodium hydroxide from spent liquors of non-sulphur pulping processes. The various details of Dars process has been studied and worked out in detail by the Research Group led by Dr. Geoff Covey of Australian Paper Manufacturers Ltd. (A.P.M). DARS is of great interest as it can be employed with soda - AQ pulping to give a simpler, cheaper and odour free process than the conventional Kraft Pulping.

In this paper are presented some important details of the DARS process and the present "State-of-the-art" of this new process.

History of Development of D.A.R.S.

The basic details of DARS were first worked out by Toyo Pulp Company of Japan¹.

The process and the Chemistry have been well described by Kiiskila and coworkers. Basically speaking, the process also known as Ferrite process involves the evaporation of the spent liquor and then burning it with ferric oxide in a suitable furnace to form a suitable product of sodium ferrite. It is believed that organics burn off and the residual sodium carbonate reacts with ferric oxide as shown below.



The product is then treated with water to regenerate sodium hydroxide and ferric oxide as shown in equation ... (2)



The ferric oxide can be used repeatedly

In fact the use of ferric oxide to produce market caustic soda from soda ash was patented by Lowig as early as 1883².

It was used sporadically until about the time of the first world war, and since then it has been used extensively in U.S.S.R. Interest in this process has been revived from time to time particularly in Japan in 1920's and 1960's.

In 1977, Australian Paper Manufacturers Ltd. (APM) entered into a licensing and development agreement with Toyo Company to develop the DARS principle and to find a suitable equipment for a commercial process.

The Chemistry of DARS

The compound formed by reaction of Na_2CO_3 with Fe_2O_3 contains Iron in the oxidation state of + 3 known as sodium Ferrite.

*Based on the information collected by the author during the visit to Australia under "South-East Asia Cooperation Trust Fund Scheme".

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Physical Properties of Sodium Ferrite

a) Crystal Forms

Sodium Ferrite has three different crystal forms, α , β & γ . The low temperature form of sodium ferrite (NaFeO_2) is FeO_2 . This is rhombohedral. Above 760°C there is a transition to β - NaFeO_2 which has an ortho rhombic form. At high temperatures say at about 1000°C β - NaFeO_2 changes to γ -Ferrite which has a tetragonal lattice^{5,6,7}. This data is important for design of a reactor as changes in phase are often accompanied by changes in hardness of the material.

Formation of Sodium Ferrite

Sodium Ferrite is normally prepared by the decarboxylation of sodium carbonate in the presence of ferric oxide. The reaction is carried out at temperatures below 858°C , the melting point of sodium carbonate and the reaction is of solid-solid nature⁸. The studies of Mazel has shown that the reaction between Ferric Oxide and sodium carbonate starts at 500°C , while Tseft and Salibaeu indicated that Na_2CO_3 begins to dissociate in the presence of ferric oxide at 670°C .

Effect of Temperature on this Reaction

The work of Mitusi and Yasuda⁹ on the effect of temperature at a number of different molar ratios of the reactions on the causticizing efficiency showed a rapid rise in the efficiency at about 700°C and the relatively flat profile above 800°C .

Kiiskila and Valkonen⁸ published results showing the effect of temperature on the decomposition of Na_2CO_3 . It was observed that after 15 minutes no further conversion was achieved if the temperature was above 900°C .

Early work by Covey and coworkers⁸ showed no further conversion of sodium carbonate at 1000°C after 20 minutes. Later work by the same group indicated a similar effect even at 900°C , but however at 800°C , the conversion was much lower and even after 1500 minutes, it was still below than that obtained in the higher temperature reactions. The reactions at temperatures between 800°C and 900°C were also studied in detail by research group at APM.

From the perusal of all these results it was felt that there appeared to be three distinct regions in the reaction between Fe_2O_3 and Na_2CO_3 . The first which occurs

at about 825°C is a solid - solid diffusion of the reacting components. The second region occurs at $830^\circ - 860^\circ\text{C}$ (Na_2CO_3 melts at 851°C) and shows an increased reaction rate with increasing temperature. This is to be traced to the increased mobility of sodium carbonate due to melting enabling diffusion into the ferric oxide and increasing the reaction rate. The final region shows little change in the causticity or sodium ferrite formation with temperatures above 900°C , because the reactants react almost fully. At lower temperatures, as would be expected, this phenomenon takes place after longer reaction time.

