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by

Carl [illegible]

Paper [illegible] in Sweden
Sixth SIDA/ [illegible]
for [illegible]

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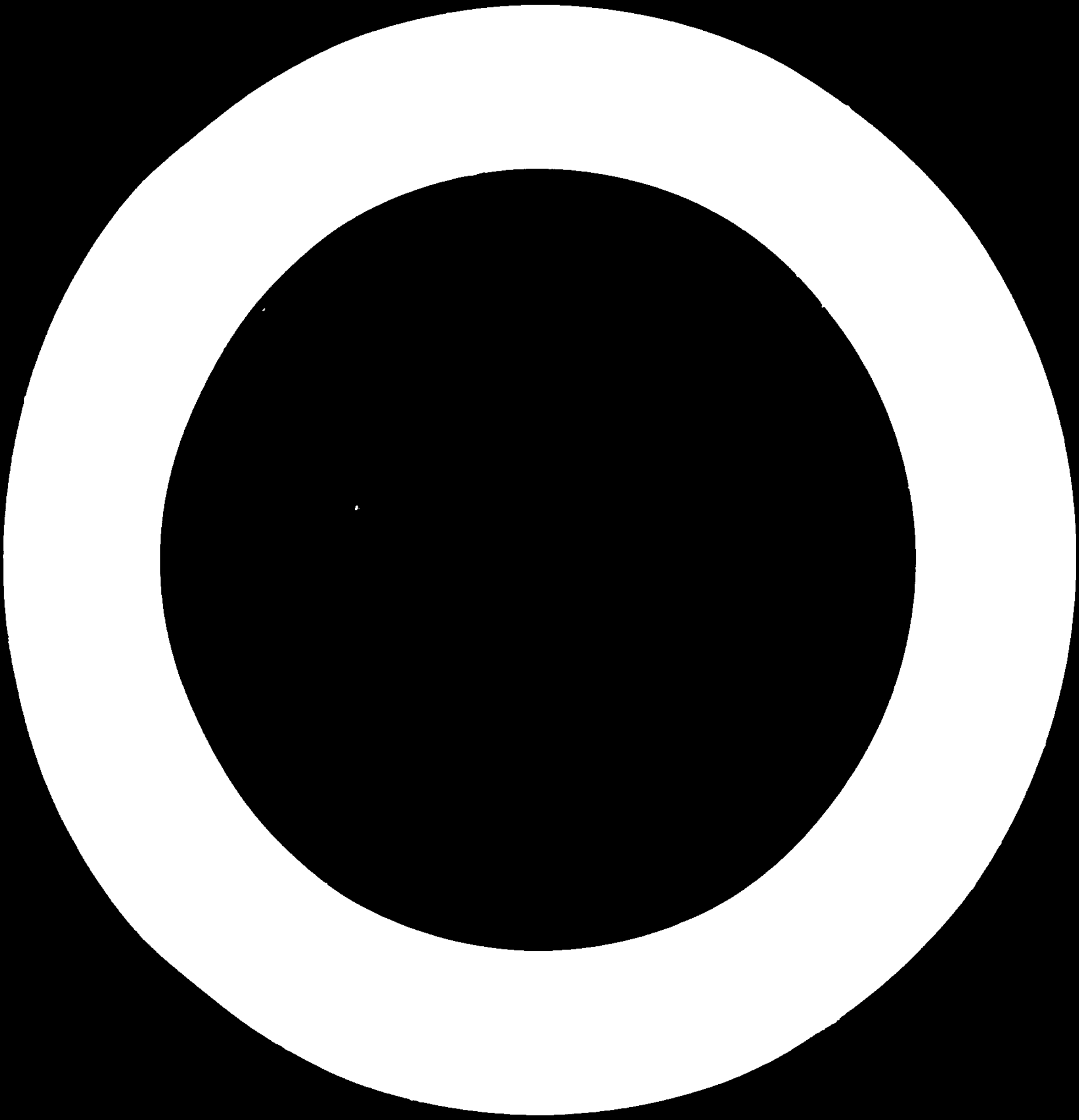


PREFACE

This special paper "Environmental aspects of the pulp and paper industry" has been prepared upon the request of the General [illegible] Techniques Section, Industrial Technology Division of UNIDO to be presented in the 6th SIDA UNIDO/SSIF In-Plant Group Training Programme for Engineers in the Field of Pulp and Paper Industries, [illegible], 1974.

In the preparation of this paper an attempt has been made to [illegible] give an account of the reports of the Environmental [illegible] and especially the practical findings and recommendations [illegible] same. As sources articles appearing in Svensk Papperstidning [illegible] magazines and other special reports compiled by manufacturers of environmental equipments have also been used. Concerning the [illegible] about "Water" information and facts have been taken from two [illegible] namely; Water and its Impurities by T R Camp and Water Purification and Wastewater Treatment and Disposal by G M Fair, J C Geyer [illegible].

As the sulphite process is getting of less importance for the manufacturing of pulp it has not been included in the paper. However, the steps regarding environmental control measures used in the same [illegible] to that used in the sulphate process. This applies also to the [illegible] mical process. In the sulphite process problems regarding the [illegible] of condensate from the evaporation of the waste liquor seem to [illegible] of the existing differences in respect to the sulphate process. [illegible] using calciumbisulfite as a process chemical problems will [illegible] large emission of sulphur dioxide and calciumsulphite powder.

In the preparation of the paper valuable assistance has been given by Mr Karl-Erik Lekander, who has been the responsible officer of the [illegible] Environmental Project.

Mar[illegible]

Carl Gustav [illegible]

Page

WATER

In one form or another water occurs practically everywhere, very [illegible] quantity from an almost unlimited supply in the oceans to [illegible] in desert regions. It occurs in the atmosphere as water vapor, [illegible] and precipitation, on the earth's surface in [illegible], [illegible] streams, in [illegible], and in the oceans. Beneath the [illegible] surface it occurs in different [illegible] areas according to which [illegible] is classified.

Although at any instant by far the largest portion of the total water supply is stored in the oceans, a constant circulation is taking place. Evaporation from the ocean's surface is continuous. Although much of the moisture so evaporated condenses and falls directly on the ocean, a considerable portion is carried by the winds on the land areas where it is precipitated as rain, hail, sleet, or snow or condensed as dew or frost on the surface of vegetation and other objects. [illegible] all the moisture in the form of dew and frost either is evaporated [illegible] or is [illegible] by vegetation and then transpired through the vegetation pores. That which falls as precipitation, however, has a much more varied experience. Some is re-evaporated before it reaches the earth. Another is intercepted by vegetation, buildings, and other objects, and part of this is re-evaporated directly. Another portion runs off from ground surface into the streams and is returned to the sea. Still another portion percolates into the ground. For this portion there are numerous outlets: part of it is held by capillarity at or near the surface and is evaporated therefrom, another part is used by vegetation and returned to the air through the process of transpiration, still another portion joins the ground water and slowly finds its way to the streams, appearing after days, months, and sometimes much longer periods as ground water flow, and finally an amount that is usually insignificant but in a few drainage basins is of considerable importance, flows back to the oceans. The natural transfer of water from one stage to the other, mainly caused by the differences in temperature created by the sun and the heat [illegible] the earth [illegible] day and night, is called the hydrological cycle. The cycle is demonstrated in the diagram no 1.

Our existence is in many ways dependent on water. It is essential to all life, human as well as both animal and vegetable. Indeed, it is a [illegible] of life itself, since protoplasm of most living cells contains [illegible] water, and any substantial reduction in this percentage is disastrous. Most of the biochemical reactions that occur in the metabolism of living cells involve water, and all of them take place in water, [illegible] has often been referred to as the universal solvent. Yet man's assessment of the value of water is very low until he finds himself without it. Most of the surface of the earth is covered with water. this is salt water, to be sure, but most of the habitable land masses have adequate [illegible] water resources. Water is plentiful, therefore, that man believes [illegible] should be free or, at most, very cheap. As a result, water supplies of good quality continue to be developed and extended on an emergency basis and, with very few exceptions, are never quite adequate for human needs. One of the principal reasons for the rarity and an adequacy of public

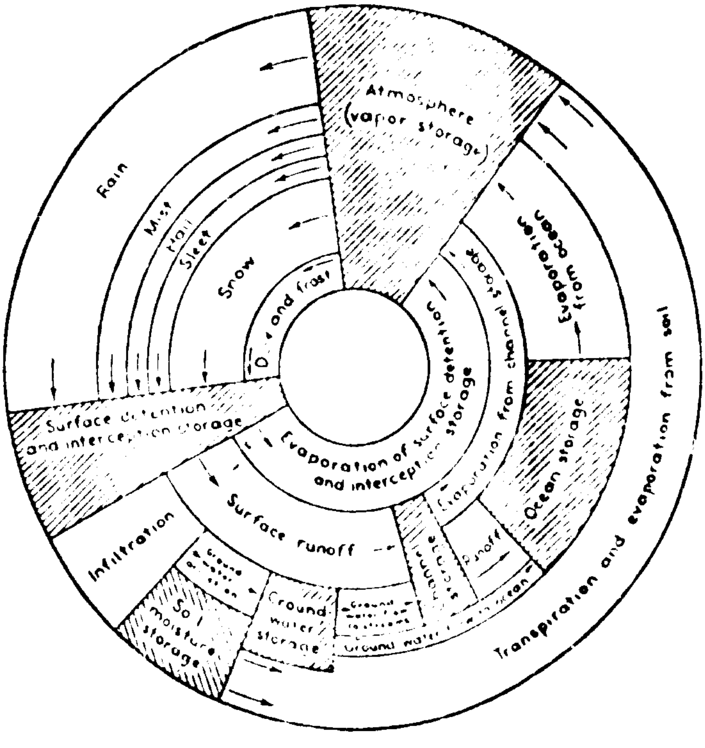


Figure 4:1 The hydrologic cycle. Read diagram counterclockwise.

water supplies in the developing countries is the widespread belief that water should be free.

Man uses water not only for drinking and culinary purposes but also for bathing, washing, laundering, heating and air conditioning, for agriculture, stock raising and gardens, for industrial processes and cooling, for water power and steam power, for fire protection, for [illegible] wastes, for fishing, swimming, boating and other recreational [illegible], for fish and wild life propagation, and for navigation.

Every activity of man involves some use of water. For many of these uses, the water must be withdrawn from a watercourse; for others, it is not withdrawn. Often, the water which is withdrawn is returned to the water course, either with pollutants or with an increase in temperature, or both, and if taken from large watercourses, this water used over and over again by downstream communities, with further impairment in quality each time.

The competition for our water resources is certain to become more and more keen in the years to come. This increase will occur not only among the various types of uses that now exist but among the new uses that will develop. With the advent of unforseen developments and with a steadily increasing congestion of population, the competition for our water resources is certain to increase as time goes now.

In adjustment of conflicts and for proper solution of the many problems arising in connection with them, complete data on our water resources and a full understanding of the principles of hydrology and maintaining the quality of the water become a vital necessity.

Physical Properties of Water

It is characteristic of liquids, including water, that the [illegible] and ions of which the liquids are composed are [illegible] in a relatively constant volume, although they are free [illegible] respect to one another. Foreign molecules, ions or particles [illegible] are also free to move about, subject to the [illegible] small drag forces created by the motion. Some understanding [illegible] physical properties of pure and impure water is an essential [illegible] an adequate grasp of the characteristics which [illegible] quality [illegible] treatability of natural and polluted waters.

Among physical properties of water of importance in its hydrologic and quality management are its molecular structure, density, viscosity, vapor pressure, surface tension, resistance to diffusion, power of solution and suspension, light absorption, heat capacity and heat absorption. Nearly all of its physical properties, as well as its chemical and biological properties, are temperature-dependent. Indeed, their variation with temperature is so great that we often speak of temperature [illegible], rather than temperature-dependent properties, as controlling the behavior of water.

Molecular

Molecules of liquid water occupy a volume of $2.97 \times 10^{-11}\ \mu^3$ (29.7 in Angstrom units A^3). The mean pure space between the molecules is about 30.7 Å.

In ice the molecules occupy, unequaly a slightly larger volume, namely, $3.23 \times 10^{-11}\ \mu^3$ ($32.3\ A^3$).

In the vapor state the equivalent size of the molecules is about $3.5 \times$ [illegible] A). They move at a high velocity, exerting a pressure $p = \frac{1}{3} N m v^2$ in conformance with the kinetic theory of gases. Here N is the number of molecules in a unit volume of gas, on the mass of each molecule, and v^2 the mean square of the velocity of the molecules.

Density and Viscosity

Density variations in deep bodies of water result in seasonal stratification and overturning of lakes and reservoirs and consequent wide variations in water quality. Density is also an important element in the short-circuiting of settling tanks as well as larger bodies of water, viscosity, similarly, in chemical coagulation or flocculation.

Density is expressed in one of three ways:

1. as mass density or mass per unit volume
2. as specific weight or weight per unit volume
3. as specific gravity

The density of liquid water at different temperatures is as follows:

Temperature C	0	4	10	20	30	100
Density	0.9999	1.0000	0.9997	0.9982	0.9957	0.9584

Pressure has little effect on the density of water. Dissolved impurities change the density of water in direct proportion to their concentration and their own density, but they leave the volume of water unaltered.

The viscosity of water is expressed in one of two ways:

1. as absolute or dynamic viscosity μ, or mass per unit length and time $(ml^{-1}\ t^{-1})$
2. as kinematic viscosity $\nu = \mu/p$, or length squared per unit time $(l^2\ t^{-1})$

At common water temperatures the viscosity of water is as follows:

Temperature C	0	4	10	20	30	[illegible]
Dynamic viscosity (μ), centipoises	1.79	1.57	1.31	1.01	[illegible]	[illegible]
Kinematic viscosity (ν), centistokes	1.79	1.57	1.31	1.01	[illegible]	[illegible]

The viscosity of water is one centipoise at 20.20 °C.

Vapor Pressure and Surface Tension

Vapor pressure is a controlling factor in evaporation whether from [illegible] water surface or from sewage sludge being dried. The pressure exerted [illegible] the water vapor is known as its partial pressure and equals its relative volume in the atmosphere. It is generally expressed in the same terms [illegible] barometric pressure (mm Hg at 0 °C), for example equilibrium values [illegible] common water temperatures are as follows:

Temperature	0	4	10	20	[illegible]	[illegible]
Vapor pressure (p) mm Hg	4.58	6.10	9.21	17.5	[illegible]	[illegible]

The interfacial tension between a liquid and a gas is essentially a property of the liquid alone. The dimensions of surface tension are energy per unit area or force per length $(m t^{-2})$. It is for pure water against air relatively great. At common water temperature the tension is as follows:

Temperature C	0	4	10	0	30	[illegible]
Surface tension (δ) dynes/cm	75.6	74.8	74.2	72.8	71.2	[illegible]

Diffusion of Substances and Gas Transfer into and from Water

Even without mechanical mixing the concentration of substances in [illegible] solution in water, both molecules and ions, will eventually [illegible] form. However, this equalization process on diffusion is extremely [illegible]. The rate of diffusion is limited by the [illegible] on the [illegible] liquid. The rate of diffusion per unit area [illegible] is

$$c \frac{ds}{dt} = - D_c \frac{dc}{ds}$$

where $c \frac{ds}{dt}$ is the quantity of particles per sec diffusing through 1 sq cm of a boundary in the direction of s, $\frac{ds}{dt}$ is the diffusive velocity, $-\frac{dc}{ds}$ is the concentration gradient and D_c is the diffusion coefficient. Einstein has derived the value of this coefficient

$$D_c = \frac{1}{3\pi d\mu} \frac{RT}{N}$$

where $3\pi d\mu$ is the Stokes drag for particles of diameter d in a fluid of viscosity μ. R is the gas constant and N is Avogadro's number and T is the temperature in °K (°C + 273).

The diffusion coefficient of dissolved oxygen in pure water is about 2.03×10^{-5} at 20 °C. The Stokes-Einstein relation, above equation, tends to indicate that the effect of the impurities in the water on the value of D_c for a particular substance, is depending on the viscosity of the medium.

The two-film theory (Lewis and Whitman) of the adsorption of a gas by a liquid is based on the assumption of a gas film and a liquud film located at the interface, through which gas must pass by molecular diffusion and beyond which the concentration of the gas is uniform. It has been found that in most problems relating to water and wastewater treatment, the resistance of the gas film need be considered. The time rate of solution (or extraction) of the gas is as follows:

$$\frac{dc}{dt} = K_L a\ (c_s - c)$$

where:

c = the concentration of the dissolved gas in the body of the liquid at time t

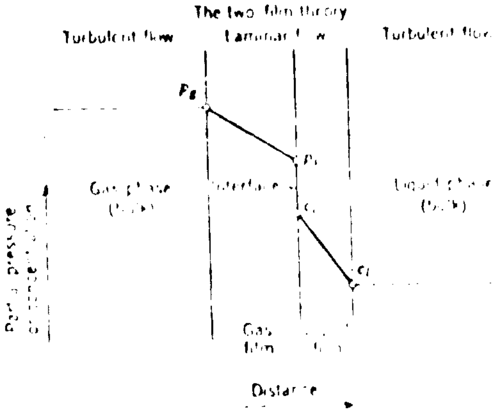
c_s = the concentration of the dissolved gas at the gas-liquid interface (the saturation concentration)

a = the interfacial area per unit of volume of liquid

K_L = the liquid film coefficient

$K_L = \frac{D_c}{L}$ for an unbroken film, where L is the thickness of the film.

With moving gas bubbles, however, shear is always present to continously change the liquid film. Similarly in flowing streams and in tanks or reservoirs, motion of the liquid is always present in varying degrees to change the liquidfilm. Where the film is being continously replaced or renewed the valuee of K_L is determined by the value of D_c and the rate of renewal of the liquid film. The two-film theory is demonstrated in the following figure.



Pressure and concentration gradients in gas and liquid films near the interface.

Figure 9:1

The rate of gas dispersion in water on the other hand depends upon the rate of molecular diffusion, eddy diffusion by convection and eddy dif- fusion by agitation.

In accordance with Daltin's law of partial pressures, the molecules each gas in a gas mixture exert the pressure they would if they were present alone, and the sum of these partial pressures equals the total pressure thus $pV = V \Sigma p$.

In accordance with Henry's law the saturation concentration of a gas in a liquid, such as water, is directly proportional to the concentration, or partial pressure, of the gas in the atmosphere in contact with the liquid:

$$c_s = k_s p$$

where

c_s is the saturation concentration of the gas in the water (ml/litr

p the partial pressure of the gas phase

k_s the proportionality constant, or coefficient of absorption (ml/litre

Example: What is the equilibrium concentration of oxygen in pure water at 0 °C exposed to air under a barometric pressure of 760 mm?

Solution: The absorption coefficient k_s is for oxygen at 0 °C 49,3 ml/l. Because dry air normally includes 20.95 % of oxygen by volume and air is contact with water is generally saturated with water vapor, the partial pressure of oxygen is 0,2095 x (760 - 4.58) = 157 mm Hg 4,58 being the vapor pressure of water at 0 °C. The volume concentration of oxygen therefore is: 49,3 x 157/760 10,2 ml/litre, and because 1 ml of oxygen weighs 2 x 16 x 10 3/22,412 = 1,43 mg, the weight concentration of oxygen is: 1,43 x 10,2 = 14,6 mg/litre.

Table 10:1

Absorption Coefficients of Common Gases in Water

Gas	weight at 0 °C and 760 mm Hg g/l	Absorption Coefficients at temperature °C			
		0	10	20	30
Hydrogen H_2	0.08988	21.4	19.6	18.2	17.0
Methane CH_4	0.7168	55.6	41.8	33.1	27.6
Nitrogen N_2	1.251	23.0	18.5	15.5	13.6
Oxygen O_2	1.429	49.3	38.4	31.4	26.7
Ammonia NH_3	0.7710	1.300	910	711	-
Hydrogen Sulfide H_2S	1.539	4.690	3.520	2.670	-
Carbon dioxide CO_2	1.977	1.710	1.190	878	665
Sulfur dioxide CO_2	2.927	79.800	56.600	39.700	27.200
Chlorine	3.214	4.610	3.100	2.260	1.770

Solution and Suspension of Solids

How a solid dissolves in water is not comparable to the solution of ideal gases. Solubility is a function of temperature, the nature and structure of the solid, and the nature and concentration of water impurities. As a general rule the solubility of solids, in contrast to the solubility of gases, increases with the temperature, but it may vary considerable within different temperature ranges.

The rate of solution of solids in water, like that of gases, is proportional to the degree of undersaturation of the solid in solution. However, it varies directly with the surface area of the solid and inversely with the volume of the liquid. The larger the surface area of the solid per unit volume of water, therefore the more rapid is its solution.

Suspended solids are so coarsely divided that they are visible to the naked eye, either directly or because they absorb or scatter light. They cause turbidity and include substances emptied into water, lifted into it by scour, or developed in the water by chemical precipitation or the growth of living organisms, notably algae.

Absorption of Light

Absorption of solar energy by water is important in three respects: 1. chlorophyllaceous organisms utilize radiant energy and increase the amount of cell substance (photosynthesis). 2. bacteria and other living organisms are killed, and color, especially natural color, is bleached by mainly ultraviolet light, 3. absorbed energy is converted into heat. Not all the solar energy directed onto a body of water penetrates the water surface. Some is reflected, its amount increasing as the incident angle becomes more acute. Accordingly the period of daylight is [illegible] shorter in water than in the atmosphere. Reflection increases as the water surface is ruffled by wind.

Heat Absorption and Transfer

Most of the energy absorbed from the sun by a natural body of water is converted into heat. If the sun's rays were monochromatic and warming took place only by radiation, while the absorptive capacity itself remained uniform, the temperature of the water would decrease logarithmically from the surface to the bottom. Selective absorption, however, steepens the gradient within the upper layers. Even more radial shifts are included by conduction and convection. Radiant energy absorbed by the bottom is released in the form of longer wave lengths. These are trapped by the overlying water. Bottom sediments themselves are cooler than the overlying water in summer and warmer in winter; the deeper the deposit, the greater, the difference.

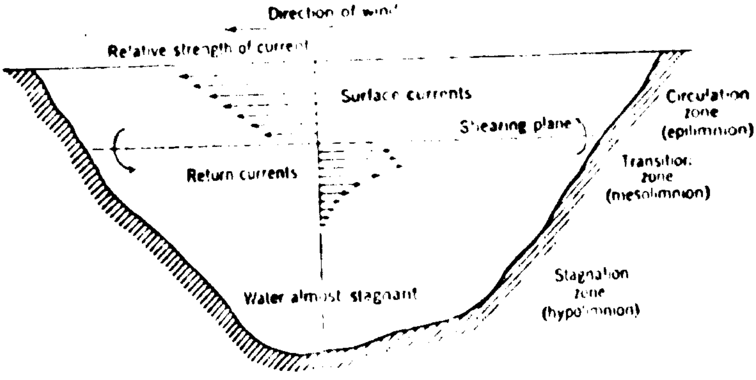
Because the specific heat of water is about 4 times that of air and the mass of water is also relatively much greater, the temperature at the interface would be the water temperature, were it not for wind and water movements. Of the two, air motion is normally the more vigorous [illegible] heat is distributed through bodies of water both horizontally and vertically, by wind action. Exclusion of wind-induced currents by ice cover explains why winter heat losses are small in spite of the lower specific heat and higher conductivity of ice.

Equilibrium is upset also by temperature changes caused by heat transfer from one fluid to another, including changes in temperature produced evaporation. If a surface water is cooled, either by contact with cold air or by evaporation, it becomes denser and sinks. Vertical (convective) currents are set in motion, and heat is transferred within the mass of water itself.

If the water temperature lies below the wet-bulb temperature of the overlying air, the water is warmed by the air; there is no thermal convection in either fluid; and little change of heat takes place. If, on the other hand, the water temperature is higher than the wet-bulb temperature of the air, the water is cooled by evaporation; thermal convection currents are set in motion in both fluids; and the interchange of heat becomes considerable.

Thermal Resistance to Mixing

Water driven to the windward shore of the lake builds up a head which generates return currents. Depending on shore topography these currents travel at or below the water surface.



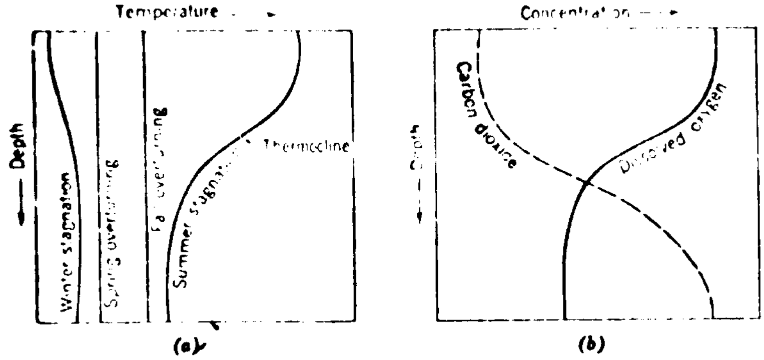
Direction and relative horizontal velocity of wind induced currents in a lake or reservoir (idealized). (After G. C. Whipple, G. M. Fair, and M. C. Whipple, *Microscopy of Drinking Water*, 4th ed., Wiley, New York, 1928.)

Figure 12:1

The returning water is displaced downward in coves and laterally where points of land put out from shore. The vertical distribution of wind-induced currents in an idealized consection of lake or reservoir is illustrated in above picture. The depth of the return currents depends on the water temperature. The greater the decrease in temperature with depth, the greater is the thermal resistance to mixture and the more will the return currents be confined to upper layer of water. By thermal resistance is meant the resistance of colder and therefore, denser and lower-lying water to be displaced by warmer and, therefore, lighter and higher-lying water. A shearing plane divides the surface currents that follow the wind from the return currents that run counter to the wind.

Thermal Stratification and Seasonal Change

The interplay of temperature, density and wind during the different seasons of the year produces a sequence of characteristic patterns of thermal stratification in lakes and reservoirs. The figure below shows such a series for the temperature gradients of water in the middle latitudes of the temperate zone.



Vertical gradients of temperature and water quality in lakes, reservoirs, and other deep bodies of water (idealized). (*a*) Characteristic thermal gradients; (*b*) oxygen and carbon dioxide gradients during summer stagnation.

Figure 13:1

During the winter the water immediatly below the ice stands substantially at 0 ° C, although the ice itself is often much colder at and near its surface. At the same time the temperature at the bottom of the lake or reservoir is not far from that of maximum density (4 ° C). The water is in comparatively stable equilibrium and is inversely stratified in terms of temperature but directly in terms of density.

Bacterial Decomposition of Organic Matter in Water

The decomposition of organic matter in water and wastewater is due to the presence of bacteria and other microorganisms. Bacteria use the organic matter for food and break it down to simpler compounds, most of which are rejected as wastes. The saprophytic bacteria, which subsist upon dead organic matter or mineral matter and are usually harmless to man, are mainly responsible for this process of degradation. Although pathogenic bacteria (disease germs) are often present in sewage and in water polluted with sewage, their proportionate numbers are usually so small that they are negligible factors in the decomposition of dead organic matter. The natural food and environment of the pathogens is the living body of the host. These bacteria, therefore, do not multiply readily in sewage or polluted water.

The growth and multiplication of bacteria in water depend upon the presence of compounds containing carbon and nitrogen in a form capable of being assimilated by the cells and capable, also, of furnishing energy to the cells. Since the ingestion of food by bacteria is accomplished by the passage of the compounds through the cell walls, it is expedited if the food material is finely divided. Small bacterial cells require food material which is composed of small, relatively simple molecules dispersed in true solution. Some of the larger bacteria are capable of ingesting more complex molecules, and many protozoa can ingest particles of colloidal size.

The energy for the respiration of bacterial cells is supplied by wet combustion or oxidation of the chemical compounds broken down by the bacteria. If the oxidation is accomplised by the use of molecular oxygen gas dissolved in the water, the breakdown process is called aerobiosis; if it occurs by the transfer of hydrogen from the compound to a hydrogen acceptor other than molecular oxygen, the process is called anaerobiosis. Bacteria requiring molecular oxygen for their growth and multiplication are called aerobes, and those whose growth requires the complete absence of dissolved oxygen are called anaerobes. Most bacteria are facultative anaerobes and obtain their energy for growth either aerobically or anaerobically, depending upon the character of the organic matter available, the amount of dissolved oxygen, and their own specificity towards the compounds available.

Almost any type of organic compound, saturated and unsaturated fatty acids, hydroxy acids, keto-acids, di- and tribasic acids, alcohols, carbohydrates, amines, amino acids, amides and aromatic compounds, may be used as a source of carbon and of energy. Only a small part of the compound destroyed, however, is used for cell-building; the remainder is by-product waste as far as the growth of the microorganism is concerned.

The rate of decomposition of organic matter is greatest when the bacteria are undergoing active multiplication. When the number of bacteria in a culture gets large, the accessibility of the food supply to the organism diminishes, because of the interfer . of the products of decomposition and other causes. A point is soon reached where the rate of [illegible] of food supply by the organisms is insufficient [illegible] reproduction [illegible], the rate of decomposition [illegible] eventually the number of bacteria also [illegible] organic matter with the liberation of all [illegible] attained. [illegible] carbon [illegible] Anaerobic [illegible] nitrogenous organic matter [illegible] factor or [illegible]

Ordinary [illegible] them [illegible] The [illegible] about [illegible]

Table 15.[illegible]

Type of organism	Energy-yielding reaction and source of carbon	Source of nitrogen
Heterotrophs		
(a)	Utilization of carbon compounds more reduced than CO_2, i.e. organic carbon compounds	Array of a[illegible] and enzymes [illegible]
(b)	"	Sin[illegible] amino ac[illegible] particularly try[illegible]phane
(c)	"	Ammonia, [illegible] nitrite
Autotrophs		
(d) Facultative chemosynthesizing aerobes	Oxidation of thiosulfate, H_2, CO, CH_4, yielding energy for assimilation of CO_2	Ammonia, [illegible]
(e) Chemosynthesizing aerobes	Oxidation of NH_3, nitrite, yielding energy for assimilation of CO_2	
(f) Chemosynthesizing "sulfur" aerobes	Oxidation of H_2S and thiosulfate yielding energy for assimilation of CO_2	Ammonia

[illegible]	Energy yielding reaction and source of carbon	Source of nitrogen
[illegible]	[illegible] H_2S $\xrightarrow[\text{Energy}]{\text{Radiant}}$ $HCHO + 2S + H_2O$	Ammonia
[illegible]	[illegible] $+ H_2O$ $\xrightarrow[\text{Energy}]{\text{Radiant}}$ [illegible] $+ O_2$	Ammonia
[illegible]	[illegible] $+ H_2O$ $\xrightarrow[\text{Energy}]{\text{Radiant}}$ $HCHO + O_2$	Fixation of N_2 gas

From the standpoint of nutritional requirements, Knight classified bacteria as shown in Table 15. The heterotrophs require organic compounds for their metabolism, whereas the autotrophs are able to subsist on inorganic compounds. The heterotrophs are mainly responsible for the decomposition of sewage organic matter, although in the latter stages of the aerobic processes of sewage treatment and of self-purification of polluted rivers the autotrophic nitrifying bacteria play important roles. It has been shown that the presence of carbon dioxide surrounding the cell is essential to the growth of most bacteria but the part played by CO_2 is unknown except in the case of the autotrophs and a few heterotrophs who use CO_2 as a hydrogen acceptor. CO_2 is an end product in the metabolism of the heterotrophs and hence is normally present around the cells.

Chemical reactions induced by bacteria usually take place at constant pressure. If the heat evolved in the reaction is written as a part of the equation, the reaction is called a thermochemical reaction and the heat evolved is called the heat of reaction. For example in the equation:

$$\underset{\text{gas}}{H_2} + \underset{\text{gas}}{1/2\ O_2} \longrightarrow \underset{\text{liquid}}{H_2O} + 68.317\ \text{kcal}$$

When any subtrate undergoes bacterial decomposition, heat is necessarily evolved in order to provide the energy for the growth and maintenance of the bacteria. The process as a whole is, therefore, exothermic. Some of the reactions which correspond to steps in the process may be endothermic, however, provided the energy yielded in the rest of the process is more than sufficient to overcome the deficit.

The energy required for the work and growth of living cells is obtained by the cells through the decomposition of foodstuffs [illegible]. The maximum amount of energy that can be obtained from organic compounds is that resulting from their complete burning in air at high temperature; hydrogen is oxidized to water and carbon to carbon dioxide, the energy being given off as heat. Spontaneous reaction of this sort, which will run by itself, is of no use to the cell. The cell can use only enzyme-catalyzed reactions which take place in such a way that the energy released is not lost as heat but is utilized by the cell. The process by which the cell obtains its energy is called respiration.

Under otimum conditions of growth, bacteria divide about every half hour. The conditions affecting the growth rate are the presence of water, the size of the cells, the temperature, the concentration and availability of food supply, the pH value, and the presence of poisons and predatory organisms in the medium. Of less importance is the content and composition of mineral salts in the medium unless the metals take part in enzyme action. In the case of aerobes, the presence or absence of an adequate supply of dissolved oxygen in the medium is an important factor which determines whether growth will take place or not; in the case of facultative anaerobes, the presence or absence of oxygen determines the rate of growth.

Under strictly aerobic conditions, ammonia may be oxidized to nitrite and nitrate through the action of the nitrifying bacteria, Nitrosomonas and Nitrobacter. These organisms are obligate autotrophs, Nitrosomonas oxidizing only ammonia and Nitrobacter only nitrites. The energy obtained from these reactions is used for the assimilation of carbon which is obtained from carbon dioxide or bicarbonate, not from organic carbon compounds.

Nitrification is an important contributory factor in the depletion of oxygen from sewage and polluted water, but its [illegible] delayed for several weeks pending the development of a suitable environment for the organisms.

When a pure culture of bacteria is inoculated into a suitable culture medium, it is found that multiplication of the viable organisms does not proceed at tne geometric rate which would be indicated by a constant generation time. There is a short period of no growth followed by a short lag phase during which there is positive acceleration in the rate of multiplication. The third period is the logarithmic growth phase indicated by a constant generation time. This the maximum rate of growth. This period is followed by one of negative growth acceleration and then by a period of substantially constant numbers as the limiting bacterial population is reached. The concentration of accessible food in this period

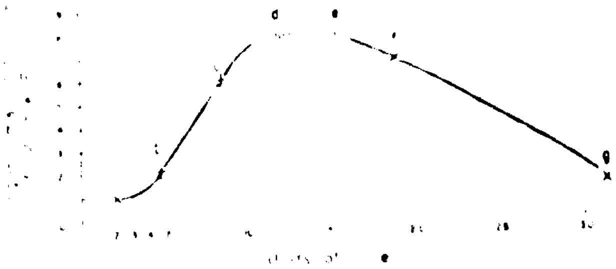


Figure 1 [illegible] phases of [illegible] (after Bakalar)

[illegible] sustain life [illegible] not adequate for reproduction. [illegible] death rate and a final phase with [illegible] decrease in bacteria resulting from death.

In the absence of dissolved oxygen, the bacteria turn to other sources of oxygen [illegible] more energy that can be obtained without oxygen. Both nitrates and sulfates are used by bacteria as a source of oxygen. The energy yield is high when nitrates are used to oxidize the food molecule, but with sulfates, the energy yield is little better than with anaerobic decomposition without an oxygen source.

Sulfates are known to be decomposed in sewage sludge digestion tanks which, when operated properly, produce negligible amounts of H_2S gas. When the pH of the digesting sludge is low, H_2S gas may be produced.

The concentration of sulfates in water is an important factor in determining whether H_2S will be evolved. Where H_2S is evolved in the anaerobic decomposition of bottom deposits in a polluted stream or estuary, it will usually be oxidized chemically to sulfates if there is sufficient dissolved oxygen in the overlying waters and if the H_2S gas does not rise in large gas bubbles along with CO_2. When the tide rises and covers flats in a polluted tidal estuary, polluted water high in sulfates will seep into the sands of the flats. When the dissolved oxygen in the water in the pores is exhausted by bacterial decomposition of the organic pollutants, the sulfates in the pore water are then broken down. When the tide recedes, the H_2S gas in the pores of the exposed sand flats is released to the atmosphere, causing odor nuisances. If the incoming tidal waters contain sufficient dissolved oxygen, the odors will be reduced or abated at high tide.

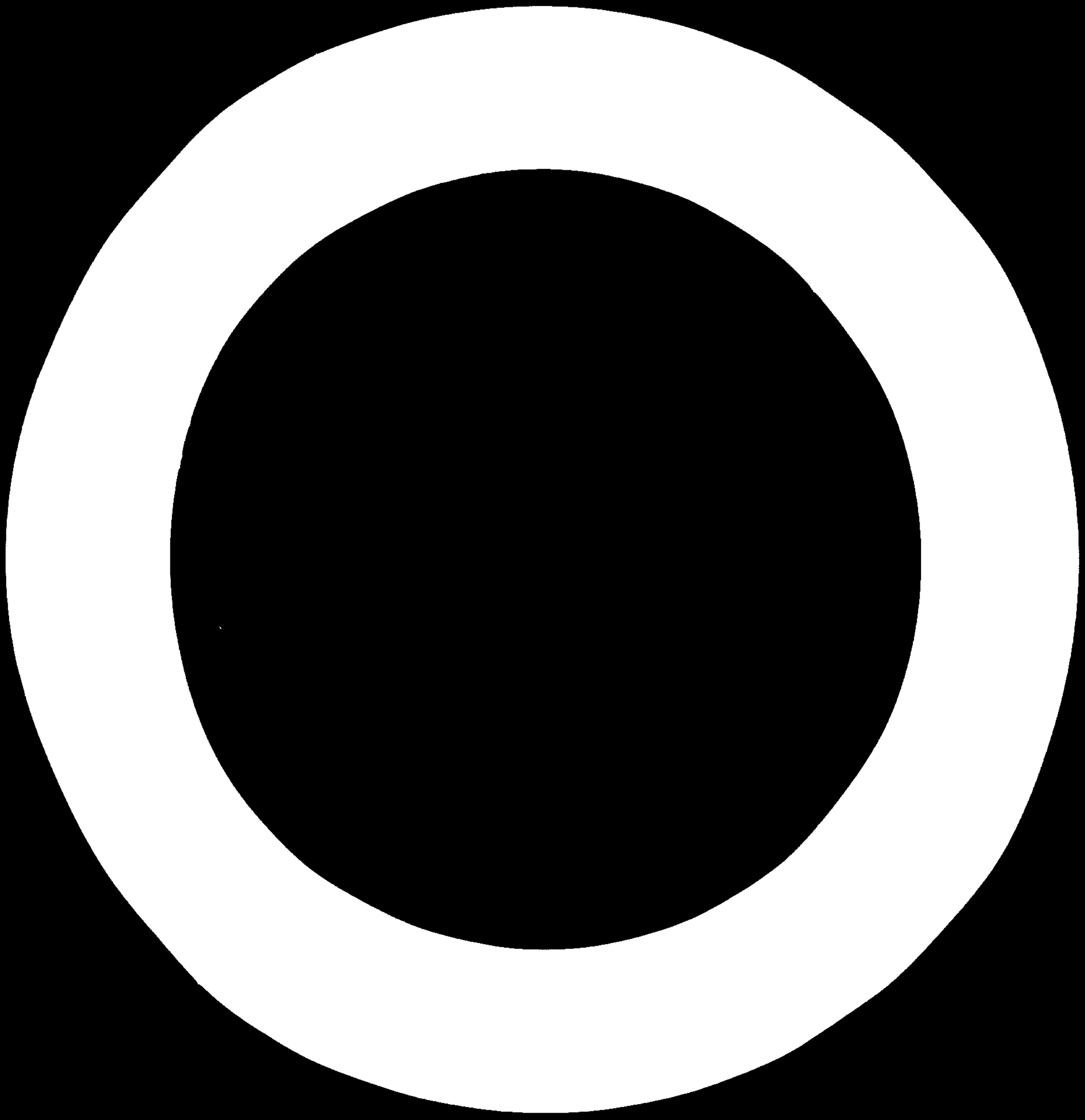


Table [illegible] 1

[illegible] NATURAL WATERS

[illegible]	[illegible]	[illegible]	Gases	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	CO_2		Ca^{++} Mg^{++} Na^+ K^+ Fe^{++} Mn^{++} Zn^{++}	[illegible] [illegible] SO_4 NO_3 Cl HS[illegible] [illegible] HPO_4 H_2PO_4 OH
[illegible]			N_2 O_2 CO_2 SO_2		H^+	HCO_3 SO_4
[illegible]	[illegible] organic wastes	Vegetable [illegible] matter organic wastes	CO_2 NH_3 O_2 N_2 H_2S CH_4 H_2 Odor vectors	Vegetable [illegible] matter organic wastes	Na^+ NH_4^+ H^+	Cl HCO_3 NO_2 NO_3 OH HS^- Organic radicals
Living organisms	[illegible] diatoms and minute animals	Viruses, bacteria, algae and [illegible]				

Table 20.2

SOLUBILITY OF GASES IN PURE WATER IN CONTACT WITH THE PURE GAS AT A PRESSURE OF 1 ATM.

Temp. (°C)	Nitrogen* [illegible]% N_2 + 1.185% A		Oxygen* O_2		Hydrogen* H_2		Methane* CH_4		Carbon dioxide* CO_2		Hydrogen sulfide* H_2S		Sulfur dioxide* SO_2		Ammonia** NH_3	
	$[N_2]$ [illegible]	mg/l	$[O_2] \times 10^3$	mg/l	$[H_2] \times 10^3$	mg/l	$[CH_4] \times 10^3$	mg/l	$[CO_2]_T \times 10^3$	mg/l$_T$	$[H_2S]_T \times 10^3$	mg/l$_T$	m$_T$	mg/l$_T$	m$_T$	mg/l$_T$
0	[illegible]	29.4	2.18	69.8	0.959	1.9[illegible]	2.48	39.8	[illegible].4	3360	208.3	7100	3.[illegible]	[illegible]6,700	52.3	471.[illegible]
5	0.9[illegible]	26.1	1.913	61.2	0.912	1.84	2.14	34.3	63.5	2790	177.4	6040	3.03	[illegible],300	45.[illegible]	[illegible]
10	0.8[illegible]	23.[illegible]	[illegible]696	54.3	0.872	1.7[illegible]	[illegible].364	29.9	53.25	2345	151.6	5160	2.5[illegible]	[illegible],600	40.1	3[illegible]
15	0.[illegible]	21.1	[illegible]524	48.[illegible]	0.841	1.70	1.645	26.4	45.45	2000	131.4	4475	2.34	[illegible]00	35.2	3[illegible]
20	0.[illegible]	19.3	[illegible]384	44.3	[illegible]812	1.64	1.475	23.[illegible]	39.1	1720	115.2	39[illegible]5	1.80	[illegible]400	30.9	3[illegible]
25	0.[illegible]	17.9	1.263	40.4	0.783	1.58	1.342	21.5	33.9	1495	101.8	3470	1.51	[illegible]00	27.9	3[illegible]2
30	0.599	16.8	1.163	37.2	0.758	1.53	1.233	19.7	29.65	1305	90.9	3090	1.26	[illegible]3,700	23.8	[illegible]
40	0.5[illegible]8	14.8	1.029	32.9	0.734	1.48	1.057	16.9	23.65	1040	74.1	2520	[illegible]91	[illegible]4,800	19.9	252.0
60	0.456	12.77	0.868	27.8	0.714	1.44	0.872	14.0	16.0	704	53.1	1810			14.0	19[illegible]
80	0.427	11.96	0.786	25.1	0.714	1.44	0.79	12.7			40.9	1394			9.1	1[illegible]
100	0.423	11.85	[illegible]	24.[illegible]	0.714	1.44	0.76	12.2			36.1	1230				

*From Landolt-Bornstein, "Physikalisch-chemische Tabellen," Table 131, p. 763, Berlin, Springer, 1923.

**From Landolt-Bornstein and Mellor, Joseph William, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 8, p. 19[illegible], London, New York, Longmans, [illegible] 1928.

†T signifies total solubility.

Table [illegible]

SUGGESTED WATER QUALITY TOLERANCES FOR INDUSTRIAL USE

Industry or Use	Turbidity (ppm)	Color (ppm)	Hardness (as CaCO$_3$) (ppm)	Fe (ppm)	Mn (ppm)	Total solids (ppm)	Alkalinity (as CaCO$_3$) (ppm)	Odor Taste	H$_2$S (ppm)	Other requirements
Air conditioning	–	–	–	0.5*	0.5	–		Low	1	No corrosiveness or slime formation
Baking	10	10		0.2*	0.2	–	–	Low	0.2	Potable**
Brewing										
Light beer	10	–	–	0.1*	0.1	500	75	Low	0.2	Potable, NaCl less than 275 ppm, pH 6.5–7.0
Dark beer	10	–		0.1*	0.1	1,000	150	Low	0.2	Potable, NaCl less than 275 ppm, pH 7.0 or more
Canning										
Legumes	10		25–75	0.2*	0.2		–	Low	1	Potable
General	10	–		0.2*	0.2			Low	1	Potable
Carbonated beverages	2	10	250	0.2 (0.3*)	0.2	850	50–100	Low	0.2	Potable, Organic color plus oxygen consumed less than 10 ppm
Confectionery		–		0.2*	0.2	100	–	Low	0.2	Potable, [illegible] for hard candy, low for [illegible]
Cooling	50	–	50	0.5*	0.5	–		–	5	No corrosiveness or slime formation
Distilling										
Gin and spirits	10	–	–	0.1*	0.1	500	75	Low	0.2	Potable, NaCl less than 275 ppm, pH 6.5–7.0
Whiskey	10	–	–	0.1*	0.1	1,000	150	Low	0.2	Potable, NaCl less than 275 ppm, pH 7.0 or more
Blending	–	–				–	–	–	–	Distilled or special treatment
Food, general	10	–		0.2*	0.2		–	Low	–	Potable
Ice	5	5	–	0.2*	0.2	170	–	Low	–	Potable, SiO$_2$ less than 10 ppm
Laundering	–	–	50	0.2*	0.2		–	–	–	
Plastics, clear, uncolored	2	2	–	0.02*	0.02	200	–	–	–	
Paper and pulp										
Groundwood	50	200	180	1.0*	0.5		–		–	No grit or corrosiveness
Kraft pulp	25	15	100	0.2*	0.1	300		–	–	
Soda and sulfite	15	10	100	0.1*	[illegible]	200				
High-grade light papers	5	5	50	0.1*	0.05	200		–	–	No slime formation
Rayon (Viscose)										
Pulp production	5	5	8	0.05*	0.03	100	Total 50, OH 8	–	–	Al$_2$O$_3$, SiO$_2$, [illegible] less than 8, 25 and 5 ppm respectively
Manufacture	0.3	–	55	0.0	0.0	–	–	–	–	pH 7.8 to 8.3
Tanning	20	10–100	50–135	0.2*	0.2	–	Total 135, OH 8	–	–	
Textiles										
General	5	20	–	0.25	0.25	–	–	–	–	
Dyeing	5	5–20	–	0.25*	0.25	200	–	–	–	Constant composition, Al$_2$O$_3$ less than 0.5 ppm
Wool scouring	–	70	–	1.0*	1.0	–	–	–	–	
Cotton bandage	5	5	–	0.2*	0.2	–	–	Low	–	

*Limit applies both to iron alone and to the sum of iron and manganese.

**Potable means complying with drinking water standards of the U.S. Public Health Service.

The Oxygen Balance in Polluted Waters

Natural surface waters and tidal estuaries contain organic impurities under decomposition by bacteria and other microorganisms. The bacteria utilize the oxygen dissolved in the water in their feeding processes, and the dissolved oxygen is in turn replenished from the atmosphere. Where green plant life, such as green and blue-green algae, is plentiful in the water oxygen is also supplied during daylight as a by-product of the photosynthesis of carbohydrates from carbon dioxide and bicarbonates.

If the concentration of decomposing organic matter is excessive, which may be the case if the water is polluted with sewage or organic industrial wastes, the dissolved oxygen concentration may be lowered to a level which is harmful to fish and other aquatic life or it may be lowered to a concentration near zero at which anaerobic decomposition takes place with the production of gaseous by-products and black water. The gaseous by-products are carbon dioxide, methane and, to a lesser extent, hydrogen sulfide and mercaptans. The sulfide compounds cause foul odors and react with metals in the water to form black precipitates, resulting in black water. In many cases where sulfide odors are present in the atmosphere above the water surface, the sulfides may react with paints on buildings, boats and structures, to discolor or blacken the paint.

Many polluted waters are analyzed routinely by water pollution control agencies during the warmer and drier months when oxygen levels are lowest and the rate of bacterial decomposition is greatest. Dissolved oxygen, BOD, and other determinations are made on samples collected from selected sampling stations at selected time intervals throughout the critical months. Such analyses are useful in measuring the extent and nature of pollution and in locating the points of minimum oxygen concentration, but they are usually not an adequate basis for oxygen balance studies to estimate the allowable pollution loads and to plan means for pollution abatement.

The most important purpose of oxygen balance studies is to estimate the allowable pollution loads at existing or potential points of pollution. The difference between the allowable and the existing or potential pollution load represents the removal which must be accomplished at each polluting point.

In oxygen balance studies to estimate allowable pollution loads, oxygen furnished through photosynthesis by green plants should not be relied upon because there is no assurance that it will be available during critical low flow periods. Studies should, therefore, be made of existing receiving water conditions to estimate how much, if any, of the oxygen supply is from green plants. The rate of supply of dissolved oxygen from atmospheric reaeration may be estimated for existing conditions from BOD and dissolved oxygen analyses, provided corrections are made for oxygen supplied through photosynthesis and due account is taken of the settling out of decomposable organic matter and the BOD added from bottom deposits.

Oxygen balance studies are of use only where there is always a flow in the receiving waters.

Where large quantities of exhaust cooling waters at high temperature are discharges into the receiving waters, the temperature of the receiving waters may be raised well above that which would be expected under natural climatic conditions. This is a form of pollution known as thermal pollution, which is of growing economic importance on industrial streams. It is of twofold economic importance, reducing the value of the stream water for cooling purposes as well as increasing the difficulty and cost of organic pollution abatement. Thermal pollution is also damaging to fish and other aquatic life. Consideration will have to be given in some cases to reduction in thermal pollution as a legitimate part of a pollution abatement project.

The design flow conditions to be used for tidal estuaries, lakes or oceans should be those which will produce the worst conditions at critical points or in critical areas. Usually the worst conditions are during warm and dry weather when the flow in the streams is a minimum.

Saturation Concentration of Dissolved Oxygen

The saturation concentration of dissolved oxygen in distilled water at various temperatures in contact with air containing 20.95 % oxygen by volume on the dry basis and at sea level (760 mm of Hg) is shown in figure 23:1 for both dry and saturated air.

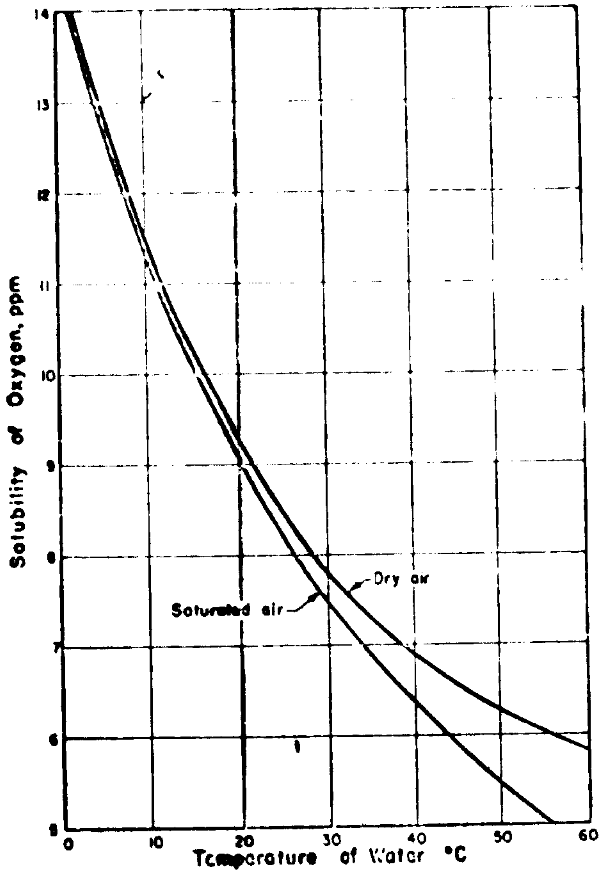
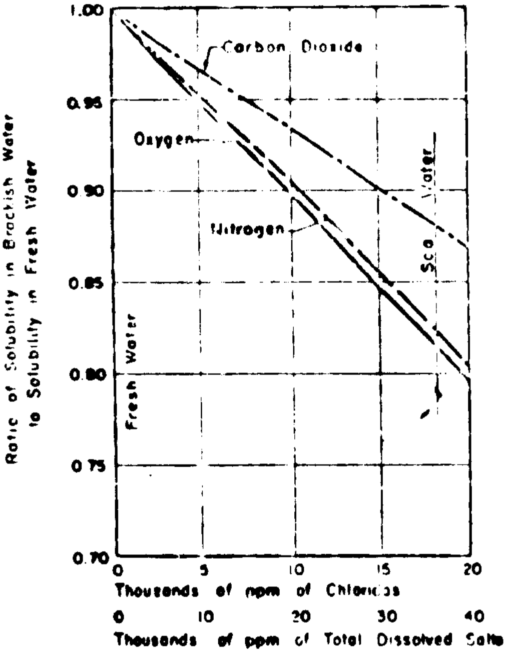


Figure 23:1 Solubility of oxygen in distilled water in contact with air at 760 mm containing 20.95% oxygen.

The solubility of dissolved oxygen is also less in brackish and sea water than in fresh water, as shown by figure 24:1. The same indicates that as the salinity increases the solubility of oxygen decreases, being only about 82 % as great for sea water as for fresh water.

The Dissolved Oxygen Sag Curve

Oxygen balance studies of a polluted stream usually result in one or more dissolved oxygen profiles along the course of the stream. Such a profile is referred to as a dissolved oxygen sag curve and is illustrated in figure 24:2.
The objective of pollution abatement is to remove sufficient pollution so that the minimum oxygen concentration at the bottom of the sag is not less than some predetermined standard, 4 or 5 ppm for propagation of fish and 1 to 2 ppm to prevent odor nuisance.



Effect of dissolved salts in sea water on solubilities of nitrogen, oxygen and carbon dioxide.

