

Fate of chlorate during ECF bleached pulp wastewater treatment

Ma. Noel Cabrera,^{a*} Mikko Martikka,^b Olli Dahl,^c

Chlorate discharges to the environment are important to control due to the fact that they show some toxicity to certain algae species and could change the aquatic ecosystem. Chlorate toxicity is linked to nitrate concentrations and aerobic conditions. The toxic effect of chlorate in plants exists because plants commonly use nitrate as nutrient, but when chlorate is present they can uptake chlorate instead of nitrate. Subsequently the lower the nitrate concentration is in the water the higher is the toxicity of chlorate. In the wastewater treatment plant of modern pulp mills an anoxic zone can be used at the beginning of the activated sludge pond with the purpose of removing chlorate from the system. In this study, chlorate, ORP, dissolved oxygen, TOC, COD and temperature were measured in several parts of the wastewater treatment system of three Kraft pulp mills with ECF bleaching and different aerobic treatment configurations (with and without designed chlorate removal zone). In these mills chlorate is completely removed in the wastewater treatment system and normally before reaching the chlorate removal zone, when it exists. In parts of the system where low oxygen content and reductive media conditions are reached (i.e. stabilization basins, sedimentation basins) chlorate is eliminated, probably due to its suitability as an electron acceptor by microorganisms. Consequently no particular treatment is needed to remove chlorate; the conditions achieved in the stabilization ponds in the modern mills are enough to complete chlorate reduction. After these trials were done, one of the mills tested, with a capacity of 1.100.000 ADt/year of Kraft ECF-bleached eucalyptus pulp, removed the anoxic zone to increase the aerated area. The results shows that no changes in the chlorate discharge to the receiving watercourse were observed; being these values normally below the instruments detection limits (0.04 mg/L and 0.5 mg/L)..

Keywords: Chlorate; Wastewater treatment, Anoxic zone, ECF bleached pulp.

*Contact information: a: Forest Process Engineering Group, Chemical Engineering Institute, Faculty of Engineering, Universidad de la República, Montevideo-Uruguay, ncabrera@fing.edu.uy b: Department of Forest Products Technology, School of Chemical Technology, Aalto University, Espoo-Finland, mikko.martikka@aalto.fi; c: Department of Forest Products Technology, School of Chemical Technology, Aalto University, Espoo-Finland, olli.dahl@aalto.fi *Corresponding author: ncabrera@fing.edu.uy*

INTRODUCTION

Most occurrences of chlorate in the natural environment are from anthropogenic origin. Historically, chlorate has been used for weed control in agriculture, at concentrations of 20 to 40 g/L. Nowadays; chlorate is used for the production of chlorine dioxide which is industrially mainly used as bleaching agent and disinfectant (Logan, 1998; Gordon and Rosenblatt, 2005).

In the 80's, brown algae ecosystems in the Baltic Sea were studied to document the effects of chlorate in Kraft pulp mill effluents. (Rosemarin *et al.* 1990; Rosemarin *et al.* 1994; Lehtinen *et al.* 1991). Studies concentrated on the undesirable effects on local algal communities caused by the coastal pulp mill effluents containing high levels of chlorate. The most sensitive species were marine brown algae, the kelps (i.e. *Macrocystis*) and *Fucus*, which were vital components of the coastal ecosystem. Both chlorate alone and pulp mill effluent containing chlorate were tested, confirming that chlorate was causing the effect. The toxic effect of chlorate in plants exists because plants in aerobic conditions commonly use nitrate as nutrient, but when chlorate is present they can uptake chlorate instead of nitrate. The lower is the nitrate concentration in the water, the higher is the toxicity of chlorate. In the Baltic Sea, there is almost no nitrate, so the toxic level of chlorate to bladder wrack there is about 20-30µg/L. (Stauber 1998)

In Elemental Chlorine Free (ECF) bleaching, chlorate is mainly formed by the reaction between hypochlorous acid and chlorous acid formed in situ or by the decomposition of chlorous acid (Ni *et al.* 1993). The formation of chlorate corresponds to a loss of 20 to 35% of the original ClO_2 charge. This is because chlorate formation involves a loss of available chlorine since chlorate can neither delignify nor bleach pulps.

Chlorate removal.

Chlorate could be removed from the wastewater by chemical or biological methods. Chemically chlorate in pulp mill wastewater could be eliminated or diminished with sulphur dioxide (SO_2), iodine (I_2) or ferrous chloride (FeCl_2). (Germgård 1989). According to Germgård (1989) with a relation of four mol SO_2 per mol of chlorate, the chlorate is completely removed in 50 minutes and in less than 20 minutes a removal of approximately 90% is reached. Besides, when using sulphur dioxide to eliminate chlorate the sulphur compounds in the final effluent could be harmful...

