Experience with Full-Scale and Pilot-Scale Biopaq UASB Anaerobic Treatment of Pulp, Paper and Boardmill Effluents

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ABSTRACT

Since 1981 when the first experiments for treatment of paper mill effluents with UASB reactors were carried out, many more tests and applications in this field took place. Five full-scale plants are now operating with several paper- and boardmill effluents. Successful pilot work has been conducted in at least six different pulp-, paper and boardmills.

This paper deals with the full-scale as well as the pilot-scale results. The pilot-studies that are discussed, relate to the treatment of effluents of board- and TMP-pulp production in Austria, paper production in Germany and France, NSSC-pulp production in Canada and paper production in Scotland. Much emphasis is put on sub-optimal wastewater characteristics such as high concentrations of sulphate and high suspended solids, low temperature and low wastewater strength. Results demonstrate that efficient anaerobic treatment is still feasible under the described sub-optimal circumstances. A method has been developed for dealing with toxic influences from tannin compounds.

INTRODUCTION

It has been four years now since the first full-scale applications of UASB reactors for pulp and paper mill effluents became reality. An earlier paper on this topic (Habets 85a) deals with the results of a research and development program that was started in 1981 and concluded in 1983 with the erection and start-up of two full-scale plants. Technically as well as economically the operation of the full-scale plants proved to be very successful.

Subsequently, more pilot-plant work. has been done and at least three more full-scale UASB reactors have been realized for pulp- and papermill effluents. Another five full-scale plants are being constructed by our company or by licensees of our process Licencing of the BIOPAQ UASB process is arranged in a number of countries now, for instance Germany, Austria, Brazil, Canada, Finland, U.K. India, France and USA. The mother company, PAQUES BV in the Netherlands is the central point where research and development take place and experience is gathered from all over the world. From here, the know-how is passed on to all licensed areas as and when required.

This paper deals with anaerobic treatment of various pulp-and paper-mill effluents under pilot-scale as well as full-scale circumstances. Speciel attention is paid to aspects such as diversity of effluents, low temperature, low COD, high COD, high concentrations of sulphate and suspended, solids. After some information on several types of effluents and influences, results of full-scale operation will be reported and recent pilot-plant results from different pulp- and paper-mill effluents will be presented and discussed.

2. VARIOUS EFFLUENT TYPES AND INFLUENCES

The nature of pulp-and paper-mill effluents is mainly a result of the various pulping and/or papermaking pr cess. Especially pulping processes can produce severe water pollution and it become increasingly evident that anaerobic techniques can be applied as an attractive alternative to solve this problem.

Pulping effluents we have successfully tested originated from TMP (therma mechanical pulping), NSSC (neutral

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sulphite semi-chemical) production and CTMP Chemi - Thermom echanical Pulping). Pilot-plant work is scheduled for SEC (sulphite evaporator condensate). The latter type results from acid sulphite pulping. CTMP pulping is gaining popularity because of its high yields and its growing suitability to a variety of uses. Therefore the emphasis is very much on research into the treatability of CTMP effluents.

Toxicity problems (acquatic as well as anaerobic) are often introduced by bark constituents and by bleaching processes (Virkola' 85). Methods to reduce these toxicities have been developed.

Paper-mill effluents — which have already undergone anaerobic treatment successfully, are those from plants producing sanitary paper, corrugated medium, testliner, board, folding boxboard, gypsumboard - liner and several other types based on recycling - paper as raw materials. Suboptimal process circumstances for anaerobic treatment can be caused by suspended solids, sulphate, wastewater temperature and concentration Treating paper-mill effluents, one sometimes has to deal with temperatures of 20°C to 30°C which falls below the optimal range necessary for mesophilic anaerobic bacteria. As a consequence biochemical activity of the biomass will be at a lower level. Dilute wastewater (COD less than 1000 mg/l) often exists in combination with a lower temperature. Their contribution to lower efficiencies is due to shorter hydraulic retention times and lower substrate levels. At temperatures ranging from 20° to 25°C and influent COD's of about 1000 mg/l, the resulting biogas production is only 0.25 instead of 0 40 m³/kg COD-removal. An important reason for this is the increased solvability of methane, carbondioxide and hydrogensulphide in the waterphase The solvability of the last two gas compounds increases more than that of methane as the temperature drops; therefore the relative methane content of the biogas increases with decreasing temperatures. Diagram 2 shows CO_2 and H_2S concentrations in the biogas at changing reactor temperatures.

