## OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

## DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

## FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

## CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

RESTRICTED

21399

DP/ID/SER.A/1748
29 January 1996
ORIGINAL: ENGLISH

15p
-[illegible]

**HIGH LEVEL ADVISORY SERVICES FOR THE BAIKALSK PULP AND PAPER MILL**

SI/RUS/94/801/11-53

RUSSIAN FEDERATION

**Technical report: Assessment of the waste water situation at BPPM***

Prepared for the Government of the Russian Federation
by the United Nations Industrial Development Organization.
acting as executing agency for the United Nations Development Programme

*Based on the work of Prof. Dr. L. Huber.*

Backstopping officer: R. M. Viegas Assumpcao
Chemical Industries Branch

United Nations Industrial Development Organization
Vienna

---

* This document has not been edited.

V.96 80482

# TABLE OF CONTENTS

## 1. Introduction

In keeping with the job description, this expertise deals primarily with the question of the external waste water treatment and sludge disposal at the Baikalsk Pulp and Paper Mill. It includes an assessment of the in-plant situation, manufacturing included, in so far as this affects water consumption and the production of waste water.

## 2. Fresh water supply

The mill draws all the fresh water required from Lake Baikal. The specific quality of the lake water, with its low electrolyte and salt content, was one of the main reasons for choosing this location for the mill. The low silicon and iron content of the water played a particularly important role in this respect.

Table 1 : Lake Baikal water

| | 40m | 0 . 5m |
|---|---|---|
| pH | 7.9 - 8.0 | 7.5 - 7.8 |
| $KMnO_4$ consumption (mg / l) | 0.6 - 0.8 | 1.1 - 1.3 |
| $BOD_5$ (mg / l) | 0.4 - 0.6 | 0.6 - 1.4 |
| $O_2$ content (mg / l) | 11.8 - 12.2 | 9.0 - 9.4 |
| Evap. residue (mg / l) | 69 - 76 | 92 - 119 |
| $PO_4$ - P (mg / l) | 0 - 0.02 | 0 - 0.03 |
| $NH_4$ - N (mg / l) | 0 - 0.015 | 0 - 0.025 |
| $NO_3$ - N (mg / l) | 0.3 - 0.5 | - |
| $SO_4$ (mg / l) | 6.1 - 6.6 | 7.1 - 9.8 |
| Cl (mg / l) | 0.6 | 1.8 - 2.6 |
| Alkalinity (mval / l) | 0.9 - 1.1 | 1.1 - 1.4 |
| Al (mg / l) | 0 - 0.015 | 0 - 0.08 |
| Fe (mg / l) | trace | 0.05 |
| Mn (mg / l) | trace | trace |
| Si (mg/l) | 0.72 | 0.78 |

Analytical data show in addition very low concentrations of organic substances and of inorganic nutrients such as phosphorus and nitrogen compounds.

Water is withdrawn through two pipelines, with the pump stations located approximately 500 m apart on the lakeshore. Through pipeline I) water for the manufacturing process is drawn from a depth of 40m at a distance of some 100 m from the lakeshore. The maximum withdrawal rate is 10 000 $m^3$ / h; as a rule, however, only 3 000 - 4 000 $m^3$ / h are withdrawn of which , in turn, some 60 $m^3$ / h are fed into the town of Baikalsk's drinking water supply. This water is additionally disinfected by means of UV irradiation and can, if necessary, also be fluoridized. The town also has other sources of drinking water; the specific water consumption is 750 l / p / d, which is unusually high even by Russian standards.

Through pipeline II) water for the power plant is drawn from a depth of 12 m; the maximum withdrawal rate is 8 000 $m^3$ / h, although the quantity effectively required is only 3 000 $m^3$ / h. The cooling water is not treated.

Water streams I) and II) are measured continuously.

2.1 Water treatment

The water withdrawn through pipeline I) for the manufacturing process is pumped to the mill (6 pumps with different delivery rates) , where as a rule it is used directly. Six sand filters are available to remove excessive amounts of solid material which the water might at times contain - e.g. due to stormy conditions on the lake.

The water withdrawn via pipeline II serves initially as a coolant. The collective stream of 3000 $m^3$ / h is then split up and used as follows:

- 800 $m^3$ / h for steam raising
- 450 $m^3$ / h for the town's hot water supply
- 750 $m^3$ / h for pulp manufacture
- 1 000 $m^3$ / h direct to waste water treatment plant.

To discharge 1 000 $m^3$ / h of clean cooling water into the waste water treatment plant is not in keeping with usual procedures; the rain water entering the system during rainy periods renders this unnecessary. The possibility of using these 1000 $m^3$ / h in the manufacturing process should therefore be considered. This, however, would necessitate modifying the waste water regulations so that the mill is not forced to observe partially unrealistic and exaggerated limiting values by means of dilution. The water-saving potential is at any rate a convincing argument for using this water in the manufacturing process.

The water used for raising steam is desalinated by means of ion exchangers (anionic/cationic), which results in 150 $m^3$ /d of regeneration effluents. These effluents are largely neutralized by mixing them with each other before they are discharged into the waste water treatment plant.

## 2.2 Water consumption in the manufacturing process

The amount of water used in manufacturing is calculated from systems I) and II) to be approximately 750 $m^3$ / h + 4000 $m^3$ / h + 400 $m^3$ / h = 5150 $m^3$ / h. This corresponds to an average water consumption of some 280 $m^3$ / t pulp, excluding the water needed for power generation.

The water consumption divides up as follows:

| | |
|---|---|
| 1. Paper machine | 25 $m^3$ / h |
| 2. Pulp drying | 360 $m^3$ / h |
| 3. Fresh water treatment, steam generation | 700 $m^3$ / h |
| 4. Bleaching plant | 1370 $m^3$ / h |
| 5. Cooking, brown stock washing and screening | 600 $m^3$ / h |
| 6. Lime regeneration | 42 $m^3$ / h |
| 7. Concentration and incineration (cooling water) | 2300$m^3$ / h |
| 8. Wood debarking | 30 $m^3$ / h |
| 9. Repair shop | 70 $m^3$ / h |
| 10. Effluent treatment plant | 60 $m^3$ / h |
| Total: | 5587 $m^3$ / h |

Although the water consumption in the various departments was measured specifically, there are considerable limitations with respect to the reliability of the individual figures. In the absence of a Sankey diagram for the overall manufacturing process, these figures can only be used to a limited extent in an assessment. The deficit of 437 $m^3$ / h between 5150 $m^3$ / h and 5587 $m^3$ / h is likewise a result of this circumstance.

## 3. Waste water sources and quality

The centrally treated waste water originates from the pulp and paper mill and its peripheral facilities as well from the town itself.

### 3.1 Pollutant content of Baikalsk town's waste water

There are practically no industrial or commercial enterprises producing effluent which could affect the waste water quantity or quality to any appreciable extent (bakery, milk bottling facility and pig farm with 230 animals).

The town of Baikalsk's waste water situation can be characterized as follows:

| | |
|---|---|
| • Sewage volume 1994 (daily average) from the town | 10 011 $m^3$ / d |
| • Sanitary sewage from the pulp and paper mill | 2 000 $m^3$ / d |
| | 12 011 $m^3$ / d |

This corresponds to an average per capita sewage volume of 728 l / d.

The collective sewage is fed without pre-treatment into the pulp and paper mill waste water treatment plant. The following effluent loads can be derived arithmetically from the known population figures:

| | | | | |
|---|---|---|---|---|
| $BOD_5$ in suspension | 16 500 x 60 g / p / d | = | 990 | kg / d |
| $BOD_5$ as sediment | 16 500 x 40 g / p / d | = | 660 | kg / d |
| COD | 16 500 x 120 g / p / d | = | 1 980 | kg / d |
| N | 16 500 x 11 g / p / d | = | 181.5 | kg / d |
| P | 16 500 x 3.5 g / p / d | = | 58 | kg / d. |

The concentrations of the municipal sewage components, monitored continuously by the mill, are unusually low due to the extremely high dilution factor resulting from the very high specific water consumption:

16.7 mg / l for the $BOD_5$
67.4 mg / l for the COD
2.7 mg / l for P
10.8 mg / l for N.

As far as $BOD_5$ levels are concerned, discharge levels here already correspond to those of a well-functioning biological sewage disposal plant. It would thus make no sense to provide for independent treatment of this waste water using biological processes, particularly not if there is a denitirifcation stage. The elevated P levels result presumedly from the use of detergents that contain phosphates. The collective waste water from the town is fed via a collective sewer of some 5 km length to the waste water treatment plant at the mill.

