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The BOD_5 and Toxicity of Effluents from Sulphite Pulping for Newsprint

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THE BOD_5 AND TOXICITY OF EFFLUENTS FROM SULPHITE PULPING FOR NEWSPRINT

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ABSTRACT

High yield bisulfite pulp mills, which are integrated with many eastern Canadian newsprint operations, produce acutely toxic effluents with extremely high organic loadings. This paper describes the results of an experimental program, sponsored by Environment Canada and carried out at the Pulp and Paper Research Institute of Canada, to measure the toxicity and five-day biochemical oxygen demand (BOD_5) of laboratory-produced sodium base bisulfite pulps covering a yield range from 60 to 80%. Strength characteristics of these pulps were also determined in order to find the critical level of yield giving the pulp quality still suitable for newsprint production. Significant reductions in toxicity and BOD_5 loadings are achieved by increasing pulp yield, but it is not possible to comply with Environment Canada Pulp and Paper Effluent Regulations solely by increasing yield.

RÉSUMÉ

Les fabriques de pâtes au bisulfite à haut rendement qui, dans l'est du Canada, sont intégrées à de nombreuses fabriques de papier journal, produisent des effluents très toxiques, dont la teneur en matières organiques est très forte. Le présent rapport dévoile les résultats d'un programme expérimental entrepris à l'Institut canadien de recherches sur les pâtes et papiers, sous le parrainage d'Environnement Canada; le programme avait pour objectif de mesurer la toxicité et la demande biochimique d'oxygène en 5 jours (DBO_5) de pâtes au bisulfite de sodium, préparées en laboratoire, et d'un rendement situé entre 60 et 80%. On a aussi déterminé les propriétés mécaniques de ces pâtes, afint de trouver le rendement critique où la qualité des pâtes convient encore à la fabrication du papier journal. On parvient à réduire la toxicité et la DBO_5 de façcon notable, en augmentant le rendement des pâtes, mais il est impossible de se conformer au Règlement sur les effluents des fabriques de pâtes et papiers, par ce seul moyen.

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1. INTRODUCTION

High-yield bisulphite pulp has achieved widespread use as the chemical fibre component in the production of newsprint in eastern Canada, but sulphite mills have come to represent an urgent environmental problem in the Canadian pulp and paper industry. Its effluent waters: (1) increase the biochemical oxygen demand of the receiving waters; (2) are a source of suspended solids; and (3) contain components that are toxic to fish. Environment Canada Pulp and Paper Effluent Regulations specify permissible limits of BOD_5 (Table 1) and the deposit of suspended solids, and also contain a fish-toxicity specification.

TABLE 1. PERMISSIBLE DISCHARGE OF BOD_5 SUBSTANCES FROM SULPHITE MILLS

TOTAL YIELD OF SULPHITE PULPS	EXISTING MILLS		NEW, ALTERED AND EXPANDED MILLS	
% ON OVEN DRY WOOD	LB/ADT*	KG/ADT**	LB/ADT*	KG/ADT**
55 or less	255	127.5	170	85.0
55 to 65	170	85.0	115	57.5
65 or more	150	75.0	75	37.5

* pounds per air dry short ton

** kilograms per air dry metric ton

Several alternatives are being investigated for solving the sulphite-mill effluent problem, including:

1. Reduction or elimination of chemical furnish by producing higher quality mechanical pulps (thermomechanical and others).

   Several manufacturers of pulping and papermaking equipment have conducted trials of the production of high quality thermomechanical pulp. However, complete replacement of the chemical pulp by thermomechanical pulp in newsprint furnish has not yet been achieved commercially.

2. Replacement of sulphite furnish with purchased chemical pulp.

   Some newsprint mills in eastern Canada use lower yield semibleached kraft pulp (48% yield), instead of sulphite pulp as their chemical fibre furnish.

3. External treatment of effluents.

   In Canada, no mill-scale biological treatment plant has yet been built for processing the effluents from a sulphite-newsprint mill. The main difficulties seem to be that the presence of lignosulphonates in the effluents inhibits the biological oxidation of carbohydrates, and that additional treatment is required for the disposal of sludge. In addition, for such an enormous BOD load, an extremely large treatment system would be required.

4. Chemical recovery of sulphite liquors.

   Recovery of spent liquors can be achieved by a number of methods as shown schematically in Figure 1. At pulp yields of 70% and higher, a chemical saving of $8-10 per air dry ton of pulp can be realized with the installation of a recovery process. However, net heat savings are limited at these yield levels. Some of these systems appear to be economically favourable for a mill producing at least 300 tons per day of pulp. Unfortunately, the bisulphite pulping units at eastern Canadian newsprint mills are generally small (100-250 a.d. tons per day), so that recovery of chemicals cannot be justified on economic grounds alone.

The present investigation represents another approach to solving the environmental problems which arise from sulphite pulping. The underlying notion was that ultra-high-yield bisulphite pulping, which solubilizes less of the wood substance, might produce effluents that could fall within the regulations for BOD_5 and toxicity.