The presence of suspended solids is another important characteristic to be considered with paper-mill effluent. At a temperature of 30°C it normally takes about 20 days to digest paper fibres. This means that relatively large particles would have to be retained in the reactor for a long time. However, due to large quantities of small gasbubbles produced in the reactor, paperfibre floatate and are washed out of the system. Smaller suspended solids (i.e emulsions) can be converted more efficiently and their settleability is improved drastically. As a rule of thumb the UASB reactor can be exposed to average concentrations of suspended solids at a level of 10 percent of the inlet COD values. Higher concentrations can be tolerated as well but will cause corresponding decreases in total efficiency, therefore facilities to remove solids are sometimes recommended.

Effluents from pulp-and paper-industry often contain sulfur compounds due to chemical pulping (use of sulphite for delignification) or paper sizing (use of aluminium sulphate) respeetively. In case of competition for hydrogen, methane bacteria normally loose the battle against sulphate reducing bacteria and if enough sulphate is present, all hydrogen will be consumed by sulphate reducing bacteria :

$$4H_2 + CO_2 \text{ ——— } CH_4 + H_2O$$

displaced by

$$4H_2 + H_2SO_4 \text{ ——— } H_2S + 4H_2O$$

This has an unfavourable effect on :

— The efficiency of the process : 1 mg of $S^{2-} = 2$ mg of COD.

— The biogas quantity : max. 30 pnrcent loss

— The biogas quality : 1 to 5 percent H_2S

Besides one sometimes has to cope with odour problems, sulphide in the reactor may cause toxicity to methanogenesis and the anaerobic plant needs special protection against corrosion.

3. FULL - SCALE RESULTS

Information on full-scale plants that are operating or will be operating soon on-pulp and paper-mill effluent is shown in Table 1.

The results of the operating plants are still monitored by us and in the following part performance data are discussed.

TABLE—1 : OPERATING DATA ON FULL—SCALE BIOPAQ REACTOR IN PULP—AND PAPER—INDUSTRY

Company	Type of paper production	Reactor volume m³	Flow m³/d	Inlet COD kg/m³	Temp °C	Vol. [1]) loading kg COD/m³.d	HRT h	COD [2]) efficiency %	year of installation
Ceres (NL)	Board	70	100	6300	35	9	17.0	70	1983
Roermond Papier (NL)	Corr. medium Testliner	1000	3000	3500	30-40	11	8 0	75	1983
Celtona (NL)	Sanitary tissue	700	2900	1200	20-25	5	5 8	60	1984
Industrie-water (NL)	Folding box-board Corr. medium Testliner Envelop paper etc.	2200	10800	1000	28	5	4.9	75	1986
Davidson (UK)	Linerboard	1600	5000	2880	35	9	7.7	70	1986
Mayr Melnhof (Austria)	Folding box-board	1500	6000	2500	35-40	10	6.0	65[3])	1987
MacMillan Bloedel (Canada)	NSSC pulp Corr. medium Hard board	11000	6500	20000	35	12.5	41.0	65[3])	1987

REMARKS 1) Loadings are calculated on total reactor volumes.

2) BOD efficiencies are 10 to 15% higher.

3) Anticipated results.

TABLE–3
AVERAGE RESULTS OF PILOT PLANT WORK AT C. DAVIDSON & SONS

	influent (mg/l)	effluent (mg/l)	removal (%)
COD non-filtered	2417	980	59.4
COD filtered	1628	590	63.8
Filterable solids COD	789	390	50.6
BOD_5	1200	272	77.3
Sulphate	1204	575	56.4

It has been shown that the contribution of filterable solids to COD is about 33 percent. At reactor loadings, mainly between 6 and 12 kg COD/m³.d, a 50 percent removal of filterable solids COD is still established. The total COD removal is suppressed both by the presence of these solids and of sulphate. The produced sulphide has been responsible for about 10 percent of the efficiency loss. Diagram 3 shows how reactor efficiency is influenced by the quantity of sulphate conversion. The curves appear to run in opposite directions most of the time.

3.1. Ceres

The 70 m³ UASB reactor of Ceres was started up in April 1983 and its operation is still quite stable. The mill produces board from recycled paper. The water circuit is closed up quite far and the process water is at a temperature of 55°C. It once occurred that the reactor was accidentally heated up to 55°C and it then required a recovery period of about 4 weeks. One problem for the anaerobic process is a fairly high water-hardness (Ca> 1000 mg/1). This leads to $CaCO_3$ precipitation in the effluent gutters. Periodical cleaning is therefore required.