The overall conclusion to be reached is that due to the excessively high water consumption in and around the town of Baikalsk the concentrations of the waste water components are so low as to be highly unsuitable for or even to exclude the use of a biological sewage disposal plant for the separate treatment of this waste water ($BOD_5$ sludge load too low, no sludge growth) . Since a technological solution to this problem makes no sense, the only answer is to increase the drinking water and sewage rates sufficiently to make the consumers cut down on their excessive use of water. The current rates of 63 rubels per $m^3$ drinking water and 76 rubels per $m^3$ sewage are no incentive for a more ecomical use of water.

3.2 Rain water

Approximately 10 % (25 hectares) of the total mill premises of 250 hectares is drained by means of a rain water sewer system. The rain water is collected mainly from paved surfaces, roofs etc. The total annual rainfall is 760 mm, with most of the precipitation occurring in the months June - August, the least in the months January, February and March. The amount of rain water collected averages between 100 - 300 $m^3$ / d.

3.3 Mill effluents

3.3.1 Debarking facility

The wet debarking facility has capacity for 3 500 $m^3$ / d (D = 0.6) or 2 100 t / d of wood. It comprises three lines, each with two debarking drums. The bark accounts for 6 % of the processed wood. The overall facility has a volume of 400 $m^3$ and can be operated in two different ways (A and B) with respect to water consumption and effluent volume.

| | A<br>non-cyciic | B<br>cyclic |
|---|---|---|
| Fresh water | 30 $m^3$ / h | 30 $m^3$ / h |
| Hot water from evaporators | 400 $m^3$ / h | 50 - 60 $m^3$ / h |
| Total | 430 $m^3$ / h | 80 - 90 $m^3$ / h |

The water consumption corresponds to the volume of effluent produced.

The effluent treatment facility for each line consists of:

- sedimentation tank 1st stage with 400 $m^3$
- WACO filter
- sedimentation tank 2nd stage with 200 $m^3$.

So little sludge is form.ed that the sedimentation tanks only need to be cleaned once a year.

Effluent from the cyclic operation is characterized as follows:

| | |
|---|---|
| SS (mg / l) | 300 |
| BOD (mg / l) | 898 |
| COD (mg / l) | 2 212 |
| $KMnO_4$ consumption (mg / l) | 1 900 |
| lignin (mg / l) | 340 |
| phenol (mg / l) | 55 |
| resin acid (mg / l) | 145 |

A dry debarking facility is being erected in 1995, which can process 1/3 of the wood.

### 3.3.2 Digester plant

The plant contains 24 digesters in two lines. They discharge collectively into a blow pit. The building features a system of channels to take up spills. Due to the poor structural and technical condition of the digesters only 8 - 9 are in operation at any one time. Spills occur 2 - 3 times a week. The channel system can be kept closed by means of gates and shut-off devices until the effluent has been tested chemically (pH, alkalinity, $KMNO_4$, SS) and a decision made by the engineer in charge as to the further treatment of the effluent. If the effluent is strongly contaminated it is fed into the black liquor system ; if it is only weakly contaminated it is sewered into two buffer tanks with a capacity of 200 000 $m^3$, where it is stored until it can be disposed of later via the central waste water treatment plant.

Highly contaminated effluent is produced at the rate of 80 $m^3$ / h by condensation of the vapour from the blow pit. This effluent is characterized as follows:

| | |
|---|---|
| $KMNO_4$ consumption (mg / l) : | 360 |
| methylated sulfur compounds (mg / l) : | 46 |

| | |
|---|---|
| mercury (mg / l) : | 11 |
| phenols (mg / l) : | 14 |
| resin acids (mg / l) : | 95 |
| lignin (mg / l) : | 560 |

This effluent is highly toxic for aquatic life; it is still acutely toxic for daphnia even when diluted 1:3700. It is accordingly fed into the black water system of the waste water treatment plant. With technological modifications to the blow pit system (no direct condensation), substantial improvements with respect to the effluent could be achieved.

3.3.3 Concentration and incineration of the black liquors

The black liquor removed from the brown stock washers is supplied to a four-stage, four-line evaporation plant, system ROSENBLAD. With a 92 % recovery rate, some 90 $m^3$ of liquor are produced per cooking operation. Before the liquor is concentrated, fibrous material is removed with filters. The incoming weak black liquor is concentrated initially to 42 - 43 % SS. The solid material content is increased to 60 - 62 % in the down-stream evaporators. The condensates resulting from the evaporation process are collected separately as

- steam condensate
- foul condensates,

the former of which is reused directly. The contaminated condensates have been subjected since 1988 to a novel catalytic oxidation process developed by the Irkutsker Institute for Hydrocarbon Synthesis. This process, which involves the use of a heterogenous antimony catalyst embedded in a matrix of polyethylene, results in the almost complete oxidation of organic carbon and sulfur compounds. The conversion takes place without the application of pressure at a temperature of 90°C and requires an air throughput of 1 : 5 to 1 : 10 relative to the quantity of effluent. The process provides a highly efficient means of converting reduced sulfur compounds to sodium thiosulfate (about 80 %) and sodium sulfate (about 20 %). The degrees to which various sulfur compounds are oxidized are as follows:

| | |
|---|---|
| $H_2S$ | 100 % |
| mercaptans | 95 - 98 % |
| dimethyl sulfide | 95 - 99 % |
| dimethyl disulfide | 92 - 96 % |
| phenols | 80 % |

Only one of two available facilities is required. The treated effluent is reused in its entirety. This means that the evaporation plant produces no effluents that have to be treated in the central waste water treatment plant.

For concentrating the white liquor resulting from cord manufacture there is an additional three-line, seven-stage evaporation facility. It will be possible to use one of these lines, which is currently not required, to concentrate the effluent from a future $O_2$ delignification facility.

The water consumption (primarily cooling water) for concentration and incineration is about 2 300 $m^3$. Of this, some 500 $m^3$ end up slightly contaminated (non-return water). This effluent is fed directly into the central waste water treatment plant (black stream) and is characterized as follows:

| | |
|---|---|
| pH : | 11.4 |
| $KMnO_4$ consumption (mg / l) : | 130 |
| Na (mg / l): | 180 |
| methylated sulfur compounds (mg / l) | 0.3 |
| resin acids (mg / l) | 35 |

1 800 $m^3$ / h are stored temporarily ( t = 40°C ) and then used in various manufacturing areas such as debarking and bleaching.

3.3.4 Brown stock washing and screening

The brown stock is passed directly from the blow pit to the brown stock washing facility. Washing takes place in 6 stages with 3 RAUMA-REPOLA filters. As wash water use is made of condensates from the evaporation plant or of warm water.

The pulp concentration during washing is 6 - 8 %, the wash water consumpton approximately 8 - 9 $m^3$ / t or 90 $m^3$ / h. Brown stock washing guarantees a recovery rate of only 92 %; the loss of sodium sulfate is calculated to be some 40 kg $Na_2SO_4$ / t. COD and BOD losses are correspondingly high. A few years ago the $Na_2SO_4$ losses were still around 100 kg / t. There are plans to improve the black liquor recovery rate to 99.5 % by installing a pressure screen. The brown stock screening facility comprises two parallel lines with four stages. The degree to which screening is cyclic is low. The process must therefore be seen to a greater or lesser extent as an additional pulp washing stage. The entire system has a volume of 3000 $m^3$. The effluent produced corresponds to the fresh water consumption of some 750 $m^3$ / h per line. That amounts to about 77.3 $m^3$ / t. From the point of view of volume, screening thus represents a very important source of effluent. The effluent is characterized as follows:

| | |
|---|---|
| pH | 10.8 |
| BOD (mg / l) : | 134 |
| COD (mg / l) : | 390 |
| $KMnO_4$ consumption (mg / l) : | 150 |
| lignin (mg / l): | 130 |
| Na (mg / l): | 80 |
| $SO_4$ (mg / l): | 65 |
| $S^{--}$ (mg / l) : | 0.3 |
| phenols (mg / l): | 14 |

The manner in which brown stock washing is currently performed is not state of the art. It must be a primary aim of improvement to render this stage either completely or at least to a large extent cyclic, among other things to reduce the sodium sulfate losses.

The unusable fibers (rejects) go to the paper machine.

