# Towards Higher Chemical Recovery Efficiency

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**Introduction**

A chemical recovery unit in a sulfate pulp mill serves dual purpose in recovering valuable chemicals and generating steam, thereby increasing the economy in terms of chemicals and fuel. Thus, when one refers to the efficiency of a recovery unit, it mainly implies both chemical and thermal efficiencies starting from brown stock washing in the pulp mill to lime mud washing in the recovery plant. Hence to improve the efficiency of this unit, proper controls have to be exercised from pulp washing to mud washing stages.

**Discussions**

A detailed discussion on the above mentioned sections is given as follows for attemping better efficiency at each stage.

**1. Brown Stock Washing**

The aim of pulp washing is to free the pulp from the dissolved inorganic and organic solids by displacing the so-called black liquor by fresh warm water. On simple calculation, it can be observed that one tonne of pulp requires about seven tonnes of wash water to displace the mother liquor completely. But in practice this figure goes as high as 10 tonnes of wash water due to inherent inefficiencies in the washing plant. Even after using this amount of wash water, some mother liquor is left behind with the unbleached washed pulp which is known as liquor entrainment. Consequently, there are always bound and unbound chemical losses with the pulp

The economics in increasing the number of washing stages in a countercurrent washing system is well discussed in the literature. It may, however, be mentioned that the economics of washing is connected with the cost of steam, cost of chemicals, operatiotal cost, etc· which vary from mill to mill. For example, a mill with low steam cost at the evaporator plant can afford to keep higher dilution factor to reduce liquor entrainment in the washing plant; whereas other mills with higher fuel cost may ill-afford to have such a higher dilution factor.

There is a tremendous improvement in the washing system of late. The principle of diffusion washing system is slowly coming back with the development of more efficient equipments. This would allow a very low dilution factor with lesser chemical losses i. e. chemical losses as low as 12 kgs/tonne of pulp as against 18 kgs/tonne expressed as $Na_2SO_4$. It should also be noted that the chemical losses can be reduced by keeping low liquor to wood ratio using the same amount of wash water. Also if the white liquor concentration is maintained high in cooking, more black liquor will be required to adjust liquor to wood ratio. This would mean that less black liquor with higher concentration will go to the recovery plant. thereby reducing chemical losses in recovery. cycle.

**2. Black Liquor Oxidation**

Black liquor oxidation is getting more popular in the modern kraft mills mainly to reduce pollution. There are several processes for carrying out black liquor oxidation in Industry. Several other advantages of black liquor oxidation are stabilization of volatile sulphur compouuds, reduced corrosion of equipments, reduction in salt-cake and lime consumption, increase in total solids in weak black liquor, etc. The basic principle of black liquor oxidation lies in bringing about an efficient contact of air with black liquor at optimum process conditions. This reaction will bring down $Na_2S$ level of black liquor to 0.9 gpl. When $Na_2S$ level is below one gpl, the oxidation reaction of organic sulphur compounds starts vigorously in converting more volatile sulphur compounds to less volatile ones which are reduced to $Na_2S$ in the recovery furnace. This naturally increases the sulphidity with reduced salt-cake consumption. It was

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observed that sulphur recovery could be boosted up to 60% as against the original 50% by employing black liquor oxidation. As per our experience and also with the help of available data on the black liquor oxidation, it can be said that a saving of Rs. 11.00 to Rs. 12.00 per tonne of pulp is possible.

Attempts should be made to recover the sulphur losses both from digester relief gases and blow vapours to have still better sulphur recovery.

**3. Black Liquor Evaporation :**

An increase in black liquor concentration by 1% will result in a saving of about Rs. 4.00 per tonne of pulp. It is most important that the evaporator plant is operated at optimum efficiency with maximum number of effects possible. For example, it can be estimated that if one effect is by-passed then in place of one tonne of steam, 1.23 tonnes of steam is required. This would mean an additional cost of about Rs. 8.00 per tonne of pulp. Therefore, it is advisable either to by-pass an effect for tube cleaning for short time or to have a standby body. Thus the tube cleaning teachniques employed are of great importance to save cleaning time.

Depending on the types of scales, attempt should be made to deaccelerate the formation of scales by taking preventive steps suh as removal of fibers and silica from black liquor, water boiling and flushing out the scales. Furthermore, white liquor clarity, saltcake reduction and presence of dissolved refractory materials such as aluminium, chromium etc. in green liquor should be checked to ensure reduced scaling problems in the evaporator tubes. It is also to be noted that if black liquor oxidation is carried out, care has to be taken to avoid prolonged time for oxidation since under this condition the oxidised constituents have a tendency to form scales in the evaporator tubes. It has been observed that black liquor obtained by using eucalyptus wood or mixed hardwoods of some species have tendency of sudden increase in viscosity of black liquor, thereby plugging the evaporator tubes very often. Hence it is necessary to discuss the details of basic design aspects of the evaporator plant before it is ordered.

The selection of correct type of descaling technique also plays an important role, which can reduce the down time of any effect. In addition to the mechanical descaling cutters, chemical boiling technique can also be employed. Sulphamic acid and/or sodium hexametaphosphate in hydrochloric acid are quite effective for mild scales. Similarly, thermal shocks are also employed to dislodge the scales.

The chemical losses in this plant are mainly due to liquor contamination in the foul condensate. Proper liquor concentration and operational control can curtail the liquor entrainment. In long tube evaporators, demister pads are being employed to reduce liquor entrainment.