Thus, under contract to the Environmental Protection Service of Environment Canada, the Pulp and Paper Research Institute of Canada undertook a brief investigation of the relationships between total pulp yield, effluent toxicity, and BOD_5 loading for the high-yield sodium-base

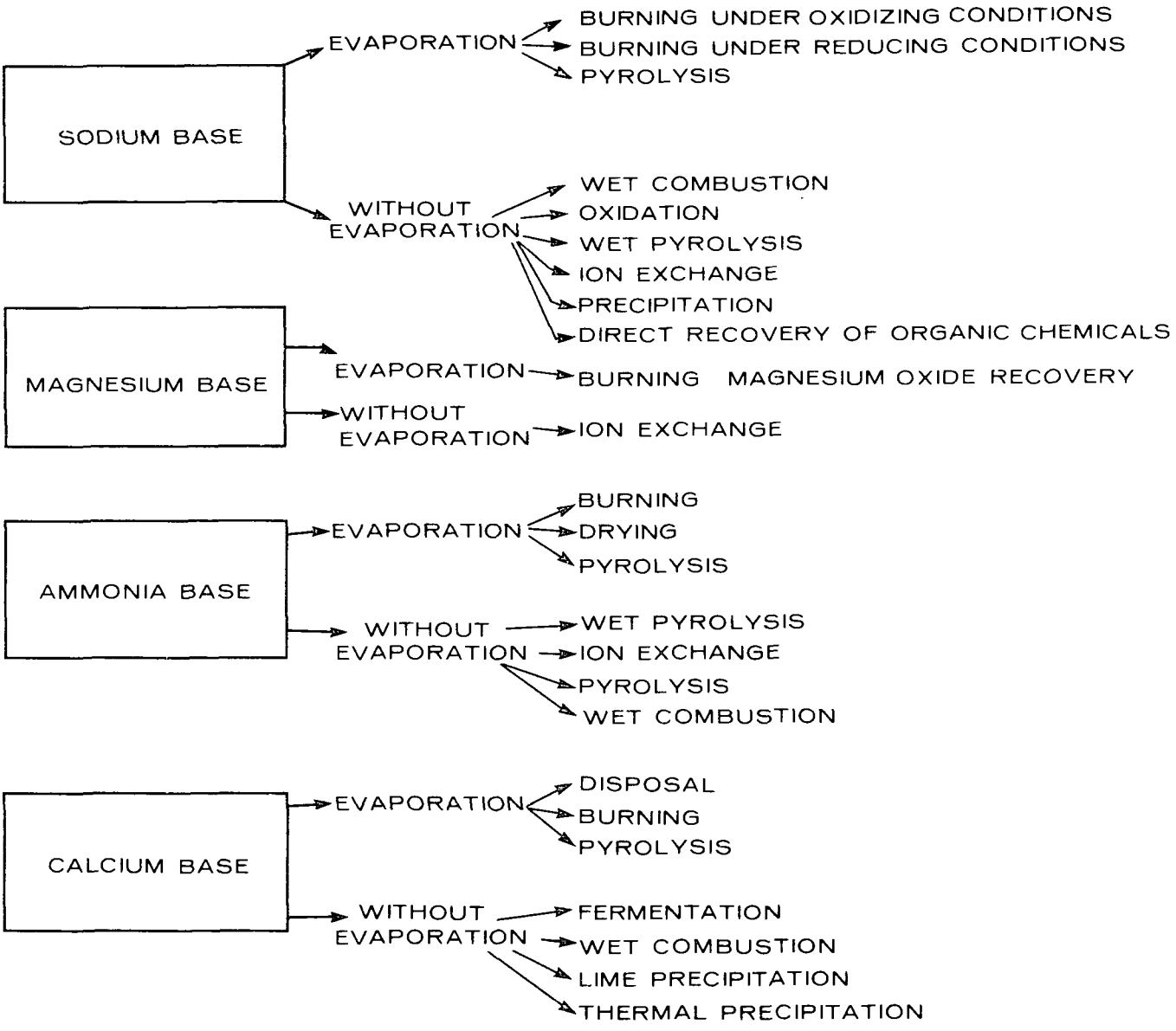

Figure 1 Spent Sulphite Liquor Recovery (1)

bisulphite process. In addition, the pulp characteristics were measured to determine the highest yield compatible with newsprint manufacture.

The first objective of the research was to determine the levels of BOD_5 reduction that might be achieved by pulping to higher yields.

The second objective was to determine the reductions in toxicity that might be accomplished solely by increasing the yield of pulp. Although the toxicity regulation requires that 80 percent of the test fish survive for 96 hours in a sample of 65 percent effluent and 35 percent water, the toxicity of the high yield spent sulphite liquor has to be evaluated in terms of total sulphite newsprint mill effluent. In a newsprint mill, the sulphite spent liquor may constitute 2 to 4% of the total mill effluent.

2. EXPERIMENTAL

2.1 Pulping

The cooks were performed in a 20-litre experimental digester, with a charge of 2.5 kg (o.d.) of wood chips for each cook. A chip blend, containing 70% balsam fir and 30% black spruce, was used for pulping. The chips were sorted to remove knots, rot, and substandard material, and were screened. After a standard steaming procedure, a sodium base bisulphite liquor, containing 2% combined SO_2, was added to the chips at the liquor-to-wood ratio of 4:1 (wood moisture excluded). The pH of the pulping liquor was maintained near 4.0. The maximum cooking temperature, 160°C, was reached in 3 hours and cooking time at the maximum temperature was varied in order to obtain pulp yields within the range of 60 to 80%. The cooking conditions to attain each yield are presented in Table 2.

