



Review

Scale deposits in kraft pulp bleach plants with reduced water consumption: A review



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ABSTRACT

The general tendency in the pulp industry towards reduced fresh water consumption and minimum effluent causes major deposit problems in mills. Chemical pulp bleach plants are affected by several types of mineral deposits, the most frequent being calcite, barite and calcium oxalate. In this review, the phenomena leading to scaling in chemical pulp bleaching are discussed, together with strategies for limiting deposits. The merits of various chemical methods in estimating scaling risks are compared. Chemical speciation methods are used throughout this review to gain a better understanding and prediction of scaling phenomena. Coupled chemical process simulations are anticipated to be a crucial way of solving deposition problems in bleach plants.

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1. Introduction

The pulp industry has made great efforts to reduce its specific water consumption over the last few decades. This has helped to reduce the environmental burden on natural resources, and to secure water supplies for the industry in regions with scarce water resources (Ali and Sreekrishnan, 2001; Lovelady et al., 2007; Tewari et al., 2009). With the increasing closure of bleach plants, many dissolved species accumulate in process loops, which may lead to scale deposits. The most frequent types of scale in bleaching lines are composed of calcium carbonate, calcium oxalate and barium sulphate (Bryant, 1996; Ulmgren, 1997). Various methods may be used to prevent deposits, such as metal removal (by acid washing and/or chelation). In severe cases, the bleach plant has to be shut down, as only hydro-blasting techniques and/or acid cleaning procedures can remove the most encrusted deposits. In order to reduce scaling, it is crucial to understand the physicochemical

parameters that govern the phenomenon, in the conditions of a closed bleach plant (i.e. at high ionic strength, and in the presence of dissolved wood organics and fibres). Chemical speciation methods are an invaluable way of predicting scaling risks (Ferguson, 2002).

The objective of this work is to review the main causes of scale deposition in bleach plants with reduced fresh water consumption, and to compare the relevance of various chemical methods in estimating scaling risks. The main phenomena are illustrated thanks to chemical speciation calculations. The importance of pH regulation in chlorine dioxide bleaching is reviewed. Also, the potential interest for magnesium-based salts in chemical pulp bleaching is discussed. Strategies for limiting deposits in closed bleach plants are then reviewed. Finally, the potential of coupled chemical process simulations for resolving scaling problems in bleach plants is examined.

2. Water management in a closed bleach plant

In the kraft pulping process, wood chips are conditioned with steam, before impregnation with white liquor (NaOH and Na₂S) and cooking (at 145–170 °C for a few hours). The cooked chips are then washed, and the filtrate (=weak black liquor) is then concentrated with evaporators. The strong black liquor is burnt in the recovery boiler, to reclaim heat and chemicals. The green liquor (Na₂S and Na₂CO₃) thus produced is regenerated to white liquor by a re-

Abbreviations: ECF, elemental chlorine free; TCF, totally chlorine free; ADT, air-dried tonne (of pulp); IAP, ionic activity product; S, supersaturation; SI, saturation index; LSI, Langelier saturation index; RI, Ryznar index; EDTA, ethylenediaminetetraacetic acid; DTPA, diethylenetriaminepentaacetic acid; COD, chemical oxygen demand.

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caustification process. The resulting pulp (brownstock) can be subjected to a bleaching sequence, for direct use on a paper machine in integrated mills, or further dried to be sold as market bleached pulp.

The bleaching process for chemical pulp consists of a sequence of oxidative stages. The degraded lignin is solubilised with intermediate alkaline extraction stages, and removed by washers. The use of chlorine for chemical pulp bleaching has been phasing out over the last 2 decades, for environmental reasons. Nowadays, 90% of bleach plants throughout the world run either an Elemental Chlorine Free sequence (ECF, using chlorine dioxide as the main bleaching chemical) or a Totally Chlorine Free sequence (TCF, with combinations of oxygen, ozone and hydrogen peroxide stages). The share of TCF in worldwide bleached pulp production remains stable at about 6–7%. An example of an ECF sequence could be ODEDD (oxygen delignification, followed by chlorine dioxide, alkaline extraction, then 2 successive chlorine dioxide stages) while a TCF sequence could be OQZP (oxygen delignification, followed by a chelation stage, then ozone, then peroxide), with numerous possible variations among mills (see Table 1 for bleaching stage codes).

The pulp industry has made considerable efforts over the last few decades to reduce its fresh water consumption and environmental impact. Water resource conservation and limiting the volume of filtrate to be treated by the integrated waste water treatment plant are strong incentives for the industry to reduce fresh water consumption. The bleach plant typically accounts for half of the total water consumption in a kraft pulp mill (Patrick et al., 1994; Towers and Turner, 1998). The specific water consumption for bleach plants has been decreasing from 50 to 35 m³/ADt in the 1980's to 25 m³/ADt today on average (IPPC, 2013). Modern pulp mills specifically designed with closed circuits may reach specific water consumption levels as low as 12 m³/ADt for the bleach plant (Bajpai, 2012). However, such low water consumption leads to the build-up of dissolved organics and salts. This causes greater scaling problems.

