THE RECOVERY OF SODIUM SULPHITE COOKING LIQUOR

Submitted to the Faculty of Graduate
Studies and Research in Partial
Fulfilment for the Degree of M.Eng.
in Chemical Engineering.

May, 1939

Gordon H. Gribbins

PREFACE

In the investigation of this problem the major part of the time was spent in the construction, erection and adaptation of the required equipment to incineration of waste liquor.

A great deal of space could be filled describing the various mechanical difficulties encountered; for example, considerable time was spent in attempting to adapt a belt and pulley auxiliary drive mechanism to rotate the furnace. This was eventually scrapped and a chain and sprocket drive used. It is deemed advisable, however, to omit such descriptive details from this treatise, as they would be uninteresting and of minor value to future readers.

At this point I would like to express my appreciation to Dr. J.B.Phillips, the director and instigator of this research, and to Mr. J. Holden for his valuable suggestions.

TABLE OF CONTENTS

INTRODUCTION

Many investigations have been carried out which conclusively show that sulphite pulp prepared by digestion with sodium sulphite is much superior to that obtained using the present calcium base process. Higher yields, easier bleaching properties, and a strength rivalling Kraft, especially in the case of resinous pines, are the major benefits reported(1).

It is evident that were such a process economically feasible it would be of considerable value, especially to pulp mills in the vicinity of large tracts of pine forests. Unfortunately, the economy of the process depends upon the efficient recovery of the relatively high-priced sodium salts from the spent liquors. A number of fundamental investigations have been attempted, but none of these have yet been attended with any degree of commercial success.

It was the purpose of this investigation to study the recovery of sodium salts through the combustion of waste liquor in a gas-fired rotary furnace. Unfortunately, a number of factors militated against the active prosecution of the problem and retarded the progress of the research to a degree not initially anticipated.

LITERATURE SURVEY OF SODIUM SULPHITE RECOVERY SYSTEMS.

The methods for the recovery of the sodium from waste sulphite liquor all involve first of all incineration of the concentrated liquor in a suitable furnace. The ash or smelt produced is then dissolved, refined, and the resulting solution treated with sulphur dioxide to regenerate sulphite or bisulphite.

The ash from incineration consists mainly of sodium in the form of carbonate, sulphide, and sulphate, accompanied by lesser amounts of thiosulphate and sulphite. These substances when treated directly with sulphur dioxide react in the following manner:

carbonate--------------------bisulphite or sulphite
sulphite---------------------bisulphite
sulphate---------------------inert
thiosulphate-----------------inert
sulphide---------------------thiosulphate, polythionates, free sulphur.

Consideration of these reactions shows that the problem resolves itself naturally into three distinct divisions:

(1) A study of those conditions which tend to give maximum yields of bisulphite or sulphite.

(2) Methods which may be used to prevent the accumulation of sulphate and thiosulphate in the system.

(3) The elimination of thiosulphate, polythionates and free sulphur, since these compounds interfere in the cooking process by converting sodium sulphite to sulphate before the pulping action is completed. In addition sodium thiosulphate stains the pulp.

It has been stated that the percentage of sulphide in the liquor for sulphiting should not exceed 12% of the total soda present. This will normally give about 5% of total soda as thiosulphate, which is the allowable limit that may be present without having any serious injurious effect on the cooking.(1) (2)

In the alkaline sulphate process the cooking liquor consists mainly of sodium hydroxide and sodium sulphide. It appears probable therefore that the ash from the sulphite process could be used in the sulphate system. An arrangement whereby a sulphite and a sulphate plant can be operated in conjunction has been devised. It is claimed that 75% of the sodium used as base recovered, and that the saving in bleach alone offsets this 25% loss.(3) However, where a sulphite plant is to be operated alone it is necessary to refine the products of the incineration. Some of the recent proposals for carrying this out will now be considered.

A: CRYSTALLIZATION PROCESSES.

In these processes the incinerating action on the concentrated waste liquor is carried to the smelting stage. The standard stationary furnaces used in the soda and sulphate recovery systems are directly applicable.