TABLE 2. COOKING CONDITIONS

	COOKING CONDITIONS				PULP PROPERTIES		
NUMBER	TIME AT TEMP. (MIN)	pH OF LIQUOR	CONCENT. SO_2 (%) COMBINED	CONCENT. SO_2 (%) TOTAL	TOTAL PULP YIELD (%)	KAPPA NUMBER	ELREPHO BRIGHTNESS (%)
1	165	3.8	2.00	3.97	59.2	93	44.7
2	135	3.9	1.99	3.97	61.1	104	43.7
3	110	3.8	1.98	3.96	67.5	133	46.4
4	80	3.7	2.02	4.04	72.5	141	49,0
5	50	4.2	1.99	3.95	77.9	146	50.9
6	28	3.9	2.04	4.06	81.5	-	50.6

Time to maximum temperature - 180 minutes

Maximum cooking temperature - 160°C

Liquor-to-wood ratio - 4:1

Wood blend - 70% balsam fir and 30% black spruce

2.2 Refining and Washing

After cooking, the chips were refined in two passes (plate clearance 0.020" and 0.010", respectively) through a Sprout-Waldron 12" laboratory refiner. The pulp was then thoroughly washed until a filtrate volume of 615.3 litres was obtained.

2.3 Testing

The volume of blow-liquor from each cook was measured, and the sample was then tested for BOD_5 and toxicity.

The BOD_5 concentration of the wash filtrate was determined to permit the calculation of total BOD_5 loading in terms of lb per a.d. ton of pulp production and kg per a.d. metric ton of pulp, respectively.

For toxicity tests, the static bioassay procedure (Table 2) was based on that given in the "Guidelines for the Pulp and Paper Effluent Regulations" published by Environment Canada (1972), [2] and work by Sprague [3].

TABLE 3. CONDITIONS FOR BIOASSAY TESTS

Fish Species: Rainbow trout (*Salmo gairdneri Richardson*)

Bioassay:

pH	:	6.5 - 7.5
temperature	:	11 ± 1°C
pre-aeration time	:	30 - 45 minutes
dissolved O_2	:	near saturation at prevailing temperature (9-12 mg/l)
dilution water	:	well water hardness = 260-290 as $CaCO_3$ pH = 7.2 - 7.6

DATE 1974	TEST SERIES	NUMBER OF FISH PER TEST	VOLUME OF TEST SOLUTION (l)	AVG. LENGTH OF FISH (cm)	AVG. WEIGHT OF FISH (g)	FISH * DENSITY (l/g)
March 12	3534	5	10	8.2	6.2	0.32
March 14	3535	5	10	8.2	6.2	0.32
March 19	3536	5	10	8.2	6.2	0.32
March 27	3538	10	10	3.4	0.5	2.00
April 1	3539	10	10	3.4	0.5	2.00
April 2	3540	10	10	3.4	0.5	2.00

* Because of the seasonal shortage of fish of a fixed size range, different sizes of fish were used. However, routine standardization tests of fish showed the responses of 10 mg/l of O-chlorophenol to be acceptable for the present purpose of exploratory toxicity testing.

Total yield, Kappa number and brightness of each pulp was determined. The pulps were evaluated by 5-point P.F.I. mill runs for the following properties: tear factor, breaking length, burst factor, stretch, fold, bulk and capacity. All physical properties were determined using Canadian Pulp and Paper Association Standard Methods or modified PPRIC procedures.

3. RESULTS AND DISCUSSION

3.1 BOD_5 Loading at Various Pulp Yields

As expected, the quality of effluents from high yield bisulphite pulping improves with increasing pulp yield. Table 4 and Figure 2 show the decrease in BOD_5 loads with increasing pulp yields.

TABLE 4. BOD_5 LOADINGS.

TOTAL PULP Yield (% on oven dry wood)	BLOW-LIQUOR				WASH-LIQUOR				TOTAL BOD_5 LOADING	
	VOLUME (l)	BOD_5 (mg/l)	BOD_5 (lb/ADT)*	(kg/ADT)**	VOLUME (l)	BOD_5 (mg/l)	BOD_5 (lb/ADT)*	(kg/ADT)**	(lb/ADT)*	(kg/ADT)**
59.2	8.40	39,400	310	155		262	196	98	506	253
61.1	7.60	31,900	286	143		293	212	106	498	249
67.5	8.64	25,500	235	117.5	615.3	293	193	96.5	428	214
72.5	8.75	31,100	270	135		273	167	83.5	437	218.5
77.9	7.93	21,100	155	77.5		298	169	84.5	324	162
81.5	8.40	11,000	82	41		181	98	49	180	90

* lb/ADT - pounds per air dry short ton

** kg/ADT - kilograms per air dry metric ton

The decrease in effluent BOD_5 loading with increasing pulp yield, relative to loading at 65% yield, is tabulated in Table 5. Values in the table were obtained by graphical interpolation from Figure 2 relative to 65% yield level. The reduction in BOD_5 is very small at 70% yield and becomes appreciable only when the yield reaches 80%. Much of this reduction may be due to the absence of such sugars as mannose, glucose, and galactose [4].

