

Kraft Mill Odour Control Goes with Energy Economy

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SUMMARY

The paper discusses the sources of sulphur losses in an alkaline mill recovery system. These malodorous gaseous discharge is due to total reduced sulphur (T.R.S.) compounds. The main contributors to T.R.S. in a kraft process are the recovery furnace, direct contact evaporator, multi effect evaporator, smelt dissolving tank, brown stock washers and lime kiln. Quantities of T.R.S. emissions from different units have been given.

INTRODUCTION

Recovery process was developed during the beginning of 20th Century only to recover the valuable chemicals from the spent cooking liquor. As technology improved a thought was given to energy recovery in addition to chemical recovery. Later on a large recovery furnace was considered essentially as a steam generator rather than as an equipment for chemical recovery. The concept of recovery unit has further changed and as on to-day, is a system which has efficient energy and chemical recovery with minimum odour emission and maximum reliability/availability.

One may think that the odour control may not be necessary in the present context, as we are not having any statutory regulations on emissions. But if we look into the chemical and energy aspects of a recovery unit, a conclusion can be arrived that any control to reduce emissions goes together with energy conservation. In fact the odour emissions from a recovery unit can be taken as a parameter to judge the total performance of the unit.

While the sodium recovery of the cycle is generally 88-94%, the sulfur recovery of the cycle would be 80-86%. In a mill with higher sodium recovery lesser salt cake is added as make up, sulfidity tends to decrease because of higher sulfur losses as malodorous emissions. Thereby a lower limit of sulfidity may be reached that affects the rate of pulping and its quality, which necessitates the addition of elemental sulfur in the furnace.

The most critical of the malodorous gaseous discharge are the total reduced sulfur (TRS) compounds. Components usually included are hydrogen sulfide, methyl mercaptan, dimethyl sulfide and

dimethyl disulfide. Other similar components are also present but usually not identified.

The principal potential contributors of TRS in the kraft process are the recovery furnace in combination with the direct contact evaporator, multiple effect evaporator, smelt tank, brown stock washers and lime kiln. The range of emissions from a kraft mill operated under non-optimum conditions is given in the Table-I.

RECOVERY FURNACE

The burning of black liquor provides the source of particulate and gaseous sulfur emissions from a recovery furnace. Malodorous emissions are generally associated with incomplete combustion. As reported by Murray and Rayner ⁽¹⁾, Thoen Dehaas, Tallent and Davis ⁽²⁾, and Clement and Elliot ⁽³⁾, the recovery furnace when operated properly with sufficient combustion air is not a source of malodorous gas discharge. R. K. Bhada, *et al.* ⁽⁴⁾ predicted the influence of operating variables on odour emission. From this analysis the following conclusions obvious:

1. Increase in total air to unit as a percent of theoretical air increases the SO_2 emissions.
2. Increase in primary air temperature decreases the emission.
3. Increase in heating value of solids decreases the emission.
4. Increase in black liquor solids concentration decreases the emission.

It is evident from the above points that any effort to decrease the emission from the furnace by controlling the operating variables will increase the unit thermal efficiency. Proper recovery furnace operation under controlled conditions has resulted in discharge gas concentration less than 1 PPM Hydrogen sulfide with an increase in thermal efficiency ⁽¹⁻³⁾.

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Another important factor which has to be considered apart from emission and thermal efficiency of a recovery unit is its availability. The most influencing parameter which determines the availability of the recovery unit is fumes carryover from the furnace bed. Unfortunately any control to decrease fumes carryover by changing the above mentioned and other operating variables, like air distribution between primary and secondary, molar ratio of S/Na₂ in black liquor, chlorine content in black liquor, increases the emission. Hence, optimisation of operating variables has to be made to decrease the emissions and fumes carryover and to increase the unit thermal efficiency (^{4,5}).

DIRECT CONTACT EVAPORATOR

The days when fuel costs were low and liquors were exceptionally difficult to concentrate, direct contact evaporators received attention as a means to supplement the work of a multiple effect evaporators.