(1). Combustion and smelting in a reducing atmosphere to give the carbonate and sulphide; aqueous solution of the hot smelt and subsequent cooling to crystallize out the carbonate. This precipitate is then removed from the mother liquor by filtration and converted to the sulphite.(4) (5)

(2). Combustion and smelting in an oxidizing atmosphere to give the carbonate and sulphate. The smelt is then dissolved and the carbonate can either be precipitated out directly, or the solution carbonated to precipitate the bicarbonate.(6) (7) (8) (9)

Since methods are available for converting both the sulphide and the sulphate left over in these refining methods to usable compounds, (i.e., carbonate or sulphite) it is therefore evident that these crystallization processes hold considerable promise.

B: HAGLUND PROCESS.(10)

The cooking liquor used in this process is sodium bisulphite.

It is stated that the ash obtained after incineration of the concentrated waste liquor is purged from sulphides and thiosulphates by a "special process". The partially purified ash is then dissolved in water and mixed with finely crushed limestone. This suspension is pumped through a battery of reaction chambers where it comes in contact with sulphur dioxide gas, through action of which calcium carbonate and sodium sulphate are converted into the insoluble calcium sulphate and sodium bisulphite.(11)

$$Na_2 So_4 + Ca (H So_3)_2 \longrightarrow 2 Na H So_3 + Ca So_4.$$

This gives a satisfactory method for converting the sulphate, but since it is not yet generally accepted it is logical to assume that the "special process" for removing the sulphide and thiosulphate from the ash is not economically sound.

One disadvantage to the Haglund cooking process is that the neutral cook using sodium sulphite (full Keebra) gives a better pulp than the acid cooking process.(1)

C: CONVERSION OF SULPHIDE TO CARBONATE(12).

From Thorpe's "Dictionary of Applied Chemistry" we find that there are three possible methods for converting sulphide to carbonate.

(1) Add an equivalent quantity of sodium bicarbonate to a solution of the sulphide. On evaporation to dryness yields of sodium carbonate as high as 96% are obtained.

(2) Passing excess carbon dioxide into a solution of the sulphide.

(3) Addition of alumina to the sulphide solution, and passing heated air through to form sodium aluminate, which on treatment with carbon dioxide yields the carbonate.

Based on the first method the following steps for the complete conversion of the ash on an industrial scale have been proposed.

(1) Spent liquor evaporated to 55% solids. Heat for evaporation obtained from (2) (waste heat boiler).

(2) The concentrated liquor sprayed into a suitable furnace and incinerated. The quantitative composition of the ash will depend to a large extent on furnace conditions. Losses of sodium replaced either with the sulphate or the

carbonate. If the sulphate is to be used it would be introduced into the furnace, if the carbonate used introduced at step (5).

(3) The ash then mixed with sodium bicarbonate. The bicarbonate used is prepared from step (6). It should remain 50% moisture to react most favorably with the sulphide.

(4) The mixture heated to a temperature above 200 degrees centigrade. The following reaction occurs:

$$Na_2 S + 2Na H CO_3 - 2 Na_2 CO_3 + H_2 S.$$

The hydrogen sulphide eliminated is conducted to the sulphur burner in the acid plant and burned to produce sulphur dioxide to be used in step (7).

(5) The above material dissolved in H_2O and insoluble substances separated by settling or filtration. The clear solution consists of $Na_2 CO_3$.

(6) CO_2 added to the solution to remove sufficient ppt'd $Na H CO_3$ to be used in step (3).

(7) The carbonate solution diluted and sulphited.

$$Na_2 CO_3 + 2H_2O + 2 SO_2$$

$$- 2 Na H SO_3 + H_2O + CO_2$$

D: OTHER METHODS FOR CONVERTING SODIUM SULPHATE(13).

Sodium sulphate may be converted to the sulphide and hence to the carbonate by treating with (a) coal (b) reducing gases, carbon monoxide or (c) water gas. A highly reducing atmosphere in the incinerator under favorable temperature conditions might therefore serve as a method for removing sulphate and sulphide.

E: THE KEEBRA PROCESS(2).

In the recovery of black liquor from the semi-Keebra process (alkaline, sodium hydroxide and sulphite) it was found that with smelting or high temperature incineration that it was impossible to keep the sulphide content low. Claimed that low temperature rotaries operated with scarcely any auxiliary fuel should be used.

