CONTROL OF SULPHITE PULPING WASTES IN THE UNITED STATES

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ABSTRACT

Statistics indicate that US capacities for acid and neutral sulphite pulping are presently at about the same level, running about 10000 short tons daily for each type of pulp. It is projected that acid sulphite will remain at about this level over the next ten years while the production of neutral sulphite will probably double. Most of the spent liquor from the operating mills is burned with or without chemical recovery. For acid sulphite liquor handling systems magnesium and ammonia base are employed to about an equal degree, there being only one sodium base mill. Neutral sulphite liquor recovery systems are either the Institute of Paper Chemistry Process or the Mead process. Most liquor incineration systems employ the fluidized bed furnace. An effort is being made to adapt this unit for magnesium base liquor incorporating chemical recovery.

Effluents from acid sulphite mills employing chemical recovery contain about 20 per cent of the original BOD load. Biological treatment in the forms of the activated sludge process and the aerated stabilization basin have been applied in full scale to treat the effluents from both magnesium and ammonia base operations, producing BOD reductions averaging in excess of 85 per cent. The manufacture of by-products continues to consume around 10 per cent of the acid liquor, some being marketed as crude evaporate and the remainder converted to speciality chemicals. The number of companies involved in this business is decreasing.

Neutral sulphite effluents are treated by various means. When associated with kraft operations the liquor is invariably diverted to the kraft recovery system as make-up. Remaining effluent is generally treated with the other mill discharges by clarification and biological oxidation. Three mills use land disposal and the same number discharge to the treatment systems of large municipalities. One mill recovers formic and acetic acids from the liquor and sells the remaining raffinate to a kraft mill.

At the present time the United States has the capacity for producing somewhat over 21000 short tons daily of acid and neutral sulphite pulps. While manufacture of the former has been declining in recent years, the latter has steadily increased and at present the capacity for producing neutral sulphite semi-chemical pulp exceeds that for acid sulphite by approximately 1500 short tons daily. Projections indicate that acid sulphite capacity will probably remain quite stable while that for neutral sulphite will continue to increase in the next few years.

Obviously the major water pollution load emanating from these processes has been contained in the spent cooking liquors. Elimination of the discharge of these is well underway in the United States and, with the possible exception of a few mills manufacturing by-products or having ocean outfalls, will be eliminated altogether within the next few years.

In the case of acid sulphite this is coming about through switching to kraft pulping, changing the chemical pulping base and burning the liquor (with or without chemical recovery), production by-products, and the dismantling of small, high production cost mills. At present, fifteen of the thirty-eight operating mills burn the liquor, long continued operation of eight others is doubtful and most of the remainder are definitely committed to burning in the near future. The tonnage equivalent of the fifteen mills now burning liquor is about half of the total. *Table 1* shows the status of the acid sulphite mills as it stands for the present and the immediate future.

Table 1. Base employed and disposition of spent cooking liquors from acid sulphite pulp mills in the United States

Base	No. of mills	% of total	Cap. t/d	% of total
Calcium	10	50	3610	38
Magnesium	9	24	3500	37
Ammonia	9	24	1945	21
Sodium	1	3	400	4
Totals	38		9455	
Chem. recovery	8	24	3490	37
Burn NH_3 liquor	5	11	730	8
Fluidized bed	2	5	410	3
By-product mfg	8	21	1325	14
Ocean outfall	3	8	840	9
Future uncertain	8	21	755	8
Land disposal	1	3	40	<1
Total burning	15	40	4630	49

Examination of *Table 1* reveals that with regard to bases other than calcium, magnesium is the most favoured, with about the same tonnage of this type being manufactured as of calcium base pulp. Smaller mills appear to favour ammonia while little effort has been made to produce soda base pulp. This is evident since the one mill employing it, constructed about ten years ago, was not eminently successful and the many sodium base recovery systems proposed[1] have, for one reason or another, not been sufficiently attractive to warrant their application. This situation could change in the future.