Effect of Temperature on Sodium Recovery

At higher temperatures there is a slight drop in the sodium recovery, which was attributed to the volatilisation of Na_2O . However, it has also been found at low temperatures also, there is an decrease in the sodium recovery especially when there is an excess of Fe_2O_3 which is probably due to the formation of the unreactive $\text{Na}_3\text{Fe}_5\text{O}_9$.

Effect of Stoichiometry

From the work of Matusi and Yasuda⁹ it was found that at temperature below 840°C , although excess of ferric oxide at temperatures below 840°C improved the causticising efficiency at higher temperature there was very little gain in raising the molar ratio above 1.6. Studies at APM also showed that an excess than the required molar quantities is needed to obtain the highest causticity. APM experience has also shown that combustion of black liquor organics and causticisation of the sodium carbonate formed is possible in a fluidised bed at temperatures as low as 800°C . The excess of ferric oxide also reduces any tendency the bed may have to sinter by providing the surplus reaction area thus minimising the quantity of free molten sodium carbonate in the bed.

Effect of Water Vapour

The presence of water vapour was found to have a beneficial effect¹⁰. It is claimed that the steam activates the reactants, and improves conditions of ionic diffusion and crystallisation of the product.

Hydrolysis of Sodium Ferrite

The decomposition of sodium ferrite, when reacted with water is generally described by equation (2) given earlier in the paper. This is however, an over simplification of what really occurs.

Effect of Hydrolysis Temperature

Matusi and Yasuda⁹ report that ferrite is stable below 35°C and found that Na₂CO₃ could be extracted at this temperature. Decomposition was rapid at 40–60°C and complete at 70°C; no information was provided on the particle size or actual hydrolysis times. Malyshev and Kazabrotsky¹¹ found that the ease of hydrolysis increased with sintering temperature.

Kulkarni et al.¹² have demonstrated that the extraction should be preferably carried out at 90°C. At 20°C 18% of Na₂O was recovered, with the reaction time being maintained at 15 minutes. At 80°C for the same 15 minutes reaction time, the alkali extracted was 76%. At 90°C, about 90% of the Na₂O was recovered and also the time factor did not show any significant change in the amount of Na₂O extracted.

Effect of Hydroxide Concentration :

Matusi and Yasuda⁹ carried out the hydrolysis of sodium ferrite in solutions of caustic soda upto 350 g/l. The results indicate that the degree of extraction of sodium hydroxide falls with increasing concentration of hydrolysis solutions when the concentration of sodium hydroxide exceeds 260 g/l the alkali extraction percentage drops substantially. Works by APM research group⁸ also confirmed the decrease in degree of decomposition as the concentration of NaOH increases.

Development of D. A. R. S. Technology

The Research group headed by Geoff Covey at APM translated the Chemistry of DARS to develop a commercially viable and Technologically feasible, "State-of-the-art" recovery system.

The present section describes how the technology was developed by APM group getting over one difficulty after another.

a) Combustion

Various types of furnaces were considered by APM group for combustion stage. They were Rotary kiln, Smelting furnace, Spray incenerator, multi-hearth furnace, and fluidised bed combustion furnace.

In fact, the rotary kiln furnaces were used by Toya Pulp Company of Japan to burn black liquor-Fe₂O₃ mixtures.

From the extensive studies conducted at APM, Maryvale, it was found that fluidised bed showed the maximum promise. This approach offered relatively low cost, stable operation, good potential for heat recovery and a comparatively wide range of equipment size.

Fluidised bed processes have been used in the past for chemical recovery in the pulp industry, but these have been quite different from the type of operation used with DARS. Agglomerating fluidised beds have provided an important service to the pulp industry by offering almost the only economical means of disposal of semi-chemical black liquor, but they are usually found to be difficult to operate.

In a DARS fluidised bed the process is essentially non-agglomerating so the need for very close control of temperature is removed. As fluidised beds are rapidly defluidised it would be considered necessary to operate below the melting point of sodium carbonate (viz. below 850°C). However, as the bed is non-agglomerating it is possible to operate fairly close to the melting point. Under these conditions the reaction between the sodium carbonate and ferric oxide is in the solid/solid region and the rate is fairly low. Therefore to obtain adequate conversion in a reasonable time (i. e. with an optimum fluidised bed volume) it is necessary to maintain a short diffusion path and the obvious way to achieve this was to use small particle size ferric oxide. However, use of small particles in a non-agglomerating bed requires the use of very low gas velocities and so the required bed cross section for a given combustion capacity becomes economically unattractive.