With the full Keebra process (neutral, sodium sulphite) it was stated that it is possible to use the residual liquors over and over again upon addition of a further amount of sulphite(14).

RECOVERY SYSTEMS UNDER PRESENT DAY ALKALINE PULPING PROCESSES

It is probable that any system for the recovery of sodium sulphite waste liquor will be similar to that used for the sulphate or soda process, at least in so far as the type of equipment is concerned. Hence, it is of advantage to consider some of these systems which are in common use.

(A) The Murray-Waern-System

This is the most satisfactory system at present on the market using a rotary incinerator, operated in conjunction with a stationary smelting furnace. In the rotary unit the concentrated liquor is dried by the hot gases from the smelter and the combustible material partially burned out. In the smaller unit the remainder of the combustible material is burned out, the chemical ash fused, and then drained to the dissolving tank. Among the auxiliary equipment are included: a waste heat boiler; air heater, disc evaporator, gear pump for feeding the liquor and an induced draft fan.

Noteworthy features of the system are:

(1) The patented seal between the rotary incinerator and the smelter to effectively render the system gas tight.

(2) The drip feed or coarse spray used to minimize entrainment of liquid particles in the gas stream, which would be dehydrated and burned in suspension, resulting in loss of ash up the stack.

(3) The water cooled liquor injection pipe used to prevent blocking of the line through premature carbonization.

(4) The system functions under induced draft, hence its operation is not accompanied by leakage of obnoxious gases, is easier controlled than forced draft, and most important, eliminates the unexplainable "back draft" often found in rotary installations.

(B) The Babcock-and Wilcox-Tomlinson and Wagner Systems. (16)(17)

Both of these systems use a stationary furnace or smelter. These stationary furnaces are essentially large, vertical, refractory lined vessels, having ample room for the stages of dehydration, combustion and smelting to take place. The concentrated black liquor is usually injected under pressure with air in the form of a coarse spray against the walls of the furnace. Air is supplied in most installations by means of a forced draft fan. No auxiliary fuel is required, the heat of reaction of the organic combustible matter in the liquor being such that a temperature as high as 1700° Fah. may be produced in the upper zone of the furnace.

THE ROTARY VERSUS THE STATIONARY FURNACE FOR SODIUM SULPHITE RECOVERY

The principal objection to the rotary furnace alone is that it is practically a certainty that expensive equipment such as a Cottrell Separator will be necessary to remove the light ash from the flue gases. The main advantage is: that since the operation is continuous, conditions of combustion may be varied over wide limits. There is the possibility that optimium conditions may be found such that the ash obtained will contain only small quantities of objectional materials.

The major disadvantage to the stationary furnace at present is the smelting action (i.e. high operation temperature) which gives rise to high sulphide content. Even with this disadvantage, however, the furnace offers possibilities when operated in conjunction with the Crystallization Refining Processes as formerly discussed. Again, there is no reason why a stationary furnace could not be operated carrying the action only to the final combustion stages, eliminating smelting altogether. Considerable advantages are gained in that the system is mechanically simpler and easier to control than the rotary furnace, and can be designed and operated in such a manner as to practically eliminate ash loss up the stack.

From this discussion it would appear that the qualities inherent to a stationary furnace appear to be superior to those of a rotary, yet, the quality of continuous and widely variable operation is of such importance that it warrants further study of the rotary furnace.

PROPOSED FIELD TO BE INVESTIGATED

It was proposed to determine what variations in the constituents of the ash could be obtained by altering the conditions of incineration.

We have seen that previously proposed refining methods all involve treatment of the ash after incineration. If refining could be accompanied during combustion in the furnace it is evident that the process would be much more feasible, at least from an economic consideration.

In view of the reactions offering possibilities as previously discussed, it can be seen that the major factors which may be varied so as to produce a desirable ash are:

(1) Addition of substances during or previous to incineration, e.g. sodium bi-carbonate, calcium carbonate.

(2) Temperature.

(3) Incinerator atmosphere, i.e. reducing or oxidizing.