A total of eight mills manufacture by-products ranging from simple evaporates used for road binder and cattle food additives to some fairly sophisticated formulations and intermediates. Four mills produce the latter which are used in adhesives, dispersants, tanning agents, drilling mud additives, etc. Two mills make fermentation products, namely ethanol and torula yeast. All these products account for about ten per cent of the liquor solids produced. These operations are described in detail by Pearl[2] and in a *Chemical and Engineering* staff report[3]. By-products manufacture does not in all cases represent a complete or permanent solution to the liquor problem.

Liquor disposal from neutral sulphite semi-chemical pulp mills is further advanced than that of the acid mills largely because of the integration of many of them with kraft recovery systems. This is because the pulp produced is moved in the same markets as much of the kraft pulp and the wood species situation at many mills favours the combination of the two processes. As indicated in *Table 2*, twenty-eight of the thirty-nine NSSC mills burn the

Table 2. Methods of handling NSSC spent liquor in the United States.

Method of handling	No. of mills	% of total	Cap. t/d	% of total
Gross recovery	17	44	4880	44
Recovery	3	8	1375	12
Fluidized bed	4	10	1140	10
Burn NH_3 liquor	4	10	1310	12
By-products mfg	2	5	625	6
To sewage plants	3	8	615	6
Land disposal	2	5	475	4
None	4	10	615	6
Total burned	28	72	8705	80
Total other methods	7	19	1715	16
Total all methods	35	90	10420	95

spent liquor, seventeen of them employing cross recovery. Pulp tonnage equivalent of the total liquor burned is about eighty per cent, forty-one per cent being through cross recovery. Actually the liquor from all but four mills is disposed of in one manner or another, and at one of those not disposing of it, tremendous dilution is provided by the receiving stream the year round. Actually the liquor from thirty-six of the thirty-nine NSSC mills representing about ninety-five per cent of the total manufacturing capacity is disposed of satisfactorily, at least for the present.

It will be noted also from *Table 2* that only three mills employ chemical recovery, all using the Institute of Paper Chemistry soda base process. Fluidized bed burning of soda base liquor is practised by four mills and an equal number cook with ammonia base liquor and burn together with bark. It can be safely predicted that before long all NSSC liquor will be satisfactorily handled in the States. Unbalance which has existed in cross recovery systems from time to time will become a thing of the past.

Only two NSSC mills manufacture by-products. One of these separates out acetic and formic acids from spent liquor by a solvent extraction process[4] and delivers the raffinate from the process to a kraft mill for use as make-up. The second mill evaporates the liquor by submerged combustion producing road binder[5].

Despite much initial interest in wet combustion and the atomized suspension burning technique, neither of these processes were carried beyond the pilot plant phase for handling spent pulping liquors in the States.

It was demonstrated by Opferkuch[6] a number of years ago that NSSC liquor could be treated biologically together with sanitary sewage. This has been proven to be the case by three mills which discharge into public treatment facilities.

Under ideal soil and drainage conditions, land disposal of the spent liquor can be employed. Whilst this is not likely to prove a permanent method of operation, it is at present used to handle the liquor from two NSSC mills.

Unfortunately, disposal of the cooking liquor does not by any means eliminate the pollution load discharged by either type of sulphite mill. Decker seal pit water from the wet room, condensates from digesters and evaporators as well as bleachery wastes constitute the major source of the residual load. Bleachery waste is almost entirely a problem of the acid mill since the bleaching of NSSC in the United States is almost defunct. Bleaching effluent has become an increasing problem for the mills pulping with ammonia base liquor because of the heavier pollution load produced in brightening this pulp. Floor drains, tank overflows and aprons and the acid plant contribute in varying degrees to the continuous load.

The major individual factor causing pollution problems in the case of both waste streams is their oxygen demand. With regard to suspended solids NSSC pulping is by far the worst offender because of the relatively large amount of fines washed from the pulp. Also to be considered are solids contained in wood preparation effluents and accessory pulp lapping or papermaking operations.