It has been estimated that about 50% of the total sulfur emission to the atmosphere emanates from the direct contact evaporator (⁶) even the evaporation plant and digester house are considered. Obnoxious gases are released through the interaction of flue gas and black liquor in the direct contact evaporator.

The most comprehensive investigation of variables influencing hydrogen sulfide emission from a direct contact evaporator has been conducted by Murray and Rayner (¹). The studies show that an important factor in release of hydrogen sulfide is the decrease in liquor pH caused by absorption of carbon dioxide from the flue gas. Lower liquor pH and high sodium sulfide concentration in the liquor favour hydrogen sulphide emission. Analytical work by Babcock & Wilcox has determined reactions that can be assumed to occur in direct contact evaporator as follows :

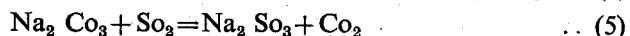
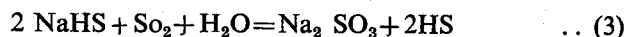
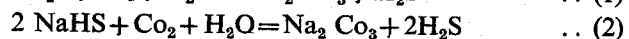
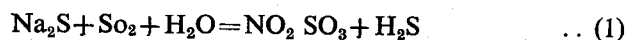
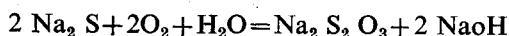


Table-II gives the typical gas analysis before and after direct contact cyclone evaporator with unoxidised liquor on dry volume basis (³). There are two known methods of controlling malodorous gas emission: (a) Elimination of sodium hydrosulfide/sodium sulfide from black liquor by liquor oxidation. (b) Elimination of direct contact evaporator.

WEAK LIQUOR OXIDATION—Weak liquor oxidation helps to control only the emissions from multiple effect evaporators. Weak liquor oxidation has not been broadly applied because of attendant liquor foaming problem. Various approaches to oxidation with minimum foam formation are still under study.

Multiple effect evaporators produce low volume, high concentration, non-condensable gases containing malodorous compounds. This stream can be incinerated advantageously in the lime kiln or in the recovery or power boilers instead of going for weak liquor oxidation.

HEAVY LIQUOR OXIDATION—In order to prevent methylmercaptans and apparent alkyl sulfide stripping from direct contact evaporator, the entering liquor could be oxidised (heavy liquor oxidation) to a point where the remaining sodium sulfide concentration approaches zero. During heavy liquor oxidation the unstable compounds of sodium are oxidised to stable sodium thiosulfide.



Eventhough liquor oxidation seems to present the added benefits of increased sulfidity, evaporation of water from liquor, these benefits are not expected to off set the disadvantages of oxidation.

Since the oxidation reaction is exothermic in nature, the heating value of the liquor decreases. The magnitude of loss depends on the amount of sulfide oxidised. The heating value was determined (⁸) for a sample of unoxidised liquor from the multiple-effect evaporator at 50% concentration and also for the same liquor sample oxidised under controlled laboratory conditions by passing oxygen through the sample. In the dry state, oxidised liquor was found to have a gross heating value of 5980 BTU/lb, whereas unoxidised liquor was reported at 6140 BTU/lb.

In the oxidation equipment, the exothermic heat of reaction can only be used for hot water production instead of steam generation which is a noticeable disadvantage. However, concentration of liquor in the oxidation process increases slightly. The economics of this occurrence is such that it saves 1 Kg of 35 psig steam in the multiple effect evaporator at the expense of 4 kg of high pressure steam in the recovery unit, since that concentration of liquor in the oxidation system occurring on 1:1 basis. Grace, T.M. (⁷) says "the net steam production from a recovery unit using black liquor oxidation and direct contact evaporator is 4% less than for a direct fired system". Moreover the power requirement for oxidation is 0.5 to 0.9 HP/Tonne of pulp, depending upon the Na₂S concentration and liquor density. The decrease in heating value of the liquor due to oxidation increases emission from the recovery unit.