### 3.3.5 Bleaching plant

In order to manufacture the various grades of pulp such as

- cord pulp
- viscose-grade pulp
- paper-grade pulp

the mill makes use of the following different bleaching sequences:

| | |
|---|---|
| cord pulp | $C - E_1 - H_1 - A - E_2 - D_1 - H_2 - D_2 - A$ |
| viscose-grade pulp | $C - E_1 - H_1 - E_2 - D_1 - D_2 - A$ |
| paper-grade pulp | $C - E_1 - H_1 - H_2 - D_1 - D_2$ |

In the case of paper-grade pulp, further reductions in the bleaching sequence are possible. The total chlorine used for cord and viscose-grade pulp divides up as follows:

| | | |
|---|---|---|
| | Total chlorine | 70 kg / t |
| Of this: | elemental chlorine | 45 - 50 kg / t |
| | chlorine dioxide | 12 - 14 kg / t |
| | hypochlorite | 6 - 13 kg / t |

The water consumption derives from the following data:

| | |
|---|---|
| a) fresh water | |
| - cord pulp : | 120 $m^3$ / t |
| - viscose-grade pulp : | 80 $m^3$ / t |
| - paper-grade pulp : | 80 $m^3$ / t |
| b) warm water: max. | 30 $m^3$ / t |
| c) hot water: max. | 25 $m^3$ / t |
| d) circuit water for pulp drying: max. | 20 $m^3$ / t |
| e) deionized water: max. | 10 $m^3$ / t |
| f) clean condensates from white liquor conc.: max. | 10 $m^3$ / t |

Since some fresh water streams are interchangeable, the actual consumption is

| | |
|---|---|
| cord pulp: | 180 $m^3$ t |
| viscose-grade pulp: | 136 $m^3/t$ |

These quantities represent at the same time the amounts of effluent produced. With cord pulp, effluent is produced at 11 stages in the bleaching process and with viscose-type pulp at 8 stages. The individual component streams are sewered into the white or black water system depending on the degree of contamination. The discharges from C and $E_1$ totalling 700 $m^3/h$ or 70 $m^3$ / t, are utilized in two separate streams (C = 500 $m^3/h$ and $E_1$ = 200 $m^3/h$) for washing the waste gases and condensates from the digester plant. A wash tower is available specifically for this purpose. The chemical nature of the waste water from the C and $E_1$ stages, after having been used as wash water, is as follows:

| | C stage (500 $m^3/h$) | $E_1$ stage (200 $m^3/h$) | after joint use |
|---|---|---|---|
| pH : | 2.4 | 11.7 | 3 - 6 |
| $KMnO_4$ consumption (mg / l) : | 54 | 1300 | 300 |
| $Na^+$ (mg / l) : | 14 | 480 | 160 |
| $Cl^-$ (mg / l) : | 130-150 | 600 | 200 |
| COD (mg / l) : | - | - | 50 |
| BOD (mg / l) : | - | - | 23.8 |
| $G_D$ : | 190 | - | 50 |

This waste water is then fed into the black water system. The discharge volumes from the other bleaching stages amount to:

110 $m^3$ for cord pulp

60 $m^3$ for viscose-grade pulp

These effluents are fed into the white water system; because their compositions fluctuate very strongly there are sometimes problems with their treatment in the central waste water treatment plant.

3.3.6 Pulp screening and drying

Bleached stock screening and drying is performed in a dual line, two stage facility using centricleaners and SC screens. Of the screening water, that is

300 $m^3$ / for the cord pulp line
60 - 80 $m^3$ / h for the viscose pulp line,

some is used again (bleaching) and some goes into the white water system. This water is weakly contaminated and has the following composition:

| | |
|---|---|
| pH | 3.2 |
| $KMnO_4$ consumption (mg / l) : | 50 |
| $BOD_5$ (mg / l) : | 50 |
| COD (mg / l) : | 139 |
| $Na^+$ (mg / l) : | 1.9 |
| $Cl^-$ (mg / l) : | 0.6 |
| SS (mg / l) : | 80 |

Extensive reuse of the water is prevented by the high proportion of fine fibers. An appropriate filter could in future be useful here.

3.3.7 Chemicals Treatment and Recovery

Of the 5 recovery boilers, three are in constant use, one is in reserve and one is defective. Green and white liquor treatment produces a total of 150 $m^3$ of effluent per hour. This effluent comprises some 120 $m^3$ / h of clinker water which is subjected to wet-ash removal and then, following mechanical treatment (in ponds) sewered to the waste water treatment plant, and 20 - 30 $m^3$ / h water which is used for gas washing.

### 3.3.8 Boiler House

In the boiler house approximately 3 000 $m^3$ / h of fresh water are required per hour, primarily for cooling purposes. This volume of water divides up as follows:

2150 $m^3$ / h steam turbine cooling
350 $m^3$ / h further cooling requirements in the boiler house
500 $m^3$ / h fire extinguishing.

Some of the steam turbine cooling water, which has a temperature of 30 - 40°C, is used again as follows:

350 $m^3$ / h steam generation
400 $m^3$ / h pulp washing (in part following desalination)
400 $m^3$ / h hot water supply for the town of Baikalsk (the temperature of the water is first raised to max. 90°C in winter and 70°C in summer).

A volume of 1 000 $m^3$ / h is supplied directly to the central waste water treatment plant.

The steam generating plant comprises 5 units which are fired exclusively with lignite and bark. The mean proportion of ash amounts to 16 - 20 %, the sulfur content to 0.8 - 1.2 %. The ash is removed in a the wet ash removal facility, which is also used for the combustion residues from calcination and from the incineration of sewage sludge. The total water consumption divides up as follows:

1285 $m^3$ / h boiler house
150 $m^3$ / h calcination
65 $m^3$ / h sludge incineration

---

1500 $m^3$ / h total water consumption for wet ash removal.

The wet ash removal water is treated mechanically in settling ponds located some 5 km from the mill. The overall retention time in the ponds is about 5 1/2 days. Originally there were three ponds with a total volume of 2 million m³ for treatment of the waste water from the wet ash removal facility. One of these ponds, with a volume of 750 000 m³, is already completely full of ash; a second pond, also with a volume of 750 000 m³, has been in use for 3 years and will probably suffice for the next two years. The third pond, which has a capacity of 500 000 m³, is still in reserve. Prospects for the future include

- provision of further pond capacity, which is likely to be difficult (environmental considerations)
- the use of ash e.g. in the production of cement (nearest cement works in Angarsk).

As a result of cyclic reuse of the mechanically treated water the volume of waste water does not exceed 450 m³ / h. The quality of this waste water, which is sewered to the central waste water treatment plant, is shown below:

| | |
|---|---|
| pH | 9.5 |
| SS (mg / l) : | 121 |
| evaporation residue (mg / l) : | 665 |
| alkalinity (mval / l) : | 6.6 |
| COD (mg / l) : | 219 |
| $H_2S$ (mg / l) : | 1.2 |

The relatively high COD load in the waste water is caused by the component stream from the sludge incineration plant, where the temperature is too low for complete oxidation of the organic compounds (the ash contains 20 % organic material).

The wet ash removal procedure and the sewering of the waste water into the mill's central waste water treatment plant must be regarded as extremely problematic, since

a) the organic waste water load is increased substantially

b) the treatment facilities in the central waste water treatment plant are subjected to an unnecessary hydraulic and salt load and undesired material (salts) is not removed.

3.3.9 Production of Clorine Dioxide

The chlorine dioxide required for bleaching is produced from sodium chlorate in a Mathieson-type plant. The sodium chlorate is currently purchased from the Bratsk Pulp and Paper Mill, but there are delivery difficulties.
The concentrated sulfuric acid produced as a by-product at the rate of 0.3 $m^3$ / h is used as a neutralizer in the digester plant.

3.3.10 Production of Tall Oil

No waste water is produced during tall oil production.

3.3.11 Paper machine

Rejects from brown stock screening are processed in the paper machine to wrapping paper at a rate of approximately 30 t / d. Waste water is produced at a rate of some 25 $m^3$ / h or 600 $m^3$ / d, which corresponds to a specific waste water volume of 30 $m^3$ / t. The waste water has a $BOD_5$ load of 120 mg / l and a COD load of 82 mg / l.