3 2. Roermond Papier

The reactor at Roermond Papier was started up in October 1983 and after 6 months of operation it produced its own granular sludge. After anaerobic treatment the effluent is post-treated in an aerobic plant that was built as early as 1977 The combination of anaerobic and aerobic treatment results in very high total removal efficiencies (COD 97.1%, BOD_5 99.7%), lower total costs than previously and a very reliable operation Total costs were brought down due to reduced power requirements for aeration and steam production from biogas. Reliable performance is a fact due to low sludge volume indexes that are realized in both the anaerobic plant (10 ml/g) and in the aerobic plant (50 ml/g). The BIOPAQ UASB reactor proved to be able to handle peakloadings of upto 25 kg COD/m³.d.

3.3. Celtona

This third full-scale BIOPAQ plant was started in November 1984 at the sanitary paper mill of Celtona. Temperature and COD concentrations of the combined effluent streams are relatively low, but pilot-plant work had previously shown (Habets 85a) that good results could be achieved, despite these sub-optimal circustances.

Because of the low COD and temperature (high hydraulic load and low biochemical activity) the design of the reactor was based on the hydraulic load. Therefore volumetric loads do not look very impressive. Results of the full-scale plant are illustrated in Diagram 1. COD–removal appears to be about 60 percent at temperatures ranging from 18°C to 26°C and influent COD's ranging from 700 to 1300 mg/1. Specific gas production is only 0.25 m³/kg COD-removal and Diagram 2 shows the composition of the biogas at different temperatures.