FIGURE 7 8

Variation de la DBO5 selon le rendement (lessive bisulfatique)

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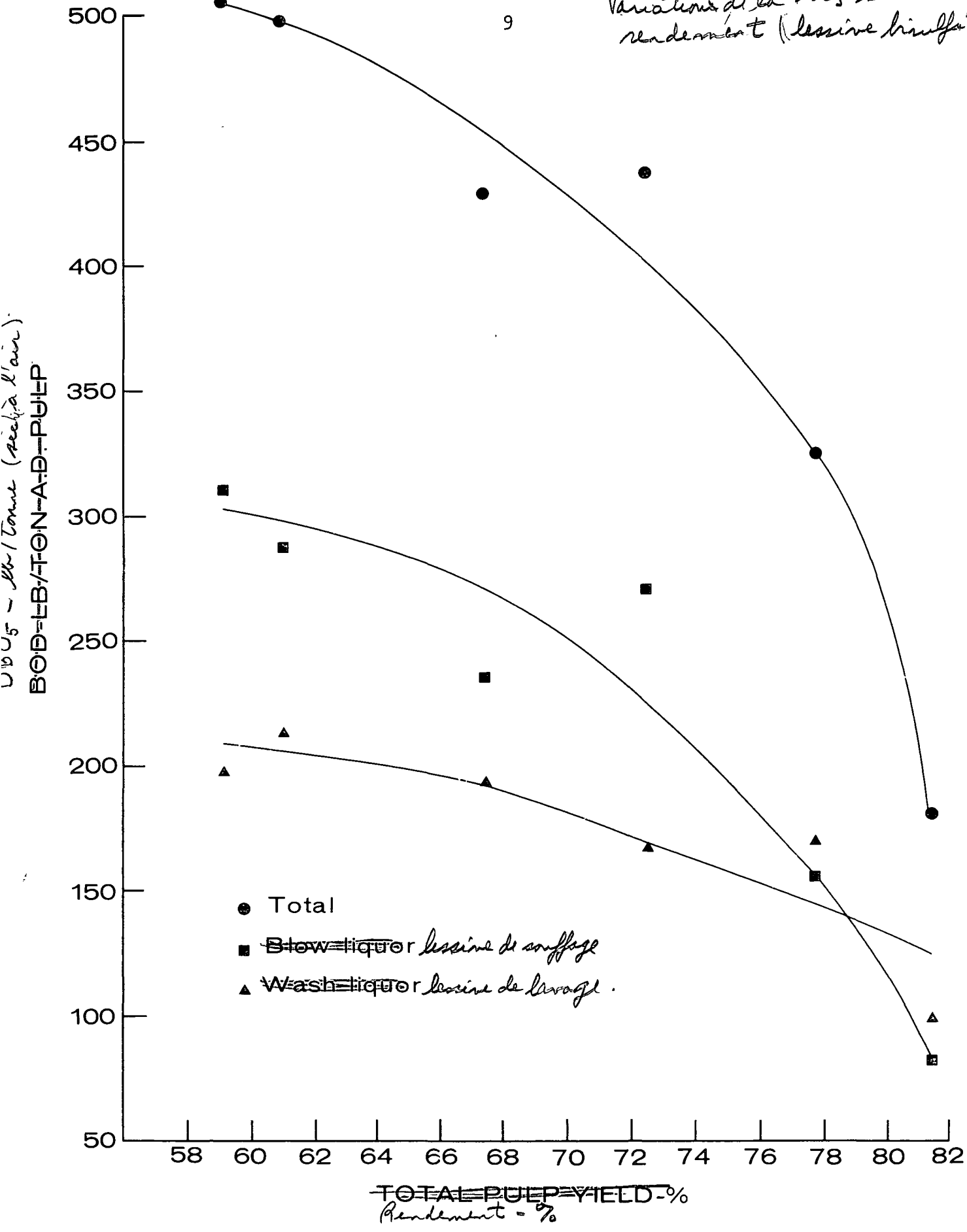