## 4. Waste Water Treatment

The total volume of waste water sewered to the central waste water treatment plant is made up of:

- 5000 $m^3$ h white stream
- 1400 $m^3$ / h black stream
- 450 $m^3$ / h wet ash removal water
- 400 $m^3$ / h domestic waste water from town and mill

8150 $m^3$ / h total volume

Below is a list of almost all the component streams which are discharged from the mill into the central waste water treatment plant:

Effluent Streams discharged from the Mill into the Waste Water Treatment Plant

1. Wet debarking
2. Dewatering: black liquor regeneration
3. Dewatering: pulp cooking (spills)
4. Dewatering: black liquor concentration
5. Brown stock washing
6. Brown stock screening
7. Gas washing: black liquor oxidation
8. Blow-off condensate (digester plant)
9. Regeneration water: ion exchangers
10. C bleaching stage
11. Alkaline extraction stage
12. $D_1$ bleaching stage
13. $D_2$ bleaching stage
14. H bleaching stage
15. Cold alkaline improvement
16. Dewatering: pulp bleaching
17. Pulp acidifcation with $SO_2$ (bleaching plant)
18. Waste water from pulp screening
19. Pulp dewatering: screens
20. Sludge dewatering: centrifuge
21. Waste water from wet ash removal facility
22. Sludge flotation
23. Sanitary sewage from mill
24. Municipal sewage from Baikalsk town.

In the absence of a Sankey diagram it is extremely difficult to define the individual waste water streams which are sewered to the waste water treatment plant in terms of volume; accurate chemical analysis is equally difficult.

The actual volume of waste water produced in 1994 was 6 620 $m^3$ / h. This corresponds to a specific waste water volume of approximately 331 $m^3$ / t of pulp, when the municipal waste water is subtracted.

The waste water is treated in two different systems with the following inputs, although a certain degree of flexibility is maintained, e.g. in apportioning the municipal sewage:

System A

- 5900 $m^3$ / h white stream
- 700 $m^3$ / h black stream (50 %)
- 450 $m^3$ / h wet ash removal water
- 200 - 400 $m^3$ / h domestic waste water

System B

- 700 $m^3$ / h black stream (50 %)
- 0 - 200 $m^3$ / h domestic waste water

The two systems are largely analogous in design, but differ in their waste water capacities.
They comprise the following functional units:

- receptor and buffer tanks for spills and waste water surges
- neutralization tanks
- blending and pre-aeration tanks
- activation plant with clarification stage.

4.1 Receptor and buffer tanks

In order to prevent upsets in subsequent waste treatment operations, both System A and System B has a receptor and buffer tank with a volume of 130 000 and 70 000 $m^3$ respectively. These are usually needed once a week.

### 4.2 Neutralization tanks

The open neutralization tanks (concrete) are for pH equalization and for adjusting the alkalinity for subsequent chemical precipitation. The retention time is 10 minutes. The tank in Plant A has a volume of 825 $m^3$, that in Plant B a volume of 200 $m^3$. The pH of the incoming waste water is as a rule between 5 and 10; it is adjusted to a value between 6.0 and 8.0, either by self-neutralizaion or through addition of HCl or NaOH. As a rule, the latter is required more often. Activated sludge is added at the same time to effect a sludge concentration of 1 g / l. The tanks are aerated and their content thus circulated; the oxygen concentration is 4-5 mg / l. The stripping of volatile substances (S compounds from the digester plant) results in unpleasant smells.

### 4.3 Pre-aeration and blending tanks

Additional safety is provided by pre-aeration and blending tanks with retention times of 2 - 3 1/2 hours. These tanks are rectangular cascade tanks. Plant A has two such tanks each with 3 cascades and a total volume of 2 x 3 600 $m^3$. Plant B has one tank with two cascades and an effective volume of 1 890$m^3$. Aeration is adjusted such that there is an oxygen content of 4 - 5 mg $O_2$ / l. The activated sludge concentration is approximately 1.5 kg SS /$m^3$. The aeration system, comprising pipes with 7 mm - diameter holes, is no longer state of the art and is highly prone to corrosion.

Pretreatment of the waste water in neutralization, pre-aeration and blending tanks results in a marked reduction in the COD load, namely by

34.4 % in System A
40.1 % in System B.

This has direct consequences for the activation plant.

## 4.4 Activation plant

The dual-system activation plant is dimensioned as follows:

| | Plant A | Plant B |
|---|---|---|
| Effective volume ($m^3$) : | 4 x 14 040 | 2 x 11 520 |
| | = 56 160 | = 23 040 |
| Length per cascade (m): | 78 | 64 |
| Width per cascade | 9 | 9 |
| Depth (m) | 5 | 5 |

Plant A has 4 basins, each comprising 4 cascades of the same volume; plant B has two basins with a smaller total volume. The first cascade in each case is used exclusively for sludge regeneration, with the waste water entering the second cascade. It is doubtful whether a prodedure of this kind makes sense, since the sludge is already subjected to intense aeration in the sludge return channels. This means that the sludge load is raised unnecessarily and there is a substantial loss (25 %) in effective activation volume. Aeration is effected by medium-bubble diffusers, the plastic-lined pipes having air-escape holes of 5 mm diameter.

The oxygen loads of 5 kg $O_2$ / kg $BOD_5$ in plant A and 19.2 kg $O_2$ / kg $BOD_5$ in plant B are extremely high; addd to this, substantial quantities of $O_2$ are introduced in the neutralization and pre-aeration tanks. Future improvements to the waste water treatment plant must aim at making the sludge activation process much more efficient, amongst other things by introducing $O_2$- electrode control of the oxygen supply, and thus reducing the running costs for the plant considerably.

With a 100 % sludge return a sludge concentration of 2 - 4 kg SS / $m^3$ is maintained. An influent $BOD_5$ load of 7500 kg / d in plant A and of 2100 kg / d in plant B results in the following $BOD_5$ sludge loads:

Plant A = 0.06 kg $BOD_5$ / kg.d
Plant B = 0.045 kg $BOD_5$ / kg.d

The COD loads are as follows:

Plant A = 0.28 kg COD / kg.d
Plant B = 0.16 kg COD / kg.d

This means that both plants have a very low pollution load, so that total nitrification and sludge stabilisation is possible. Under these conditions a very extensive reduction in organic carbon compounds may be expected, even when sludge activity is starting to decrease. The cascade arrangement promotes this reduction. Due to the elevated effluent temperatures both plants are operated

between 25 - 32° C in summer
between 16 - 20° C in winter.

Since pulp effluents have a deficiency in essential nutrients of phosphorus and nitrogen, P is added in the form of superphosphate and N as ammonium hydroxide in a proportion of 100 ($BOD_5$) : 4 (N) : 1 (P) in the neutralization tank. The pollutant reduction levels obtained in the two plants are as follows:

| | Plant A | Plant B |
|---|---|---|
| $BOD_5$ | 88.8 % | 93.0 % |
| COD | 69.5 % | 54.7 % |
| AOX | 60.0 % | 60.0 % |

The amount of settleable matter in the waste water, especially that in the white and black streams, is of particular significance because it is an indicator for the fibre losses from the mill. Based on 1994 figures the amount of settleable matter can be calculated as follows:

| | mg / l | t / d |
|---|---|---|
| Black stream (1994) : | 172 | 5.1 |
| White stream (1994) : | 71 | 8.7 |
| Total waste water (1994) : | - | 13.8 |

Since the suspended matter is mainly of fibrous content, the daily losses via the waste water can be calculated at some 3.1 % of production. The absence of a mechanical retention or sedimentation facility preceding biological treatment also means that large amounts of suspended solids accumulate in the activated sludge and the chemical precipitation sludge, from which they have to be removed. This procedure has technical disadvantages and is uneconomical, and it should be modified without delay. The fibrous material could then be used in the Paper machine, a useful way of recycling it.

Clarification takes place in conventional-type sedimentation basins. There are 5 round basins for plant A, each with an effective volume of 4626 $m^3$ (diameter 42 m, depth 3 m, surface area 1256 $m^2$) and two for plant B, each with a volume of 1360 $m^3$ (diameter 24 m, depth 3 m, surface area 453 $m^2$). Suction de-sludgers of Russian make are in use. These clarification capacities give rise to the following essential operating data:

| | Plant A | Plant B |
|---|---|---|
| Retention time (h): | 2.55 | 3.0 |
| Effluent vol. ($m^3$ / $m^2$ / h) | 1.4 | 1.0 |

The clarification stage is thus adequately dimensioned.

## 4.5 Chemical precipitation and flocculation

In order to further reduce the pollutant content in the waste water, the biologically treated effluent streams from plants A and B are jointly subjected to chemical precipitation. The main aims of this treatment are:

- precipitation of the alkali lignin components (industrial use)
- reduction in colour
- elimination of organochlorine compounds
- reduction in the aquatic toxicity
- removal of o-phosphate.

As precipitating agents use is made of aluminium sulfate or aluminium potassium sulfate in a quantity of 1.4 mg Al / l (3 mg Al / l?) and an anionic polyelectrolyte (polyacryloamide of Russian production) in a quantity of 0.2 mg / l. The daily consumption of aluminium sulfate is 59 t.