FIGURE 1 : RESULTS OF FULL-SCALE ANAEROBIC TREATMENT AT CELTONA, TWO MONTHS AFTER START-UP

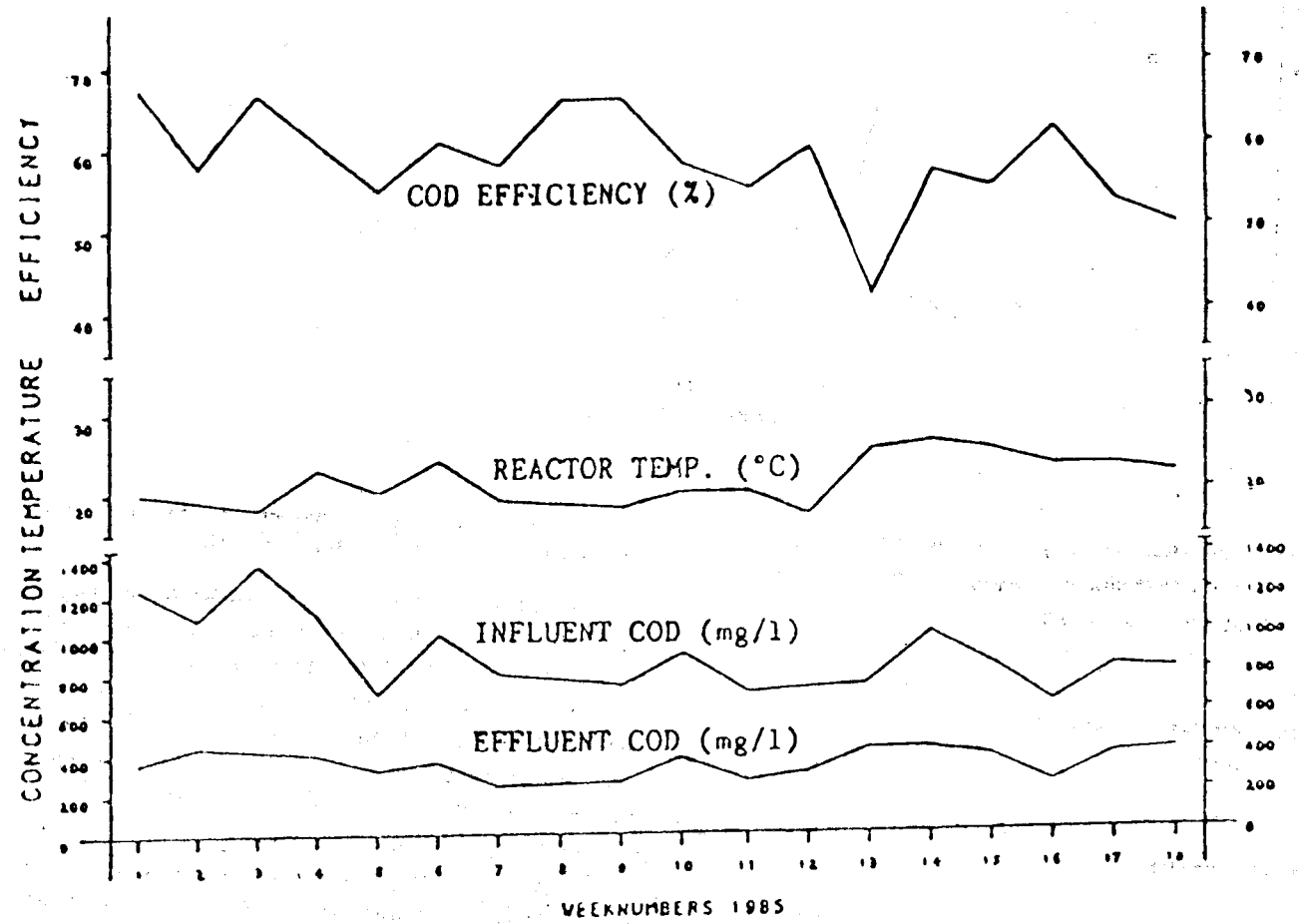
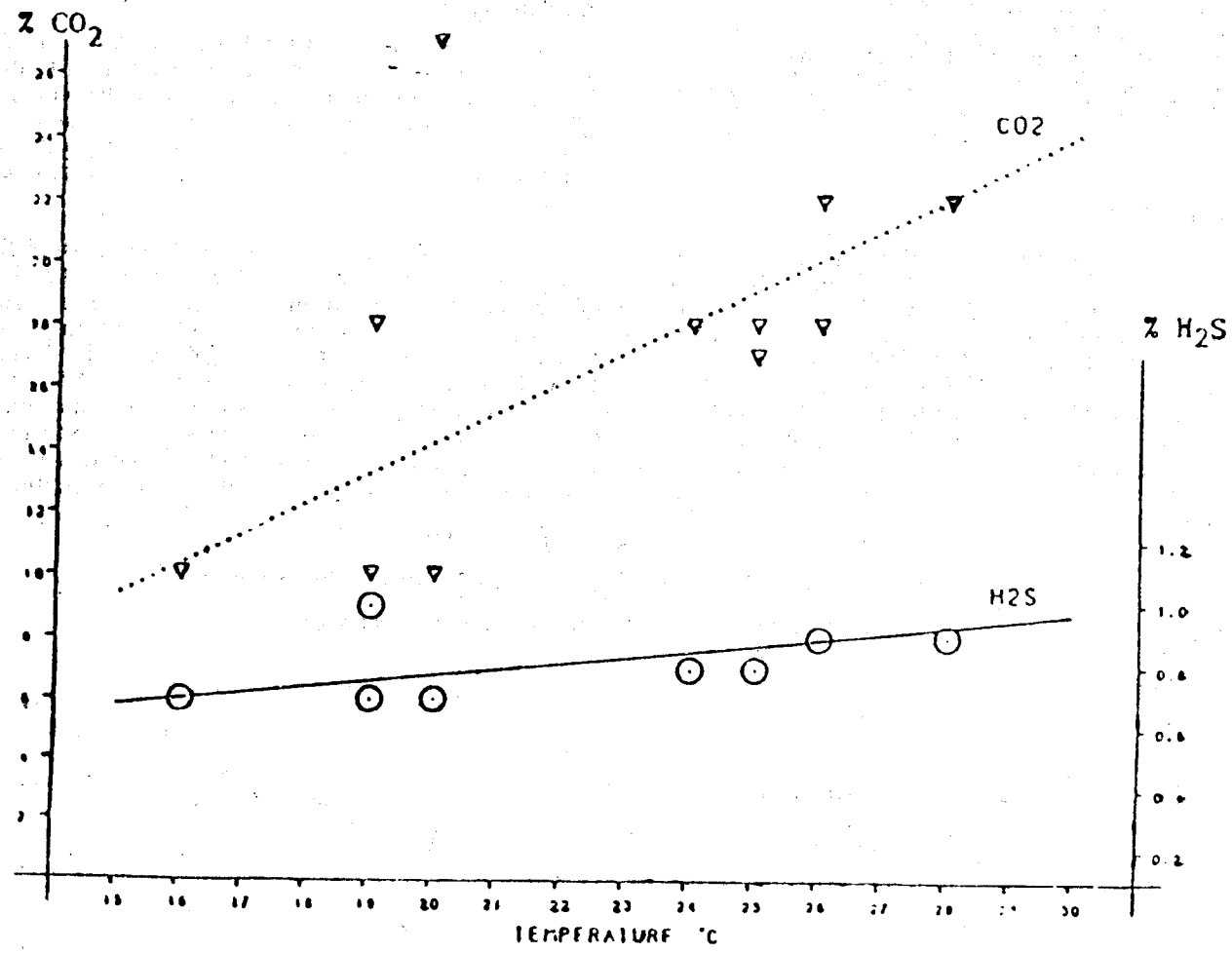


FIGURE 2 : CO_2 AND H_2S CONCENTRATION OF BIOGAS VERSUS REACTOR TEMPERATURE



After more than half a year of successful operation results were not satisfactory anymore and it was discovered that lack of nutrients and accidental introduction of oxygen into the reactor inlet caused a gradual deterioration of the sludge activity. After certain measures had been taken, removal efficiency improved again to the original levels.