Lachenal *et al.* (1998) worked in the reduction of the adsorbable organic halides (AOX) and chlorate formation in chlorine dioxide bleaching by the addition of dimethyl sulphoxide, (namely DMSO). With an addition of 1% of DMSO in the pulp, a reduction in AOX of 40 to 50% is achieved (Joncourt *et al.* 2000). However, the reaction competes with the regeneration of chlorine dioxide, and consequently reduced the delignification degree. Yoon *et al.* (1999) studied the effects of DMSO, sulfamic acid, hydrogen peroxide and sodium chlorite in chlorate formation. They found that DMSO, sulfamic acid and hydrogen peroxide reduced the chlorate formation with a slightly decrease in delignification efficiency.

There are some studies about chlorate removal by biological systems in pulp mill wastewaters. Germgård (1989) made different laboratory trials with aerobic (simulating an aerated lagoon) and facultative systems (0.2 mgO₂/L), in order to imitate the no mixing parts of the lagoons. He used tap water and chlorate as wastewater. During each experiment the temperature and pH maintained constant.

There was no elimination of chlorate in aerobic systems, whereas complete elimination of chlorate was achieved in facultative system after four days. Additionally, the results with different working temperatures showed that there is no chlorate removal at 50°C and at 35°C the reaction is faster than at 25°C; these facts suggest biological removal. In low oxygen concentration systems at pH above 7, 90% removal efficiency is obtained in one and a half hour. (Germgård 1989)

Alm (1990) studied the chlorate reduction in two systems of 4.5 m³ of volume, working in continuous mode, one with oxygen saturation (8 mgO₂/L) and the other one without addition of oxygen (1.5 to 2 mgO₂/L), using aerated pond sludge as inoculum and treating mill wastewater. After one month, the chlorate content in the outlet of the non-aerated pond decreased to almost zero, while the aerated pond does not removed chlorate.

Welander *et al.* (Yu and Welander 1990, Malmqvist and Welander 1992, Malmqvist *et al.*, 1993) studied the biological removal of chlorinated compounds in three wastewater systems: aerobic, anaerobic and anaerobic/aerobic. The aerobic system reached a very good removal of BOD but the chlorate removal was zero however in the anaerobic and in the anaerobic/aerobic system the removal of chlorate was complete. In other works (Basta *et al.*, 1995, Basta *et al.*, 1996) anaerobic/aerobic systems were utilized in the treatment of bleaching wastewaters. The removal of chlorate was complete in all the effluents treated.

Malmqvist and Welander (1992) and Malmqvist *et al.* (1993) studied the anaerobic removal of chlorate in laboratory and pilot plant scale. Malmqvist and Welander (1992) worked with bleaching wastewater in a continuous anaerobic laboratory reactor and found that the product of the biological reduction of chlorate is chloride and the chlorate can be completely removed from the bleaching wastewater.

There are some works (Logan, 1998a, Logan *et al.*, 1998b, Coates *et al.*, 1999, Van Ginkel *et al.*, 1995) that have tried to identify chlorate respiring microorganisms. In these works it is stated that chlorate could be used by some microorganism as an electron acceptor in anoxic or anaerobic conditions. The end product of the reductive metabolic process is innocuous chloride. Some species of chlorate respiring microbes that are facultative anaerobes are thought to be related to denitrifying organisms. According to Van Ginkel *et al.* (1995) chlorate may be reduced by assimilatory and dissimilatory nitrate reductases present in microorganisms. They found chlorate reductive microorganisms in river samples, anoxic sediments from a ditch, surface soils from a public garden and a wastewater treatment plant treating primarily domestic sewage. Microbial reduction of chlorate was supported by different organic chemicals such as mono and dicarboxylic acids, alcohols and aminoacids and two inorganic compounds: sulphidric acid and molecular hydrogen (Logan 1998a). Under denitrifying conditions gas formation but not chloride production was observed, indicating that nitrate inhibited chlorate respiration. (Van Ginkel *et al.*, 1995)

Malmqvist et al. (1991) studied the mechanism of the chlorate removal in the anaerobic treatment. As previously mentioned, chloride (not chlorite as was supposed previously in this work) is formed in the same extension as the chlorate is removed. Acetate was consumed and presumably oxidized to carbon dioxide (and water) which was present as an end product. When no acetate is available, other organic compounds could act as electron donors. In aerobic system, oxygen is favoured to chlorate as electron acceptor in microbial systems, whereas in anaerobic systems chlorate is chosen by the bacteria as an electron acceptor. According to Malmqvist et al. (1991) the growth yield was of 1.9 to 3.8 grams per equivalent of available electrons. This suggests that the reduction of chlorate to chloride involved a biological transport system and probably is coupled with an electron transport phosphorylation. In the work of Coates et al., (1999), they studied a broad spectrum of environments to try to determine the ubiquity and diversity of organisms capable of chlorate reduction. In this work they isolated thirteen of these organisms. The entire chlorate reductive microorganism isolated were strict respires and could not grow on anoxic basal media in the absence of a suitable electron acceptor. But they could couple the complete oxidation of acetate in basal media with chlorate. As mentioned by Logan (1998a) little is known about biochemical pathways used by microorganisms for electron transport using chlorate.

