Ozone Bleaching Technology : A Review

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ABSTRACT

Bleaching of pulp using chlorine and chlorine compounds will be a matter of the past in the near future. Ozone bleaching has already taken the centre stage. This paper summarises the development so far achieved in ozone bleaching technology.

INTRODUCTION

In pulp and paper industrty, due to environmental reasons, there was an urgent necessity to reduce and eliminate dioxins and halogenated organic compouds (AOX) in the discharge of pulp mill wastewater. This allowed some of the processing liquors to be recovered and recirculated and large volumes of bleach plant effluents, to be reduced. The rapid technical development in cooking and bleaching process has enhanced the posibilities of recycling effluents, in both Elemental Chlorine Free (ECF) and Total Chlorine Free (TCF) bleaching process. Minimising the volume of effluent from bleaching system, is the first step needed to be taken to realise low Environmental impact mills. Modern mills in developed countries, have an effluent of 20 m^3 per tonne of pulp. The volume will be further reduced in the near future. As a result of the success of the Green Movement world wide, tremendous market pressure has come to bear upon paper mills. Growing number of paper producers are clamouring for pulp produced by so called environmentally benign processes. Recent EPA regulations have proposed drastic restriction in AOX levels from non-TCF bleaching. It seems that a grass root bleached mill will have to be designed with closed cycle capability, in order to be permitted. However, the changing nature of kraft delignification and bleaching, in response to combined public, market and regulatory pressures, has moved many existing mills into the position of adopting full closure of effluent.

As a consequence, this not only decreased the volume of waste water being discharged to the receiving water bodies, but also increased potential for elemental Chlorine Free (ECF) or Total Chlorine Free (TCF) bleached pulp mill, to become a future reality in the early 1970's.

Results of Research in Ozone Bleaching Technology

Research in the field of oxygen and ozone pulp bleaching and some laboratory and pilot scale studies were conducted in many mills in European and Scandinavian countries. The objective was, reduction of BOD and COD levels from the bleach plant effluents. The experiments were conducted giving high importance to oxygen delignification and it became a commercial reality in a number of mills. But much of the early research on ozone was not without acute problems, indicating some unacceptable trends when using ozone. While the use of oxygen began to increase and appeal of ozone wanted, certain developments in the industry during the 1980's returned ozone to the centre stage. Gaseous mixing of bleaching medium, was done in high consistency pulp. But mixing of gases with medium consistency pulp was made easy by deploying shear - type mixers. The initial problems encountered with ozone bleaching was, not achieving the target of brightness and strength of pulp, and high expense of ozone bleaching, when compared to chlorine bleaching.

High presence of AOX and dioxin in bleach plant effluents forced mills to use oxygen based bleaching agents, oxygen, ozone and hydrogen peroxide. The advent of chlorine dioxide bleaching reduced AOX and dioxins in the effluent and ECF bleaching became the order of the day. Some mills that opted for total TCF pulp started using ozone as part of the bleaching sequence. But, still ozone bleaching was exorbitantly expensive. Slow but steady development in ozone

generation processes, to make it less expensive was a big turning point, which accepted ozone stage on commercial basis by many mills.

Drive initiated by what is known as "greening" of the bleaching process, was the most important contributing factor that gave impetus to ozone, as a bleaching agent. Regulatory agencies and market forces, put a ban on chlorine as a bleaching chemical. The above factors have led to successful commercialisation of ozone bleaching in many operating mills and new green field mills.

Ozone generation technology in the early stages could produce only 1-2% by weight of ozone, and ozone was produced form air. With high purity oxygen, the concentration was 2,4% . Ozone generation systems of this kind were used in water treatment plants. Generation of ozone from air was very power intensive. Later developments in ozone generation technology could produce 5% by weight. However, though it took about a decade, in the early 1990s concentration of ozone could be raised to 8-11% with power efficiency, which was very attractive. This development renewed the interest in its application and many pulp mills took up ozone bleaching commercially.

Driving Forces

The European countries, particularly Germany, which imports most of its bleached pulp, depends on Scandinavian countries for their bleached pulp requirement. Green peace movement passed regulations prohibiting Germany to use bleached pulp bleached with chlorine compounds. To maintain their market, Scandinavian countries took the burden of producing TCF pulp. With the Environmental Protection Authorities (EPA) stipulation becoming stricter to eliminate chlorine, mills determined that ozone was the best option to TCF pulp. Naturally many countries followed suit. In America through EPA regulations are not very strict on AOX emissions, many mills opted for ozone bleaching to cater to import and social commitments. In Brazil, which is one of the main suppliers of pulp to Europe, some mills commissioned ozone bleach plants and many more are in the line. Although, the capital cost of this type of bleach plant is 25-30% higher than the conventional sequence of bleaching, the overall results reported by many mills in America demonstrate the effectiveness of the process. Effluent volume is less than half of that from the conventional bleach plants, as are colour, COD. BOD and AOX. There is no deterioration of pulp quality and brightness exceeds specifications. Using ozone at about 8% by weight in oxygen, the bleach chemicals costs have been reduced by more than 40%. Scandinavian countries, South Africa and Brazil are also commercially turning to ozone bleaching, indicating that ozone bleaching is here to stay.

