*Final Report*

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# REPORT ON OXYGEN BLEACHING STUDY FOR AGRO BASED PAPER MILLS

*Sponsored by:*

**DEVELOPMENT COUNCIL FOR PULP, PAPER AND ALLIED INDUSTRIES**

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# REPORT ON
# OXYGEN BLEACHING STUDY FOR AGRO BASED PAPER MILLS

# EXECUTIVE SUMMARY

The progress in Research & Development, technological innovations and their adoption in industry has resulted in resource optimization and hence waste minimization. This is particularly true for the pulping and bleaching of fibers for paper & board manufacture. In addition, the increasing awareness on environmental and sustainability issues coupled with customer preference for eco-friendly products had led to developments in the use of oxygen, ozone and hydrogen peroxide in place of chlorine and chlorine derivatives.

Although oxygen has been in use in pulp bleaching since the last 3 decades, its importance grew after the detection of polychlorinated dioxins & furans in the pulp & paper mill effluents and sediments in rivers & lakes in 1980's. In Scandinavia, nearly all pulp mills use oxygen in bleaching and in USA nearly 40% of the mills use oxygen either in the pre-bleaching stage or in the bleaching. The progress has been very slow in the Indian paper industry as only a few large mills have introduced use of oxygen in bleaching.In the small agro based pulp mills, there was hardly any mill using oxygen in bleaching.

The project was conceived to introduce an oxidative / oxygenated alkali extraction stage in a conventional chlorine-extraction - hypochlorite (CEH) bleach sequence in a 50 TPD pulp mill using bagasse, wheat straw & rice straw as pulping raw materials.

In order to generate process parameters for designing the plant, Central Pulp & Paper Research Institute, Saharanpur was commissioned to carry out laboratory scale trials on CEH and CEoH bleach sequences and optimize the process parameters. The laboratory results indicated reduction in chlorine consumption and improvement in bleached pulp brightness in CEoH sequence. In addition, the COD and BOD of bleach effluent were reduced. Based on the data collected, the basic engineering was developed by Indian Agro Paper Mills Association (IAPMA), while the detailed engineering was carried out by M/s. Chemprojects Engineering & Design (P) Ltd, New Delhi.

Although the oxygen bleaching equipment for large scale pulp mills were either imported or fabricated in India, there were no known suppliers for equipments suitable for small pulp mills. It was essential to scale down the equipment size, which required an in-depth knowledge in design philosophy and exceptional risk concept and management. The system was to be fully automated not only from point of controlling the operational parameters, but also from a complete safety point.

Specifications for each critical equipment had to be made and got fabricated, instrumentation logic diagrams had to be conceived, specifications of instruments and their procurement made from indigenous suppliers. Instead of going to a single supplier for the system, individual items of equipment and instrument had to be bought and assembled. The overall exercise, though perceived to be risky, has been fruitable, and has resulted in considerable capital cost saving.

The erection of the plant was carried out by an organization of repute. The commissioning and initial plant operation was under the supervision of IAPMA technical wing.

After successful completion of the trials, it was observed that the pulp brightness reached the target level of 80% ISO whereas the tensile & tearing strength improved by 20 and 7% respectively. The later improvement ultimately resulted in reduction of long fibered pulp addition to the furnish. The COD and BOD values in the mill effluent have been lowered.

The cost benefit analysis indicates substantial saving due to introduction of Eo stage in the bleaching system resulting in pay back period of investment less than two years. In addition, there are intangible benefits of improved paper quality as well as environmental benefits.

The short payback period has proved that environmental benefits and cost benefits can go together. Thus the mills can combine economy and ecology. The project's long term objectives will be met, if more mills opt for the Eo-stage. IAPMA can offer them expertise in design, selection & procurement of equipment & controls and commissioning of the plant.

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# PREFACE

From the environmental point of view, paper manufacture is a complex business with a wide range of impacts. Its use of natural raw materials, large amount of energy, chemicals and water, coupled with a wide range of emissions ensure that it has a high environmental profile. There are environmental pressures from a number of angles and they can be placed into two groups, namely - legislative requirements and other pressures like the market, consumer and stakeholders.

## *Legislative requirements*

Historically, the law has been the driving force behind any change in our environmental performance. The tradition has been to do the minimum necessary to meet the standards needed by legislation. To do only the minimum necessary was seen as perfectly reasonable. The "end of pipe" treatments was considered the only option. Its cost was high and considered to be a "nil return" investment.

## *Market Forces*

The consumer, who is more informed today, demands not only nonpolluting products, but also environmentally friendly production processes. This gives rise to the so called "Integrated pollution control (IPC) with its emphasis on the use of the best available technology (BAT); this represents a more holistic approach to minimization of the environmental impact of an activity.

## *Environmental compulsion enforce:-*

a) a better understanding of the paper making process and its impact on environment.

b) an eco-management system, which improves control of raw materials, energy use and waste management and ultimately results in cost control.

## *Methods of treatment for pollution abatement*

To address the pollution problems, there are two routes:-

(a) End of pipe treatment - in lagoons, activated sludge etc.

(b) Pollution prevention - decrease discharge of polluting materials from the fiber line.

The second method is preferable as it is better to negate these effects by avoiding formation of pollutants at source.

## *Main source of pollution from pulp & paper mill*

The raw material (wood, agro residues etc.) contains approximately 25-27% lignin (for wood) or 15-20% lignin (agro residues). At the cooking stages the lignin content is reduced to about 5%. As the lignin causes darkening of pulp, more lignin has to be removed and this is done in a bleach plant.

The main bleaching chemicals used in India are chlorine and chlorine compounds. In the bleaching of pulp, chlorine in elemental form or its compounds are used to break down the lignin. Chlorinated organic compounds are formed such as dioxins (2,3,7,8, TCDD) which are reported to be bi-accumulative, carcinogenic and mutagenic to marine and human life.

Since bleaching process is not a part of the closed system, it is responsible for most of the emissions discharged from the pulp mill. The bleach plant effluent accounts for 60-70% of COD and 80-90% colour load of the waste water from the entire mill. Traditionally, the bleaching sequence used in the Indian Paper Mills are CEH/CEHH. Some large pulp & paper mills also use chlorine-di-oxide in addition to CEH sequence. Discharge of chlorinated organics compounds, dioxins etc. measured in terms of AOX from bleach plants is the major environmental problem (see annexure I).

With the introduction of the oxygen use, emissions could be reduced by half. By replacing $Cl_2$ with $O_2$ or $H_2O_2$ an effluent free of AOX can be achieved.

## *Use of oxygen to replace chlorine in Pulp delignification*

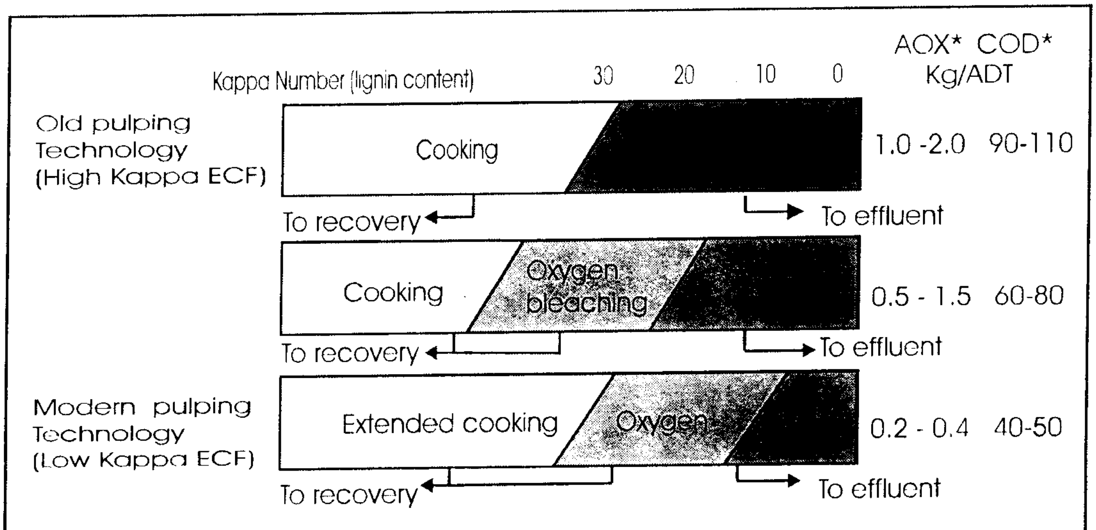
Oxygen is used in the pulp deliginification in various ways. Oxygen is added to the washed brown stock pulp before it goes to the bleach plant. The idea is to reduce the pulp lignin by 50%. Thus for a softwood pulp with a kappa number of 30, the BOD, COD and AOX levels are 100, 250 and 4-6 respectively, By eliminating elemental chlorine, the levels of the above pollutants get reduced to 50, 100 and 2 Kg/t of pulp respectively.

## *Trends in Europe & North America on use of Oxygen in pulp delignification*

Although there were no commercial plants in 1970, the progress in adopting oxygen in bleaching has been very rapid. In 1996, 50% of chemical kraft pulp production had Oxygen Delignification (OD) plants in Scandinavian countries. Presently in Finland, Sweden and Norway almost 100% kraft pulp mills have an O.D. stage. In Japan it is 80% and in North America it is 40%.

Using modern pulping methods and OD stage, the post - OD kappa has reached 10 for softwood and 8 for hardwood pulp.

The chart below shows the effect of modern cooking by OD and ECF bleaching on the AOX and COD.




*) After primary treatment, whole mill effluent (after secondary treatment the discharge levels would be about 50% lower for both AOX & COD

## *Use of oxygen in Alkali Extraction*

When the pulp in presence of alkali is treated (mixed thoroughly) with oxygen, more lignin can be extracted and the result is a lowering of pollutants (both AOX and COD) and an improvement in pulp brightness and viscosity. Almost all kraft mills in the western world have an Alkali extraction (EO) stage in their bleaching system.