Reduced water consumption in the bleach plant is achieved through counter-current washing of the pulp. The fresh water is only used to wash the pulp after the last bleaching stage, and then recirculated backwards to wash the pulp from previous stages. Non-contact water such as condensate from black liquor evaporation may be fed into the water system to reduce the mill's overall water consumption. Direct counter-current washing has the potential to reduce water consumption to very low amounts. However, this increases the load in the effluent in the first bleaching stages and results in increased scaling problems. Therefore, common practice is to separate the alkaline and acidic effluents (see Table 1). This results in the so-called jump-stage counter-current washing strategy for effluent management in the bleach plant (Dence and Reeve, 1996; Suess, 2010). It consists in applying counter-current washing to the acidic and alkaline circuits separately (see Fig. 1). This is critical in limiting scaling problems, as the

acidic effluent is loaded with dissolved calcium which may precipitate if used to wash pulp from an alkaline extraction stage for instance. Besides, backward washing of alkaline pulp with cation-rich acidic filtrate will cause enhanced cation build-up in the bleach plant, due to re-adsorption on fibres at alkaline pH (Bryant, 1996). Efficient pulp washing technology is essential for closed bleach plants. Mineral deposits in pulp washers limit washing efficiency: this increases the carry-over of dissolved substances, which cause over-consumption of bleaching chemicals during the next stage.

It is possible to reduce fresh water consumption by recycling the alkaline filtrate from the oxygen delignification washer for brownstock washing, and then sending this ultimate filtrate to the recovery cycle (Fig. 1). This effluent is usually suitable for evaporation and burning in the recovery boiler, as it rich in dissolved organics and poor in metal ions (Dence and Reeve, 1996). Nowadays, both ECF and TCF bleaching sequences start with an oxygen delignification stage. Oxygen delignification may be considered as an extension of the cooking process. Here we consider it to be part of the bleaching sequence to show the intricate structure of water circuits in closed mills and the impact on deposits. Using oxygen delignification as Best Available Technology makes it possible to dissolve more organics from pulp before it enters the bleach plant. In a closed mill, these organics end up being burned in the recovery boiler. This is very important from a water management point of view, as it limits the dissolved organic load in the next bleaching stage. This makes it possible to reduce bleach plant water consumption further and to decrease the consumption of bleaching chemicals.

Industrial experience has shown that it is difficult and not cost-effective to run a bleach plant with water consumption below 5 m³/ADt (Rapson and Reeve, 1973; Rapson, 1967). In Europe, no bleach plant currently operates with less than 12 m³/T (IPPC, 2013). This confirms that it is economically difficult to run a bleach plant with a high degree of closure. This would require re-using the acidic effluent in some way. In order to reach zero effluent, acidic effluent must finally be recycled to the recovery cycle. Therefore it must be cleaned of its chloride content, otherwise corrosion could endanger the evaporators and recovery boiler (Maples et al., 1994). Treating acidic filtrates to remove metal ions is a technological challenge. Various processes have been proposed: evaporation and electro-dialysis (Johansson et al., 1995), lime precipitation (Ulmgren, 1997), or acidification, stripping of HCl and evaporation (Myreen, 1993). Even after adequate treatment of the acidic effluent, the chloride concentration may become unacceptable for re-use and cause corrosion problems (Pattison et al., 1981; Rapson and Reeve, 1973). In addition, enhanced scaling problems become impossible to handle (Maples et al., 1994; Patrick et al., 1994). Total closure of the water circuits in pulp mills is not currently a viable strategy (Axegard et al., 1997; Basta et al., 1998).

While it is possible to achieve low water consumption with an ECF sequence, complete closure is however problematic. In a totally closed circuit, all filtrates are finally sent to the recovery cycle (Brooks et al., 1994). Some studies report that bleach plant closure may be better achieved with a TCF sequence, as no chloride build-up occurs (Bajpai, 2012; Johnston et al., 1997; Patrick et al., 1994). However, efficient peroxide bleaching requires prior removal of transition metal cations by a chelation stage or an acid washing stage (in order to limit metal-catalysed decomposition of hydrogen peroxide) (Bouchard et al., 1995; Colodette et al., 1988; Li et al., 2000; Wekesa and Ni, 2003). The corresponding washing effluent loaded with salts cannot be recycled to the recovery cycle without appropriate and costly treatment. Note that some state-of-the-art ECF mills now include an acid washing stage before the D0 stage (Colodette et al., 2008). This is intended to remove hexenuronic

Table 1
Nomenclature of typical chemical pulp bleaching stages and effluent quality.

Code	Bleaching stage	Type of effluent
O	Oxygen delignification	Alkaline
E	Alkaline extraction ^a	Alkaline
P	Hydrogen peroxide bleaching	Alkaline
Z	Ozone bleaching	Acidic
Q	Chelation stage	Acidic
A	Acid stage	Acidic
C	Chlorine stage	Acidic
D	Chlorine dioxide bleaching	Acidic

^a Extraction may be reinforced with oxygen (EO) and peroxide (EOP).

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