It has been proved that commercial operation of substitution of chlorine with ozone in ECF bleaching sequence can reduce the volume of effluent from pulp mills significantly, by circulating a portion of process water from bleach plant to be recycled and processed in the chemical recovery system. The actual reaction of ozone in the bleaching process is complex and numerous. Ozone has a high potential for oxidation and reacts rapidly. Ozone reacts with lignin rapidly. Ozone reacts with ligning during delignification. However, the capacity of ozone to remove substantial quantity of lignin is limited, as it can only aid lignin depolymerisation.

Disadvantages and Limitations

Despite commercial success of ozone bleaching, there are areas, which need much improvement and optimisation, to make ozone bleaching a more generally accepted option for existing and future mills. This is because of vast variety of raw materials used, cooking process adopted and requirement of end product.

Presently, ozone bleaching, though adopted by many mills driven by pollution abatement considerations, has several disadvantages. The ozone generators are exorbitantly expensive. Mixing technology has to be considerably developed, to make ozone replace other bleaching agents. The pulp has to be free from carried - over organics and dissolved metallic ions, before the ozone stage. That means extra washing to be done while using ozone. It is critical to wash the dissolved solids prior to ozone treatment, because they react quickly with ozone, consuming a more costly chemical, that cannot be added in significant quantities.

The ozone generation technology is still energy-intensive, in spite of some recent developments. High concentration of ozone has to be attained to make it a single - stage medium-consistency-bleaching agent. Research is still on to find the desirability of medium consistency and high consistency bleaching when ozone is used. Though medium consistency bleaching is more widely accepted, the low concentration of ozone achievable is a limitation. Development of mixers should lead to improvement in better gas mixing. As in the case of other bleaching chemicals, process variables like pH, temperature, retention time etc. also play an important part in ozone bleaching. These variables will have to be optimised. Carry-over of

recycled solids and dissolved metal ions will have to be almost totally removed in the washing stage before the pulp is subjected to ozone bleaching, to improve effectiveness of the ozone bleaching.

Build up of inert in mill liquor systems will present more difficulties in mills that recycle bleach plant effluent. These metals promote catalysts of oxidation free radicals, which attach cellulose and impart adverse effect on chlorine dioxide. In addition, metals such as calcium, magnesium and aluminium can form precipitates, which lead to scale formation in process equipment. Recycle of alkaline effluent to the post oxygen washers increases the total solids carried over into the bleach plant and increase the bleach chemical requirement for both the ECF and TCF sequences. In other words, carry over of organics and lignin to the bleaching system will hamper ozone bleaching process, as ozone will be absorbed by these chemicals, further enahcncing the quantity of ozone used and hence the cost.

Sequences adopted

Mill that uses ozone stage presently either for ECF or TCF pulp, use different sequences depending mainly on factors like pulping methods, brightness target and end product. For ECF, sequence of OZEoD or OA (ZD) EOD sequence can be used. Mills using chelants (Q) adopt a different sequence. There are mills using QP (ZQ) (PO) and get required end brightness. It is reported that bleaching process involving ozone and peroxide are more attractive and use QP (ZE) P and (ZE) QP sequence.

CONCLUSION

Due to significant developments in ozone bleaching, it is possible today to design an ozone stage to meet the process requirement. From a cost stand point. designing the ozone system for flexibility is the most important factor because ozone equipment is the highest cost -factor. However, bleaching process involving ozone-bleaching reduces the cost of water and wastewater treatment plants considerably, as there is a 75% reduction in effluent discharged due to recycling of process water. General trend of pulp industry to achieve "closed effluent" concept and the long-term visions of totally Effluent Free Pulp Mills rely on, ozone-bleaching-process. Total elimination of gaseous chlorine as a bleaching chemical, will induce interest in modifying the bleaching process by using ozone, in combination with ECF or TCF pulp production. Regulatory limits on AOX and other effluent parameters compelled with improvement in ozone generator-efficiency, will surely make more and more mills adopt ozone bleaching.