SHORT DESCRIPTION OF THE ROTARY FURNACE AND AUXILIARIES.

See Figure I. - page 17.----

The rotary A itself is of 4-inch Shelby tubing, (Stainless Steel) 18 inches in length. It is refractory lined to withstand the high temperatures and the corrosive action of the waste liquor and flue gases, and is well lagged on the outside with magnesia.

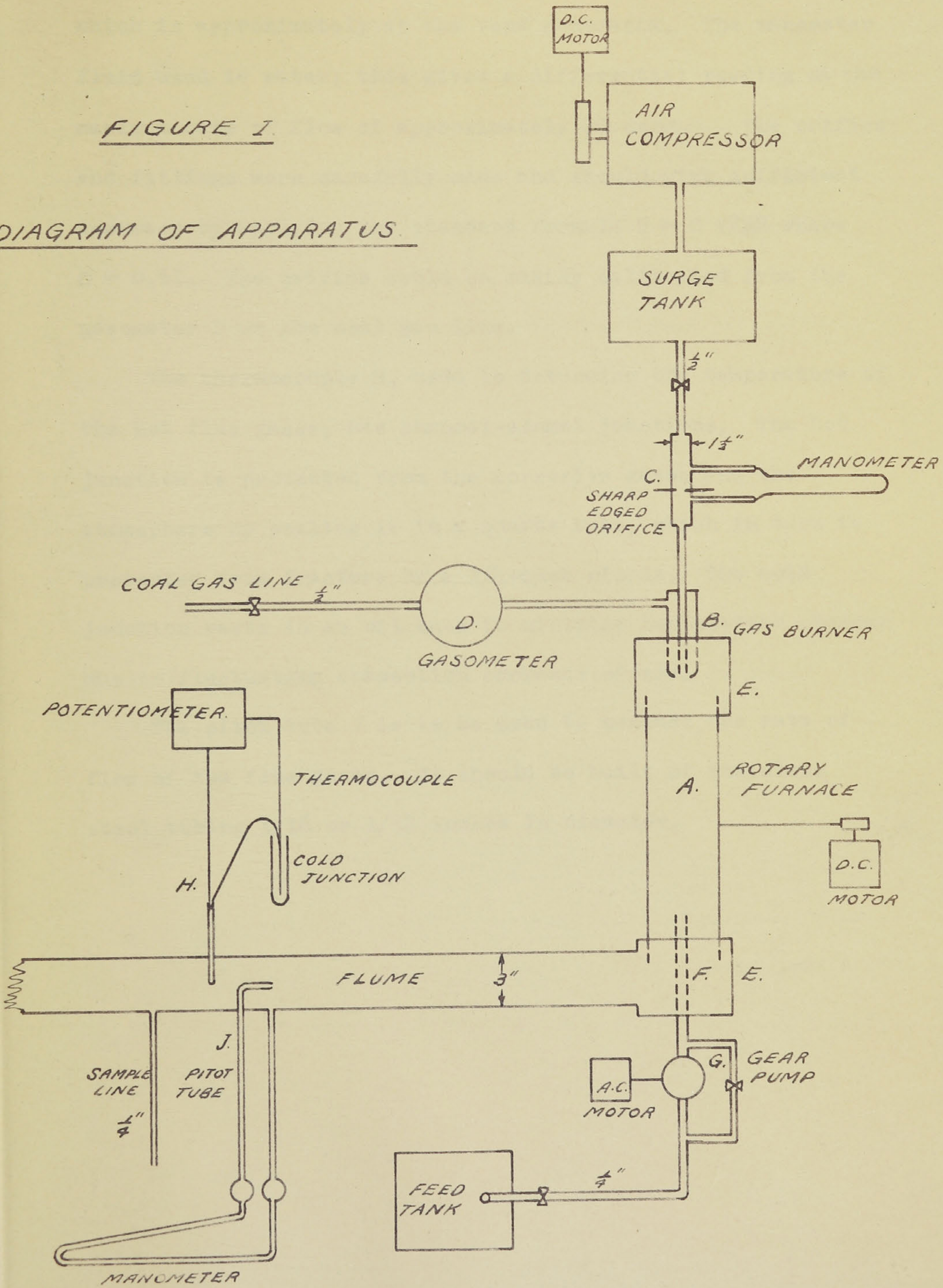
The furnace ends E are simply 3-inch standard Tees with one series of threads machined out to fit snugly over the rotary tube.