Figure 2 B.O.D5 of Spent Sulphite Liquors at various pulp yields

TABLE 5. PERCENTAGE REDUCTION IN BOD_5 WITH INCREASING PULP YIELD

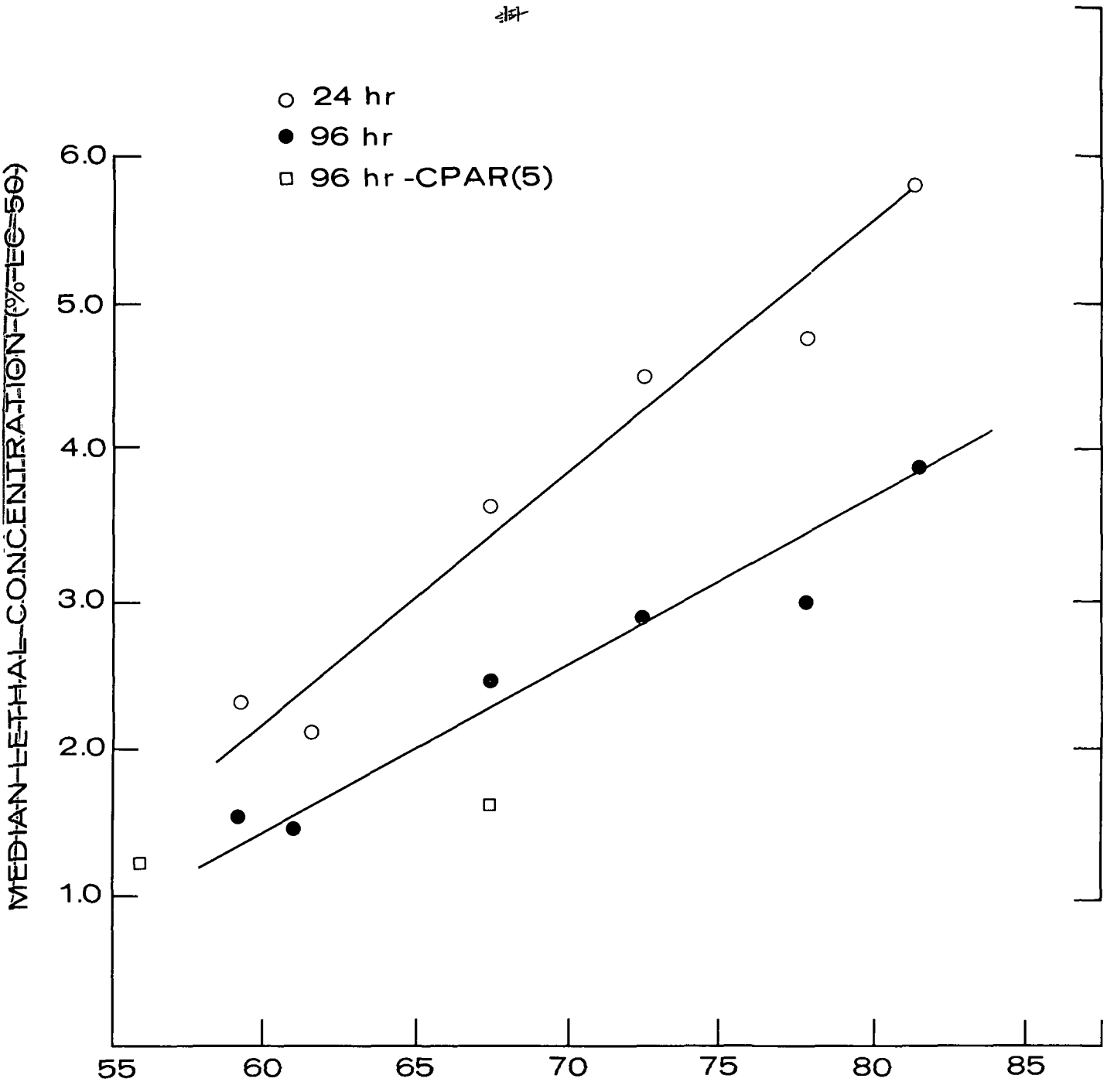
TOTAL PULP YIELD % ON OVEN DRY WOOD	% DECREASE IN BOD_5 LOAD		
	BLOW LIQUOR	WASH LIQUOR	TOTAL LIQUOR
65	0	0	0
70	12	9	11
75	32	20	23
80	59	33	45

3.2 Toxicity at Various Pulp Yields

Figure 3 shows the relation of total pulp yield to the toxicity of the blow-liquor expressed as 24 hour, and 96 hour LC50 values. LC50 is defined as the concentration of sample in which 50% of the fish survive for stated test period. The actual LC50 values as well as comparison of blow-liquor at six yield levels is presented in Tables 6 and 7. Toxicity is reduced as pulp yield increases, with considerable improvement relative to 65% yield shown at 75% yield. A very large toxicity reduction was observed at 80% yield.

TABLE 6. TOXICITY OF SPENT SULPHITE LIQUOR

TOTAL PULP YIELD % ON OVEN DRY WOOD	BLOW-LIQUOR TOXICITY 24 hr LC50 %	96 hr LC50 %
59.2	2.30	1.55
61.1	2.10	1.45
67.5	3.60	2.45
72.5	4.50	2.90
77.9	4.75	3.00
81.5	5.85	3.90



LC_{50} (%)

Rendement — % Bois sec absolu

FIGURE 8 Y

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Toxicité (LC_{50}) vs Rendement (pâte bisulfitique)

Figure 3 Median lethal concentrations versus Sulphite pulp yield

TABLE 7. PERCENTAGE REDUCTION IN BOD_5 WITH INCREASING PULP YIELD

TOTAL PULP YIELD % ON OVEN DRY WOOD	% DECREASE IN TOXICITY *	
	24 hr LC50	96 hr LC50
65	0	0
70	26	28
75	54	54
80	80	82

* Relative to toxicity of blow-liquor at pulp yield of 65%, graphically extrapolated from Figure 3.

