

## EFFECT OF DIOXINS REDUCTION WITH ECF CONVERSION IN KRAFT PULP BLEACHING MILLS IN JAPAN

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### Abstract

Effects of elemental chlorine free (ECF) bleaching on the reduction of dioxins were investigated for 17 domestic pulp mills in Japan. Dioxin concentrations were measured and compared in the bleached pulp, in-mill process effluents for bleaching, and whole mill effluents before and after the ECF conversions.

Even before the ECF conversion, dioxin concentrations in the bleached pulps were below 0.5pg-TEQ/g in approximately the half of the mills investigated. After the ECF bleaching process was introduced, the generation of dioxins was dramatically suppressed in all of the mills: dioxin levels were reduced by more than 98% after the ECF conversion. Similarly, the concentrations of dioxins of the in-mill process effluents after the conversion also dramatically decreased by more than 98%, strongly indicating that the shift of bleaching process to the ECF bleaching effectively suppresses the generation of dioxins. The dioxin levels in the whole mill effluents after ECF conversion of the mills were below 1pg-TEQ/L that is the environmental standard in Japan. Furthermore, some isomers of dioxins specifically generated by chlorine bleaching process were not detected in the whole mill effluents, confirming that the ECF conversion dramatically and effectively suppresses the emission of dioxins into our environment.

### Introduction

Since the severe pollution of organochlorine compounds in the Baltic Sea and the significant dioxins generation by chlorine bleaching process in pulping became public, the worldwide movement was intensified to shift to non-chlorine bleaching process. By 1994, Scandinavian countries completed the conversion of pulp bleaching process to non-chlorine bleaching.<sup>1</sup> In the U.S., the Cluster rule strongly promoted the pulp and paper industry to shift the bleaching to non-chlorine process.<sup>2</sup> As the non-chlorine bleaching, the elemental chlorine free (ECF) bleaching has commonly been used worldwide, whereas application of the totally chlorine free (TCF), a process using no chlorine compound has been limited in Nordic countries.

Japanese pulp and paper industry has also made a lot of efforts to reduce organochlorine compounds including dioxins by introducing advanced technologies such as oxygen delignification and partial substitution of chlorine by ClO<sub>2</sub> in the chlorine bleaching process. In addition, the pulp bleaching process has been recently converted to ECF bleaching to suppress the generation of chloroform. To date, about 90% of bleached pulp in Japan is produced without using the chlorine bleaching.

In the U.S., after the Cluster rule became effective, a survey on the outcome of the ECF conversion was intensively conducted for a numerous number of mills. Only few reports, however, are available for direct comparison in the same mill between before and after the ECF conversion. In Japan, we have investigated the environmental impact of the process change in bleaching during the transition stage of the ECF conversion in Oji paper cooperation and Nippon paper industries. From year 2000, these two corporations have conducted the ECF conversion on 17 mills. In this study, effects of the ECF conversion on the reduction of dioxins were investigated. Results are presented with respect to the improvement in the generation and emission of dioxins after the ECF conversion.

**Materials and Methods**

Dioxins were analyzed for the bleached pulp, in-mill process effluents for bleaching, and whole mill effluents in 23 lines of 17 mills where the ECF bleaching was introduced to the KP bleaching process from 2000. ClO<sub>2</sub> is used for 1st bleaching stage (D-ECF) in 18 lines, whereas O<sub>3</sub> is used for the same bleaching stage (Z-ECF) in 5 lines. The bleached pulp samples were prepared by air-drying the wet pulp of each in-mill process. In-mill process effluents were sampled at 1st bleaching stage (C stage and D/Z stage, before and after the ECF conversion, respectively) and at 2nd bleaching stage (E stage).

Analysis of dioxins was conducted according to JIS K0312. Besides the 29 toxic dioxins, 1,3,6,8-TCDD, 1,3,7,9-TCDD and 1,2,7,8-TCDF were also analyzed to identify the origin of dioxins. The detection limits of 2,3,7,8-TCDD were 0.2pg/L for effluent samples and 0.02pg/g for pulp samples. For calculating the toxicity equivalent quality (TEQ), only the values above the detection limits were used.

The reduction ratio is calculated, based on the complete results of 20 series in 14 mills. Median is used as numerical value.