The two precipitating agents are added in the given amounts to two separate mixing chambers, first aluminium sulfate and then polyelectrolyte, with a mixing time of 1 minute in each case.

The water is circulated using pressurized air and the pH during precipitation kept between 5.2 - 5.5. The actual flocculation and precipitation occurs in 6 round flocculation clarifiers with the following dimensions:

| | |
|---|---|
| diameter: | 54 m |
| effective capacity | 10500 $m^3$ (per clarifier) |
| surface area | 1975 $m^2$ |
| depth | 3.3 m |

The average effluent retention time in the clarifiers is 5.8 h.The overfall weirs have an edge length of 400 m and tooth-type sills; the effluent flows over them from both sides.

Although only very small amounts of aluminium are used for precipitation ( 0.08 mg Al / l due to waste water regulations governing discharges into Lake Baikal), the efficiency with which $BOD_5$ and COD are removed is relatively high (1994). In terms of the amounts contained in the incoming effluent,

64 % of the COD and
57.1 % of the $BOD_5$

were eliminated. The average solids content in the discharge was 5 - 10 mg / l. Isolated measurements pointed to a high reduction in AOX of 59 %.

The overall efficiency of biological and chemical treatment in terms of AOX reduction is thus approximately 83 %.

In order to keep the pH more or less neutral ( 6 - 7 ), the collective effluent is treated for 2 - 3 minutes with aqueous sodium hydroxide in a mixing tank. on inspection of this facility quite a lot of floc drift was noticed. This is due at least in part to the condition of the overfall weirs, where some of the sills are missing.

Some 6 - 7 % of the treated effluent is sludge; the water content of the sludge is 99.3 - 99.5 %.

## 4.6 Waste water ponds

The last treatment stage comprises three successive aerated ponds , with the following effective capacities:

| | |
|---|---|
| pond 1 : | 80 000 $m^3$ |
| pond 2 : | 114 000 $m^3$ |
| pond 3 : | 60 000 $m^3$ |

Total retention time is approximately 1 1/2 hours. The average depth is 3 m. The waste water is aerated by means of sunk perforated pipes, by means of which the oxygen concentration can be kept at 6 - 8 mg $O_2$ / l. In 1994 a $BOD_5$ load of 0.6 t / d and a COD load of 8.0 t / d entered the ponds. These loads were reduced to 50 % and 10 % respectively.

No further reduction in AOX is to be observed in the ponds. As a result of the large amount of sludge which collects, the ponds have to be de-sludged once a year. There is floating equipment for this purpose ( catamaran with pump). Water blooms caused by green algae were observed repeatedly in the ponds, as also a colonization by fish and daphnia.

## 5. Sludge treatment and incineration

Biological and chemical treatment produce 1100 $m^3$ of sludge per hour, with a solids concentration of 2.2 kg / $m^3$. Of these 1100 $m^3$, 180 $m^3$ / h come from the clarification stage of the activation plant and have a solids content of 6 kg / $m^3$, and 920 $m^3$ / h (1.5 kg / h) come from the precipitation stage. The sludge is first of all concentrated to a solids content of 20 kg/$m^3$ in a six-unit flotation facility. The flotation tanks, of the VNIIB type, are dimensioned as follows:

| | 3 tanks old | 3 tanks new |
|---|---|---|
| volume ($m^3$) : | 170 | 190 |
| depth (m) : | 4 | 4 |

Flotation is effected in the collective waste water stream according to the depressurization principle, using flocculators ( DP 1 from Allied Colloids, anionic polyacryloamide or N 250 P from Sunfloc, Japan ) in quantities from 5 - 6 kg / t sludge dry matter. The sludge water, with a solids content of 0.25 g / l, is returned to the chemical precipitation facility because the organic pollution (COD) is very low.

Further dewatering to 200 kg / $m^3$ dry matter is effected in 2 or 3 Centripress units from the firm KHD, which were installed in 1994/95. As dewatering agent use is made of anionic polyelectrolyte (ZETAG) in a quantity of 3 kg / t. The sludge water, with a solids content of 0.1 g / l, is likewise returned to the chemical precipitation facility. The concentrators and centrifuges in former use are no longer in operation.

The sludge is incinerated in a HITACHI-BABCOCK furnace at a temperature of 700°C. Higher incineration temperatures are currently not realized due to the substantial energy costs involved. This means that there is danger of dioxin formation from the adsorbed organohalogen compounds. In 1994 no sludge lignin was sold; the rotary drier used for making it was accordingly not in operation. The sale of sludge lignin is in the long term no safe disposal method.

## 6. Analytical monitoring of the waste water treatment plants

There is a laboratory with 22 employees for the analytical monitoring of the waste water treatment facilities. A very rigid and comprehensive monitoring system provides for the testing of up to 40 parameters at up to 35 sampling sites. The following parameters are monitored:

settleable solids
$BOD_5$, $BOD_{50}$
pH
evaporation and combustion residues
alkalinity
scum
COD
$KMnO_4$ consumption
ammonium
nitrite
nitrate
chloride
sulfate
phosphate
phenols
aluminium
hydrogen sulfide, methyl mercaptan
dimethyl disulfide, dimethyl sulfide
colour
terpentine
ether-extractable resins and fats
chlorine
anionic tensides
lignin
methanol
furfurol
formaldehyde

sulfate soap
hydrocarbons, oils
daphnia toxicity

AOX and organochlorine compounds (chloroform) are measured by the local institute for ecotoxicology (Prof. Beim). The analytical methods used must comply with the national regulations (Russian Temporary List of Methods that can be used to measure the Content of Pollutants in Natural and Waste Waters, 1990). The authorized methods include only few of the advanced instrumental methods such as IC, IR, GC, HPLC or AAS, which means that use must be made, at least in part, of long-outdated, time-consuming, chemicals-intensive and thus expensive methods; this situation reduces the efficiency of the laboratory considerably. Alone the use of $O_2$ electrodes in the laboratory instead of the WINCKLER method would mean considerable savings in oxygen determination. Attempts on the part of the mill to introduce state-of-the-art analytical methods meet with failure because they are not accepted by the authorities. Particularly problemmatic is the fact that for some of the substances with limiting values laid down in the waste water regulations, analytical methods are prescribed for which these substances are below the detection limit (e.g. $H_2S$, anionic tensides).

A particularly unusual aspect of the monitoring activities is the fact that daphnia toxicity is measured daily. It is unlikely that this is done anywhere else in the world with such frequency.

A necessary parameter that is not monitored is the algae toxicity. This parameter would cover an important chain in the biocoenosis of Lake Baikal. A weekly measurement should be sufficient here.

Further tests are carried out sporadically by the Institute of Ecology in Baikalsk in order to obtain a toxicological assessment of the waste water, in particular of the water discharged into Lake Baikal. These include tests with

- saprophytic bacteria
- green algae (Scenedesmus spec.)

- crustaceans (Limnogammarus cyaneus, Limnogammarus verrucosus)
- insect larvae
- molluscs
- fish (Phoxinus phoxinus, Thymallus arcticus).

## 6.1 Quality of the treated effluent

Table contains the mean values obtained by the in-plant laboratory for the treated waste water discharged into Lake Baikal.

Table : Mean values waste water discharge into Lake Baikal

| | | | | |
|---|---|---|---|---|
| Waste water volume | 158 945 | $m^3$ / d | - | |
| Temperature | 19°C | | - | |
| SS | 2.8 | mg / l | 445 | kg / d |
| Evaporation residue | 513 | mg / l | 81.5 | t / d |
| Scum | nn | | - | |
| pH | 6.3 | | - | |
| $KMnO_4$ consumption | 18 | mg / l | 2.86 | t / d |
| Colour | 46 | | - | |
| $BOD_5$ | 1.9 | mg / l | 301.9 | kg / d |
| $BOD_{50}$ | 9.3 | mg / l | 1.48 | t / d |
| COD | 45 | mg / l | 7.15 | t / d |
| Ammonium | 0.43 | mg / l | 68.3 | kg / d |
| Nitrite ($NO_2$ - N) | 0.001 | mg / l | 158.9 | g / d |
| Nitrate ($NO_3$ - N) | 0.65 | mg / l | 103.3 | kg / d |
| Phosphate | 0.007 | mg / l | 1.1 | kg / d |
| Oxygen | 7.6 | mg / l | - | |
| Hydrogen sulfide | nn | | - | |
| Dimethyl sulfide | 0.026 | mg / l | - | |
| Dimethyl disulfide | 0.062 | mg / l | 9.85 | kg / d |
| Tall oil | 0.85 | mg / l | 133.5 | kg / d |
| Phenol | 0.017 | mg / l | 2.7 | kg / d |
| Terpentine | 0.07 | mg / l | 11.1 | kg / d |

| | | | | |
|---|---|---|---|---|
| Aluminium | 0.07 | mg / l | 11.1 | kg / d |
| Chloride | 108 | mg / l | 17.2 | t / d |
| Sulfate | 170 | mg / l | 27.0 | t / d |
| Hydrocarbons/oil | 0.06 | mg / l | 9.5 | kg / d |
| MBAS (anionic tensides) | 0.08 | mg / l | 12.7 | kg / d |
| Furfurol | 0.04 | mg / l | 6.4 | kg / d |
| Formaldehyde | 0.05 | mg / l | 7.9 | kg / d |
| Methanol | 0.001 | mg / l | 158.9 | g / d |
| Lignin | 4.2 | mg / l | 667 | kg / d |
| AOX | 1.23 | mg / l | 195.5 | kg / d |
| Chloroform | 0.135 | mg / l | 21.5 | kg / d |

