Oxidation equivalents, OXE—an alternative to active chlorine

N. Roland Grundelius

ABSTRACT: As an alternative to active chlorine, it is proposed that the oxidation power of a substance be expressed by the unit "oxidation equivalent, OXE." Oxidation equivalents allow the different chlorine containing bleaching chemicals to be assimilated into one system together with oxygen, hydrogen peroxide, and ozone. The chemicals can be converted to OXEs and be expressed as OXE Cl_2 per metric ton of 100% oxygen bleached pulp and OXE H_2O_2 per metric ton of 90% bleached pulp. An entire selective delignification demands 100 OXE per metric ton of 100% pulp and kappa unit removed. OXE provides a tool for studying the coordination of all stages of a bleaching sequence. Its use could be a valuable tool when design and performance of bleaching sequences are discussed.

KEYWORDS: Bleaching, chlorine compounds, costs, oxidation, oxygen bleaching, sequences, units of measurement.

Oxidation equivalents—OXE

As an alternative to active chlorine, the oxidation power of a substance can be expressed in the unit "oxidation equivalent, OXE"[1]:

1 OXE = that quantity of substance which receives 1 mol electrons when the substance is reduced.

The concept oxidation equivalents allows the different chlorine containing bleaching chemicals to be assimilated into one system together with oxygen, hydrogen peroxide, and ozone. The chemicals can be converted to oxidation equivalents (**Table I**) and be expressed as OXE Cl_2 per metric ton 100% oxygen bleached pulp, OXE H_2O_2 per metric ton of 90% bleached pulp, etc.

The conversion factors for chlorine dioxide and hypochlorite in Table I refer to the quantity of each compound, ClO_2 and NaClO, respectively. If chlorine dioxide and hypochlorite are expressed as active chlorine the conversion factors will be identical with those for chlorine, 35.46 g/mol e^- and 28.20 OXE/kg.

Table I shows the number of e^- per mol to completely reduce chlorine, chlorine dioxide, and hypochlorite to chloride ion, Cl^-, and also oxygen, peroxide, and ozone to O^{2-}. Such a complete reduction occurs when chlorine, hypochlorite, oxygen, and peroxide react with the residual lignin. The remaining chemical when a bleaching stage is terminated is recovered in the same oxidation state as the chemical charged. However, chlorine dioxide in a chlorine dioxide stage is partly oxidized to chlorate ions. Sometimes the presence of chlorite ions can be established. These facts mean that less than 5e^- per mol are active when chlorine dioxide reacts with residual lignin. The formation of chlorate and chlorite ions depends on the bleaching conditions. Consequently, a true conversion factor to OXE depends on the number of electrons per mol participating in the oxidation of residual lignin. In chlorine dioxide bleaching, 4–4.2 e^- per mol is a probable number. In ozone bleaching, it is questioned whether all 6 electrons per mol are transferred in pulp bleaching. Therefore, it is recommended that the maximum oxidative power, 5 e^- per mol for chlorine dioxide, and 6 e^- per mol for ozone, be utilized in OXE calculations. It is important to note that this principle is already accepted when chlorine dioxide is converted to active chlorine.

"Residual chlorine" and "residual peroxide" can correspondingly be replaced by "residual equivalents," for instance OXE per metric ton of 90% bleached pulp.

[1]Grundelius, R., 1991 International Pulp Bleaching Conference Proceedings, Stockholm, Volume 1, p. 49.

Grundelius is senior research scientist with Stora Technology, S-791 80 Falun, Sweden.

Comparison of bleaching sequences

Distribution of oxidative power

Three bleaching sequences are compared. They represent different generations. The first sequence is the old standard sequence for a kraft pulp with a high charge of elementary chlorine, Cl_2, and also with a hypo stage. The extraction stages are not reinforced. The second sequence starts with oxygen prebleaching followed by sequential bleaching with 40% chlorine dioxide in the chlorination stage. The first extraction stage is reinforced with oxygen and the second one with peroxide. The second sequence comes close to 1990 technology for a softwood kraft pulp in Sweden. Also the third sequence begins with oxygen prebleaching. No bleaching chemicals are used in the X-stage. This stage is utilized to remove heavy metals, which otherwise partly decompose peroxide in the following stage.