This problem was solved by APM Research group in the following way.

Operation above the melting point of sodium carbonate (i.e. outside the region normally considered feasible for fluidised beds) permits the use of large (1-2 mm) particles of ferric oxide. This results in good fluidisation at high fluidising velocities while giving efficient ferric oxide use.

Additionally, the higher temperature improves combustion dramatically. Indeed the pilot plant in APM was operated with very little excess air with very low carbon monoxide, no measurable hydrocarbons in the flue gases and no measurable unburnt

carbon in the bed product. The use of large particles of ferric oxide also simplified material handling and gave other process advantage.

b) Leaching

Complete hydrolysis of sodium ferrite and subsequent extraction of NaOH to form a concentrated solution with minimum generation fine iron-oxide particles is a key-step in the implementation of the DARS process.

As discussed earlier, the hydrolysis reaction (the main reaction in leaching) is retarded by increased sodium hydroxide concentrations.

Therefore, for efficient sodium recovery, counter current is necessary. The experiments in APM demonstrated that although large particles of ferrite are leached more slowly than are the fine particles, the decrease in rate is not very large, and leaching large particles was found to give three distinct advantages.

a) The residues is of the required size for the fluidised bed (This is desirable for a non-agglomerating bed).

b) It permits easy separation of liquids and solids between the stages. Further, as particles can easily be made to move in the opposite direction to the liquid it is possible to obtain several equilibrium stages-in suitable continuous contact counter current leacher.

c) It is possible to mechanically separate the liquid from large solids to a much greater extent than from fine solids. With large particles it is possible to go above 90% solids while with fine particles it is not possible to go above 70-75% solids by mechanical means. This has very large effect on the thermal efficiency of the process as any water retained with ferric oxide must be evaporated in the fluid bed and this causes a direct reduction in the steam raising potential of the system.

The effect of temperature on leaching has already been discussed.

Ken Maddern¹⁸ lists out the important factors which were taken into consideration during the design of the ferrite leaching system in the DARS World's first DARS plant having a recovery capacity equivalent to 200 TPD O.D. unbleached pulp.

1. The leaching temperature should be as high as practicable but below the solution boiling point to

avoid breakdown of the solids due to the boiling action.

2. The most efficient leaching configuration will be the pure counter current contacting. Based on the diffusion model this would require a minimum of 6 minutes solids residence-time at 95°C for 95% removal of the water soluble sodium under perfect conditions.

On the same basis a stagewise counter-current system would require 3 to 4 perfect stages.

3. The leached solid is very susceptible to attrition and mechanical action must be minimised to prevent excessive generation of fines.

4. The production of high strength sodium hydroxide solution requires careful attention to equipment fabrication and metallurgy to avoid caustic embrittlement.

The effect of impurities :

The efficiency of any process is measured by its ability to operate under varied conditions. Contaminant non process elements (NPE) enter the pulping chemical cycle in the wood, iron oxide, process water, makeup chemicals and as process equipment corrosion products. The impurities that enter via wood are Ca, Mg, K and both non fibrous raw materials silica. The metallic impurities that enter the cycle along with the ferric oxide are Si, Al, Cr, Ti etc. In addition anions like chloride, sulphate also enter in the system. If these are cycled with the white liquor, impurities may build up to such a level that they interfere with pulping process (possibly discolouring the pulp) or be deposited as scales in the evaporators. If they are cycled with ferric oxide they may be inert, they may also react with ferric oxide so that some quantity of ferric oxide is unavailable for causticisation. Studies conducted at APM's laboratories and elsewhere have clearly indicated that washing of the product from fluidised bed with cold water ($\sim 30^{\circ}\text{C}$) in order to dissolve out soluble NPEs with out causing hydrolysis of sodium ferrite.

It was also noticed in these studies cold water washing of ferrite can lead to some disadvantages, as the impurities removed will be in the form of sodium salts thus leading to sodium loss. Depending on the quantity of sodium removed by cold washing, and the nature of impurities removed, further treatment of this wash water may be required.

Covey⁸ has suggested that it is possible to precipitate silica, alumina, sulphate and some heavy metals by treating the wash water with lime. In this case the lime consumption is small as it is only used to precipitate unwanted ions, and it is rejected after use. The treated wash water would then be returned to the pulping chemicals.