## *The Indian scenario*

With liberalisation of Indian economy and globalisation of market, the trade practices are closely linked with the environment. Apart from public pressure, court rulings on pollution vrs. trade disputes have always gone against the polluters. Therefore, the industry needs more focused attention for adoption of cleaner production technologies and practices.

Indian pulp & paper mills have realized that environmental protection and profitability do not necessarily clash. The pulp and paper industry is particularly fortunate that use of modern pulping & bleaching technologies ensures that resources are being utilized completely, efficiently and effectively, which ultimately improves the mills profitability.

A few large mills have already adopted use of oxygen in the alkali extraction stage whereas one mill has gone for oxygen delignification in the pre-bleaching stage.

The equipment and technology used in these mills are imported and hence entail high capital cost.

There is hardly any small agro residue based pulp with an oxygen alkali extraction stage in India and perhaps none anywhere. The plant scale study of Eo bleaching in small agro based paper mills under the present context with indigenously developed equipments at affordable cost will possibly attract many more to follow the route.

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# THE PROJECT

## *Introduction*

Considerable technological developments have been taking place from time to time in the area of pulp bleaching. Due to environmental considerations, conventional bleaching chemicals – chlorine and chlorine compound are being gradually replaced by Oxygen, ozone, peroxide etc. Use of oxygen in bleaching operations is gaining importance in reducing energy, bleaching chemical cost and pollutional loads. Emphasis is mainly on the use of oxygen as a bleaching chemical in pre-bleaching stage as well as in alkaline extraction stage.

Although a number of large wood & bamboo based pulp mills in India have adopted oxygen bleaching, particularly in the extraction stage and have been able to reduce the level of total polluting emissions from the bleaching plant, it is perhaps the first organized systematic attempt to introduce oxygen in alkali extraction stage in a small size agro residues based pulp mill (50 TPD). The technology and equipments for the oxygen fortified alkali extraction stage for large mill are mostly imported and their cost has been an impeding factor for other mills specially for smaller ones to follow. The perception among the small mill owners as well as the mill operators was that the part replacement of chlorine compounds with oxygen adds to the capital as well as operating cost.

Laboratory stage studies carried out in India and abroad have revealed that introduction of oxygen reinforced extraction in the conventional CEH bleaching of agro residues pulp results in a number of benefits leading to the lower pulp bleaching cost with respect to energy and chemical requirement and improved product and effluent quality. It is in this context the present project was conceived to set up a demonstration unit for oxygen reinforced extraction stage in a CEH bleaching system in a running agro based mill and conduct trials with indigenously developed equipments to optimize the operational parameters and demonstrate the benefits of the system.

## *Objectives*

The plant scale study was taken up by IAPMA with the following main objectives: -

(i) Optimize the basic bleaching process parameters with introduction of oxygen at the extraction stage in a running small agro based paper mills,

(ii) Evaluate its effectiveness with respect to pulp & paper quality and pollution reduction.

(iii) Develop cost effective indigenous equipment for sustained operation,

(iv) Create confidence with practical data for its replication in other small agro pulp and paper mills.

## *Selection of agro based paper mills for the study*

After preliminary evaluation of a number of pulp & paper mills producing writing & printing paper based on agro residues, a willing unit, Shiva Paper

Mills Limited, situated in Rampur district of Uttar Pradesh, was selected for the studies for retrofitting oxygen reinforced extraction (Eo stage) in their existing C-E-H bleaching system.

Shiva Paper Mills produces about 70 tonnes per day of various grades of writing & printing papers mainly based on pulp from wheat straw, rice straw, bagasse, sarkanda etc. Transportation, storage and conveying systems for depithed bagasse to the digester house in Shiva Paper Mills Limited, Rampur (U.P.) are shown in the Photographs (i), (ii) &(iii). The mill uses soda process for pulping and conventional C-E-H sequence for bleaching to achieve a brightness of about 75% ISO. Different stages of pulping and bleaching are shown in photographs (iv) to (ix). The average bleached pulp production of the mills is 50 MT per day. A diagram of the existing bleaching system of the mills is shown in Fig.1.

Flow Sheet showing Multistage Bleach Plant
CEH

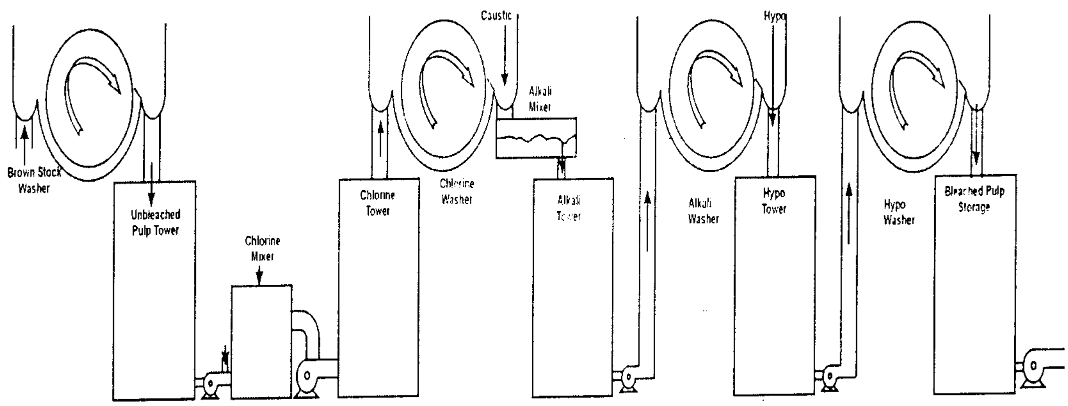


Figure 1

# *Development of Design parameters*

## Laboratory studies on Oxygen Bleaching

In order to generate data for basic engineering and sizing of the plant and equipments for Eo stage, a laboratory scale experiment on C-E-H & C-Eo-H sequences of bleaching of the mill pulp was carried out at different conditions. The results of the laboratories studies conducted at Central Pulp and Paper Research Institute (CPPRI) are recorded in Table 1.

Table 1 : Effect of Oxidative Extraction on Mixed Pulp (from Shiva Paper Mills)

| Sl | Parameters | Blank | Reaction Vessel Pressure | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1.5 kg/cm² | | | | 2.0kg/cm² | | | |
| | | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| 1 | **Unbleached Pulp** | | | | | | | | | |
| | Kappa Number | 31.6 | 31.6 | 31.6 | 31.6 | 31.6 | 31.6 | 31.6 | 31.6 | 31.6 |
| | Brightness (% ISO) | 28.5 | 28.5 | 28.5 | 28.5 | 28.5 | 28.5 | 28.5 | 28.5 | 28.5 |
| | Intrinsic viscosity ($cm^3$/gm) | 1025.8 | 1025.8 | 1025.8 | 1025.8 | 1025.8 | 1025.8 | 1025.8 | 1025.8 | 1025.8 |
| 2 | **Chlorination Stage** | | | | | | | | | |
| | Chlorine added (as available chlorine %) | 7.9 | 7.9 | 7.9 | 7.9 | 7.9 | 7.9 | 7.9 | 7.9 | 7.9 |
| 3 | **Eo-STAGE** | | | | | | | | | |
| | NaOH added (%)* | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| | $O_2$ dosing ( Kg)* | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| | $O_2$ Pressure (Kg/cm²) | 0 | 1.5 | 1.5 | 1.5 | 1.5 | 2 | 2 | 2 | 2 |
| | Reaction time (Min.) | 60 | 15 | 30 | 45 | 60 | 15 | 30 | 45 | 60 |
| | End pH | 11.1 | 11 | 10.9 | 10.9 | 10.8 | 11.4 | 11.4 | 11.2 | 11.2 |
| | Brightness (%ISO) | 42.8 | 44 | 45.4 | 47.2 | 49.2 | 46.5 | 47.6 | 48.5 | 50.8 |
| | Kappa Number | 7.44 | 6.29 | 6.16 | 5.66 | 5.36 | 6.03 | 5.7 | 5.36 | 5 |
| | Intringic viscosity (cm3/gm) | 867.5 | 832 | 825 | 823 | 818 | 787 | 778 | 772 | 764 |

* *Optimized separately*

Table 2 provides the findings of the lab scale study with respect to changes in pulp properties after introduction of oxygen at the optimum conditions i.e. 5 Kg $O_2$/tonne of pulp with reaction vessel pressure at 2 kg/cm$^2$.

Table 2 : Laboratory Studies on C-E-H And C-Eo-H Pulp Bleaching

| **Particulars** | **C-E-H** | **C-Eo-H** |
|---|---|---|
| ***Unbleached Pulp:*** | | |
| Permanganate number (40 ml) | 15.0 | 14.2 |
| Intringic Viscosity CED (cm$^3$/g) | 791.0 | 666.3 |
| Brightness ISO% | 34.08 | 33.07 |
| ***Alkali treated pulp:*** | | |
| Permanganate number (40 ml) | 5.22 | 2.5 |
| Intrinsic Viscosity CEd (cm3/g) | 611.0 | 522.3 |
| Brightness ISO % | 32.33 | 43.51 |
| ***Hypo Stage:*** | | |
| Intrinsic Viscosity (cm3/g) | 359.0 | 297.9 |
| Brightness ISO % | 76.8 | 78.95 |

## Basic & Detailed Engineering

Based on the laboratory data, the basic engineering for the process was developed and the detailed engineering of the bleach plant for retrofitting Eo stage was carried out. With a view to have safety and control in operation, complete instrumentation and automation systems were incorporated. A flow diagram of the complete system is shown in Fig.2.