While the problem of pollution cannot always be solved entirely through in-mill control, it can be reduced appreciably. This procedure is mandatory if high degree treatment must be afforded in order to keep the treatment system of reasonable size and uniform performance.

Obviously the first step toward this end is to provide adequate washing and evaporator capacity for the pulp tonnage produced. The second is to provide sumps for collecting periodic strong liquor losses owing to process upset, leaks and accidents from which they can be returned to process at appropriate locations and at suitable rates.

The third step is to provide retention basins to which the effluent can be diverted during periods of mill upsets or wash-up. The contents of these can then be pumped to the receiving stream or treatment works at controlled rates during periods of normal operation. Proper treatment plant design provides sufficient capacity over that of the normal waste load to handle the basin contents.

Excellent descriptions of such control measures are presented by Barton, Byrd *et al.*[7,8]. These measures were provided at the last acid sulphite mill to be built in the States. This mill was erected by the Charman Paper Company and put into operation in 1968. Because of stringent water pollution regulations set as a result of the high quality and usage level of the receiving stream, activated sludge treatment was provided. To maintain this treatment at required performance levels, good internal control was mandatory. Those employed are described by Barton *et al*[7].

Lowe[9] reported on mill tests conducted to determine the effects of recycling white water within a NSSC corrugating board mill, through which he was able to ascertain the minimum fresh process water requirement necessary before problems arising from this practice became intolerable. The difficulties observed as a result of closing the system were as follows: variable paper quality; decreased wet felt life; increased slime deposits; higher maintenance; increased scaling; greater chemical additive demands; build up of contaminants from waste paper. It was found that these problems could be minimized at an effluent discharge of only 2000 gallons per ton of product, but the problems experienced were severe at the 1000 gallon level. This is very much lower than the water usage of most systems of this type. The author claims that this practice both reduced the overall pollution load of the mill and provided a more uniform distribution of it to the aerated stabilization basin in which the effluent is finally treated. A flow diagram of the entire system is shown in *Figure 1.*

Primary treatment for the removal of settleable solids is provided by over half of the sulphite mills. *Table 3* shows the situation with respect to this

Table 3. Effluent treatment by sulphite mills in the United States

	No. of mills	% of total	Cap. t/d	% of total
Primary treatment				
Acid mills	15	40	4365	46
NSSC mills	25	60	7950	71
Totals	39	50	11865	59
Secondary treatment				
Acid mills	2	5	550	6
NSSC mills	12	31	3405	31
Totals	14	18	3955	19

practice which is expected to become almost universal before long if the State regulations approved by the Federal Government are to be met.

In most instances circular, mechanically cleaned clarifiers are employed for handling the combined dilute wastes from the mill. Where a kraft mill is operated at the same site the waste water from attending NSSC operations is combined with it for treatment. However, when wet barking is practised, the effluent from this operation is frequently treated separately because its peculiar properties can upset clarifier operation.

The second most important undesirable characteristic of the dilute wastes is generally their biochemical oxygen demand. For sulphite mills this is, as a rule, much higher than that of kraft mills. In the case of acid sulphite, this is because of the high acetic acid content of the condensates and, for NSSC, the difficulty experienced in washing the pulp well allows relatively high concentrations of sodium acetate to appear in the seal pit water. Then too some of the older mills are not provided with modern washing systems so that this appears in the machine white water. High degree bleaching of acid sulphite