As far as chlorides are concerned, it was found in practice at APM's pilot plant that chloride in the black liquor volatilises in the fluidised bed.

To remove some of the impurities building up as a dead load, Maddern¹³ has suggested a preferential use of DARS white liquor⁵ to provide a bleed off.

Pilot Plant Operational Experience of DARS

Actually the first commercial installation of DARS process has come up recently at the Bumie Mill of Associated Pulp and Paper Mills Ltd. at Burnie, Tasmania, Australia. The operational experience of this first DARS plant has not been published so far. However, the details of working of DARS pilot plant at Maryvale Mills of APM are available.^{8,14,15} The pilot plant was under operation for about 2½ years.

A simplified flow sheet of the Research pilot plant is shown in figure.

This pilot plant of 3 Tons per day chemical pulp capacity has been in operation more or less continuous three shift basis during the period 1980-82.

The pulping section was consisting of a 5 m³ batch digester together with batch diffusers for chemical pulp and a live bottom blow tank to permit semi-chemical pulp.

The black liquor is evaporated in a single effect long tube evaporator and is then fired in the fluidised bed reactor. Supplementary fuel was required during start up. Fluidisation was easy to control, there was very little agglomeration or attrition with very little scale formation in the fluidised region. The particles were not sticky and it was possible to slump or restart the bed without difficulty.

The fluidised bed was originally 1 meter in diameter. Combustion efficiency was excellent with very low carbon monoxide and nitrogen oxide levels. The combustion performance was also very insensitive to liquor type. Even liquor from pulping of 100% overmature

eucalyptus which has high phenol content and poor swelling characteristics could be burned without difficulty.

The good combustion at low excess air together with stable fluidisation achieved resulted in a dramatic increase in the through put of the fluidised bed. As the liquor burning capacity increased beyond that of ancillary systems and in order to bring the system back into balance, the diameter of the fluidised region was reduced to 750 mm. The bed operated with a moderate excess of ferric oxide over the stoichiometric amount. Recycling of ferric oxide had no deleterious effect on the performance. Pelletisation proved to be an effective and simple means of returning fines to the system as strong particles.

The heat recovery systems were appropriately designed and heat recovery from flue gases was comparatively - straight forward tubes immersed in the bed did not show evidence of erosion or fouling and good heat transfer coefficients were obtained.

The solid bed product, consisting mainly of sodium ferrite and excess (unreacted) ferric oxide passes through a second bed which acts as a solids cooler/combustion air preheater. Actually this fluidised bed contains water cooled tubes.

The fluidised bed where the combustion takes place has a refractory distributor plate and a combustor in the wind box for the start up. Gases leaving the bed pass through a cyclone and venturi scrubber prior to venting through an induced draught fan. The gas cleaning method has proved to be effective and suspended particulate matter levels in the flue gases were below 250 mg/Nm³.

Leaching was done in ferrite leacher by counter current extraction with hot water at 95°C or so.

Process Advantages of DARS

DARS has a number of advantages over other Chemical Recovery Processes.

1) DARS is applicable over a wide range of mill sizes. Even for a small paper mill viable recovery units can be built.

2) There is an elimination of recausticising section, thereby leading to considerable savings of equipment cost and space needed for causticising.