Figure -2

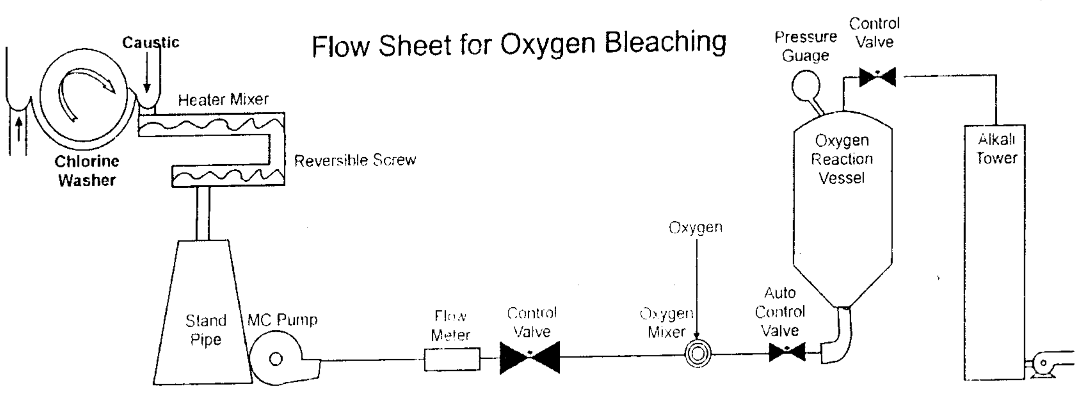


Figure 2

## *Equipments Fabrication and Procurement*

Scaling down of the plant and equipment size to a system suitable for the small pulp mill capacity of Shiva Paper Mills Limited, required indepth knowledge in design philosophy and exceptional risk concept and management. The system was fully automated not only from the point of controlling the operational parameters but also from a complete safety point.

All the plant & equipments for Eo stages as shown in Fig 2 were got fabricated in reputed workshops in the country based on the design parameters and specifications of the individual equipment developed by IAPMA with a view to reduce the overall capital cost of the plant and easy availability of the spares. All the instruments were also procured from indigenous manufacturers and suppliers. Photographs from (x) to (xxii) are showing different stages of Eo.

## *Erections and Commissioning of Demonstration Plant*

The complete erection and commissioning of the Eo plant was carried out by an organization of repute in the field under the supervision of IAPMA and was completed in about 2 ½ months' time. The plant was available for commissioning trials by 30th November, 2000, however the actual commissioning trials were started from 15th December, 2000 after necessary rectification and alteration in the system to form an integral part of the mill.

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# PLANT TRIAL

Initial trial was taken with the oxygen of approximate 93% purity procured in cylinders. However, later a capsule of 5m3 capacity was installed to get continuous supply of oxygen at 99% purity as shown in photograph No. (xiv) and (xv). The original idea of installation of an oxygen generator was given up to reduce the burden of maintenance and operation of additional equipment.

## *Optimization of Operational Parameters*

The important process parameters for oxygen reinforced alkali extraction stage are reactor pressure, temperature, reaction time, pulp consistency, pH and oxygen dosage. Although the process parameters as established at lab scale trial were available for guidance, the plant trials for processing the pulp through Eo stage was taken with variations in pressure in the reaction tower from 1.5 to 4 kg/cm2 (Reaction vessel photograph Nos. xvii and xviii). Similarly, the dosing of oxygen was also optimized after feeding the oxygen with different quantities. With a number of experiments, it was found that the best result was obtained at the pressure of 2 Kg/cm2 at an oxygen feed of 4.5 kg/tonne of pulp. The other conditions of the pulp at Eo stage were maintained as under.

| | | | |
|---|---|---|---|
| (a) | Pulp consistency | - | 10% |
| (b) | Reaction temperature | - | 70-72°c |
| (c) | Retention time in reaction tube | - | 30 mts. |
| (d) | Retention time in alkali tower | - | 20 mts. |
| (e) | Reactor pressure | - | 2kg/cm2 |
| (f) | Oxygen feed rate | - | 4.5 kg/tonne of pulp |
| (g) | pH | - | 11.5 |

## *Performance of the Indigenously Developed Equipments*

The critical equipments like M.C Pump and Oxygen Mixer, shown in photograph Nos. xi & xii, were indigenously designed and manufactured for small size of the plant for satisfactory performance. However, these equipments needed improvements, which were carried out by the manufacturers during the operational trials. The functioning of safety valves and other instruments were found satisfactory.

## *Results of Trials*

(a) Pulp Quality

During the trial runs the pulp quality was evaluated at CPPRI for P.C. No., Brightness and viscosity at each stage of the bleaching sequence. The same properties of the pulp were also evaluated before the oxygen was fed into the system. The comparison of the pulp quality before and after the oxygen introduction into the bleaching system is shown in Fig.3

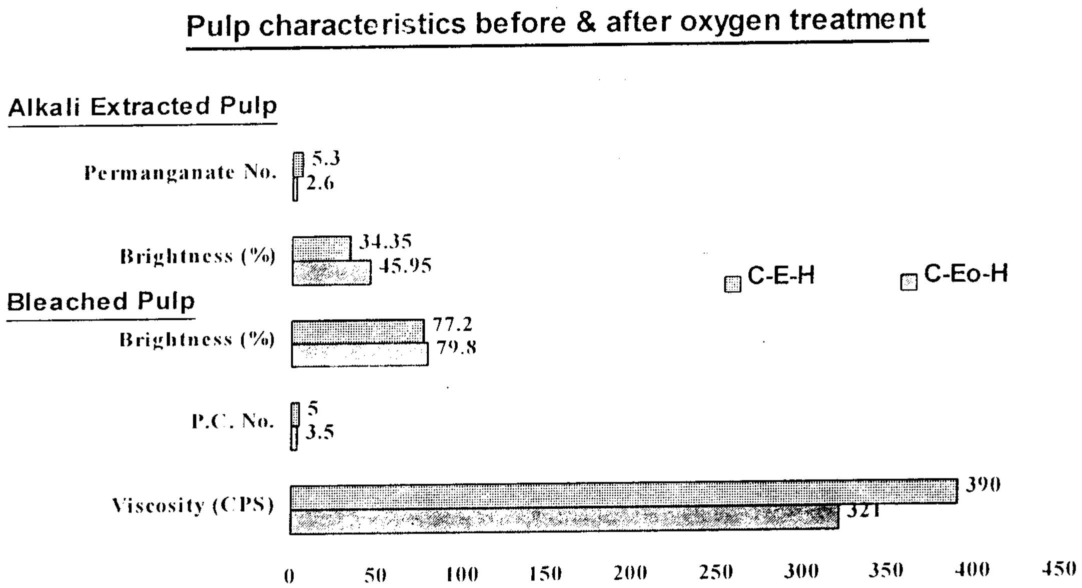


*Figure 3*

It can be seen that C-Eo-H bleaching produced a pulp of brightness of 79.8% ISO, which is 2.6 points higher over the brightness of the pulp produced by C-E-H sequence. It has been observed that with the stabilization of the plant operating conditions the pulp brightness has further improved and reached a value of 80% ISO. Fiber classification shows marginal increase in longer fibres and reduction in fines.

The physical strength properties of the finished paper increased in terms of breaking length, tear factor, burst factor, ash content and brightness for the paper produced with the oxygenated pulp. The tabulated results are shown in Annexure A1 & A2 and their comparison has been indicated in Fig.4

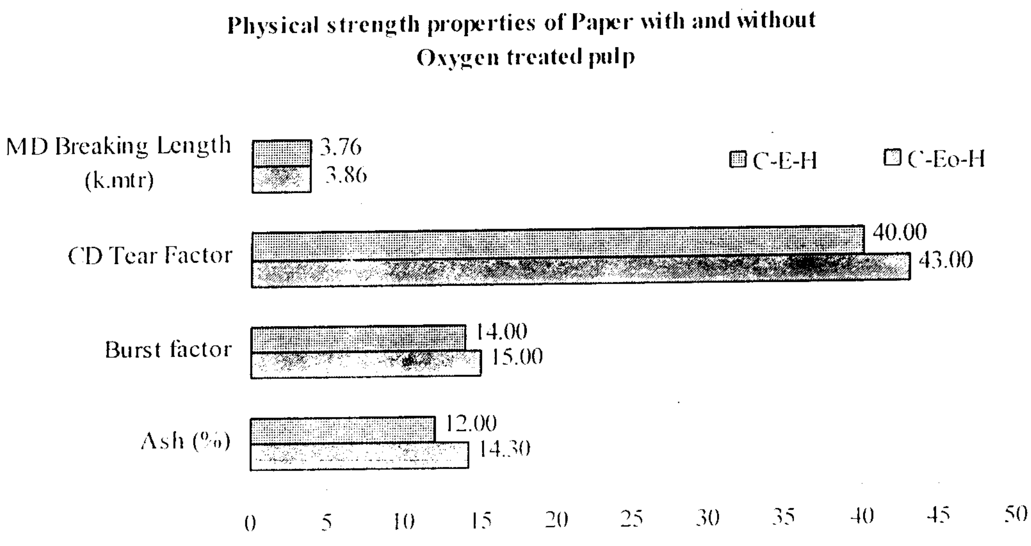


*Figure 4*

Introduction of Eo stage has shown significant improvement in the physical strength characteristics of the bleached pulp. On an average tensile and tearing strength improved by more than 20% and 7% respectively while the bursting strength did not change. This ultimately has resulted in the improvement in the runnability of the paper machine and reduction in paper breaks, thus increasing productivity of the paper machine of the mill. There has been considerable improvement in brightness and colour stability as shown by lower P.C No after $O_2$ treatment. It may be noted that inspite of lower viscosity of the oxygen treated pulp; the physical strength properties show a higher trend.

### *(b) Reduction in Chlorine Consumption*

The decrease in pollutants such as chlorinated organics, BOD, COD and Colour in bleach plant effluent is proportional to the bleach chemical consumption. Effect of oxygen in the bleaching system has remarkable reduction in chlorine consumption, specially at the hypo stage and the tabulated results are shown in Annexure-B. The comparison of chlorine consumption is indicated in Fig 5.