Assessment of the individual parameters leads to the following results:

a) Temperature

On account of the high dilution, an average discharge temperature of 19°C (13 - 24°C) is not a problem for Lake Baikal, even if temporary lens-shaped layer ing can occur in the deep water of the lake.

b) pH

The average discharge pH of 6.3 (6.2 - 6.4), which is altogether extremely stable throughout the year, is within the neutral range and is thus ecologically compatible, even if the water of Lake Baikal has a pH of 7.5 - 8.0.

c) BOD

As a result of the very intensive, multi-stage effluent treatment the waste water discharged from the mill has an unusually low average $BOD_5$ content of 1.9 mg / l (1.3 - 2.9 mg / l); this means that there are hardly any biologically degradable products still contained in the waste water. As far as Lake Baikal is concerned, this residual pollutant load of 302 kg / d is negligible. The $BOD_{50}$ content, which averages 9.3 mg / l, is a further indication of the above-average degree to which the waste water is purified. Further improvement with respect to the removal of oxygen-consuming matter is not possible.

d) COD

The extensive waste water treatment results in a COD level of 45 mg / l, which is ununsually low for pulp and paper mills. In this connection, however, the high specific water consumption per tonne of pulp produced must be taken into consideration since it automatically results in a higher degree of dilution than is the case in a sulfate pulp and paper mill, which produces less than one third of this specific effluent volume. It can generally be assumed, however, that a further reduction in COD concentrations is not possible with conventional waste water treatment processes.

e) Nitrogen compounds

On account of the low nitrogen content of the pulp effluents to start with, these even requiring the addition of ammonium to ensure undisturbed biological degradation, the waste water discharged from the mill contains very small amounts of

| | | | | | |
|---|---|---|---|---|---|
| ammonium, with | 0.43 | mg / l | or | 63.3 | kg / d |
| nitrate, with | 0.08 | mg / l | or | 103.3 | kg / d |
| nitrite, with | 0.001 | mg / d | or | 0.15 | kg / d |

Any inadmissible pollution of Lake Baikal can be excluded, on the basis both of the lakewater concentrations and of the waste water load.

f) Phosphorus

As is the case with nitrogen compounds, only very small amounts of phosphorus compounds or phosphates are contained in pulp effluents. Effective biological treatment thus necessitates additional phosphorus. The phosphorus contained in the municipal sewage from the town of Baikalsk is not sufficient to meet this need. The phosphorus content ( 0.007 mg / l ) of the waste water discharged into Lake Baikal is far below the eutrophication limit for lakes ( 20 mg / l (VOLLENWEIDER).

g) Evaporation residue, chloride, sulfate

The waste water treatment facilities are not able to reduce the quantitites of inorganic ions such as cloride, sulfate or sodium, which constitute the major proportion of the evaporation residue. The quantity of salts discharged into the lake can only be reduced by in-plant measures , e.g. by avoiding effluents from wet ash removal. A reduction in the $Na_2SO_4$ losses incurred during brown stock washing can also be included in this catalogue of measures.

h) Aluminium

With an aluminium content of 0.07 mg / l the effluent discharged from the mill has practically the same aluminium concentration as the lake. When one takes into account the fact that the Selenga has average Al concentrations of 2 - 3 mg / l when it flows into Lake Baikal, the Al discharged from the mill can be ignored.

i) Settleable matter

By virtue of the altogether good mechanical sedimentation that takes place in the waste water treatment facilities, the waste water discharged into the lake contains only 2. 8 mg / l (1.8 - 4.4 mg / l) of settleable matter, which means a total infeed of 445 kg / d. It may be assumed, moreover, that some of this particulate matter is already biomass (plankton) from the waste water ponds.

j) Various specific organic products (furfurol, methanol, hydrocarbons, anionic tensides, formaldehyde)

The concentrations and pollutant loads of various specific organic products in the collective mill discharge are so low that any significant pollution of the lake can be excluded. The question must be asked, however, whether parameters such as anionic tensides (MBAS) provide useful information at all on pulp effluents.

k) Sulfur compounds ( $H_2S$, DMS, DMDS, methyl mercaptan)

Hydrogen sulfide and organic sulfur compounds are destroyed and degraded - for the most part oxidatively - to such an extent by the in-plant and external treatment that only ecologically harmless traces can be detected in the collective discharge.

l) Organochlorine compounds

The use of elemental chlorine, chlorine dioxide and hypochlorite for pulp bleaching results not only in the formation of products extracted from wood (primarily lignin and its breakdown products), but also in organochlorine compounds, which are included in the collective parameter AOX. Approximately 83 % of the AOX is eliminated by the biological and, in particular, by the chemical precipitation treatment and is removed by way of the sludge formed.

Despite these measures the mill still discharges 1.23 mg / l of AOX - which corresponds to a daily load 193 kg / d - into the lake. Although AOX is hardly useful as an ecotoxicological parameter, concentrations and loads of this level are not authorized for Lake Baikal. Chloroform, as a component of the AOX, is also contained in the discharge in a concentration of 0.135 mg / l, although complete removal would be expected in view of the very intensive aeration in many parts of the waste water treatment plant.

m) Daphnia toxicity

The exceptionally comprehensive monitoring of the collective waste water discharge into Lake Baikal, with the daily Daphnia test, shows quite clearly that for this test organism there is no aquatic toxicity of the undiluted discharge. The indicative value of this biological test method must be considered very high in terms of the general harmfulness of the waste water.

## 7. Process restructuring recommendations based on various studies

With a view to restructuring the manufacturing process along more environmentally friendly lines, the BPPM commissioned a number of institutes and firms to draw up expertises and/or offers which focus especially on cooking and bleaching. Among the recommendations and expertises already submitted are those from :

- SUNDS DEFRIBRATOR
- VOEST - ALPINE / LENZING TECHNIK
- SIBERIAN INSTITUTE OF PULP AND BOARD
- OBUMPROM - St. Petersburg.

The firm SUNDS DEFIBRATOR, which has relevant laboratory experience in the manufacture of chemical pulp (viscose) under TCF conditions, recommends as bleaching sequence O-Z-P; the hydrolysis step in cooking (use of super-batch process) is retained. SUNDS provides all the technical equipment. The processing safety of the method of manufacturing corresponding dissolving pulps is guaranteed.

The recommendations from VOEST-ALPINE / LENZING TECHNIK for the manufacture of dissolving grade kraft pulps are likewise based on the assumption of a pre-hydroysis step in cooking and include a TCF-based bleaching sequence. Important aspects of the process are:

- use of the Visbatch process
- use of oxygen as first and second bleaching stage (oxygen-alkali treatment)
- medium consistency ozone bleaching
- peroxide bleaching stage
- acid washing and chelation using EDTA or DTPA (0.2 % in terms of pulp).

The necessary use of chelating agents such as EDTA and DTPA to inactivate Fe, Mn, Co and Cu ions, which cause the undesired and uncontrollable formation of peroxide and ozone, poses a new specific environmental problem for Lake Baikal when these agents are used in the required amounts. EDTA and DTPA are, on the one hand, biologically either completely non-degradable or only partially degradable, and, on the other hand, are clearly algae-toxic (especially DTPA, with an acute toxicity of approximately 0.6 mg / l). An added disadvantage is the heavy-metal remobilization effect of these agents which, from the point of view of the lake, is ecologically incompatible. Research on organic chelating agents with good biological degradability is currently worldwide insufficiently advanced - in particular their ecological testing, e.g. methyl and ethyl glycine diacetic acid - to enable their direct use. This means that the component effluent streams from acid washing, which involves the use of chelating agents, must be subjected to specific treatment which allows the practically complete removal of these substances.