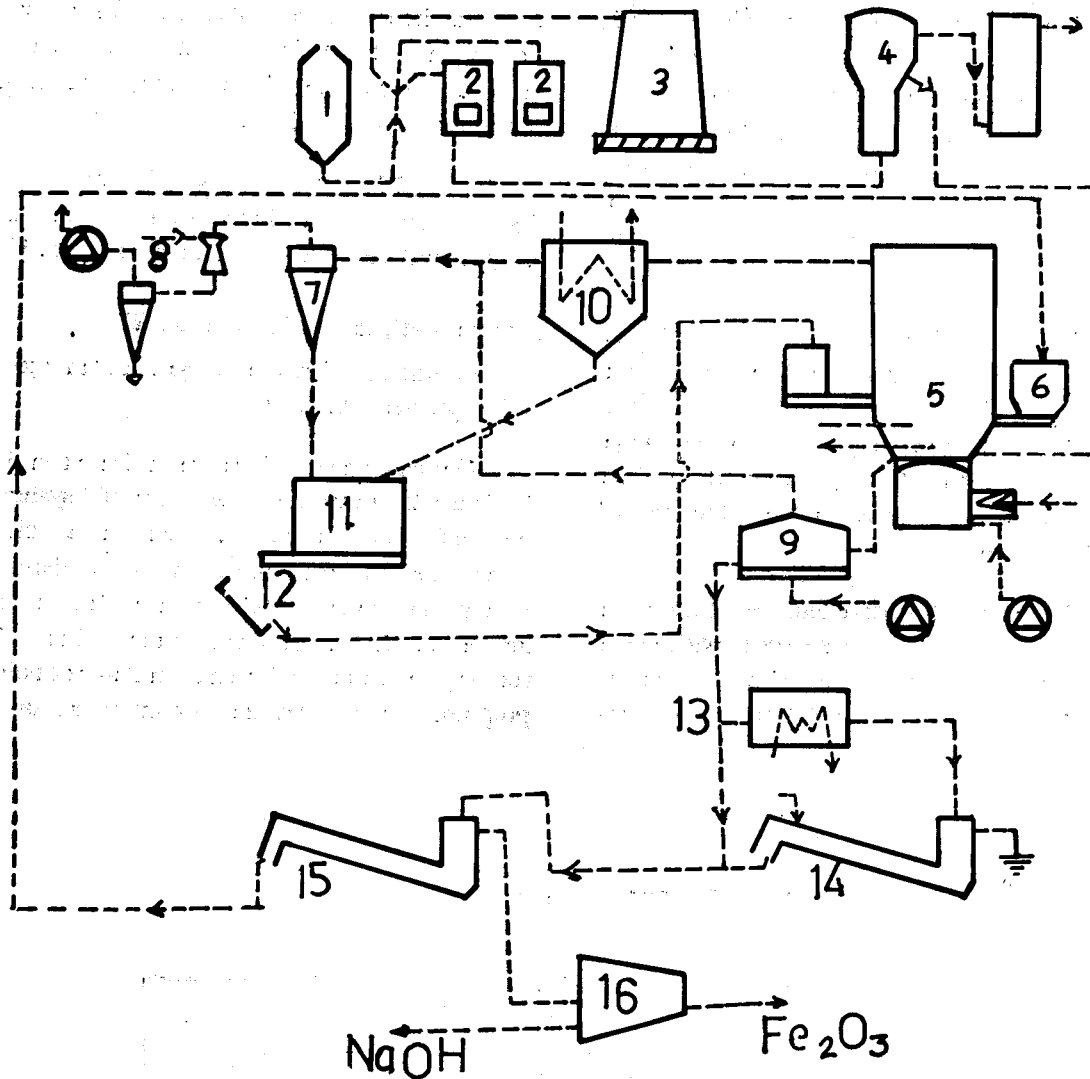


Fig. Simplified Flow Sheet of DARS Pilot Plant
in its Final Form.

- | | |
|--------------------------|-------------------------------|
| 1. Digester | 9. Product Cooler |
| 2. Batch diffusers | 10. Model Waste - heat boiler |
| 3. Live-bottom blow tank | 11. Dust Silo |
| 4. Evaporator | 12. Pelletizer |
| 5. Fluidized bed | 13. Secondary cooler |
| 6. Ferric Oxide Silo | 14. Cold Waste Stage |
| 7. Cyclone | 15. Ferrite leacher |
| 8. Venturi Scrubber | 16. White liquor centrifuge |

3) Elimination of lime kiln and its high fossil fuel use.

4) Safety in operation. Reaction of sodium ferrite with water is not explosive unlike the reaction of smelt with water. In fact, during the pilot plant operations weak black liquor and even water were injected into the hot fluidised bed without any hazardous consequences.

5) The sodium hydroxide produced by DARS has two advantages over that produced by lime causticising: higher causticity and if required higher concentration. The causticity of DARS liquor is generally in the range of 92-95% compared with 80-85% produced by lime causticising. This means a considerable reduction of dead load in the system.