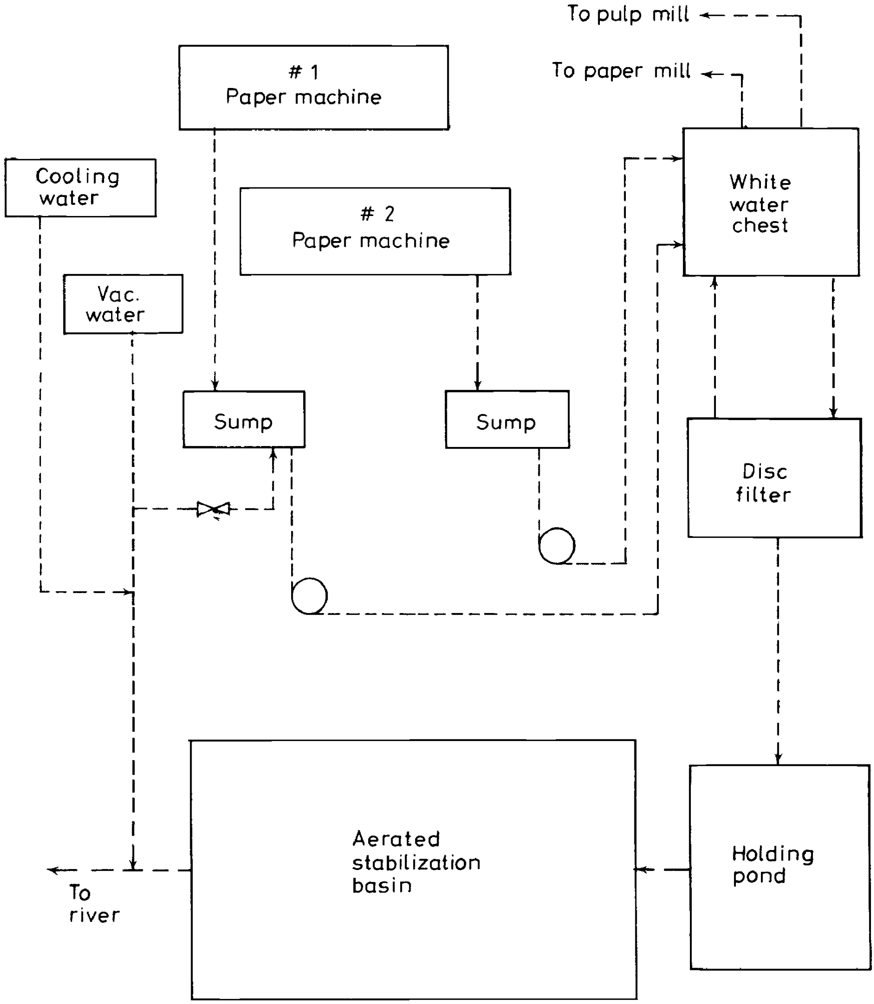

Figure 1. Water recycle in a NSSC mill.

and normal bleaching of NSSC pulp both produce effluents high in oxygen demand.

To date, biological treatment is the sole method being applied for treating these wastes to reduce their BOD. Effluent from two acid sulphite mills and twelve NSSC mills receive this treatment. Methods employed include the activated sludge process, aerated stabilization, storage oxidation, as well as irrigation and soil percolation. In all, fourteen mills treat to this degree.

Because of their generally smaller size and greater age, and the high costs attending the provision of liquor handling facilities, the sulphite mills in the States are not as far advanced as the kraft mills in the secondary treatment of dilute effluents. The fact that of a number of the larger ones discharge into very large bodies of water has also been a limiting factor. The effluent requirements of the future will exert a strong restraining influence on growth of acid sulphite pulping in the States.

Another consideration is the inability of biological treatment to remove appreciable amounts of lignin compounds as well as colour from the effluents irrespective of the degree of BOD reduction achieved. Approaches to this problem will be discussed further on in this presentation since it might be as well to review the present application of the biological oxidation processes first.

One example is that provided by the Charmin Paper Co. at their acid sulphite mill in Pennsylvania[7]. Decker seal pit water together with the condensates, bleachery effluent and return flowage from a detention basin which holds bypassed wastes are neutralized to pH 6.5 with lime and nutrients are added. At the entrance to the aerators, the stream, which contains up to 35000 pounds of BOD-5 daily at a concentration averaging 2400 mg/l, is mixed with sufficient return activated sludge to maintain a mixed liquor suspended solids level of around 5000 mg/l. Two one million gallon capacity aeration basins equipped with three 150 h.p. mechanical aerators each are employed. Aerator loading runs as high as 120 pounds of BOD_5 per 1000 cu. ft of capacity. Effluent from the aeration basins passes to an 85 foot diameter clari-flocculator and thence to the receiving stream. During periods of sub-normal operation, the effluent, or part of it, can be diverted to a holding basin for return to the head end of the treatment plant at a controlled rate.