EXPERIMENTAL PART.

Materials and methods

With the objective to study the behaviour of chlorate species in the wastewater, different parameters were measured in various parts of the treatment systems at three mills. Temperature, dissolved oxygen, pH and redox potential were measured in situ. Chlorate, chlorine dioxide and chlorite analyses were done immediately according to Wartiovaara (1982) method. TOC and COD were determined at the laboratory using APHA Standard Methods.

Mill A

Mill A produces softwood pulp mainly from pine and spruce. The annual production is about 350.000 tonnes using an ECF bleaching sequence (D_0 - E_{OP} / E_{OP} - D_1 - P_0). The wastewater is treated in an activated sludge plant. Scheme of the wastewater treatment is presented in Figure 1. The red points in the scheme show the sampling points. The sampling points "Equalization basin in" and "Equalization basin out" were situated in the equalization basin. The mill was sampled in two opportunities.

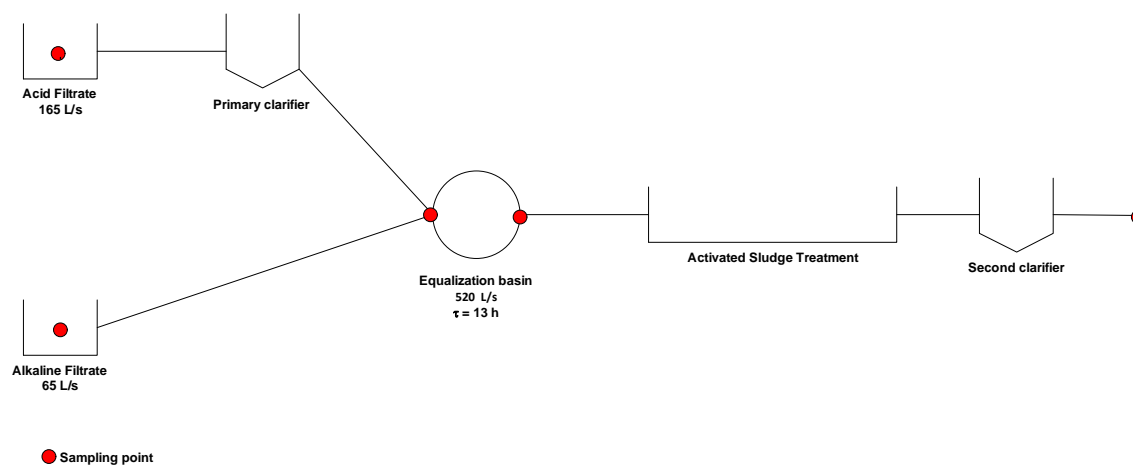


Figure 1 . Scheme of Mill A wastewater treatment.

Mill B

Mill B produces 630.000 tonnes of softwood ECF pulp per year. The wastewater treatment plant also treats integrated paper mill wastewater and urban wastewater of the near city (60.000 inhabitants). The treatment system (Figure 2) includes an activated sludge treatment with an anoxic selector before the aeration basin.