6) One of the most attractive features of DARS is its flexibility. The process functions over a wide range of black liquor-concentrations, and therefore concentration at which liquor is fired and the extent of heat reco-

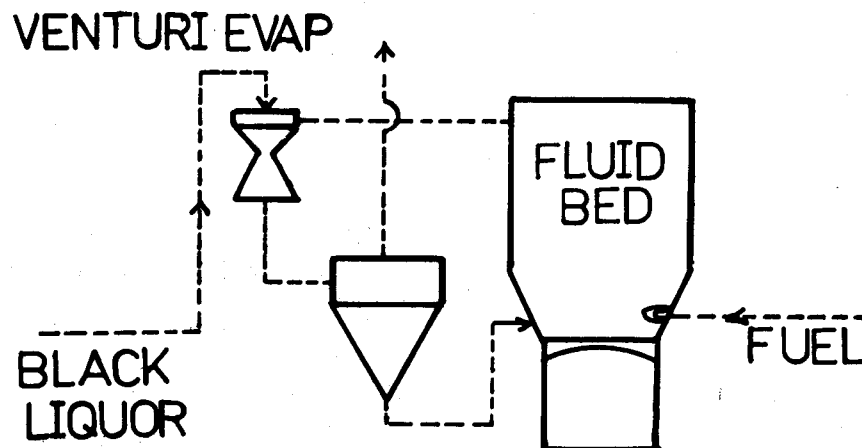
very practised can be governed solely by economic factors in that particular mill for which recovery is needed. Acceptable liquor firing concentrations can be as low as 40% solids¹⁴.

7) DARS shows promise of being well suited to the recovery of spent liquor from pulping of the non-woods, and the systems tolerance of silica.¹⁵

Process Options Available in DARS

As stated earlier, the biggest advantage of DARS is the process flexibility.

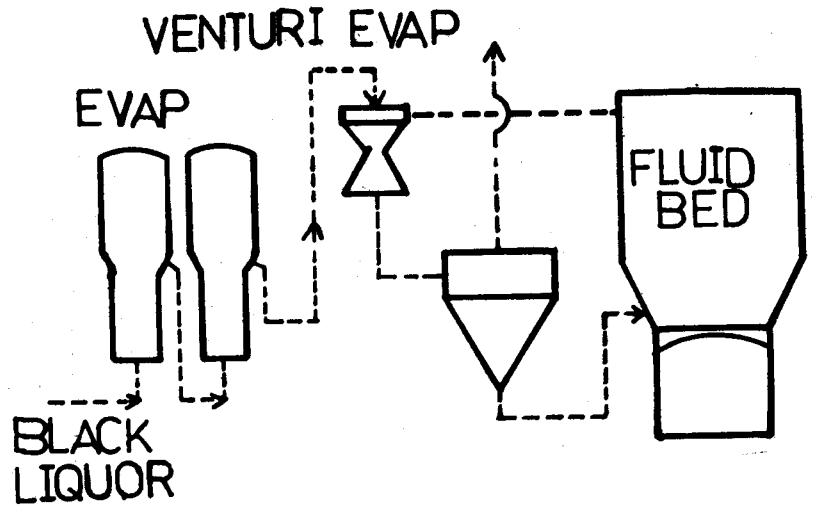
The major possibilities are indicated in figures 2 to 5. Figure 2 shows the possibility of system in which the black liquor is concentrated in a direct contact evaporator and then burned in the fluidised bed reactor with a small quantity of auxiliary fuel to compensate for the shortfall in the black liquor solids. This approach may be attractive for small mills-producing chemical pulp and this involves the minimum capital cost.