3.3 Pulp Properties at Various Yields

Table 8 lists the pulp strengths, opacity and brightness of each experimental pulp. The tear factor, burst factor, tensile, and fold at different yields are illustrated graphically in Figure 4.

TABLE 8. PULP PROPERTIES

TOTAL PULP YIELD (% on od w)	TEAR FACTOR	BURST FACTOR	BREAKING LENGTH (meters)	STRETCH (%)	DOUBLE FOLDS	BULK (cc/gram)	OPACITY (%)
59.2	70	91.1	12,385	2.90	1,650	1.45	70.0
61.1	66	90.8	12,072	2.76	1,622	1.42	69.0
67.5	60	88.4	11,646	3.04	976	1.47	68.5
72.5	60	77.0	11,331	2.93	1,227	1.48	70.0
77.9	58	74.6	10,255	2.63	606	1.52	73.4
81.5	55	57.0	8,883	2.19	235	1.69	78.7

Pulp strength properties are recorded at 500 ml CSF

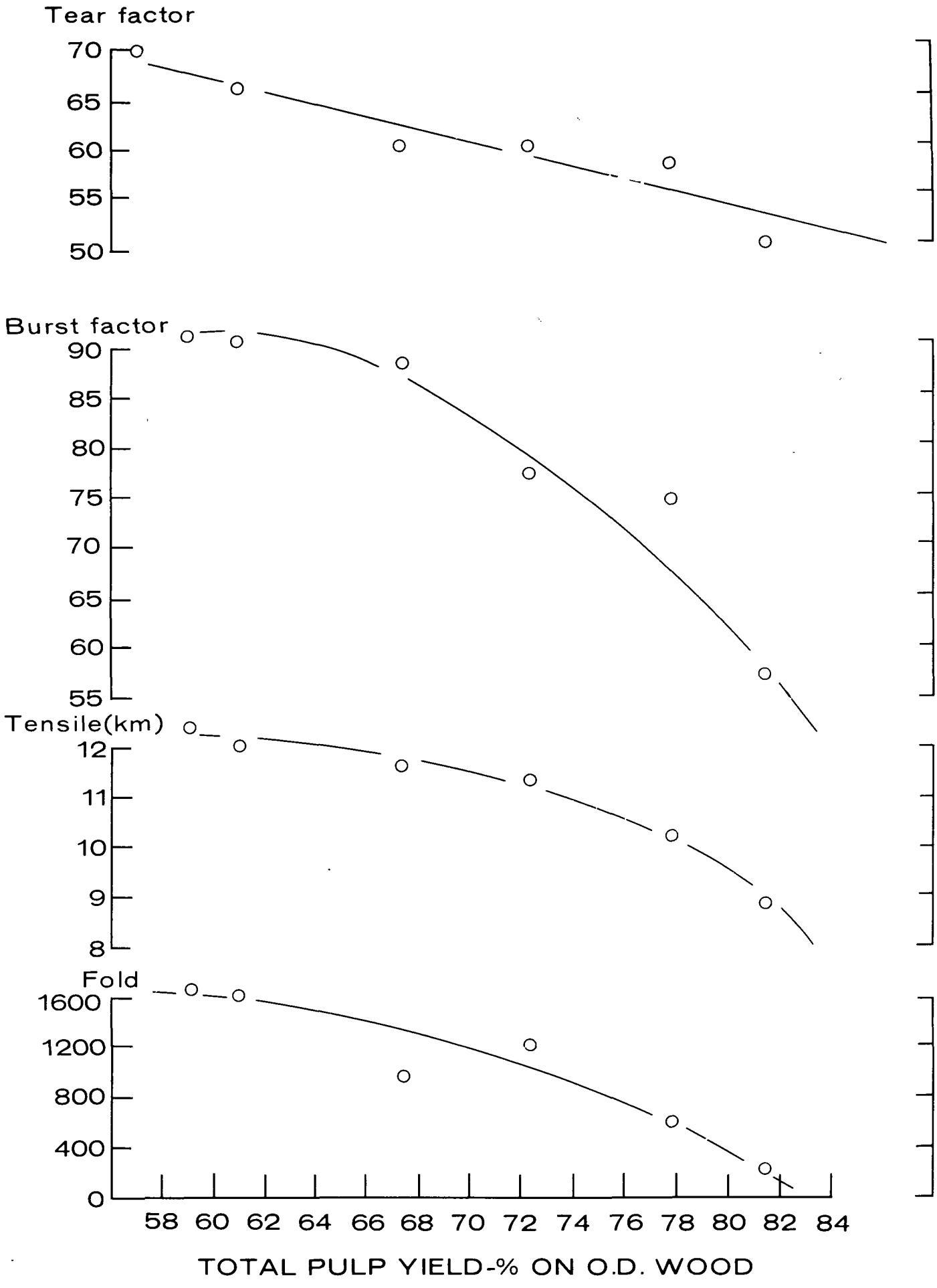

Figure 4 Physical properties of pulp at various yields

Table 9 was obtained by extrapolation from Figure 4 with 65% yield as a reference. The pulp strength characteristics at 500 ml CSF are considered for comparison in Table 9.