ELIMINATION OF DIRECT CONTACT EVAPORATORS—Considering the available technology and energy consumption of black liquor oxidation, many countries decided to eliminate direct contact evaporators, which have proved to be the major source of odorous emission and increased energy consumption.

In systems using direct contact evaporators, flue gas leaves the boiler at a temperature of 350°C, but in a system without direct contact evaporator, the flue gas temperature can be dropped as low as 140–150°C. A temperature of minimum 140°C is necessary to satisfy the warm electrostatic precipitator requirements. As a rule, a 20°C change in exit gas temperature varies the thermal efficiency by approximately 1%. A thermal efficiency difference of 5% is obvious between the systems with and without direct contact evaporators. If we look closer into the direct contact evaporator operation, conclusion can be arrived that the energy corresponding to 5% difference in efficiency is not being utilised efficiently. The evaporation ratio of the direct contact evaporator is about 1:1, whereas the same can be done in a multiple effect evaporator with a ratio of 4:1.

While there is a drop in gas temperature across the direct contact evaporator, the combined heat of the gases and the evaporated water leaving the evaporator is nearly the same as the total heat of the gas entering the evaporator. Any small difference may be accounted for by radiation losses, leakage and heat absorbed or given up by the remaining liquor.

Table-III shows a comparison of heat balance of a chemical recovery unit equipped with a direct contact evaporator and with no direct contact evaporator (8). With identical amounts of black liquor solids and salt cake make-up, a difference in efficiency of 3.4% can be seen. Apart from drop in thermal efficiency by the use of direct contact evaporators, consumption of power also increases to the tune of 7 HP/Tonne of pulp.

Robertson (9), compared thirteen different systems to reduce the purchased fuel cost (Table -IV), and found that the fuel cost is low for the new combustion engineering and B & W systems. The new combustion engineering system uses air contact evaporator instead of flue gas contact evaporator and in the B & W system solids are being fired directly from the multiple effect evaporators at the desired concentration and an extended surface economiser is used to recover the heat from the flue gas.

Elimination of direct contact evaporator increases smoothness of the liquor and pH stability. Smoothness and pH stability of the liquor are essential to maintain stable flame in the furnace, and to improve electrostatic precipitator performance.

MULTIPLE EFFECT EVAPORATORS

To-day, experience and technology are available to make possible the installation of multiple effect evaporators that will produce concentrated liquor at 60 to 65% solids consistent with established liquor burning characteristics.

Recovery boiler installations in Sweden, Norway, Finland, Italy, Spain and other European countries operate without direct contact evaporators. For

example in Sweden, the country where fuel efficiency assumed top priority than any other country, there are 45 units operating without direct contact evaporators.

However there is a reluctance in America to accept that multiple effect evaporators can be designed and satisfactorily operated at solids discharge concentration compatible with recovery furnace operation. This attitude is to longer extent, the result of poor operation, some thirty years ago, with high concentration, forced circulation evaporators in many mills. Contributing most to poor experience with tube fouling, was the use of steam at 100 to 125 psig in contrast to maintaining steam pressure at less than 50 psig saturated as currently recommended. The high pressure gave a much higher metal temperature which caused rapid scaling. Kraft mill pulp washing and causticising have been further improved over years so that fibre and calcium in the liquor going into the evaporators are greatly reduced.

Continuity of operation requires recognition of the design and cleaning problems posed by heavy liquor operation. Available experience from operating installations demonstrates techniques to evaporate liquor at high solids without interruption of pulp production.

The two alternatives available for strong liquor effect at the time of design are natural and forced circulation. Forced circulation strong liquor effect is the most constructive design. In a typical sextuple, natural circulation long tube (LTV) evaporator, the final liquor concentration is attained in a forced circulation stage. Weak liquor at 13% solids enters both the fifth and sixth effects by a feed arrangement. Soap skimming is provided at 30% solids concentration after the third effect to prevent the possible fouling in the following stage.