Figure 24:1

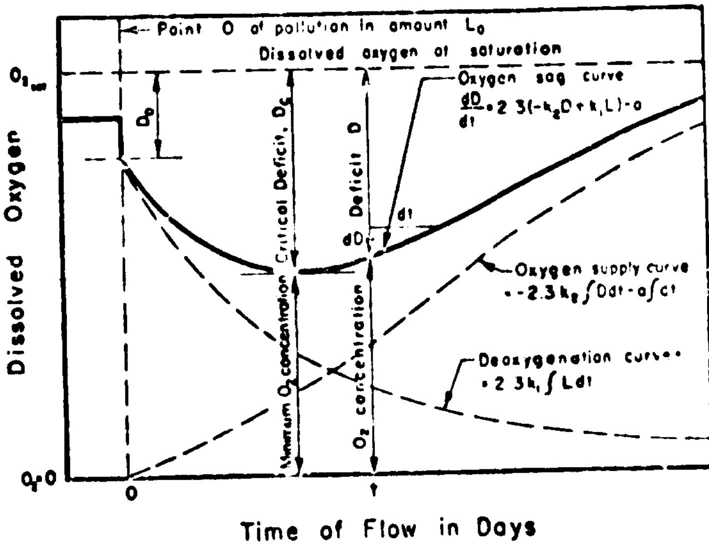


Diagram of simple oxygen sag curve

Figure 24:2

Figure 24:2 is a simple oxygen sag curve for a nontidal watercourse with only one pollution load. The initial dissolved oxygen concentration drops suddenly at the point of pollution, if there is an immediate oxygen demand associated with the wastes or if the wastes are voluminous as compared to stream flow and contain little dissolved oxygen. The initial BOD load, L_0, is the net demand after mixing with the receiving waters and after satisfaction of the immediate demand. The BOD of the receiving waters just upstream from the point of pollution must also be taken into account in estimating L_0. The difference between the saturation concentration and the actual concentration at any station is known as the oxygen deficit, D. At any station, the rate of change of the oxygen deficit with time of flow downstream, which defines the shape of the oxygen sag curve, is as follows:

$$\frac{dD}{dt} = 2.3\,(-k_2D + k_1L) - a$$

where D is the oxygen deficit in ppm, L is the first stage oxygen demand in ppm, t is the time of flow in days, k_2 is the atmospheric reaeration constant in days^{-1}, k_1 is the deoxygenation constant in days^{-1}, and a is the oxygen production in the euphotic zone by photosynthesis in ppm per day.

It is evident from figure IV.2 and equation that the dissolved oxygen concentration at any station is the algebraic sum of the initial concentration at an upstream station, the oxygen added from the atmosphere and from photosynthesis between stations, and the amount of oxygen used in the bacterial decomposition of the polluting organic matter in the water. The critical deficit D_c is reached at the bottom of the sag when the slope $\frac{dD}{dt}$ is zero and the rate of supply of oxygen is equal to the rate of deoxygenation.

The critical deficit is, therefore:

$$D_c = \frac{2.3\,k_1L_c - a}{2.3\,k_2}$$

where L_c is the first stage demand at the bottom of the sag. Conversely if k_1, k_2 and a are known, the allowable first stage demand L_c for any selected critical deficit D_c, may be estimated as follows:

$$L_c = \frac{2.3\,k_2D_c + a}{2.3\,k_1}$$

It should be noted that above equations apply to the station at the bottom of the oxygen sag if D_c is less than the saturation concentration. Oxygen balance computations are usually started from a point just upstream from the first point of pollution, and proceed downstream with trial-and-error solutions for each reach. It is possible, however, to start oxygen balance computations at the bottom of the sag, even though the location of this point is unknown with respect to pollution loads, and to work upstream to determine the allowable pollution loads. Above equation may be used to compute L_c whether or not there is settling out of BOD, addition of BOD from the bottom deposits, or both; however, these factors must be taken into account to compute upstream values of L and D.

In a grossly polluted stream, the dissolved oxygen concentration may be reduced to zero at the bottom of the sag as shown in figure 26:1.

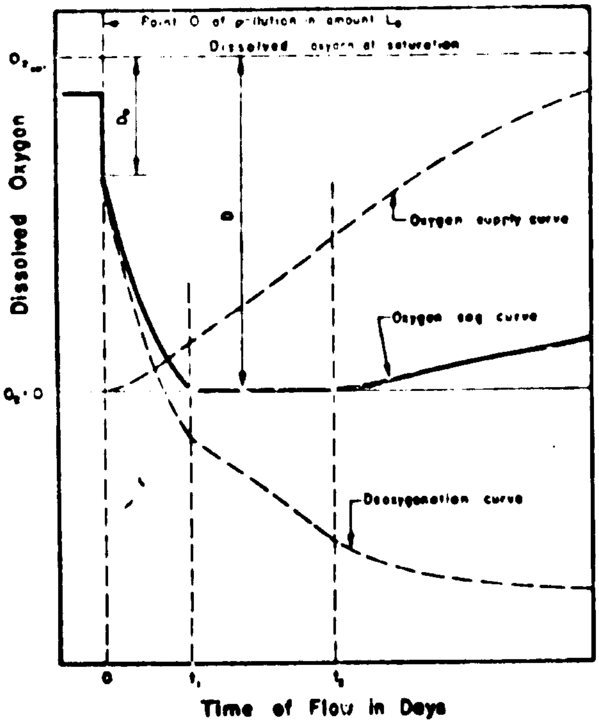


Figure 26:1. Diagram of oxygen sag curve with oxygen concentration reduced to zero

It should be noted that, even though the concentration is zero in the reach $t_2 - t_1$, oxygen is nevertheless being supplied by reaeration from the atmosphere (and possible by photosynthesis) and the rate of supply is a maximum because D is equal to the saturation concentration. Therefore, the rate of deoxygenation in the reach $t_2 - t_1$ is limited by, and equal to, the rate of oxygen supply.

The rate of deoxygenation will decrease from the point of pollution to point t_1, at which point there will be a discontinuity as the rate is controlled by the oxygen available rather than by the BOD. At point t_2, the rate of deoxygenation again becomes proportional to the remaining value of L, and downstream from point t_2, dissolved oxygen is supplied faster than it is utilized by the bacteria. The value of L at point t_2 may be computed from equation above. The time interval $t_2 - t_1$ may be computed by nothing that the oxygen used in the reach is equal to the amount of dissolved oxygen supplied.

ANALYSES OF [illegible] AND EFFLUENT WATERS

In order to be able to reduce the influence of discharged effluents from the pulp and paper industry it is necessary to have knowledge about the relations between the effect upon the environment and the parameters of the process. Our knowledge of how the discharged effluents affect the water environment or the recipients is not complete and the existing methods to determine specific values are thus quite doubtful. The discharged waste water from the pulping process is coloured, contains lignin, suspended materials and substances which will have a biological oxygen demand (BOD_7). Certain discharges can also be toxic.

The oxygen demand of the discharges depends upon in the first place the content of biochemical oxidizable substances, mainly methanol, terpenes and carbohydrates. The colour in the effluents comes mainly from their content of lignin but also to a great extent from modified carbohydrates.

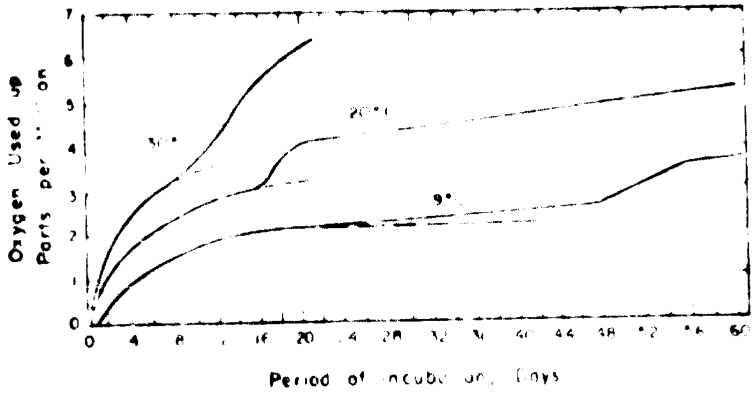
In the following the most common methods of analyses applied in the investigations of waters concerning environmental effects are briefly described.

Suspended Matter in Waste Water

The fibre content in white water is determined by measuring the amount of suspended material (SCAN W6:71 see appendix). Eventually can a correction be made for solid, unorganic compounds by after the determination to incinerate the sample. The suspended matter content value is reported in mg/l.

Biochemical Oxygen Demand of Industrial Effluents

The rate at which dissolved oxygen is used up in fresh sewage or sewage polluted waters has been studied extensively by many. The biochemical oxidation has been found to proceed in a manner similar to a unimolecular chemical reaction, that is, the rate is approximately proportional to the remaining concentration of unoxidized organic matter, measured in terms of oxidizability, and it is a function of the temperature. See the following figure no 29:1.



The general course of the oxygen demand curve

Figure 29:1

The amount of oxygen used up is called the BIOCHEMICAL OXYGEN DEMAND **or BOD** for a particular time and water temperature. BOD tests have **become** standard practice and are now widely used. The standard procedures for the test are described in Standard Methods for the Examination of Water and Wastewater, American Public Health Association. In **Sweden** normally the method **developed** by the Scandinavian Pulp, Paper **and Board** Testing committee is used (SCAN-W[illegible], see appendix [illegible]). In many **countries** an incubation period of 5 days is commonly applied. The period of 7 days specified in this method is convenient for laboratories **working** a 5-day week.

The BOD of sample of sewage, industrial wastes or polluted water is a **measure** of the concentration of decomposable organic matter in the **sample**. It has become the most useful single determination [illegible] the routine examination of sewages, industrial waste and treatment plant effluents and, especially, in the examination of the receiving waters in **pollution** studies. The BOD concept involves not only the amount of organic material which is decomposable by bacteria but also the time [illegible] **at which** it will decompose **aerob**ically. The BOD test [illegible], therefore, [illegible] **used** as a laboratory model of the deoxygenation process in the receiving **water**.

The concentration of decomposable organic matter in wastewater or polluted water is not directly **measurable** and is of little importance except **that** it controls the **demand** for dissolved oxygen. The associated dissolved oxygen demand on the other hand, is of major importance, and this **is measured** by the BOD test. **Decomposable** organic matter may be reduced **in** concentration **by a number of** different processes in treatment plants or polluted waters. Since the amount of the associated oxygen demand, rather than the amount of organic matter, is the parameter of interest, it has become common practice to use the term "BOD" interchangeably with the term "decomposable organic matter" in discussions of pollution loads and changes in amounts of organic matter. It is important to note that the quantities are of oxygen and not organic matter.

The BOD test has been subjected to adverse criticism because of the long period required for its completion, 5 days or more, and substitute chemical tests have been sought. Chemical tests may be used, to determine the concentration of chemically oxidizable organic matter, but the result is not the same as the biochemically oxidizable organic matter and it throws no light on the biochemical time rate.

The BOD test is performed by determining the dissolved oxygen content of the sample at the beginning, and after various incubation periods at the desired temperature. If there is insufficient dissolved oxygen in the sample for the complete test, oxygen is added in dilution water or by aeration. It is most important that the bacterial seed be the same as in the waste or polluted water and that the nutrients and minerals be representative of the polluted water.

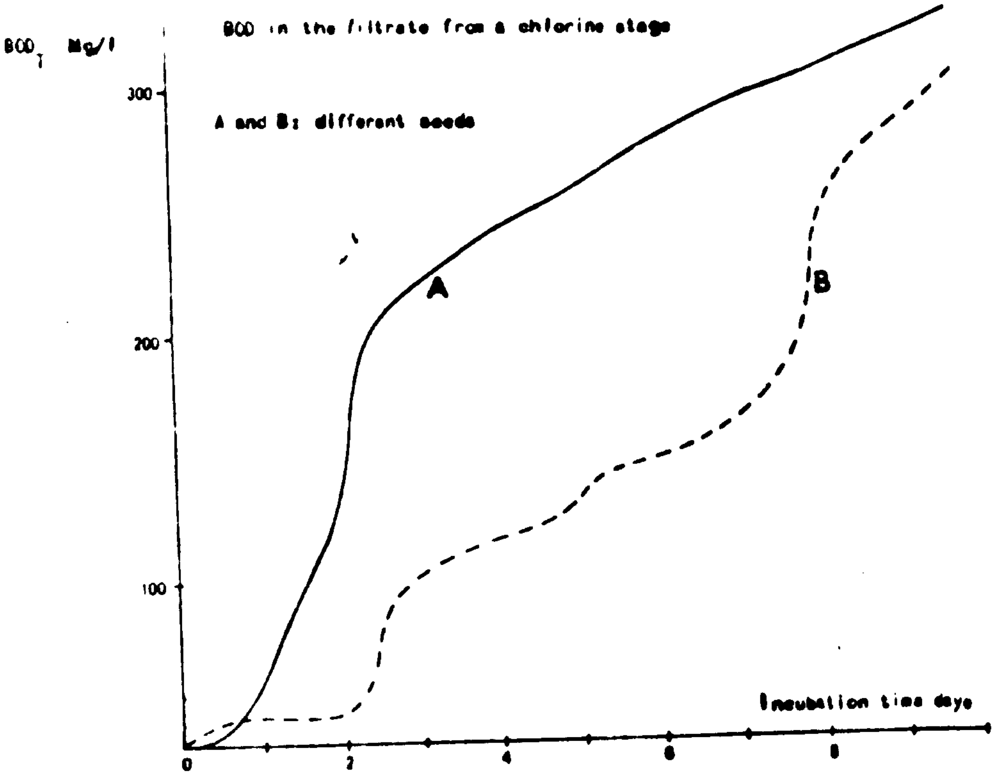


Figure 30:1

In conformity with all biochemical processes when measuring BOD_7 the oxygen consumption shows in the beginning a slow phase the so called incubation period. A period of intensive oxygen consumption is then followed, whereafter the same decreases again. This is demonstrated by curve A in the diagram shown in figure 30:1.

The curve B in the same diagram on the contrary shows a considerably more complicated course with repeated growth and stagnation periods. Both of the curves correspond to the same sample of effluent water from a chlorine stage. The different courses are explained by a difference in the quality of the bacterial seed. However, it must be pointed out that the difference which has been shown in this case is greater than that normally obtained when measuring BOD_7 in effluents from chlorine filters. The BOD_7-values can be considerably spreaded although relatively independent of the time, but if a bacterial seed is chosen which is more adapted to chlorine effluents a less spread of the same is obtained. When measuring BOD in the filtrate from the alkali stage the spread is still smaller. BOD_7 is reported as biochemical oxygen demand in mg per litre.

Chemical Oxygen Demand of Industrial Effluents

Potassium permanganate was first used as a reagent to determine the oxygen demand, OC, by organic matter (SCAN-W1:66, see appendix). This reagent has now been superseded by potassium dichromate, and the values obtained are known as the dichromate oxygen consumed, DOC, or the chemical oxygen demand, COD. Since the carbon and hydrogen, and not the nitrogen, are oxidized by the chemical oxidants, the COD is sometimes erroneously assumed to indicate the total carbonaceous organic matter present. For most organic compounds oxidation is 95 to 100 % complete with the dichromate method. Oxidation of short chain alconols and acids, is 85 to 95 % complete if a silver catalyst is used. Benzene, toluene and pyridine are not oxidized by this method whether the catalyst is used or not. The COD test is not a satisfactory substitute for the BOD determination, but it may be used to reduce the number of BOD tests which might otherwise be required, if the results of the two tests are correlated on occasional replicate samples.

COD is reported as chemical oxygen demand in mg per litre

Total Organic Carbon in Industrial Effluents

The deficiencies of the COD test can be avoided if instead the total amount of organic carbon in the sample is determined. This analyse can be performed according to two principles:

- Combustion of all organic material to CO_2 which then is detected by different methods

Pyrolyses of organic material to CH_4 which is then either oxidized to CO_2 for IR detection or is determined directly with a flame ionization detector

An analyses of TOC gives a measure of all carbon compounds (divided into organic and inorganic carbon) in the sample. TOC is thus a sort of BOD providing that all carbon compounds can be broken down. The carbon compounds which in the first place make up the BOD_7 value are the carbohydrates while for instance lignin has a very low BOD_7 value. TOC-value is reported in mg/l.

Colour in Industrial Effluents

The colour of an effluent is usually measured as the strength of the same light absorption as a chlorine-platinum solution has at a certain wave length (400 nm). This test is usually made according to ASTM (3) method.

When determining the colour of filtrate from the bleach plant which contain active chlorine it is necessary to make the sampling, dilution and buffring in a reproducable way as time between these working moments influence the measured value obtained.

After neutralization the colour of the filtrate increases with the time. Eventually this depends on an air oxidation of the sample and as a consequence formed chromophores. The colour increases also with the time when the sample has been standing from the time it has been taken and to the time the test is performed. Most likely the phenomena is related to the rest chlorine of the sample. When the sample is neutralized hypochlorite is formed which effectively bleaches the coloured groups in the lignin. The lower the rest chlorine content is the less hypochlorite is formed and the less the bleaching effect will be.

Hydrogen Sulphide in Waste Water

This method applies to all kinds of waste water. If the sample contains sulphur dioxide, a modification in the testing procedure should be used. See appendix description of SCAN-W4:69 method and note 1.

After acidification of the sample the hydrogen sulphide is stripped off by a stream of nitrogen, absorbed in an alkaline phosphate buffer solution and determined colometrically by the methylene-blue method. The test value is reported as sulphide concentration in mg of S_2/l.

Non-Volatile matter in Waste Waters

The dry matter content of waste water is the ratio of the mass of the dried residue of the evaporated sample to the original volume of the sample, the drying having been carried out at 105 °C ± 25 °C.

The loss on ignition is the difference between the dry matter content and the residue on ignition, reported as mg/l.

Settleable Matter in Waste Water

The test (specified in SCAN-W7:72 method, see appendix) is intended for measuring the amount of settleable matter present in a sample of waste water.

The sample [illegible] volume is withdrawn and then allowed to settle for a specified time, generally 10 minutes. The supernatant water is removed by suction and the remainder is filtered. The solid matter so obtained is dried and weighed. After calculation it is reported as settleable matter content, mg/l.

Magnesium in Waste Water

The sum of magnesium and calcium is determined volumetrically with EDTA solution. In a separate titration the calcium is determined, and the amount of magnesium is obtained as the difference in mg/l. (SCAN-W2:67, see appendix).

Phosphorus in Waste Water

The sample is wet-combusted with hydrogen peroxide and concentrated sulphuric acid to convert all phosphorus compounds to ortophosphates. Addition of molybdic acid produces a yellow complex; this is reduced by ascorbic acid to a blue complex, which is determined colometrically. The phosphorus content is reported as g per litre or in ppm. (SCAN-W8:73, see appendix).

Regarding additional methods of analyses of industrial waste water we wish to refer to the literature in this field of environmental pollution control and especially to the Standard Methods published by the Water Pollution Control Federation (WPCF), 3900 Wisconsin Avenue, Washington, D C 20016, USA.

Sodium content of wet pulp

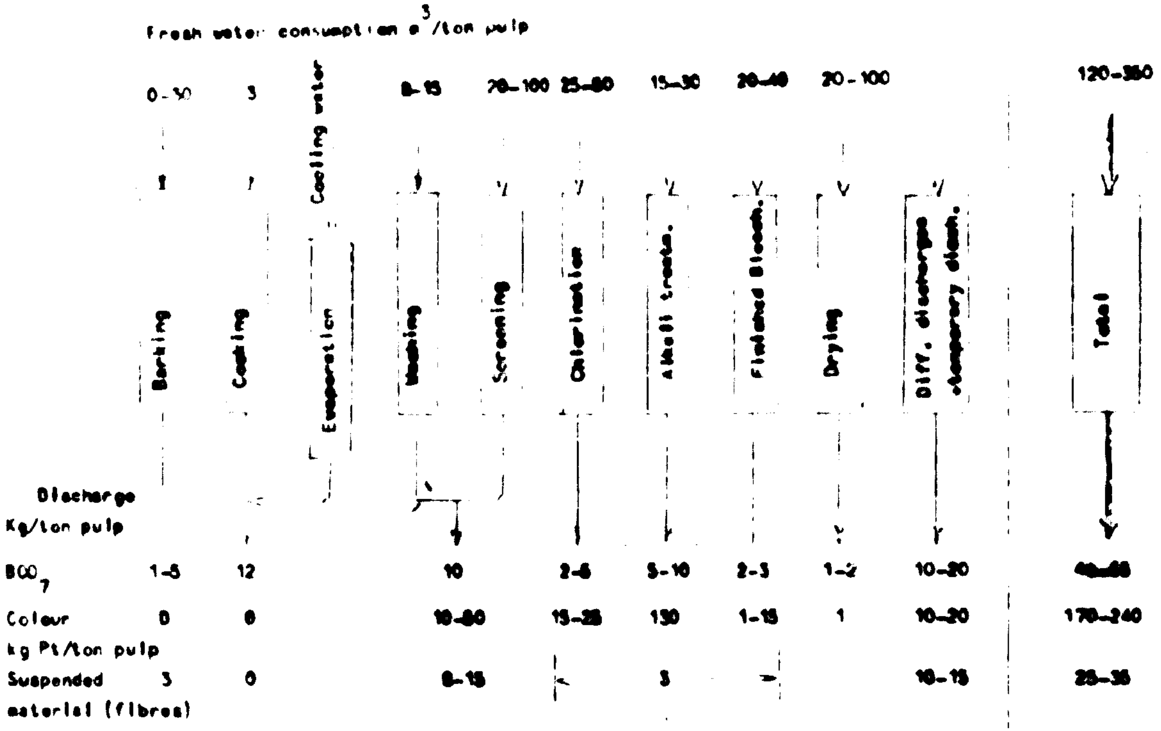
The sodium content of wet pulp is defined as the amount of sodium that can be extracted from a sample of the pulp with hydrochloric acid under specified conditions.

The pulp sample is diluted to a pulp concentration of about 2 % and acidified with hydrochloric acid. The sodium content of a sample of the liquid phase is determined by atomic absorption spectrophotometry or flame photometry. The dry matter content of the pulp is determined gravimetrically and the sodium content is calculated; it is expressed in kilograms of sodium sulphate per metric ton of oven-dry pulp. (SCAN-C 30:73, see appendix)

THE SULPHATE PROCESS

The technique of this process is very well described in the literature and there is no need of describing the same in this paper. It seems more essential to focus the attention to the effluent water from this process and the environmental influence it can have on the recipient.

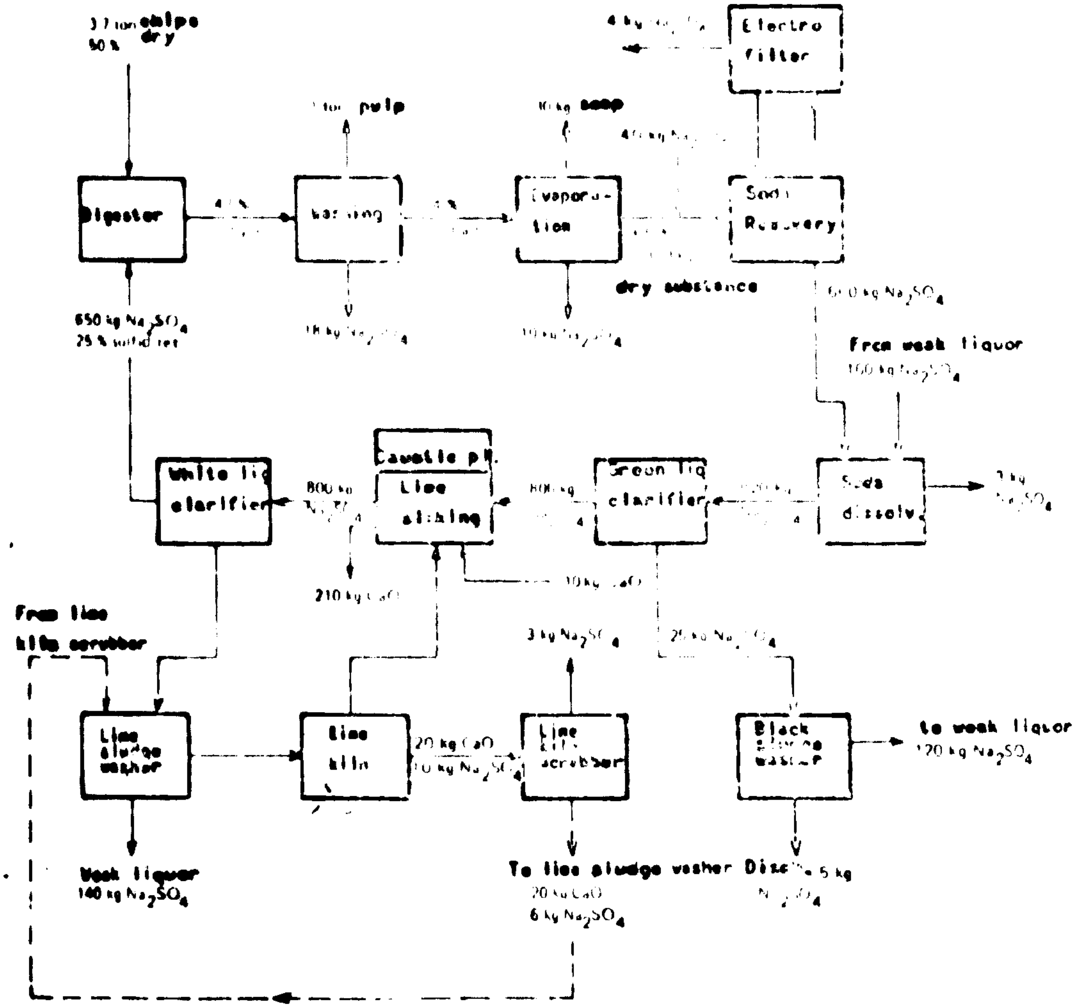
According to the investigation made by the SSVL environmental project [illegible] the magnitude of effluents to water and air from sulphate mills were divided approximately according to the following figure 34:1. In the same the consumption of fresh water is also indicated. Considerable improvements have been made since this investigation was made.



Discharged effluents from sulphate mills to receiving waters

Figure 34:1

In the next figure 35·1 the chemical balance is demonstrated. One should also observ that discharges of inorganic sludge from the green liquor clarifying, reburning of lime/causticizing and fiber and bark sludge are included.



Chemical balance and discharges of chemicals

Figure 35:1

Air emissions from sulfat mills are of two kinds, dust and gases. Dust is mainly coming from the soda recovery boiler as sodium salts and from the lime kiln as lime dust. The emitted gases are mainly containing sulfur compounds together with water vapor and carbondioxide from the burning of the liquor. Gases in greater amount are emitted from the soda recovery boiler, lime kiln, digesters, washers and tall oil plant. In table 36.1 the amount of gases emitted and the sources are listed.

Table 36:1

Emission to the air

Source	Compound	Amount
Soda Recovery	Bad smelling	10 mg/m^3 flue gas
Lime Kiln	Sulfurcompounds	100 " " "
Tall oil cooking	Hydrogen sulfur and	
Digesters	organic sulfur	
Washers	compounds	
Evaporation		
Soda Recovery	Sulfurdioxide	5 - 20 kg/ton pulp
Lime Kiln		0.1 " "
Odourdestruction		2 - 6 " "
Soda Recovery	Dust	200 - 1000 mg/m^3 flue gas
Lime Kiln		200 - 2000 " " "
Bark Burning		500 - 2000 " " "
Bleach Plant	Chlorine Chlorinedioxide Sulfurdioxide	Temporary emissions and ventilation emissions
Unidentified emissions	Bad smelling Sulfur compounds	

Cooking, washing and screening

Cooking

The cooking of wood chips can take place in batch or continous digesters.

The noncondensable gases when the batch digester is reliefed from pressure contains besides nitrogen, carbondioxide, methanol, myratic acid also very ill smelling organic sulfurcompounds as hydrogensulphide, methylmercaptan (MM), dimethylsulphide (DMS) and dimethyldisulphide (DMDS). Most of the last compounds may have condensated together with the raw terpentine. The black liquor, obtained during the cooking and containing alkali and liquor compounds, is in a continous digester with a washing zone drawn off from this and the steam released in two steps in two flash cyclones. The steam from the first flash cyclone is used in the presteaming of the chips and the steam from the second flash cyclone is utilized for the preparation of hot water. From the condensate from the released steam raw terpentine can be separated. The black liquor goes to evaporation and burning.

Washing

As the black liquor contains biochemically oxygen consuming substances, sulphides and other environmental polluting compounds in a high concentration it is necessary to wash the pulp free from this liquor as far as it possible also so that it can be further treated in the process.

For washing of sulphate pulp different types of apparatures are used, which are discontinous as well as contineous. The latter types are now dominantly being installed. Of great importance for an effective washing of the pulp has the counter current washing in the continous digesters.

1. Diffusers were formerly very common, but are now more and more replaced by continous washing equipments. In this the washing is done by replacement of the black liquor succesively by pure warm water. Although the diffusers can give a good washing result if correctly dimensioned in relation to the production, they have several weaknesses. The long washing time makes them require lot of space and they have a not so good flexibility in regard to capacity. The course of the washing in them is instable and it occurs that the zone of displacement happens to be uneven or irrigular, when unnormally large amounts of washing liquor is required - high dillution - in order to achieve a good result. The reproducable washing effect is therefore not adequate and is not meeting the requirements in respect to pollution control, as modern washing equipments do.

2. Filter washing is carried out through repeated dilution, dewatering and displacement on usually four drum filters in serie. The washing liquor is normally pure warm water or condensate added to the last filter. The repeated dilutions to a low consistancy with following dewatering require large buffert volumes for dilution liquor - filtrate - from each

filtering step. Air, which is sucked through the pulp layer on the filter drum, causes foam in the black liquor, which also requires large filtrate volumes. In addition to this complicated systems for killing the foam and recovery of the liquor in the foam must perhaps be installed. The large volumes of the liquor makes the system rather slow with great time delays at production changes before equilibrium has been reached.

These disadvantages mentioned are mutual for all types of filter washers and independent of manufacture or construction. Open filter washers - vacuum filters - create less good working environment as large amounts of moist vapor containing bad smelling sulfur compounds are released. This problem has been solved by pressure filters which have a completely closed hood, as they are working under pressure instead of vacuum.

3. Screw presses have in some cases been used in combination with filters for washing of sulphate pulp. As well screw presses as disc presses of the Davenport-type are used for washing of other kinds of pulp, mainly NSSC-pulp.

Installation of presses of some kind in the last stage of the washing has its advantages. With presses it is namely possible to reach higher pulp concentrations, 40 - 45 %. The quantity of liquor following the pulp will then thus be very small.

The degree of washing efficiency for the press step is depending on an effective mixing and equalization, when the pulp is diluted before the press, which sometimes is difficult to achieve.

4. Hi-Heat washing in the washing zone of a continous digester takes a time of 2 - 5 hours which is considered to have the same effect as 1 - 3 washing filters. The following washing is made easier as there will be no foaming problem. This counter current washing is very effective, and at least 4 hours should be given it to be performed. For pulp with a high Kappa-number it is recommendable to prolong the washing time.

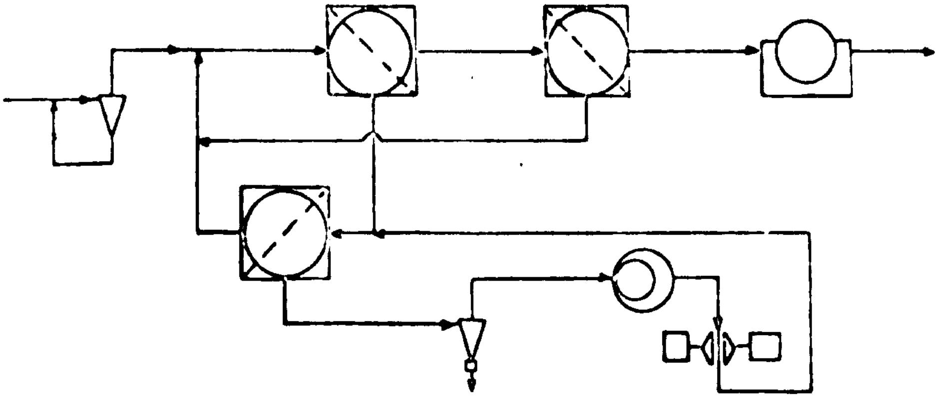
5. The continous diffuser (radial washing) is more and more used as a complement to the build in hi-heat washing. Through such a combination a completely closed system is obtained, when as well bad odours as mixing in of air in the black liquor causing foam is avoided. The washing in diffusers takes place through displacement at unchanged pulp concentration, 8 - 10 %.

Screening

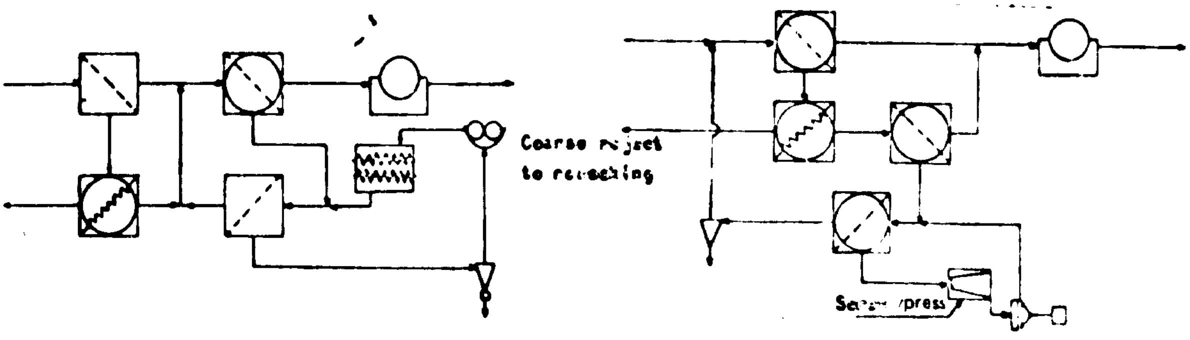
Screening of the unbleached pulp is aimed to seperate an to remove larger and smaller impurities such as uncooked pieces of chips, knots and not completely defiberized fiber bundles from the out of the wood liberated cellulose fibres. This separation is accomplished in screens, where the pulp at a low concentration - in general 1 - 3 % - is forced to pass through screen plates with holes in different sizes and form, through which the accepted pulp fibres can pass.

As a complement to screens so called centricleaners or vortex cleaners are used. In these the centrifugal force is utilized in order to separate particles which are heavier than the fibres e g sand and even bark pieces. In this cleaners the pulp concentration is between 0.5 - 1 %.

Screening equipment and other auxiliary equipment can be arranged in many different ways. In a traditional screening department in a sulphate mill large praticals as knots are separated from the pulp in a so called knotter. Thereafter a fine screening of the pulp takes place in two or several steps. An example of such a screening system is shown by the flow diagram in figure 39:1.



Closed screens, alt. A



Closed screens, alt. B

Closed screens, alt C

Figure 39:1

In certain cases the accepted pulp from the primary step is passed another screening step consisting of either ordinary screens or centrifugal cleaners. This is called double screening, which is used when higher cleaneness of the pulp is required.

When the knotters are placed before the washers, because of mixing in of air in the black liquor, foaming will be a problem. Furthermore relatively much of the black liquor will follow with the reject to the handling of the knots. It is therefore preferable to let the coarse reject follow the pulp through the washing section. It is also common, that the coarse reject mostly containing uncooked pieces of chips or knots is deverted back to the digesters for recooking. In this case it can be of advantage to separate the coarse reject before washing, as the chemicals in the same in a natural way are returned to the liquor system at the same time as the cooking liquor will not be diluted.

Reduction of Environmental Polluting Effluents

Cooking

From well operated digesters during normal conditions there should be very small amounts of effluents.

Sealing water to pumps and so on is normally pure. Because of leakage around the shaft it can be contaminated by black or white liquor and terpentine.

Cooling water from condensors is normally pure. In the case there is leakage in the heat exchange, the warm water can be contaminated. Then it is unusuable.

Steam condensate from the heat exchanger can be contaminated by black liquor if there is a leakage. In that case the condensate must be diverted to the sewer.

Condensate reliefed, when the pulp is blown from the digester to the blow tank, is in general very much contaminated by sulfur compounds and terpines depending upon now the terpentine recovery system is functioning. These compounds make the condensate quite odourous. It contains also dissolved alcohols, mainly methanol, which gives a high biochemical oxygen demand.

The approximate amount of condensate from the digester blow and the amount of contaminates are given in the following table no 40:1.

Table 40:1

		Batch digesters	**Contin digesters**
Approximate amount of liquor	**ton/ton pulp**	**1.0 - 1.2**	**0.4**
Sulfur	**kg S/ton pulp**	**0.2**	**0.1**
Biochemical oxygen demand	**kg BOD_7/ton pulp**	**5**	**3**

Condensate from the digester blow is normally so very much contaminated that it should be transferred to a condensate purification system. The general principles for such a system will be described later when dealing with the evaporation of black liquor.

Washing

The amount of black liquor solids, which are remaining in the pulp after washing is dissolved into the water used in the screening and is then carried with the effluent from the same into the recipient. This is called the washing loss.

The washing loss is defined as the sodium content in the washed pulp expressed as sodiumsulphate per ton 90 % pulp (kg Na_2SO_4/ton of pulp). It is fairly easy to quickly determine the Na-content in the water phase of the pulp. The relation between the Na-content and the content of organic dry solid substance - or BOD_7 - in the waste liquor is also fairly unambiguous as long as the washing loss is in the order of 15 - 20 kg Na_2SO_4 per ton of pulp or higher.

At lower washing losses greater consideration must be taken to the difference between "easy washable" and "total" sodium in the pulp because of sorption phenomena. The method to get out the sodium (washing loss) out of the pulp is getting then more important. Less sodium content will then be of less interest from an economical point of view, while colour, BOD_7, liquor etc still can be of importance in regard to the environmental pollution degree caused by the effluent. The washing loss defined as above should not be used as a measure of the degree of pollution.

Dilution

$$DF = V_{shower} - (L_{pulp} - L_{liquor}) \text{ ton/ton 90 \% pulp}$$

V_{shower} = Shower water flow ton/ton pulp

L_{pulp} = Liquor in the leaving pulp ton/ton pulp

L_{liquor} = The amount of original liquor which contains corresponding amount of solid substance as the washing loss ton/ton

The main part of the remaining black liquor in the pulp after washing goes with the screening effluents to the sewer. In a traditional mill this effluent discharge corresponds to about 25 % of the total BOD_7 discharged from the mill and to about 50 % of its total discharge of liquor. The washing department is therefore one of the most important points to which attention should be paid, if one wishes to decrease the degree of environmental pollution. The effect of the washing can be improved either by increasing the dilution or by instalment of several or more effective pulp washers.

The simplest way is to increase the amount of waste water and thereby the dilution. This presupposes that the liqour evaporation have capacity enough.

From an economical point of view the optimal dilution is reached when the value of the last regained solid substances is balancing the marginal evaporation cost. Commonly it is demanded that the washing loss shall be reduced to max 8 kg Na_2SO_4/ton of pulp.

When installing equipment in a new washing department the choice of equipment depends upon what kind of equipment there are in the digester room. In a Kamyr-digester with an inbuilt four hours Hi-Heat washing sector most of the washing of the pulp is taking place. With additional two washing steps it is then possible to reach a washing loss of 8 - 10 kg Na_2SO_4/ton of pulp.

After batch digesters in general five washing steps is required in order to reach a washing loss of 8 - 10 kg Na_2SO_4/ton of pulp.

When chosing washing equipment as a role a machine which is closed against the atmosphere releases less odorous gases. A machine, which can work at high pulp concentration, is less liable to discharges to the recipient due to affluent liquor.

Screening

Most of the open screens are operating most efficient at a pulp concentration of 1 - 2 %. This means that before the screens 40 - 90 m^3 water per ton of pulp must be added. Because of the construction of the screens dilution and sealing water must be added in an amount of 10 - 50 m^3 per ton of pulp. It is not unusual that with adding all water together the consumption in a conventional screen room is as much as 150 m^3 water per ton of pulp or more.

Through internal reuse of white water from the screens it has been possible to bring down the consumption of fresh water to about 50 m^3/ton of pulp. It is possible, however, to bring down the same to 20 - 25 m^3 water per ton of pulp.

The effluent from the screens contains a certain amount of black liquor substance. This quantity is in general equal to that existing in the pulp after the last washing step (= washing loss). This water has a brown colour and contains a certain amount of fibres. In order to reduce the degree of pollution several purification methods has been tried mainly precipitation with alum and lime. Usually the precipitation of the effluent from the screens is carried out together with other effluents, e g from the bleachplant or the pulp drying machines. Often the precipitate is different to dewater and it is therefore difficult to dispose the same.

Closed Screening

With closed screening it is understood, that desired concentration is obtained by dilution with water, which is removed from the pulp after the screening in order that the [illegible] concentration [illegible] before and after the screens. No other addition of water [illegible] required than that which is leaving the system with the rejects. [illegible] talk about a closed screening, the handling of the rejects must [illegible] [illegible] as far as possible.

Recovering of the coarse reject can be said to be a first step [illegible] to close the reject handling. However, there are other [illegible] to make use of this reject at the same time as the requirement for a closed [illegible] system is satisfied.

[illegible] to be able to solve the special problems, which arise when the screening system is closed, it is necessary that the used equipment is [illegible] closed and constructed so that foaming of the liquor is avoided. [illegible] pressure screens are safe. Also [illegible] screens, which work under vacuum can also be used, if they are correctly operated.

Fine reject has in general such a form that it can be returned to the main pulp stream after beating or [illegible] without affecting the quality. As coarse reject contains material which is less cooked, and therefore [illegible] difficult to [illegible] and [illegible] afterwards [illegible] the main stream. For certain qualities [illegible] to do this, however, when [illegible] going to be bleached. The screening [illegible] be demolished entirely and with the help of a system for hot stock or in-line refining, the coarse and finer particles can be desintegrated with the accepted [illegible].

In figure 43:1 and 44:1 a proposed flow diagram is shown, in which the screening system is closed with a closed reject handling respectively in-line refining in combination with a continuous digester.

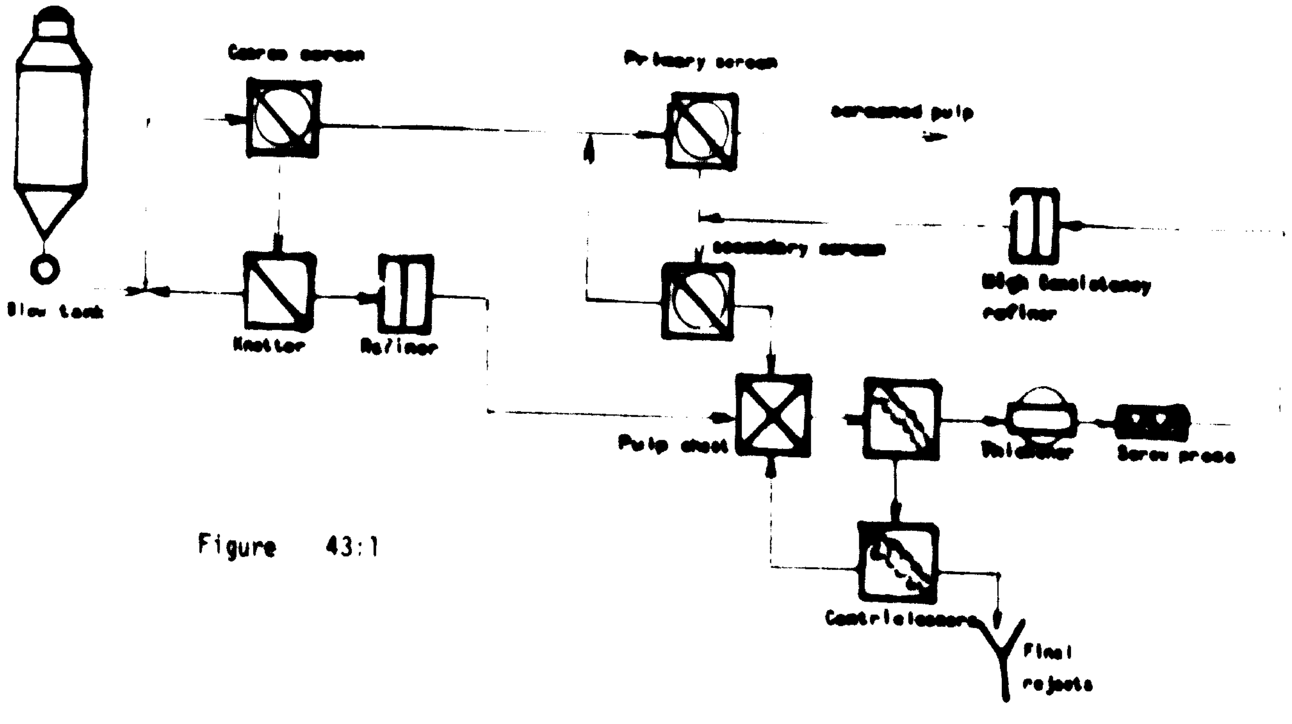


Figure 43:1

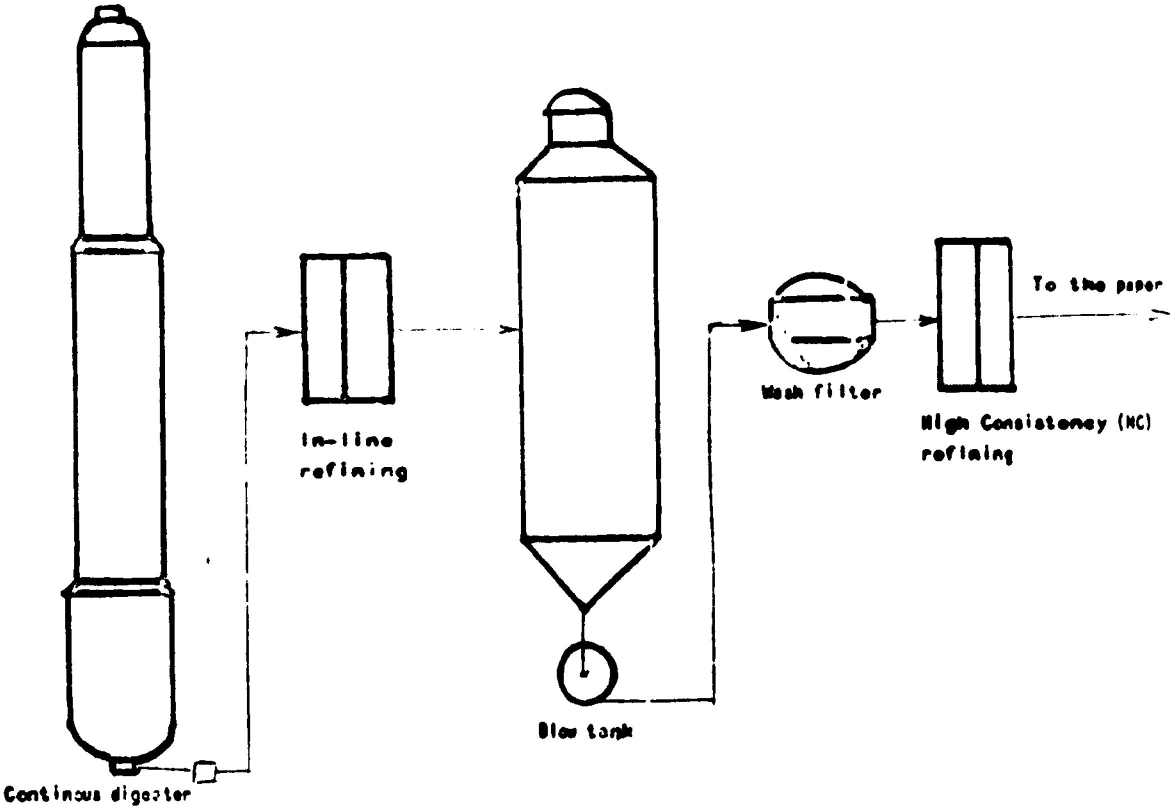


Figure 44:1

Integrated Washing and Screening

In most of the new mills the washing and the screening will most likely be integrated into a closed unit. In such a system the thickner in the screen room will be the last washing stage. The white water from the screening will then be used for the washing of the pulp. Under normal conditions no effluent water will go to the sewer.

Closing of the system washing-screening will at least have two consequences which must be observed. On one hand the temperature in the screening will be much higher than usual, on the other hand the remaining black liquor substances in the pulp will be carried on to the following department, bleach plant or paper mill.

The high temperature possibly 70 - 90^0 C or more, will require special attention to the equipment how this is formed. The screens must be closed and in the reject handling equipped with hoods and ventilation facilities.

Carry over of black liquor substance from the washing via an open screening system to the following departments is normally neglected depending upon the effective soaking of the pulp which takes place in the screening. The cleaned washed pulp contains a few kilos of dry substance (TS) and BOD_7 oxygen consuming substances.

Pulp from the screening with a washing loss of 10 kg Na_2SO_4 per ton contains five to ten times as much TS and BOD_7 as the above mentioned clean washed pulp. If the screening is closed without any other measures are taken, about 50 % of these impurities will be transferred to the following department.

If this pulp is pumped to a conventional chlorine bleaching, the consumption of bleaching chemicals will increase due to the black liquor substance and thereby cause higher running costs. The transferred amount of BOD_7 will increase the BOD_7 discharge from the chlorine stage. Furthermore the quality of the pulp can be lowered due to irreversible precipitation of in the black liquor dissolved substance.

Sorption Phenomena

The relation between remaining sodium as sulphate, alkalilignin and biochemical oxygen demanding substance in sulphate pulp, which has been washed in different ways has been studied.

It has been shown that the amounts of sodium, alkalilignin and BOD substance in the filtrate from the washing were higher than the calculated amounts being in equilibrium. This shows that the components, which before the washing was sorbed on to the fibre phase, had desorbed to the filtrate.

Furthermore the laboratory trial results indicate, that the transport of materia from the interior of the fibre out to the solution takes place more rapid the more the pulp is delignified, and that there is no appreciable difference between sodium and lignin.

However, there is a difference between different pulps and also different fibres. For instance the sorption effect is much more apparent with a bagasse filter. It is also commonly known that bagasse pulp is more difficult to wash than softwood pulp. Therefore the bagasse fibre requires a larger amount of wash water than softwood pulp and usually in the washing operation a dilution factor which is two times higher must be used.

Anyway the practical concequences of the sorption effects are among other things, that the environmental pollution degree is not directly proportional to the "washing loss" that is the total content of sodium in the pulp.

Pressing of Unbleached Pulp

Lately there has been an increasing interest for the use of presses as the last stage in the washing. Trials have been carried out to investigate their effect.

When sulphate and bisulphite pulps are pressed it could be established, that the pressed out liquor had a lower concentration of sodium and lignin than the liquor, to which the pulp was in equilibrium before the pressing started. The more the pulp is pressed the lower the concentration will be. This circumstances will lead to a not satisfactory effect of the washing operation.

Total BOD_7 as a function of total Na in different sulphate pulp
Pulp consistency = 10 %

- ● *kappatal 28*
- ▲ *kappatal 40*
- ○ *kappatal 38*
- △ *kappatal 48*

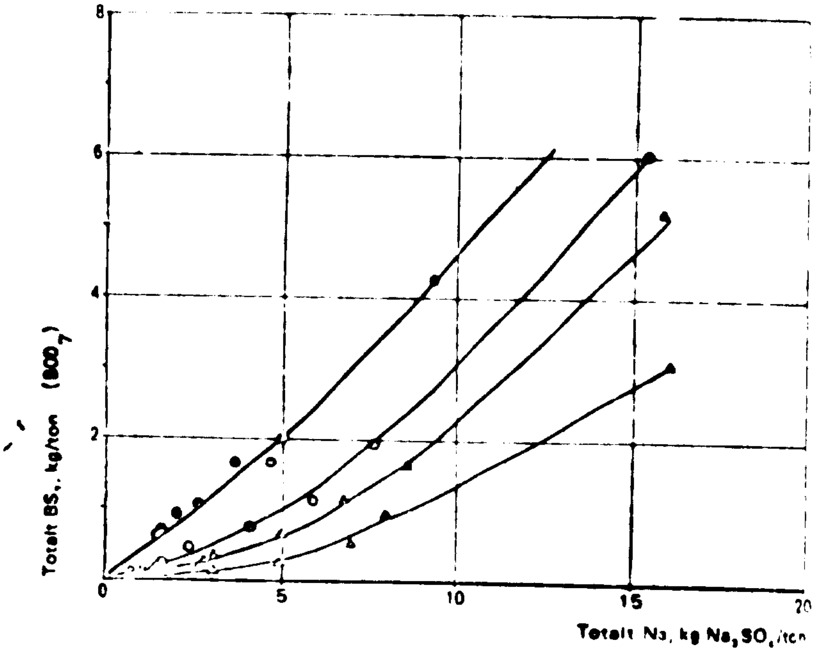
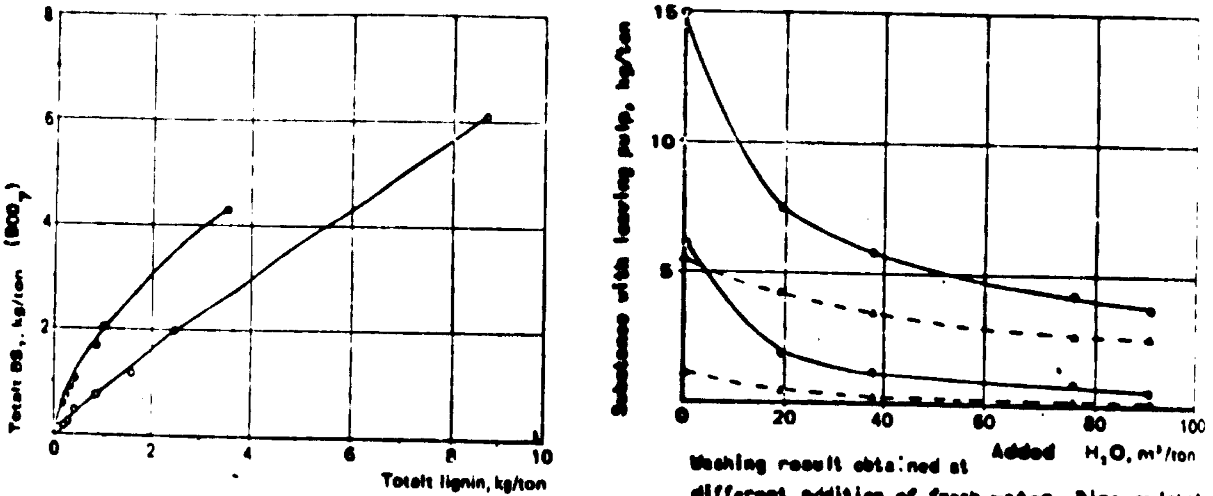


Figure 46:1



Total BOD_7 as a function of total lignin.
Consistency = 10 %

- ● *sulfsulfat, kappatal 28*
- ○ *sulfsulfat, kappatal 38*

Washing result obtained at different addition of fresh water. Pine sulphate

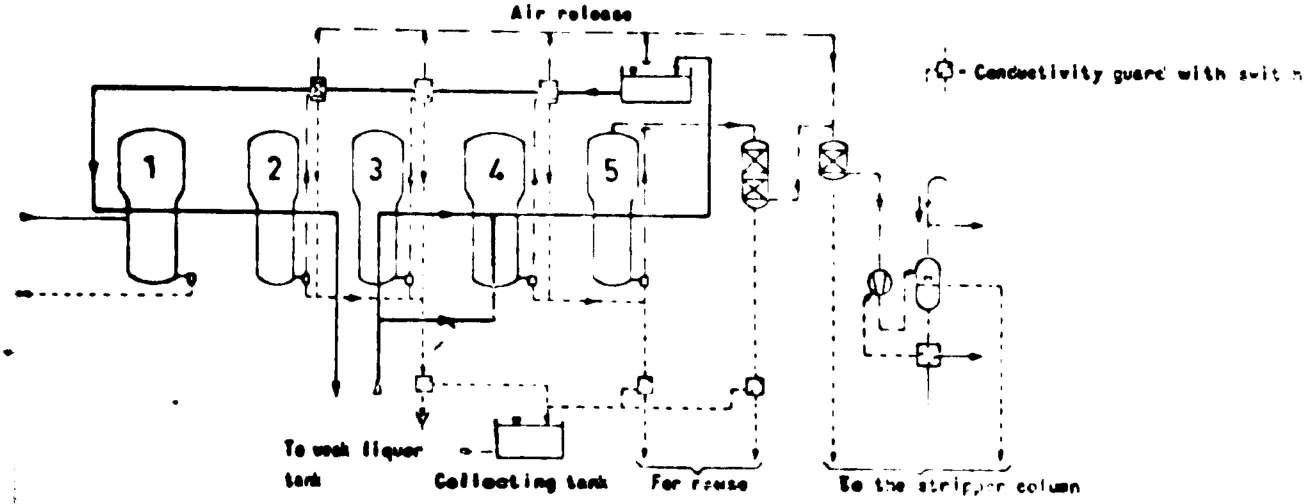
- ○ *totalt Na (som Na_2SO_4)*
- △ *sorberat Na (som Na_2SO_4)*
- ● *totalt BS*
- ▲ *sorberat BS*

Kappa number = 3[illegible]
Consistency = 10 %

Figure 46:2

Black Liquor Evaporation

In order to be able to burn the recovered black liquor obtained through the washing of the pulp most of its water must be removed be evaporation. This will take place in several steps, and the usual system consists of five so called Kestner apparatures, which work under vacuum. The units are numbered according to the flow of the steam. No 1 is the one to which live steam is supplied. In the following steps (or effects) the steam vapor from the black liquor in a preceding step is utilized for heating. From the last effect the liquor vapor goes to a surface condensor, in which remaining heat content is used for heating water. The principle of a five effect evaporator is shown i figure 47:1.