TABLE 9. PERCENTAGE REDUCTION IN PHYSICAL PROPERTIES WITH INCREASING PULP YIELD

TOTAL PULP YIELD % ON OVEN DRY WOOD	DECREASE IN PULP STRENGTH PROPERTIES - % *			
	TEAR FACTOR	BURST FACTOR	TENSILE KM	DOUBLE FOLDS
65	0	0	0	0
70	5.0	7.0	4.0	17.0
75	9.5	17.0	10.0	42.0
80	15.0	30.0	21.0	72.0

* Relative to strength at 65% yield, graphically extrapolated from Figure 4.

Tear factor, burst factor, and tensile were decreased by 9.5, 10, and 17%, respectively, when the pulp yield was increased to 75%. Experience dictates that these quality reductions are probably the maximum tolerable without affecting paper machine operation. Further strength reductions may cause operational problems. However, it may be noted that the pulps were processed using a very small laboratory refiner at constant plate clearance. It is probable that commercial scale refining equipment would minimize any detrimental strength reduction.

Figure 5 shows an improvement in optical properties of pulps with increasing yield.

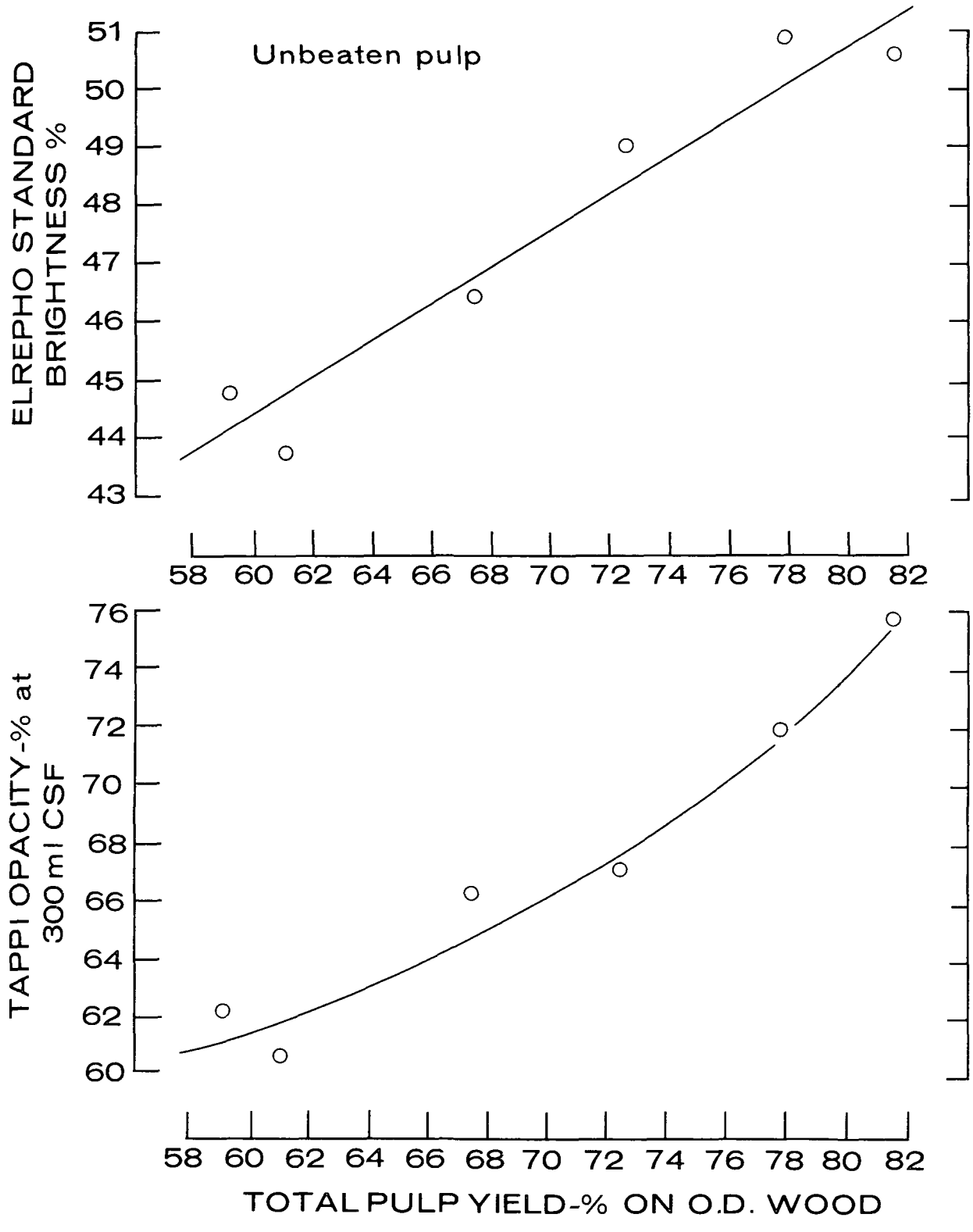

Figure 5 Improvement in optical properties with increasing pulp yield

4. CONCLUSIONS

From the results of BOD_5 measurements, there is no doubt that conversion of all existing mills to the high yield process would significantly reduce the organic loading to the receiving waters. For sulphite mills integrated with newsprint operations, the present organic loadings are represented by bar one in Figure 6. Bar two represents the loadings assuming the conversion of all mills below 65% to 65% yield. Bar three represents the loadings assuming the conversion of all mills to 80% yield. However, this process cannot be used to comply with Environment Canada's regulation for BOD_5 of 37.5 kg/ADT (Figure 6).