The forced circulation stage is divided into three sections, each having its own circulation system. One section is washed continuously with liquor from the second effect at 35% solids. The liquor then passes through the two pass, first LTV effect.

Liquor leaving the first effect at 52% solids is concentrated to 64% in the other two sections of the forced circulation concentrator operating in series. Final liquor concentration of 65% is achieved by flashing.

A three section concentrator will provide the capability of continuous cleaning in one section with a throughput of lower concentration liquor. The sections will be switched in a sequence so that each is cleaned on a routine schedule.

ODOUR CONTROL FROM OTHER EQUIPMENTS

Malodorous gas streams from other equipments can be thermally incinerated with advantage in lime

kiln or recovery unit. In the new systems, high-concentration, low-volume gas streams from the multiple effect evaporators and digesters, and low-concentration, high-volume gas streams from the brown stock washers are being incinerated in the recovery unit or lime kiln.

The presence of organo sulfur compounds are of minor significance from the smelt dissolving tank. The organo sulfur compounds could not exist at the smelt temperature. Their presence in the dissolving tank vent gases could be attributed to outside sources such as drafted gas from the furnace reduction zone, water used in the smelt tank. However methods are available and practiced to recover heat and chemicals from the dissolvent.

For a soda recovery boiler having an output of steam 50T/hr, the losses of heat and chemicals from the smelt dissolving tank exhaust are 1.5-2 T/hr and 1-10kg/hr (as sodium oxide) respectively (10).

TABLE—I

S. No.	Potential Source	TRS*
1.	Digester Relief and blow (Batch)—	0.63-4.52
2.	Brown Stock Washers —	0.13-0.41
3.	Multiple effect evaporators	
	(a) Oxidised Liquor —	0.21-0.52
	(b) Unoxidised Liquor —	0.26-4.6
4.	Recovery furnace before DCE —	1.03-5.14
5.	Recovery furnace after DCE	
	(a) Oxidised Liquor —	0.17
	(b) Unoxidised Liquor —	5.7-33.2
6.	Smelt dissolving tank —	0.005-0.13
7.	Lime Kiln —	0.01-0.63

*Values represent emissions as lb of Hydrogen sulfide/tonne of air dry pulp.
Source : Air pollution control and industrial energy production—Noll. Davis Donlass.

TABLE-II

GAS ANALYSIS BEFORE AND AFTER
DIRECT CONTACT CYCLONE EVAPORATOR
WITHOUT UNOXIDISED LIQUOR
DRY VOLUME BASIS

	Before Cyclone	After Cyclone
Oxygen, %	1.1	—
Combustibles, %	0	—
Hydrogen sulfide, ppm	0.1	86.5
Methyl Mercaptum, ppm	nil	3.4
Dimethyl sulfide and Dimethyl- disulfide, ppm	nil	1.0

TABLE—III

STEAM GENERATION COMPARISON
BETWEEN DIRECT CONTACT EVAPORATION
SYSTEM AND DIRECT FIRED SYSTEM

	Direct con- tact eva- poration	No con- tact eva- porator
Solids from evaporator, %	50.0	60.0
Liquor temperature, °F	200	220
Firing Concentration, %	61.0	60.0
Air Heater	Steam Coil	Recirc. ah
Exit Gas temperature, °F	325	360
Gas weight leaving econ., lb/hr	304.000	305.000
Gas weight leaving direct contact evap., lb/hr	322.000
Gas volume to precipitator, ft ³ /min (actual)	115.500	110.500
Steam flow., lb/hr.	225.000	223.009
Steam-to-steam coil air heater, lb/hr.	14.600	...