**4. Black Liquor Incineration :**

The main sources of chemical losses are from this unit in a chemical recovery plant. It is said that chemical carry-over, even in a well controlled furnace, is about 100 kgs/tonne of pulp as sodium sulfate. In a kraft mill the sulfate content in the flue gas dust is about 80% remaining being combustibles, sodium carbonate, sodium hydroxide, sodium chloride etc. This sodium chloride is particularly dangerous as it accelerates corrosion reaction of white liquor on mild steel. Efforts are being made to eliminate sodium chloride at this stage only. Attempts were also made to keep sodium chloride concentration at lower level by bleeding off adequate quantity of weak white liquor into multistage bleaching.

For recycling the carry-over chemicals in the flue gas, catchalls or hoppers are provided where the velocity is reduced so much as to drop down dust aggregates. The dust is either collected by an electro-static precipitator or a venturi scrubber giving 90% efficiencies. To improve this figure to 98% and also to recover the waste heat from flue gases, scrubbers requiring only low pressure drops are being employed after the electrostatic precipitator. Venturi scrubber evaporators give 90% dust recovery and also increase the thermal efficiency by recovery of waste heat to stack. The low investment involved and saving in fuel cost are making this unit more and more popular despite the high power consumption involved to maintain the required differential of 30 inches of water across the venturi for efficient scrubbing.

Another source of losses of recoverable chemicals is from the dissolver stack. By modifying the steam atomising nozzle, the carry-over from the stack are curtailed to a great extent. Further improvement in arresting the dissolver vent losses is reported by installation of a mist separator. This installation can reduce the dissolver vent losses from 8 to 0.5 kg. of sodium sulfate per tonne of pulp, thereby increasing the over-all recovery by 1%. Alternatively, it can also be connected to electrofilters inlet with controlled dampers.

Reduction of salt-cake is another most important factor. Lower reduction results in high dead chemicals in circulation, which means more chemical losses. However, excess salt-cake is to be avoided to avoid digester heater fouling. Further, excess salt-cake forms complex compounds particularly with the mineral constituents of the wood. Complete conrol is necessary to get maximum reduction possible in the furnace. The efficiency of the furnace operation is reflected in the reduction figures in green liquor. As the reduction analysis of the smelt consumes long time, it is difficult to exercise this control in the furnace operation immediately. An indirect quicker method is to find out green liquor sulphidity to control the operation. It was found necessary that the char bed temperature should be kept on lower side to keep down the chemical carry-over. This can be possible only when adequate quantity of salt cake is added along with controlled combustion. Similarly, free alkali in the black liquor should be high so as to get low melting smelt to avoid smelt pool troubles even at the low furnace temperature. It has also been reported that the melting point of the smelt will be lowest at the sulphidity of 32%. Thus the sulphidity in the range of 28 to 34% is desirable for smooth furnace operation.

To reduce the chemical carry-over and their consequent condensation on the boiler tubes, it is also necessary to reduce air temperature, to maintain low char bed level and to have a fine spray at the liquor injection zone of the furnace. The primary, secondary and tertiary air should be so adjusted as to have maximum turbulance at the secondary air port level. Minimum auxiliary fuel should be used as and when necessary to reduce chemical carry-over.

### 5. Green Liquor Causticizing

In causticizing department the process control plays a very important role. The chief source of nuisance is the lime. The quality of lime changes quite frequently and, therefore, each quality of lime will have different characteristics in slaking, causticizing, mud settling and mud washing. It calls for ingenuity of the operator to narrow down process variations.

The authors have carried out complete process evaluation of the causticizing section and could locate the points of least resistance. When a better control is exercised at these points, the product uniformity was improved. Thus the wide variations in the lime quality could be well taken care of by process control.

As is well-known, clarity of green liquor, lower concentration of green liquor, high reaction and slaking temperature and mode of green liquor addition to lime have definite effect on the completion of reaction and filter cake washability. If lime sludge reburning is to be done, it is essential to keep $Na_2O$ content as low as 0.3% to avoid operational difficulties.

### Conclusions

Strict process control can bring about better chemical and thermal efficiencies in any pulp mill. The following table indicates the potential sources, where the chemical efficiency can be increased.

| | Losses in Kgs. as $Na_2SO_4$ per tonne of pulp | | Losses, in % | |
|---|---|---|---|---|
| | Present | Future | Present | Future |
| 1. Brown Stock washing. | 20.0 | 15.0 | 2.95 | 2.21 |
| 2. Evaporator condensate. | 1.0 | 0.5 | 0.15 | 0.08 |
| 3. Stack losses. | 25.0 | 15.0 | 3.68 | 2.21 |
| 4. Dissolver Vent. | 10.0 | 1.0 | 1.50 | 0.15 |
| 5. Miscellaneous. | 15.0 | 10.0 | 2.21 | 1.50 |
| Total | 71.0 | 41.5 | 10.49 | 6.15 |
| Recovery efficiency % | — | — | 89,51 | 93,85 |

Under the present trend of rapid rise in prices of chemicals and raw-materials, it is absolutely necessary to make all efforts in further improving chemical and thermal recovery efficiencies. Any additional capital investment for new equipments will be justified if they can increase the over-all recovery efficiency. It is only regular process evaluation and consequent better process control that will boost up the economics of the recovery plants.

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