The gas burner B is of a construction similar to the standard laboratory blast burner, with the air in the inner tube and the coal gas flowing in the annular space. A 1-1/2 inch cap, drilled centrally 3/4 inch and machined to a taper is used for a nozzle.

The sharp-edged orifice C for measuring the flow of air was made from hard steel plate. The diameter of the orifice is 0.406 inches, and the ratio, diameter of orifice to diameter of tube equals 0.252 inches, which is within the range of standard practice for gases. The upstream manometer tap is placed at a distance of 2 inches from the orifice, and the downstream tap at a distance 0.6D (D = diameter of pipe),

FIGURE I

DIAGRAM OF APPARATUS



which is approximately at the vena contracta. The manometer fluid used is water; this gives a differential reading at the maximum rate of flow of approximately 20 cent. The orifice and fittings were carefully made and should give sufficient accuracy by applying the standard formula $U = C\sqrt{2gh}$ where $C = 0.61$. The orifice could be easily calibrated from the gasometer D on the coal gas line.

The thermocouple H, used to determine the temperature of the hot flue gases, has chromel-alumel junctions. The hot junction is protected from the corrosive gases and the atmosphere by sealing it in a quartz tube, which in turn is protected from fracture by a 1/4-inch nipple. The cold junction rests in an oil bath to minimize temperature changes due to fluctuating convection currents of air.

The pitot tube J is to be used to measure the rate of flow of the flue gases. It should be built of stainless steel tubing 1/16 or 1/32 inches in diameter.

THE OPERATION OF THE FURNACE.

It is desired in the incineration to approach as closely as possible to conditions applicable to commercial operation, hence a process of continuous combustion under constant equilibrium conditions should be used.

The conditions of incineration will depend to a large extent on the following variables, which should be carefully regulated and measured for each run.

(1) fuel ratio; gas: air

By varying this ratio both the temperature and incinerator atmosphere can be changed. In an industrial installation the use of an auxiliary fuel would be prohibited, since there is sufficient fuel value in the concentrated waste liquor to support its own combustion.

(2) Speed and inclination of rotary.

(3) Rate of liquor feed.

The upper limit here is the rate of feed that will result in continuous operation without quenching the apparatus. The rate at which the liquor travels through the furnace can be controlled by varying either or both of (2) and (3) above.

THE PREPARATION OF WASTE LIQUOR.

(1) Once the furnace is operating satisfactorily, it would be necessary to obtain a supply of waste sodium sulphite cooking liquor. Proposed to cook jack pine under conditions which would produce a pulp and liquor comparable to that which would be obtained in the commercial sulphite process(18). To carry out this operation use should be made, if possible, of the large experimental digester in the Forest Products Mill. With the small laboratory digester only 900 cubic centimetres of liquor can be obtained per run. The consistency of the weak waste liquor only ranges from 10 to 12% solids, and must be evaporated to 50% solids. Therefore with an initial 10% liquor, only get 180 c.c. of concentrated liquor per cook. As quite large quantities of liquor are required to make even one test with the furnace, since steady conditions must be reached if the results are to be of any value, it is evident that this laboratory digester presents a very inefficient and laborious means of obtaining the waste liquor.

(2) Evaporation of the liquor to 50% solids. There are two evaporators in the Chemical Engineering laboratory which could be used for this purpose, a small vacuum evaporator , and a larger forced circulation evaporator. The liquor is

very foamy, which necessitates careful control of the process. The progress of the evaporation can be followed by withdrawing samples from time to time and determining their specific gravity. (range 1.045 to 1.27).

In order to test the operation of the furnace before going to the trouble of preparing some sodium base liquor, it was deemed advisable to use readily available calcium bisulphite liquor. The burning characteristics of this liquor will be the same as the sodium sulphite liquor. Howard Smith Paper Mills Limited kindly co-operated and supplied 20 gals. of their spent liquor. This was evaporated down to 50% solids and incinerated in the gas-fired rotary furnace.