3 4. Industriewater

This is the name of a combined wastewater treatment plant of three different paper mills. The anaerobic pretreatment plant has been built for similar reasons as at Roermond Papier, namely to expand the treatment capacity of the existing facilities.

The BIOPAQ plant was started up in January 1986 and Table 2 shows how the results improved gradually in the beginning of 1986. This improvement was caused by the growth and the development of new gradular sludge. Sludge volume indexes of the aerobic post-treatment sludge of 300 ml/g have been replaced by indexes for below 100 ml/g. A sodiumhydroxide gaswasher is successfuly used for H_2S scrubbing, before the biogas is burned for power generation (150 KW). As wastewater temperatures are higher than expected, biogas production rates are are also higher than predicted (see Habets 1987 for complete report).

TABLE—2

RESULTS OF THE BIOPAQ PLANT AT INDUSTRIEWATER IN THE BEGINNING OF 1986

(WEEKLY AVERAGES)

Week nr.	Influent[1] COD mg/l	Influent[1] BOD_5 mg/l	Effluent COD mg/l	Effluent BOD_5 mg/l	Reactor Temp °C	Biogas m^3/d	Removal Efficiency COD %	Removal Efficiency BOD_5 %
3	986	528	454	200	24	889	55	62
4	865	432	329	142	27	665	62	67
5	933	473	358	1 0	28.5	–[2]	62	70
6	724	322	304	117	27	885	58	64
7	819	407	306	111	27	–[2]	63	73
8	916	461	320	123	27	1080	65	73
9	902	421	320	124	27	1122	64	70
10	905	456	328	121	28	1810	64	73
11	756	364	273	89	28	1149	64	75
12	975	476	282	96	29	2195	71	80
13	993	471	272	101	28	2315	73	78
14	897	447	265	89	28	1887	70	80
15	742	329	211	73	27 5	840	72	78

REMARKS

1) Reactor feed increased from 400 to 450 m^3/h in week 12.
2) Not recorded
3) Biogas contents is $CH_4 : CO_2 : H_2S = 80 : 17.5 : 2.5$

3. 5. C. Devidson & Sons (Scotland)

Similar to the other cases mentioned, the decision to buy a BIOPAQ plant was made after extensive pilot work had been completed. During the pilot testing, concentrations of sulphate and suspended solids in the mills-effluents were quite high, up to 1700 and 1000 mg/l respectively. Despite this the results were satisfactory (Newns '86 and later on in this paper). In the meantime paper production has been modified to neutral sizing, which reduces concentrations of sulphate and suspended solids remarkably. Therefore results of the full-scale operation are better than those achieved during pilot tests. As legislation for sulphide discharge is very strict in the U.K., sulphide in the effluent of the reactor is oxidized with pure oxygen.

3 6. Mayr Melnhof (Austria)

At this boardmill, Purator, our licensee in Austria, is realizing two BIOPAQ reactors of 750 m^3 each. The plant will be in operation in summer this year. Pilot test results are discussed later on in this paper.

3. 7. MacMillan Bloedel (Canada)

Erection of the anaerobic wastewater treatment plant of MacMillan Bloedel will be completed in 1988. This year a current additional pilot-plant demonstration with a 20m^3 BIOPAQ reactor at the mill site will be completed. Results of a 1.4 m^3 BIOPAQ pilot study are described by Hall '86 and summarized in the following part of this paper.

3. 8 Tillmann Zulpich (West-Germany)

This papermill produces similar products as Roermond Papier and the anaerobic plant (150 m^3), which will start-up this Summer, will pretreat the waste water before it flows into the existing aerobic facility.

3. 9. Emin-Leydier (France)

The mill produces corrugated medium and testiliner from recycled paper. A 6 months' pilot study was completed in March 1986 and completion of the full scale plant (1000 m^3 reactor) is scheduled for Summer this year.

3. 10. Lake Utopia (Canada)

Paques Lavalin, our licensee in Canada recently went into a full scale contract with this company located in New Brunswick, which produces NSSC pulp and corrugated medium. The COD-load is 6000 kg/day and Paques Lavalin will operate the plant during six years and in return the client will purchase all the produced biogas.