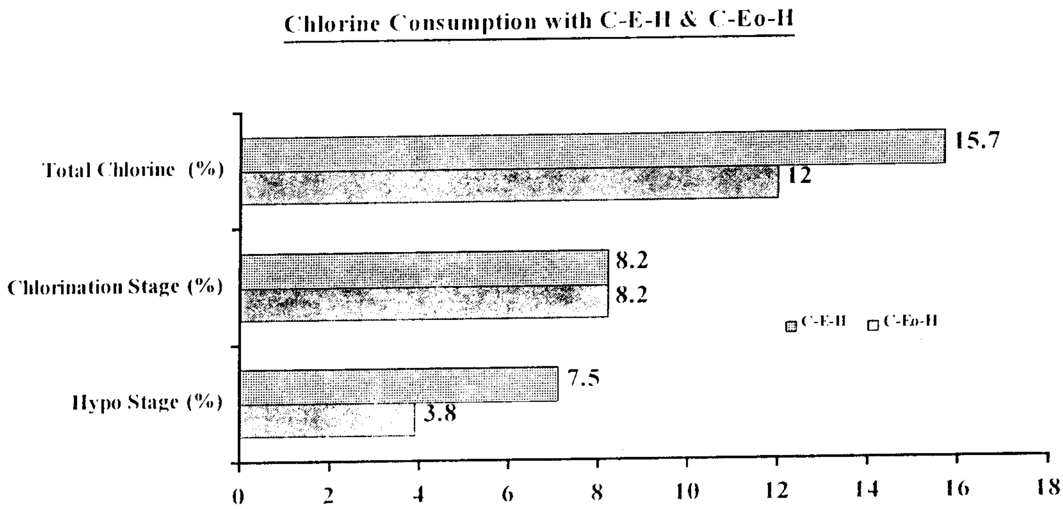


*Figure 5*

It can be seen that introduction of C-Eo-H has resulted in the reduction of chlorine demand at hypo stage from 7% to 4% to reach the brightness level of around 80% ISO. Hypochlorite consumption reduced by 30-40 kg/t of pulp resulting in reduction of chlorine and lime consumption of the mills. Overall chlorine consumption in the bleaching section of the mill reduced by around 24%.

## *(c) Fiber Classification*

Fiber classification of the pulp with and without oxygen bleaching was carried out and is tabulated in Annexure C. The results reflect the small increase in longer fibres and decrease in shorter fraction. As a result, the addition of soap stone powder in the pulp was increased from 12% to 14.3% thereby effecting saving of equal quantity of fibre (pulp) in the paper. This has made significant impact on the overall economy of the paper cost.

Table 3 : Effluent Characteristics

| | C-E-H | C-Eo-H | % REDUCTION |
|---|---|---|---|
| **Alkali Back Water** | | | |
| COD mg/l | 3338 | 2630 | 21.3 |
| BOD mg/l | 652 | 723 | (-)10.9 |
| Colour Pt-Co Units | 5814 | 4791 | 17.6 |
| **Combined Effluent** | | | |
| COD mg/ltr. | 7909 | 2052 | 73.7 |
| BOD mg/ltr. | 503 | 421 | 16.3 |
| Colour Pt-Co Unit | 7797 | 3423 | 56.1 |

## *(d) Effluent Characteristics*

A perusal of table 3 reveals that introduction of Oxygen in the extraction stage has marked effect on the final effluent characteristics, specially on COD, BOD and colour values which were lower by 74%, 16%, and 56% respectively.

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# ECONOMIC IMPACT OF "*Eo*" STAGE

The cost benefit analysis carried out has shown that the introduction of Eo stage required additional operating cost of Rs. 317.00 per tonne of pulp for addition of oxygen, additional energy requirement for Eo stage and other operational expenses whereas there was a direct saving of Rs. 622.00 per tonne of pulp as a result of reduction in chlorine demand in the hypo stage by a minimum 30 kg/t of pulp, reduction in lime requirement and fiber saving due to increased filler loading. Taking into account of net economic gains after adjusting the interest impact on capital, pay back period works out to less than two years. Indirect benefits have not been taken into economic evaluation such as improved machine runnability, resulting in higher production, improved product quality and improved effluent quality. Taking into consideration of all these factors, retrofitting of Eo stage has proved to be a very attractive option for the agro based pulp & paper mills.

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# CONCLUSIONS

A complete indigenously procured demonstration plant of oxygen bleaching of about 50 TPD capacity for C-Eo-H bleaching of agro residues pulp has successfully been installed and commissioned at Shiva Paper Mills Limited, Rampur, Uttar Pradesh and has been in continuous operation since January 2001. This C-Eo-H bleaching system for agro residues has established the following advantages: -

a) Improved pulp brightness
b) Improved strength characteristics of bleached pulp
c) Reduced chlorine consumption
d) Lower effluent toxicity with respect to BOD, COD and effluent colour,
e) Improved paper machine runnability
g) Improved product quality
h) Overall cost reduction
i) Installation of the system at affordable cost.

The studies have clearly demonstrated the benefits of oxygen-reinforced extraction in the conventional bleaching of agro residues pulp. It was established that Eo stage could be retrofitted in the existing bleaching system with indigenously available equipments, with much lower investment level as compared to imported equipments. The pay back period as well as the level of investment is attractive even for medium size pulp and paper mills.

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# DEMONSTRATION & DOCUMENTATION

A CD for the complete system of Eo stage bleaching system in operation has been made and was presented in the Paperex'2001 with a view to demonstrate the viability of oxygen fortified bleaching in small agro based pulp and paper mills.

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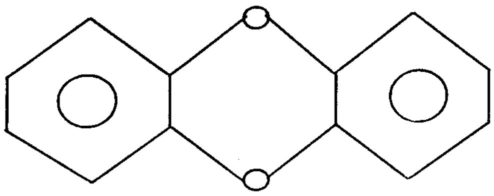
Annexure I

# ABOUT DIOXINS AND AOX

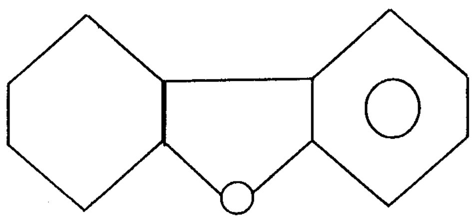
## *What is dioxin?*

The increasing public interest in the adverse environmental effect of the industrial world has led scientists to the identification of many toxic by-products from these industrial processes. One such class of compound, which has received much publicity, are the dioxins, which are two different but similar classes of compounds.

The basic structures of these compounds are -

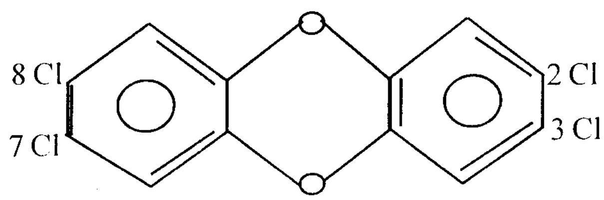


*Dibenzo - Dioxin*



*Furan*

All processes that use chlorine have the potential of changing these naturally occurring nontoxic dioxins and furans into chlorinated dioxins and furans. 2,3.7,8 - TCDD is probably the most toxic substance known to man.




*2,3,7, 8 TCDD*

TCDD accumulates readily in animal tissues, especially in lever and fatty tissues. Although dioxin is soluble in water, it tends to accumulate in fish that ingests sediments and food organisms.

Dioxins are not used in the pulp & paper industry, but they are generated as undesirable by-products of processes involving chlorine.

In the bleaching of pulps, chlorine in elemental form or its compounds are used to break down lignin. As a result, the non-chlorinated dioxins and dioxin precursors are converted into chlorinated dioxins such as TCDD.

Several unfortunate incidents have been reported in which humans were exposed to large amounts of dioxin. A number of these individuals developed sever skin disease (chloraemia). Some studies have shown a relationship between stomach cancer, soft tissue sarcomas and leukemia and dioxin exposure.

## *Sources of Dioxin*

There are several sources of dioxin. Large amounts are released from incomplete incineration of organic materials including gasoline and municipal solid wastes. Municipal solid waste incinerators are the largest contributors of dioxin (60% of U.S. generation). The second largest contributors are the fuel combustion (15%), forest fires (4.5%), metal furnaces and the paper industry (3 %).

## *Dioxin and the paper industry*

The bleach plant of the pulp mill uses chlorine gas as such and its derivatives such as Hypochlorite and chlorine dioxide. Toxic carcinogenic and mutagenic chlorinated compounds are formed during the bleaching process, Chlorination and alkali extraction stages contribute maximum pollution in terms of Dioxins and colour. The formation of AOX is dependent on the type of bleaching sequence. An approximate estimation of AOX can be made from the equation.

*AOX (for softwood)* $= 0.07\text{-}0.11\ (IC + {}^{H}/_{2} + {}^{D}/_{5})$

*where C = elemental chlorine charge; H= Hypochlorite charge, av.* $Cl_2$ *(=1.5 x NaOCl) and D = chlorine dioxide charge (av.* $Cl_2$ *(2.3 x* $ClO_2$*)*

## *Toxicity & Carcinogenicity of Chlorinated Compounds*

The level of understanding of the toxic compounds is bleached kraft mill effluent has increased considerably. The C and E stage effluents represent the largest portion of chlorinated compounds. The material that biodegrades or remains in the environment should be of little concern as it will have little impact. The fraction that is less than 1000 molecular weight (MW) is of most concern because this material can penetrate into a cell through the cell membrane and has the potential to bio-accumulate and this is of most concern.