Under-flow from the clari-flocculator is returned partially to the process and the remainder wasted. This latter portion has presented the most difficult problem with regard to operation of the process because of its resistance to dewatering, despite the provision of a two-stage centrifuge system to accomplish this. The first machine, which serves as a thickener, is a disc-nozzle type centrifuge. The slurry discharged from this unit, after the addition of poly-electrolyte is fed to a solid bowl centrifuge, the cake from which is disposed of by land fill. A serious nozzle clogging problem was encountered in the operation of the thickener but this has since been overcome. It was found that the thickened sludge responds to heat treatment producing a granular cake which is readily dewatered on a vacuum filter. Application of this process is now under consideration.

This process has reduced the BOD of the waste in excess of 85 per cent. Together with the suspended solids removal system of the papermill, an effluent of very high clarity is produced.

The other activated sludge plant treats acid sulphite effluents of the Cosmopolis, Washington mill of the Weyerhaeuser Company and has been described by Morgan[10]. This plant treats a mixture of condensates from the pulping and magnesium base recovery system together with caustic extraction effluent from the bleachery. This flowage amounts to around 1.65 mgd and carries a BOD load of from 30 to 120 thousand pounds daily. Extended aeration–activated sludge treatment was chosen to oxidize this waste. Because of the wide swings in load caused by pulp grade changes, two aeration basins were constructed and the piping arranged so that they can be operated either in parallel or in series. Each is equipped with eight 75 h.p. surface aerators and has a capacity of 5.5 million gallons. This provides a nominal detention period of five days.

Premixing of the wastes provides a neutral stream to which nutrients are added. Whilst influent temperature ranges from 68 to 146°F, it has not proved to be a problem since blending and cooling owing to turbulence in the aeration basins cool it to below 100°F.

A 50 foot diameter clarifier follows the aeration basins. The underflow from this unit can be returned to the influent or diverted to a land fill area for disposal. Generally 100 per cent recycle is practised so that the sludge removed from the system is well stabilized.

BOD_5 reduction efficiency has ranged from 83 to 95 per cent, the lower values corresponding with aerator failures. After correction of such difficulties, an average reduction of 88 per cent was recorded with the influent BOD_5 averaging 4000 mg/l or 55000 pounds per day. Installation of this process has allowed the mill to more than meet effluent quality requirements and is considered a success by both management and the regulatory agencies.

Dilute NSSC wastes are treated in aerated stabilization basins at six mills in combination with unbleached and bleached kraft effluents. Another employs the activated sludge process to handle the combination[11] with only one mill treating it alone by aerated stabilization[9]. No difficulties have arisen in oxidizing these wastes biologically either alone or in combination with others since both the rates and degrees of oxidation observed are normal. The only effect it has had on treatment systems in general is to increase the quantity of primary sludge collected and decrease dewaterability. This is due to the high suspended solids loss in the form of fines attendant to the manufature of this pulp.

Irrigation disposal of weak NSSC wastes, which is practised by two mills, can be successful if properly installed and managed[12, 13]. Fodder crops are grown on the disposal area and this is a particularly economical and effective system for small mills discharging into streams having a low summer flow. However a large area of suitable land is required[14].

Extensive research and development work is underway in the States on alternatives to the present methods for reducing the pollution load after recovery. Since a substantial portion of the BOD load from acid sulphite mills is contained in the condensates in the form of acetic acid, Clark, Lang and De Haas have worked out a method for reacting it with caustic soda and making acetic acid and sodium sulphite of acceptable quality[15, 16]. Application for this process is dependent upon the quantity that can be made at a single location as well as the markets for it.