4. RECENT PILOT PLANT STUDY RESULTS :

During the past year pilot-plant studies have been realized at six different pulp- and paper-mill effluents. Two of these were undertaken with 3.75 m³ reactors processing effluents comparable with Roermond Papier (same products), namely one in West-Germany by our licensee Passavant Werke and one in France by ourselves. Both test periods took about four months and confirmed that COD and BOD removal efficiencies were resp. 75 and 85 percent at average volumetric loadings of about 10 kg COD/m³.d. Sludge growth was about 0.05 kg ds/kg COD removal and biogas production was 0.40 to 0.45 m³ /kg COD removal.

At C. Davidson in Scotland, gypsumboardliner is produced from waste paper and the BIOPAQ process was exposed to high concentrations of suspended solids and sulphate. The average results of the 8 months' study with a 3.75 m³ reactor are summarized in Table 3.

Another pilot-study where sulphate influenced the results was at Mayr Melnhof in Austria, where folding boxboard is produced from waste paper. The BIOPAQ pilot had a volume of 13m³ and the trial lasted about four months. Diagram 4 shows the COD and sulphate conversions during a one month period in which volumetric loading was increased from 6.5 to 13 kg COD/m³ d. Average influent COD was 2500 mg/l, gas production varied from 20 to 40 m³/d and the H_2S concentration in the gas was 6 to 4 percent. Diagram 4 shows a COD removal efficiency increasing from 58 to 68 percent. As the effluent was analysed on sulphide content as well, COD due to sulphide could be calculated. This shows, that sulphide has been responsible for a reduction of COD efficiency by about 10 percent. Or, in other words, that the real removal efficiency of the organic substance is 79 percent at the end of the period. It is also remarkable that the best performance was reached during the highest volumetric loadings. VFA—levels in the effluent show, that no sulphide toxicity is noticeable at all, although the sulphide levels increases to 180 mg/l. The examples from practical work – where COD/SO_4 ratios were about 2– have also shown, that not all sulphate is being reduced and that sulphide present in the biogas is only 10 to 20 percent of the total sulphide produced.