A large fraction of the lignin-derived material from bleaching is greater than 1000 MW and hence it is of low concern. The low molecular weight chlorinated phenolics cause acute toxicity and mutagenicity. It is known that chlorinated compounds which include chlorinated resins, fatty acids, chlorinated phenolics and dioxins are partly responsible for contributing effluent colours, acute and chronic toxicity, mutagenicity and carcinogenicity. Some non-chlorinated compounds such as resins and fatty acids are also toxic.

## *Measurement of AOX*

In order to find a parameter for monitoring bleach effluent, the Swedish Forest Industry Research Laboratory (STFI) came up with total organic chlorine (TOCL). The method for determination of TOCL is based on adsorption on a column of XAD resin, then separation and analysis of total organic chlorine compounds (TOCL). This method has been replaced by the AOX method. Here the material is absorbed onto activated carbon, the carbon is washed with a nitrate solution to remove the chloride ion, the carbon and the adherent organic matter are burned, the combustion gases containing HCl are scrubbed and the chloride ion is quantitatively determined by the microcoulometric titration. To convert TOCL to AOX, one has to multiply by a factor 1.4.

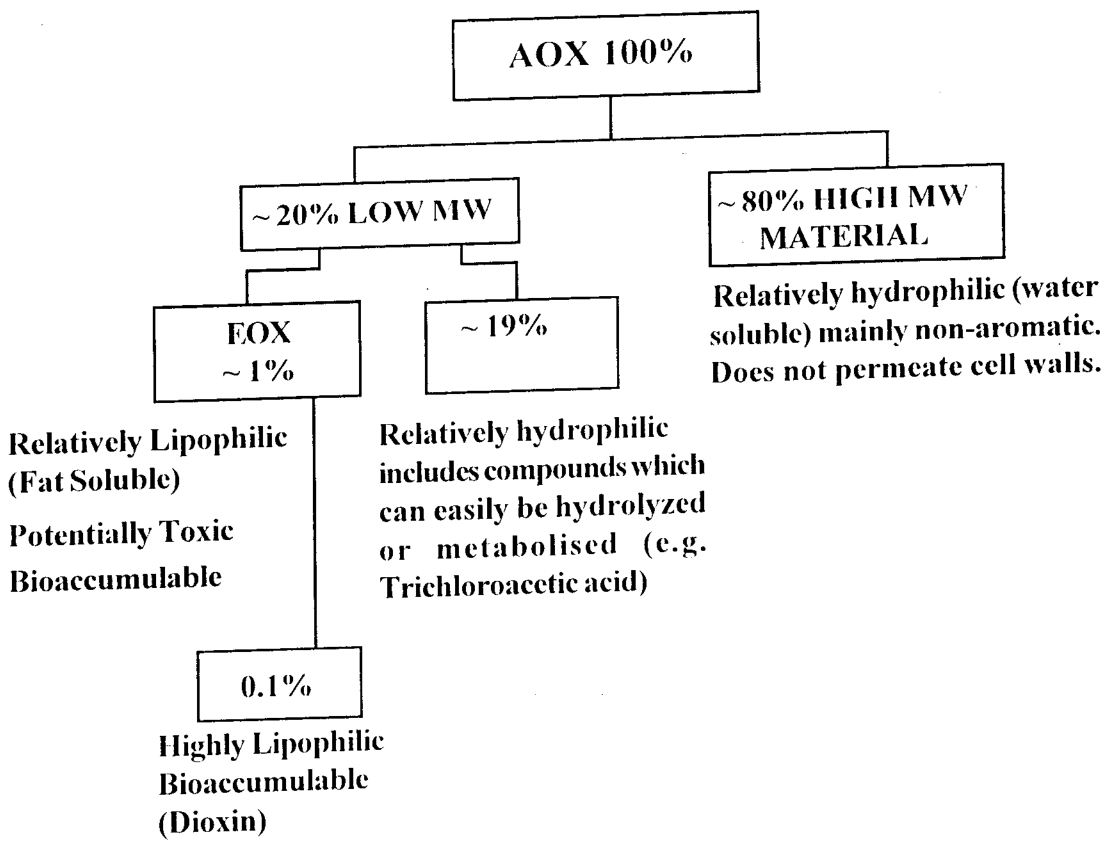
Thus

*1 TOCL x1.4 = 1 AOX*

AOX has become the parameter for most of the regulatory agencies world-over.

## *Distribution of chlorophenolic compounds:*

The measured AOX level does not represent 100% harmful compounds. The low molecular fraction is hardly 20% in bleach effluent from wood. The extractable organic chlorides (EOX) constitute only 1% of AOX, which are relatively lipophilic and are potentially toxic and bio accumulable. Only 0.1% are highly lipophilic and bio-accumulable. Chart shows the different components in AOX:-




DISTRIBUTION OF CHLORO-PHENOLIC COMPOUNDS

## *Limitations of AOX as a parameter for environmental damage*

As mentioned earlier, AOX - value does not really indicate the dioxin level. The extractable organic chlorides (EOX) or the extractable persistent organic chloride (EOPX) is a more relevant parameter to correlate environmental damage. The EOPX involves an alkaline hydrolysis step to simulate the ability of organisms to break down the organics.

USA has its cluster rules because they believe that they are some 12 chlorinated phenols which are considered harmful. The cluster rule incorporates maximum limits of different polychlorinated phenols.

Sweden has laid down that AOX-level for chlorine free paper should be below 0.1 kg/t paper.

The Central Pollution Control Board (CPCB) in India has adopted a maximum limit of 2 kg/T. paper, expressed as TOCL or 2.8 kg/T paper of AOX for large mills. This is likely to be reduced further down in the coming years.

### *AOX regulation*

Many of the countries in Europe, North America and Australia have set maximum limits for AOX in the mill effluent. The set standards for AOX in the discharge effluent are given in table -

Discharge AOX limits (Kg/t. pulp)

| | 1999 | 1995-2000 | 2000-2005 |
|---|---|---|---|
| Australia | 1.5 | - | - |
| Canada | 1.5 | - | - |
| Finland | 1.4 | 1.4 | 1.0 |
| Germany | 1.0 | -- | -- |
| Japan | 1.5 | -- | -- |
| Norway | 1.0-2.0 | -- | -- |
| Sweden | 1.2-1.5 | 0.3-1.0 | 0.3-0.5 |

<u>*USA follows the cluster rules, with the following items:-*</u>

| | Max. | Av. monthly |
|---|---|---|
| AOX, kg/t pulp | 0.951 | 0.623 |
| BOD, kg/t pulp | 4.52 | 2.41 |
| Chloroform, mg/t pulp | --- | 6.92 |
| Dioxin, pg/l | below 10 | 6.92 |
| Furan, pg/l | below 31.9 | --- |

Chlorinated phenols below detection (mass spectra)

## *Methods of reducing the AOX level in pulp & paper mill effluent*

Various methods practiced in industry for reduction of AOX in pulp mill effluent are:

A. Low kappa of pulp entering the bleached plant - the formation of chloro-organics can be reduced by bleaching a pulp with low lignin content. This is achieved by modified cooking methods. The various modified cooking methods to achieve a low kappa pulp are :-

(i) Extended delignification by addition of chemicals, which accelerate the lignin removal - polysulphide or/and Anthraquinone. This is achieved without any modification of equipment.

(ii) Extended delignification with modification of equipment (digester)

The various techniques used in the industry are :-

(a) Modified continuous cooking (MCC)

(b) Extended modified continuous cooking (EMCC)

(c) Isothermal cooking (ITC)

(d) Low solids pulping (LSP)

(e) Various systems modified batch cooking such as rapid Displacement heating (RDH), super batch and Enerbatch. All these processes increase pulp yield & pulp strength and lower cooking chemicals demand and improve washing.

B. **Reduction in consumption of chlorine or its compounds, used for bleaching.** This is achieved in optimizing the parameters of bleach chemical dosages, number and sequence of stages in a multistage bleach plant.

C. **Use of alternate bleach chemicals in place of chlorine such as oxygen, ozone and Hydrogen peroxide.** More recently a new chemical polyoxometalate (POM), which is an inorganic enzyme analog, promises good results in bleaching, but it does so in a much cleaner way. The decomposition products of all these chemicals are $CO_2$ and $H_2O$.

******()******

**Annexure A1**

## Physical Strength Properties of Paper (CEH Bleaching)

| GSM | Breaking Length (M) | | Tear Factor | | Burst Factor | Ash% |
|---|---|---|---|---|---|---|
| | MD | CD | MD | CD | | |
| 56 | 3571 | 1904 | 28.5 | 38.7 | 15.0 | 11.5 |
| 56 | 3511 | 1964 | 31.4 | 39.2 | 13.3 | 12.5 |
| | 3954 | 1919 | 35 | 44 | 14.0 | 12.0 |
| | 3735 | 1896 | | | | 12.5 |
| | 3742 | 2100 | 28 | 37 | 14.0 | 12.0 |
| | 4060 | 2060 | 29 | 41 | | 11.0 |