Evaporator unit- Conductivity measuring instruments and switching system

Figure 47:1

Reduction of Environmental Pollution Effluents

Condensates from the evaporators and the digesters contain the below listed amounts of polluting substances.

Table 48:1

Condensate		Total condensate from digesters		Total condensate from evaporators	
Type of digester		Cont	Batch	Cont	Batch
BOD	kg/ton pulp	2.6	4.9	9.0	5.5
Dry substance	" "	0.05	2.0	3.4	
Sulphide	" "	0.07	0.15	0.28	
Fiber in the liquor to evaporators					
Average mg/kg liquor			16		
Max " "			50		

As can be seen from above table the content of BOD substances in condensate from continous digesters is lower than those from batch digesters, while it is the revers regarding BOD substances from the evaporators. The total amount of BOD substances is, however, about the same, 11 - 12 kg/ton of pulp in both cases.

30 - 50 % of the BOD content in the evaporator condensates are coming from the surface condensor and the rest from the evaporator bodies themselves.

The relation between the degree of pollution and different factors has been investigated. For instance it has been proved that a relation between the solid carry over and the volume load in the last effect is existing.

There is not a clear relation between BOD and kappa number, dry substance and viscosity, and other factors.

When installing a evaporator station, which desirably should give the least degree of pollution consideration shall not only be taken to capacity, heat economy and so on but also to such questions as the following:

- incrustations and liqour quality
- talloil recovery
- washing of uncrusted surfaces
- dry substance carry over in the separators

- p[illegible] [illegible] the [illegible]
- control
- evaporation to high [illegible]
- separation [illegible]
- purification [illegible] in column apparatus
- [illegible]

Incrustation and Liquor Quality

In order to [illegible] without problems, the degree of reduction [illegible] and the degree of caustization must be as high as possible. Preferably extra additions of sodium sulphate from the [illegible] plant [illegible] plant should not be made to the weak liquor. If this is done very easy precipitation of unorganic salts in the form of Na_2SO_4 and Na_2CO_3 in the evaporator tubes takes place [illegible] concentration and temperature. These incrustations are, however, easy to wash away with weak liquor or water. If the clarifying [illegible] plant [illegible], precipitations of calcium compounds is obtained, which are not so easy to remove by washing. Incrustations containing silica are still more difficult to remove. These are quite common when pulping such material as bamboo, straw and so on. These must be removed by mechanical means or special treatment with chemicals. Precipitation of lignin can also occur, e g if the pH is getting low, which can happen if liquor from semichemical pulp is mixed with black liquor. The problem will be avoided if NaOH is added.

Incrustations can also be obtained, if the liquor is containing to much tall oil. This can also cause foaming in the last evaporator stage.

When operating with a good quality liquor incrustations can still occur. These are normally removed with intervals of 2 - 7 days. Incrustations can be obtained if the evaporation is operated with super heated steam and if the liquor contains fibres. With almost without exception all evaporator stations are equipped with filters, which remove the fibres in the liquor from the washing. A higher fibre content than 20 mg per liter on a 80 mesh screen is not tolerable.

If the evaporators have stainless steel tubes there are generally no problems with incrustations on the steam side of the same.

In Sweden all evaporators are equipped with stainless steel tubes.

Washing of Incrusted Surfaces

The most common methods to wash the evaporators is to replace the weak liquor to evaporator 1 with water, condensate or mixed liquor, which is allowed to pass body 1 and 2 and them pumped to the thick liquor tank, weak liquor tank or mixed liquor tank all according to change of the solid content. The wash liquor can also be circulated within the evaporator 1 and 2 during the washing itself. The whole time the evaporatorstation is operating with limited live steam, which means, that a certain amount is evaporated from the first two bodies and also from the three last ones, in which the liquor is run as usual.

This described wash system is not particularly good in respect to environmental pollution. For instance if mixed liquor is used for the washing, methanol will enter the wrong condensate. Furthermore the station is disturbed too much and there is a risk of dry substance carry over. With this washing method the liquors do not enter the ordinary tanks and therefore there is also a risk to overflow these. It is necessary to maintain a sharp control of the washing during the two hours it lasts.

To remove incrustations of silica, lime or fibres by this washing method cannot be done. The cleaning of the tubes must be done mechanically, through high pressure hose or by special chemicals.

Dry Substance Carry Over in Separators

With respect to increased BOD material in the condensate, but also because of economical reasons a reduction of BOD from 300 to 100 g/ton evaporated water has been achieved in some mills.

Before in order to reach 300 g/ton it was a question of dimensioning the expander vessel large enough. The conditions required was also that the evaporator were operating evenly and without pulsations.

One way to improve the conditions is to return the liquor, which is separated, when the vapor from one body goes into the steam distribution chamber of a following body. The inlet can be arranged tangentically or radically.

By this methods the amount of dry substance in the condensate from respective bodies can be halfed. The cost for making this arrangement is neglible, as only a small pipe with a seal for the returning of the separated liquor to a suitable point in the evaporator can be installed.

The same or even a better effect can be achieved by installing a cyclone in the separator.

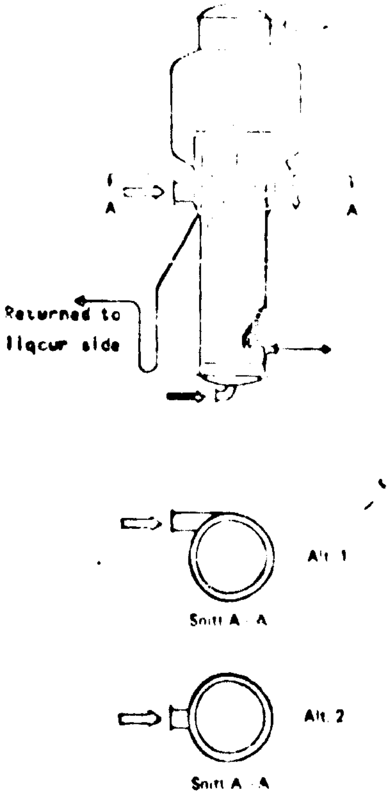
A further step towards a cleaner condensate is achieved, if a secondary separator in the form of lamellas dimensioned for the vapor volume is introduced after the primary separator. This one can be placed in the separator or in the steamline.

A degree of separation of about 90 % can be achieved by these arrangements. The following can be concluded regarding the dry substance carry over:

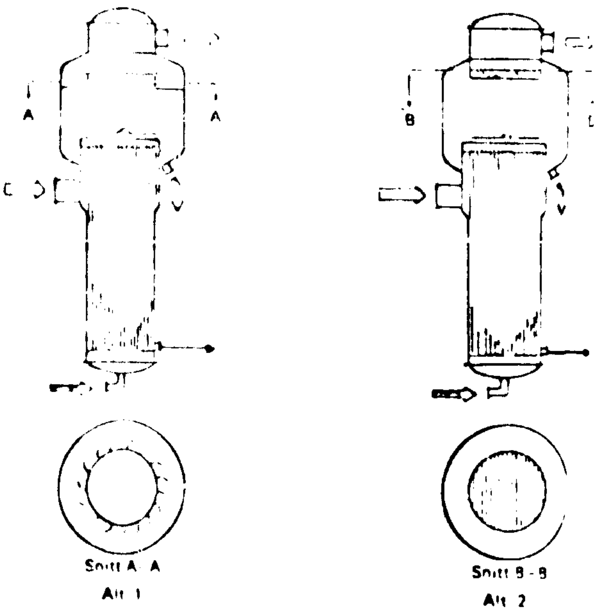
- The primary separation steam - liquor should be improved according to certain recommendations

- In new evaporator plants it should be arranged so that the liqour separated in steam lines and steam inlets can be diverted
- New and existing evaporator plants can be complemented with cyclons or lamella separators, where the latter ones are most suitable in the last effect, where the steam velocity varies a lot and the droplet [illegible]
- If the separators are correctly dimensioned an amount of 100 g/ton evaporated water as [illegible] in the total condensate can be reached

Cyclone separators as well as screen separators so called demisters are not so effective.



Drop separator - Steam distribution chamber



Drop separator - cyclon and profile separator

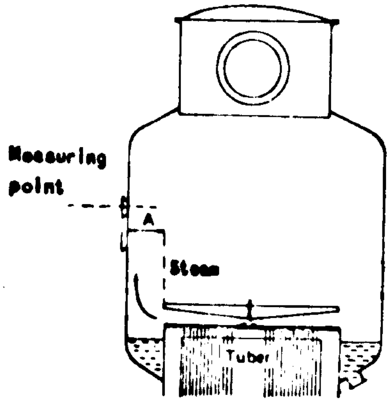


Figure 50:1

Table 52:1

		Lamella separator	
Pulp prod ton/day		300	
Preasumptions			
Evaporator capacity ton/h		100	
Before drop separator:			
Dry substance loss g/ton evap		200	
Dry substance loss kg/ton pulp		1.6	
Type of separator	Demister	Lamella separator	
		"single"	"improved"
After drop separator.			
Dry substance loss g/ton pulp	(100)	25	2
Dry substance loss kg/ton pulp	(0.8)	0.2	0.2
Pressure drop mm w s	60	20	80
Gain BOD_7 kg/ton pulp	(0.3)	0.4	0.5

Pulsations in Evaporators

In order to prevent pulsations in evaporators the following points should be observed:

- Great care should be taken when planning the control equipment and the systems for air releasing and the planning of liquor- and concendaste handling
- Buffer vessels for the liquor between the single evaporators should be installed. These can eventually at the same time be made so that they can function as expansion vessels.
- There should be possibilities to add certain evaporators cool thin liquor quickly if necessary.

Control

In general the control equipments equipment has the objective to assist the operation of the evaporators so that an optimal utilization of their capacity and at the same time as much as possible eliminate disturbances, whic among other things can cause carry over of liquor in the separators, can be achieved.

An optimal utilization of the capacity means that the pressure of the live steam and the dry substance in the thick liquor are kept at such a level, that the frequency of washing of the evaporators maintains acceptable.

The pressure before the surface condensor has a great importance.

Conductivity alarms should be installed in each outgoing condensate line, so that [illegible] can automatically be diverted to the sewer or to the [illegible] where [illegible] condensate is collected. Safety controls are required in order to prevent damages, such as dry evaporation in mainly the thick liquor bodies. If the liquor pumps to such bodies stop, the [illegible] should automatically be shut off.

[illegible]

With modern [illegible] a dry substance content of 62 to 63 % can be achieved. If a higher dry substance content is desired hitherto in general double forced circulation apparatuses have been installed. A calculation shows, that the profitability is not particularly high for the investment [illegible] these apparatuses. There are, however, other aspects, difficult to value, which compensates the lower profitability. The following points should be observed:

1. The dry substance content in the liquor after the Kestner evaporators are chosen to about [illegible], when there are final liquor thickeners. The risk of difficult incrustations in the last body can then be reduced. The forced circulation apparatuses are washed alternatively. Thus they are made so that a higher incrustation is occuring.

2. It will be easier to govern the burning of the liquor in the recovery boiler, because the carry-over of dried liquor particles in the flue gases will be less.

3. Theoretically a higher specific load of the recovery boiler can be allowed. This will mean a reduced investment cost for the recovery boiler. It is difficult to determine how much the load of the boiler can be increased. However, it is not to optimistic to calculate with an increase of 2 to 3 %.

4. The temperature will be higher in the lower part of the furnace. Thereby a higher degree of reduction can be encountered. At the same time most possibly the content of [illegible], which causes corrosion, can be reduced. Furthermore the content of H_2S in the flue gases can be reduced, which is valuable from the point of environmental pollution.

5. The risk for a so called "black" hearth will be exceedingly small, which will mean improved operating conditions of the recovery boiler.

The conclusion is that the evaporation to a high solid content (~ 65 %) can be recommended.

Treatment of Condensates and Evil Smelling Gases

Process Technique

When manufacturing sulphate pulp at several points of the process evil smelling gases and condensates are formed. The smell is caused by the sulph[illegible] [illegible]de and organic sulphides. The condensates have in certain cases a [illegible] biochemical oxygen consumption, which is mainly caused by [illegible], mainly methanol.

The smelling gases as well as the condensates are an apparent environmental problem. Several systems have been developed in order to reduce the [illegible] the environment and the recipients. Several of the Swedish sulphate mills have already or planning to introduce some type of gas and condensate purification. In the following a short description with general principles for such systems is given.

Odorous and oxygen consuming condensates are formed partly during the cooking and partly at the evaporation of the liquor. Together they have an oxygen consumption of 11 - 12 kg BOD_7/ton of pulp. However, the distribution between the digesters and the evaporation depends upon the arrangement of the digesters. From a continous digester the condensates has a lower oxygen consumption than from batch digesters. The reversed condition is prevailing for condensates from the evaporators. The distribution of the oxygen consumption in the evaporator condensates is such that 1/3 of this falls upon the condensates from the evaporators.

A general principle in order to reduce the environmental influence of the condensates is to try to separate these in the first place and reuse them in different places in the process. The separation of evaporator condensates is based on the fact that condensate from different apparatuses are differently contaminated. In the following table fig 54:1 average values for flow and amounts of contamination for the essential types of condensates are given. This values are valid for a mill with continous digester and the liquor flow in the evaporators is 3-4-5-1-2.

Figure 54:1. Flows and degree of contamination for different types of condensates from a mill with a continous digester

Condensate from		Approximate flow ton/ of pulp	BOD_7 kg/ton of pulp	Sulfur compounds kg S/ton pulp
Flash tanks	**(a)**	**0.4**	**3**	**0.1**
Terpentine separator	**(b)**			
Apparatus 2 and 3	**(c)**	**3.2**	**0**	**0**
Apparatus 4 and 5	**(d)**			

Condensate from		Approximate flow ton/ of pulp	BOD7 kg/ton of pulp	Sulfur compounds Kg S/ton pulp
Surface condenser	(e)	4.5	7	0.2
Secondary condenser	(f)			
Vacuum pump sewer	(g)	0.3	2	0.3
Total		8.4	12	0.6

Reduction of Environmental Polluting Effluents

Stripping of Condensates in a Still Column

A usual method to purify condensate is to lead the flows from the digesters, secondary condensor and the vacuum pump pit to a still column. Togehter they make about 0.7 ton/ton pulp.

The still column, in which the condensates shall be freed from the sulphur compounds, is alternatively a separate arrangement as in the figure below or can be integrated with the evaporator station. In the first alternative the column is operated with live steam and in the second alternative with steam released from the liquor. When live steam is used the consumption of the same is about 0.2 ton/ton of condensate. The purification effect in regard to methanol is about 90 %. The release of sulphur compounds will be nearly complete. The released gases are lead to the lime kiln or a separate furnace, where they are burned.

The purified condensate can be reused in the process as a replacement for warm water suitable as wash water in the wash room, screen room or for the sludge filter.

The methanol containing condensate from the latter part of the evaporator station can be reused in the wash room or in the caustizing plant. When using it for washing of pulp it is necessary to limit the quantities so that they correspond to the dilution. The showers in the filters should also be so sectioned that pure water can be added in the last shower. About 40 % of thus added methanol quantity follows the black liquor back to the evaporators, 40 % goes with the pulp and most of it goes then to the sewer, while the rest, 20 % evaporates to the air.

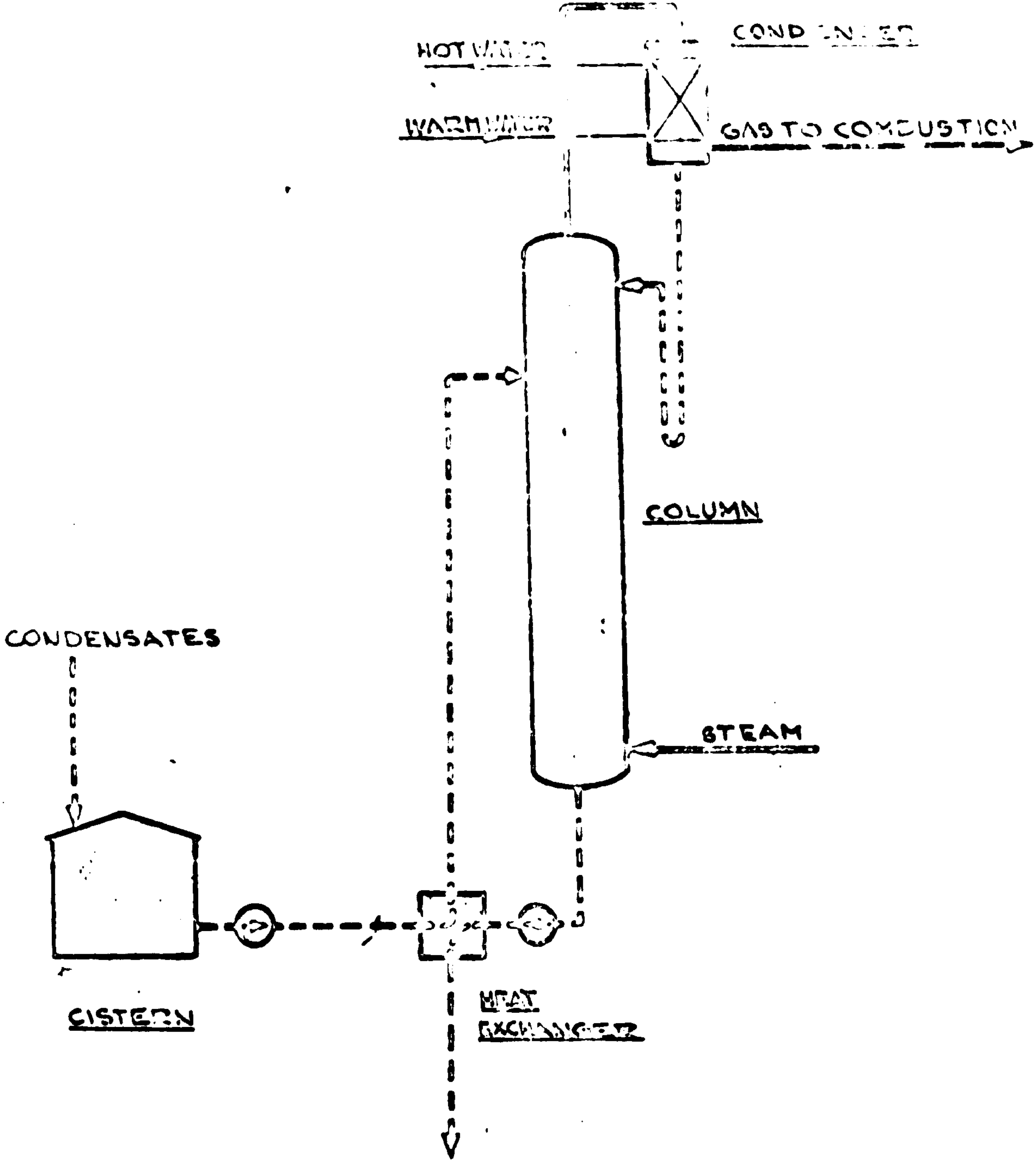

HOT WATER
COND INLET
WARM WATER
GAS TO COMBUSTION
COLUMN
CONDENSATES
STEAM
CISTERN
HEAT EXCHANGER

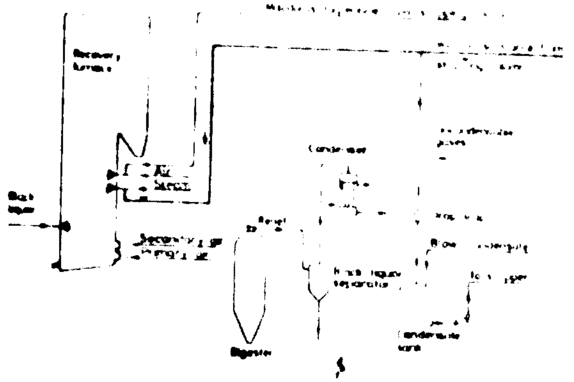
Figure 56:1

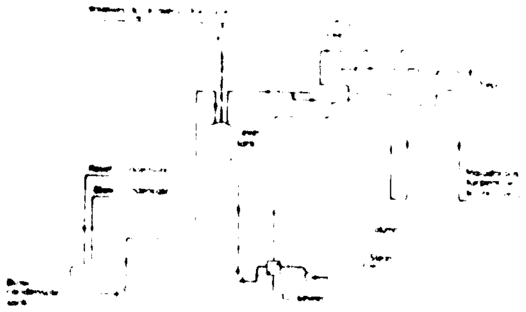
By stripping and reuse of the condensate in this manner the discharged effluent with [illegible] can be reduced from [illegible] to about [illegible]

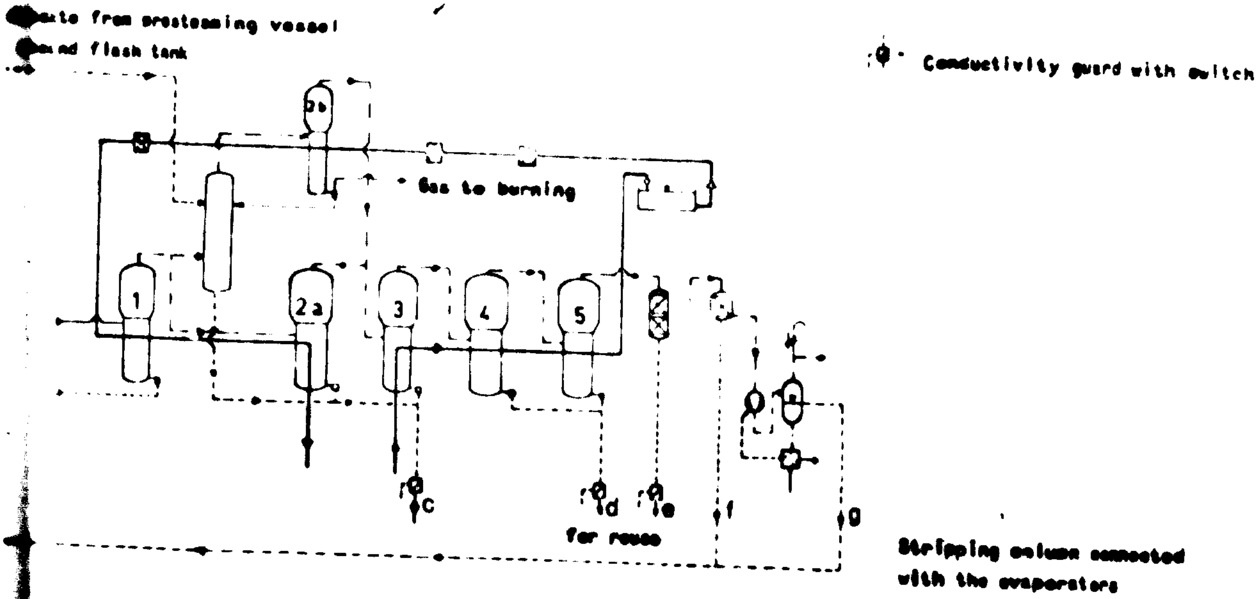
Burning of the odorous gases

The odorous gases are in principle of two types. Partly it is the uncondensable [illegible] for condensation, which contain high amounts of [illegible]. The total amount of gas from continuous [illegible] relatively small. Partly there are coming great amounts of very small [illegible] from tanks and wash filters and so on. These gases can be destroyed by using them as combustion air in a [illegible] furnace.

In the following figure [illegible] another system for condensate purification is shown, which now has been installed in several Swedish mills.







Stripping column connected with the evaporators

In this case the stripping column has been integrated in the evaporator station and is operated with a part stream of liquor steam from the first effect. In the case there are several evaporator stations the collected amount of condensate is so great that the whole steam flow is needed from the first effect in one of the stations in order to operate the column.

When collecting and transporting the odorous gases it should be obsered that they in mixture with air are explosive within a con entration limit between about 2 to 50 %. Because of safety one should therefore work with diluted gases under 2 % or alternatively with highly concentrated gases.

In order to decrease the risk for explosions and reduce the damages which may be caused a combination of arrangements is used as flame guards, explosion diaphrames, liquor seals, velocity guards, locks, automatical air releases etc. In systems where concentrated gases are handled a slight over pressure should be maintained in order to avoid leakage of air into the same. The dimension of lines should be chosen so that the velocity of the gas with an ample marginal is maintained greater than the velocity of burning.

Except for the risks of explosions it should be observed that the odorous gases are poisonous even at relatively low concentrations. This is especially applicable to hydrogen sulphur. In order to minimize the risk for poisoning the system should be so formed that eventual leakage of gases from the same can be taken care of by ventilation and the gases diluted to not dangerous concentration.

Burning of gases in the lime kiln has several advantages. First of all a complete oxidation of the sulphur compounds takes place and therefore no special measures are needed in order to avoid the escape of the formed sulphur dioxide as this is absorbed by the lime. In order to eliminate the explosion risk the gas should be diluted with air to about 25 % of the lower explosion limit before the gas is introduced in the kiln. This can simplest be done by mixing in the same with the combustion air.

Alternatively the gas can also be burned in bark or oil furnaces or in a separate furnace. However, some of these can be of disadvantage when disturbances in the operation of these furnaces occur.

Liquor Burning, Causticizing, Lime Reburning

Reduction of Environment Polluting Effluents

The effluent discharge to receiving water from a soda recovery plant should in a well operated mill be very little contaminated. Mainly it consists of sealing water. The wash liquor from an eventually installed scrubber is diverted to the causticizing plant. Almost neglible amounts of chemicals in the produced warm water in the scrubber is for instance diverted to the bleach plant.

From process technical point of view there is no necessaty to discharge water from the causticizing plant to the recipient except from the points, namely the washing of grits from slaker-classifier and soda sludge or green liquor sludge from the sedimentation in a green liquor clarifier. The green liquor sludge is washed with water in a separate washing tank or on a special washing sludge filter.

The soda sludge contains mainly sulphides of iron and other heavy metals. Through removing of this sludge from the system a built up of these metals in the white liquor is prevented. However, the sludge is not so easy to wash and difficult to dewater. A small quantity of alkali and alkali sulphide is therefore lost. The amount of liquor leaving together with the soda sludge can normally be of the magnitude of 0.1 ton/ton of pulp.

Regarding effluents to the recipient from the lime reburning there are risks for overflows from mainly sludge silos and oil tanks. The greatest discharge of effluent is however coming from the scrubber. From a scrubber of the Peabody type one can calculate with a liquor amount in the order of 10 - 20 m^3/h at the production of 900 tons per day.

Soda Recovery Boiler

The soda recovery boiler is one of the most air polluting sources of a sulphate mill. A lot of interest has been devoted to the same by the SSVL project. A project "Computor control of the soda recovery boiler" is being carried out at Gruvön's sulphate mill. In connection with this project an improved construction of the furnace spray nozzles has been made by which the amount of liquor can easely be varied. How the conditions in the boiler influences the primary emission has also been studied.

The amount of soda dust which follows the flue gases from the furnace is of the magnitude of 50 - 60 kg/ton of pulp. Most of this dust is sodium sulphate. Sodium carbonate and sodium chloride are also present. The chloride content is of course dependent upon the chloride content in the black liquor system. At a too great an excess of air a sticky dust can be obtained, which sticks to the heating surfaces and thereby decreases the heat economy. This is considered to be caused by the forming of sodium-hydrosulphate. A high content of chlorides can also give a melting point depression of such a magnitude that there is a risk for stickyness of the dust.

Soda Recovery Boiler Control

Interesting studies of a new soda recovery boiler installed in Gruvön mill, Billerud AB has been made, which was included in the SSVL project. The objective of the same was to construct a control system, which utilized the ordinary equipment in such a way that a high and even production was maintained and that the emission of unburned sulphur compounds (H_2S) was minimized.

Process Description

Gruvöns mill produces about 300 000 tons of sulphate pulp and about 130 000 tons of NSSC-pulp per year. The raw material for the sulphate pulp is mainly pine wood and small amounts of spruce wood. The NSSC-pulp is solely made from birch wood.

The Alkali Recovery System

The recovery of black respectively "red" liquor from the two different cooking processes takes place in a combined recovery system so called "Cross Recovery System" according to the figure no 60:1 below.

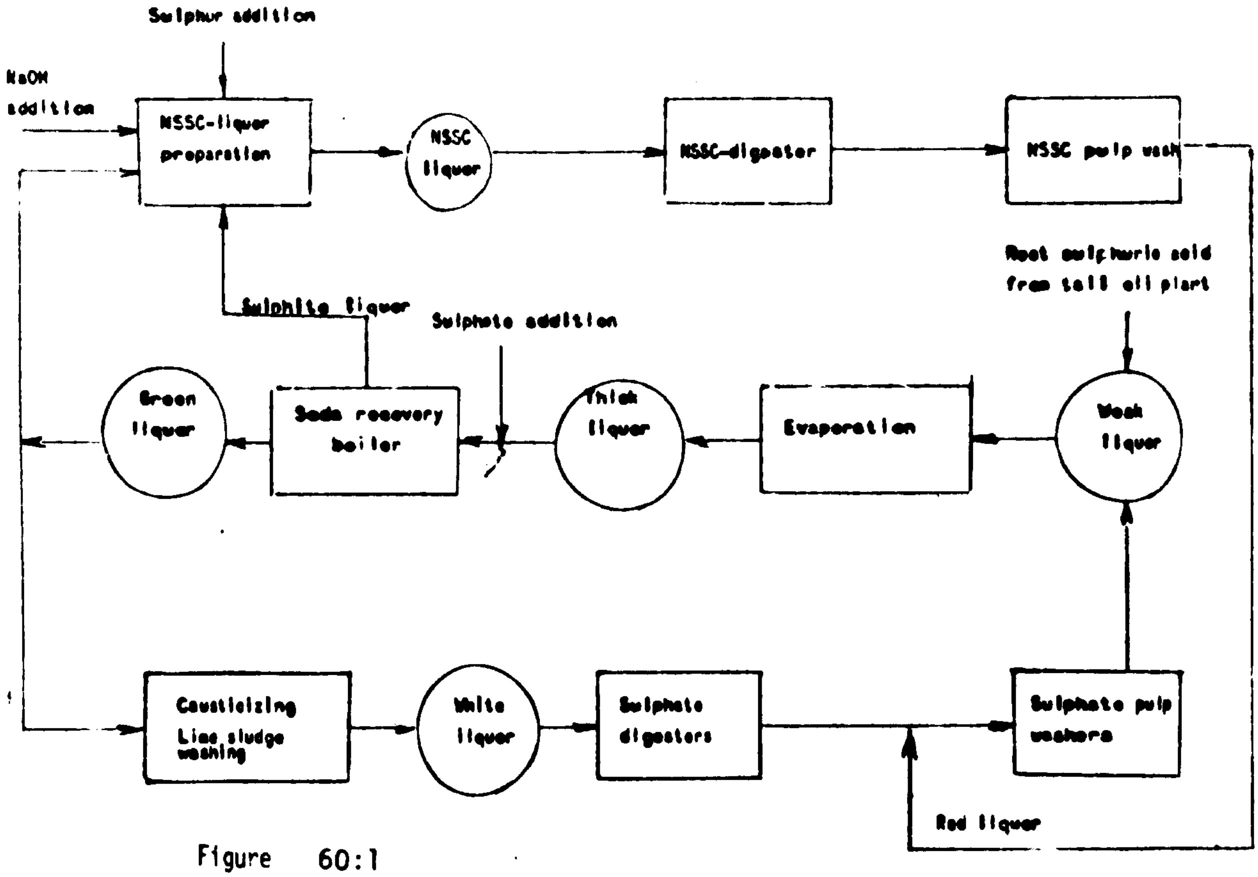


Figure 60:1

In the table no 61:1 on the next page is shown the chemical composition of cooking liquors and respective black and red liquor.

Table 61:1

White liquor		Black liquor		NSSC-cooking liqour		Red liquor	
	Mol %		Weight %		Mol %		Weight %
$(NaOH)_2$	57,9	C	37,3	$(NaOH)_2$	8,5	C	25,3
Na_2CO_3	14,6	H	4,1	Na_2CO_3	19,6	H	3,3
Na_2S	24,7	O	35,1	Na_2S	12,5	O	43,0
Na_2SO_4	2,8	Na	19,6	Na_2SO_3	50,7	Na	18,2
		S	3,9	Na_2SO_4	8,4	S	10,2
				$Na_2S_2O_3$	0,3		
	100,0		100,0		100,0		100,0

The analyses of white liquor is based upon:

Degree of reduction	90
Degree of Causticization	8
Sulphidity	30

Cooking liquor for the sulphate process is white liquor made in the conventional way from green liquor recovered in the recovery boiler. The cooking liquor for the NSSC-process is made from green liquor from the soda recovery boiler sulphite enriched caustic soda, which is obtained in a gas scrubber by absorbing SO_2 in the flue gases from the recovery boiler in a NaOH-solution, and of added chemicals. The latter are compensating the chemical losses, which is different from an ordinary sulphate mill where these are compensated by sodium-sulphate.

Under normal production conditions the chemical part from the red liquor is 15 % of the total dry substance amount to the evaporators. At disturbances in the production of sulphate pulp the share of red liquor can be higher.

The variations in the composition of the liquor are normally slow due to large storage tanks between the digesters and the soda recovery boilers. As the red liquor is directly mixed into the black liquor, the relation between red/black liquor can vary considerably.

Evaporation and Recovery Boilers

The evaporation of the liquor is carried out in two conventional 5-stage evaporator stations each with an evaporator capacity of about 180 tons/hour. Additionally there are two booster evaporation thickners with forced circulation which increase the dry content of the liquor to about 65 %. The evaporator stations are run in parallel with the utilization of mutual storage and soap collecting tanks for weak liquor, mixed liquor, secondary liquor and thick liquor.

Construction Details

The injection of liquor takes normally place via one or several spray nozzles. Because of the size of the boiler the same is equipped with two movable spray nozzles in each opposite wall in the furnace. The greatest problem is arising every time the load of the boiler has to be changed, and the spray nozzle must be shut off and taken out to be replaced by a nozzle of a different size. This means great disturbances in the operation of the boiler. Therefore a variable liquor spray nozzle has been constructed, which can considerably eliminate this problem.

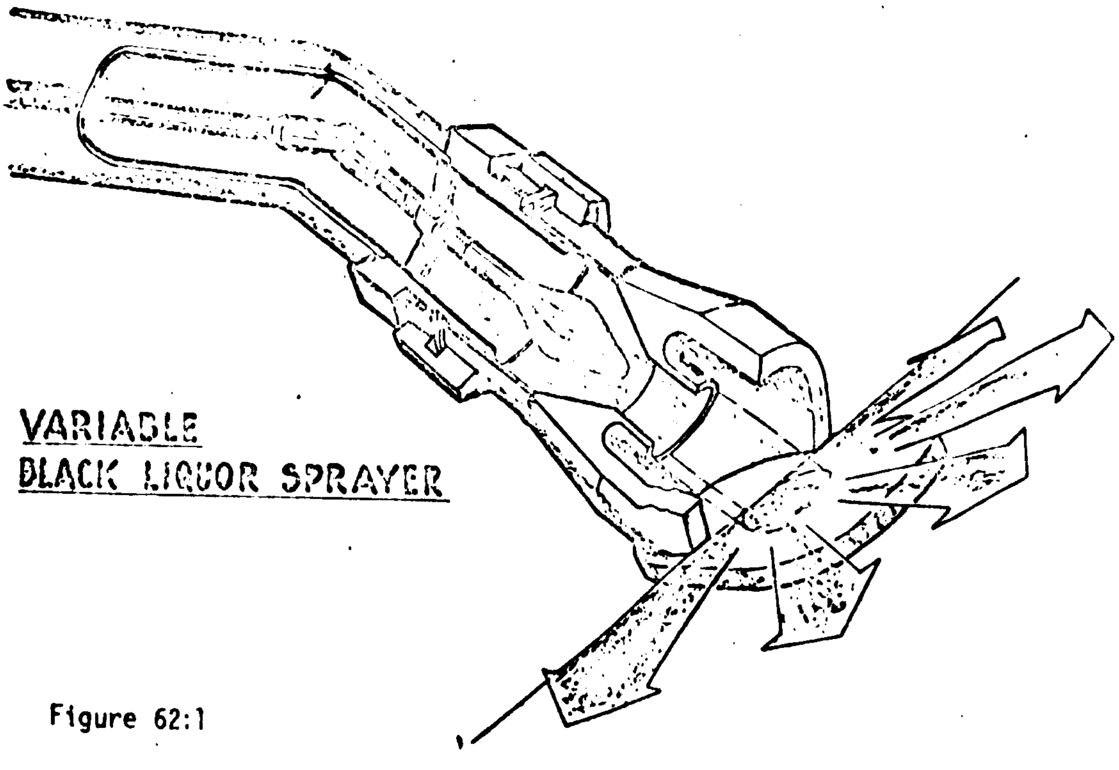


Figure 62:1

Gradually occuring coating on the spray nozzle distribution plate can cause variations in the distribution of the liquor. In order to prevent this the combustion air is supplied to the furnace via a great number of air ports, which are mounted in the four walls of the boiler at four different levels.

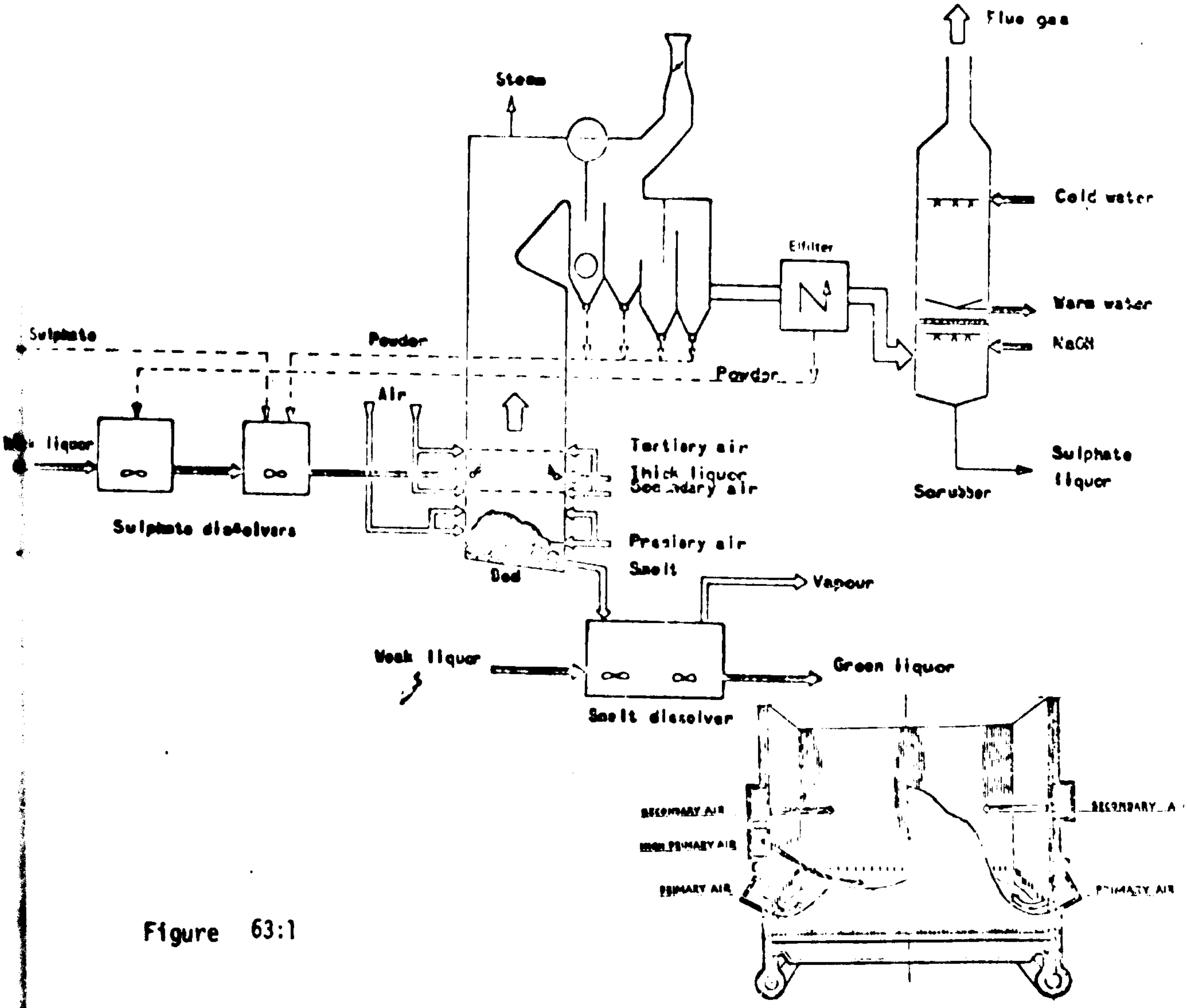


Figure 63:1

The two lower levels of ports are connected to one so called primary air fan and the two upper levels to a secondary fan. The opening of each air port can be manually adjusted. Furthermore before the air ports there are a number of manually handled dampers, with which individual air pressure can be adjusted in different air registers around the boiler accoring to the judgement of the operator of the boiler. In practice it is difficult to reach an even or against the liquor injection corresponding air distribution. Gradual build up of coatings around the air ports influences furthermore the air distribution. One has tried to solve this problem in two ways, partly through intermittent and automatical remove of the formed coating, partly to prevent or to detain the formation of plugs in the air ports.

This is done by letting the air blow over the surfaces or places where coatings are beginning to form. The ports are therefore provided with an insert, which is made tight against the air register front. A ring formed column is formed between the insert and the normal port. All air is blown into this column. Consequently no air is blowing wihtin the insert. Thus a hollow air stream is formed. See the following figure no 64:1 which shows the principle of this arrangement. The air insert is provided with a sharp edge in the front. The insert can be manually moved so far in past the center of the tubes that the formed coating can be brushed off.

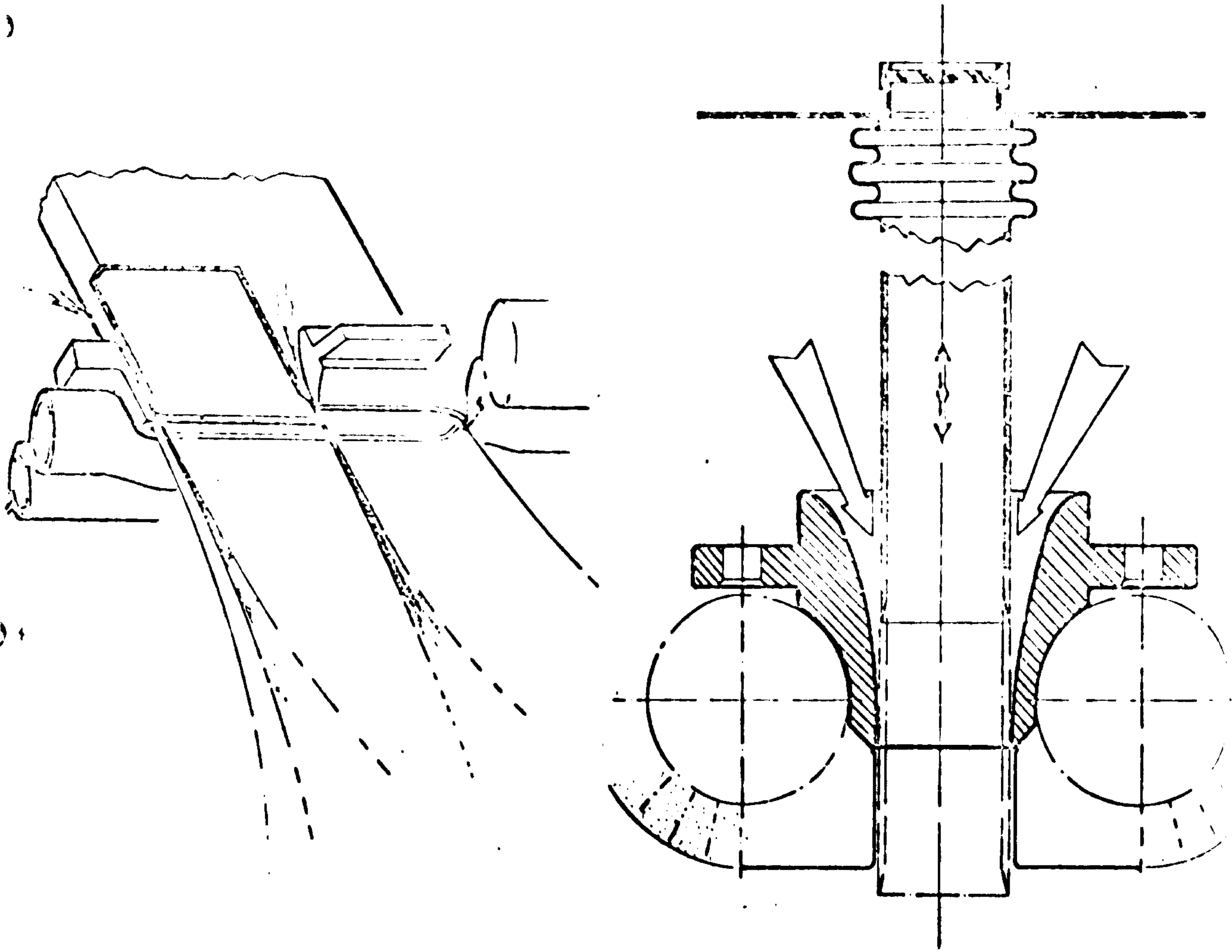


Figure 64:1

The air pressure obtained at the most upper air level is often too low. In this place the best possible mixing of the air with the flue gases is desired in order to keep down the H_2S-content in the same.

If the soot-blowing system is not correctly dimensioned great problems with clogging of the economiser part of the boiler can arise. Certain close sections in the flue gas channels have also been the cause for cloggings, which limite the capacity of the boiler. If this is the case the channels have to be altered and a higher pressure in the soot-blowing apparatuses used.

Circulating sodium sulphate powder coming partly from the ash pockets under the economisers partly from the electro-static precipitators is as usual mixed into the liquor before it is sprayed into the furnace. Variations in the amount of powder result in a varying chemical composition of the liquor spray, which cause disturbances in the operation of the boiler. In order to decrease these variations the order in which the soot blowing apparatuses are being used, has been spaced in such a way that the best equalization has been obtained. There are two separate computers on each side of the boiler which regulate the soot-blowing apparatuses. Two soot-blowers are always working at the same time, but they blow different parts of the economiser and/or superheater.

The following figure no 65:1 shows the arrangement and a flow diagram of the biggest recovery boiler in Gruvön mill.

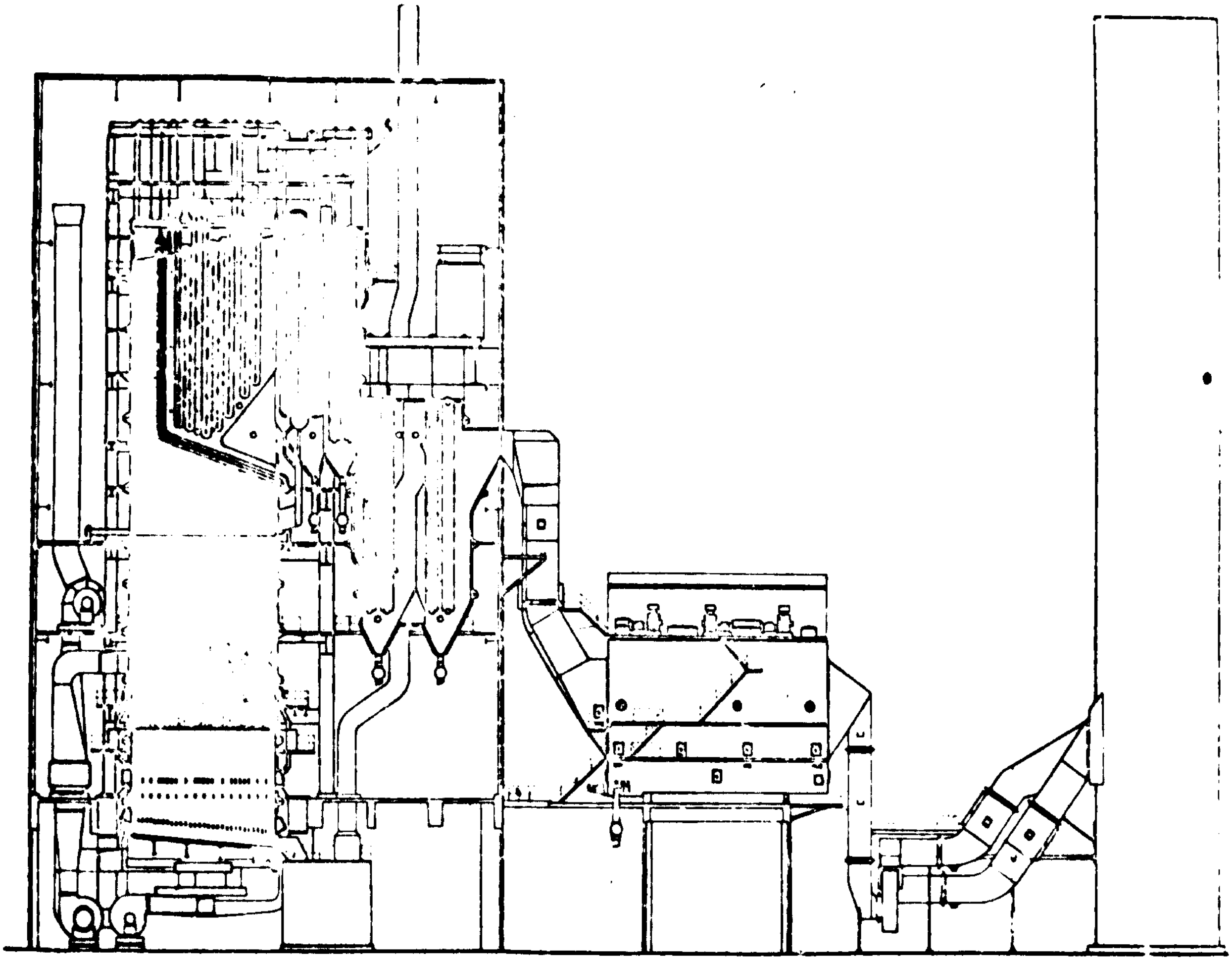


Figure 65:1

Main dates of the soda recovery boilers at Gruvon mill

		T3	T4
Nominal capacity	tp 90/day	375	760
Calculated max capacity	"	450	1 025
Dry substance flow	ton/h	21	43
Steam pressure	abs press	34	65
Steam temperature	°C	380	480
Feed water temperature	°C	115	135
Air temperature after air preheater	°C	120	150
Flue gas temperature after economiser	°C	125	155
Steam production	ton/h	76	156
Flue gas flow	Nm^3/h	110 000	216 000
P-air fan flow	Nm^3/h	62 000	130 0
P-air fan pressure	mmWs	280	465
S-air fan flow	Nm^3/h	62 000	130 000
S-air fan pressure	mmWs	480	613
Combustion surface	m^2	2 340	5 210
Furnace area	m^2	50,5	8 x 11,5
Furnace height	m	16	22
Furnace volume	m^3	805	2 000

A similar soda recovery boiler installed in Värö mill is shown in the attached figure no 66.1

5

Results Obtained

The study of the control system started in may 1973. The following summary of the results obtained can be made.