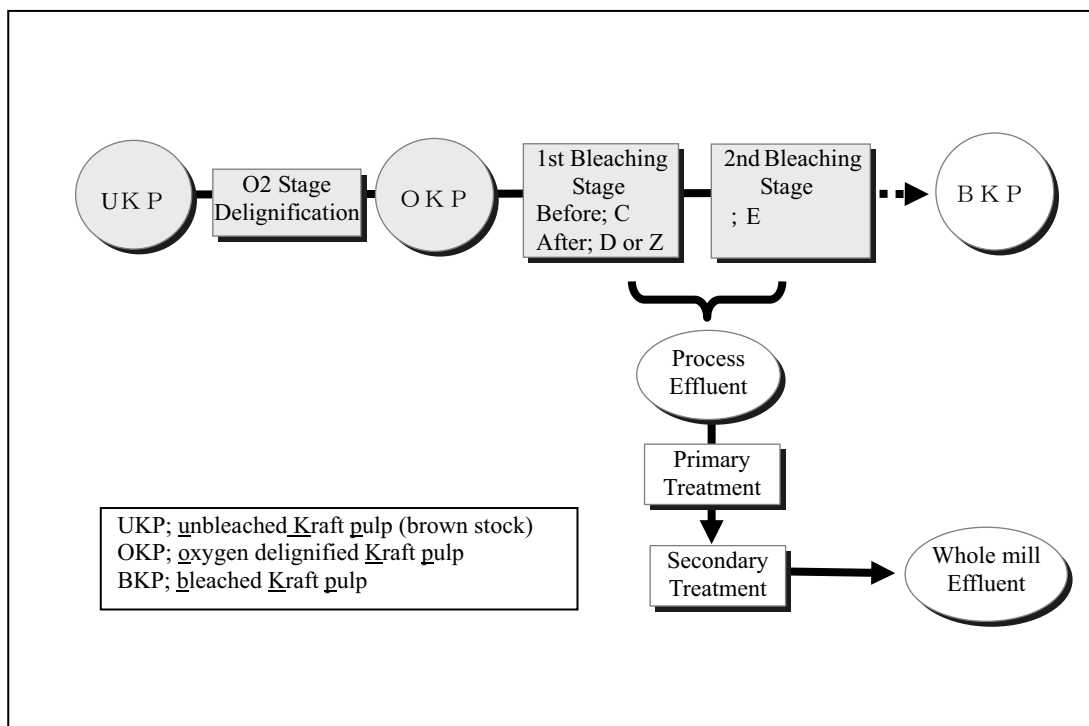


Fig. 1 Process of pulp bleaching

**Results and Discussion**

In Nordic countries, as a result of ECF conversion the dioxin levels of the paper made from the bleached pulp decreased to 0.5pg-TEQ/g dramatically.<sup>3,4</sup>

Even before the ECF conversion, dioxin concentrations in approximately the half of the mills investigated were below 0.5pg-TEQ/g, on account of having equipped with oxygen delignification process and bleaching process with partially substitution of chlorine by ClO<sub>2</sub>.

After the ECF conversion, dioxin levels of the bleached pulp decreased almost below 0.5pg-TEQ/g, and the reduction ratio was 98%. Especially, dioxin levels in the half of these pulps were below 0.02pg-TEQ/g which was thought to be virtually dioxin free level. Not only Z-ECF but also D-ECF using ClO<sub>2</sub>, suppressed the dioxins generation effectively (Fig.2).

The dioxin levels in-mill process effluent decreased below 10pg-TEQ/L with 19 lines of 23 lines, and the dioxin concentrations in the 2nd bleaching stage effluent was higher than that of in the 1st stage. Similar to the pulps, the dioxin levels of the in-mill process effluents were reduced more than 98%. It is confirmed that the ECF conversion dramatically and effectively suppresses the generation of dioxins in pulp bleaching process.

Both of the dioxins isomers 2,3,7,8-TCDD and 2,3,7,8-TCDF which specifically generates in chlorine bleaching were not detected from bleached pulp or bleaching process effluents in ECF converted mills. It clearly shows that ECF converted mills can produce virtually dioxin-free pulp.

pg-TEQ/g (μg-TEQ/Ton)