Annexure A2

## Physical Strength Properties of Paper (CEoH Bleaching)

| GSM | Breaking Length (M) | | Tear Factor | | Burst Factor | Ash% |
|---|---|---|---|---|---|---|
| | MD | CD | MD | CD | | |
| 56 | 3733 | 1964 | 34 | 44 | 15.0 | 11 |
| | 4166 | 2244 | 37 | 40 | 17.0 | 13 |
| 50 | 3850 | 1900 | 35 | 44 | 14.5 | 11 |
| 58 | 4067 | 2068 | 39 | 40 | 17.0 | 16.5 |
| 56 | 3976 | 1695 | 34 | 44 | 14.5 | 12.5 |
| | 4444 | 1988 | 37 | 45 | 16 | 13.5 |
| 56 | 3900 | 1900 | 31 | 39 | 14.0 | 13.0 |
| | 4444 | 2150 | 35 | 45 | 16.0 | 12.0 |
| 56 | 3986 | 1844 | 30 | 41 | 15.5 | 11.0 |
| 50 | 4333 | 2000 | 36 | 44 | 17.5 | 14.5 |
| 56 | 3264 | 1600 | 28 | 34 | 13.0 | 16.0 |
| 70 | 3555 | 1642 | 33 | 42 | 14.0 | 15 |
| 58 | 3680 | 1666 | 36 | 44 | 14.0 | 15.5 |
| | 3900 | 1896 | 38 | 46 | 15.0 | 16.5 |
| 58 | 3646 | 1685 | 32 | 39 | 13.5 | 15.0 |
| 56 | 3811 | 1839 | 34 | 42 | 16.0 | 16.5 |
| 56 | 3690 | 1637 | 36 | 44 | 14.0 | 14.0 |
| | 3928 | 1904 | 38 | 48 | 15.0 | 17.5 |
| 56 | 3570 | 1666 | 34 | 44 | 14 | 16 |
| | 3772 | 1871 | 35 | 45 | 15 | 12.0 |
| 56 | 3400 | 1637 | 36 | 44 | 14 | 16 |
| 45 | 3900 | 1904 | 38 | 48 | 15 | 17.5 |

Annexure B

| Effect of Oxygen Bleaching (Reduction in chlorine consumption) | | | | |
|---|---|---|---|---|
| Sl. No. | Pulp Production | Total $Cl_2$ % on pulp | $Cl_2$ in Hypo stage (% on pulp) | |
| 1 | 44.0 | 16.7 | 7.0 | Before Oxygen Bleaching |
| 2 | 44.0 | 15.5 | 7.0 | |
| 3 | 42.8 | 14.8 | 7.2 | |
| 4 | 43.0 | 15.0 | 7.1 | |
| 5 | 43.6 | 16.7 | 7.2 | |
| 6 | 43.0 | 11.2 | 3.7 | After Oxygen Bleaching |
| 8 | 43.0 | 12.0 | 3.9 | |
| 9 | 37.0 | 11.8 | 3.7 | |
| 11 | 43.0 | 11.0 | 4.5 | |
| 12 | 44.0 | 12.5 | 3.9 | |
| 13 | 44.0 | 11.8 | 4.2 | |
| 14 | 42.0 | 13.0 | 4.0 | |
| 15 | 36.0 | 12.0 | 4.0 | |
| 16 | 33.0 | 13.0 | 3.6 | |
| 17 | 48.0 | 12.6 | 3.6 | |
| 18 | 42.0 | 13.1 | 3.9 | |

Annexure C

## Fiber Classification

**WITHOUT OXYGEN**

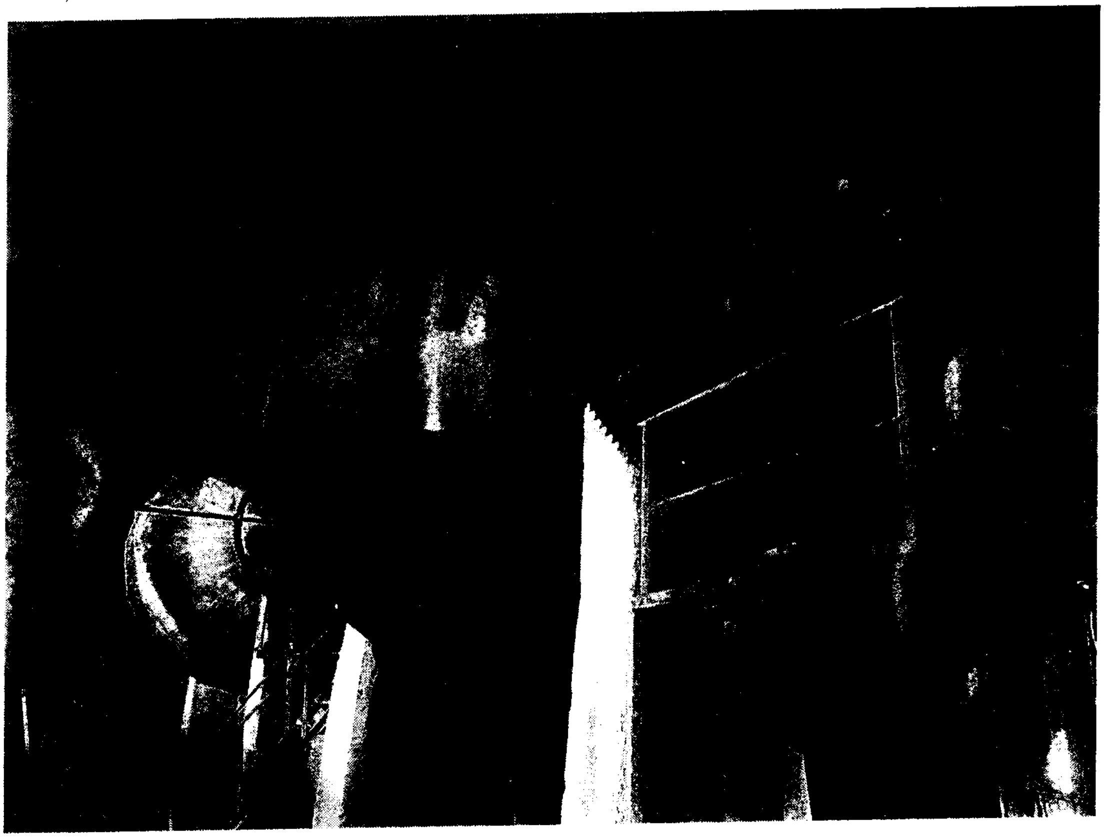
| +30 | +50 | +100 | +200 | -200 | °SR | Brightness % | Viscosity |
|---|---|---|---|---|---|---|---|
| 21.68 | 16.5 | 20.9 | 16.88 | 24.02 | 30 | 78 | 6.91 |
| **WITH OXYGEN** | | | | | | | |
| 22.82 | 15.64 | 22.81 | 14.96 | 23.77 | 27 | 80 | 6.5 |
| 22.10 | 18.91 | 23.64 | 12.95 | 22.40 | 28 | 80 | 7.16 |
| 23.64 | 16.95 | 24.82 | 11.98 | 22.61 | 27 | 81 | 7.30 |
| – | – | – | – | – | 28 | 80 | 7.1 |