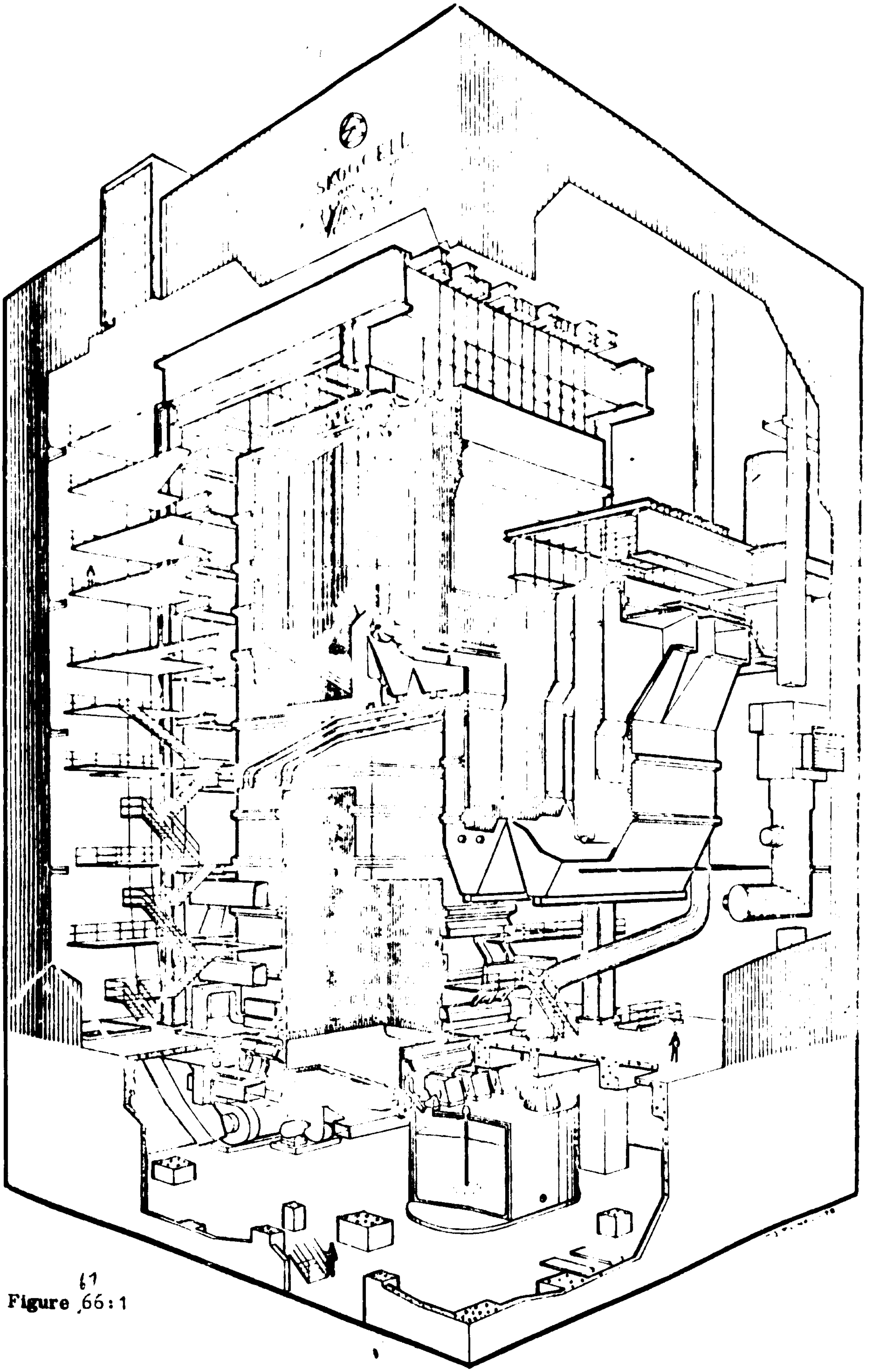
Capacity

The boiler has been operated steady at a load corresponding to [illegible]00 tons of sulphate pulp per day. At few times the dry substance flow corresponded to about 1 000 tons per day.

The capacity was limited by the air fans and also earlier by cloggings in the economiser part. After installation of tertiary air fans an improvement was achieved and there were no limitations caused by air flows or by the load of the furnace itself.

Degree of reduction

During a testing period the average degree of reduction was 93,8 % ± 3,5 %. The boiler was during the same period working at a constant load of 85 % of its maximum capacity.



67

Figure 66:1

Degree of efficiency

Based upon measured data the degree of efficiency was estimated to about 75 %. 15 kg of sodium sulphate per ton of pulp was then added.

SO_2-content in the flue gases

The average value for the SO_2-content before the scrubber has been around 1 000 mg/Nm^3. Great variations have, however, occured, even when the boiler has been operated with other noticable variations. In the scrubber about 90 % of the SO_2-gases are absorbed.

H_2S-content in the flue gases

At periods when the load has been around the nominal capacity the H_2S-emission has been very little. The main reason for higher H_2S-content has been the over loading of the air supply system. H_2S emission of temporary duration can be caused by the following reasons:

change of liquor spray nozzles
cleaning of the nozzle plate
cleaning of air ports
adjustment of air ports
adjustment of air flow
formed caves in the hearth
fall downs of liquor lumps from the wall

Conclusion

The project study was carried out with the help of a process computor, which had great advantages as several alternative control strategics could be tried. The following conclusions in short could be made:

1. Through better knowledge of the behavior of the recovery boiler, accurate control and thorough supervision the boiler could be operated more even. This has contributed to a reduction of air polluting emissions from the same.

2. The best result from both process and environmental preservation point of view was obtained if the steam production was held as constant as possible. Thereby variations in the furnace temperature, the size of the hearth bed, smelt flow and emission was equalized.

The presence of hydrogensulphide in the flue gas depends upon uncomplete combustion. In order to eliminate the hydrogensulphide in the fluegas it is required that:

O_2-content in the flue gas is high enough (in general 3 %)
the mixing in of air in the upper part of the furnace (tertiary air) is good
the boiler is operated as even as possible
temporary disturbances due to manual operation of the boiler are as small and short as possible

All rapid adjustments, both manual and automatic, should be avoided, as they in general cause an increase of both SO_2- and H_2S-content in the flue gas temporarly.

3. The main points in a control system for a soda recovery boiler can be summerized as follows:

> Variations in the physical and chemical properties of the supplied liquor shall be equalized before entering into the boiler furnace. The total flow of air, which is nearly proportional to the steam production, shall be held as constant as possible. Variations in the excess of air (O_2-content in the flue gas) depending upon variations in the chemical composition of the liquor, shall be compensated by controlling the air and the liquor flow. If the air pressure can be held constant at the same time as the air flow is varied a variable black liquor spray is required. The soda powder from ash pockets and from the electro static precipitator should be collected in a container and from this in determined proportions fed to the black liquor.
> Eventual equalization of the variations in the SO_2-content in the flue gas should be done by adequate additions of chemicals to the liquor, as an even sulphide content in the smelt and at the same time even SO_2-content in the flue gas only can be achieved if the relation S/Na in the injected liquor is even.
> Extensive adjustments of the production should be followed according to fixed schedule, so that relations between liquor and air flow as much as possible are maintained.

Measurement and Calculation of Primary Emission

One has observed variations between different recovery boilers and different operations of the same in the sulfur emission, which are difficult to explain. The objective of the study of the recovery boiler in Gruvön mill has also been through detailed measurements in a recovery boiler and calculations of the balance for adequately small parts of the same to try to describe the soda recovery process. In consideration to the high temperatures it is likely that the chemical reactions in the different parts of the furnace will reach almost equilibrium. As a consequence of bad mixing in the boiler and of the high viscosity of the gases at existing temperature most likely, however, there are inhomogenities as well horisontally as vertically.

Furthermore the objective for this investigation has been to establish basic facts, which make it possible to estimate the effect of different changes in the operating conditions regarding emissions of sulphur (S) and sodium (Na) and the possibility to control and also reduce the same.

One condition for the investigations has also been to study the recovery boiler under normal operating conditions, that is at nominal load.

The figure no 69:1 on the next page demonstrates the measured flows of sodium and sulphur at normal conditions. The width of the arrows is corresponding to the magnitudes of the flows. The rectangle indicates the recovery boiler itself. The figures, which indicate the size of the emission, are expressed in per cent of the amount of sodium respectively sulphur in the thick black liquor injected in the furnace.

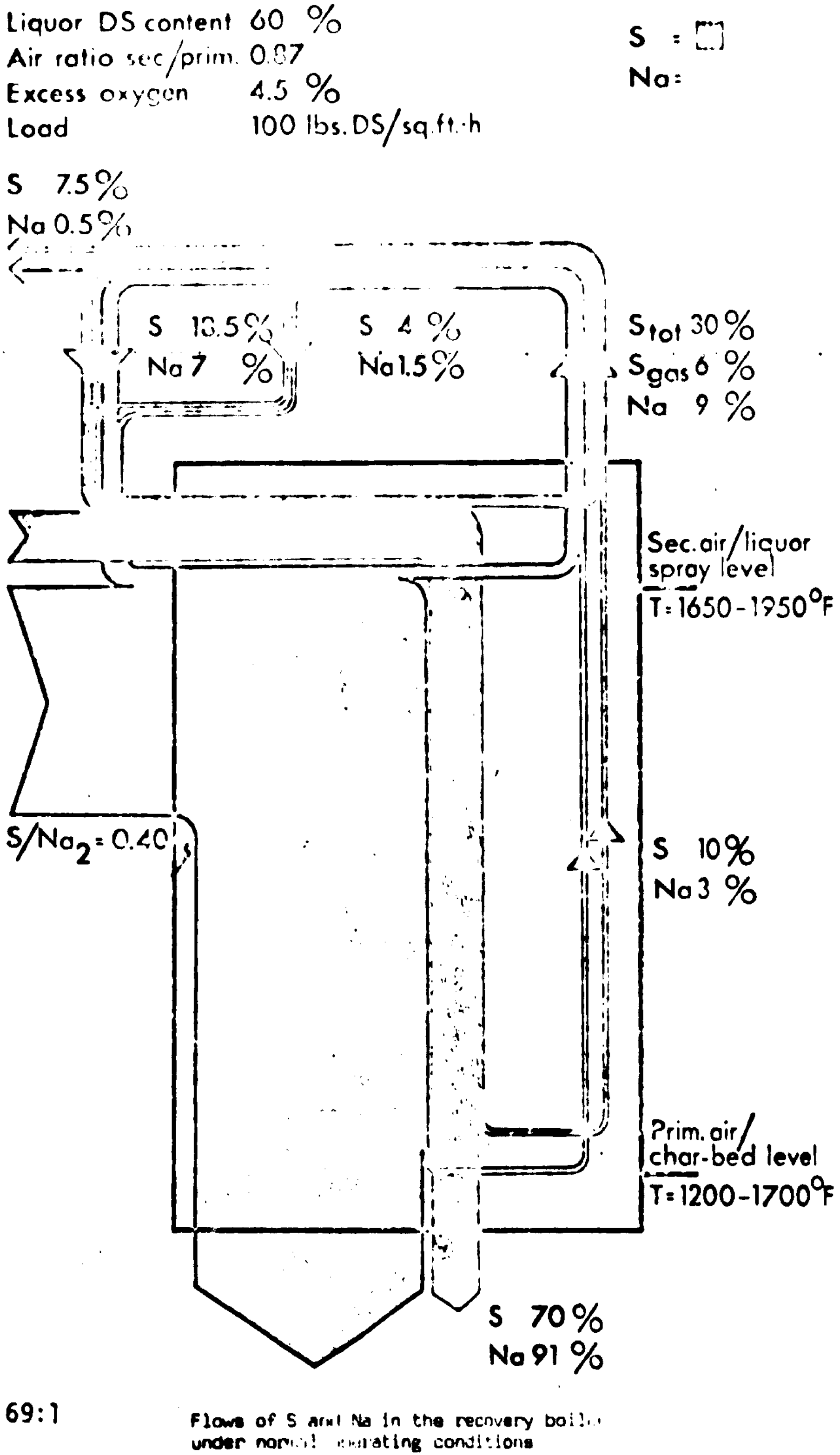


Figure 69:1 Flows of S and Na in the recovery boiler under normal operating conditions (nominal load).

The total emission of sulphur and sodium consists of emissions from the bed of the smelt and from the seconday air/liquor injection level. Normally the emission from the bed level is somewhat less than that from the seconday air/liquor injection level.

In the flue gas channels about 1/5 of the totally emitted sodium powder is separated and then collected in the soot or ash pockets. The main part of the remaining rest is caught in the electro static precipitators. The total separation of powder before the scrubber is about 95 %.

In the table below the composition of the smelt in the bed and in the spout is indicated

Table

		Bed		Spout
Na_2CO_3	mol %	59,7	(35,8)	59,8
Na_2S	mol %	33,2	(56,0)	31,8
NaOH	mol %	6,2	(7,2)	5,6
Na_2SO_4	mol %	0,8	(0,1)	2,5
S	mol %	0,1	(1,0)	0,3
Carbon	weight %	5,0 (8,0)		0,5
Degree of reduction %		97,5	(99,8)	92,0

The composition of the smelt coming from the spout is fairly constant. The degree of reduction is lower in this smelt than that one in the bed, and it varies more.

The composition on the bed is about the one given in the above table. In general it applies that the process chemistry of the recovery boiler with fair approximations can be described with "lokal" chemical equilibriums in regard to for instance the bed, or part of the same, and the adjoining gas phase. The temperature in the bed is in general nearly following the melting point curve for the system Na_2S - Na_2CO_3. Therefore besides flowing smelt there exist solidified "smelt" in the bed. It is assumed that this can contribute to the termal and physical stability of the bed. At complete solidification (temp = 750 °C) a rich $NaCO_3$ and a rich Na_2S solid phase precipitate, which is normally so well mixed, that a sample taken from the bed shows the original gros composition of the smelt. Locally in the bed a segregation can take place because of differences in density, so that single sample with deviating composition, e g high Na_2S-content, can be found. The column with paranteses in the table exemplifies this.

The content of carbon in bed is about 5 %. In the case the bed has an unnormally low temperature, as in "black" spots, the same is in general higher. In one sample taken out from the bed a carbon content of 8 % was measured.

The condition for a forming of carbon takes place when all the water has been evaporated from the thick black liquor when it is falling down towards the surface of the bed and that at the same time the temperature is lower than 800 °C. The precipitation of carbon is thus depending on the temperature, and it is taking place near the surface of the bed, where "black" spots are formed.

The sulphur as hydrogensulphide from both the bed and the liquor particles emits to the gas phase above the bed. However, when passages are very much formed in the furnace, the degree of combustion can locally be high, which causes sulphur dioxide to be formed. Sodium emits primarly in the form of gas as Na and NaOH, which then sublimates and forms the powder. The composition of the gas and the powder above the bed is shown in the following table no 71:1.

Table 71:1

	Measured	Theoretically calculated
H_2	3	3 %
H_2O	4	12 %
CO	6	5 %
CO_2	13	14 %
O_2	5	0 %
N_2	68	65 %
CH_4	0,1	0 %
H_2S	300	365 ppm
SO_2	1	1 ppm
Na NaOH	1,5	1, 5 % of added Na

In principle the gas in the furnace is in equilibrium. However, passages containing partly not consumed combustion air exist. Traces of not burned gases as H_2, CO and H_2S can alco exist. When the relationship sulphur-

sodium is sufficiently big the powder exists almost entirely as pure Na_2SO_4 in the upper part of the furnace. The amount of carried over **liquor** particles are quite small.

How the temperature is distributed in the bed as well as in the vertical part of the furnace is of special interest. The figure below demonstrates how the temperature is distributed when taking a cut through the bed. From the same one can distinguish three zones. The hotest zone, the white ring, arises at those places, where the primary and high primary air are hitting the bed surface. Because of the limited reach of the air jets the middle part will be somewhat cooler. The air will also not reach the furnace walls and because of the cooling effect of the walls the temperature will be lower.

TEMPERATURE DISTRIBUTION IN CHAR BED

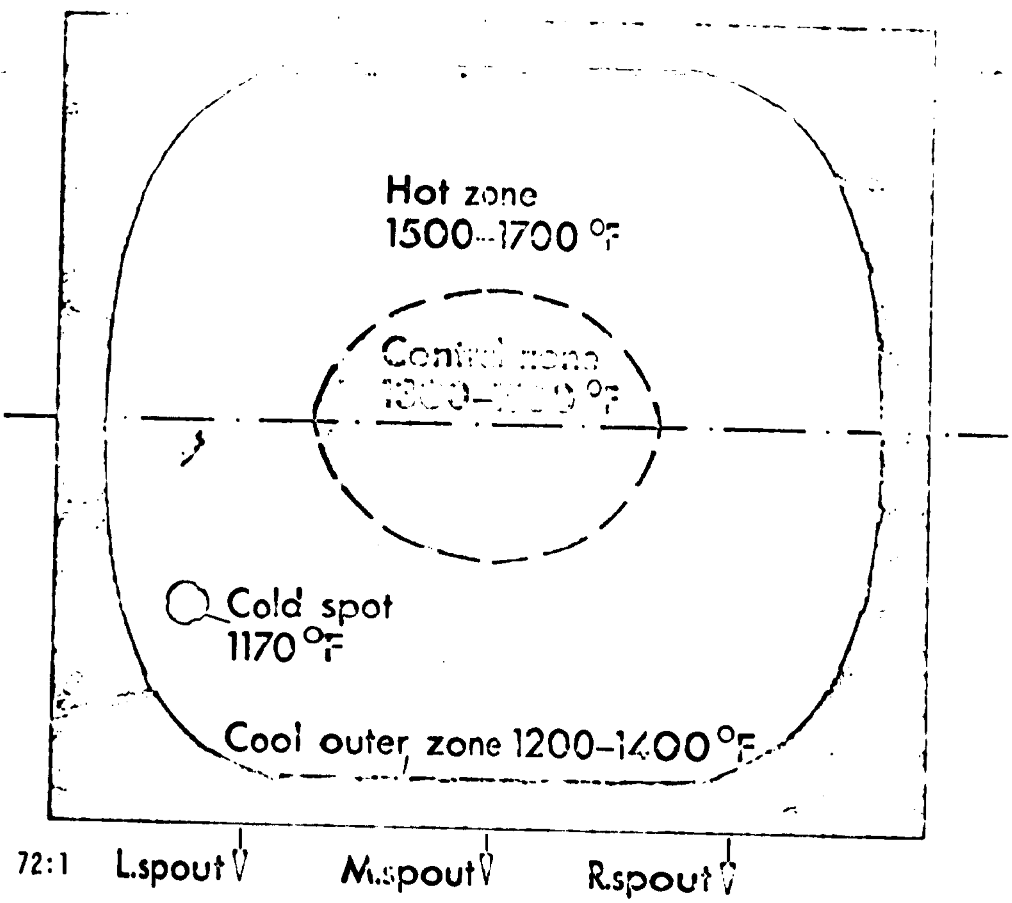


Figure 72:1

In the next figure no 73:1 it is shown that the distribution of the **temperature** is important. Through analyses of gas samples taken from **places** above parts of the bed with different temperatures it has been **found a** distinct dependence upon the pressure what concerns the emission of sulphur. With the assistance of the temperature and the local degree of combustion above respective parts of the bed it is possible to make a fairly good estimation of the maximal respectively minimal sulphur emissions from the bed.

A normal distribution of the temperature in the vertical part of the furnace is shown in figure no 73:1.

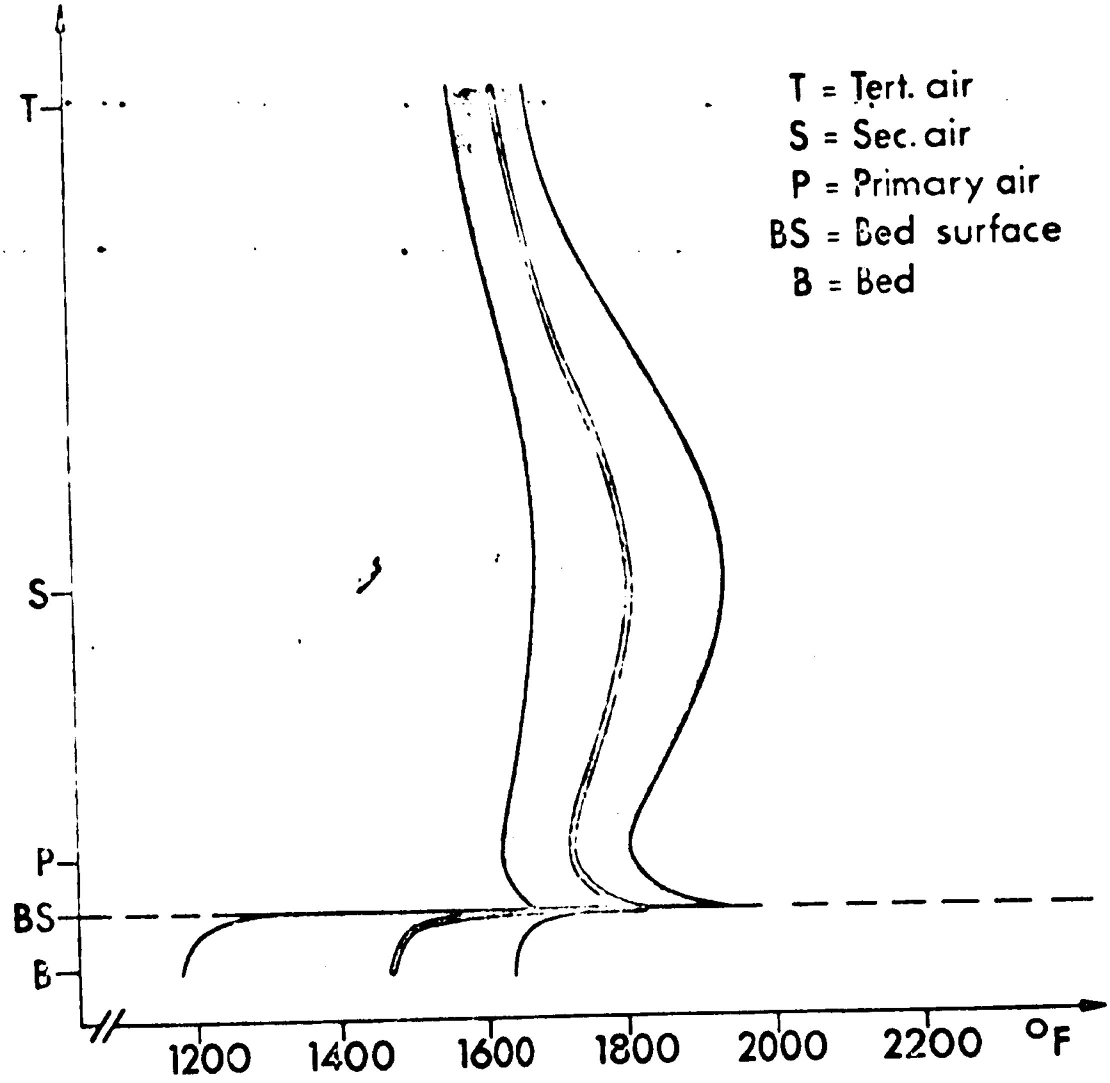


Figure 73:1

The grey field indicates the spread of the temperature in respective levels. The thick black curve indicates the averages. The figure indicates that there are two temperature maxima, one at the surface of the bed and one around the secondary air level. Between these there is a minimum near the area of the primary air level. The maximum of the temperature - eventually in a thin gas layer close to this - depends upon the reaction of carbon to carbon monooxide, which is strongly exotermical. At the final combustion around the secondary air level also strong exotermical reactions take place, as burning of carbon monooxide to carbon dioxide and hydrogen to water vapor.

The profile of the temperature increases in width at the secondary air level which indicates that there are inhomogenities in the different parts in a cut made across the furnace. Consequently there are also different degrees of combustion in the same. By studying how the profile is getting more narrow higher up in the furnace, one can get an idea how well the combustion air has been dispersed, and consequently also about the homogeneity in the last stage of the combustion of the flue gas.

Conclusions

1. The emission of sulphur and sodium originates both from the bed and from the secondary air/liquor spray level.

2. The emissions of sulphur dioxide and hydrogen sulphide consists of a smaller part of the total sulphur emission from the boiler. The main part of the sulphur found as powder of the emitted sodium, and only the rest will emit in a gas form. Relatively small changes in the primary sulphur and sodium emission can therefore to a great extent influence the SO_2 emission.

3. Primarly the sulphur is emitted from the bed from those areas, which have a low temperature. An essential part of the sulphur emission is created in the liquor spray level.

4. Sodium emits to a large extent from liquor particles and areas in the bed, which have a high temperature. The temperature determines in general the extent of the sodium emission.

5. Irregularities in the temperature increases the emission of sulphur as well as sodium. It is therefore important to maintain a constant temperature all the time.

6. Increased dryness of the air promote decreased emission of sulphur dioxide.

7. Primarly the sulphur is emitted from hydrogen sulphide.

8. Incomplete combustion in the upper part of the furnace forms hydrogen sulphide in the flue gas. In order to prevent this besides an adequate amount of air an effective mixing in of air in this part of the furnace is required.

From environmental pollution point of view it is necessary to study the soda recovery process as well as the whole sulphate process itself. It is obvious that more sophisticated methods are required in order to control the sulphate process. In certain cases perhaps an entirely new control technique must be applied. It does not seem right that the losses of chemicals in the different parts of the sulphate process shall be compensated just in the recovery boiler. Perhaps the losses should be compensated at those points in the process where they occur, and thereby resulting in a better control of the chemicals circulating in the process.

BLEACHING

In order to characterize environmental polluting effluents to the receiving waters (recipient) such terms as biochemical oxygen demand (BOD), colour (Pt), chemical oxygen demand (COD), total organic carbon (TOC), "lignin", suspended materials (SM) and so on are used. Our knowledge about the relations between these factors and their influence upon the environment is quite incomplete. Therefore efforts should be made to establish these relations. The methods of measurement are encumbered with quite a lot of uncertainties in certain cases. This is especially true for the determination of BOD_7 of certain effluents.

In the following table 76:1 environmental polluting effluents from a relaviely modern sulphate mill with a conventional bleach plant and condensate treatment are listed.

Table 76:1

Source	Discharge kg/ton of 90 % bleached pulp		
	BOD_7	Colour (Pt)	"Lignin"
Digesters - washing - screening	4,5	15	5
Condensate	2,5	-	-
Bleach plant	13	165	44
Temporary discharges	3	10	3
Total	23	190	52
The share of the bleach plant %	56	87	85

Among the factors, which are of importance in regard to polluting effluents from the bleach plant, the following can be mentioned:

The content of lignin in the unbleached pulp
The degree of washing of the unbleached pulp

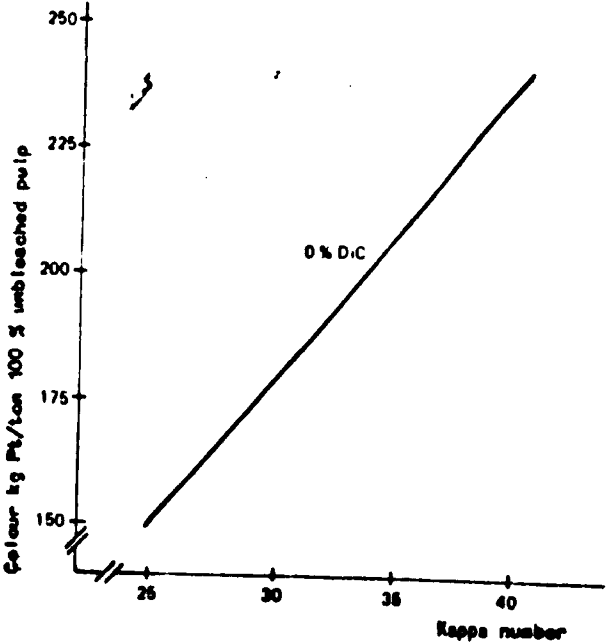
The carried out conditions during the bleaching as
degree of delignification in the primary bleaching
used bleaching chemicals
bleaching sequences
temperature etc
final brightness and strength properties required

Furthermore to a certain extent the degree to which the bleach plant has been closed and the filtrate from washers has been brought back in the system has also an influence on the environmental pollution.

The Content of Lignin in the Unbleached Pulp

How effluents from a bleach plant is influenced by the Kappa number of the unbleached pulp studies have been made in a laboratory, where a serie sulphate pulps with Kappa numbers from 23 to 45 was made in a laboratory digester. The following conclusions could be made:

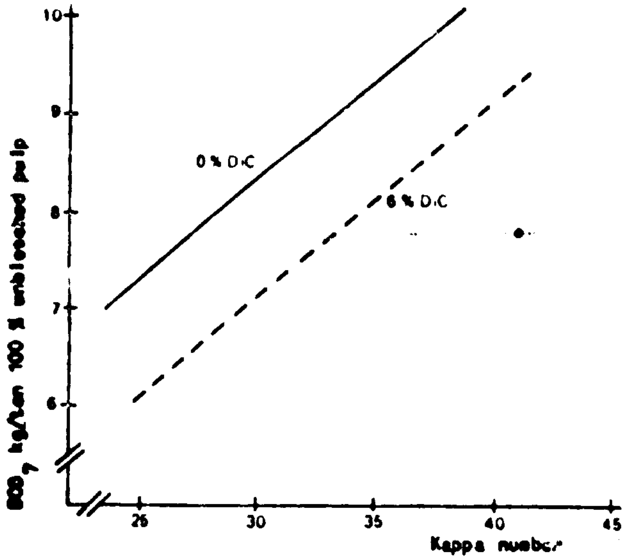
The colour of the effluent is linearly depending upon the release of the lignin which is presumed to be directly proportional to the lignin content of the pulp. The colour intensity of the effluent from C and E stage is given as a function of the Kappa number of the unbleached pulp in the following figure 77:1.



Colour discharge from primary bleaching of unbleached sulphate pulps with different Kappa number

Figure 77:1

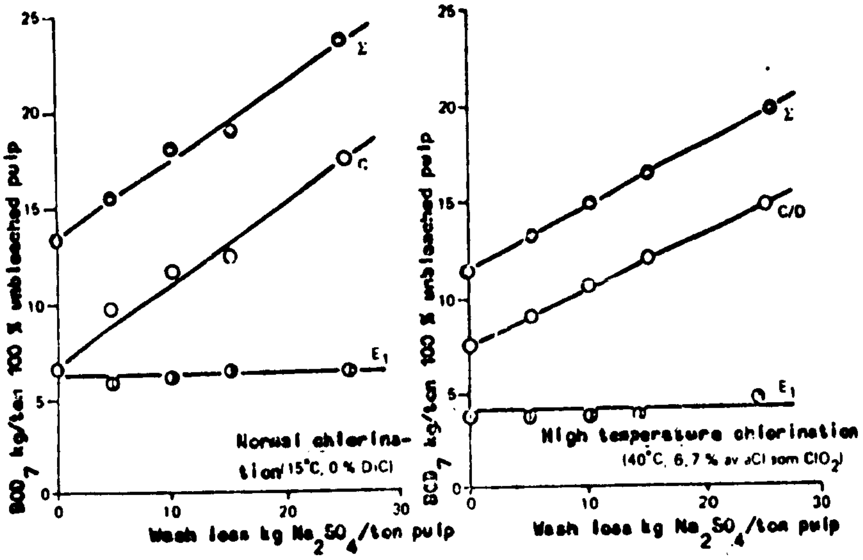
The BOD_7 of the effluent from the C and E stage is also linearly depending upon the release of lignin. Mixing in of chlorine dioxide results in a lower BOD_7 in the effluent, about 1 kg/ton of pulp lower over the whole interval of yield. The total BOD_7 as a function of the Kappa number is given in the following figure no 78:1.



Total BOD_7 from primary bleaching of unbleached sulphate pulps with different Kappa number

Figure 78:1

By increasing the delignification during the cooking it is possible to reduce the environmental pollution effect of the bleach plant. How far it is possible to go is among other things depending upon which pulp quality one tries to produce. Naturally it is depending also upon the cost of wood and chemicals and so on.



BOD_7-discharge from C- and E-stage and total discharge (Σ) at different wash losses.

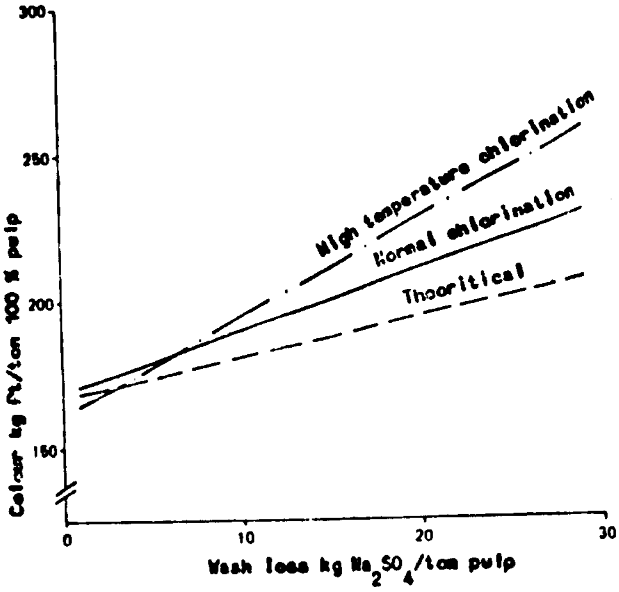
Figure 79:1

The Degree of Washing

How much the unbleached pulp has been washed influences among other things the consumption of chemicals during the primary bleaching and also the properties of the effluent. A laboratory investigation was carried out with a well washed sulphate pulp, when the wash losses was simulated by mixing the pulp with between 5 and 25 kg Na_2SO_4/ton of pulp in the form of black liquor.

The demand of chlorine increased linearly with the wash loss at chlorination to the same rest chlorine content. Each kilogram of sulphate required 1.3 kg chlorine and additionally an increased alkali charge of 0,2 kg NaOH in the first alkali stage.

The BOD_7 in the effluent from the chlorine stage increased with increased wash loss according to the diagram in figure no 80:1 , while the effluent from the alkali stage was not affected.



Colour discharge, actual and theoretical, from C- and E-stage at different wash losses

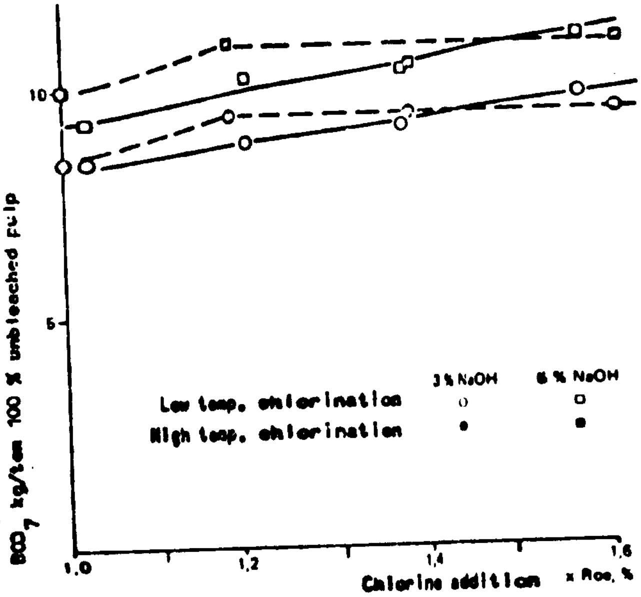
Figure 80:1

In regard to the colour of the effluent the condition is somewhat different. Most likely the lignin in the black liquor becomes more intensified coloured through the chlorination, which is shown in figure 80:1 above.

Bleaching Conditions

Factors of polluting character in the effluent from bleach plants are mainly determined by the degree of delignification in the primary bleaching (CE) and by the final brightness of the pulp required. The degree of delignification in the primary bleaching is directed by the addition of chlorine and alkali. The final brightness is achieved partly by the primary bleaching and partly by the addition of chemicals as hypo chlorite, chlorine dioxide in the final bleaching stages.

At constant conditions in the alkali stage increased chlorine addition results in a certain increase of the BOD_7-discharge from the primary bleaching. See figure no
This fact is, however, connected to an decrease of the Kappa number after CE-bleaching. See figure no 81:1.



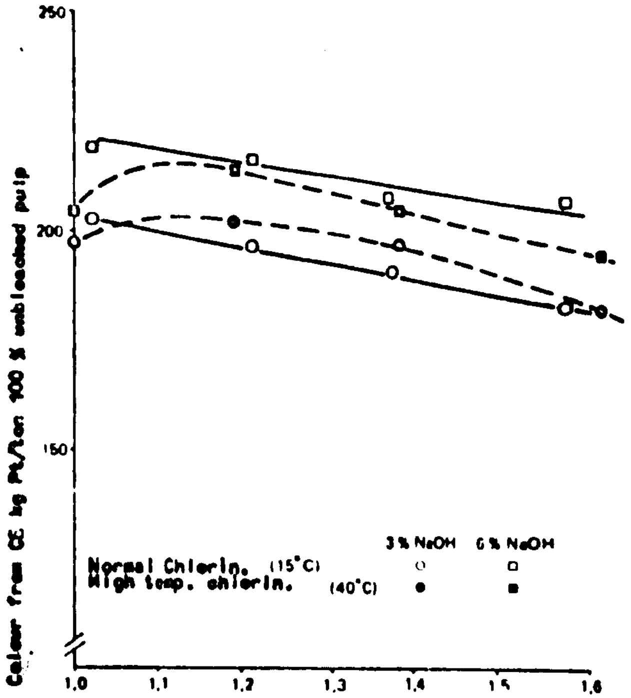
BOD_7-discharge from primary bleaching at different chlorine additions and constant conditions in the alkali-stage.

Figure 81:1

At normal chlorination (low temperature chlorination) a single relationship between the Kappa number after CE and the BOD_7-discharge from this stage exists.

The discharge of BOD_7 from the CE-stages at chlorination at 40 °C is depending upon the Kappa number after the CE and the alkali addition in the E-stage. At the same Kappa number the discharge increases, when the addition of alkali increases.

When the addition of chlorine increases and the conditions in the alkali stage are constant a slight decrease of the colour discharge at normal chlorination is taking place, which shows in figure no 82:1.
When chlorination is taking place at 40 °C the colour discharge increases in the beginning somewhat with the increased addition of chlorine. At addition over about 1,2 x Roe number the colour discharge decreases again.

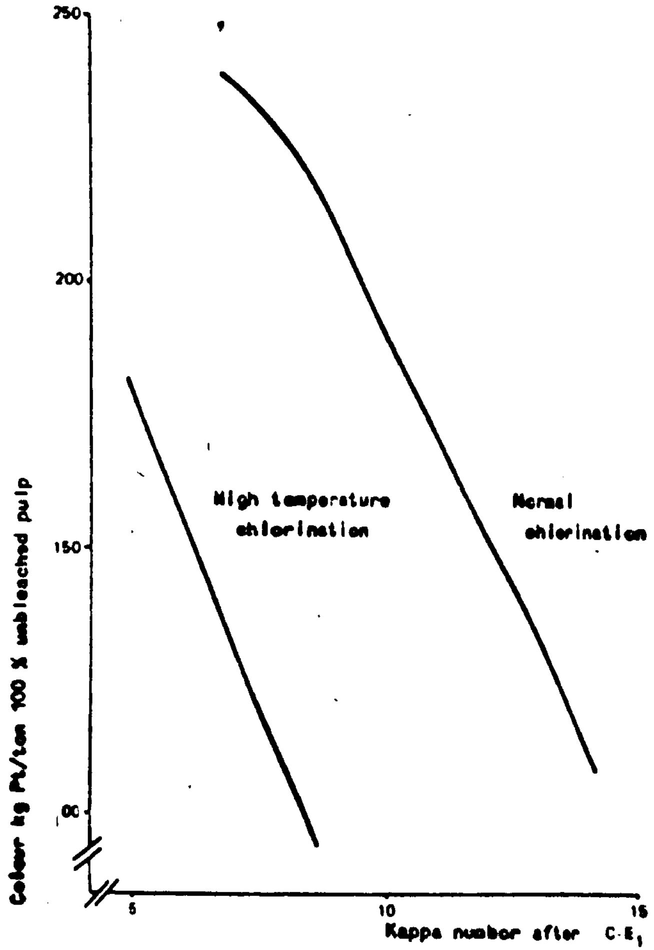


Colour-discharge from primary bleaching at different chlorine additions in the C-stage. Constant conditions in the alkali-stage.

Figure 82:1

Increased addition of alkali in the E_1-stage results in an increased colour discharge at constant chlorine addition. This is valid as well at normal chlorination as high temperature chlorination with mixed in chlorine dioxide (chlorination at 40 °C).

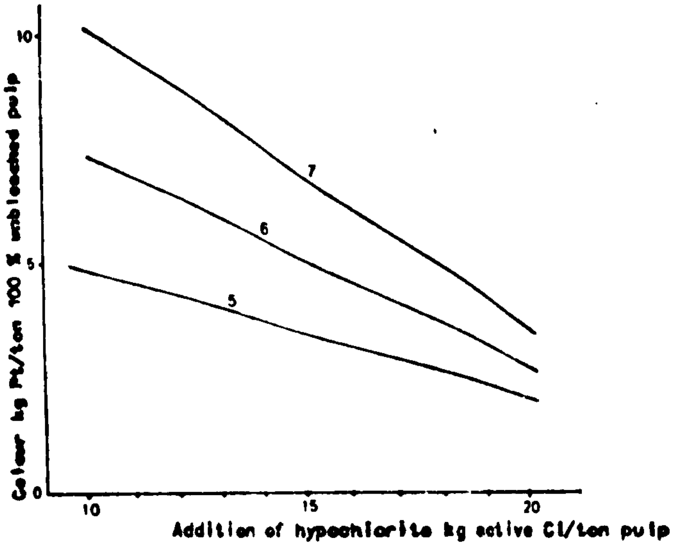
From the following figure no 83:1 it can be seen how the colour discharge from the primary bleaching changes when the Kappa number after CE has been varied with the addition of alkali.



Colour-discharge from primary bleaching, when the Kappa number has been varied after the CE-stage with the addition of alkali

Figure 83:1

The discharge of colour from the hypo-stage (CEH) is very low in comparison with the same from the CE-stages. It increases somewhat with increasing Kappa number after the CE-stages. However, this increase is small in comparison with the change of the colour discharges from the CE-stages, which is affected by the changes in the Kappa-number after this stage, which is shown in the following figure no 84:1.



Colour-discharge from hypo-stage at varied addition of hypochlorite. The Kappa number after CE-stage is the parameter.

Figure 84:1

An increase of the final brightness of fully bleached pulps can result in considerable increases of the BOD_7-discharge, when the bleaching conditions are pressed.

Modified Bleaching Technique

The total discharges of BOD_7 and colour (Pt) calculated on 90 % dry bleached pulp from sulphate and sulphite bleach plants are grouped together in the following table no
The figures are based on an investigation made by the SSVL Environmental Care Project in 1971.

Table 84:1

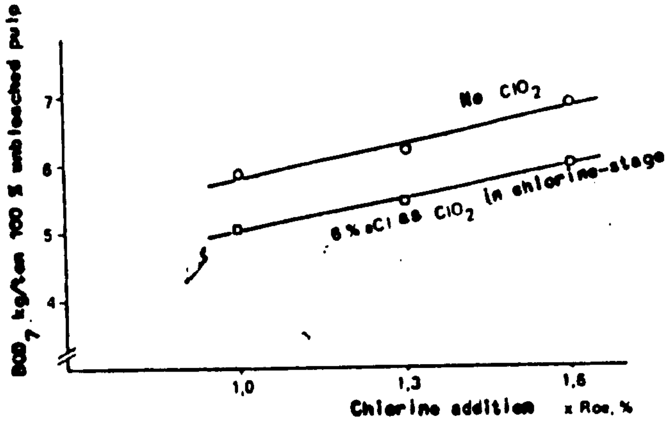
Bleach stage	Sulphate		Sulphite	
	BOD_7 Kg/ton	Colour Kg Pt/ton	BOD_7 Kg/ton	Colour Kg Pt/ton
C	4,6	7	5,8	25
E	4,8	138	4,7	41
Final bleaching	2,6	9	1,1	0(0,1)
Total	12,0	154	11,6	66

The discharge of BOD_7 is concentrated to the chlorination and the first alkali stage (about 75 % of the total discharge). When bleaching sulphate pulp the dominating discharge of colour comes from the alkali stage, while when bleaching sulphite pulp the discharge of colour from the chlorination as well as the first alkali stage is relatively large. Consequently it is important to find such measurements which reduce effluent discharges from the chlorination and the first alkali stage.

Chlorine Dioxide in the First Bleach Stage

An environmental effect can be achieved by adding chlorinedioxide to the chlorine stage, whereby colour as well as BOD_7 from the C- and E-stage discharged to the recipient will be decreased. The discharge of biochemical oxygen consuming substance from the C-stage increases with increased chlorine addition. See the following figure no 85:1.

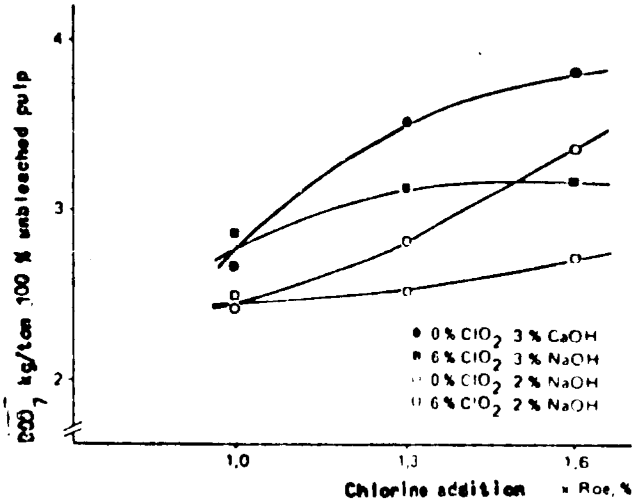
The addition of chlorine dioxide (6 % of totally active chlorine) will lower the BOD_7 discharge about uniformly with approximately 15 %.



BOD_7 discharge from C-stage at vaying chlorine addition

Figure 85:1

The discharge of biochemical oxygen consuming substance from the E-stage depends partly upon the addition of chlorine in the previous C-stage and partly upon the addition of alkali in the E-stage. See the following figure no 86:1.



BOD$_7$-discharge from E-stage at varying chlorine addition in preceding C-stage

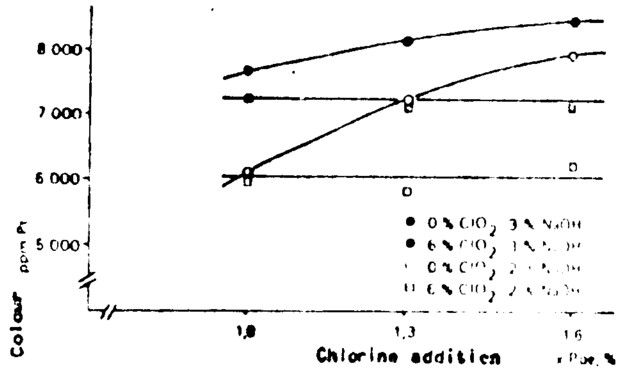
Figure 86:1

When chlorine dioxide (6 % of the added chlorine) is added in the C-stage the discharge will decrease. At small additions of chlorine the effect is limited. However, at normal addition of chlorine (1,3 x Roe number) a decrease of 10 % of the discharge is obtained. At excess chlorination the BOD$_7$ discharge will decrease with 20 % if chlorine dioxide is added.

The discharge of coloured substance is concentrated to the E1-stage in the bleach plant. The addition of chlorine dioxide in the chlorine stage will decrease this large discharge of coloured substances. The filtrate from the chlorine stage is, however, not affected.

At chlorination without addition of chlorine dioxide the colour of the alkali effluent discharged will increase with increased addition of chlorine. Increased addition of alkali in the E-stage will also make the discharge more intensive coloured. This effect is most apparent when the addition of chlorine is rather low. See the following figure no
A pulp consistency of 6 % in the alkali stage corresponds to a discharge of 125 kg Pt/ton at 1,3 x Roe number (3 % alkali).

The addition of chlorine dioxide has the effect that the colour does not change at increased addition of chlorine. At a total chlorine addition = 1,3 x Roe number an addition of 6 % chlorine dioxide decreases the colour with about 15 %, at excess chlorination this colour decrease will be about 20 %.



Colour-discharge from F-stage at varying chlorine addition in the C-stage

Figure 87:1

This method of adding chlorine dioxide in the C-stage will result in higher costs for chemicals, if at the same time the temperature is increased in this stage. However, an increase in the temperature will reduce the environmental effect. This procedure demands also chlorine dioxide resistant equipment in the chlorine stage.

The difference in investment costs for new plants compared with the alternative chlorine bleaching and chlorine - chlorine dioxide bleaching is small, as the cost for brick lining of the chlorine tower, which is necessary in order to protect the same against chlorine dioxide, is slightly higher than the cost for rubber lining of the same.

Hypochlorite in the First Alkali Stage

An environmental effect can be achieved by the addition of hypochlorite in the first alkali stage, as this decreases the coloured substances in the effluent by almost 30 % discharged to the receiving water.

This decrease seems to be fairly linear with increasing addition of hypochlorite. In the E_1-stage a colour reduction of 20 % at a charge of 10 kg hypochlorite/ton pulp and c. 10 % with at the same of 20 kg hypochlorite/ton of pulp can be achieved. The corresponding total reduction of discharged coloured substances from the whole bleach plant will be 15 respectively 25 to 30 %. At the higher addition of hypochlorite the addition of chlorine dioxide should take place in the chlorine stage in order to maintain a good quality of the pulp. The discharge of BOD_7 decreases also somewhat and about 15 %.

The discolouring ability of the hypochlorite can depend upon the fact, that this bleach chemical oxidizes quinoides and phenolic lignin elements to aliphatic uncoloured fragments, eventually all the way to carbondioxide and muratic acid. Thus a proportion of the hypochlorite added reacts with the lignin, which still should have been extracted in the alkali stage, and a discolouring of the effluent is consequently taking place.

At moderate additions of hypochlorite, less than 10 kg/ton of pulp, no extra costs for chemicals will be expected as less chemicals can be added in the final bleaching. At higher addition of hypochlorite the costs for chemicals will increase if a certain brightness of the pulp will be maintained, partly because of the cost for hypochlorite, partly because chlorine dioxide must be added in the first chlorine stage. This is necessary in order to maintain the viscosity of the pulp.

New Equipment and New Bleaching Chemicals

As a new bleaching chemical it is possible to use ozon instead of chlorine in the primary bleaching of pulp. The used bleaching liquor from a ozon stage should be brought back to the recovery boiler and be burned in the same. Bleaching with ozon is, however, not yet fully explored. Although bleaching with ozon seems to give a lower viscosity of the pulp the strength properties of the same are not affected. Today ozon is more expensive than oxygen gas. However, it may have some advantages as more simple equipment can be used and less amounts of chemicals have to be added.

The most important application of the peroxide bleaching is most likely sequences for the manufacturing of semi bleached pulp of the type DP, CP or OP. (DP = chlorine dioxide-peroxide, CP = chlorine-peroxide, OP = oxygen-peroxide). The paper properties of the pulp made according to the sequences DP or CP are satisfactory. The sequence OP should be able to make a semi chemical pulp without effluents.

Chlorine monoxide can replace chlorine in the primary bleaching and chlorine dioxide in the final bleaching of the pulp. Bleaching of pulp in the first stage with chlorine monoxide decreases the discharge of coloured substances in the effluent and also the BOD_7 in the same with 40 respectively 20 %.

In order to decrease the environmental polluting effluents from the bleach plant new bleaching equipments shall give a direct decrease of the discharged polluting substances and/or decreased effluent volume. A decreased amount of polluting impurities can be achieved through a reduction of temporary discharges (better control of the bleach system) or through reduction of normal discharges (high yield bleaching - bleaching in gas phase). A decreased volume of the discharged effluent can be achieved by new methods of washing the pulp (radial washing, press washing), and through a new bleaching technique (closing up of the bleach plant, bleaching at higher pulp concentration, dynamic bleaching, puls bleaching, displacement bleaching). A reduced effluent volume does not give a reduced environmental pollution, but the handling of the effluents are less costly.

Oxygen Bleaching

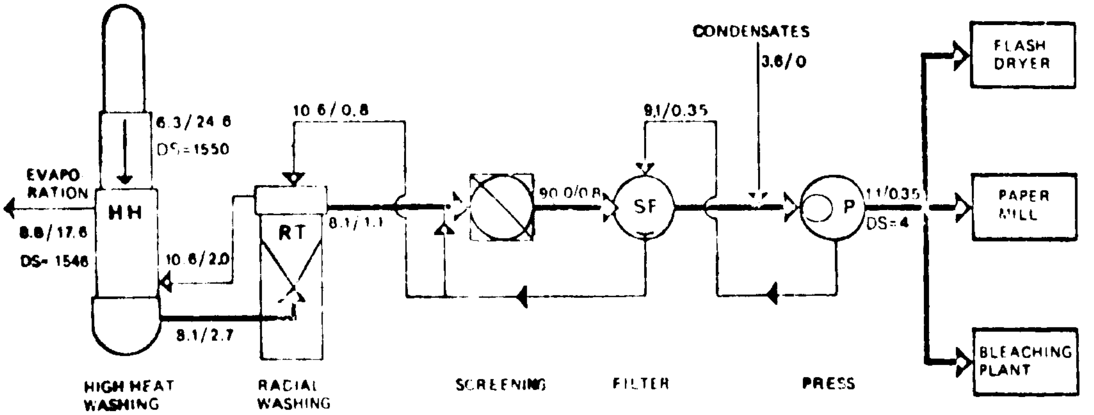
Oxygen bleaching is characterized by the treatment of chemical pulp with oxygen at a high pressure and increased temperature in the presence of alkali. The destruction of the cellulose is reduced by magnesium inhibitors. In comparison with the conventional bleaching it is possible to achieve apparent advantages from the environmental pollution point of view by using the oxygen bleaching, providing the oxygen stage is placed in a suitable way regarding the washing of the pulp and further fitted into the alkali recovery system. The destruction of organic material and the recovery of inorganic chemicals can take place via the recovery system of the sulphate mill without bringing the chlorite content in the liquor system to such a level that corrosion will be a dangerous factor.

From an environmental pollution point of view an essential factor to be considered is - because of quality reasons - how far the delignification of the pulp in the oxygen stage can be allowed to be carried out, and how big an amount of lignin will remain in the pulp to the following bleaching stages. When bleaching a sulphate pulp to a brightness of 92 % SCAN it is normally estimated that besides the oxygen stage further five stages, for instance C/D, E, D, E, D, are required.