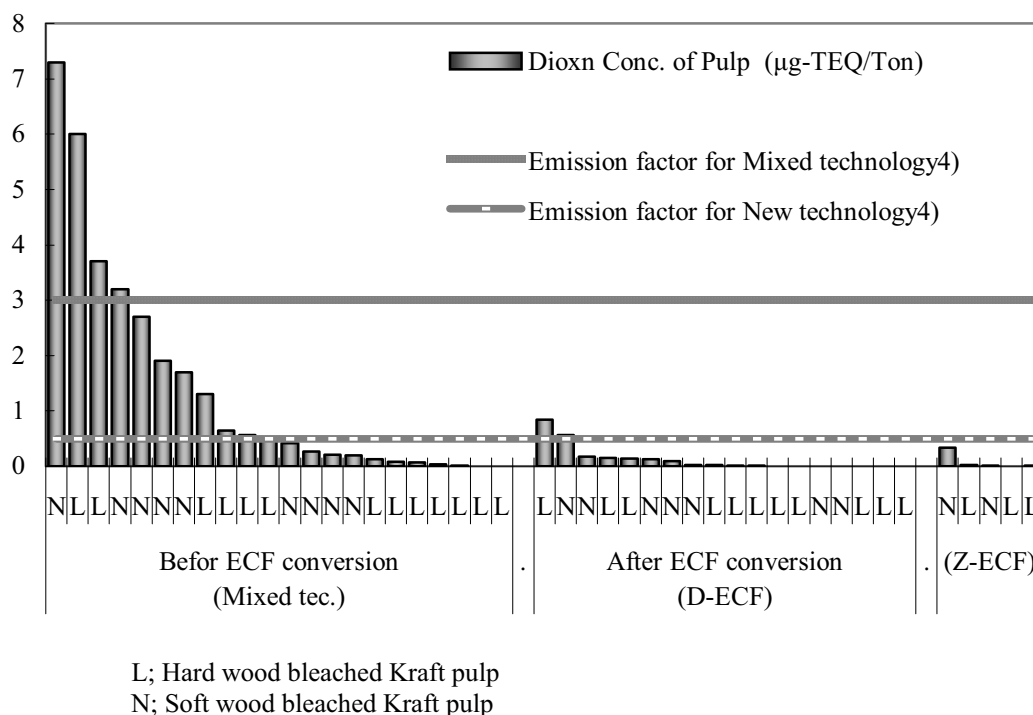


Fig. 2 Dioxin levels of bleached pulp

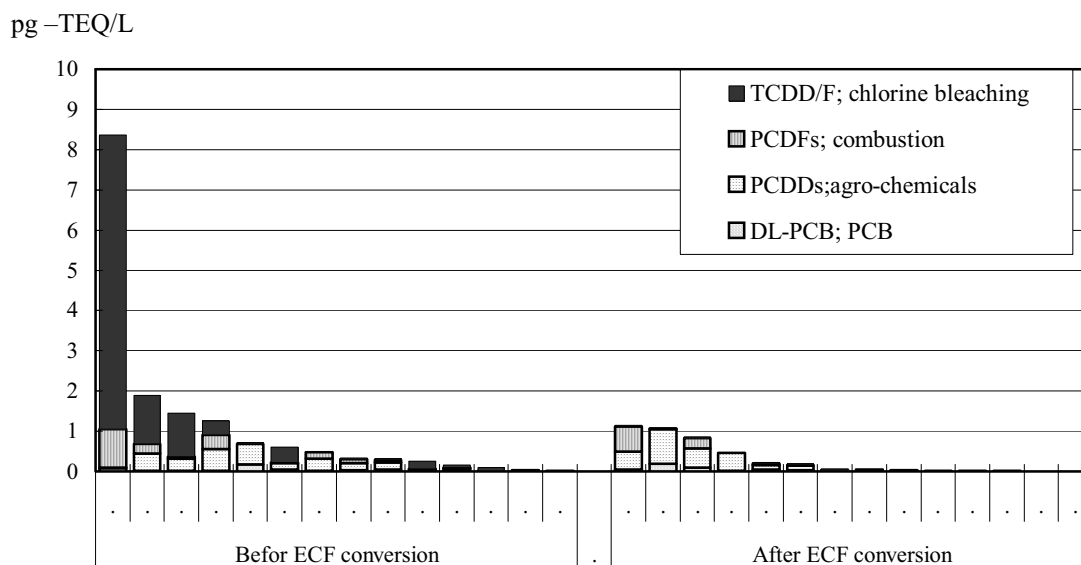


Fig. 3 Dioxin levels of whole mill effluent

In the whole mill effluents, the dioxin levels before the ECF conversion had been less than 10pg-TEQ/L that is the limit value for whole pulp-mill effluent in Japan. The dioxin levels after the ECF conversion decreased almost below 1pg-TEQ/L that is the environmental standard in Japan, and the reduction ratio was 70%. Surprisingly, the dioxin levels in the half of mills effluents were even below 0.1pg-TEQ/L. The level is thought to be zero-emission level. It is confirmed that the ECF conversion dramatically and effectively suppresses the emission of dioxins into our environment.

As shown in Figure 3, small amount of dioxins were remained in some whole mill effluent even after the conversion to ECF. It is well known that PCDDs and PCDFs derived from agro-chemicals or the combustion were ubiquitous.<sup>5</sup> We have reported that raw water in one of pulp mills was contaminated dioxins, which source is agro-chemicals.<sup>6</sup>

As expected, dioxins specifically generated by chlorine bleaching process were not detected in the whole mill effluents in all investigated mills. It clearly shows that the effect of dioxins reduction in bleaching process of ECF conversion has reached to also whole mill effluents. By solving for the remaining problem in several mills, pulp and paper industry is led to dioxin zero.

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