# PHOTOGRAPHS

**Photograph No.(i)** ⟶ ***Proceurement of Bagasse***

**Photograph No.(ii)** ⟶ ***De-pithed Bagasse***

**Photograph No.(iii)** ——▶ ***Conveying***

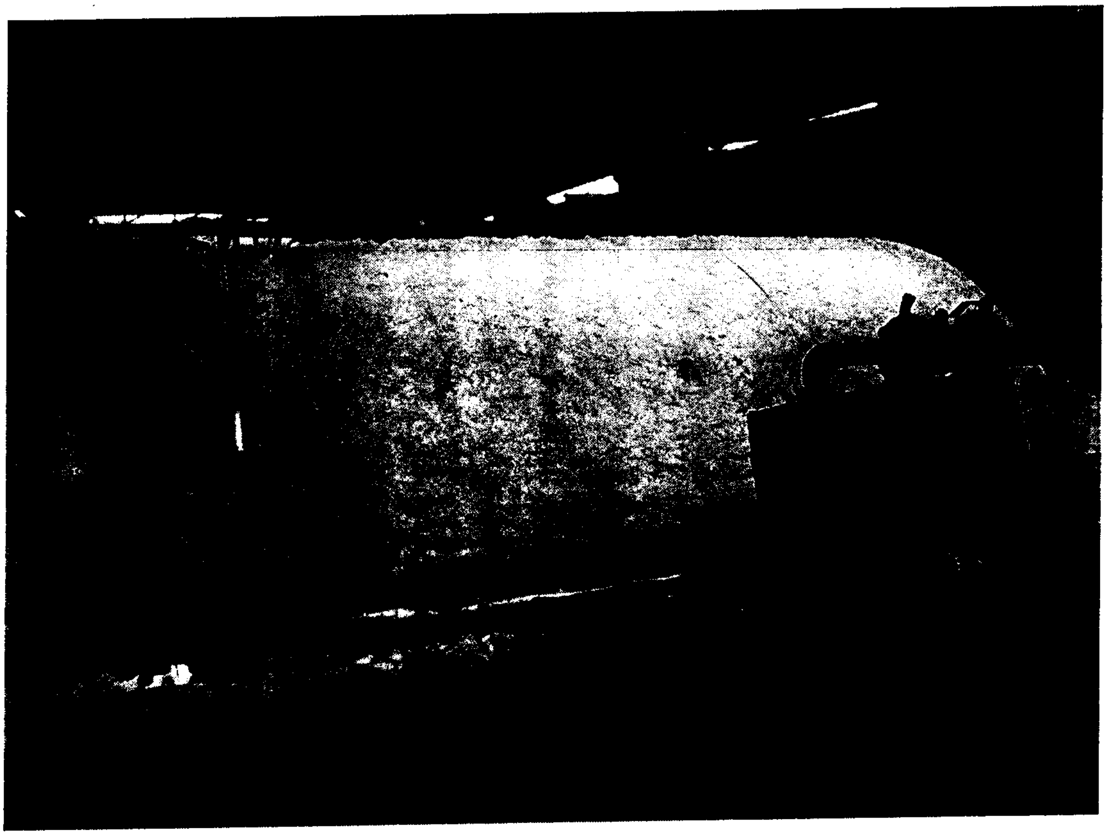


**Photograph No.(iv)** ⟶ *Digesters*

**Photograph No.(v)** ⟶ ***Blow tank***

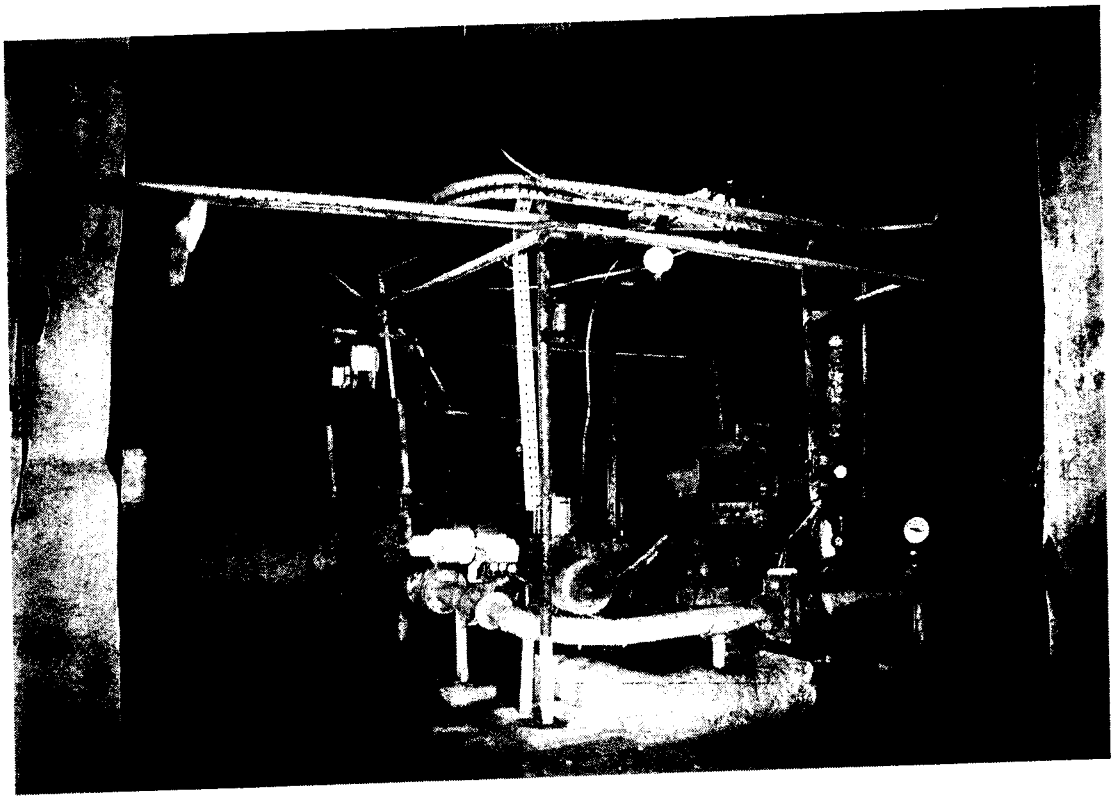
**Photograph No.(vi)** ⟶ ***Brown stock washer (unbleached pulp washing)***