In order to obtain a good recovery of effluent liquor from the oxygen bleaching and reduce the environmental influence of the bleach plant in an economically satisfactory way it is required that the oxygen stage is integrated in a closed washing and screening system. In many cases it can also be necessary as alkali in the oxygen stage entirely or partly to use sulphur containing alkalies in order to avoid an excess of alkali in the mill. This has been studied at one of the mills in Sweden. The results from this investigation and several other ones are commented in the following.

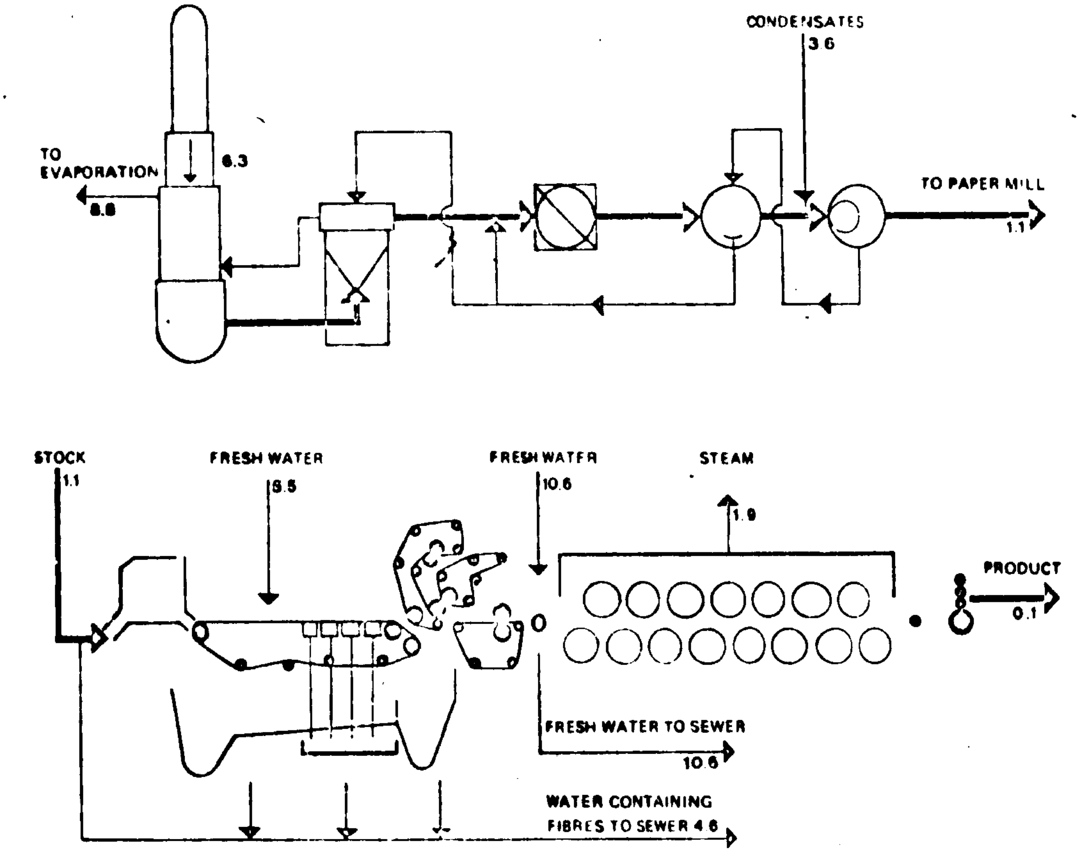
At the mill trials efforts were made to fairly exactly establish how far the delignification in the oxygen stage can be carried out when bleaching sulphate pulp add when considerations were taken to the pulp quality and to environmental effects anticipated in connection with these trials. As basis for forming an estimate of the different mill trials as referens was used a period when NaOH was added as alkali in the oxygen stage, and when the white water system around the oxygen stage was open. The results from this referens period showed a good conformity with trials in the laboratory.

By closing the white water system waste liquor from the oxygen stage was brought back with the pulp to the oxygen reactor. It was found that the waste liquor from the oxygen bleaching did not affect the quality of the oxygen bleached pulp or the consumption of chemicals in the oxygen stage.



Flowsheet for totally closed kraft mill. Figures indicate ton liquid per ton of pulp (90 %) / percentage by weight of dry solids. DS = kgs of dry solids per ton of pulp (90 %).

Figure 90:1



Flowsheet for totally closed kraft mill (cf fig. 7), including paper mill. Figures indicate ton liquid per ton of pulp.

Figure 90:2

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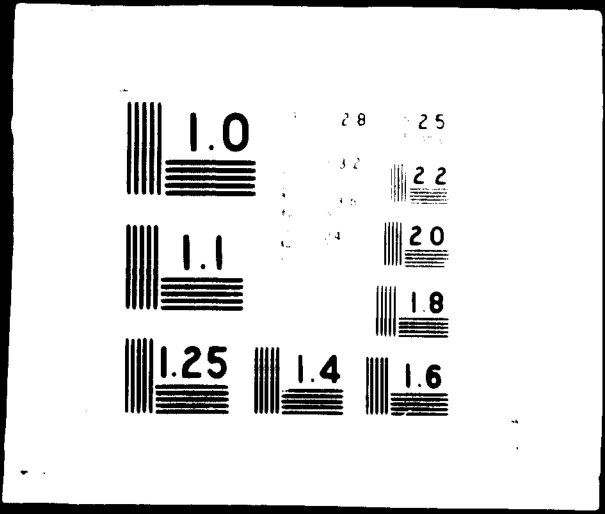
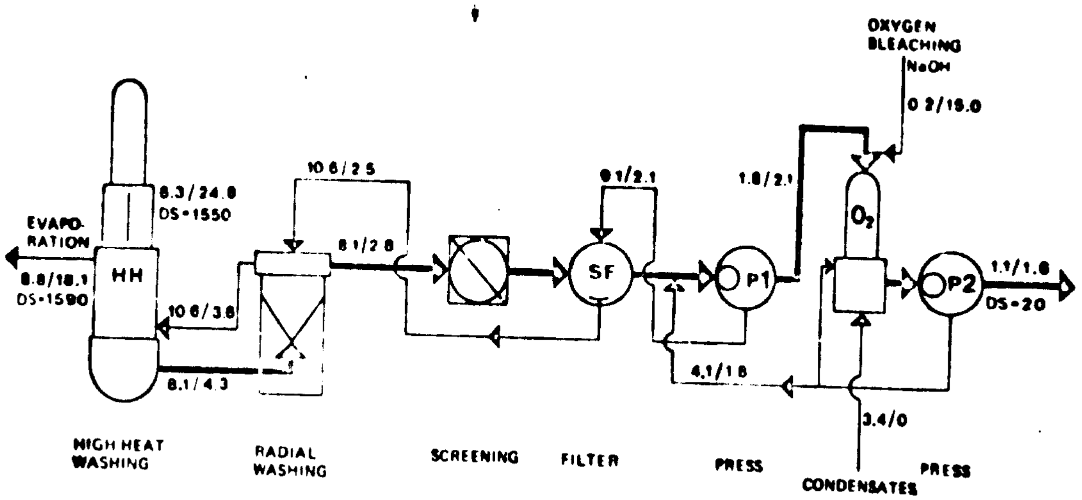
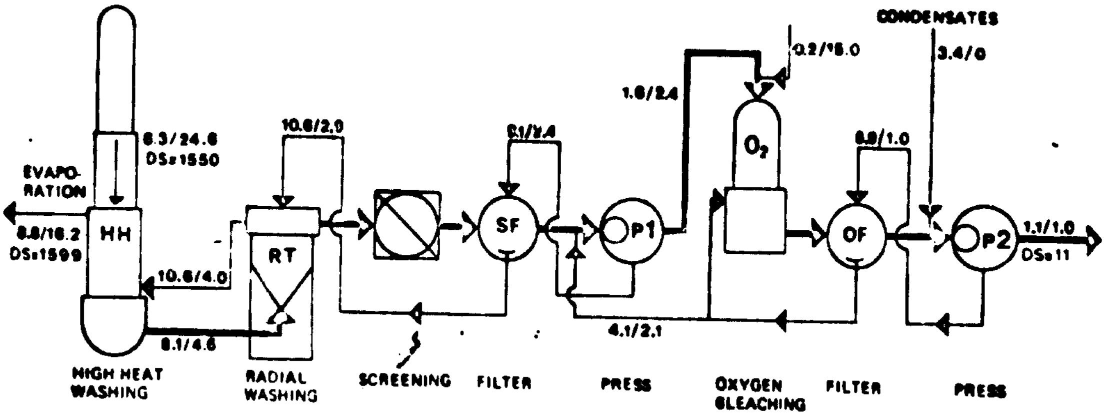




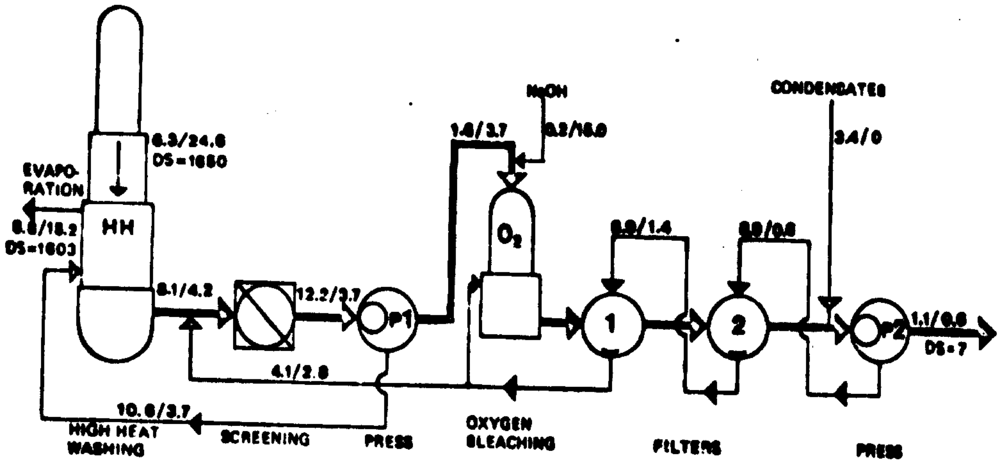
. Flowsheet for totally closed kraft mill, including oxygen bleaching I. Figures indicate=fig. 7. In the oxygen bleaching is dissolved 30 kgs of dry solids per ton of pulp (90 %).

Figure 91:1



Flowsheet for totally closed kraft mill, including oxygen bleaching II. Figures indicate=fig. 7 and 9.

Figure 91:2



Flowsheet for totally closed kraft mill, including oxygen bleaching III. Figures indicate=fig. 7 and 9.

Figure 92:3

The effect of black liquor (not oxidized) in the oxygen stage was also studied partly by adding the same before the stage and partly by installing a closed screening system before the oxygen stage. The presence of black liquor caused a certain impairment of the quality of the oxygen bleached pulp especially in respect to the viscosity of the same. Furthermore the black liquor caused an increased consumption of oxygen but a decreased alkali demand. If one wishes to produce a fully bleached pulp with strength properties comparable with those in pulp bleached with conventional bleaching sequences, it is recommended to ensure that the amount of unoxidized black liquor dry substance, which follows the pulp into the oxygen reactor is not exceeding 20 kg/ton of pulp.

At the conditions, which were existing during the period, when the screening system was closed, the washing on the filters, which followed after the oxygen stage, was more effective for inorganic material than it was for organic material.

From both mill and laboratory trials the following conclusions could be made:

1. The final shape of the chlorine stage is of great importance for the finally bleached pulp its strength properties and its viscosity. With chlorine dioxide present in the chlorine stage a significantly higher viscosity and tearing strength of the pulp was obtained. Additionally the environmental polluting discharges became smaller.
2. Strong delignification in the oxygen stage (≥ 60 %) resulted in lower strength properties of the finally bleached pulp compared with a pulp bleached in a conventional 6-stage bleach plant.
3. Bringing back waste liquor from the oxygen bleaching to the following chlorine stage resulted in a certain decrease of the viscosity providing chlorine dioxide was not added in the chlorine stage. When black liquor was transferred to the chlorine stage in a conventional sequence the result was also a decreased viscosity.

White liquor and green liquor besides NaOH was also tried in the oxygen stage. When solely white or green liquor was used a distinct impairment of the viscosity of the oxygen bleached pulp was obtained, while the oxygen consumption also increased. When half of the alkali was NaOH and the other half white liquor or green liquor a fair viscosity could be maintained. Through the use of only white liquor, which had been oxidized negative effects regarding the viscosity and the chemical consumtion could be avoided.

In summing up the mill trials and the laboratory trials, which were carried out with pulp from the mill it can be concluded, that with a oxygen sequence OC/DEDED a delignification of about 53 % (Kappa-number after the oxygen stage 15,5 - 16) produced a pulp with the same strength properties as a pulp bleached in a conventional sequence CEHDED. How big a degree of delignification which can be allowed in practice depends to a large extent upon which variations in the lignin content of the unbleached there are. Therefore a rigid control of the cooking of the pulp is an important complement to the oxygen bleaching.

When establishing the effects of the environmental measurements it must be pointed out that regretably the determination of the BOD_7-values is rather uncertain. The reduction of the values when changing from the CEHDED-sequence to the OC/DEDED-sequence at about 53 % delignification, about 20 kg unoxidized black liquor substance per ton of pulp to the oxygen reactor and about 80 % waste liquor recovery, will be about the following percentages:

BOD_7 (Biochemical oxygen demand)	45 - 50 %
COD (Chemical oxygen demand)	55 - 60 %
Colour (Pt)	70 %

The degree of delignification seems to be of less importance in regard to the BOD_7-value than to the colour.

The introduction of oxygen bleaching results in an increased load of 3 to 5 % on the recovery boiler caused by a higher amount of dry substance. In a mill where the recovery boiler is the bottle neck this will mean a reduced production. When oxidized white liquor is used to 100 % in the oxygen stage an increased capacity in the causticization and reburning of the lime is required, which can be about 7 %. The transfer of waste liquor from the oxygen stage can also require increased capacity in the evaporator room providing the washing of the pulp after the oxygen stage is not sufficiently effective.

The increased investment costs for the installation of an oxygen bleach plant is about:

10	million SwCr for a capacity of 300 tons/day 90 % unbleached pulp
22 - 23	million SwCr for a capacity of 900 tons/day 90 % unbleached pulp

If a recovery of 80 % after the oxygen stage shall be achieved, the two filter stages must function very well, if the above mentioned gains of the environmental measurements shall be fulfilled.

At a oxygen price of 0,20 SwCr/kg the yearly operating costs compared with those for a conventionel bleach plant will be about the same in the first case but about 1,9 million SwCr lower at a production of 900 tons/day.

An interesting application of oxygen bleaching is in the manufacturing of semi bleached sulphate pulp, which has been studied at Husum mill. A pulp with a brightness of 50 - 55 % SCAN was produced. This pulp has been afterwards tried as an enforcing pulp in newsprint paper with a very good result.

At the same mill the bleaching sequence OCED has also been tried. A brightness of the pulp of 89 % SCAN was obtained during the trial period of three weeks.

At the Norweigian University of Technology one has among other things studied the sequence OC/DPD. With a peroxide addition of 0.9 % and an addition of 2 % chlorine in the chlorine dioxide stage a brightness of 92 % SCAN with acceptable viscosity of the pulp was obtained.

When birch or hardwood pulp is bleached with oxygen, the gain regarding the environmental care in absolute figures is lower than oxygen bleaching of pine sulphate pulp. This is due to the fact that the lignin content of unbleached birch or hardwood pulp is lower than in pine or softwood pulp. When the delignification is carried quite far, over 50 %, a strong decomposition of the cellulose will take place as well as at the same time a lower yield and viscosity is obtained. A suitable Kappa-number after the oxygen stage seems to be 9 to 10.

Oxygen bleaching of magnefite pulp has also been studied. A delignification of a magnefite pulp (Kappa-number 30) to about 50 % required about 20 kg NaOH per ton of pulp. The delignification in the presence of only $Mg(OH)_2$ became as low as 10 - 20 %. This will mean that in the recovery of the waste liquor from an oxygen stage in a magnefite mill sodium salts will be introduced in the recovery system. Furthermore this will mean that the economical conditions for an introduction of oxygen bleaching is considerably less in a magnefite mill than in a sulphate mill.

Pilot oxygen bleaching plant for bleaching of pine sulphate at Husum mill

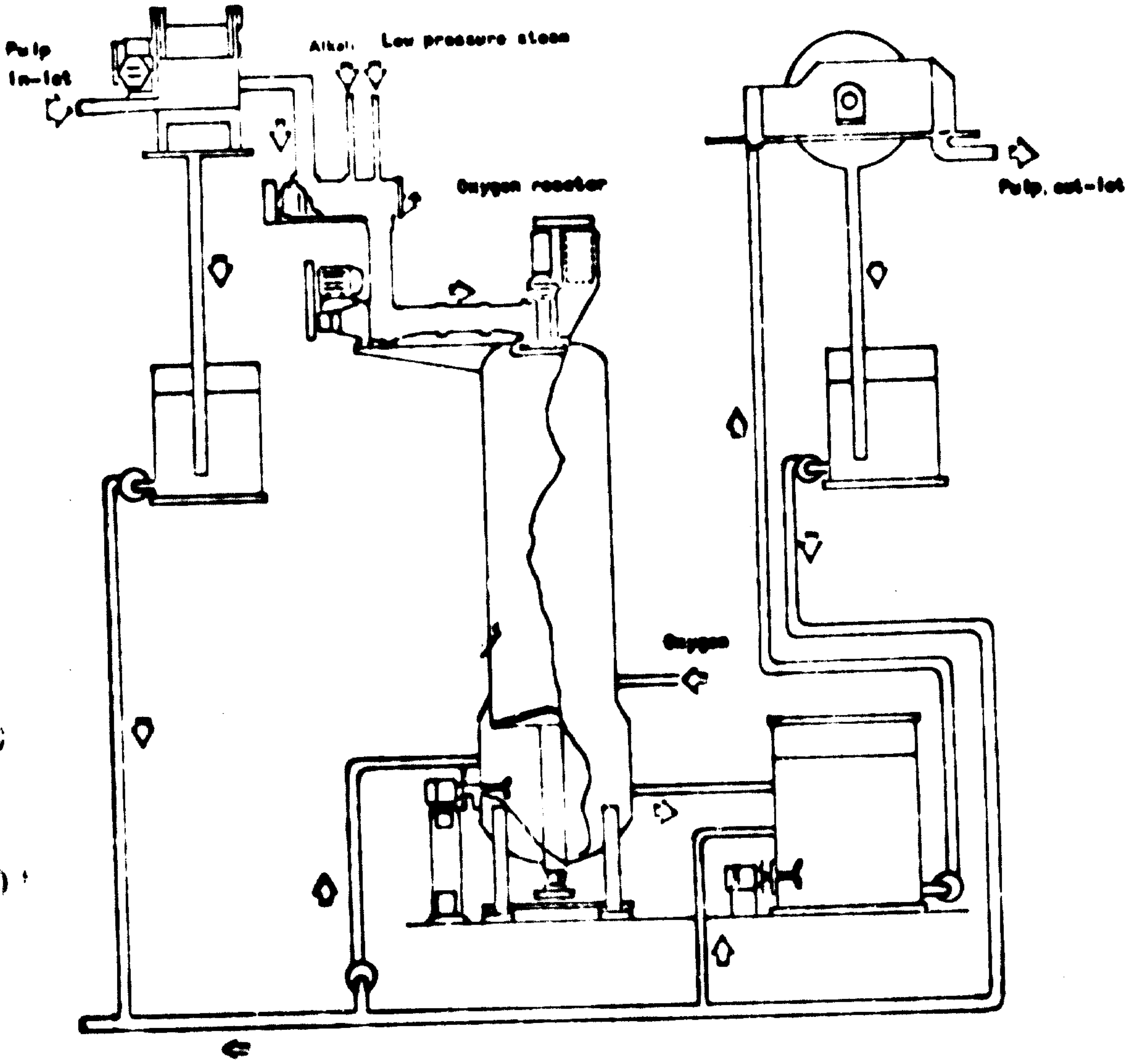


Figure 96:1

Table 96:1

Properties and discharges for different bleaching sequences

Property		Sequence					
		CEHDED	OC/DEDED	CEDED	OC/DE/HD	OC/DE/HD	OC/DED
Kappa-number after oxygen stage		-	13,2	-	12,0	9,8	12,7
Delignification in the oxygen stage %		-	61	-	65	71	63
Brightness	% (SCAN)	92,5	93,4	90,7	90,0	89,5	89,9
Viscosity	cm^3/g	1 004	865	1 007	856	759	850
Viscosity	P (TAPPI)	(82)	(52)	(83)	(50)	(36)	(49)
Tear factor at 7000 m breaking length		170	174	157	158	152	(152)
Discharges							
BOD_7	kg/ton 90 % unbleached pulp	17,3	8,5	18,0	9,7	7,9	9,9
COD	- - " - -	74,5	33,3	78,0	31,9	26,0	31,7
Colour (Pt)	- - " - -	186	42	180	30	21	36

Remark: There exists a relation between intrinsic viscosity and the TAPPI viscosity, which can be found in the literature

Closing of the Bleaching System

The closing of the water system in a bleach plant is primarly carried out in order to reduce the consumption of water and thereby the amount of waste water. From environmental care point of view the closing of the system results in a decreased load on an external purification stage at the same time as the handling costs of the water is decreased. The same results also in a decreased discharge of fibres and most likely also marginal reductions of the discharged quantities of BOD$_7$ and coloured substances. Furthermore it can result in a saving of heat.

The closing of the chlorine stage will not result in changes of the properties of the pulp, but it can cause operative disturbances. However, it will result in increased costs for alkali in the E$_1$-stage.

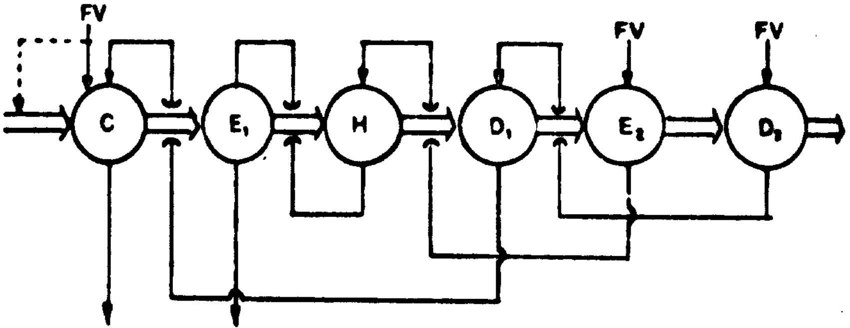
The returning of hypochlorite white water will give small advantages in respect to the environmental care as for instance reduced colour in the E$_1$-filtrate and no effect on the properties of the pulp. When applied it can reduce the costs for chemicals in the stage mentioned.

It is possible to contemplate at least three main principles for the closing of the water system in a bleach plant. See the following figures.

A. Returning the white water (filtrate) in one acid and one alkaline line.

B. Bringing back the white water (filtrate) in a strict counter current stream.

C. A mixed counter current washing comprising of a combination of A and B. This type of closing is recommended by many among other things with the motivation that it will be able to give the lowest costs for chemicals.



A. Return in one acid and one alkaline line

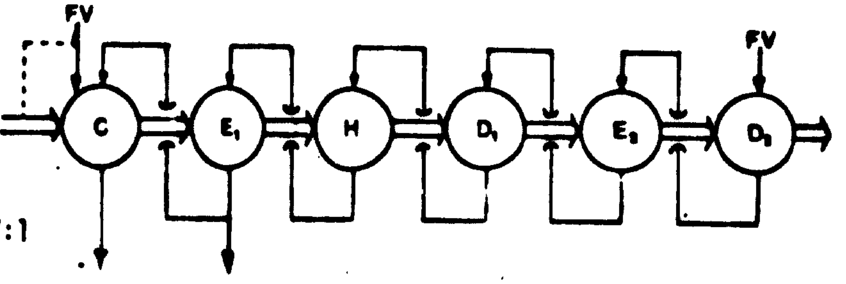


Figure 97:1

B. Return in strict counter current line

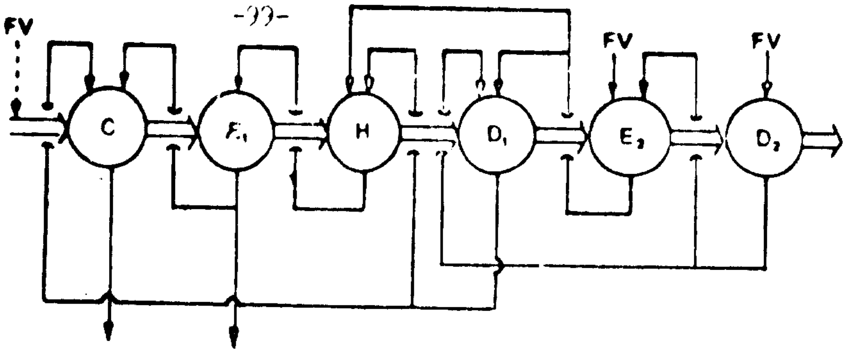
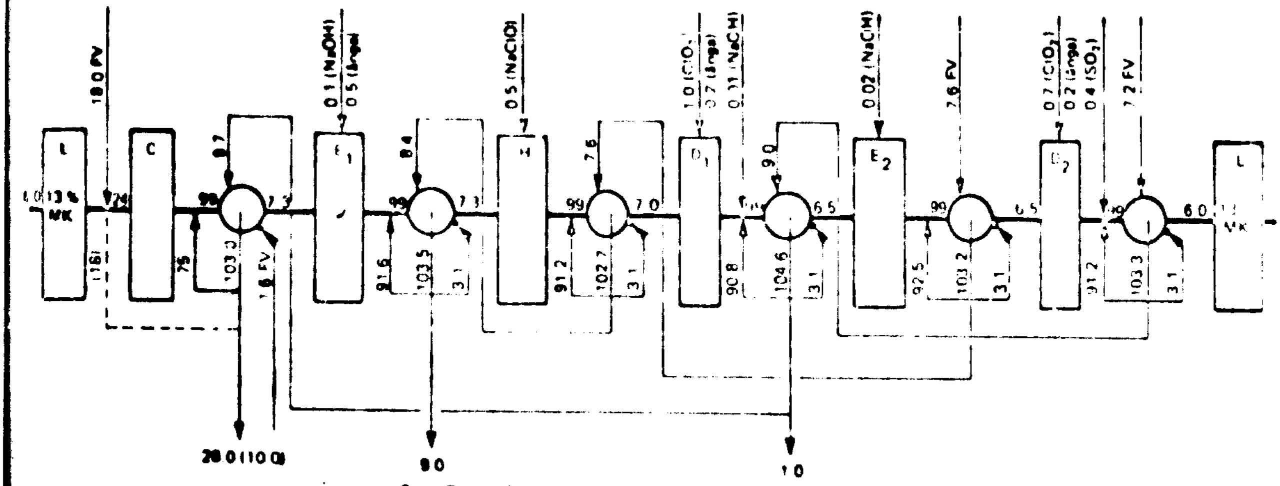


Figure 98:1 c "Mixed counter current washing"



Bas Ton H_2O/ton 90 % blekt massa

Σ Färskvatten 34.4 (18.4)

Σ H_2O med kemikalier 2.7

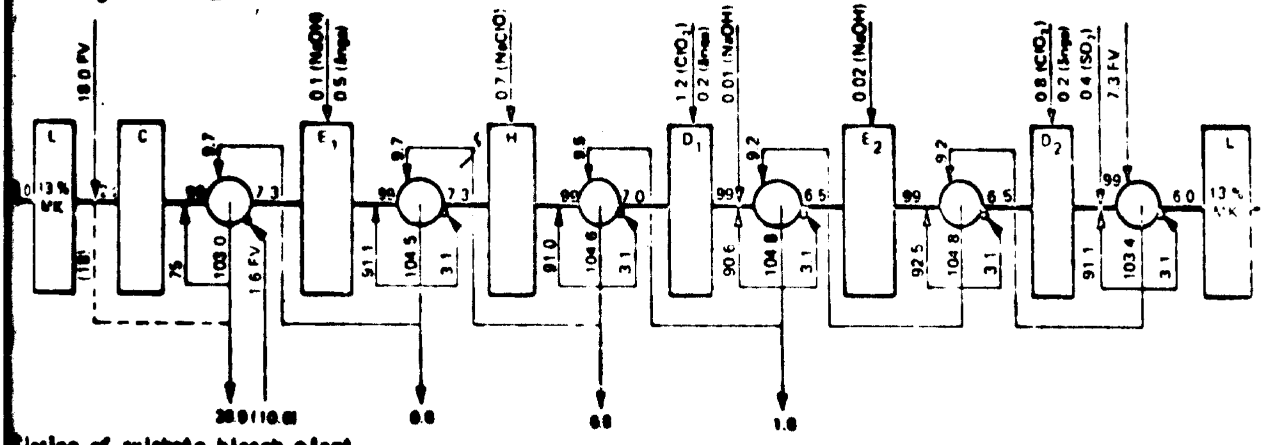
Σ H_2O som ånga 0.9

Total in 38.0 (20.0) ton/ton massa

Σ Avlopp 38.0 (20.0) ton/ton massa

Closing of sulphate bleach plant
Alt 1. (Alt 2)

Figure 98:2



Closing of sulphate bleach plant
Alt 3 (Alt 4).

Bas Ton H_2O/ton 90 % blekt massa

Σ Färskvatten 28.0 (8.0)

Σ H_2O med kemikalier 3.2

Σ H_2O som ånga 0.9

Total in 31.0 (13.0) ton/ton massa

Σ Avlopp 31.0 (13.0) ton/ton massa

Figure 98:3

The following alternatives for the closing of the white water system from process and operative point of view has been investigated.

1. Returning in an acid and one alkaline line (A). Open chlorine stage
2. Returning in an acid ond one alkaline line (A). Closed chlorine stage
3. Returning in a strict counter current stream (B). Open chlorine stage
4. Returning in a strict counter current stream (B). Closed chlorine stage

The amounts of discharged water in the four alternatives has been calculated, and the result is shown in the following table.

Table 99:1

Alternative	Effluent discharge m^3/ton 90 % bleached pulp
1	38
2	20
3	31
4	13

The first alternative corresponds to what can be achieved with the best technique of today without any great disadvantages.

The next alternative no 2 is considered to be able to cause complications in the form of foaming on the chlorine filter resulting in decreased capacity difficulties to control the temperature during the chlorination and so on.

Alternative no 3 can give problems when acid and alkaline liquids are mixed on the chlorine filter and in maintaining the correct temperature in the hypo chloritesstage.

Alternative no 4 will give the same complications as alternative no 2.

Treatment of Waste Liquor from the Bleach Plant

Besides a modification of the bleaching or the introduction of new bleaching processes as oxygen bleaching it is possible to reduce the effect of the waste waters from the bleach plant upon the environment by treatment of certain discharged effluents in different ways. The costs are in that case very much depending upon the magnitude of the amounts of waste water discharged, which shall be treated, that is upon the degree of the closing of the system in the bleach plant.

There exist treatment methods, which have a practical application, while others are being developed. Today mainly precipitation with lime and biological purification (in combination with other discharged effluents) is in practical use. In Japan a precipitation with iron and lime is applied.

Methods which are being developed comprises among others treatment with ionexchangers, adsorption by active carbon, amine extraction and reversed osmosis.

Lime and Iron/Lime Precipitation

In principle the method using lime for the precipitation is carried out by treating the filtrate from the two E-stages, after this has been used in the wood room. The precipitation is carried out with lime added as milk of lime. The lime sludge is separated by sedimentation. The sludge is dewatered further after an addition of lime mud. Thereafter it is fed to the kiln for reburning.

Based upon laboratory investigations the consumption can be determined, and the following results listed in the table below have been obtained.

Table 100:1

	Primary alkali stage		Screens + primary alkali stage	
	300 t/d	900 t/d	300 t/d	900 t/d
Specific costs SwCr/ton 90 % unbleached pulp	9,70	7,15 - 7,80	13,85	9,65 - 9,80
CaO addition, t/d	23	69	30	90
Decrease in BOD$_7$ %	about 30		about 30	
" " Pt-colour %	80 - 90		80 - 90	

The method of using iron/lime for precipitation is carried out by using an iron solution (Fe^{2+} - Fe^{3+}), which is made by dissolving iron metal in the form of scrap in waste water from the C-stage on the bleach plant. This iron solution is mixed with the waste water (filtrate) from the E-stage. Lime is then added in order to increase the pH. There will then take place a precipitation of Fe-organic (and most possibly also Ca-organic) substances and Fe-hydroxide. The precipitated substance is forming flocks, which are seperated by sedimentation. The sludge is afterwards thickened, dewatered and burned.

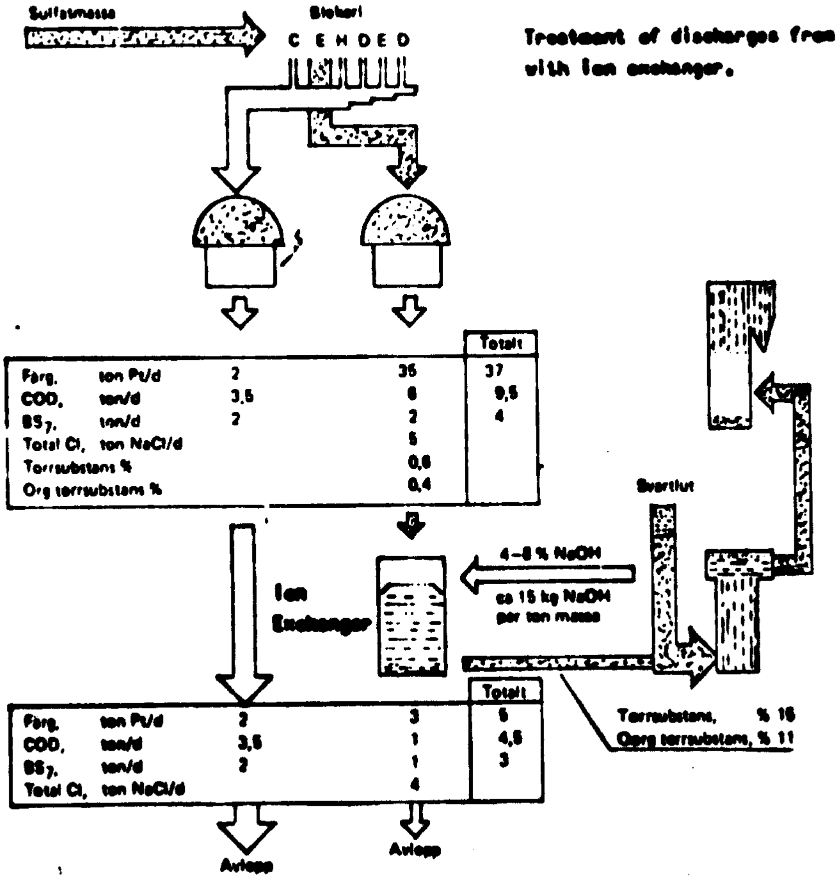
Biological Purification

Biological purification of effluents from the bleaching in combination with other effluents has got its application in USA and Canada in a number of mills. The reduction of BOD_5 is supposed to be between 60 and 80 %. Biological purification will be dealt with later in this paper.

Ion-Exchangers

Among the methods being developed a special interest should be given the treatment of waste water from the first alkali stage with ion-exchangers. The method, which has been developed by the Uddeholms AB, is now being retried in full scale in order to confirm earlier obtained laboratory results. These indicate a purification effect in practise of 95 % for coloured substance and 60 % for BOD_7.

The following figure shows how a treatment of waste water from the bleach plant is carried out with ion-exchangers.



Treatment of discharges from the bleach plant with ion exchanger.

Figure 101:1

Active Carbon

At St Regis Paper Co, Pensacola, Florida, USA development work is carried out to produce active carbon as a biproduct from the recovery system in the sulphate mill, and investigations are being made to use tha same for the purification of the waste water from the bleach plant. These investigations will be reported very soon.

Reversed Osmosis

The use of reverse osmosis for the concentration of different discharged effluents from the forest industry is since 1966 being investigated by the Institute of Paper Chemistry (IPC), Appleton, Wisc., USA. The costs for purification of waste water from bleach plants are considered to be too high at present.

TEMPORARY DISCHARGES

The total discharges from a pulp mill can be divided partly in "normal process discharges", which depend upon the lay out of the process and upon the equipment used, partly in temporary discharges. These are such discharges, which to an essential degree surmount those for the process and for the equipment normal discharges or which in some other way are not normal for the process during the operation.

The temporary discharges can be divided in three main groups according to cause:

Faults in the equipment (Example: A hole in the filter cloth)
Human factors (Example: Forgotten valve to the sewer)
Mishandled control (Example: Running over of liquor tanks when the process is operated out of the line)

According to investigations made and all information collected the temporary discharges correspond to 20 - 50 % of the total discharges of chemicals and to 30 - 50 % of discharged fibers from the mill.

Temporary discharges are often of a short nature (10 minutes). The extremly short discharges can therefore only be discovered either by continous measurements and control of sewers or by taking samples with short intervals.

Investigations made in the Swedish pulp and paper industry revealed that through temporary discharges about 80 000 tons of fibermaterial are lost yearly to the recipients. Furthermore it was established that temporary discharges of chemicals from the sulphate mills corresponded to about 100 000 tons per year as Na_2SO_4. The value of the lost substance is estimated to about 10 SwCr per ton of produced pulp.

Below some of the most common reasons for temporary discharges are listed:

Faults in equipments

Digesters	Leakage in heat exchangers
Screen room and Bleach plant	Torn holes in the filter cloth, inferior sealin of the filter drums
Liquor system general	Leakage in pumps. If the sealing water is leaking into the liquor the evaporators are more loaded
Tanks and Pulp chests	Not correct indicating level indicators cause over flows Pipe fractures close to the tanks can result i large discharges
General	Power failures result in serios disturbances in the operation, which often are followed by temporary discharges

Mismaneuvering

Digesters	Blowing over of liqour from the blow tank is easely done, if its blown too warm. The large gas volumes is then overloading the blow tank
Wash room	Overloading results in foaming and over flows from the wash filters
Screen room	Rejects are temporarly diverted to the sewer, and from there they are pumped to the sedimentation instead of being returned to the system
Bleach plant	Unevenly cooked pulp from the digesters can result in diffuculties to add correct amounts of chemicals in the bleaching stages, which easy can cause increased discharges
Evaporator room	Foaming and over flows because of overloading. If the skimming of tall oil is not functioning, a condensate is obtained, which cannot be reused and thus has to be discharged
Tanks and Pulp chests	If a too high production level is demanded temporary discharges are forced forward, especially if the pulping section has a higher capacity than the liqour section
Causticization	Over flows of mixersand liquor tanks. Over flow of water from the lime kiln scrubber
External purification systems	Fiber recovery installations and settling basins are overloaded
General	Start and stop routines are often such that temporary discharges cannot be avoided

Human factors

Evaporator room	Mismaneuverings at coupling or decoupling of the evaporator effects when being washed can result in foaming and discharges of liqour
Bleach plant	Discharges of gas force the personnel to leave the plant
Tanks and Pulp chests	Over flows
General	Mismaneuverings because of lack of training, not sufficient operating instructions or inattentiveness

There are reasons why temporary discharges are so little observed in spite of the considerable consequences, which they have in regard to the environment and the costs being caused the industry.

The temporary discharges are often caused by human factors. The operator or the foreman does not always have time to take all flows, levels, buffer-storages and so on, which influence the process, into consideration. Sometimes this can mean that temporary discharges will not be known to the managemant.

Another cause is the conflict between the choice of temporary discharges and an undisturbed production. Because of economical reasons a temporary discharge is prefered than a loss of the production.

Measurements in order to avoid Temporary Discharges

The Possibility of Controlling the Process

Already when laying out a flow diagram for a process one should have in mind the possibilies to avoid temporary discharges. At an early stage in the planning start and stop routines should be discussed as well as also interlockings and catastrophy routines. The control should be so arrange that the operator with so simple maneuvers as possible can increase or decrease the production. The risks connected with different disturbances in the operation shall be weighed against each other so that a maximal security at a resonable cost is obtained. This philosophy shall then reflect itself in the operating instructions. In this the personnel shall be given clear and unbiased instructions, which also concerns the operation in adjacent departments. The operating personnel have often difficulties to se "their" equipment as a part of a long production chain. When there is a question about how much buffer tanks between departments shall be filled, conflicts can arise between the same.

Dimensioning of Process Equipment and especially Tanks and Chests

In general tanks within single process departments are a part of the process itself. Their main purpose is to give enough retention time or equilibration of fluctuations of concentrations of the through flowing media. The volume of the tanks are so determined, that required retention time is achieved at maximal production.

Tanks and chests between different process departments function as intermedia storages and must be dimensioned so that one department can be operating even if departments before or after the same are stopped.

A third category of tanks are those so called collecting reservoirs. These make an extra buffer capacity and in the same various discharges are collected.

To determine the volume of a collecting reservoir is not as simple as t dimension a process tank. If one only considers the time it takes for an overflow from a tank within the process because of for instance lack of information (incorrect instrumentation) or watchfulness, moderate volumes are adequate in comparison with the tanks within the process itself.

It is easier to estimate a suitable volume of a collecting reservoir, if one desires to have the reservoir on hand in order to make it possible to empty the ordinary process tanks for inspection and maintenance. A collecting reservoir shall then be so dimensioned, that one or several tanks can be emptied to the same without anything going to the sewer. If such aspects are laid upon the dimensioning one collecting reservoir will in most cases be so big, that it can receive unintentional overflows from process tanks during normal operation or at stop and start during a sufficient long time, so that measurements are ready to be taken before the collecting reservoir in its turn will over-flow.

A mill should have collecting reservoirs, which form the last link in the chain. For instance it is suitable to place a collecting reservoir one before and one after the soda recovery boiler, as it is unsuitable to mix pure inorganic liquor with black liquor. The content in the collecting reservoir should slowly be returned to a suitable point in the process. An example how this can be made is shown in the figures on page

Damming up of Equipment

In a sulphate mill there is a great number of tanks for liquor and oil, e g thinn liquor, intermediate liquor, mixing liquor, thick liquor, green liquor, weak liquor, white liquor and oil for burning. Furthermore there are tanks for e g sulphuric acid and sodium hydroxide. Safeguards in the form of dammings or embankments are required according to regulations only for certain inflamable material. However these regulations cannot be applied for above mentioned different kinds of liquor. However, in order to make possible a satisfactory safeguard against temporary discharges, every tank should be provided with overflows to collecting reservoirs. If this is not possible they should be provided with an adequately designed overflow to embanked pond or placed within a damming or an embankment. The latter should have such a size that the operating personnel will have time to take measures against overflows, before its volume is completely utilized.

The damming should not have any outlet. Rain water and eventuel overflows shall be removed via a pump pit within the damming itself. The ground should be made tight so that no out flow via the ground water is taking place. Such overflows should be returned to the process.

Superintendence

In order to avoid that tanks are leaking because of for instance corrosion, they must be regularly inspected, when the degree of corrosion is measured, and other measures are made to detect leakages in the same.

In order to prevent overflows to occur and secondly to collect overflows and leakages in concentrated form to be reused a protection system can be laid out in the following manner:

Continous measurement of the level in all tanks

Sounding alarms for high levels from a separate gauge
Embankment outside the tank
Sounding alarm for high level inside the embankment

The size and the frequency of overflows depend to a large extent upon the attention from the personnel. In order to facilitate a better superintendence every tank should be provided level measuring instrument (indicating or registrating). Besides this the tank should be provided with an alarm for high level (about 95 % full), which receives its impuls from a separate gauge.

In the pulp industry an efficient measurement of the level is made difficult because of the properties of the liquor to incrust, corrode, foam, sediment and so on.

All equipment for the superintendence of tanks and embankments should be regularly controlled in order to prevent faults and to maintain a high operating security.

Internal Measures in the Process Departments

As a principle for all internal measures in the process departments process and discharge systems and sewer systems should be so planned that discharges can easily be collected so close to the source as it is possible and so that it can be returned the shortest way to the process.

These measures are of the following type:

Equipment shall be so dimensioned that unnecessary bottle necks exist in the process

Interlock the equipment electrically so that start respectively stop take place in a correct order

Around equipment where overflows often occur embankments with separate outlet to a suitable reservoir should be made

The equipment should be on levels so that spillways can be arranged from a process technical point of view in a suitable manner

All equipment for collecting temporary discharges shall be dimensioned according to the largest possible discharge expected

All environmental protecting equipment should be so formed, that the personnel will have a minimum of extra work. Otherwise it will be difficult to maintain the same at good working conditions

Examples of these measures are demonstrated in the figures on page

The Lay Out of the Sewer System

Included in the measurements against temporary discharges are not only the installation of buffer tanks, dimensioning of equipment, superintendence and control but to a large extent also a correct lay out of the sewer system. The sewer system shall be so differicienteed and so flexible that the continous and temporary discharges from the different departments of the mill can be returned, diverted for treatment or only discharged, if no treatment is required.

In the conception sewer system the final outlet of the discharges to the recipient is of course included.

Under certain conditions it can be relatively easy to plan a sewer system, if there is no need to take a changing attitude from the authorities or decided changes in the process or relocation of certain parts of the process into consideration.

In spite of these reservations it can be appropriate to have a model to work from. Therefore a SSVL-group has made studies of a few newly laid out sewer systems and tried to combine these in an ideal solution, which is demonstrated in the attached figure.

Each discharge is guarded by a system in which sampling equipment and measuring gauges.
At normal operation purified discharges can be contaminated due to operating disturbances or break downs of machineries. Conductivity guards give then an alarm and by these contaminated water is diverted to those waste liquor containing discharges, which shall again treated in the evaporators. At installations of this type a throrough superintendence and control of these guards must be exercised so that the unnecessarly diverted water into the evaporator system, thus not will cause increased operating costs. A single liter/min which unnecessarly is diverted this way will result in an extra cost for steam of about 600 SwCr per year to evaporate, and it requires an extension of the evaporator and the recovery boiler capacity for about 5 000 SwCr.

Basically it is common to distinguish between three types of industrial sewer systems, namely such ones for sanitary water, rain and cooling water and process water.

According to common practice the sanitary water is directed to the community for treatment, while rain water and cooling water, which is regarded as pure, directly can be discharged to the recipient.

The process water discharge is divided in a number of separate systems before the purification of the same.

Water containing bark sludge is directed through a special sewer to a settling basin for treatment.

Fiber containing discharges contain such large amounts of fiber that it must be separated before it is finally treated to recover the same.

This is done in a sedimentation basin. After the same the pipes are combined again.

It can be suitable to arrange a special system for process water, which contains dissolved organic substances and chemicals but not fibers. This can be applied to floor drains from the digester house and the alkali preparation department and to excess condensate. These drains are connected through collecting reservoirs to be treated for recovery of the chemicals.

From a bleach plant acid and alkaline discharges are diverted normally separated, and a mixing of these take place at a suitable point outside the mill. It is then directed in the same pipe to the sedimentation basin or eventually as fiber free water to the recipient.

When combining different discharges there is a risk that hydrogen suplhide and other poisonous gases can be formed. Great care must therefore be excersiced that the water seal against the mill department is functioning all the time.

Training

It cannot be enough emphasized the importance of the training of the personnel in environmental protection care. It is difficult to limit this training to a special part. The best result will be obtained if the training is integrated in the normal training of the mill personnel.

ilaga

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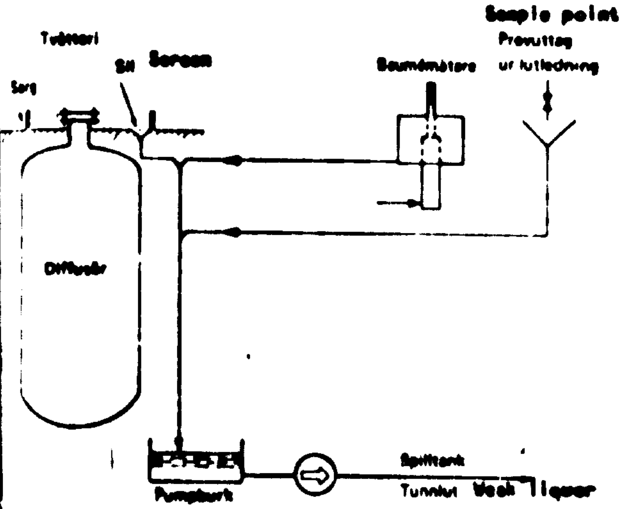
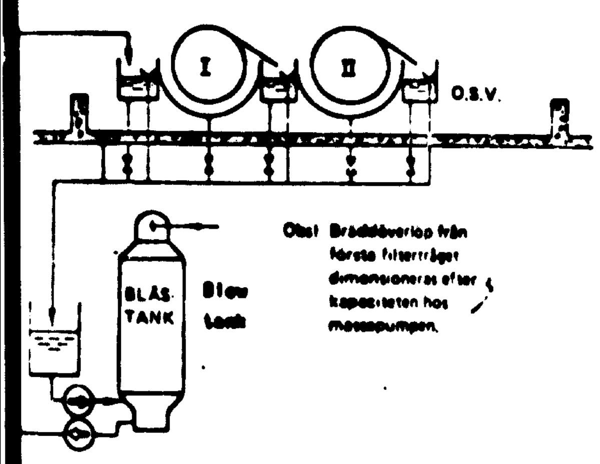
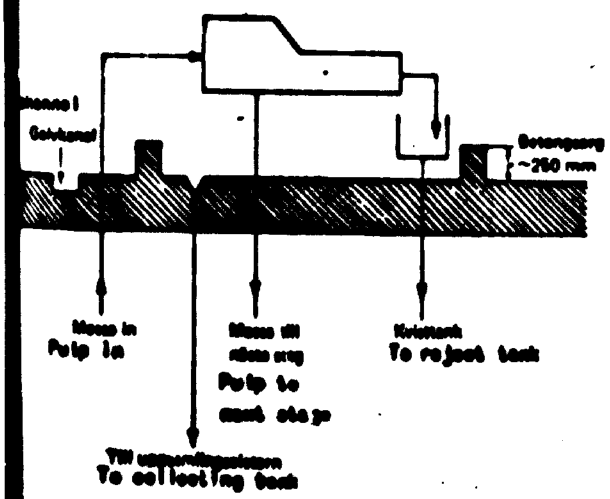


g 1 *Invallning av diffusörhuset.*



Obs! Bräddöverlop från första filterträget dimensioneras efter kapaciteten hos massapumpen.

g 2 *Invallning av filterhuset.* **Embankment of washers**



3 *Invallning av kvistfångare.*
Embankment of knotters

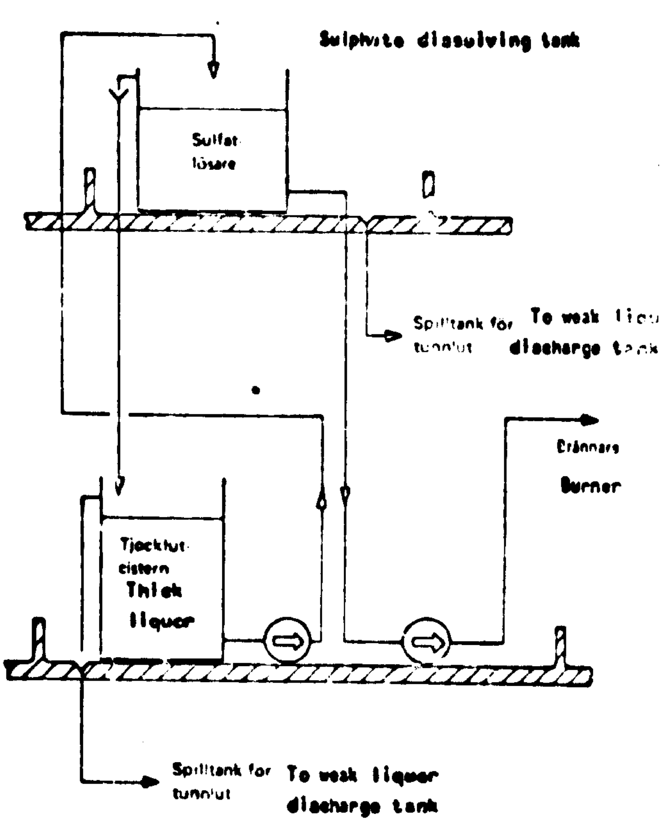


Fig 4 *Invallning av sodahus.* **Embankment of soda recovery plant**

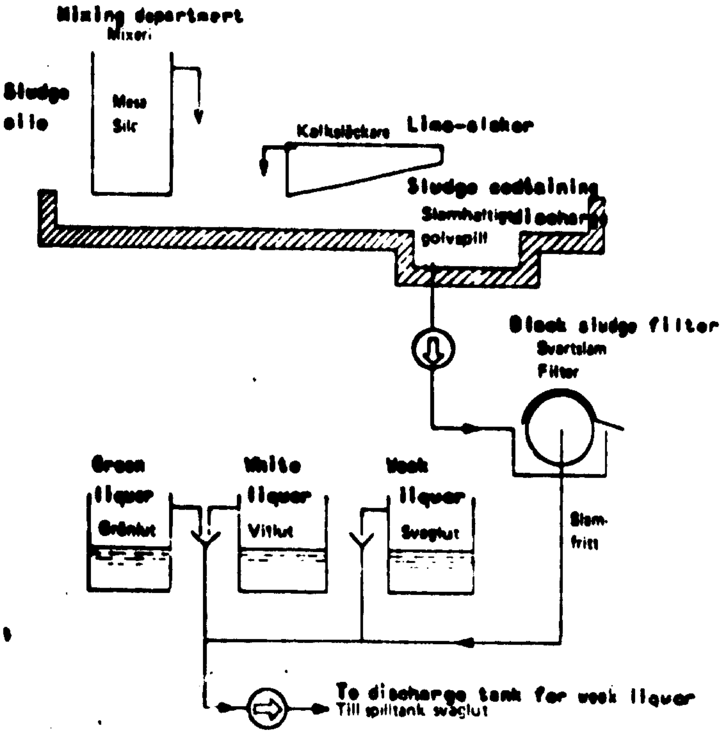


Fig 5 *Invallning och överlopp i mixeri.*
Embankment of over-flows in mixing department

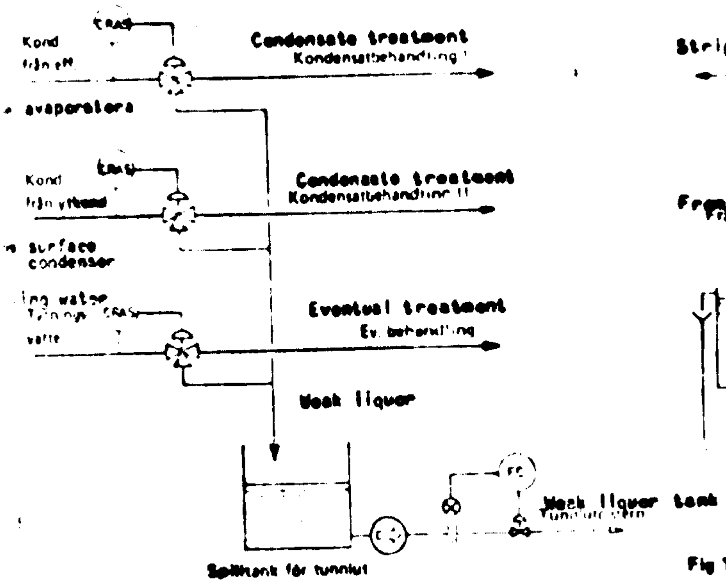
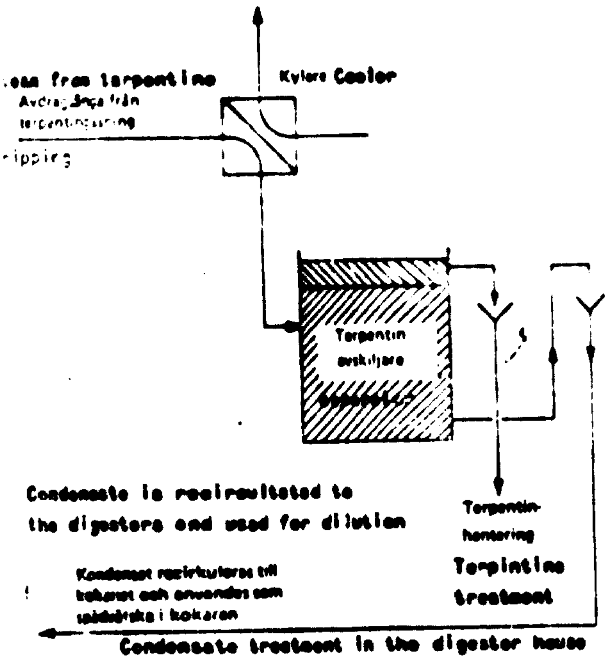


Fig 11 *Kondensatvakt vid indunstningsanläggning.*

Condensate guard in evaporator plant



Condensate treatment in the digester house

Fig 12 *Kondensatbehandling i kokeri.*

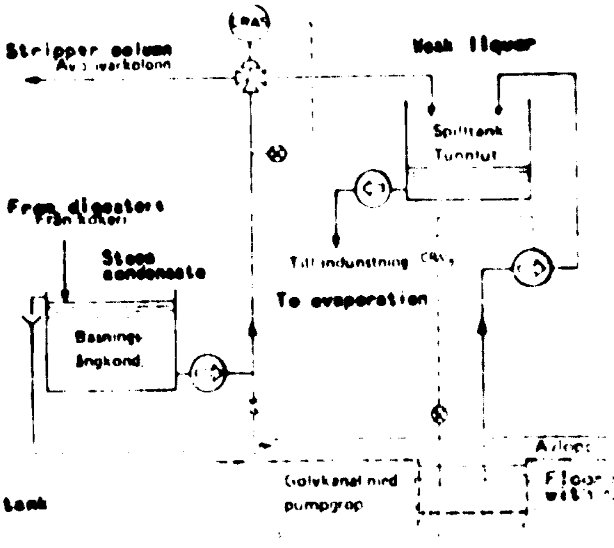
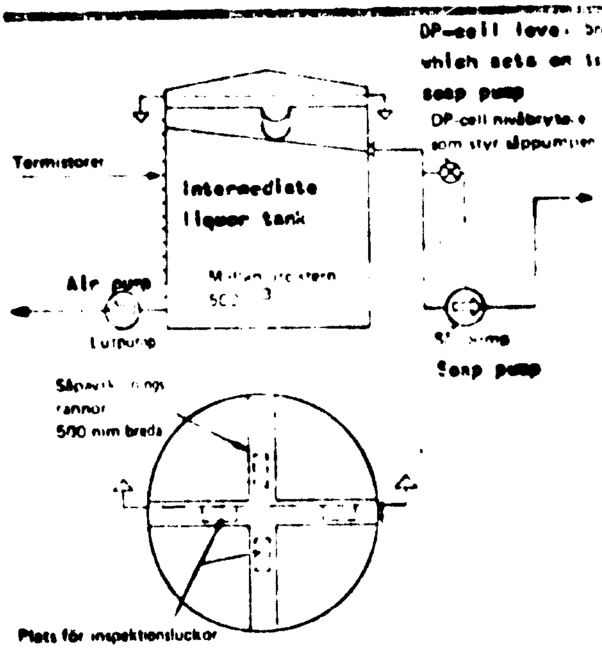


Fig 13 *Kondensatbehandling.* Condensate treatment



Separation of soap in intermediate liquor ta...