Nor, despite the favourable effects of high-yield operation on toxicity, would there by any hope of meeting the official toxicity standards, although the toxicity might come very close to the permissible limits in the total effluent from a newsprint mill, where the spent sulphite liquor would be considerably diluted.

The properties of pulps prepared during this investigation seem to indicate that 75% is the maximum yield at which pulps can be obtained that are compatible with the needs of newsprint production. However, it is possible that ultra-high-yield bisulphite pulps (80% plus) with adequate strength properties might be obtained from large refiners, operating under mill conditions and at high consistency.

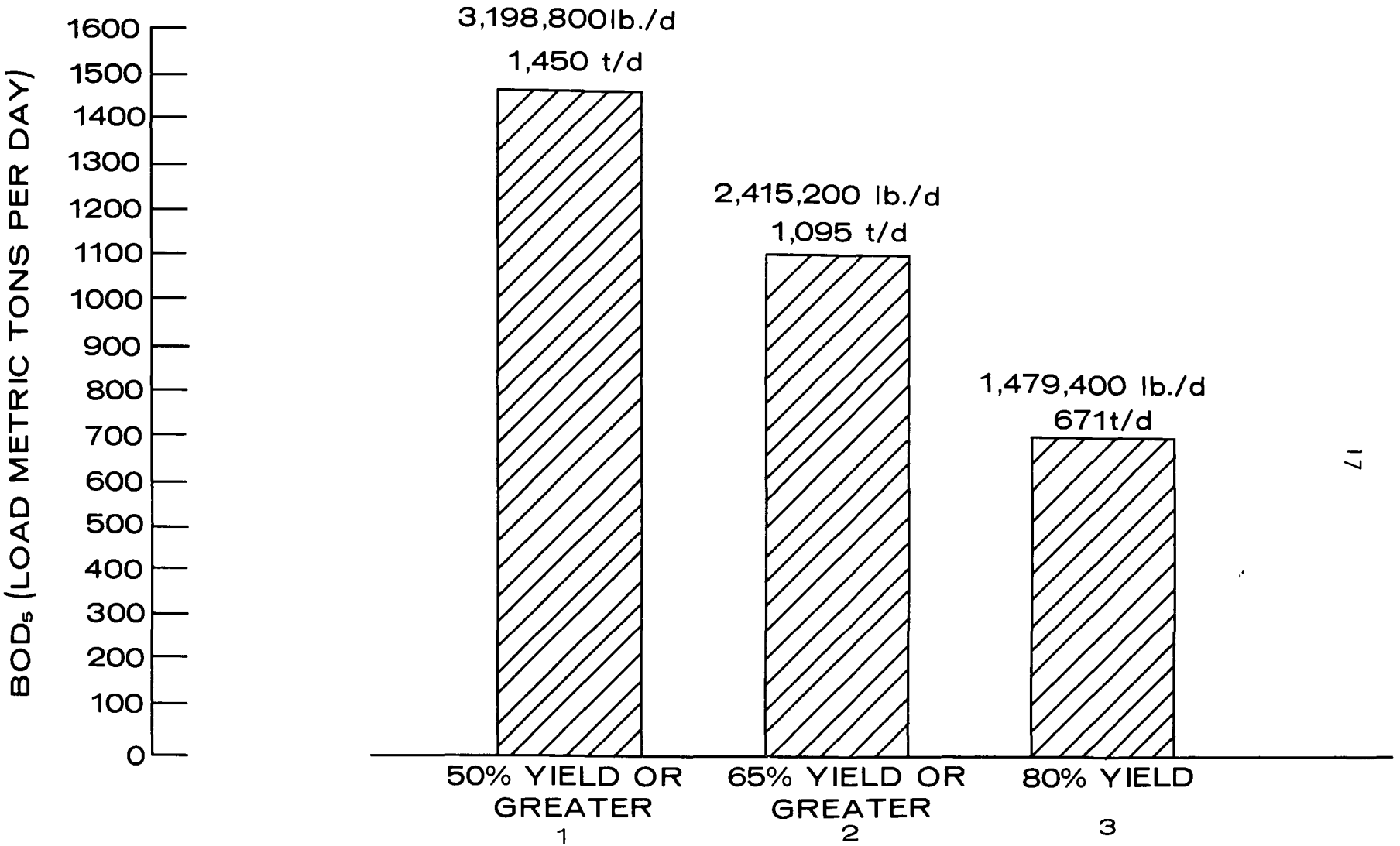

Figure 6 Potential BOD_5 loads from Canadian Sulphite mills by conversion to higher pulping yields

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