MINIMUM CAPITAL COST NON-AUTOGENOUS OPERATION

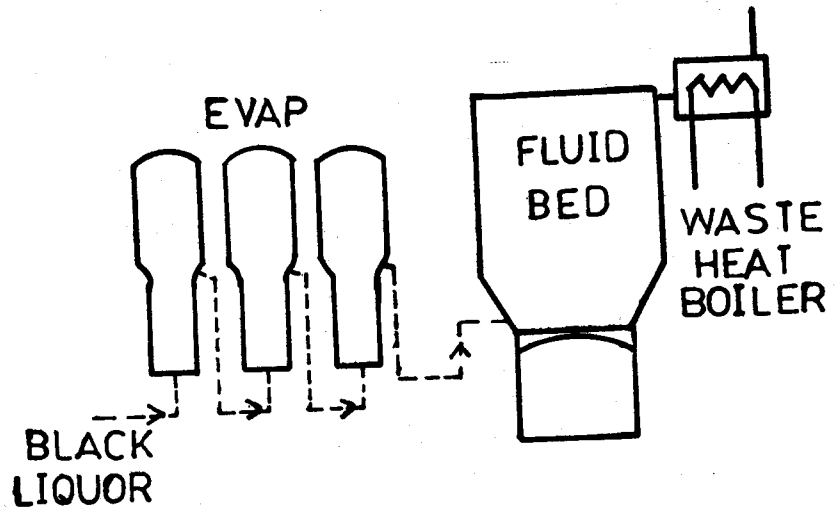
ARRANGEMENT OF DARS

FIGURE 2



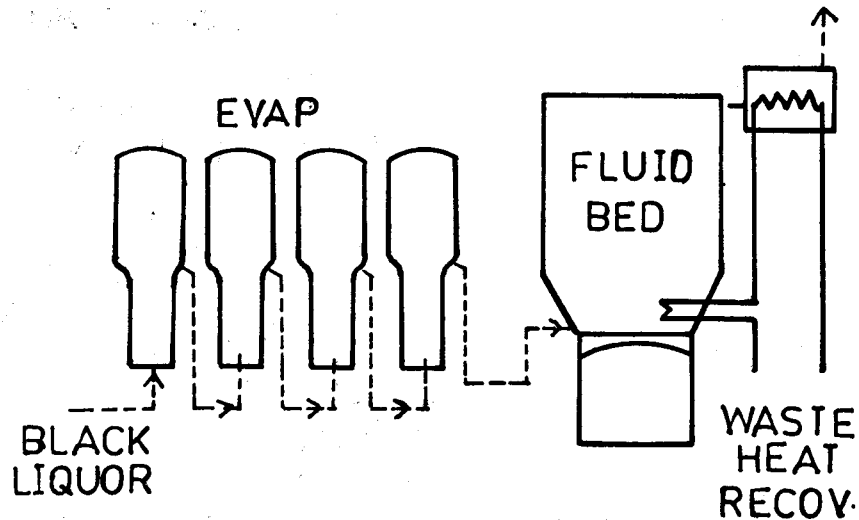
LOW CAPITAL COST AUTO GENOUS OPERATION
ARRANGEMENT OF DARS

FIGURE 3



DARS WITH SIMPLE HEAT RECOVERY

FIGURE 4



DARS WITH MAXIMUM HEAT RECOVERY

FIGURE 5

Another low capital cost arrangement is shown in figure 3. In this arrangement liquor is fired to the fluidised bed at the autogenous concentration viz 45%. This concentration is reached by using a venturi evaporator (or other direct contact evaporators) and a small set of steam heated evaporators.

A natural extension of the system is to one which has heat recovery also. Figure 4 shows system which is simple but gives a substantial steam generation. Black liquor is evaporated to the autogenous concentration and burned in the bed with steam being generated from the flue gases. This arrangement is particularly suited to mills with viscous liquor which cannot readily be concentrated to the level required for safe operation of a smelting furnace without the use of a direct contact evaporator.

Figure 5 shows the maximum thermal efficiency from DARS. Liquor is taken from the evaporators at upto the maximum practical concentration and fired to the fluidised bed. Heat is recovered from both flue gases and the fluidised region.

Cost Savings in DARS

a) Capital

From the study of a number of case studies presented by Covey it is evident that the relative capital cost of DARS versus conventional technology varies from mill to mill, but as a guide-line in the recovery area, a savings of about one third can be expected for DARS.

b) Operating Costs

It is projected that the operating costs of DARS will also be less, Kulkarni et al have worked out for a 30 Tons per day mill, the operating costs of DARS will be less by 15 lakhs per annum compared to conventional recovery system.

c) Labour Cost

Labour cost of DARS process will be less when compared to the conventional process, as this avoids the recausticising section and lime Kilns.

d) Maintenance

The equipment for DARS is generally simpler

than that used in kraft, there are less process steps and conditions are less corrosive which means lesser maintenance costs.

Conclusions

It is very clear from above, and with the experience of successful operation of DARS pilot plant for 2 years for black liquor from 3 TPD pulp mill, the same process can be scaled up for the small soda pulp mills of 10-30 TPD.

The capital cost of this recovery equipment will be paid back in short time as the sodium hydroxide which is now being drained can be recovered upto 90%. The recovery of sodium and the elimination of black liquor from the effluent streams will also considerably reduce the effluent treatment costs, thus thereby significantly improving the financial health of the small paper mills.

Further details of this potentially attractive process can be obtained by contacting APM headquarters at Samberwell, Victoria, Australia.

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