Fig 14 *Såpavskiljning i mellanlutcistern.*

Comprimation of soap foam by circulation pumping
Komprimering av såpskum med rundpumpning

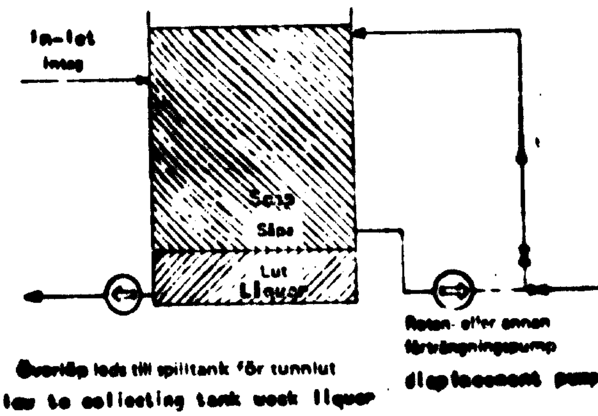
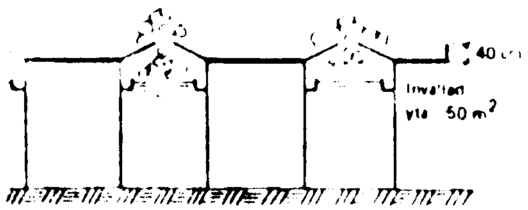


Fig 15 *Såpavskiljning.*
Soap separation

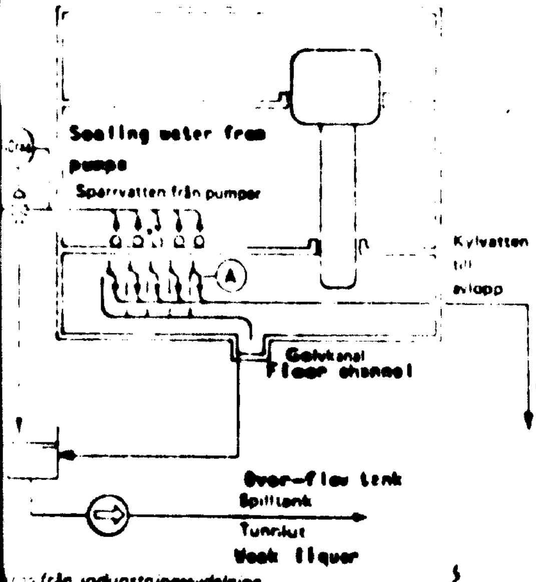
mbankment of the type of three soap tanks
Typen av 3 såpcisterner à 40 m^3 invallade

s rymd ~ 20 m^3

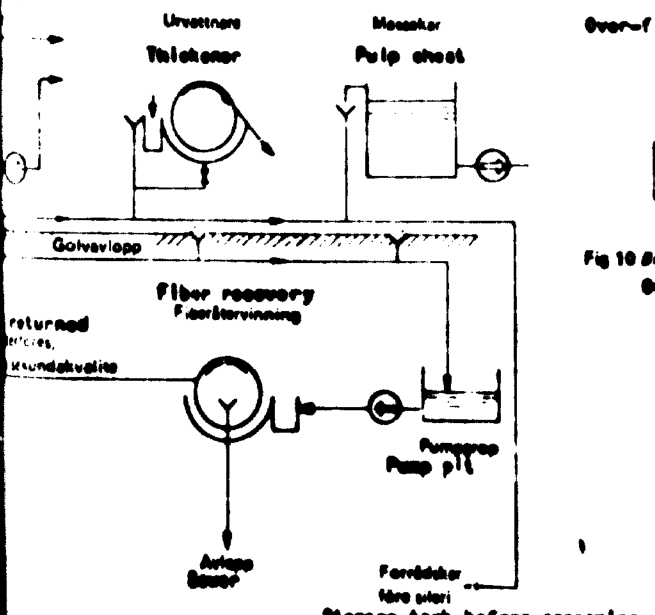


ad yta i detta fall 50 m^2 = large surface embanked
och släcker såpskummet cools down and kills foam

ning vid såpavskiljning Embankment of soap separation

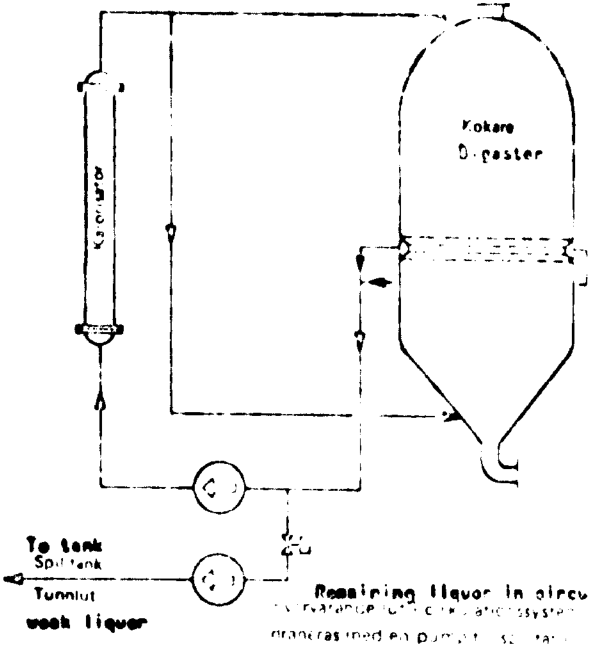


från indunstningsavdelning
charge from evaporator room



Storage tank before screening

rhos och bräddöverlopp i sileri. Floor gutters and over-flow in screen room



Remaining liquor in circulation
Kvarvarande lut i cirkulationssystemet
dräneras med en pump till spilltank
system is drained with pump to over

Fig 9 *Dränering av ledningssystem i satskokeri*

Draining of line system for batch digesters

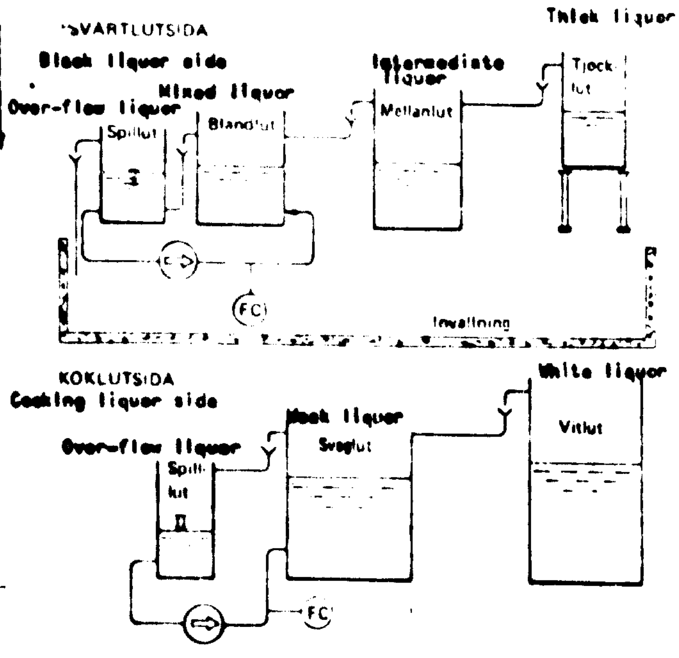


Fig 10 *Bräddoverlöp för cisterner.*
Over-flow from tanks

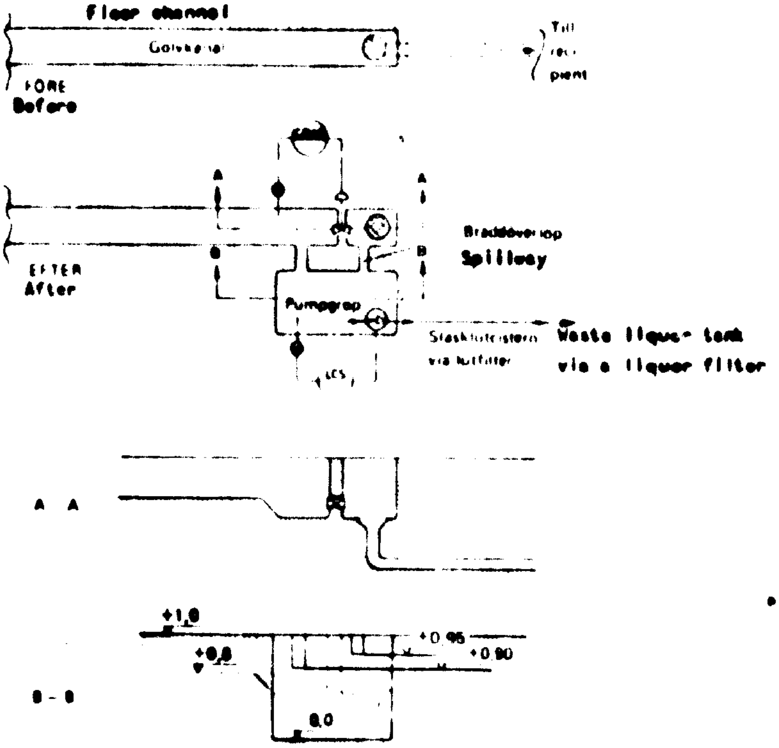


Fig 16 Ombyggnad av avloppskanaler i koker, tvätteri, indunstning eller mixeri. Rebuilding of discharge channels in digester, screening, evaporator or mixing department

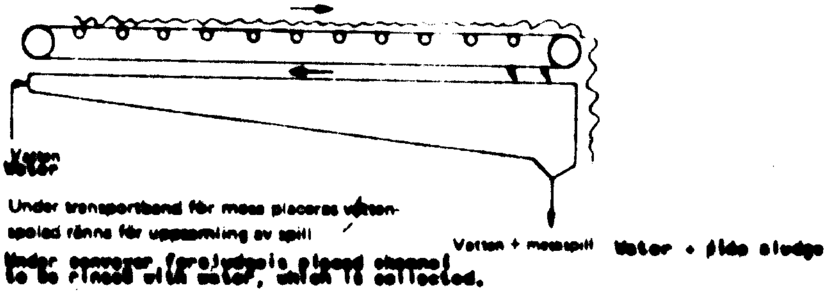


Fig 17 Återföring av massaspill i mixeri. Returning of sludge over-flows in the mixing department

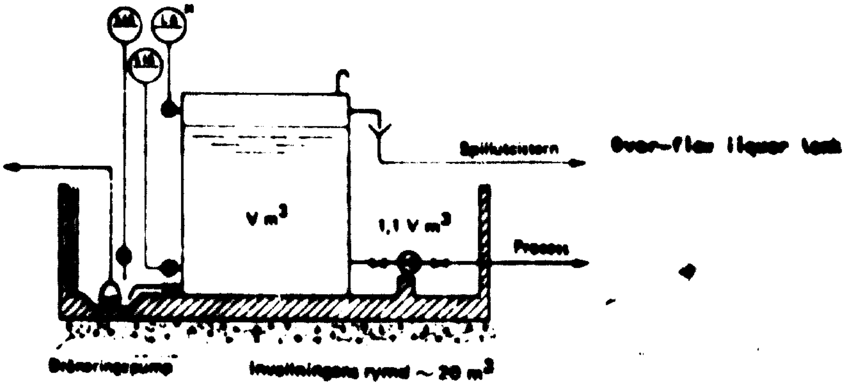


Fig 18 Invallning av cisterner och apparater. Embankment of tanks and apparatuses.

EFFLUENT CONTROL BY CLOSING THE WATER SYSTEM IN THE PAPER MAKING PROCESS

Overflow water created in the paper making process contains materials in different forms as suspended particles and dissolved compounds. The suspended material are mainly fiber fragments and fillers as kaolin, while the dissolved materials consist of wood substances as carbon hydrates, lignin and resin compounds. All these materials will follow the excess water from the paper machines to the recipient, unless they are not removed by some kind of purification treatment of the white water. From the viewpoint of environmental control thus the handling of the white water is the main problem.

However, there are two good reasons for being concerned about the effluents from a paper machine and its white water system. These are to:

1. Reduce pollution of the receiving water
2. Retain all valuable substances and expensive raw materials, which are existing in the excess process water

It is self-evident that the lower the volume of water can be kept the easier, economically as well as technically, the elimination of the pollution hazard caused by the solids and the dissolved and colloidal materials can be carried out. In order to achieve this consequently it is necessary to close the white water system so that excess water from the paper making process is minimized or completely eliminated.

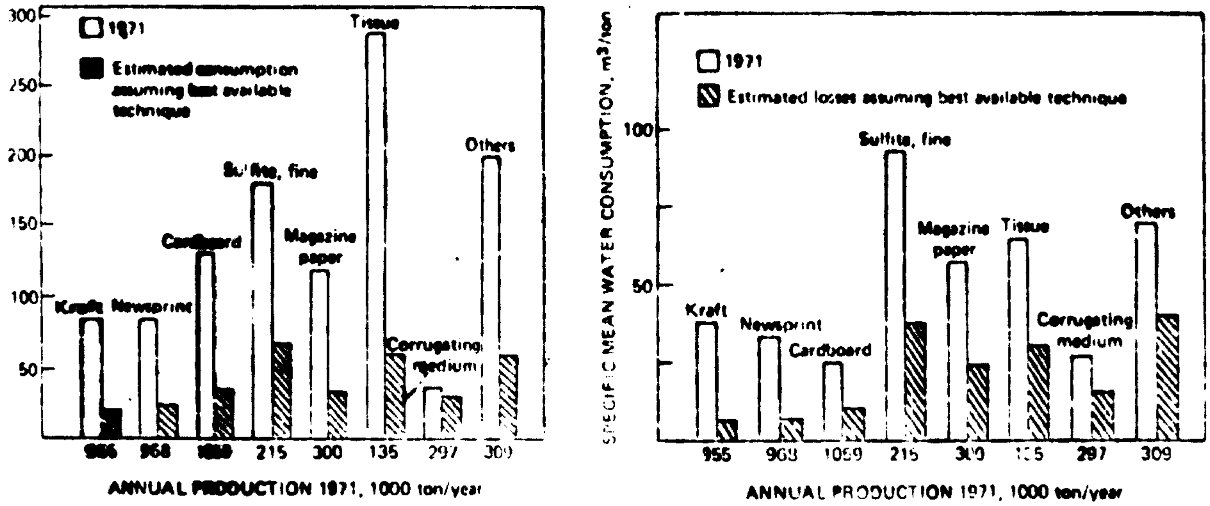
A subproject group of the Environmental Care Project (SSVL) carried out an extensive research and development program in order to find from economical point of view the most optimal means to solve the environmental problems of the paper industry. The results reported have been reviewed in several articles. Thus we wish to refer to the article by S Martin-Löf and co-workers with the title "Establishment of a closed system for the paper making process". In this paper we will only deal with some practical aspects regarding how the closed systems should be arranged, which are based upon said report.

Present and Future Conditions

According to the investigations made by SSVL in the paper industry regarding the degree of closeness of the white water systems of the paper machines this varies between different types of machines. The following figures exemplifies this both in regard to specific water consumption (m^3/ton of paper) and to the loss of material (kg/ton of paper) for different kinds of paper produced. The lowest values represent estimated losses assuming best available technique and are related to the best conditions, which have been able to be achieved in practice during a long period of time without observing any negative effects on the operation or the paper quality. Thus the figures are related solely to those conditions which exist during continous and normal operating conditions. Thus so called temporary or accidental discharges should be added to the given values.

Accidental discharges are caused partly because of mechanical failures, partly because of the necessaty to open the system for cleaning the machine when running certain qualities.

Short trials have been performed, when the closing of the system has been carried still further. The problems, which have arisen at these occasions, have been of a more colloid-chemical nature rather than of a mechanical character.



Fresh water consumption and loss of dry solids for various Swedish paper mills.

Figure 115:1

The stock, fresh water, broke and white water systems of the paper machines must fulfill many demands. These vary from product to product, and the lay-out of the systems must be applied to the local conditions. Furthermore the composition and colloid-chemical properties of the paper stock and the white water vary quite a lot. Because of all these factors a specific system solution which functions well in one mill, cannot simply be applied in another mill.

Closed System Solutions

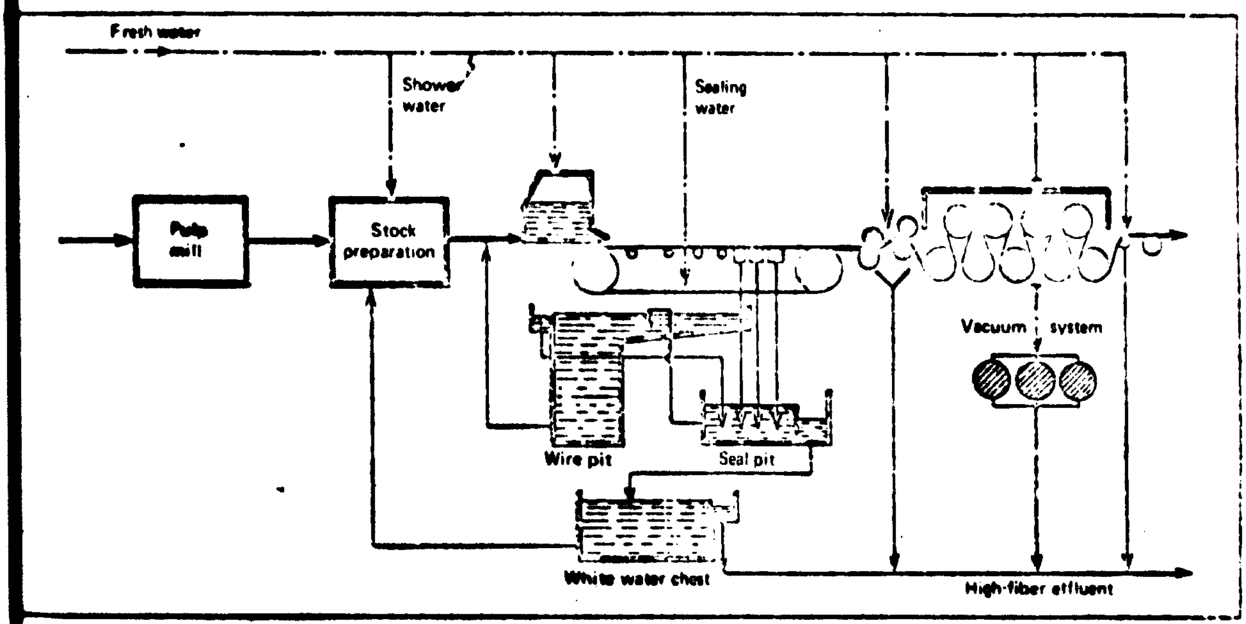
The amount of effluent water which leaves a paper mill is determined entirely upon how much water is added to the mill.

> Water, which comes into the paper mill, comes out as effluent.
>
> Water, which has transported fibers, contains fibers, fiber substances and dissolved colloidal material and fillers in some cases.

In order to reduce the effluent from the paper mill in the first place it is necessary to reduce the amount of water going into the same. Secondly the water, which does not necessarly have to come into the fiber carring system, shall be entirely kept apart from the same. Furthermore the water quantity, which must go into the fiber carring system, must be purified.

1. Open and closed systems

In figure no 116:1 a classical entirely open system is illustrated. For each ton of paper produced a couple of hundred cubicmeters of water pass through the mill. Each cubicmeter of water carries 0,5 to 5 kg substance to the sewer. The discharged quantities are completely unacceptable, why such systems hardly exist anymore.

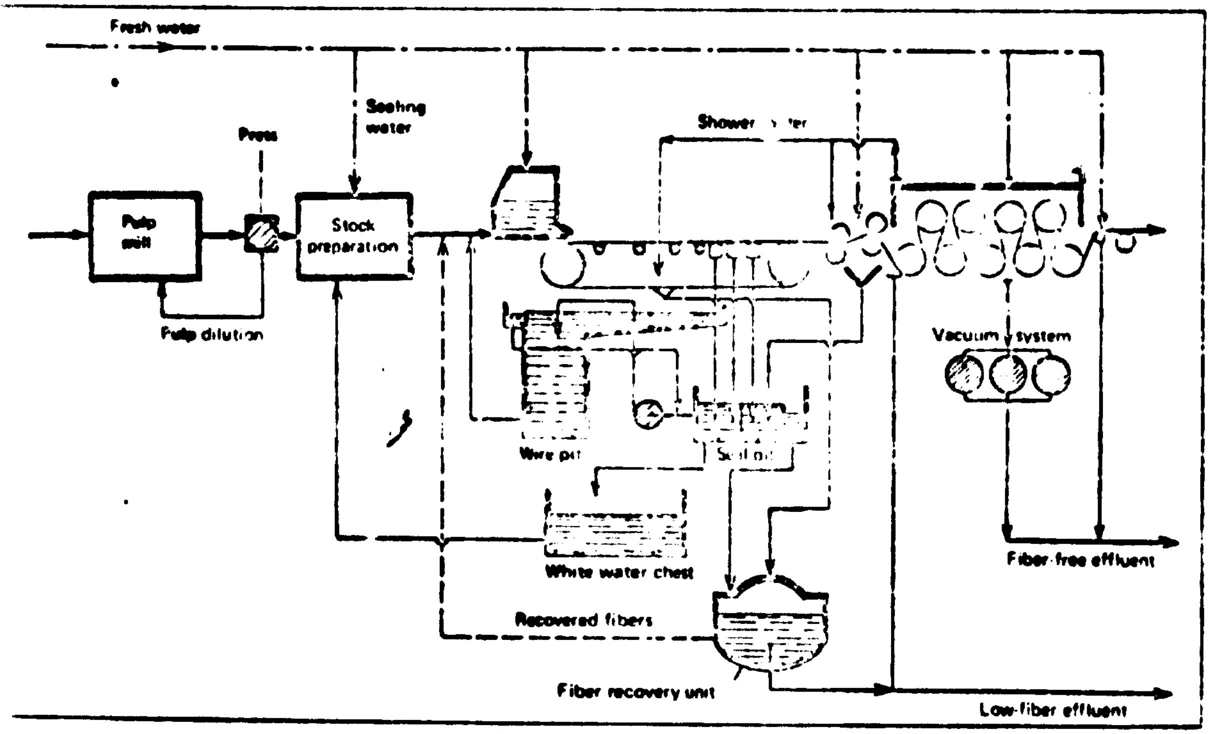


Open white water system.

Figure 116:1

In the next figure no 117:1 a common relatively open system is shown. The pulp from the pulp mill carries about 30 m^3 water/ton of paper. Sealing and shower water is added in the stock preparation and on the paper machine. Additionally sealing and cooling water for the vacuum pumps and cooling water for the steam condensor, motor drives, pope and so on are added. All the added water, about 100 to 200 m^3/ton are collected in a combined discharge. Therefore the same will carry fibres. The white water, which is discharged, is the one from the paper machine having the lowest concentration.

The content of solid substance can be of the order of 250 mg/l corresponding to 0.25 kg/m^3. The discharged solid substance will then be about 25 to 50 kg/ton finished product.



Closed white water system.

Figure 117:1

In order to decrease the consumption of fresh water and at the same time the amounts of effluents a such equipment (stuffing boxes, spray pipes, vacuum systems etc) is required, which uses very small amounts of fresh water or which can work with fibre-poor or fibre-rich water.

Furthermore the following conditions are required:

Systematical returning of fibre carring water to points in the process where it can be tolerated. For instance at the adjustment of the concentration dilution can be done with not purified white water.

The addition of water to the process must be minimized. This can be done by reducing the addition of fresh water and by reducing the amount of water transporting the paper stock.

All excess white water shall be purified internally in a fibre recovery unit. This water should be the poorest in regard to fibres.

Not all fibre-carring water as cooling water shall be diverted directly to the recipient, if it cannot be used instead of a necessary fresh water addition. This requires that there is a complete separation of fibre-carring and not fibre-containing water.

A system where above points have been observed is illustrated in figure no 117:1.
The amount of water coming with the pulp to the paper mill is small, as the transport water has been replaced by white water.

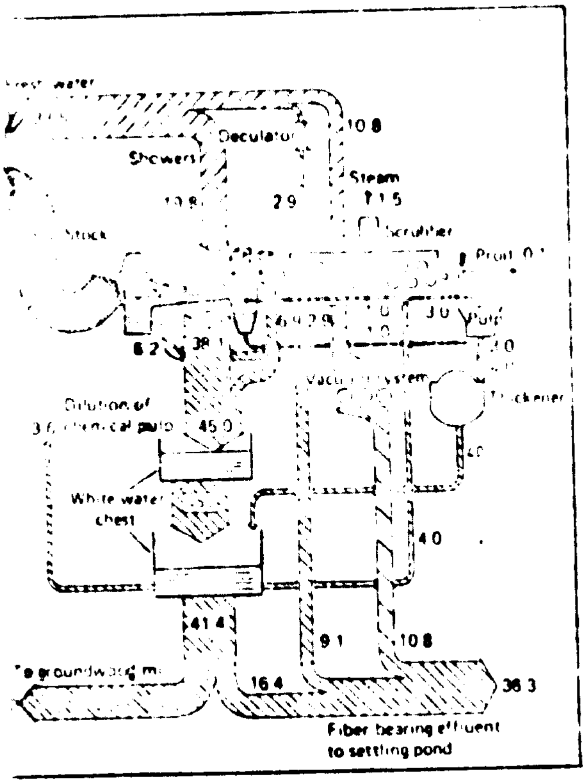
The return water from the wet section of the paper machine can be divided into different types depending upon the content of fibres.

Fibre-rich water from the wire table
Fibre-poor water from the wire showers
Relatively fibre-poor water from the separators after the suction boxes

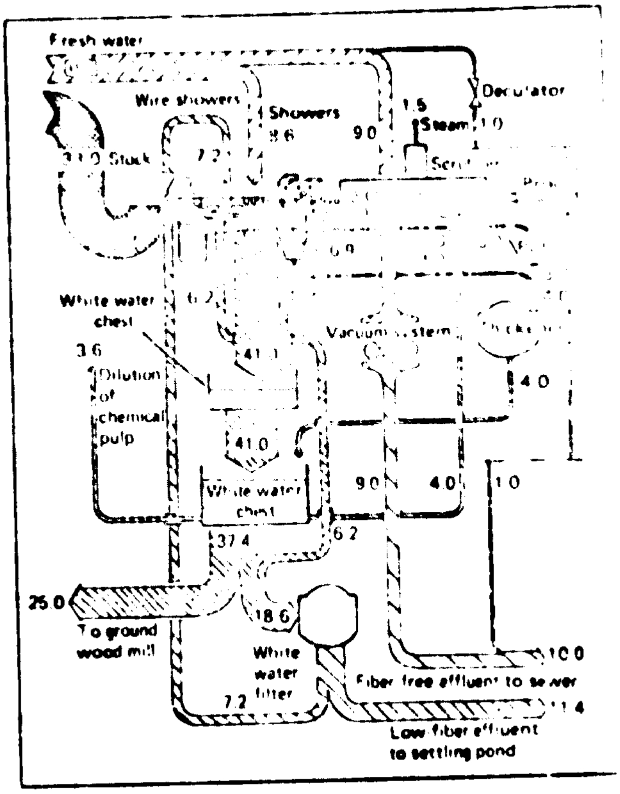
The most fibre-containing water is returned directly to the fan pump with the addition of the relatively low fibre-containing water from the separators after the wet suction boxes. The most fibre-poor water (wire wash water, separated water from the dry suction boxes and water from the press part) shall be diverted to the fibre recovery equipment. Thereafter it can be reused as shower water in several places.

The water consumption in a closed system of this type can with the today's best available technique be brought down to about 20 m^3/ton of paper. As the amount of filterable substance in the leaving water can be maintained in a magnitude of 50 mg/l a totally stable discharge in the order of 1 kg/ton or 0,1 % of the production can be achieved. To this discharges caused by disturbances in the operation should be added.

This example shows how in reality the discharged amount of filterable substances can be reduced from the quite unacceptable level of 20 to 30 % in the entirely open mill to 2,5 to 5 % in the conventionally closed mill and further to 0,15 % of the production at a systematically carried out closing of the paper machine system.



Example of water balance (m^3/ton) for a newsprint ma- ne, open system.



Example of water balance (m^3/ton) for a newsprin machine, closed system.

Figure 119:1

Placing of White Water Filter and Broke Pulper

The placing of the white water filter and an eventual broke thickener in the system is very essential, In some systems an adjustment of the concentration of the broke takes already place in the dissolver for wet respectively dry broke, while for other types of paper it is necessary to use a thickener for the broke before it is returned via a chest to the process.

The filtrate from the broke thickener has in general an amount of fibre, which in the same order as that in the white water from the suction boxes. The concentration can even be higher. Depending upon the amount of fibres the white water from the broke thickener should be returned to the white water system for dilution of the paper stock or for purification in the fibre recovery equipment.

A flow diagram how the broke thickener and the filter for fibre recovery are connected with each other is exemplified in the figure no 120:1 . The unfiltered white water is used for consistency regulation in the stock preparation as well as for dilution in the dissolver for wet and dry broke.

In the chest for not purified white water a deficit of water exists even when the broke thickener is working in full. The richest water from the collecting cistern for suction box water is used for maintaining the level of the white water constant and the same is thus in that way returned to the system.

Only the richest white water in this system namely from the part of the collecting cistern mentioned, which receives water from the couch and the dry suction boxes, is diverted to the white water filter.

The preformed pulp mat on a white water filter shall not contain fine material and dissolved and colloidal substance. Therefore unbeaten pulp should be used for the preforming of the mat on the save-all.

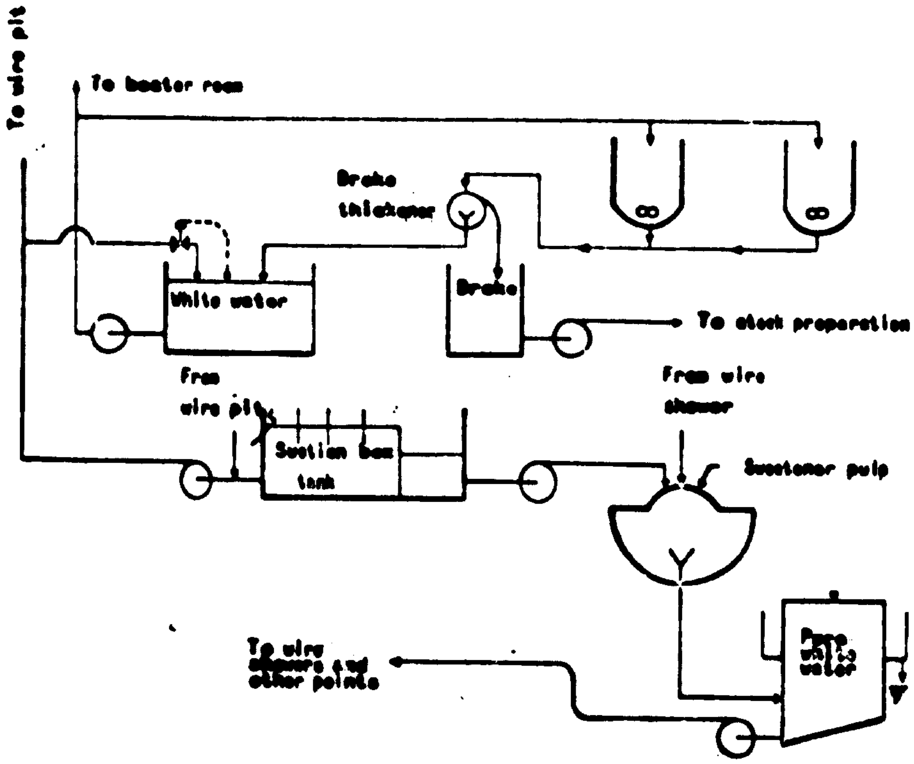


Figure 120:1

The wire wash water, which contains only a small amount of fibre material and mostly long fibres, should if possible be diverted directly to the filter.

As there must be a chest for purified white water, this can also be utilized for a certain degree of purification as by sedimentation, which is also shown in the above flow diagram. The filtrated water is directed into the chest eventually by some kind of spreading device. Water for the wire wash, showers and so on is taken out from the bottom of the chest, while overflows to the sewer or to the final purification are leaving from the top of the chest. This arrangement can increase the degree of recovery of fibres somewhat.

3. Closing of the vacuum system

The wire and the press section are usually equipped with dewatering devices, which work at low pressure or vacuum. Such devices are suction boxes, wet and dry, couch roll with one or two suction chambers, first and second press with suction boxes in the rolls and a number of felt suction boxes. The vacuum for all these suction positions is obtained from different types of vacuum pumps. The Nash liquid-ring type pumps, the Sulzer condenser turbine or reciprocating piston compressors and other types are used for this purpose in the paper machine. The Nash pumps consume relatively much fresh water. Their function depends upon the fact that a liquid ring of low temperature is maintained. If the liquid-ring gets too thin, the vacuum capacity decreases, while at a too thick liquid-ring the power consumption increases very much. The liquid-ring of the Nash pump is also to a large extent depending upon the temperature in order to maintain stable vacuum conditions. Therefore the Nash pump should be supplied with cold fresh water.

The amounts of fresh water to the Nash pumps vary usually between 50 and 400 l/min. Paper machines with a daily production of about 300 tons can thus consume about 3000 l/min fresh water in the vacuum system. If the vacuum system furthermore is not equipped with water separators in the different suction positions additional great amounts of white water from the paper sheet are added. The white water contains then a large amount of fibre materials, which will be mixed into the cooling water. The total water flow from the vacuum system is in that case about 4000 l/min.

The Sulzer turbine as a vacuum pump consumes on the other hand only small amounts of fresh water as cooling water in its bearings. When this vacuum pump acts as a condensator turbine no water is needed for its function. The Sulzer turbine is usually of such a size that only a few turbines are enough for a modern large paper machine. This will mean that the water consumption can be reduced to about 100 to 300 l/min for a paper machine of the above mentioned size.

Also reciprocating piston compressors of different manufacture are used as vacuum pumps. These pumps do not usually require any fresh water in order to function. Such pumps have been used in a couple of Swedish paper mills for about four years without any serious operating problems.

All above mentioned pumps have practically identical output capacity in regard to power input. The reciprocal piston compressor needs the least room at the same time as the sound level is the lowest.

Within the paper industry today Nash pumps are mainly used. Modern larger production units usually require 10 to 13 pumps. These are divided so that two or three are reserved for high vacuum for among other thing the suction chamber in the couch roll. The rest of the pumps operate mainly at a lower vacuum for suction boxes in the wire section, pick-up roll and suction presses in the press section and in felt suction boxes in connection with a felt washer. If each pump is supplied with sealing water in the amount required the water consumption will be about 3000 to 6000 l/min.

In order to reduce the water quantity to the whole vacuum system the following systems have been developed:

Installation of water separators and reuse of added cooling water in the wire and the press section

Installation of heat exchangers, by which the water quantity sucked from the paper sheet is cooled and then reused in the vacuum system

Utilization of different water temperatures. The sealing and cooling systems are cascade connected in two steps

Through the installation of water separators in each vacuum section as illustrated in the following figure no 123:1the fibre containing water from the paper sheet can be separated from the air before it goes into the vacuum pumps. The water separator can be fairly simple in its construction, which is demonstrated by figure no 123:1 below. The obtained water from the paper sheet is pumped from the separator to the collecting tank for the suction box water. Consequently no fibre material is added to the vacuum system, why the fresh water added to the vacuum system can be diverted directly to the recipient or alternatively after heating in a scrubber be reused as shower water in the wire and the press section.

In order to guarantee that required purity of the circulating sealing water is maintained, the water should pass a simple filter before it is delivered as shower water. In order to control the amount of sealing water the vacuum pumps are equipped with pressure and temperature guards. The water separator shall be equipped with a level control so that at all times there is a certain liquid level in the same.

An other method to reduce the fibre containing white water quantity from the vacuum system is shown in figure 123:2. In this system there has been installed a heat exchanger connected as shown in the figure. The diverted and obtained water quantity is allowed to pass through the vacuum pumps, after which it is collected in a so called vacuum pit.

The collected water is then pumped to the heat exchanger, whereby the heat content of the white water is reduced to a suitable level with cold fresh water. Thereafter the chilled white water is reused as cooling or sealing water in the vacuum system. By this method a certain excess of white water corresponding to the water quantity which comes

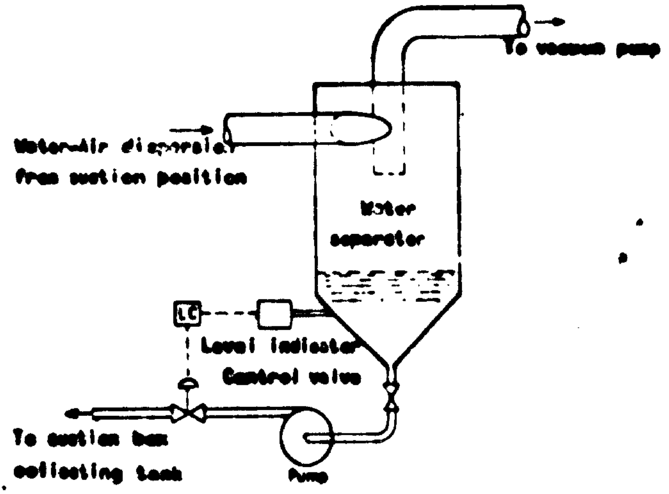


Figure 123:1

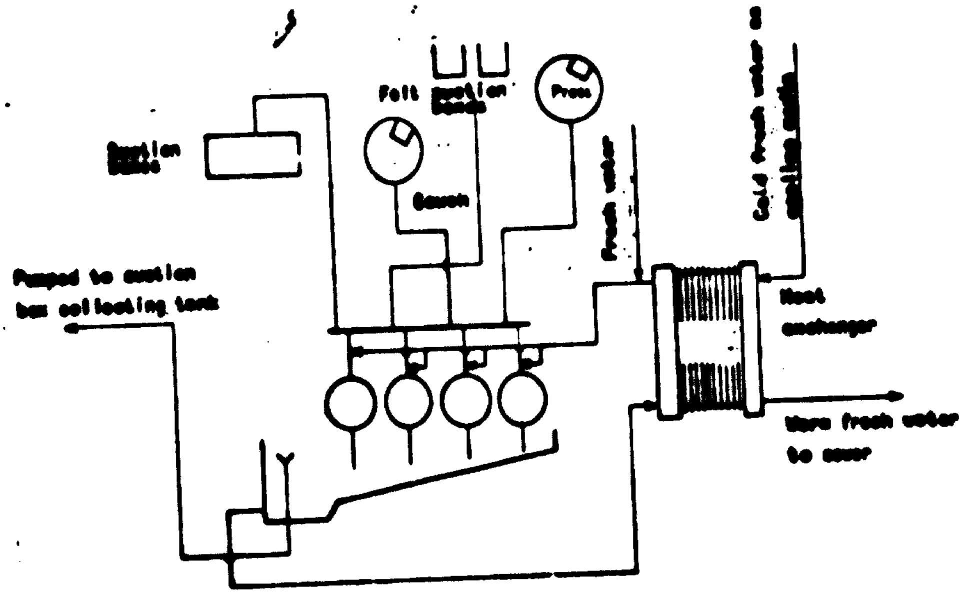


Figure 123:2

from the paper sheet exists. This white water quantity is diverted **to the** collecting tank for the suction box water directly from the **collecting** tank after the vacuum pumps. The fresh water consumed is **thus leaving** the heat exchanger somewhat warmer. It can either be **diverted** directly to the recipient together with the fibre-free discharge or it can be reused as warm shower water in the wire and the **press** section, as this water does not contain fibres.

As mentioned above there are no such problems with the Sulzer turbine **and the** reciprocating piston compressor as these are requiring less **or no** water at all. However, a certain separation must take place in **the water**-air dispersion leaving the same. Usually this will be done **in a separate** water separator to which the water-air dispersion from **all the** pumps are going. This is illustrated in figure no 124:1. **The separated** water in the separator is pumped either directly to the **internal** fibre recovery system or to the collecting tank after the **suction** boxes, where it is mixed into the white water and thus returned **to this** system. It should be observed that the fibre content in this **system** commonly will be relatively high, 400 to 1000 mg/l.

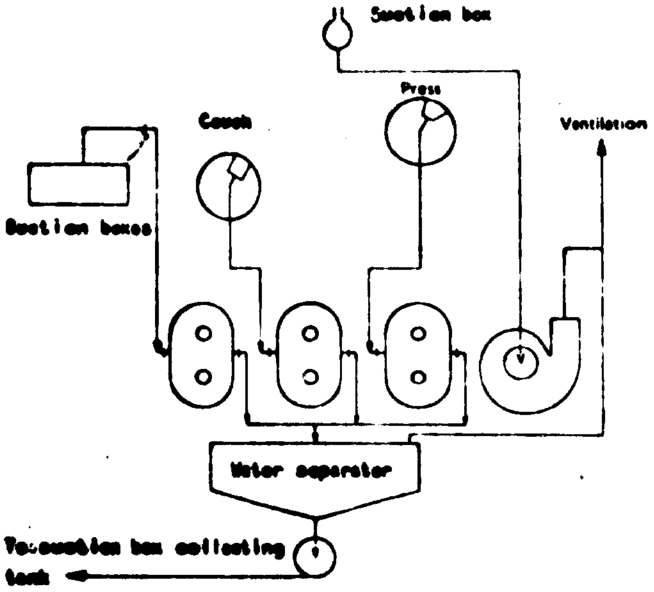


Figure 124:1

4. Shower water systems in the wire and press section

Very much water is consumed in the wire and press section of a paper machine for cleaning, spraying and wetting of the wire, press rolls and press felts. Earlier only fresh water was used for this purpose. Naturally it depends upon the fact that fresh water has been easaly available and it has been more simple to use, as at the same time the advantage of using warm water was not thought of.

A wire section is usually equipped with a shower pipe next to the breast roll, a few shower nozzles around the deckle, a shower pipe near the suction box in the couch roll, two or several edge sprays, one or several shower pipes for spraying the paper sheet down into the couch pit, two extra showers for the edge also to be sprayed down into the couch pit and finally shower pipes for each guide roll in the wire. Most of these shower positions are supplied with fresh water. In the following table the consumption of fresh water in different positions is listed.

Table 125:1

Position	Type of water FW or WW	1/min per m width	Pressure kp/cm^2
Breast roll	FW	1 x 150	Ca 3,5
Deckle showers	FW	6 x 30	Ca 3,5
Couch roll showers	FW	2 x 25	Ca 3,5
Edge sprays	FW	2 x 25	Ca 10,0
Shower pipes for spraying the sheet into the couch pit	WW	1 x 250	Ca 3,5
Sprays for edges into couch pit	FW	2 x 100	Ca 4,0
Guide roll showers	FW	5 x 150	Ca 3,5

The amounts of shower water indicated per meter wire width are refered to a modern paper machine.

From the table it can be seen that for a five meter wide paper machine with five guide rolls the water consumption for the wire section will be approximately 6.250 l/min. Of these usually 5000 l/min is fresh water and the rest white water.

In order to reduce the fresh water consumption in the wire section two different methods can be applied. First of all the consumption of water shall be reduced as much as possible, which can be done by cutting off two or three guide roll showers, take away the deckle showers and for the other showers except for the edge spray reduce the pressure of the water. The other method is based upon the reuse of unclean or cleaned wire shower water. In order to achieve a good result these two methods should be combined.

Regarding the first method a reduction of the water consumption of about 40 % be achieved in the wire section. In order to be able to perform this work on the machine a long term trimming period is required, when the operating personnel shall be made partly responsible for the maintaining of the least water consumption. It is important to keep a continous superintendence, as otherwise after a time the water consumption tends to increase.

If the shower water is reused, however, the largest reduction of the fresh water consumption on a continous basis has been achieved. For doing this several different methods have been developed. The most common one is the one when purified white water from the internal fibre recovery system is reused. The same is then used for the guide roll showers, breast roll shower and the edge spraying of the sheet into the couch pit, while the same for the whole sheet is supplied with fresh water. See the following figure no 126:1.

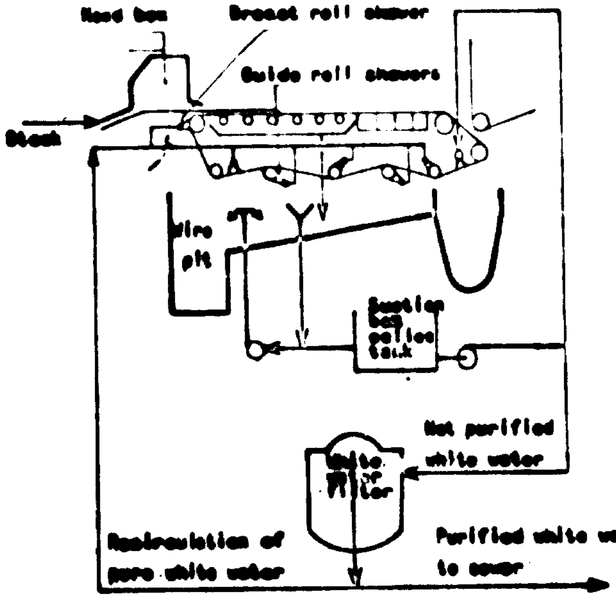
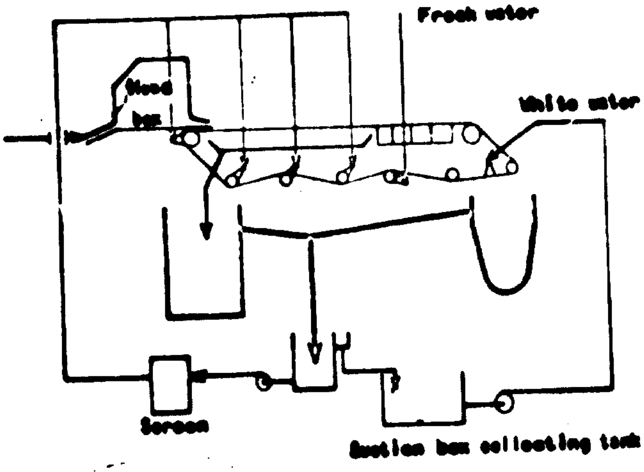


Figure 126:1

This can in this case result in a reduction of about 90 %. When white water is recirculated as shower water special nozzles are required. In principle the nozzle holes are made somewhat bigger than when fresh water is used. Furthermore the surfaces should be polished in order that the fibres in the white water shall collect on the same and cause troubles with clogging of the nozzles. By this method the recirculated water quantity ban be increased with about 15 %.

The guide roll showers are often connected in serie, so that one shower is supplied with fresh water, which is collected and mixed into the water for the other showers. This means that about 1/5 of the fresh water quantity the whole time flowing through the shower water system by which the fibre content in the same is relatively low. This shower water quantity is all the time kept separated from other white water except the 1/5 part suplied to the white water system. See the following figure 127:1 In order to get rid of eventual solid material there should be installed a some kind of a course filter. This very simple method often results in a reduction of the fresh water consumption in the wire section of about 70 %. In many modern mills instead of fresh water, water from the dry end of the machine, for instance discharges of water from the vacuum system and other cooling positions, which can be obtained as pure water.

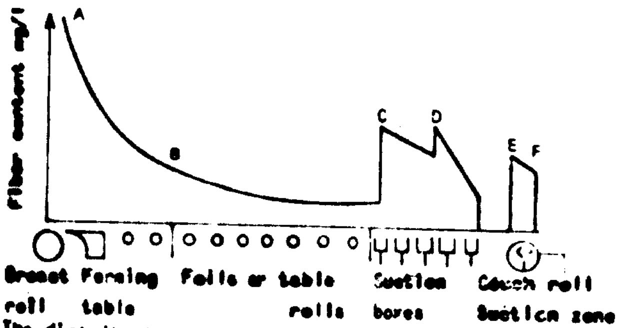


Wire showers connected in series. Fresh water added to one shower.

Figure 127:1

This water is often heated in the dryer scrubber, by which warm shower water is obtained. Thereby the stock temperature on the machine can be kept fairly high which is an advantage as better drainage on the wire is achieved.

Another method very much utilized is based on the knowledge about the variations of the white water quantities along the wire. The curve in the figure no 128:1 below demonstrates the variation in the fibre content of the white water coming from different points along the wire.



The distribution of the fibercontent in the water coming from different parts of the wire

Figure 128:1

The magnitude of the fibre content in the white water varies from machine to machine and between different types of paper products. In a paper machine producing fluting, newsprint or magazine paper the fibre content in the white water is often as high as 1500 mg/l. The dissolved and colloidal materials are of the same amount. In a kraft paper mill the fibre content seldom exceeds 500 mg/l and the dissolved and colloidal substances does not exceed 100 mg/l.

If an intermediate wall is installed at point B in the wire through the white water quantity obtained between A and B is separated from those quantities received between B and C. In this way a white water is obtained between B and C which contains relatively little fibres. This quantity can with advantage be reused as shower water, ultimately in both the breast roll shower and in the guide roll showers. By making the above mentioned changes in the process the fresh water consumption in the wire section can be radically reduced at the same time as the temperature of the stock is increased and the loss of materials is decreased. No changes in the quality of the paper should take place.

In the press section the fresh water consumption is distributed to the following points:

Sprays in the pick-up roll, sprays in the press suction roll, showers for cleaning of doctor blades and showers for cleaning of felts.

Fresh water is usually used in all these positions, why the water consumption in the press section often is high. Nobody has experience from recirculating the white water in the showers in the section. Therefore today the only possibility to save water is to cut down the consumption in each single position.

In a few machines the problem with the high water consumption has been abated by replacing the continous felt washer with an intermittent working high pressure shower. The result from these trials have been quite promising, as felts with a high content of synthetic fibres have been used. The intervals between the washings vary from case to case. Thus in some paper machines the washing of the felt is done one or a couple of times each shift, while in others the washing is done only once a week. Besides a favourable effect, which this measures have uoon the water consumption, these have resulted in a prolonged life time of the felt.