**Photograph No.(vii)** ⟶ ***Brown stock washer***

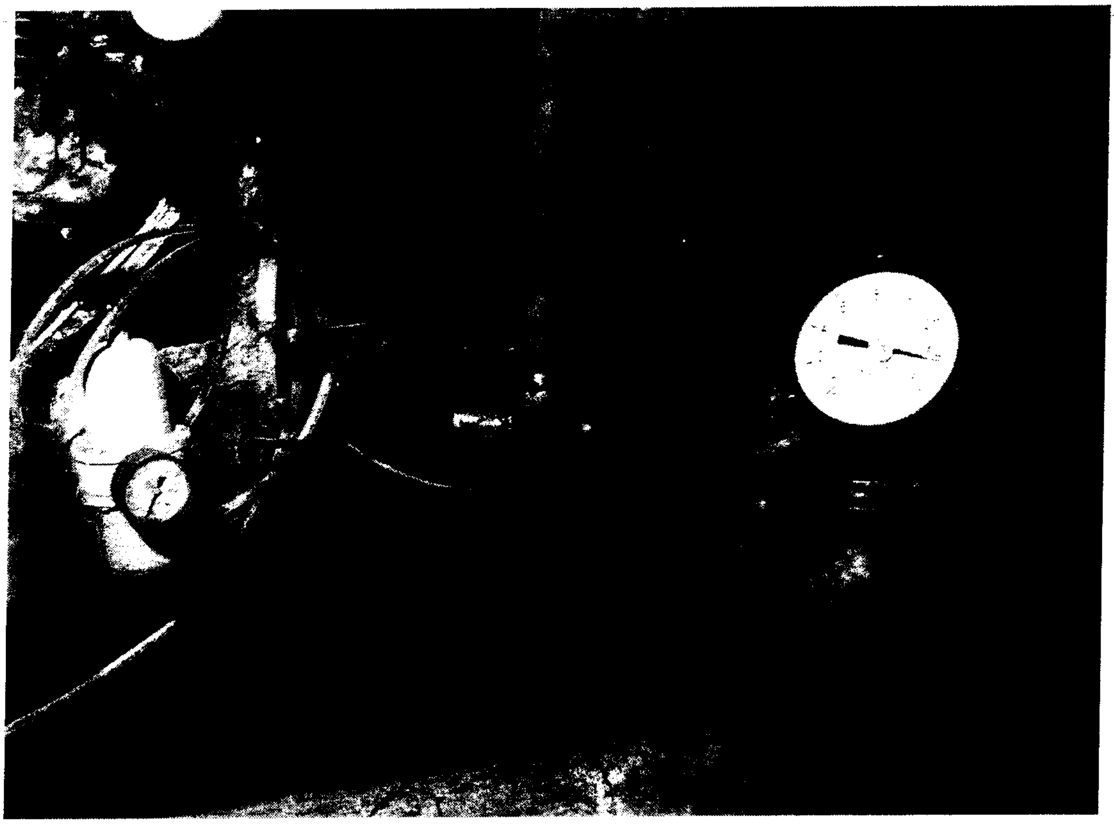


**Photograph No.(viii)** ⟶ *Chlorine washer*

**Photograph No.(ix)** ⟶ ***Alkali heater mixer***



**Photograph No.(x)** → ***Oxygen bleaching plant (full view)***

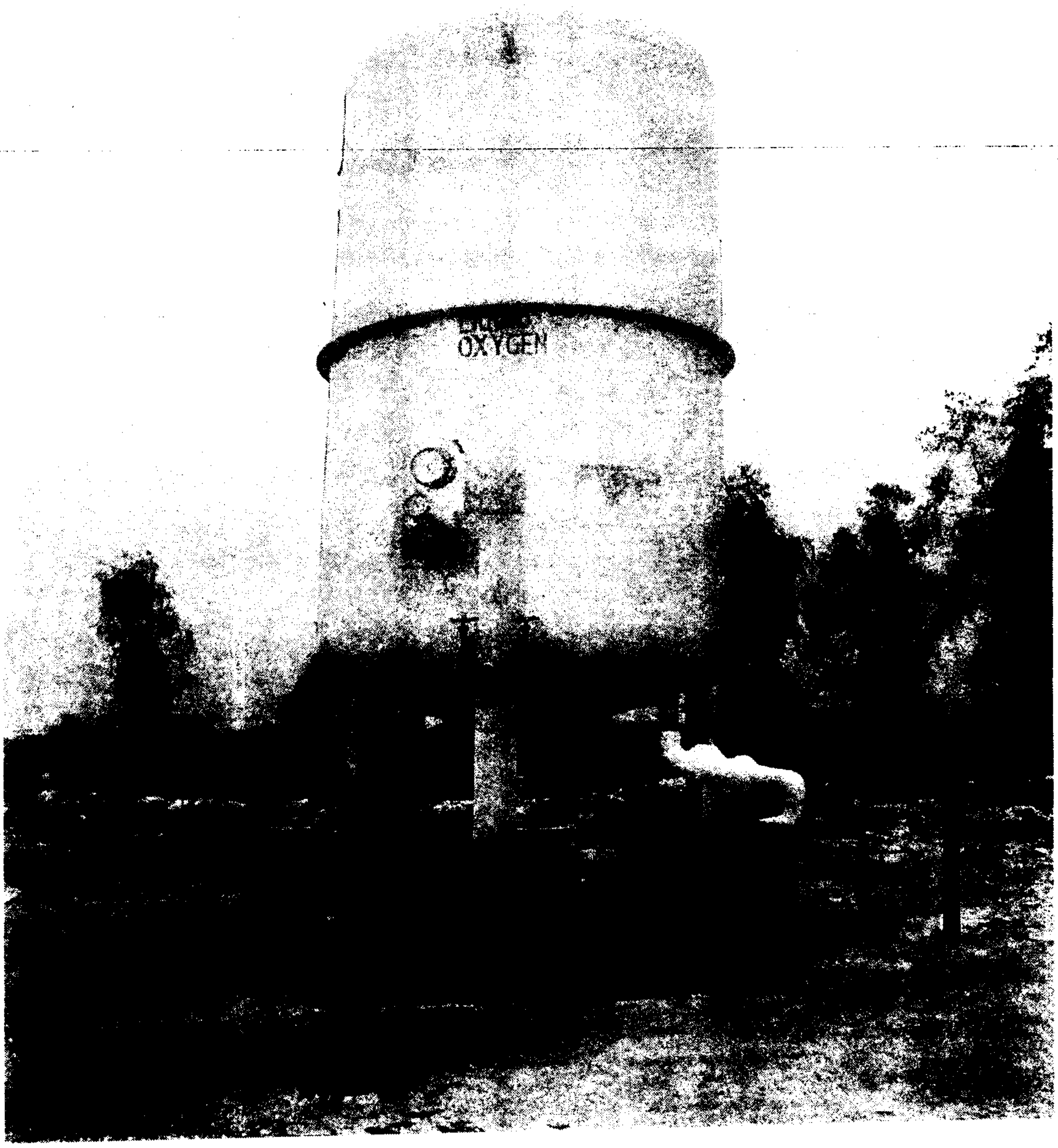


**Photograph No.(xi)** ⟶ ***Stand pipe & M.C. Pump***

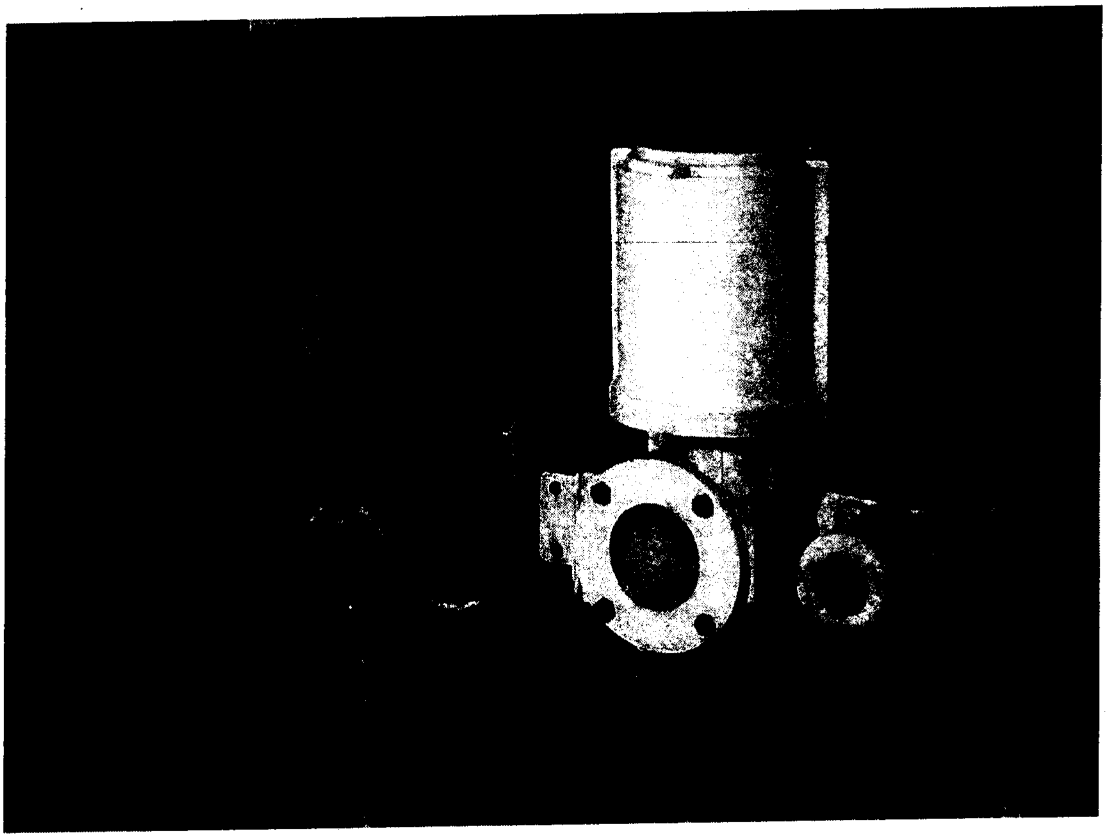
**Photograph No.(xii)** ⟶ *Oxygen Mixer*

Photograph No.(xiii) ⟶ *Oxygen Control valve*

**Photograph No.(xiv)** ⟶ ***Oxygen vapouriser***

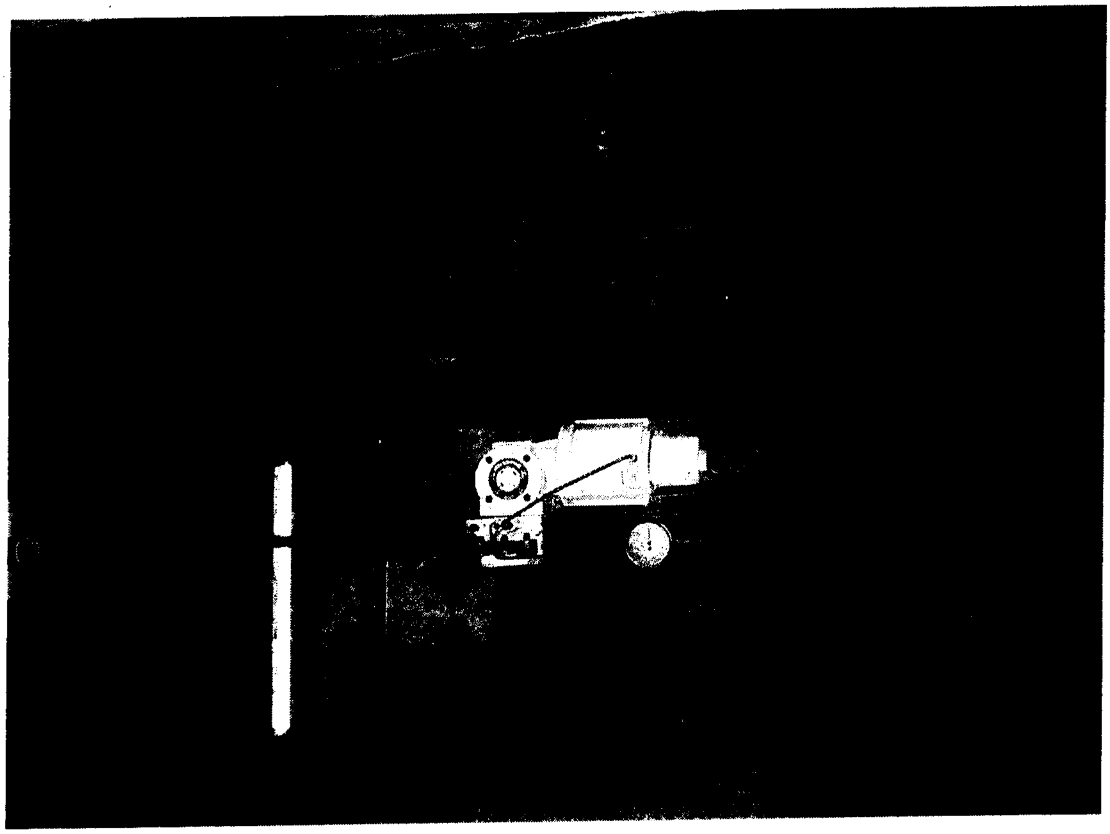



**Photograph No.(xv)** ⟶ ***Oxygen Capsule***

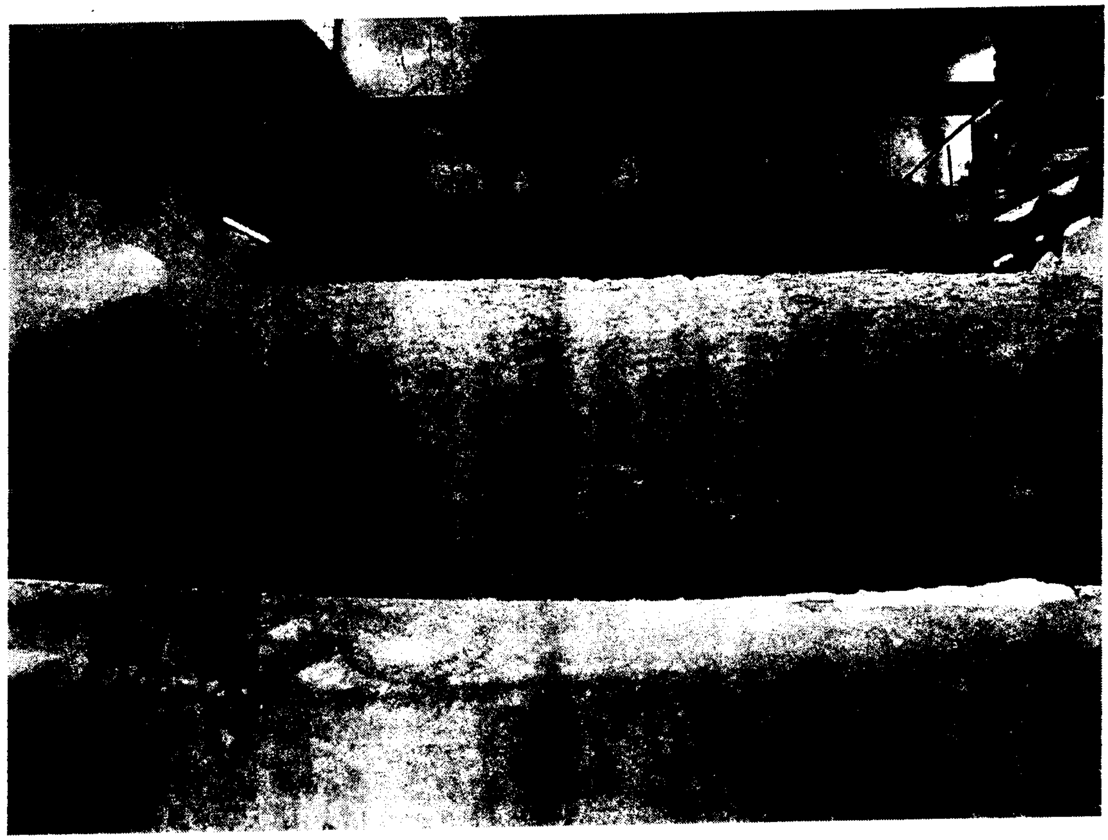


**Photograph No.(xvi)** ⟶ ***Auto control valve Before Reaction vessel***

**Photograph No.(xvii)** ⟶ ***Reaction vessel***



**Photograph No.(xviii)** ⟶ ***Reaction vessel top, showing pressure control valve and oxygenated pulp discharge line***



**Photograph No.(xix)** ⟶ *Alkali washer*

**Photograph No.(xx)** → ***Common effluent drain (Before Eo)***

**Photograph No.(xxi)** ⟶ *Common effluent drain (after Eo)*

**Photograph No.(xxii)** ⟶ ***Alkali washer shredder***