HEAT INPUT, BTU/HR

Value	6,000	6,000
Sensible heat in liquor	175	159
Sensible heat in air from steam coil air heater	253	0
Liquor heater input	28	0
Heat Input	7056 353X10 ⁶	6759 338X10 ⁶

HEAT DISTRIBUTION %

Dry Gas	4.2	5.2
Water evaporated in furnace	10.6	11.6
Water evaporated in evaporator	6.4	0.0
Hydrogen in solids	5.6	5.9
Moisture in air	0.1	0.1
Radiation loss	0.5	0.5
Unaccounted for and mfgs. margin	2.5	2.5
Molten smelt	3.5	3.6
Reduction of salt cake makeup	1.7	1.8
Reduction of sulfur in liquor	5.0	5.2
Heat in steam	59.9	63.3

A system proposed by the Leningard Technological Institute for recovery of chemicals alone comprises a spray nozzle and a separator. Such a system has been installed at the Astrabhan Mill (USSR) and gives over 80% recovery.

Another system installed on the tampella boilers, consists of a spiral heat exchanger and a blower mounted on the exhaust pipe of the dissolving tank. The chemicals are recovered by condensing the steam vapour mixture on the surface of the heat exchanger to produce hot water as by product. The condensate mixture is returned to the dissolving tank.

TABLE-IV
COMPARISON OF ANNUAL FUEL COSTS FOR THIRTEEN DIFFERENT
RECOVERY BOILER SYSTEMS

System Description	Liquor Concentration % Solids	Feed Water Temperature °C	Annual Fuel Costs Rs.	Annual Fuel Costs Difference Rs.
1. No. DCE, SCAH	—	120	59,62,968	—2,27,916
2. No. DCE, RAH	—	149	58,72,590	—3,18,294
3. No. DCE, SCAH	—	149	58,45,959	—3,44,925
4. ACE	50	149	63,07,704	+1,16,820
5. ACE	55	149	59,92,344	—1,98,540
6. DCE, No. OX.	—	149	61,90,884	O-Base
7. DCE, WITH OX.	—	149	62,50,767	8,883
8. No. DCE, RAH	—	182	58,60,800	—3,31,884
9. NO. DCE, SCAH	—	182	57,92,454	—3,98,430
10. ACE	50	182	60,71,040	—1,19,844
11. ACE	50	287	57,74,427	—4,16,457
12. DCE, NO. OX	—	182	59,74,812	—2,16,072
13. DCE, WITH OX.	—	182	60,61,770	—1,29,114

DCE = Direct Contact Evaporator

RAH = Regenerative Air Heater

SCAH = Steam Coil Air Heater

OX = Black Liquor Oxidation

ACE = Air Contact Evaporator

Comparison and made by taking one power boiler and the recovery boiler system into consideration. The power boiler efficiency has been taken as 85%.

ALTERNATIVE SYSTEMS

It can be stated that by replacing direct contact evaporators, more efficient recovery of energy is possible besides eliminating the majority or possibly all unpleasant odour. There are many low odour and low energy systems available while considering new installations as well as for converting existing installations. The new systems include :

- (a) Large economiser and air heater to drop the flue gas temperature, the liquor being fired directly from the multiple effect evaporator.
- (b) Large economiser and air heater to drop the flue gas temperature, the final liquor concentration being obtained in an air contact evaporator.
- (c) Economiser-circulation air heater system, liquor firing directly from multiple effect evaporator.
- (d) Economiser-steam air heater, liquor firing directly from multiple effect evaporator.

The design of cast iron extended surface and tubular steel economisers are standardised in such a way that it may not be a factor that influences the boiler availability. The cleanliness of the surfaces can be maintained by the use of retractable soot blowers or steel shot circulation. The air heater designs include tubular air heater with retractable soot blower and regenerative air heaters.

Replacement of direct contact evaporator, with suitable modified equipments in a operating mill is a unique problem depending upon the existing

system design and there can be no generalised conclusion in converting existing units. Two such converted units are operating in U.S.A., and many mills also selected this approach and are in the process of conversion. However, existing pulp mills have numerous options as already mentioned for converting recovery systems to have low energy consumption and low emission. The existing equipment system must be analysed together with other equipment modifications necessary, and by taking the experience of the converted units into consideration to determine the most economical conversion systems.

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