The SIBERIAN INSTITUTE OF PULP AND BOARD likewise assumes a stepwise restructuring of the mill with a guarantee of

- high pulp quality
- reduction in or elimination of environmental pollution
- improved energy utilization (reduction in steam requirement for cooking of 45 - 75 %, depending on pulp quality)
- reduction in or elimination of chlorine and chlorinated compounds consumption and their substitution by $O_2$, $O_3$ and $H_2O_2$, with stepwise transition to ECF and TCF pulp
- high degree of water reuse, resulting initially in a specific effluent volume of 12 - 25 $m^3$ / t. The ultimate aim is a TEF pulp and paper mill (totally effluent free).

**Measures proposed for the implementation of these recommendations**

Improvement of cooking technology comprising black liquor reloading and ousting and intensifying delignification by means of polysulfide and thiosulfate cooking. Cold blowing of digesters is included. Suitable equipment is available from SUNDS DEFIBRATOR, BELOIT and VOEST ALPINE.The principle of liquor reuse is described in a Russian patent: at the end of the cooking process some of the black liquor is supplied to the next digester as soon as pre-hydrolysis is completed. The process is used successfully in the Bratsk Pulp and Paper Mill. The advantage of the process lies in the marked reduction in the emission of sulfurous compounds (50 - 75 %) when the digesters are emptied, a reduction in steam consumption ( 30 - 35 %) and a reduction in white liquor consumption (5 - 10 %). Introduction of the process would not necessitate any equipment chan¢ es. In principle, further modifications of the process are possible which would bring additional savings, e.g. in water consumption (brown stc::k washing: 25 - 30 %). The following improvements can be made in a 2nd or 3rd restructuring stage:

- reduction in steam consumption of 65 - 75 %
- almost complete elimination (95 - 99 %) of sulfur compounds in atmospheric emissions .

The technological improvements in the actual cooking process concern deep delignification. Of great importance here is a new method of oxidizing the white liquor. This method involves the use of specific heterogeneous catalysts which make it possible to convert sodium sulfide into polysulfides. The use of oxidized white liquor has allowed the development of an ecologically safe technology of so-called "thiosulfate" cooking. Thiosulfate is non-toxic.

The new cooking process could be combined with ECF or TCF bleaching; for ECF bleaching use could be made e.g. of the following bleaching sequence for the manufacture of chemical or paper pulp:

$$D - E_p - D$$

Since a ɜppa number of 3 - 6 can be achieved with the proposed new cooking process (deep delignification), relatively little bleaching is necessary. With this bleaching sequence neither oxygen nor elemental chlorine is used (Russian patent). For hardwood the use of a homogeneous catalyst (1,4 dihydro - 9,10 dihydroxy-anthrachinon) is recommended (Russian patent). If quasi-classical ECF bleaching sequences are used, it is recommended that elemental chlorine be replaced by $O_2$ mixed with $ClO_2$ according to the following scheme:

$$D_0 - E - H - D_1 - D_2 - A$$

This would mean a reduction in TOCL from 3 -4 kg / t to 1.0 - 1.5 kg / t.

Additional use of peroxide brings a further improvement ($H_2O_2$ is made in Usolye - Sibirskoje). The TOCL load then sinks to 0.5 - 0.9 kg / t. The following possible bleaching sequence is recommended, in which peroxide is employed in the first stage:

$$P_1 - D_1 - E_p - D_2 - P_2 - A$$

The advantage of the recommended procedure consists in the fact that it can be implemented with the existing facilities.

The introduction of $O_2$ bleaching, with the appropriate structural modifications to the mill, results e.g. in the following bleaching sequence:

$$O - E - D_1 - P - D_2 - A$$

Combined with this there is a marked improvement in brown stock washing through use of new dewatering units such as screw presses.

The effluent from the O - E step is collected separately, concentrated and incinerated.The TOCL emission from the bleaching plants sinks as a result to < 0.5 kg / t .

As a further improvement to the bleaching process the introduction of a TCF bleaching sequence is recommended, according to the scheme

$$O - Z - P$$

This results in a COD of < 10 kg / t and a $BOD_5$ of < 2 kg / t. The use of a chelating agent is necessary here.

The investigations made by OBUMPROM, some of which were carried out in conjunction with the Bayerische Landesanstalt für Wasserforschung, resulted primarily in the following recommendations:

1. Introduction of dry wood debarking
2. Deep cooking with utilization of sulfide lignin
3. Use of ECF or TCF bleaching sequences.

If suitable machinery is used for debarking, e.g. NICHOLSON, it may be assumed that no or only very little effluent will be produced (Table).

| Table : | Debarking Effluents | |
|---|---|---|
| | current | future |
| Effluent volume | 400 $m^3/h$ | 7 $m^3/h$ |
| Lignin | 6.1 $m^3/h$ | 0.6 kg / t |
| COD | 5.0 kg / t | 0.4 kg / t |
| $BOD_5$ | 2.5 kg / t | 0.05 kg / t |

By changing over from the currently-used cooking process to the vis-batch process (VOEST-ALPINE) for example, it will be possible to obtain markedly lower kappa numbers than has previously been the case. The target is a kappa number 9. This would at the same time make a substantial reduction in atmospheric pollution possible. An improvement in brown stock washing through the introduction of pressure screens is considered as essential. This would result in a 90 to 99 % increase in efficiency, as shown below:

| | | | |
|---|---|---|---|
| Lignin | 17.1 kg / d | → | 1.7 kg / t |
| COD | 59.4 kg / d | → | 6 kg / t |
| $BOD_5$ | 19.8 kg / d | → | 2 kg / t |

OBUMPROM, St. Petersburg, recommends a step-wise restructuring of the bleaching process, changing first to ECF and then perhaps at a later date to TCF. The chemicals consumption for ECF bleaching with the sequence (O - E) - $D_1$ - P - $D_2$ - H - A is as follows:

| | | | |
|---|---|---|---|
| O - E: | NaOH | 25 - 30 | kg / t |
| | $O_2$ | 22 - 25 | kg / t |
| $D_1$: | $H_2SO_4$ | 5 | kg / t |
| | $ClO_2$ | 15 | kg / t |
| P: | NaOH | 3 - 5.1 | kg / t |
| | $H_2O_2$ | 18 | kg / t |
| $D_2$: | $H_2SO_4$ | 0.7 | kg / t |
| | $ClO_2$ | 10 | kg / t |
| | NaOh | 2.3 - 2.6 | kg / t |
| A: | $SO_2$ | 9 | kg / t |

The total chlorine consumption is thus reduced from 82 kg / t with the existing technology to 34 kg / t. A further reduction can be obtained through the use of peroxide, in particular in the case of paper grade pulp with a bleaching sequence of (O - E) - D - $P_1$ - $P_2$. If the O - E effluent is concentrated, the following reduction in pollutants can be achieved:

| | current | future |
|---|---|---|
| COD | 110 kg / t | 24 kg / t = 79 % |
| $BOD_5$ | 25 kg / t | 5 kg / t = 80 % |
| AOX | 0.8 kg / t | 0.2 kg / t = 75 % |

## 8. Recommendations for improvements concerning waste water

Based on the information collected on the

- fresh water consumption
- in-plant production effluents
- waste water and sludge treatment

a number of proposals can be made for improving the waste and waste water situation of the mill.

## 8.1 Fresh water consumption

a) The current very high water consumption by the pulp and paper mill and by the town of Baikalsk can be reduced by lowering the specific water consumption in the mill from some 331 $m^3$ / t ( = 12 110 $m^3$ / d) to 50 $m^3$ / t ( = 3 300 $m^3$ / d or 138 $m^3$ / h) and in the town from 734 l / p / d to 200 l / p / d.

At a production rate of

a) 240 000 t / a = 685 t / d
b) 200 000 t / a = 571 t / d
c) 163 000 t / a = 465 t / d

the corresponding fresh water consumption figures are

a) 1427.1 $m^3$ / h
b) 1190.0 $m^3$ / h
c) 967.8 $m^3$ / h

Under these conditions the delivery capacity of just one of the two pump stations at the lake would be quite sufficient to more than cover the water requirement of the mill and of the town of Baikalsk. Since the drinking water (UV irradiation) is supplied by pump station I, pump station II can be kept as a stand-by.

The discharge of 1000 $m^3$ / h of unpolluted cooling water (System II) directly into the waste water treatment plant contributes significantly towards raising the absolute and specific waste water volume, results in unnecessary dilution of the waste water and is a waste of water that could be used directly in the manufacturing process. Reuse of this water must be regarded as the first important step towards improving the waste water situation in the pulp and paper mill.