Conclusively it can be said that it is possible to decrease the consumption of fresh water in the press section considerable by above mentioned measures without harming the felts and their life time and affecting the moisture content in the paper sheet unfavourably after the presses.

5. The seal water system

In a paper mill a large part of the fresh water consumption is the sealing water for pumps, screens, agitators and so on. Usually there are about hundred positions where sealing water is used. The sealing water is mainly mixed into the white water system and thereby increasing the quantity of contaminated water discharged to the sewer.

By the introduction of modern sealing systems and for an improved control of the water consumption in sealing devices the discharged water quantities can be reduced considerably.

As there exist different kinds of sealing devices for pumps, it is recommendable to consult a manufacturer of these equipments concerning which kind to use in different positions.

A check valve will prevents the liquor to force itself through to the sealing gland, when the sealing water is accidently cut off. Therefore this type of valve us usually installed immediatly before the pump. Besides the obligatory check valve a screen, flow indicator, orifice plate and eventually a pressure gauge can be installed as shown in the following figure no 130:1.

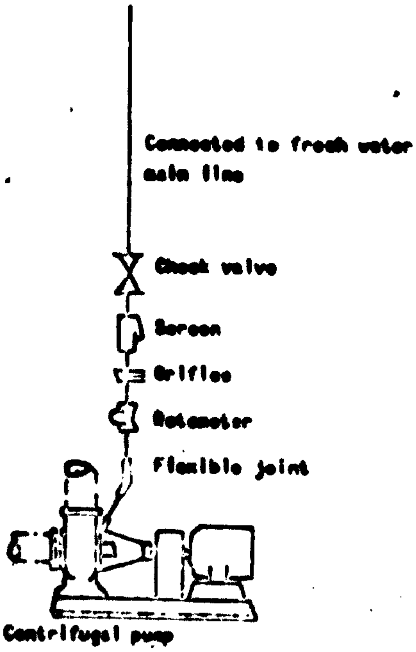


Figure 130:1

The pressure gauge is naturally valuable for the personnel for the control of the pressure of the sealing water. It should be installed next to the seal.

The purpose of a flow indicator is to indicate that the sealing water has not stopped to run. If this is the case serious harm can be done by the increased temperature in the liquid film between the sealing rings.

To have an orifice plate installed in the pipe line for the sealing water can be very suitable, as by the same a simple arrangement is obtained by which a certain control and limitation of the consumption of the sealing water can be achieved when the pump is in operation as well as it is stopped because of for instance a wire change.

In order to supply all sealings in a mill with sealing water required it is recommendable to distribute the same in an entirely separate pipe line as exemplified in the following figure no 131:1.

The pipe line system should be layed out and mounted in the mill in sections, which are provided with branches to suitably located pump groups. All the pipes should be made of stainless steel. In or order to promote a secure operation only absolutely necessary shut-off valves should be installed. Furthermore the hand wheel for the valves should be removed or the valves should be locked, so that unintentional shut-offs of the water supply cannot occur.

Directly after the in-take of the fresh water line into the paper mill a suitable amount of water is directed to a level controlled water seal. from which a feeding pump is pumping the water through some sort of micro filter. In the same particles which have a wearing effect on the equipment are removed. This is of great importance in regard to the life time of the sealing glands and so on, and that the micro filter has adequate capacity to purify the water consumed.

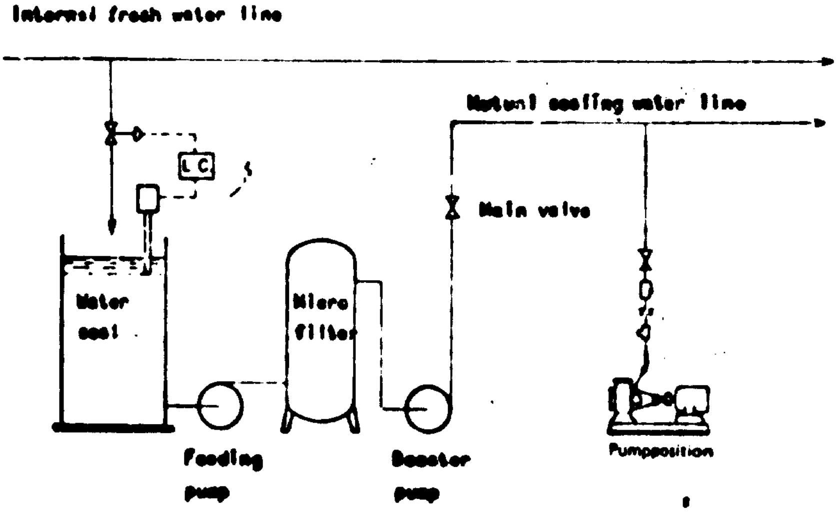


Figure 131:1

Fibre Recovery Equipments

Without comparison the filtration of the white water to recover the fibres is the most common method. Equipment for sedimantation functions very good for white water obtained when producing paper qualities with a high degree of fillers.

The following aspects on the equipment for filtration of the white water can be mentioned:

By filtration the suspension of materials is dewatered on a fine mesh cloth. Most of the white water can relatively easely freed from suspended material by retention means. Dissolved and colloidal material will normally not be separated.

When filtering white water the filter cloth cannot normally have so fine a mesh that it retains fine material. Therefore normally a more open cloth is used, upon which a filter mat of coarser material is forming the actual filter media.

At present two methods are used to form this filter cake.

By the coating method, which is often used for drum and wire filters, the filtration is taken place in two steps. In the first step the filter cake is formed. The same consists of usually unbeaten pulp. In the next step the white water is added and filtrated through the formed filter cake.

The amount of solid, which is separated from the white water, is in general considerably smaller than the amount of pulp in the filter cake. The filtrate from the first step contains rather much fibres, and it is therefore returned to the head box of the filter.

The mixing-in method is applied mainly when disc filters are used. In this case the amount of suspended material in the white water is increased by an addition of pulp so that a concentration of about 5 g/l is obtained.

Besides the concentration of the white water, type of fibre and fillers the capacity of a filter depends mainly upon the effective filter area and the available pressure difference.

The filtration process can be carried out with several types of apparatuses:

Drum filter
Belt filter
Disc filter

The drum filter consists of a vertical rotating cylinde, which is covered with a wire cloth. The latter is woven with a thread of different material, e g phosphor-bronze, stainless steel or plastic. Usually a filter cake is formed with unbeaten pulp. These filters operate often with a pressure difference, which is obtained by the level difference between the outside and the inside of the cylinder. The filtration can take place from the outside and to the inside or in the revers direction.

The belt filter consists of a drum and a trough as the above described filter. The principal difference is that the filter media consists of an endless wire, which runs off the filter to discharge the filter cake, cleaning and new forming of the filter cake with pulp.

The disc filters are built up by a number of circular discs dressed with cloth, which in the center are fitted to an horisontal shaft. Each disc consists of several sectors. Each such sector together with the corresponding sectors in the other disc are connected to a separate channel in the shaft. The water flows from both sides of the disc into the hollow sectors. The required pressure difference is created by a vacuum pump or more common with barometric drop leg. The latter requires a certain minimum of liquid load in order to be able to give a good result.

A relatively large white water chest should be installed in order to equalize the load on the filter. A chest should also be installed after the filter, which can be so dimensioned that the purified water can be utilized instead of fresh water.

When chosing the dimensions of a filter the retention properties of the fiber material must be taken into consideration. Also its compressibility should be determined so that the pressure difference and filter speed required can be calculated. In this case it is recommendable to turn to a manufacturer of filters who has such data for dimensioning a filter, which he has built up by experience.

Specific Lay-Outs of Paper Machine White Water Systems

If consequently carried out the above mentioned recommendations for closing of the paper machine systems will give drastic results in regard to partly a decreased amount of discharged solid materials as fibres and fillers and dissolved and colloidal materials to the recipient, partly a decreased water consumption resulting in considerable economical gain.

It was mentioned above that there are actually no ideal models for closing of the paper machines. Each mill and each paper machine must be given its own system closed. It would carry to far to describe all closed systems applied for different types of paper manufactured, which have been studied by the Environmental Care Project (SSVL). Instead we have allowed ourselves to include some of the flow diagrams given in a report by SSVL. When these are carefully studied a lot of valuable information can be obtained from them.

EXTERNAL TREATMENT OF WASTE WATER FROM PULP AND PAPER MILLS

Today's technique offers excellent possibilities for internal measures in order to reduce the discharges. As a complement to the internal measures a separation of the suspended materials in the effluent is required before the same arrives to the recipient. This separation can suitably take place in a sedimentation basin, which should have such a size and shape, that it can function as a "police" against temporary or accidental larger fibre discharges, e g at failures in pipe lines, holes in filter cloths etc.

In certain cases screening or filtration can replace sedimentation, for instance when a discharged water can upset the function of the basin to the disadvantage of other discharged water. This is the case regarding for instance discharged waste water from the bleach plant, which partly normally contains a small amount of fibre and partly often reduces the efficiency of the basin.

The separation of solid material from the discharged waste water is sometimes called primary treatment.

When it is judged that the recipient does not have the capacity to receive the discharged waste water the same must be purified and freed from oxygen consuming substances by a biochemical treatment and from suspended or dissolved substances by chemical precipitation. Such a purification process is called a secondary treatment

A secondary treatment can result in considerable complications in the operation of the mill without giving a corresponding gain in the environmental protection. In addition to this problem there will also be a problem with the treatment of the sludge obtained and the disposal of the same.

Sedimentation

Nowadays most mills in Sweden have special sedimentation equipments. Sedimentation means that particles are removed from the water by gravity and the sedimentation is therefore dependent upon size of the particles, the temperature of the water, the water flow and so on. Theoretically the sedimentation is only depending upon the surface area of the sedimentation equipment. Therefore - still theoretically - the sedimentation basins should have the right area but need no depth. It has been shown in practice, however, that the basins need to have a depth of almost 2 m. This means that a circular sedimentation basin should be at least 2 m deep at the periphery. This depth of the basin is natural because there must be a magazine that can be used, when the basin is loaded momentarily with a high concentration of fibre suspension. See figure 134:1 on page 134.

The load of the sedimentation basin is expressed in $m^3/m^2/h$. For all sedimentation Hazen's surface load theory should be applied. According to the same in order to be removed a particle must reach the bottom of the basin before the water leaves the sedimentation basin. This will mean that the particles should have a rate of descent which is greater than the flow velocity per sedimentation area (Q/A $m^3/m^2/h$). As some of the particles are coming into the basin under tha surface and thus have a shorter distance to fall, other particles having a lower rate of descent will also be removed.

If a particle has a rate of descent v_0 and arrives into the basin at the surface (see figure below) and reaches the bottom at the out-let, the following correlation is obtained:

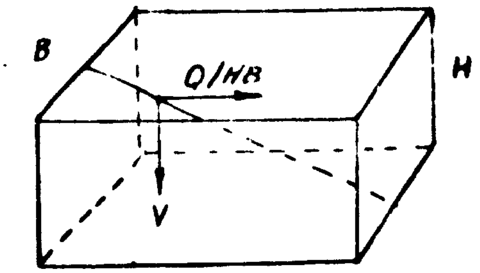


Figure 135:1

$$\frac{v_0}{\frac{Q}{H.B}} = \frac{H}{L} \quad \text{or} \quad v_0 = \frac{Q}{B.L} = \frac{Q}{L}$$

where

v_0 = sedimentation velocity m/h
B = the width of the sedimentation basin
L = the length of sedimentation basin in meter
H = the depth of the sedimentation basin in meter
Q = the flow m^3/h
A = the area of the basin in m^2

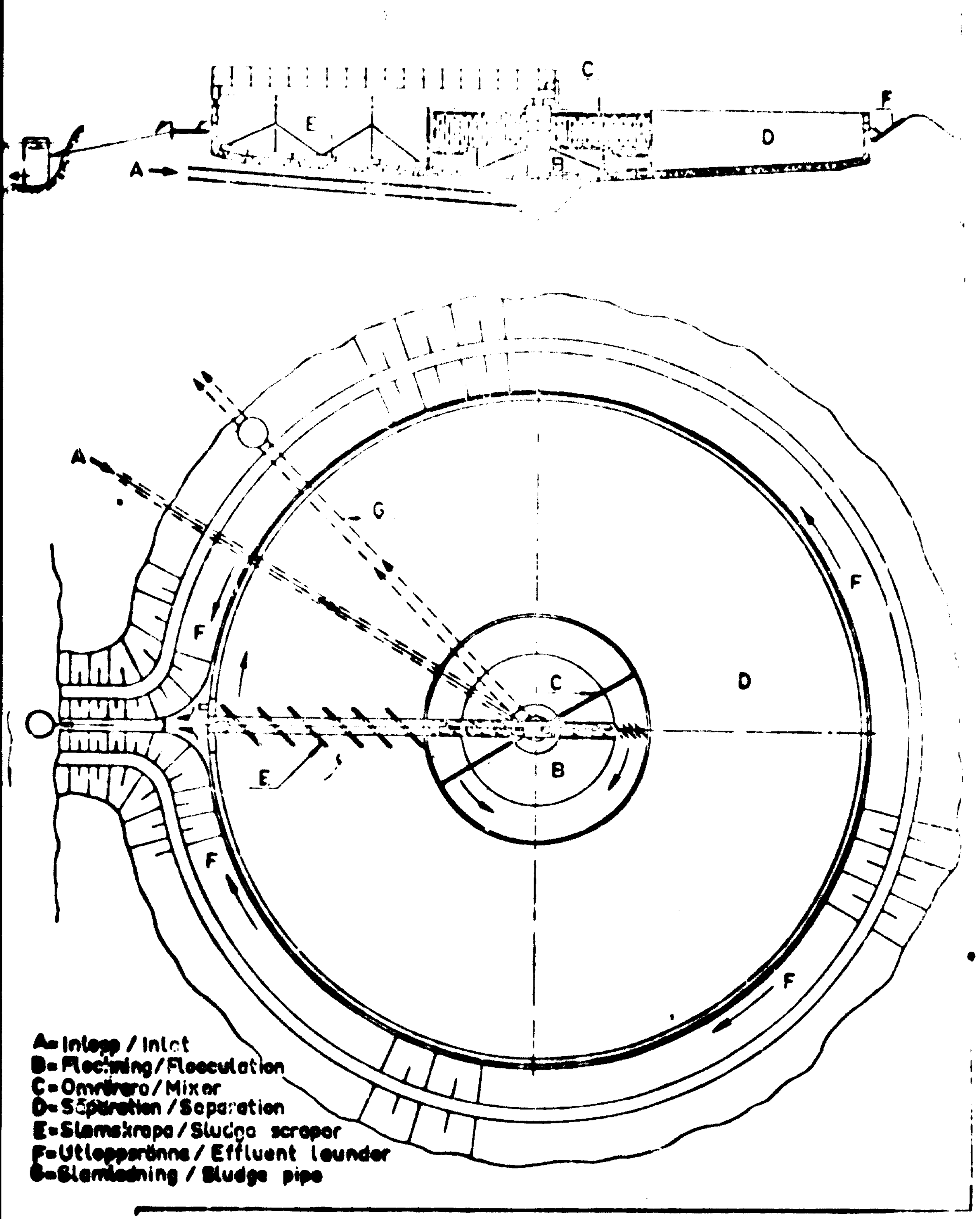

C
E
D
F
A
B
A
G
F
C
D
B
E
F
F
F
A=Inlopp / Inlet
B=Flockning/Flocculation
C=Omrörare/Mixer
D=Separation / Separation
E=Slamskrapa/Sludge scraper
F=Utloppsränna/Effluent launder
G=Slamledning / Sludge pipe

Figure 136:1

The surface load Q/A is thus equal to the limit rate of descent v_0 for those particles, which will be barely removed.

Thus depending upon the size of the particles which have to be sedimented in the basin, the load will differ from a very low to a high value. For waste water coming from fine paper mills the value is about 0,5 $m^3/m^2/h$ and for waste water coming from a pulp mill the figure is about 2 $m^3/m^2/h$.

Depending upon the internal measures taken in different mills it is advicable to investigate the waste water which should be cleaned by sedimentation. It is naturally important to find out how this water will behave in a sedimentation basin before this one is constructed and given its dimensions.

Circular sedimentation basins are mostly used in Sweden because the machinery is cheaper than for rectangular basins. In countries where there are no problems with snow and ice, the rectangular basins may probably be of greater interest.

The effects obtained by building sedimentation plants depend naturally on the quality of the incoming water, but the outlet should have a fibre content ranging from 30 to 10 ppm if the basins are functioning satisfactory.

There are also other types of fibre removing equipment. One is the vertical sedimentation basin. This functions in the manner that water is introduced into the basin at the bottom and the inflow of water creates a circulating stream in the basin. This circulation causes coagulation of the fibre content. In some mills a rather good result has been achieved with these types of basins.

Flotation

Instead of letting the fibres descend to the bottom of the tank it is possible to make them float up to the surface with the aid of very small bubbles of air. This called flotation and the method is frequently used for fibre recovery inside the mill. A typical one is the so called Sveen-Pederson saveall. As this equipment is depending upon the air pressure, it is not so useful as the sedimentation basin for the final treatment of waste water. In order to obtain a good result with the flotation equipment it is mostly necessary to introduce a coagulent into the water such as aluminium sulphate.

Chemical Treatment

Chemical treatment of waste water from pulp and paper mills is not usual for the reduction of only the fibre content. In the last years, however, chemical treatment of especially the waste water from kraft mills has attracted great interest. In the following table values obtained from an investigation in a kraft mill is tabulated.

Table 138:1

	Before sedimentation "internal measures" mg/l	After sedimentation mg/l	Flocculation after sedimentation mg/l
Fibre content	200 - 300	18 - 36	11 - 28
BOD_7	100 - 135	100	44
Colour Pt	810 - 870	740 - 772	150 - 182
•		kg/ton pulp	kg/ton pulp
Fibre content		1.8	1,2 - 1,6
BOD_7		9	3,5

Column 3 shows how the water from the sedimentation basin is reduced in BOD_7 with about 50 % by coagulation of the water with 100 g aluminium sulphate per m^3 of water. This precipitation of waste water is, however, limited to the wash effluent from the kraft mills and is unfortunately not of use for waste water from a bleach plant. The only way to reduce the BOD in the same seems to be a modified process. However, as mentioned previously new bleaching methods using oxygen under pressure have been developed. This means that at all events 50 per cent of the bleaching effluent can be reused in the chemical circulation of the kraft mill.

Biological Treatment

It has not yet been quite possible to solve the condensate problems in the sulphite process as it has been done in the kraft process. For the former condensates, therefore, there remains only the possibility of using biological treatment.

Biological treatment of effluents from forest industries is used on a full scale in the United States and also at some mills in Europe and Asia. Most of these treatment plants are built for kraft mills. The plants use mostly the activated sludge method but are constructed in different ways. The reduction of BOD_7 in these plants is normally

75 - 90 per cent. A conventional activated sludge plant consists of a sedimentation tank in which the oxidation and the BOD_7 reduction take place, and a sedimentation or flotation plant where the activated sludge is separated. As the waste water from pulp plants are poor in nutrients, it is necessary to add phosphorus and nitrogen.

The biological plant functions as follows. The first sedimentation act to reduce the fibre content. In the aeration basin the pretreated efflent is mixed with return sludge. nutrients and possibly chemicals for pH control. Aeration can be done by turbines or other sorts of aerators. In the second sedimentation basin the treated water is separated from the suspended solids. Most of this as activated sludge is returned to the inlet end of the aeration basin. The excess sludge is brought to the sludge handling station. In order to reduce the phosphorus content in the water this biological treatment plant has to be combined with a chemical treatment plant.

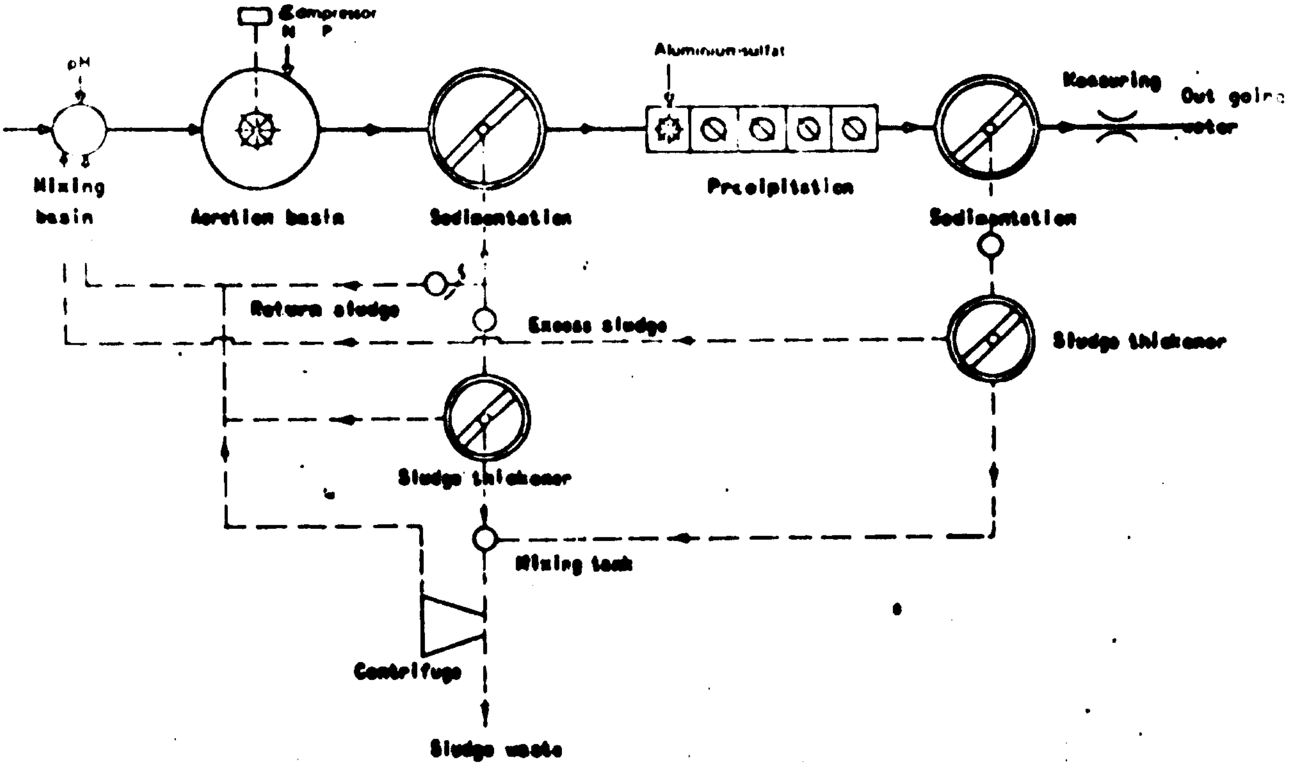


Figure 139:1

The cost of the biological treatment depends naturally upon which part of the effluent has to be treated. The estimated treatment cost in these cases is somewhere between 2 and 4 US dollars per ton of produced pulp. The figure no 139:1 illustrates a lay-out of a biological treatment plant according to the active sludge method.

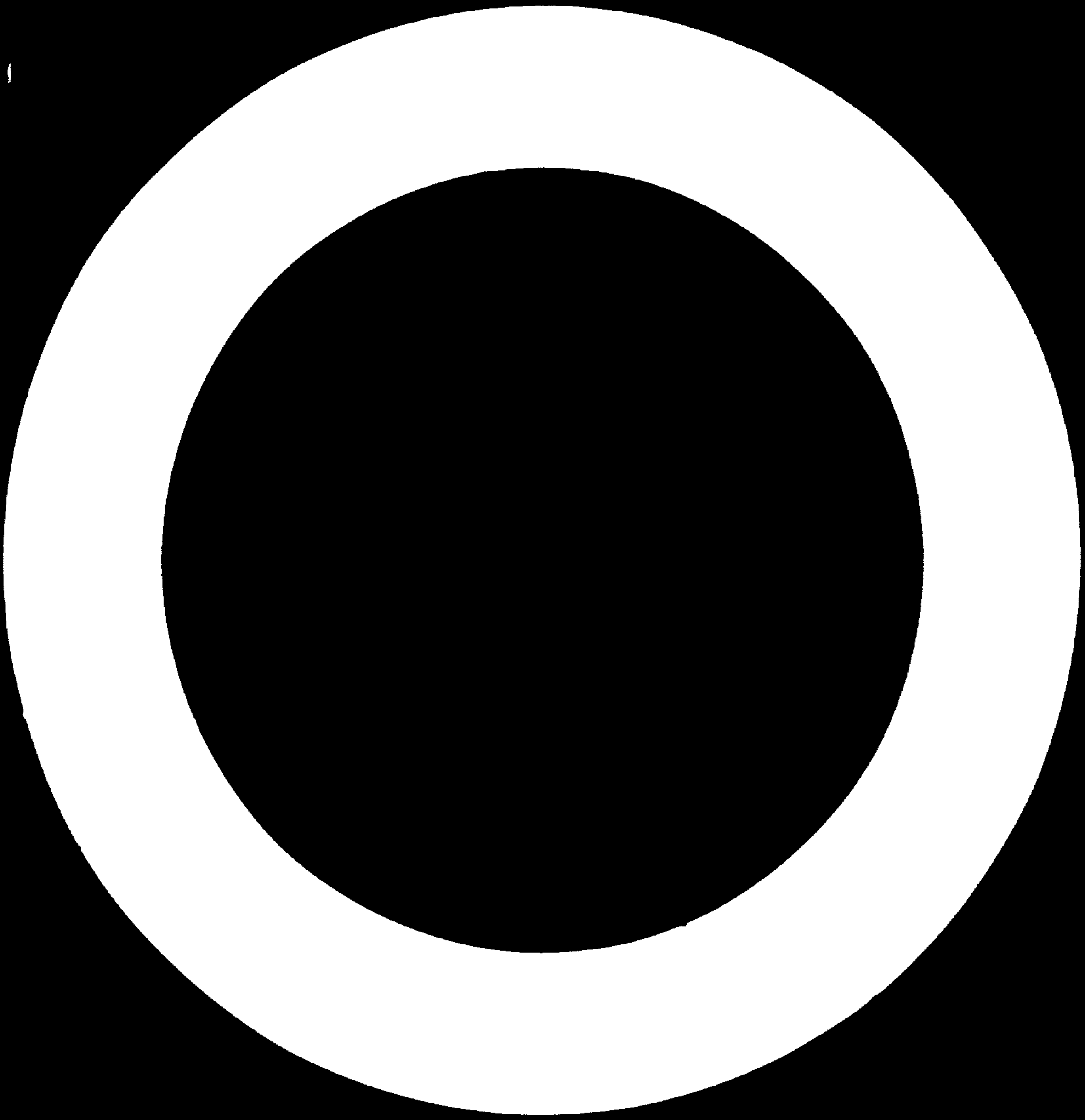
Sludge Handling

Scientists have developed methods for mechanical, biological and chemical treatment of waste waters. At the end of these processes a sludge of various character is obtained. Unfortunately so far there is no uniform solution as to how to handle this sludge.

From the sedimentation basins a sludge is taken out with a dry content of about 1 - 2 per cent. In some cases this sludge can be brought back into the production, but the sedimentation basin must then not be loaded with bark or rejects from centricleaners. Usually the sludge cannot be reused and in these cases it is dewatered to about 5 - 6 per cent dry content in special basins. Afterwards it is conditioned with some kind of dewatering apparatus. The dewatered sludge with dry content of about 30 - 40 per cent may be burnt together with bark from the wood department in the mill.

If the waste water is treated with aluminium sulphate the sludge will be very voluminous and difficult to dewater. In some cases this sludge just as well can be reused, but mostly it has to be treated. This problem was almost impossible to solve before a new type of centrifuge has been constructed in Denmark. This centrifuge makes it possible for the flocks to keep together when the water and sludge enter the slowly rotating compartment of the centrifuge, where the speed is up to 1600 revolutions per minute.

The problem is even more complicated when it is necessary to treat the effluent biologically. In Swedish sewage treatment plants it is a practice to use some kind of a digester to break down part of the organic substances in the sludge. This also reduces the bacteriological problem of the same. Sludge from the biological treatment plant of wood-processing mills has no harmful bacteriological effect. It is therefore possible to stabilize this sludge aerobically by putting it on the ground as fertilizer. This is a possible but, unfortunately, not a final solution.



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APPENDIX

SCAN-W 6:71

Accepted · September 1971

SUSPENDED MATTER IN WASTE WATER

Definition

For the purpose of this method suspended matter in waste water is defined as the matter retained when a sample of the water is filtered through a specified filter. Floating material and supernatant layers of nonaqueous liquids should be removed before the filtration.

Object and scope

The test specified in this method is intended for measuring the amount of suspended matter present in a sample of waste water.

While the test is applicable to most kinds of effluents, special care is required when filtering waters containing suspended matter that builds up a filtering layer having a smaller pore size than the actual filter (Note 1). The method is not intended for the determination of suspended oils.

Principle

The sample is filtered through a filter paper of glass fibres, and the retained dry matter is weighed. Relevant details concerning the filter are presented under «Apparatus».

Apparatus

1. Glass-fibre filters (Note 2), pore size approximately 10 μm (Note 3), 55 mm in diameter (Note 4).
2. Büchner funnels, with an inner diameter to take the filter papers.
3. Filter pump and filter flask, for the Büchner funnels.
4. Drying oven, adjustable to 105°C ± 5°C.

Preparation of sample

Remove floating material and other particulate agglomerates not dispersed on agitating the gross sample. Allow this to attain ambient temperature.

Because some kinds of effluents — for example those from kraft mills — are unstable, the samples should be analysed without delay.

Procedure

Agitate the gross sample vigorously and transfer immediately a suitable volume (generally ca. 100 ml) to a measuring cylinder rapidly and in one portion. The volume taken should contain 5 to 100 mg of suspended matter and should be chosen so that the filtering time is less than 1 min. Read off the sample volume on the cylinder scale.

Dry a filter for 1 h at 105°C ± 5°C in the drying oven. Allow it to attain equilibrium with the atmosphere near the balance and weigh to the nearest 0.1 mg. Ensure that during this procedure the filter is not contaminated by dust.

Place the weighed filter in the Büchner funnel and apply suction. Moisten the filter with a few drops of distilled water and check that it fits the funnel tightly.

Transfer the sample quantitatively to the funnel. If the time required for the sample to pass the filter exceeds 1 min, record the time needed. Rinse the cylinder with 20 ml of distilled water and use this for washing the filter. Rinse the sides of the funnel with a few millilitres of distilled water. Remove the filter carefully from the funnel and dry it in the drying oven for 2 h at 105°C ± 5°C. Allow to cool, and weigh as before. Check that the temperature and relative humidity near the balance have not changed appreciably since the filter was weighed prior to filtration.

Carry out the procedure in duplicate. The results should agree within 10 per cent.

Calculation and report

The suspended-matter content is given by the expression

$$X = 1000(a - b)/c$$

where

a = weight of filter and residue, mg.

b = weight of filter, mg.

c = volume taken for analysis, ml.

X = suspended-matter content, mg/l.

If X is at least 5 mg/l, report to 2 significant figures; otherwise report the result as «less than 5 mg/l».

The report should also state:

(a) The time elapsing between sampling and analysis.

(b) The manufacturer of the filter, its pore size (where known) and other relevant information.

(c) The filtering time, if longer than 1 min.

(d) If relevant, that suspended matter formed a filtering layer having a pore size smaller than that of the filter itself, and that the modification in Note 1 has been used. In this case, the two sample volumes should be reported. State, then, that the results are approximate.

Note 1

Many effluents from pulp, paper or wallboard mills contain minute particles which can block the filter by adhering to the walls of the pores, thus diminishing the pore size. When this happens the filtration time will be prolonged and the results will vary with the sample volume taken for analysis. In this case filter two samples, one twice the size of the other, but both rather small. Report the two results and the sample volumes and state that the results are approximate.

Note 2

Filters made of cellulosic fibres, such as Schleicher and Schüll 589 or Munktell 00R, are in common use in mill control. If such filters have been used, this should be stated specifically. The results shall then not be reported as being obtained in accordance with this standard method.

Note 3

A suitable filter is «Whatman GF/A».

Note 4

If the amount of suspended matter is large, larger filters and funnels may be used.

This method has been published in:

Norsk Skogindustri *25* (1971):12, 389—393. (English, Norwegian)
Paperi ja Puu — Papper och Trä *53* (1971):12, 735—740. (English, Finnish, Swedish)
Svensk Papperstidning *74* (1971):23, 809—810. (English)
Svensk Papperstidning *74* (1971):24, 845—846. (Swedish)

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SCANDINAVIAN PULP, PAPER AND BOARD
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SCAN-W 5:71

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BIOCHEMICAL OXYGEN DEMAND OF INDUSTRIAL EFFLUENTS

Definition

The biochemical oxygen demand of an industrial effluent is the amount of dissolved oxygen that is consumed in biochemical oxidation of organic matter under specified conditions (Note 1).

Scope

This method is designed for application to normal industrial effluents containing no other toxic or interfering substances than active chlorine, sulphur dioxide, hydrogen sulphide or other volatile sulphides.

Principle

The pretreated and suitably diluted sample is seeded with domestic sewage to initiate biochemical oxidation. Inorganic nutrient salts are added and the oxygen content is measured immediately and after an incubation period of 7 days at 20°C (Note 2).

The oxygen dissolved in the sample is determined by adding Mn^{2+} ions, which are oxidized to manganese(III))hydroxide, MnO(OH). On the addition of potassium iodide and acidification an equivalent amount of iodine is liberated and this is titrated with sodium thiosulphate.

Apparatus

1. **Glass incubation bottles of volume ca. 130 ml, with ground-in tapered stoppers. The volume of the bottles with the stopper inserted should be known to the nearest millilitre.**
2. **Constant temperature bath adjustable to a temperature of 20.0°C ± 1.0°C.**

Reagents

Check the quality of all the distilled water used in this method as described in Note 3.

1. Nutrient solutions:
   - (A) Phosphate buffer. Dissolve separately in sterile distilled water (Note 4) 8.5 g of potassium dihydrogen phosphate, KH_2PO_4, 21.8 g of dipotassium hydrogen phosphate, K_2HPO_4, 33.4 g of disodiumhydrogen phosphate, $Na_2HPO_4 \cdot 7\ H_2O$ and 3.24 g of potassium nitrate, KNO_3. Mix the solutions and dilute to 1 litre with sterile distilled water. Store in a dark, cool place. The solution easily becomes infected and has a short shelf life. Discard solutions that have become turbid or that are more than one month old.
   - (B) Magnesium sulphate solution. Dissolve 22.5 g of magnesium sulphate, $MgSO_4 \cdot 7\ H_2O$ in distilled water and make up to 1 litre.
   - (C) Iron(III)chloride and calcium chloride solution. Dissolve separately 0.25 g of iron(III)chloride, $FeCl_3 \cdot 6\ H_2O$, and 27.5 g of calcium chloride, $CaCl_2$, in distilled water. Mix the solutions and make up to 1 litre.
2. **Seed. Domestic sewage, preferably taken from the effluent from the secondary, or alternatively, the primary clarifier in a sewage treatment plant. Before use, leave the seed in contact with air in an open vessel for 24 to 36 h at 20°C. Take a portion from the centre of the liquid with a pipette and filter through surgical cotton or a paper filter (Note 5).**

3. Dilution water. Distilled water, free from copper and having an oxygen content at 20 °C of 8 to 10 mg per litre, obtained by bubbling air through the water. If compressed air is used for the purpose it should be purified by filtering. It must not contain foreign substances, such as oil, water or exhaust gases. Check the oxygen content as described under «Procedure».

4. Sulphuric acid, 0.05 M. Add 2.8 ml of concentrated H_2SO_4 ($\rho = 1.84$) to *ca.* 700 ml of distilled water and make up to 1 litre.

5. Sodium hydroxide solution, 0.1 M. 4 g of NaOH per litre.

6. Sodium sulphite solution, *ca.* 0.0125 M. Dissolve 1.6 g of Na_2SO_3 in distilled water and make up to 1 litre. As this solution is unstable, use only freshly prepared solutions.

7. Potassium iodide solution, 10 %, 10 g of KI per 100 ml.

8. Acetic acid, 8.7 M. Add 250 ml of glacial CH_3COOH ($\rho = 1.049$) to 250 ml of distilled water.

9. Starch indicator solution. Dissolve 1 g of «soluble starch» in 200 ml of hot distilled water. Add a small amount (a few milligrammes) of mercury(II)iodide, HgI_2, as a preservative.

10. Alkaline iodide solution. Dissolve separately 500 g of sodium hydroxide, NaOH, and 150 g of potassium iodide, KI, in distilled water. Mix the solutions and dilute to 1 litre. Add a solution of 10 g of sodium azide, NaN_3, in 40 ml of distilled water.

11. Manganese(II)sulphate solution. Dissolve 480 g of $MnSO_4 \cdot 4\,H_2O$ in distilled water and make up to 1 litre. Filter the solution if it is turbid.

12. Phosphoric acid, H_3PO_4, concentrated, $\rho = 1.83$.

13. Sodium thiosulphate solution, 0.1 N. Dissolve 24.8 g of $Na_2S_2O_3 \cdot 5\,H_2O$ in distilled water and dilute to 1 litre. Shelf-life limited.

14. Sodium thiosulphate solution, 0.01 N, standardized, normality known to 0.0001 N.

15. Glucose-glutamine solution. Dissolve separately in distilled water 150.0 mg of glucose, $C_6H_{12}O_6$, and 187.2 mg of glutamic acid hydrochloride, $C_5H_9NO_4 \cdot HCl$ (both substances dried over phosphorus pentoxide). Mix the solutions in a 1-litre volumetric flask and make up to the mark. The solution should be freshly prepared.

16. Iodine solution, 0.01 N. Dissolve 1.28 g of iodine, I, and 20 g of potassium iodide, KI, in 40 ml of distilled water in a 1-litre volumetric flask and make up to the mark. Let the solution stand for 24 h before use and store it in a dark, glass-stoppered bottle. Commercially available standard solutions of iodine may be used.

All chemicals should be of reagent grade (pro analysi).

Preparation of sample

Instructions for transport and storage of samples are given in Note 6.

The preparation of the sample is dependent on the presence and nature of interfering substances. These should be eliminated as instructed below. Shake the sample bottle before removing any part of its content.

(a) Active chlorine

Active chlorine is reduced in acid solution by the addition of an equivalent amount of sodium sulphite.

To 100 ml of the sample add 10 ml of the potassium iodide solution, 10 ml of the acetic acid and a few drops of the starch indicator. If a blue colour appears, titrate with the sodium sulphite solution (consumption *a* ml). The endpoint is indicated by the disappearance of the blue colour.

To a second 100-ml sample, add *a* ml of the sulphite solution and, after 10 min, potassium iodide solution, acetic acid and starch solution as above. If the solution turns blue add more sulphite (*b* ml) until the colour just disappears. Add to the sample (*a* + *b*) ml of sulphite solution per 100 ml.

(b) Sulphur dioxide

Under the conditions of the BOD determination sulphur dioxide consumes oxygen and must therefore be removed.

If the sample contains sulphur dioxide transfer a measured volume to a beaker and acidify with the sulphuric acid to pH 3 or just below. Note the volume of acid used and take this into account when calculating the dilution factor (see below under «Dilution of sample»). Pass nitrogen through the sample for about 30 min by means of a glass tube to whose lower end is connected a piece of fritted glass, or by means of some other suitable device for producing small bubbles of gas.

Check the immediate oxygen demand by titrating a known volume of the sample with standard iodine solution; 1 ml of 0.01 N iodine solution corresponds to 0.08 mg of oxygen. The immediate oxygen demand of the final test sample should not exceed 0.1 mg per litre.

(c) Hydrogen sulphide and other sulphides

Remove with nitrogen at pH 5 or lower, as described under *(b)*.

(d) Suspended material

If the sample contains suspended material it should be decided whether its biochemical oxygen demand is to be included in the test (Note 7). If it shall be included, homogenise the sample in a mixer; if it shall not, remove the suspended material by sedimentation: shake the sample and transfer a part of it to a beaker or a flask. After 30 min take the amount required from the supernatant solution.

The presence of suspended material in the test samples may lower the precision of the test.

(e) Oxygen

If the sample contains oxygen in excess of the equilibrium amount at room temperature *(ca.* 9 mg per litre)it should be removed by passing air through it.

If no interfering substances are present, or if these have been eliminated as instructed, dilute the sample as described below.

Dilution of sample

Although this method covers effluents containing a wide range of concentrations of oxygen-consuming material the oxygen content at the end of the incubation period X_7 should be within 35 to 60 per cent of the original value X_0, which is 8 to 9 mg per litre. The original sample will therefore normally have to be diluted, and several «test samples» of different dilutions must then be prepared from the same original sample. The dilution is expressed in terms of a dilution factor, *d*, which is the ratio of the volume of the diluted sample to that of the original sample.

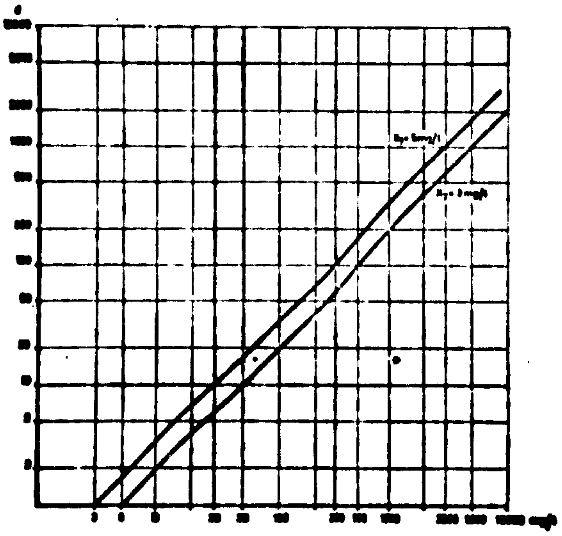

Figure 1.

The dilution factor *d* plotted against the biochemical oxygen demand, BOD_7. The two lines correspond to values of X_7 of 5 and 3 mg/l, respectively.

Prepare the test samples as follows:

Bring the samples and dilution water to a temperature of 20.0°C ± 1.0°C.

Transfer to a 1-litre volumetric flask a volume not less than 5 ml original sample, selected to give an oxygen content at the end of the incubation period, X_7, of between 3 and 5 mg per litre. If the dilution factor to be used is greater than 200, the dilution must be made in two steps. If the sample contains large amounts of suspended material use measuring cylinders.

If the approximate oxygen demand of the original sample is unknown, prepare 3 or 4 test samples having dilution factors forming a series the consecutive terms of which do not differ by more than a factor of 2.5. A suitable series is 1, 2.5, 5, 10, 25 . . . (Note 8).

Prepare each test sample in a 1-litre volumetric flask. Before making up to the mark add to the sample 1 ml of each of the nutrient solutions A, B and C (Note 9) and 1 ml of the seed. Check that the pH of the solution is between 6 and 8, and adjust if necessary with a few drops of the 0.1 M sodium hydroxide solution or the 0.05 M sulphuric acid (Note 10).

Perform all dilutions with dilution water.

Procedure

To check the procedure run 3 control samples parallel with each batch of test samples:

1. A control sample containing 25 ml of seed per litre of dilution water.

2. A control sample containing 1 ml of seed and 15 ml of the glucose-glutamine solution per litre.

3. A reagent blank containing 1 ml of seed per litre.

All 3 control samples should contain the normal quantities of nutrient salts (Note 11).

For each test or control sample rinse 5 incubation bottles with a small portion of the sample, fill them to the rim and insert the stopper. Check that no air has been trapped in the bottle.

Place 3 of the bottles in a constant-temperature bath at 20.0°C ± 1.0°C for 7 d. Exclude light to prevent growth of oxygen-producing algae. Determine the amount of oxygen in each of the 2 remaining bottles. Remove the stopper and deposit, at the bottom of the bottle, 1 ml of the alkaline iodide solution, and just below the surface 1 ml of the manganese sulphate solution. Replace the stopper, thereby expelling approximately 2ml of the solution. (This is corrected for in the calculation.) Shake the bottle, leave for 5 min and shake again. Allow the precipitate to settle — this will take about 15 min. Remove the stopper carefully and at the surface add 3 ml of the phosphoric acid; replace the stopper immediately; about 3 ml of solution will be expelled. (No correction is required.) Shake the bottle until the precipitate is dissolved.

Transfer the contents of the bottle (Note 12) to a titration flask. Titrate immediately with the 0.01 N sodium thiosulphate solution. Towards the end of the titration add a few drops of the starch solution as an indicator. Calculate the oxygen content from the expression

$$X_0 = \frac{8000\, a\, n}{b - 2}$$

where

a = volume of sodium thiosulphate solution consumed by the sample, ml

n = normality of the sodium thiosulphate solution, equivalents per litre

b = volume of the incubation flask, ml

X_0 = oxygen content, mg of O_2 per litre.

Record the mean to 3 significant figures as the oxygen content.

Determine the oxygen content in the incubated flasks after 7 d ± 6 h and record the mean as X_7.

Calculation and report

Calculate the oxygen demand from the expression

$$BOD_7 = d[(X_0 - X_7) - (C_0 - C_7)]$$

where

X_0 = oxygen content in the test sample at the start, mg of O_2 per litre

X_7 = oxygen content in the test sample after 7 d, mg of O_2 per litre

C_0 = oxygen content in the reagent blank at the start, mg of O_2 per litre

C_7 = oxygen content in the reagent blank after 7 d, mg of O_2 per litre

d = dilution factor, the ratio of the volume of the diluted sample to that of the original sample.

BOD_7 = biochemical oxygen demand, mg per litre.

Report the result to 2 significant figures. Report any pretreatments and if the seed check (control sample 1), the standard mixture (control sample 2) or the reagent blank has given values outside the ranges specified in Note 11.

If 2 test solutions made from the same original sample but having different dilution factors give different oxygen demands for the original sample, report both values, provided that the oxygen consumption lies within the limits specified (35 to 60 procent of X_0). The difference may be due to poisoning of the seed by toxic components.

Note 1

The purpose of a determination of biochemical oxygen demand is to measure the amount of organic material decomposed and oxidized by natural aquatic micro-organisms (mainly bacteria). Under the conditions of the test, however, several inorganic compounds or ions, for instance SO_3^{2-} and Fe^{2+}, consume oxygen. These interfering substances are therefore removed before the test is started

Note 2

In many countries an incubation period of 5 d is commonly applied. The period of 7 d specified in this method is convenient for laboratories working a 5-day week.

Note 3

Distilled water sometimes consumes oxygen. Check the quality of the water in this respect by determining the permanganate number of the water as taken and after it has been boiled for 20 min. The method is described in SCAN-W 1. If the difference in the consumption of 0.01 N sodium thiosulphate solution exceeds 0.15 ml the water should not be used for preparing solutions or dilution water.

Note 4

Because nutrient solution A is susceptible to bacterial contamination, sterilize the water used for its preparation by boiling for a few minutes; also sterilize the bottle for storing the solution by heating it to 120° C for 2 h.

Do not dip unsterilized objects such as pipettes into the solution. Do not return unused portions to the storage bottle.

Note 5

To avoid infection of personnel, extreme care should be exercised when handling the seed. Rinse pipettes and other glass-ware thoroughly after each test. Do not put used pipettes on laboratory benches, but use a pipette stand.

After working with the seed disinfect the hands. At the end of each working day sterilize all the glass-ware (except incubation bottles).

Note 6

Industrial effluents with a high oxygen demand and other properties (such as a high or low pH) that inhibit or prevent spontaneous biochemical processes may be stored for 1 to 4 days after sampling, preferably at 4°C.

Non-sterile samples (containing effluents from paper mills, food factories and domestic sewage) should be tested as soon as possible after sampling. Delay due to transport and other causes should not exceed 1 day. Keep the samples at a temperature of 4°C.

Note 7

For example, if the object of the investigation is to study the performance of a biological treatment with regard to degradable dissolved as well as suspended material, suspended material should not be separated.

Note 8

In selection of the dilution factors to be applied the diagram in *Figure 1* may be used as a guidance. The diagram illustrates the relationship between the BOD_7 for the original sample and the dilution factors to be selected for X_7 = 5 mg/l and X_7 = 3 mg/l.

Note 9

If the number of samples to be analysed is large it may be convenient to use dilution water containing 1 ml per litre of each of the nutrients A, B and C.

Note 10

If the pH is adjusted before the final dilutions, the properties of the sample may be altered; where possible, pH adjustments during the preparation of the sample should therefore be avoided.

Note 11

The BOD_7 of the seed (control sample 1) should fall within the range 50 to 300 mg O_2 per litre. Control sample 2 should have a BOD_7 of 225 mg ± 10 mg of oxygen per litre. A reduction in the oxygen content of the reagent blank exceeding 0.7 mg of oxygen per litre indicates that at least one of the reagents is contaminated.

Note 12

If a large number of bottles are tested it may be more convenient to use the following technique:

Cut the neck of a 100 ml volumetric flask at 101.6 ml ± 0.2 ml. Place a rubber gasket around the stem, invert the bottle and press the gasket into the mouth of an incubation bottle. Turn bottle and flask so that the flask fills. When the flask is free from air bubbles remove the bottle and transfer the aliquot (101.6 ml) to a titration flask. Titrate with 0.0125 N sodium thiosulphate solution as described above and calculate the oxygen content from the expression

$$X = 80\, n_2 f$$

where

n_2 = normality of the sodium thiosulphate solution, equivalents per litre

f = volume of thiosulphate solution consumed, ml

X = oxygen content, mg of O_2 per litre.

If the normality is exactly 0.0125, the expression reduces to

$$X = f$$

The volume of the volumetric flask is calculated as follows:

$$\frac{100 \times 130}{130 - 2} = 101.6 \text{ ml}$$

Literature

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PERMANGANATE NUMBER OF WASTE WATERS

Definition

The permanganate number of waste waters is defined as the number of milligrams of potassium permanganate consumed by one litre of waste water under standard conditions of test as specified in this method.

Principle

To the acidified sample is added a known amount of potassium permanganate at the temperature of a boiling water bath. The consumption of permanganate is taken as a measure of the content of organic matter in the sample. Unconsumed permanganate is determined iodometrically.

Scope

This method applies to waste waters and receiving waters, or dilutions thereof, containing less than 300 mg of chloride ions per litre.

Apparatus

1. Water bath with rack for sample tubes 25 mm × 85 mm (Note 1).
2. Sample tubes, 25 mm × 85 mm (Note 2).
3. Glass rods *ca* 5 mm × 120 mm, flattened at one end and bent at the other to form a handle; for stirring during titration.
4. Piston burette, 5 ml, graduated in 0.005 ml.

Reagents

1. Potassium permanganate solution, 0.01 N. Dissolve 3.16 g of $KMnO_4$ in distilled water and dilute to 1000 ml. Filter this stock solution (0.1 N) and store in a dark bottle. Dilute the stock solution to 0.01 N immediately before use.
2. Sulphuric acid, 4.5 M. Add cautiously 1 volume of H_2SO_4 ($\rho = 1.84$) to 3 volumes of distilled water.
3. Potassium iodide solution, 0.1 M. Dissolve 4.15 g of KI in distilled water and dilute to 250 ml.
4. Starch solution, 2 g per litre. Add a few grains of mercuric iodide, HgI_2, to the solution.
5. Sodium thiosulphate solution, 0.01 N. Dissolve 2.482 g of $Na_2S_2O_3 \cdot 5\,H_2O$ in 500 ml of distilled water, add 10 ml of isobutanol, $(CH_3)_2CHCH_2OH$, and 0.1 g of anhydrous sodium carbonate, Na_2CO_3, and dilute to 1000 ml. Normality known to an accuracy of ± 0.00002 N. The solution may be stored for up to 6 months.

All reagents should be of analytical grade.

Preparation of sample

Analyse the samples as soon as possible, and not later than 5 days after collection. If the storage time will exceed 2 days, store at 0 to 5°C.

Preserve samples that might contain a large number of bacteria (domestic effluents, paper mill effluents, heavily polluted receiving waters) and that cannot be analysed immediately, by adding per litre of sample 1 ml of a saturated solution of mercury(II) chloride, $HgCl_2$. Acidify samples containing chlorine, hydrogen sulphide, sulphuric dioxide or iron(II) salts with a few drops of sulphuric acid and aerate before analysis.

Allow samples containing easily sedimenting particles to settle for 1 h (alternatively 30 min). Discard the sediment and shake the solution before taking a portion for analysis. Any necessary dilution shall be made after the sedimentation. Samples not requiring sedimentation should be shaken before taking a portion for analysis.

Procedure

Transfer a 10 ml portion of the sample or a dilution thereof (Note 3) to a sample tube. Add 0.5 ml of the sulphuric acid and 2.0 ml of the potassium permanganate solution (Note 4). Place the tube in a boiling water bath for exactly 20 min and then cool immediately in cold water. Add 1 ml of the potassium iodide solution and, using starch as indicator, titrate with sodium thiosulphate solution until the blue colour disappears. Run a blank, in which 10 ml of distilled water is used instead of the sample.

Calculation and report

Carry out two determinations and calculate as follows:

$$X = 3160\, n\, c\, (b - a)$$

where

a = sodium thiosulphate solution consumed in the titration of the sample, ml.

b = sodium thiosulphate solution consumed in the titration of the blank, ml.

n = normality of the sodium thiosulphate solution

c = concentration of waste water in the portion taken for anaylsis, ml/ml.

X = permanganate number, mg $KMnO_4$ per litre of waste water.

Report the mean of the two determinations to two significant figures. Report also the storage time (if more than 5 days), the time for sedimentation (0, 30, 60 min) and, if relevant, aeration and addition of preservative.

Note 1

The heat capacity and power of the water bath should be large enough to ensure that boiling will be resumed within 2 min of the tubes having been placed in the bath. Example: Rack for 20 tubes, power of water bath 2 kW.

Note 2

Sample tubes are made by shortening standard 25 mm × 125 mm test tubes.

Note 3

Dilute waters with a high permanganate consumption to give a permanganate number of *ca.* 10 to 40 mg/l for the dilution, corresponding to a value for *a* of *ca* 0.6 to 1.6 ml.

Note 4

The use of an accurate dispensing outfit is recommended for adding the permanganate solution.

Literature

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HYDROGEN SULPHIDE IN WASTE WATER

Scope

This method applies to all kinds of waste water. If the sample contains sulphur dioxide, the modification in Note 1 should be used.

Principle

After acidification of the sample the hydrogen sulphide is stripped off by a stream of nitrogen, absorbed in an alkaline phosphate buffer solution and determined colorimetrically by the methylene-blue method (Note 2).