FIGURE 3 : COD REMOVAL EFFICIENCY AND SULPHATE REMOVAL DURING PILOT PLANT TESTS AT DAVIDSON & SONS

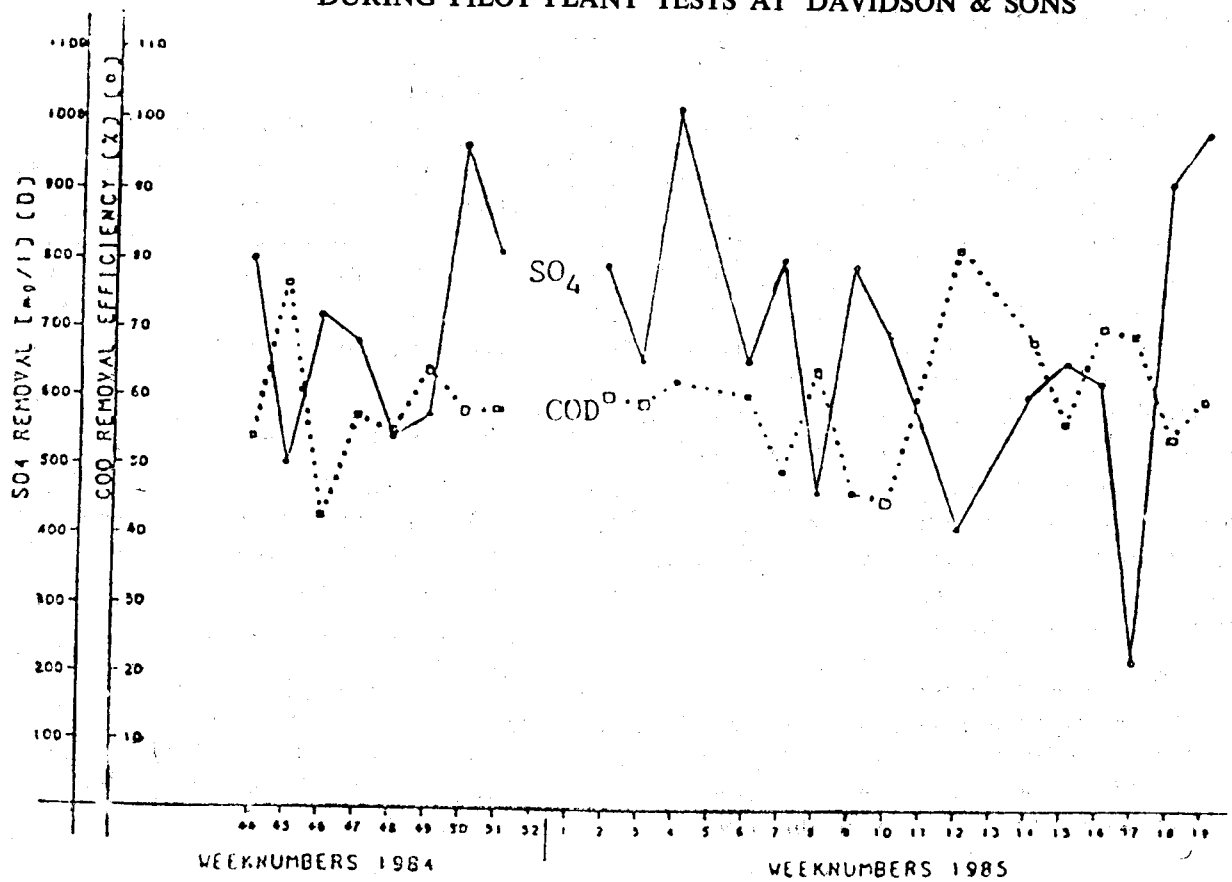
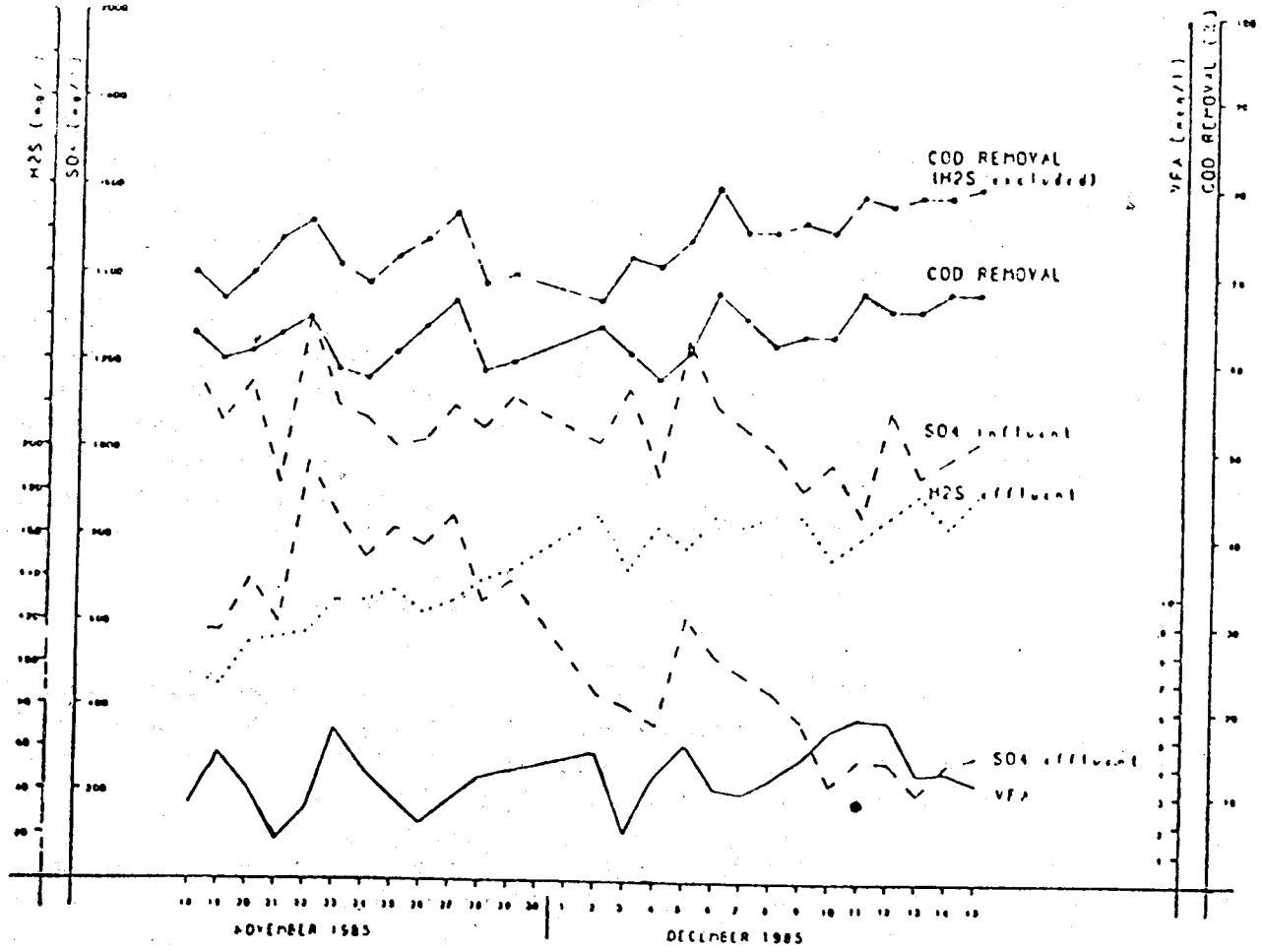


FIGURE 4 : COD REMOVAL EFFICIENCY AND SULPHATE CONVERSION REGISTERED AT A 13 m³ PILOT PLANT
(effluent from folding-boxboard production)



One pilot study has been carried on for quite some time now (more than 2 years) and takes place at a board mill in Austria. The mill produces its own pulp (TMP–process) and this causes a large amount of dissolved waste. Operation results of pilot-plants from several suppliers are being evaluated by the mill and the water authority.