OPERATION DIFFICULTIES; OBSERVATIONS; SUGGESTIONS.

Originally it was intended to use a preheating section and spray the liquor into the furnace. Unfortunately rapid carbonization occurred in the line and this had to be abandoned. There is a possibility, however, that using a weaker feed, and a high head gear pump, this preheating action may be adopted. The present feed line is of 5/8 inch pipe and the liquor is injected without spraying. Nevertheless even this is unsatisfactory since the capacity of the furnace requires a slow rate of feed, and carbonization still occurs in the heated section. To alleviate this condition a water-cooled feed line should be used.

It was also found that the feed pump has not sufficient head to give a steady flow of viscous liquor under anything but the best possible conditions. It was very difficult to operate the pump at its lowest capacity, which is approximately the maximum capacity of the furnace.

The major difficulty encountered in the operation of the furnace was an unexplainable back draft. This made it necessary to burn the liquor under a large forced draft, with the result that with the high gas velocities about 90% of the ash was carried up the stack. To accurately control the air supply and prevent this back draft an induced fan system should be installed. In addition the furnace as it stands is not of sufficient diameter in comparison to its length, hence even under normal conditions the gas velocity would be higher than absolutely necessary. Industrial rotary furnaces are built on a ratio of length to diameter of three. This furnace has a ratio of seven.

During one trial run flue gas samples were taken and analyzed.(19) A high content (2%) of carbon monoxide was found, which shows that it is possible to operate the furnace under good reducing conditions.

It is concluded that to adapt a rotary incinerator to the efficient combustion of waste liquor would be an expensive and difficult process.

BIBLIOGRAPHY

1. "The Monosulphite Process". Paper Trade Journal, 83. pp. 41,42. Dec.9.1926.

2. "The Keebra Process". James d'A. Clark, Paper Trade Journal. 83. p. 43,44. Nov.25,1926.

3. "Some Economical Aspects of Combined Sulphate and Sulphite Operation." Paper Industry.3 - p.1247.Dec.1921.

4. George A. Richter, U.S.P. 1,974,751, Sept. 25,1934.

5. "Pulping Wood Chips". George A. Richter. Chemical Abstracts. 28: 7531.

6. George A.Richter, U.S.P. 1,815,328 . July 21,1931.

7. "Recovery of Values from spent cooking Liquors obtained in Pulp Manufacture." George A.Richter. Chemical Abstracts. 25:5560.

8. George A.Richter. U.S.P. 1,906,882, May 2, 1933.

9. Recovering Substances from spent cooking liquors obtained in Pulp Production." George A.Richter. Chemical Abstracts, 27:3608.

10. "Interest grows in Sodium Sulphite Process." Pacific Pulp & Paper Industry. 8 - No.7. p. 5-6 July 1934.

BIBLIOGRAPHY - (Continued)

11. "Soluble Sulphites and their Bi-Sulphites in the Pulping of Wood."
John D.Rue. Paper Trade Journal, 81- p.54 (Oct.15,1925)

12. P.S. Bellingham, G.H. Chidester and C.E.Curran. Paper Trade Journal. 101 - T.S. p. 140-142. (Sept.12,1935)

13. "Metals and Metallic Compounds". Evans, Vol.II. P. 721.

14. "The Keebra Process for the Production of Chemical Pulp." Paper Trade Journal 77 - p.51. (Sept.6,1928.)

15. Phamplet on Murray-Waern System. The Combustion Engineering Company,Inc. 200 Madison Ave., New York.

16. "Results from the B & W-Tomlinson Process for the Recovery of Chemicals, and Heat from Kraft Black Liquor." L.S.Wilcoxson. Paper Trade Journal. P.72, (June 13, 1935.)

17. Recovery of Soda from Spent Liquor." B.D.Millidge, E.Taylor, A.A. Heimrod. Paper Trade Journal. T.S. 98-p.57. (June 28, 1934)

18. S.Coppick. Progress Report No.1. P.P. T.S.A.. 94M.

19. J.Hall. B.Eng.Thesis. May 1939.