8.2 In-plant situation

a) Despite its cyclic nature and internal effluent treatment facility, the current wet debarking procedure is the source of 1 % of the total waste water produced in the mill. The proposed dry debarking facility will make a considerable reduction in the waste water volume possible and at the same time a reduction in the respective $BOD_5$ and TOC loads.

b) The waste water situation in the digester plant reflects to a large extent the generally poor condiion of this department and the frequent spills. By modernizing the digester plant, for example with the introduction of a cold blow system, the production of highly-contaminated condensates at a rate of 80 $m^3$ / h can be prevented. Modification of the digester plant, as described in the various proposals for improving the cooking process (VOEST ALPINE, SUNDS DEFRIBRATOR) should lead to a substantial reduction in the volume of digester plant effluent and make bleaching considerably easier.

c) One of the main sources of excessive waste water pollution is brown stock washing and screening. This is due primarily to the fact that only 92 % of the black liquor is recovered. As a result there are correpondingly high losses of sodium sulfate, COD and BOD. Increasing the recovery rate to at least 99.5 % by means of suitable filters or pressure screens is one of the basic prerequisites for modernizing the mill. Extensive or complete recycling of the water used in brown stock washing and screening can be seen as a further means of significantly improving the waste water situation.

d) Another important area in which the waste water situation can be improved is the bleaching plant, where the use in particular of elemental chlorine results in the formation of high AOX loads. Conversion to ECF bleaching sequences, and in particular substitution of the chlorine stage by an O - E stage, is considered an important first step towards a decisive improvement; the AOX can be reduced by approximately 70 - 80 % in this way. With the existing white liquor evaporation capacity this effluent can be concentrated and subsequently eliminated by incineration. Intensifying the cyclic nature of the bleaching process will reduce the current specific waste water volume of some 99 $m^3$ / t to about 15 $m^3$ / t.

A considerable risk for Lake Baikal is recognized in the use of chelating agents such as EDTA or DPTA for ECF and TCF bleaching sequences. This problem can only be avoided through use - if available - of degradable chelating agents or, alternatively, by selectively treating those component effluent streams that contain these compounds.

Generally it is recommended that the bleaching plant be converted stepwise to low-chlorine and then chlorine-free bleaching sequences; in the first step the elimination of elementary chlorine will result in decisive ecological improvements due to a substantial reduction in AOX (approximately 0.5 kg / t) and due to the type of organic chlorine compounds formed (compounds with single rather than multiple substitution, which means better degradability).

However, it must be kept in mind that changing over to TCF bleaching does not greatly affect the discharge of dissolved organic matter.

Improvement in the screening of bleached pulp by more intensive water reuse (installation of filters to separate out fibrous material) is also necessary if the current high specific water consumption is to be reduced.

d) Wet ash removal, with an effluent volume of 450 $m^3$ / h, is another important source of effluent and accounts for some 5.4 % of the total waste water. These effluents have a particulrly high salt load which, even after waste water treatment, enters the lake unchanged. Changing over to a dry ash removal process or using a different fuel (oil, gas) would solve this problem.

## 8.3 Waste water treatment

a) The pulp and paper mill has a very large and efficient biological waste water treatment plant for the two separate effluent streams; for the current volume of waste water and its quality, the plant is even now not working to full capacity. The sludge contamination and the sludge age are such that sludge mineraliza tion takes place. With the proposed modernization measures, especially the reduction in waste water volume of some 1000 - 1600 $m^3$ / h (current volume: 8000 $m^3$ / h), a substantial proportion of the waste water treatment capacity will no longer be required. This applies both to the biological and to the chemical stage. It will no longer be necessary to split up the waste water into two streams.

b) As investigations have clearly shown, large quantities of fibers (13.8 t / d), which for the most part are reusable, enter the treatment plant. Most of these fibers are removed during the biological treatment stage. Provision of a preceding mechanical treatment stage (sedimentation) is considered an essential requirement for improving the mill's waste water situation; reuse of the sedimented fibers in the manufacturing process (paper machine) will moreover be of considerable economic advantage.

c) The clarifer basins were found to have a non-uniform suface load due to certain deficiencies in their structural condition. This leads to increased floc drift. It should be possible to remedy these deficits easily.

d) Power consumption in the biological treatment plant is too high. This is the result of unusually high oxygen loads of up to 19 kg $O_2$ / kg BOD and of very high oxygen concentrations in the aeration tank. Control of the oxygen supply by means of $O_2$ electrodes is an important prerequisite if the plant is to be run more economically.

e) The current method of operating the biological treatment plant, with the first cascade in each case being used only for sludge regeneration and not for waste water treatment, is inefficient. Under the current waste water conditions it represents an unnecessary waste (25 %) of aeration volume without serving any apparent purpose with regard to the plant's operational reliability.

8.4 Sludge treatment

a) The process of sludge dewatering by means of flotation and centrifugation is state of the art and requires no improvement. Problemmatic, by contrast, is the sludge incineration at 700°C, during which

- increased formation of dioxin from the AOX adsorbed by the biological and chemical sludges is probable
- organic matter is insufficiently combusted (the ash contains 20 % organic matter), which in turn affects the quality of the wet ash removal water.

A higher incineration temperature (1200°C) is therefore desirable.

8.5 Quality of the treated waste water and rulings of the waste water directive

a) As a reult of the existing in-plant and external waste water treatment facilities a very high level of purification is achieved, even when the dilution effects caused by the high specific water consumption and volume of waste water are taken into consideration. With respect to $BOD_5$ and COD, which are essential parameters for assessing the effectiveness of a waste water treatment plant, further reduction using conventional treatment methods is not possible. The combination of

- blending
- buffering and neutralizing
- pre-aeration
- low-rate activated sludge treatment
- chemical precipitation and flocculation
- waste water pond treatment

is internationally exemplary. The concentrations of nitrogen and phosphorus compounds, which have to be added in order to adequately sustain the biological treatment process, are so low in the discharge to the lake as to exclude any danger of eutrophication.

Other dangerous substances such as organic sulfur compounds, $H_2S$, furfurol and methanol are reduced to such low levels under existing conditions that they pose no ecological risk on discharge into the lake.

The almost total absence of daphnia toxicity in the collective waste water provides very convincing evidence that the treated waste water is for the most part ecologically sound.

Although AOX is not a parameter from which a defined degree of ecotoxicity can be derived, the average dicharge concentration of 1.23 mg / l or 193 kg / d reflects a situation which needs attention. The recommended modernization measures for the bleaching plant should result in a reduction in AOX, in the case of a change-over to ECF in a reduction to 0.24 - 0.36 mg / l and in the case of a change-over to TCF to virtually zero, which would make the AOX parameter superfluous.

b) In addition to the parameters laid down in the waste water directive, the introduction of a further biological test, the algae test (Scenedesmus), is recommended. This test would provide information on the effects of the mill's effluent on an essential component of the lake's biocoenosis. It would suffice if this test were carried out once a week.

c) The existing waste water directive for the mill, issued by OBLKOMPRIRODA, Irkutsk, makes a distinction between Temporary Limits and Absolute Limits, and lists 33 parameters to be measured. By general international standards the analytical monitoring of the waste water treatment plant, with the high sampling frequency and the large number of parameters measured, is unusually comprehensive. It is doubtful whether the official list of 33 parameters for the monitoring of waste water discharges is still appropriate, even if, from the point of view of Lake Baikal, extensive monitoring is certainly desirable.

At the present time the so-called "Temporary Limits" have to be observed.

Even here, limiting values are prescribed which either cannot be reached or observed by waste water treatment plants or similar facilities corresponding to the state of the art in science and technology, or which are below the analytical detection limits and therefore cannot be measured at all. This applies in particular to

mercury
aluminium
$H_2S$
nitrite

If the Absolute Limits are applied, it is likely that only the following parameters can be observed - unless the pulp and paper mill produces no more waste water at all :

methano
terpentine
extractable oils
formaldehyde
nitrate

The additional requirement contained in the directive, namely that "it is forbidden to discharge any substances into the lake which are not listed here" is absolutely impossible to fulfil.

It is recommended that the waste water directive be interpreted as far as possible in terms of product-specific pollutant levels, as is internationally the custom in the pulp and paper making industry.

d) The expenses incurred at the the Baikalsk Pulp and Paper Mill for the entire area of waste water treatment, including sludge disposal, make up approximately 10 % of the overall production costs. This is well above average by Russian standards, the usual figure being no more than 2 - 3 %.