Considerable attention has been given to the use of activated carbon for treating dilute pulp mill wastes since this material can adsorb most of the colour and a part of the BOD[17]. Regeneration is a basic requirement for the application of carbon adsorption. Recovery of the carbon can now be efficiently accomplished with some carbons[18]. Its application to sulphite waste waters is likely to be limited because of its relatively low capacity for adsorbing materials responsible for the BOD in relation to its high affinity for coloured bodies.

An extensive research and development programme on the use of reverse osmosis for concentrating the dissolved solids present in weak sulphite wastes and reclaiming process water was conducted by the former Pulp Manufacturer's Research League. This study, which included tests employing a portable reverse osmosis plant which was moved from mill to mill, was partially financed by the Federal Water Quality Administration. After extensive laboratory work with the process, this unit was assembled and operated at several mills of different types including acid and NSSC plants. In addition to concentrating solids for introduction into recovery or incineration systems and reclaiming water, the separation of acetic acid and sugars having unique properties was attempted.

While the reports covering these investigations have not as yet been published, it has been pointed out by the participants[19] that flux rates obtained were undesirably low and that membrane life fell short of that required for commercial practicability. These observations were confirmed by other investigators[20]. Very extensive effort is being expended by membrane manufacturers and others supplying hardware for these systems and it is anticipated that these shortcomings will be overcome to some degree in the not too distant future.

As an outgrowth of these studies, the Green Bay Packaging Company, which manufactures NSSC pulp and corrugating medium, has agreed to join in a project with PFQA to conduct comparative pilot plant tests of various proprietary reverse osmosis systems for concentrating weak pulping wastes to such a degree that they can be introduced into the existing fluidized bed burner handling the spent liquor. If results obtained with the most efficient unit tested appear favourable, plans call for the installation of a demonstration unit at the mill. The company is attracted to the process because it removes both BOD and colour and could possibly lead to a closed system.

It is envisaged that the bleaching effluent problem, which is becoming increasingly acute, may be eliminated or drastically reduced by developments such as those proposed by Rapson[21] or by oxygen bleaching[22]. Both of these processes return a relatively concentrated liquor low in chloride ion to the recovery system. The success of these schemes awaits further development.

REFERENCES

1. T. T. Collins and R. E. Shick, *Paper Trade J. Series* (1969–70).
2. I. A. Pearl, *Tappi* **54**, 1253 (1969).
3. Staff Rep., *Chem. Eng. News* **41**, 83 (1963).
4. W. A. Biggs, Jr. *Tappi* **45**, 385 (1961).
5. NCASI Meeting Rep., K. E. Lowe, Menasha Corp.
6. R. Opferkuch, *NCASI Tech. Bull.* No. 42 (1951).
7. C. A. Barton, *et al.*, *J. Water Polution Control Federation*, **40**, 1471 (1968).
8. C. A. Barton, San. Eng. Seminar, Univ. of Cincinnati.
9. K. E. Lowe, *Paper Trade J.* **154**, 52 (1970).
10. O. P. Morgan, *NCASI Tech. Bull.* No. 220, 24 (1969).
11. B. V. Pearman and O. B. Burns, *Proc. Purdue Ind. Waste Conf.* (1957).
12. H. C. Koch and D. E. Bloodgood, *J. Water Pollution Control Federation* **31**, 827 (1967).
13. C. N. Betts, Private communication.
14. *NCASI Tech. Bull.* No. 185, Part 4 (1965).

[15] L. H. Clark and G. G. De Haas, *Tappi* **52**, 1728 (1969).
[16] C. J. Lang and G. G. De Haas, *Tappi* **53**, 1094 (1970).
[17] *NCASI Tech. Bull.* No. 199 (1967).
[18] US Pat. 3455820 (1970).
[19] *Pulp Mfg. Res. League Annual Rep.* (1969).
[20] H. Beder and W. J. Gillespie, *Tappi*, 6th Water and Air Conf. (1968).
[21] W. H. Rapson, *Pulp Paper Mag. Can.* **68**, 12:T635 (1967).
[22] P. D. Van Derveer, *Paper Trade J.* **154**, 23, 41 (1970).