The operation procedure of our 8m² BIOPAQ reactor has been modified several times and with the concept we have now a stable reactor operation at reactor loading up to 18 kg COD/M³ d and COD removal rates of 80 percent has been achieved. The activity of the sludge was sometime suppressed by the toxic influence of tannins. These tannins originate from pieces of bark in the raw material. In the past year we have developed a method to reduce the toxicity of tannins in order to increase the methanogenic activitity in our reactors and to decrease aquatic toxicity in general. The method can also be applied to all barkpress and debarking effluents and is very efficient. After a detoxification stage was added to the pilot plant, volumetric loading rate of the reactor could be almost doubled.

The pilot-plant work on MacMillan Bloedel's effluent in Canada was initiated in June 1984 at the Wastewater Technology Centre (WTC) in Burlington, Ontario.

The wastewater consists of a black liquor from NSSC pulping (2500 m³/d with COD 40 kg/m³ and BOD 16 Kg/m³) and the combined effluent from chip

wash, paper mill and hardboard pulping (3800 m³/d with 7 kg/m³ and BOD 2.5 kg/m³). It was delivered to the WTC in 24 tanker loads during 18 months and tested at pilot-plants of different design. These different reactor types were Downflow Fixed Film, hybrid, fluidized bed and UASB. The complete evaluation of the study has been described in detail by Hall '86.

In the beginning of 1985 the original UASB pilot was modified to a BIOPAQ UASB of 1.4 m³ volume. Consequently reactor loadings could be increased from 10 to 20 kg COD/m_3.d. without upsetting the system and maintaining the excellent performance. The use of sodium-hydroxyde had been quite high in the past and could be reduced substantially compared with the other systems.

As a result of the pilot-scale testing program, it was concluded that a number of technical alternatives were available for achieving the full-scale performance criteria of 75% BOD removal at a minimum organic loading of 10 kg COD/m³.d. At this stage, MacMillan Bloedel arranged to contact ten suppliers of commercial anaerobic technologies to obtain estimates of the capital and operating costs of full-scale systems for installation at Sturgeon Falls. Performance data generated during the pilot plant tests were summarized and forwarded to the suppliers. The full-scale designs solicited were based on the 75% removal/10 kg loading criteria. However, the suppliers were given the freedom to further optima ize their designs on the basis of their interpretation of the data provided, in order to achieve the most economical full-scale system.

The assessment disclosed that the UASB technology proposed by Paques - Lavalin offered the most attractive combination of technical and economic benefits for application at Sturgeon Falls. The projected capital cost of a full-scale BIOPAQ system in 1985 was Can. dollar 0.9 M per year. At Sturgeon Falls, biogas can be used to replace an equivalent amount of natural gas. This will produce a surplus operating cost of Can. dollar 0.4M which can be applied against amortization of the capital investment.

On the basis of the projected full-scale costs, MacMillan Bloedal chose our Canadian Licensee Paques-Lavalin to supply, install and operate during one year a 20 m³ on-site demonstration plant. This plant has been in operation now since the beginning of May of 1986 and the results are used to confirm and/or refine the design of the process prior to processing with the installation of the full-scale anaerobic treatment plant.

5. CONCLUSIONS

The BIOPAQ UASB process has shown its applicability for many types of pulp- and paper-mill effluents and is being seleeted increasingly for different reasons, such as its economy, its reliable performance and our experience in this field.

Five papermills already treat their effluent anaerobically and at least another four BIOPAQ plants are under construction.

Tolerances to low temperatures, high and low COD's high hydraulic loads, high sulphate concentrations and high suspended-solids concentrations have been confirmed. A good performance has been achieved. despite sub-optimal cireumstances.

Successful longterm pilot trials have been conducted on TMP and NSSSC pulping effluents. The potential for sulphite evaporator condensates and for CTMP pulping effluent is positive nnd is being evaluated at the moment.

A detoxification process for effluents from debarking and barkpressing has been developed, so that the green light is given for treatment of pulp mill effluents containing tannlns.

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