Going from sequence 1–3 the amounts of chlorinated compounds in the bleach plant effluent (and particularly compounds with high chlorine substitution) are considerably decreased. Elimination of chlorine and reduction of oxidative power in the first tower in the bleach plant are the main reasons for lowered AOX- and TOCl-values.

Table II shows OXE partitioned in three blocks: oxygen treatment, prebleaching, and final bleaching. Oxygen treatment of unbleached pulp takes almost 50% of the total oxidative power charged. The old chlorine prebleaching and the newer oxygen treatment have about equal amounts of OXE charged, about 2000 OXE per metric ton of 90% bleached pulp. But the oxidative power is more efficient with chlorine and hypo because this combination subsequently needs only about 30% of the OXE required for oxygen bleached pulp to reach 89–90% ISO brightness, 705 compared to about 2300 OXE per metric ton of 90% bleached pulp.

An entire selective delignification demands 100 OXE per metric ton of 100% pulp and kappa unit removed. The values of total OXE per metric ton of pulp are reported to the last unit in Table II. However, it is recommended that the oxidative power of a complete bleaching sequence be reported generally to the nearest 10 units.

I. Conversion factors to oxidation equivalents, OXE

	Molecular weight	*e⁻/mol for reduction to Cl^- and O^{2-}, resp.*	*g/mol e*	*OXE/kg*
Cl_2	70.914	2	35.46	28.20
ClO_2	67.457	5	13.49[a]	74.12[b]
NaClO	74.448	2	37.22[a]	26.86[b]
O_2	32.000	4	8.00	125.00
H_2O_2	34.018	2	17.01	58.79
O_3	48.000	6	8.00	125.00

[a] = 35.46 g active chlorine/mol e⁻
[b] = 28.20 OXE/kg active chlorine

II. Block distribution of OXE per metric ton of 90% bleached pulp

	Distribution of OXE per metric ton (% of total)			
	Oxygen treatment	*Pre-bleaching*	*Final bleaching*	*Total*
1.		CEH 2171 (76%)	DED 705 (24%)	2876 (100%)
2.	0 1875 (45%)	(D40 C60) (EO) 1471 (36%)	D (E+P) D 796 (19%)	4142 (100%)
3.	0 2000 (46%)	X (E+P) 1117 (26%)	D (E+P) D 1246 (28%)	4363 (100%)

Chemical cost of an entire sequence

Consideration of chemical cost will add a new dimension to the OXE concept. Step-by-step integration of different chemicals gives a survey of an entire bleaching sequence.

In a cost/OXE diagram, a broken line can be built up. Each part of the line represents a specific chemical, the slope depends on the chemical cost per OXE. A high total OXE charge does not automatically mean a high total cost. For instance, oxygen is very cost effective. At a constant OXE charge the cost depends on the relative distribution of chemicals.

A high OXE charge is not a guarantee for high brightness. It is always a complex situation if operation economy, pulp quality, and environmental aspects are simultaneously considered. Many factors have to be balanced. Oxidation equivalents, OXE, provides a tool to investigate the coordination of all stages of a bleaching sequence.

Recommendation

It is suggested that "active chlorine" be replaced by "oxidation equivalents, OXE." The concept of oxidation equivalents allows chlorine-containing bleaching chemicals to be assimilated into one system together with oxygen, peroxide, and ozone.

OXE is a neutral concept based on pure chemistry. OXE includes all oxidizing chemicals. OXE links together the stages of a bleaching sequence. Delignification, brightness development and cost of bleaching chemicals can be combined with oxidative power, OXE per metric ton of pulp, within a particular sequence as well as compared between sequences.

The use of oxidation equivalents, OXE, has the potential of being a valuable tool when design and performance of bleaching sequences are discussed.

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