Apparatus

1. Apparatus, for stripping off hydrogen sulphide, as shown in *Figure* 1.
2. Apparatus, for standardization of hydrogen sulphide solution, consisting of a thick-walled conical flask, 250 ml, with ground-in joint and a separating funnel, 50 ml, with ground-in joints (*Figure* 2).
3. Spectrophotometer or filter colorimeter.

Reagents

1. Distilled water, to be used for preparation or dilution of standard solutions or samples, freed from dissolved oxygen by boiling and kept oxygen-free by bubbling nitrogen through the boiled water.

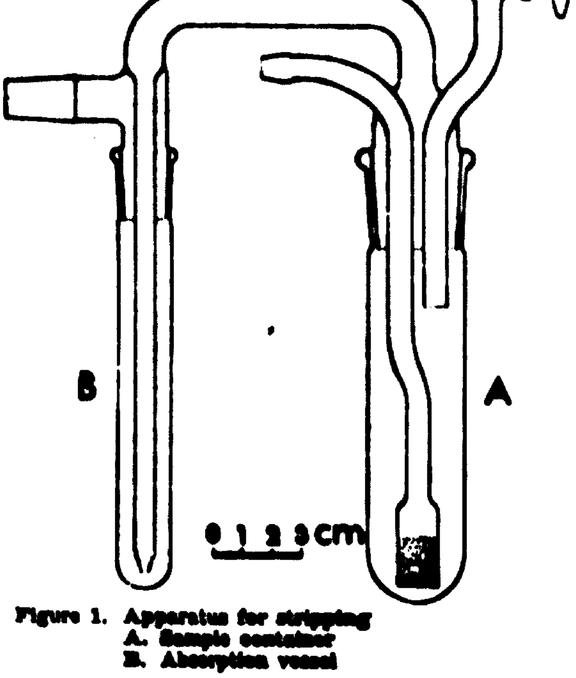
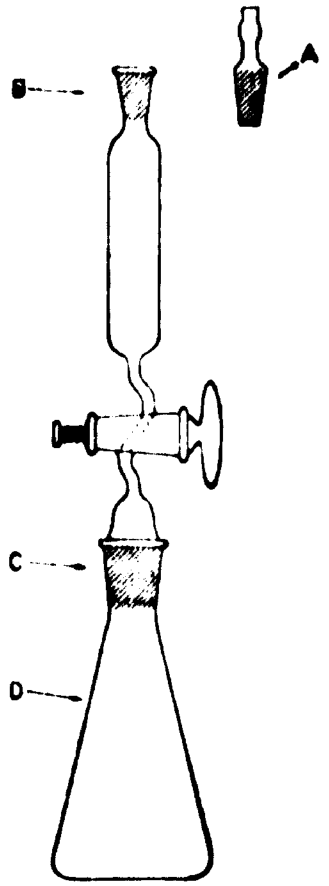


Figure 1. Apparatus for stripping
A. Sample container
B. Absorption vessel



igure 2. Apparatus for standardization
A and B. Ground-in joint no. 14
C. Ground-in joint no. 24
D. Thick-walled conical flask

2. Hydrochloric acid, *ca.* 6 M. Dilute 500 ml of HCl (ρ = 1.19) with 500 ml of distilled water.
3. Absorption solution: Dissolve 20.56 g of disodium hydrogen phosphate, $Na_2HPO_4 \cdot 2\,H_2O$, [illegible] g of sodium hydroxide, NaOH, and 1.6 g of sodium hydrogen carbonate, $NaHCO_3$, in distilled water in a 1 litre volumetric flask and make up to the mark with distilled water; adjust the pH to 10.5.
4. Amine-sulphuric acid I. Add 25 ml of concentrated sulphuric acid, H_2SO_4 (ρ = 1.84), to [illegible] ml of distilled water, cool and add 17.5 g of p-amino-N,N-dimethylaniline oxalate, $[(CH_3)_2NC_6H_4NH_2]_2(COOH)_2$. When the amine has dissolved, dilute to 50 ml with distilled water.
5. Sulphuric acid, *ca.* 9 M. Add 300 ml of concentrated sulphuric acid, H_2SO_4 (ρ = 1.84), to [illegible] ml of distilled water. Cool to room temperature.
6. Amine-sulphuric acid II. Dilute 5 ml of amine-sulphuric acid I with 495 ml of *ca.* 9 M sulphuric acid. The solution is stable for at least 1 month.
7. Iron(III)chloride solution, 1.2 %. Dissolve 2 g of $FeCl_3 \cdot 6\,H_2O$ in 100 ml of distilled water.
8. Iodine solution, 0.1 N. Dissolve 12.8 g of iodine, I_2, and 20 g of potassium iodide, KI, in 40 ml of distilled water in a 1 litre volumetric flask and make up to the mark. Let the solution stand for 24 h before use and store it in a dark, glass-stoppered bottle.
9. Sodium thiosulphate solution, 0.1 N, standardized. Normality known to an accuracy of ± 0.0005 N.
10. Starch solution, 2 g per litre. Add a few grains of mercuric iodide, HgI_2, to the solution.
11. Standard sulphide solution. Rinse a few large sodium sulphide crystals, $Na_2S \cdot 9\,H_2O$, with distilled water and transfer 1.3 g of them, while still wet, to a 1 litre volumetric flask. Dissolve them immediately in oxygen-free distilled water and make up to the mark.

All reagents should be of analytical grade (pro analysi).

Calibration

Standardize the standard solution as follows: Pipette 25.0 ml of 0.1 N iodine solution and 4 ml of 6 M hydrochloric acid into the thick-walled conical flask and connect the separating funnel (Figure 2). Evacuate the flask through the funnel by means of a filter pump, close the stop-cock and disconnect the pump. Pipette 50.0 ml of the standard solution into the funnel, suck it down carefully so that no air is admitted and rinse with about 15 ml of distilled water. Suck down the rinsing water into the flask. Repeat the rinsing once and then shake the flask vigorously. Transfer 20 ml of distilled water to the funnel, open the stop-cock and suck down the water; remove the funnel. Titrate with 0.1 N sodium thiosulphate solution using the starch solution as an indicator, and denote the consumption by *a* ml. Titrate a blank consisting of 100 ml of distilled water, 25.0 ml of iodine solution and 4 ml of 6 M hydrochloric acid. Denote the consumption by *b* ml. Calculate the sulphide concentration:

$$X = 16000\, n\, (b - a)/c$$

where

a = volume of sodium thiosulphate solution consumed in the titration of the sample, ml.
b = volume of sodium thiosulphate solution consumed in the titration of the blank, ml.
c = volume of the standard solution, ml.
n = normality of the sodium thiosulphate solution.
X = sulphide concentration of the standard solution, mg of S^{2-}/l.

The standardized solution should contain maximum 180 mg of S^{2-}/l. Dilute it immediately with absorption solution, 1 : 100, and transfer aliquots of 1.0, 3.0, 5.0 and 10.0 ml of the diluted standard solution to four 25 ml volumetric flasks. Add absorption solution to give a final volume of 10 ml. Use a fifth flask for the preparation of a reagent blank.

Mix 10 ml of the amine-sulphuric acid solution II and 10 ml of the iron(III)chloride solution. Add cautiously 2 ml of the mixture to one volumetric flask, dilute to the mark with distilled water and shake the flask vigorously. Repeat the procedure for the other flasks in the same way. Measure the absorbancy within 5 min — 2 h at 670 nm, using the reagent blank as a reference. Divide the reading by the length of the cell in centimetres. Plot the values obtained against the sulphide concentrations, expressed as milligrammes of S^{2-} per litre of coloured solution and check that the points lie on a straight line through the origin of coordinates.

Preparation of sample

When sampling, add immediately *ca.* 4 g of zinc acetate, $Zn(CH_3COO)_2 \cdot 2\,H_2O$, per litre of waste water.

Before removing a sample for analysis shake the sample bottle vigorously to distribute the zinc sulphide precipitate evenly and immediately take an aliquot for testing or dilution. If necessary use a pipette with wide opening.

Samples containing large amounts of sulphides, such as condensates, should be diluted with distilled water just before performing the test.

Procedure

After shaking the sample bottle, pipette a volume of sample not exceeding 40 ml (Note 3) into the sample container (Figure 1) (Note 1). If the sulphide content of the waste water is high only a small sample volume is taken; then add distilled water to a volume of 20 ml — 40 ml. Transfer 10.0 ml of absorption solution to the absorption vessel. Assemble the apparatus, close the stop-cock and transfer *ca.* 7 ml of 6 M hydrochloric acid to the funnel. Open the stop-cock, loosen the absorption vessel for a moment and hold it so that the tip of the glass tube is just beneath the surface of the liquid to avoid counter-pressure, thus ensuring that the hydrochloric acid runs down into the sample container as fast as possible. Close the stop-cock immediately, fasten the absorption vessel and allow a rapid current of nitrogen (*ca.* 200 ml/min) to bubble through the apparatus for 20 min.

Immediately pipette a volume containing not more than 18 µg S^{2-} of the solution in the absorption vessel into a 25 ml volumetric flask and add 2 ml of the reagent mixture as described under «Calibration». Dilute to the mark with distilled water and shake the flask vigorously. Measure the absorbancy within 5 min — 2 h at 670 nm with a reagent blank as a reference and divide the reading by the length of the cell.

Calculation and report

Carry out two determinations and calculate as follows:

$$Y = d\,e\,f/g\,h$$

where

d = sulphide concentration, obtained from the absorbancy value and the calibration curve, mg of S^{2-} per litre of coloured solution.
e = volume of the coloured solution, ml.
f = volume of the absorption solution, ml.
g = fraction of absorption solution taken, ml.
h = volume of sample taken, ml.
Y = sulphide concentration, mg of S^{2-}/l.

Report the result to two significant figures.

Note 1

If the waste water contains sulphur dioxide the hydrochloric acid should be replaced by an acetate buffer of pH 4.0–4.5 (equal volumes of 1 M acetic acid, CH_3COOH, and 1 M sodium acetate solution, CH_3COONa). Dissolve 80 g of ethylenediaminetetraacetic acid, disodium salt, $C_{10}H_{14}O_8N_2Na_2 \cdot 2\,H_2O$, per litre of acetate buffer solution to mask the zinc ions present in the sample.

Note 2

The stripping operation may be excluded if pilot tests have clearly shown that the results obtained with this type of sample are independent of stripping. In this case pipette a suitable sample volume into a 25 ml volumetric flask and add the reagents as described under «Calibration». With organic matter present chelating the iron the prescribed amount of iron(III)-chloride solution might be insufficient for complete colour development and a further addition of 2 ml of a 6 % iron(III)chloride solution or the equivalent amount of iron(III)chloride must then be made.

Note 3

To check the apparatus, treat a suitable volume of the standard solution as described under «Procedure».

Literature

1. *Bethge, P. O.:* Anal. Chim. Acta 9(1953):2, 129—139.
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This method has been published in:

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Paperi ja Puu — Papper och Trä *51* (1969):4a, 323—331. (English, Finnish, Swedish).
Svensk Papperstidning *72* (1969):6, 190—192. (English).
Svensk Papperstidning *72* (1969):7, 232—234. (Swedish).

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NON-VOLATILE MATTER IN WASTE WATERS

Definitions

The dry matter content of waste water is the ratio of the mass of the dried residue of the evaporated sample to the original volume of the sample, the drying having been carried out at 105°C ± 5°C under specified conditions.

The residue on ignition is defined as the ratio of the mass of the ignited dry matter to the original volume of the sample, the dry matter having been ignited at 600°C ± 25°C.

The loss on ignition is the difference between the dry matter content and the residue on ignition.

Scope

This method is intended for unfiltered samples of waste water having a dry matter content of less than 50 g/l.

Apparatus

1. Dishes of platinum, quartz or glazed porcelain, for sample volumes of 10 ml — 100 ml.
2. Ventilated drying oven with means for circulating the air, adjusted to maintain a temperature of 105°C ± 5°C (Note 1).
3. Electric muffle furnace, adjusted to maintain a temperature of 600°C ± 25°C.

Reagent

Ammonium nitrate solution, 1 %. Dissolve 1 g of NH_4NO_3 in 100 ml of distilled water. The reagent should be of analytical grade.

Procedure

Ignite an empty dish in the muffle furnace at 600°C ± 25°C (Note 2) and allow to cool in a desiccator. If several dishes are cooled in the same desiccator, allow a cooling time of 3 h. Weigh the dish to the nearest 0.1 mg.

With a pair of forceps remove large objects, such as pieces of bark, that are not actually suspended in the sample. Shake the bottle and measure into the weighed dish a volume of sample large enough to produce a dry residue of 15 mg — 500 mg. Evaporate the water and dry the residue for 2 h at 105°C ± 5°C in the drying oven. If the sample contains spent liquor increase the drying period to 24 h. If several dishes are cooled in the same desiccator, allow the dish to cool for 1 h. Weigh the dish to the nearest 0.1 mg.

Place the dish in the muffle furnace and ignite for 2 h at 600°C ± 25°C (Note 3). If the sample contains spent liquor increase the heating time to 4 h or until the residue is greyish-white. If the ashing is not complete, i.e. if the residue contains black particles, moisten the residue, after cooling, with a few drops of ammonium nitrate solution. Evaporate the moisture, ignite the residue at 600°C ± 25°C for 30 min and allow to cool in a desiccator. If several dishes are cooled in the same desiccator, allow a cooling time of 3 h. Weigh the dish to the nearest 0.1 mg.

Calculation and report

Calculate as follows:

$$X = 10^6(a - c)/d$$
$$Y = 10^6(b - c)/d$$
$$Z = 10^6(a - b)/d$$

where

a = mass of dish and sample residue after drying, g.
b = mass of dish and sample residue after igniting, g.
c = mass of the empty dish, g.
d = volume of waste water sample taken, ml.
X = dry matter content, mg/l.
Y = residue on ignition, mg/l.
Z = loss on ignition, mg/l.

Report the result to not more than two significant figures. State the drying and heating times used.

Note 1

If the drying oven has no means of circulating the air, evaporate the samples to dryness on a boiling water bath before placing them in the oven.

Note 2

If the residue on ignition is not required, the dish may be heated in the drying oven at 105°C ± 5°C.

Note 3

If the dry residue contains fibres it may burn with a flame; to avoid this the furnace temperature should not exceed 200°C when the dish is inserted; it should then be raised slowly.

This method has been published in:
Norsk Skogindustri *22* (1968): 10, 356—359. (English and Norwegian)
Paperi ja Puu — Papper och Trä *50* (1968): 10, 609—610. (English)
Paperi ja Puu — Papper och Trä *50* (1968): 11, 697—700. (Finnish and Swedish)
Svensk Papperstidning *71* (1968): 20, 751—754. (Swedish and English)

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SETTLEABLE MATTER IN WASTE WATER

Definition

For the purpose of this method settleable matter in waste water is defined as the matter that separates on sedimentation under specified conditions

Object and scope

The test specified in this method is intended for measuring the amount of settleable matter present in a sample of waste water.

Principle

The sample is shaken and a known volume is withdrawn and then allowed to settle for a specified time, generally 30 min. The supernatant water is removed by suction and the remainder is filtered. The solid matter so obtained is dried and weighed.

Apparatus

1. Imhoff cone (conical vessel of glass) capacity 1 litre.
2. Glass-fibre filters, pore size approximately 10 µm (Note 1), 55 mm in diameter (Note 2).
3. Büchner funnels, with an inner diameter to take the paper filters.
4. Filter pump and filter flask for the Büchner funnels.
5. Drying oven, adjustable to 105° C ± 5° C.

Preparation of sample

Remove floating material and other particulate agglomerates not dispersed on agitating the gross sample. Allow this to attain ambient temperature.

Because some kinds of effluents — for example those from kraft mills — are unstable the samples should be analysed without delay.

Procedure

Agitate the gross sample vigorously and immediately transfer 1 litre of the contents to an Imhoff cone. Agitate with a glass rod until all air bubbles have escaped.
Allow suspended matter to settle for 30 min, or, if this occurs slowly, for 60 min. Withdraw the supernatant water by means of a filter pump, taking care that no sedimented matter is lost.
Dry a filter for 1 h at 105° C ± 5° C in the drying oven. Allow it to attain equilibrium with the atmosphere near the balance and weigh it to the nearest 0.1 mg. Ensure that during this procedure the filter is not contaminated by dust.
Place the weighed filter in the Büchner funnel and apply suction. Moisten the weighed filter with a few drops of distilled water and check that it fits the funnel tightly.
Transfer the sediment quantitatively to the funnel and rinse the cone with 20 ml of distilled water; use this for washing the filter. Rinse the sides of the funnel with a few millilitres of distilled water. Carefully remove the filter from the funnel and dry in the drying oven for 2 h at 105° C ± 5° C. Allow to cool and weigh as before. Check that the temperature and relative humidity near the balance have

not changed appreciably since the filter was weighed prior to filtration.

Carry out the procedure in duplicate. The results should agree within 10 per cent.

Calculation and report

The amount of settleable matter is given by the expression

$$X = a - b$$

where

a = weight of filter and residue, mg.

b = weight of filter, mg.

X = settleable matter content, mg/l.

The report should also state:

(a) The time elapsing between sampling and analysis

(b) The manufacturer of the filter, its pore size (where known) and other relevant information

(c) The time allowed for sedimentation.

Note 1

A suitable filter is «Whatman GF/A».

Note 2

If the amount of settleable matter is large, larger filters and funnels may be used.

This method has been published in:

Norsk Skogindustri 26 (1972): 2, 47—50. (English and Norwegian)
Paperi ja Puu — Papper och Trä 54 (1972): 1, 11—16. (English, Finnish and Swedish)
Svensk Papperstidning 75 (1972): 4, 143—144. (English and Swedish)

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MAGNESIUM IN WASTE WATER

Principle

The sum of magnesium and calcium is determined volumetrically with EDTA solution. In a separate titration the calcium is determined, and the amount of magnesium is obtained as the difference.

Reagents

1. Hydrochloric acid, *ca.* 6 M. Dilute 500 ml of HCl ($\rho = 1.19$) with 500 ml of distilled water.
2. Hydrochloric acid, 1 M. Dilute 82.5 ml of HCl ($\rho = 1.19$) to 1 litre with distilled water.
3. Standard EDTA solution, 0.01 M. Dry a portion of ethylenediaminetetraacetic acid, disodium salt, $C_{10}H_{14}O_8N_2Na_2 \cdot 2H_2O$ at 80°C over a period of 2 to 3 days. Weigh 0.01 mole (3.722 g) of the dried substance to the nearest 0.001 g into a 1-litre volumetric flask. Dissolve in re-distilled or deionized water and make up to the mark. The exact molarity is

$$M_{EDTA} = \frac{0.01\,a}{3.722}$$

   where *a* is the amount of dry product taken in grammes.
4. Potassium hydroxide solution, 8 M, 450 g of KOH per litre.
5. Buffer solution, pH 10. Transfer 70 g of ammonium chloride, NH_4Cl, to a 1-litre volumetric flask and add 570 ml of ammonia, NH_3 ($\rho = 0.90$). Dilute to the mark with distilled water.
6. Potassium cyanide, solid or solution, 0.3 M. Dissolve 20 g of KCN, in distilled water and dilute to 1 litre. The reagent is poisonous.
7. Hydroxylamine hydrochloride solution. Dissolve 2 g of $NH_2OH \cdot HCl$ in 100 ml of distilled water. The reagent is poisonous.
8. Eriochrome black T indicator. Rub 100 mg of 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonic acid, sodium salt, in a mortar, with 20 g of sodium chloride, NaCl, to form a homogenous mixture. Store in a dark bottle.
9. Cal-red indicator. Rub 100 mg of 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid in a mortar with 10 g of sodium sulphate, Na_2SO_4, to form a homogenous mixture. Store in a dark bottle.

All reagents should be of analytical grade.

Preparation of sample

Shake the sample container before taking each sample for titration. Pipette a portion containing between 0.5 and 5 mg of magnesium (Note 1) into each of two conical flasks of 250 ml and dilute to 50 ml with distilled water.

Samples without turbidity can be analysed as described below without further preparation.

To dissolve any solid magnesium compounds, add to turbid samples 2 ml of 6 M hydrochloric acid, heat to boiling and cool to room temperature. Neutralize the solution with 1.5 ml of 8 M potassium hydroxide solution.

Procedure

A. *Determination of the sum of magnesium and calcium by titration.*

To one of the samples for titration add 5 ml of buffer solution, *ca.* 100 mg of potassium cyanide or 5 ml of the solution, 2 ml of hydroxylamine hydrochloride solution and *ca.* 100 mg of eriochrome black T indicator.

Titrate with EDTA solution to a colour change from wine-red to blue (Note 2). As the colour change is not instantaneous, add the EDTA solution slowly towards the end of the titration using a titrated sample for comparison. Record the amount of EDTA consumed as *b* ml (Note 3).

B. *Correction for the calcium content.*

To the second sample add 5 ml of potassium hydroxide solution and, after 5 min with occasional shaking of the flask, *ca.* 100 mg of potassium cyanide or 5 ml of the solution, 2 ml of hydroxylamine hydrochloride solution and *ca.* 100 mg of cal-red indicator. Titrate with EDTA solution to a colour change from wine-red to blue. Record the amount of EDTA consumed as *c* ml.

Calculation and report

Calculate the magnesium content as follows:

$$X = 24.32\ (b - c) M_{EDTA} \cdot 1000/d$$

where

b = volume of EDTA solution consumed in titration A, ml.

c = volume of EDTA solution consumed in titration B, ml.

M_{EDTA} = molarity of the EDTA solution.

d = volume of sample taken for titration, ml.

X = magnesium content, mg/l.

Report the result to the nearest whole number.

Note 1

If the calcium content is known to be negligible compared with the magnesium content titration B may be omitted.

Note 2

If the water sample is so strongly coloured as to mask the colour change of the indicator, prepare the sample as follows:

Evaporate 100.0 ml to dryness in a platinum dish and ash the residue at 575 °C ± 25 °C. Add 5 ml of 6 M hydrochloric acid and evaporate to dryness on a steam bath. Dissolve the residue in 5 ml of the hydrochloric acid, transfer the solution to a 100 ml volumetric flask, add 3.5 ml of 8 M potassium hydroxide solution and dilute to the mark with distilled water. Pipette two equal volumes containing between 0.5 and 5 mg of magnesium into two conical flasks and dilute to 50 ml with distilled water. Continue as described under «Procedure».

Note 3

When titrating water samples containing less than 10 mg of magnesium per litre, the colour change for titration A is not sharp. In this case modify the procedure by measuring 100.0 ml of the water sample for each titration and adding 1 ml of a 0.1 M solution of EDTA-disodium magnesium salt, $C_{10}H_{12}O_8N_2Na_2Mg$, before the titration. Titrate also a reagent blank with 100 ml of distilled water instead of the sample and record the amount of EDTA solution consumed as *e* ml. Calculate as follows:

$$X = 24.32\ (b - c - e) M_{EDTA} \cdot 1000/d$$

Literature

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PHOSPHORUS IN WASTE WATER

Scope

This method applies to all types of waste water.

Principle

The sample is wet-combusted with hydrogen peroxide and concentrated sulphuric acid to convert all phosphorus compounds to orthophosphates. Addition of molybdic acid produces a yellow complex; this is reduced by ascorbic acid to a blue complex, which is determined colorimetrically, (Note 1).

Apparatus

1. Glass bottles, 1 litre, with ground-in stoppers.
2. Kjeldahl flasks, 100 ml.
3. Combustion racks with burners.
4. Spectrophotometer or filter colorimeter.

Clean all glassware to be used in the determination with dilute sulphuric acid and rinse with distilled water. Do not use detergents.

Reagents

1. Sulphuric acid, 2.5 mol/l. Add carefully 70 ml of H_2SO_4 ($\rho = 1.84$) to 430 ml of distilled water. Cool and dilute to 500 ml.
2. Hydrogen peroxide, 30 % H_2O_2.
3. Sodium sulphite solution, 0.5 mol/l. Dissolve 6.3 g of Na_2SO_3 in distilled water and dilute to 100 ml.
4. Phenolphthalein solution, 1 %. Dissolve 1 g of phenolphthalein in 100 ml of ethanol, C_2H_5OH.
5. Sodium hydroxide solution, 5 mol/l. Dissolve 20 g of NaOH in distilled water and dilute to 100 ml.
6. Ascorbic acid solution. Dissolve 2 g of ascorbic acid, $C_6H_8O_6$, in 18 ml of distilled water. The solution is stable for one week. Store in a cool, dark place.
7. Antimony potassium tartrate solution. Dissolve 3.35 g of $K(SbO)C_4H_4O_6 \cdot 1/2\, H_2O$ in 100 ml of distilled water.
8. Sulphuric acid, 4.5 mol/l, for preparation of the molybdic acid solution. Add carefully 250 ml of H_2SO_4 ($\rho = 1.84$) to 750 ml distilled water. Cool and dilute to 1 litre.
9. Molybdic acid solution. Dissolve 4.04 g of ammonium molybdate $(NH_4)_6 \cdot Mo_7O_{24} \cdot 4\, H_2O$ in 45 ml of distilled water. Add the solution slowly, with stirring, to 200 ml of 4.5 mol/l sulphuric acid and then add 5 ml of the antimony potassium tartrate solution. When stored in a cool, dark place the solution is stable for several months.
10. Standard phosphorus solution, 100 µg of phosphorus per millilitre. In a 1-litre volumetric flask, dissolve 0.4392 g of dried potassium dihydrogen phosphate, KH_2PO_4, in distilled water, add 2 ml of 2.5 mol/l sulphuric acid and make up to the mark with distilled water.

All reagents should be of analytical grade.

Preparation of sample

Analyse the sample as soon as possible after the sampling. Keep the samples in the glass bottles with ground-in stoppers, cleaned with dichromate-sulphuric acid and thoroughly rinsed with distilled water. Add as a preservative 2 ml of 2.5 mol/l sulphuric acid per litre of sample.

Calibration

Dilute 10.0 ml of the standard phosphorus solution to 1000 ml in a 1 litre volumetric flask. From a burette measure portions of 0.5, 1.0, 2.0, 4.0, 10.0 and 20.0 ml (containing 0.5, 1.0, 2.0, 4.0, 10.0 and 20.0 µg of phosphorus) of the diluted standard solution into 50 ml volumetric flasks. Dilute with distilled water to ca. 40 ml, add 5 drops (0.25 ml) of the ascorbic acid solution, mix, and add 1 ml of the molybdic acid solution. Make up to the mark with distilled water and mix. The solutions contain 0.5, 1.0, 2.0, 4.0, 10.0 and 20.0 µg of phosphorus per 50 ml. After 5 min measure the absorbancy at 880 nm (Note 2) in a 50 mm cell, using distilled water as the reference. Determine the absorbancy of a reagent blank and subtract this value from the absorbancies of the standard solutions. Draw a calibration graph by plotting the absorbancy against the amount of phosphorus per 50 ml of coloured solution.

Procedure

A. *Orthophosphate*

To a 50 ml volumetric flask transfer a sample of not more than 40 ml, containing less than 20 µg of phosphorus (Note 3), and, if necessary, add distilled water to a volume of 40 ml. Add 5 drops of the ascorbic acid solution, mix and add 1 ml of the molybdic acid solution. Make up to the mark with distilled water and mix again. After 5 min measure the absorbancy, using distilled water as the reference in the same way as for the calibration. With every group of samples run a standard to check the calibration curve.

B. *Total Phosphorus*

To a Kjeldahl flask transfer a sample containing less than 20 µg of phosphorus and add 6 ml of 2.5 mol/l sulphuric acid and 2 glass beads. Heat the flask and boil slowly until the water has evaporated and fumes of sulphur trioxide are visible in the flask. The mixture will now normally have a dark colour. Allow to cool for at least 30 s and add one drop of the hydrogen peroxide. Repeat this procedure until the solution is colourless. Boil for 10 min, allow to cool a little, add 1.0 ml of the sodium sulphite solution for each drop of hydrogen peroxide and boil for 5 min.

Allow to cool, add ca. 50 ml of distilled water and boil until the volume is reduced to ca. 10 ml. Cool to room temperature, add 4 drops of the phenolphthalein solution and then the sodium hydroxide solution dropwise until the solution turns a faint pink. Transfer the solution to a 50 ml volumetric flask, rinse the Kjeldahl flask with distilled water and adjust the volume to ca. 40 ml; add 5 drops of the ascorbic acid solution, mix and add 1 ml of the molybdic acid solution. Make up to the mark with distilled water and mix again. After 5 min measure the absorbancy at 880 nm in a 50 mm cell with distilled water in the reference cell. With every group of samples, run a standard to check the calibration curve.

Prepare a reagent blank and measure its absorbancy with distilled water as the reference. Subtract the absorbancy of the blank from that of the sample and read off the corresponding amount of phosphorus from the calibration graph.

Calculation and report

Carry out duplicate determinations and calculate as follows:

$$X = \frac{1000\,a}{b}$$

where

a = amount of phosphorus obtained from the calibration graph, µg

b = sample volume, ml

X = phosphorus content, µg per litre

Report the result to 2 significant figures, and values below 10 µg/l as "less than 10 µg/l".

Note 1

Arsenate and silicate ions also form complexes with molybdic acid. To avoid interference from arsenate ions, ascorbic acid is used as the reducing agent; the reduction of the arsenate complex is slow and still incomplete after 1 h; by reading the absorbancy of the sample after 5 min the interference from arsenate is kept at an insignificant level. Interference from silicate ions is obtained only if the acid concentration is too low.

Note 2

If an instrument for measuring the absorbancy at 880 nm is not available, it may be measured at lower wavelengths, though not at less than 690 nm. The calibration must then be carried out at the same wavelength.

Note 3

If the sample is turbid, centrifuge or filter it.

Literature

1. Murphy, J. and Riley, J. P.: Anal. Chim. Acta 27 (1962) 31—36.

This method has been published in:

Norsk Skogindustri 27 (1973):11, 322—323. (English)
Norsk Skogindustri 27 (1973):12, 390—391. (Norwegian)
Paperi ja Puu — Papper och Trä 55 (1973):12, 975—980. (English, Finnish, Swedish)
Svensk Papperstidning 76 (1973):17, 652—655. (Swedish, English)

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Sodium content of wet pulp

Definition

The sodium content of wet pulp is defined as the amount of sodium that can be extracted from a sample of the pulp with hydrochloric acid under specified conditions.

Scope

The method is intended for use in determining the amount of cooking chemicals left in the pulp after various operations. It is recommended for determining the loss of cooking base metal from one section of the mill to another or to the environment.

It is designed primarily for the determination of sodium in pulps produced by the sulphate process but it is also applicable to pulps produced by other processes in which sodium is the base. With relevant modifications, it can be employed in the case of pulps produced by processes in which magnesium is the base metal.

Recommendations for sampling are given in the Appendix. They are intended for use in process control, especially for the purpose of reports to various authorities, but do not form a part of the standardized test procedure.

Principle

The pulp sample is diluted to a pulp concentration of about 2% and acidified with hydrochloric acid. The sodium content of a sample of the liquid phase is determined by atomic absorption spectrophotometry or flame photometry. The dry matter content of the pulp is determined gravimetrically and the sodium content is calculated; it is expressed in kilograms of sodium sulphate per metric ton of oven-dry pulp.

Apparatus

Flame photometer or atomic absorption spectrophotometer, equipped for the determination of sodium.

Because small amounts of alkali may lead to appreciable errors in the result, all vessels and glass equipment must be thoroughly cleaned with hydrochloric acid and distilled water.

Reagents and chemicals

1. Distilled water
2. Hydrochloric acid, 5 mol/l
3. Sodium sulphate, Na_2SO_4, dried to constant weight

Calibration

Prepare a stock sodium sulphate solution in a 100 ml volumetric flask by dissolving an accurately weighed amount of sodium sulphate (not less than 500 mg) in distilled water. Make up to the mark and mix well.

Prepare calibration solutions by diluting the stock solution with distilled water. Use pipettes of not less than 10 ml volume and measuring flasks of not less than 100 ml capacity. Use at least 4 concentrations of sodium sulphate, selected to cover the working range of the instrument. Store the calibration solutions in stoppered polyethene bottles.

Prepare a calibration graph by plotting the instrument reading against the sodium sulphate concentration.

Sampling

Recommended sampling techniques, including sample sizes and sampling frequencies, for use in mills with various pulp-washing systems, are given in the Appendix.

Procedure

The amount of sample, especially a gross sample, received in the laboratory is often so large that a smaller test sample must be taken. Before doing so, dilute the sample with distilled water to a pulp concentration of 2%, preferably in a plastic bucket. Mix the diluted sample by intense stirring. When necessary, disintegrate the pulp in a kitchen mixer or, if the sample is large, in a laboratory mill. Remove large shives before the analysis. While mixing, take the test sample, quickly and in one stroke, using a scoop with a capacity of about half a litre. Transfer the test sample to a glass beaker.

Add 10 ml of the hydrochloric acid and mix well for 10 min. Filter the pulp suspension through a Buchner funnel fitted with an "ashless" filter paper, for example Munktell OOR, of known oven dry weight.

Collect the filtrate in a filter flask and remove as much water from the pulp as possible by suction and by pressing with a thick glass rod having a flat end. Wash the pulp in the funnel three times with 500 ml of distilled water, pressing it each time with the glass rod.

Remove the pressed pulp and the filter paper from the funnel and dry overnight in a drying oven at 105°C. Place them in an desiccator and allow to attain room temperature. Weigh, subtract the weight of the filter paper and note the weight of the oven-dry pulp c to the nearest 0.01 g.

Dilute the combined filtrate and washings so that the sodium content is within the range covered by the calibration solutions, measure the total volume b. Check that the solution is free from fibres and other particulate matter. Determine the sodium content by flame photometry or atomic absorption spectrophotometry, following the instructions given by the manufacturer of the instrument. Check the calibration graph frequently, preferably after each determination.

Calculation and report

From the calibration graph read the sodium sulphate content, a, of the diluted filtrate.

Calculate the sodium content, expressed as the sodium sulphate content of the dry pulp, from the expression

$$X = \frac{a \cdot b}{c}$$

where

X = the sodium sulphate content of the pulp, kg/ton

a = the sodium concentration in the diluted filtrate, mg of sodium sulphate per litre

b = the volume of the diluted filtrate, l

c = the weight of the oven-dry pulp, g

Express the result in kilograms of sodium sulphate per (metric) ton of oven-dry pulp to the nearest 0.1 kg/ton.

Appendix — Recommendations for sampling

General

These recommendations relate to sampling and tests performed to determine the washing losses, *i.e.* the part of the sodium added in the cooking process which is not returned to the recovery system or any similar closed system. The procedures must be modified to suit the local conditions and therefore no precise instructions can be given. This Appendix is not to be considered as part of the standard method SCAN-C 30:73.

It is often difficult to obtain a sample from the point where the pulp leaves the system; this may not be easily accessible or the pulp may not be properly mixed. The sample should then be taken at the first accessible point downstream where the pulp is well mixed and where a minimum of diluting liquor has been added.

Recommendations are given for sampling in various types of pulpwashing systems and for calculating of the washing losses.

In the calculation of the washing losses, the amount of sodium returned to the system from a later stage should be subtracted from the amount of sodium found; on the other hand no correction should be made for sodium added to the system from an earlier stage or from the spent liquor evaporation system. The precision required when determining the parameters for calculating the corrections depends on the relative magnitude of the correction itself. The amount of sodium returned should be measured by a technique corresponding to that described in the standard method.

The sampling frequencies and the sample sizes recommended below are intended for continuous mill control for the purpose of internal and external accounting.

The composite samples obtained from a certain sampling point within a certain time interval may be combined to form a gross sample.

The recommendations do not cover tests for measuring the efficiency of a washing system, for example in an acceptance test; in this case a somewhat different technique should be used.

Sampling in different pulp-washing systems

Continuous digester with hi-heat washing

The washed pulp is blown to a blow-tank.

Recommended sampling point	First accessible point where the pulp is properly mixed, for example, on the pressure side of the pump after the blow-tank. In sampling from closed pipelines the pulp concentration should be less than 4 per cent; the sample should therefore not be taken from the blow-line.

Sampling frequency	Three consecutive random samples, taken at intervals of at least 5 min, are combined to form a composite sample.
Sample size	A random sample of pulp suspension should contain not less than 25 g of dry pulp and should weigh at least 1 kg.
Corrections in calculating the washing losses	A correction must be made for the amount of sodium added to the washing system upstream from the sampling point with washing or dilution liquor.

Radial washer

Recommended sampling point	The outlet from the washer.
Sampling frequency	Three consecutive random samples, taken at intervals of at least 5 min, are combined to form a composite sample.
Sample size	A random sample should contain not less than 25 g of dry pulp and weigh at least 250 g.
Corrections in calculating the washing losses	A correction must be made for the amount of sodium added to the washing system upstream from the sampling point with the washing or dilution liquor.

Filter washing system

Recommended sampling point	(a) The screw after the last filter. (b) The point where the pulp leaves the last filter.
Sampling frequency	(a) Five consecutive random samples taken at intervals of at least 5 min are combined to form a composite sample. (b) A series of random samples taken across the pulp web are combined to form a composite sample. In order that the composite sample shall be representative of the cross-section of the web the series should comprise one random sample per metre of filter width.
Sample size	(a) A random sample should contain not less than 25 g of dry pulp and weigh at least 250 g. (b) The sample size depends on the number of random samples required. Each random sample should be at least 70 mm by 70 mm.
Corrections in calculating washing losses	A correction must be made for the amount of sodium added to the washing system upstream from the sampling point with the washing or dilution liquor. The relation between the volume of diluting liquor and the amount of pulp should be known, as should the sodium content of the liquor.
Comments	In a random sample, the top and wire side of the pulp web should be equally represented. It is therefore recommended to remove from the filter a fairly large area of pulp web and to take the random sample carefully from this.

Washing presses

Recommended sampling point	Immediately after the press nip or at the point where the pulp leaves the press, for example, after the screw.
Sampling frequency	Three consecutive random samples, taken at intervals of at least 5 min, are combined to form a composite sample.
Sample size	A composite sample weighing not less than 250 g.
Corrections in calculating the washing losses	A correction must be made for the amount of sodium added to the washing system upstream the sampling point with washing or dilution liquor. The relation between the volume of diluting liquor and the amount of pulp should be known, as should the sodium content of the liquor.

Batch diffuser

Recommended sampling point	After the diffuser bin. Provided that the stirring in the bin is very efficient the sample may be taken in the bin itself.
Sampling frequency	Three consecutive random samples taken at intervals of at least 5 min are combined to form a composite sample.
Sample size	A composite sample of pulp suspension should weigh at least 1 kg and contain not less than 25 g of dry pulp. If the samples are taken from a pipe, each random sample should be this size.
Corrections in calculating the washing losses	It should be taken into account whether the washings are recirculated or discharged (to the re-

cipient) and whether recirculated white water is used for final washing or rinsing of the diffuser.

Displacement in discontinuous digesters and/or bins

It is assumed that the pulp is transferred to a bin or a similar container, where it is washed and drained.

Recommended sampling point	(a) Bin emptied with a conveyor -- Take the sample on the conveyor. (b) Bin emptied by rinsing -- Take the sample at the first point after the bin where pulp is well mixed.
Sampling frequency	(a) Five consecutive random samples, taken at intervals of 10 min, are combined to form a composite sample. If water is added to the bin for washing, the intervals must be increased so as to cover the entire emptying period. (b) Three consecutive random samples, taken at intervals of 5 min, are combined to form a composite sample.
Sample size	(a) A composite sample of at least 1 kg of wet pulp. (b) A random sample of pulp suspension should weigh at least 1 kg and contain not less than 25 g of dry pulp.
Corrections in calculating the washing losses	It should be taken into account whether the washings are recirculated or discharged (to the recipient) and whether recirculated white water is used for final washing or rinsing of the diffuser.

Corrections

If the pulp is diluted (for example, with white water) between the washing system and the sampling point, a correction must be made for the sodium content of the diluting liquid. The pulp concentration at the sampling point should be approximately 3%. Sampling at pulp concentrations below 2% should be avoided because the corrections will be unreliable, and large errors may be incurred in the final result.

Determine the flow of the diluting liquid with a measurement orifice or calculate it from the difference in pulp concentration before and after the point of dilution. At the same time take a sample for determination of the sodium content of the diluting liquid.

Correct also for the sodium added with washing liquid obtained from any point downstream from the sampling point.

Sampling from pipelines

The sampling device used in sampling pulp suspensions in pipelines must be designed to avoid systematic errors in the concentration of the pulp sample. A fairly high rate of pulp flow and a fairly large cross-section area of the pulp stream are required. *Fig. 1* shows the main principles of a simple sampling device designed to avoid plugging and systematic errors. In some cases more elaborate sampling devices are required; such devices are commersially available.

Some devices can be used for pulps of high concentration, for example, a type which takes out a pulp plug from the stream passing by. With such devices the risk of loosing liquid phase to the lower part of the pipe must be observed.

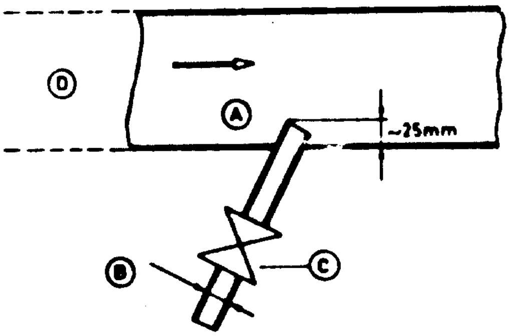


***Fig. 1.* Device for sampling pulp suspensions in pipes.**

(A) In order to minimize the hold-up of fibres the sampling tube protrudes at least 25 mm into the pipe and is set at an oblique angle. The opening of the sampling tube is cut off obliquely.
(B) Tube diameter 25—40 mm.
(C) A sampling valve with a minimum of constriction is placed in a straight section of the tube.
(D) The sampling device should not be placed immediately after a bend, especially a long, gentle bend, nor after long horizontal straight sections, especially if the pulp flows slowly.

SCAN testing methods are issued and recommended by the Central Laboratories of the Pulp, Paper and Board Industries in Denmark, Finland, Norway and Sweden. Distribution: Secretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604, S-114 86 Stockholm, Sweden.

ENVIRONMENTAL PROTECTION LEGISLATION IN SWEDEN

New environmental protection legislation went into effect in Sweden July 1st, 1969; an environmental protection law, passed by Sweden's Parliament on May 28th, and a Royal Ordinance on environmental protection.

The legislation provides comprehensive regulations concerning various kinds of environmental disturbances from industrial and municipal installations.

A new government agency, the Environmental Franchise Board, has also been established through the new legislation.

Applicability of the legislation

The environmental protection legislation applies to a wide area. It concerns the use of real estate for various kinds of operations that imply a danger to the environment. The law makes the following definition of these operations:

"the discharge of waste water, solid matter, or gases from land, buildings, or installations into water-courses, lakes, or other water areas;

"the use of land, buildings, or installations in a manner that may otherwise cause pollutions of water-courses, lakes, or other water areas;

"the use of land, buildings, or installations in a manner that may cause disturbances to the environment through air pollution, noise, vibrations, or light, or from similar causes, if the disturbance is not wholly temporary".

Rules for acceptance

An essential section of the law contains the rules stating the conditions for allowing certain operations. The basic principle behind these rules is that disturbances should be provided against in advance as far as is practicable, and that in any case unnecessary disturbance should not be tolerated.

The law states that "whosoever engages in or intends to engage in activities that have detrimental effects on the environment must take the protective measures, accept the limitations to his activities, and observe the additional precautions that reasonably may be deemed necessary to prevent or remedy injury".

The interpretative rules added to this general rule state that the duty to take protective measures etc. must be judged on the basis of what is technically possible. The operator must use the most efficient technical equipment and methods available. Technical advance must continously be utilized to improve environmental planning and protection.

The rules also state that the authorities must give due consideration on the one hand to the characteristics of the affected area and the importance of the effects of the disturbance, and on the other hand the advantages of continuing the disturbing operations and the costs for the protective measures.

This means that if there are particular circumstances, environmentally detrimental operations may be allowed in spite of their causing serious disturbance. Such circumstances would exist when there is a clearly established utilitarian advantage to society or to individuals in continuing the operations, for instance if serious unemployment were the alternative.

Advance licensing

The law requires that an operating license be sought in advance for such new industrial and other installations that will have a disturbing effect on the environment. For certain other new installations, advance notice to the County Administration is sufficient. (The categories are listed below).

A similar procedure is required for certain changes or additions to existing installations belonging to these categories. Even in cases where a license is not definitely required, the operator is free to apply for one. If the license is granted, it would then provide the operator with a certain amount of security parallel to that inherent in a court decision.

The ordinance also states that certain types of sewage may not be let out without a license. The application of this rule includes sewage from built-up areas with more than 200 inhabitants.

The ordinance also provides detailed procedural rules for the authorities that have environmental jurisdiction.

Licensing authority

Applications for licenses are considered by an administrative authority. The legislators feel that this is a better method to achieve efficiency, speed, and flexibility than judicial procedure, since the necessary discussions between the applicant and the authorities may then be conducted more informally than court procedure would allow.

A special board - the Environmental Franchise Board - has been established to deal with licensing. To a certain extent, it has court status, but it should rather be regarded as an impartial arbitral tribunal. The Franchise Board consists of a President and three more members. The President must be learned in the law, one member is a technical expert, one member must have "experience in matters belonging to the competence of the National Environment Protection Board" and the fourth member must have "industrial experience". When in the President's opinion the matter under the Board's consideration concerns municipal affairs, the fourth member should instead be one with municipal experience.

The decisions of the Franchise Board may be appealed to the King in Council. Reconsideration of stated rules and conditions is also possible to a certain extent.

Dispensation

There is, however, no definite obligation to apply to the Franchise Board. The National Environment Protection Board, and in some cases the County Administrations, may consider individual applications for dispensation from the obligation to apply to the Franchise Board.

The legislators have intended the consideration of applications for dispensation as an essential part of the new system. When dealing with such an application the National Environment Protection Board must conduct negotiations with the applicant to try and establish what conditions must be met with before the applicant may start operations. A dispensation differs from a license in not being legally binding. It may be recalled if necessary. However, a dispensation cannot be granted until careful investigations have been made. The dispensation decision will also include directives regarding precautionary measures. In practice, dispensation will imply a safeguard to the interests of the applicant. A decision to grant dispensation may not be appealed.

Inspection

The environmentally protective duties of the authorities are not limited to such matters as the scrutiny of applications. The authorities must also engage in tracing such cases where further action is necessary, inspect sources of disturbance, and supervise compliance with the regulations. The central supervision is the duty of the National Environment Protection Board, and the local, continuous supervision that of the County Administrations.

When the case arises, it is the first duty of the authorities to try and effect a voluntary adjustment. If these efforts are not successful, the authorities have such tools at their disposal as a request to the Franchise Board to prohibit continued operations or to make a number of precautions mandatory for continued operations.

Court Procedure

The basis for environmental action by the authorities is mainly to safeguard public interest, but private interest must also be taken into consideration. The legislation includes rules regarding procedure for dealing with private claims against environmental disturbances. A private individual may sue the pollutor in a real estate court, demanding prohibition against environmentally dangerous activity or a ruling establishing compulsory precautions.

The real estate courts also handle damage claims arising from such cases.

Responsibility

Violation against several of the rules in the new law are punishable by fines or a maximum one-year prison sentence.

Appendix A:

Industrial and other installations for which a license is necessary

1. mines, dressing plants;
2. sintering plants, iron works, steel works, ferroalloy plants;
3. metal works, metal refineries;
4. metal surface treatment plants;
5. cement factories;
6. plants manufacturing lime through burning shale;
7. mineral wool factories;
8. mechanical pulp mills, paper works, chemical pulp factories, fiberboard factories;
9. sugar factories;
10. starch factories;
11. dairies, powdered milk factories, ice cream factories;
12. abattoirs, meat-packing plants, refuse incinerators;
13. fishmeal factories, fish-oil factories, fish-refining and canning factories;
14. refining and canning factories for vegetables, root vegetables, fruits, berries;
15. margarin factories;
16. yeast factories;
17. bone meal factories, hide glue factories;
18. breweries, malt factories;
19. textile refining plants, textile dyeing plants, wool scouring mills;
20. laundries with a capacity exceeding 22000 lbs (10000 kilograms) per twenty-four hours;
21. tanneries or other plants for dressing of fur skins;
22. factories producing staple chemicals;
23. fertilizer factories;
24. factories producing plastics, synthetic fibers, synthetic rubber;
25. rubber factories;
26. carbon black factories;
27. pharmaceuticals factories;
28. gunpowder factories, explosives factories;
29. oil refineries, fat refineries;
30. factories producing dyes, resins, varnishes, solvents;
31. detergent factories;

32. factories producing pest and insect control chemicals.
33. nuclear power plants;
34. steam power plants and other plants using fossil fuels and with a power input exceeding 50 megawatts;
35. coal gas works, plants for production of town gas from naphtha;
36. plants for the treatment or disposal of refuse if the refuse input exceeds 50 (metric) tons annually, plants for treatment of oil refuse or other special refuse;
37. animal breeding plants with space for over 1000 slaughter hogs or over 10000 poultry;
38. plants for the drying of animal manure.

Appendix B

Emission dispensation requirements (water)

The following five categories of sewage from grounds, buildings, or installations, may not be discharged into watercourses, lakes or other water areas or into sewage disposal systems of other owners, without previous permission from the Franchise Board or a dispensation from the Environment Protection Board:

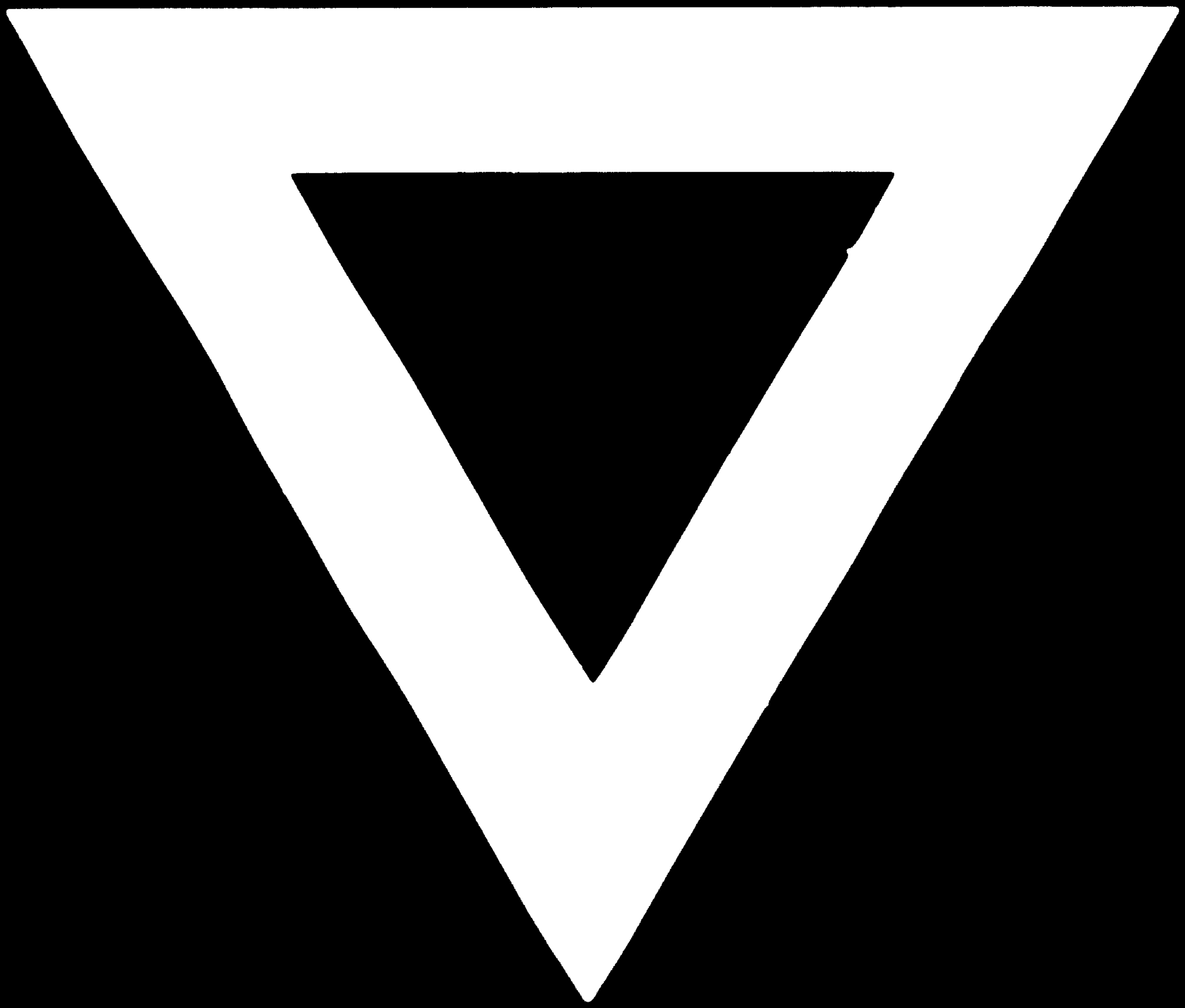
1. sewage from built-up areas with more than 200 inhabitants, or from barracks, hotels, hospitals, or similar installations intended for the use of more than 200 people;
2. juices squeezed in silo plants;
3. urine from animal byres;
4. whey (but not as spillage);
5. metal surface treatment baths, or concentrated rinsing fluid from such baths.

Appendix C

Industrial and other installations requiring advance notice to the local County Administration

1. foundries;
2. cable works;
3. crushing-mills, macadam works, stone-works;
4. asphalt works, oil gravel works;
5. plants for production of lime or lime products;
6. chalk works;
7. plants for production of mineral construction materials;
8. rock pits, stone pits, gravel pits, sand pits;
9. china factories, glazed tile factories, potteries;
10. glass factories;

11. wood impregnating plants;
12. pre-checked food factories, smoke-curing plants;
13. coffee roasteries;
14. distilleries;
15. soft drink factories;
16. plants for impregnating paper materials, plastic materials, synthetic fiber materials;
17. plastic products factories;
18. electrode coke factories, graphic factories, graphite electrode factories;
19. filler factories, pigment factories;
20. acetylene gas works;
21. laundries with a capacity exceeding 2200 lbs (1000 kilograms) per twenty-four hours;
22. waterworks serving more than 5000 people;
23. gas turbine power plants;
24. salvage dumps, plants for scrap handling;
25. plants for centralized collection of oil refuse and of other special refuse.



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