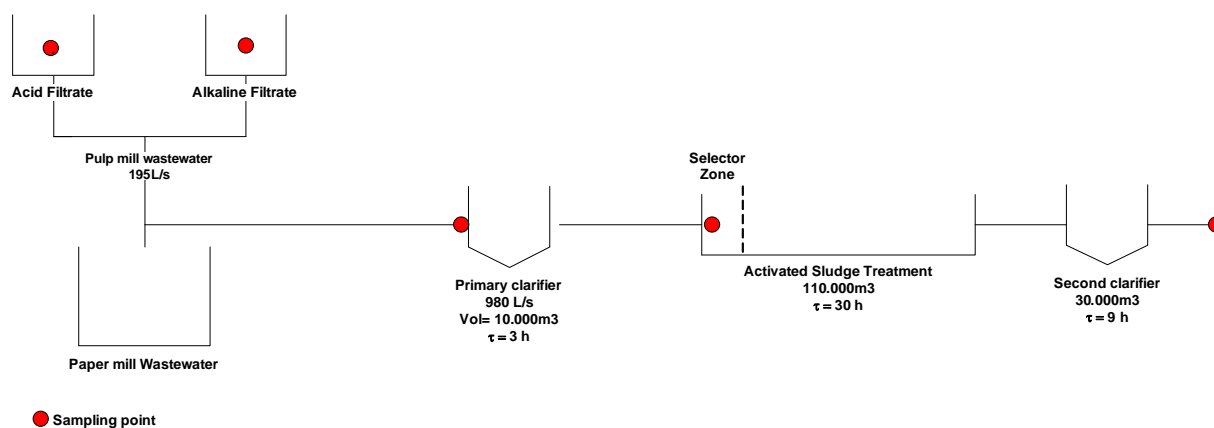


Figure 2. Scheme of Mill B wastewater treatment. The red points show the sampling points.

Mill C

Mill C is an ECF bleached eucalyptus pulp mill with a production capacity of 1.100.000 tonnes/year. The bleaching sequence used in the mill is (A/D)-E_{OP}-D-P. The

wastewater is treated in an activated sludge plant that has an anoxic selector at the beginning of the aeration basin (Figure 3).

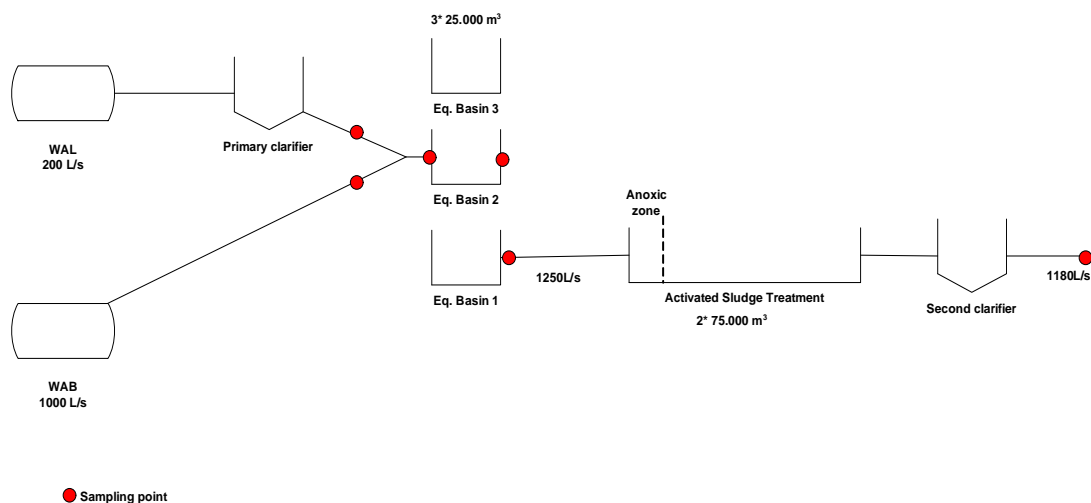


Figure 3. Scheme of mill C wastewater treatment. The red points show the sampling points. WAL: Effluents with high solid content (mainly from woodyard); WAB: Effluents with low solid content (from bleaching plant). The equalization basin works in discontinuous mode.

Mill C wastewater plant has 3 equalization basins of about 12 meters deep each one. Normally one of them is not in operation but used as an emergency basin and the other two works in discontinuous mode. During 8 hours one of the equalization basins is filled while the other one is emptied; although the basins are not completely emptied each time, a remnant of effluent remains on the bottom (about 1m). Equalization basin 2 was being filled at the time of sampling, and equalization basin 1 was being emptied.

RESULTS AND DISCUSSION.

Mill A.

Mill A wastewater treatment plant was sampled twice. In Table 1 are shown the different values obtained in both sampling occasions.

Table 1. Physical and chemical properties in different parts of mill A wastewater treatment plant. n/d: dissolved oxygen was not possible to be determined in this point because the sensor cannot operate at high temperature. DO, ClO_3^- , COD and TOC are in mg/L.

Sampling 1	pH	Temp (°C)	ORP (mV)	DO	ClO_3^-	COD	TOC
Alkaline Filtrate	10.4	> 50	200	6.4	20.0	1200	1186
Acid Filtrate	2.5	> 50	490	7.8	331	2900	573
Equalization basin in	5.2	41.2	285	2.2	55	1250	633
Equalization basin out	6.5	39	150	0.7	0	1200	493
Clarified Water	7.2	32	315	3.5	0	390	164
Sampling 2							

Alkaline Filtrate	10.0	67	185	n/d	117	3088	1215
Acid Filtrate	2.5	54	490	n/d	271	1456	657
Equalization basin in	6.2	44.5	235	1.4-2	68	1567	549
Equalization basin out	6.6	40.7	215	0.45	5	1300	468
Clarified Water	7.1	34.5	335	3.3	0	530	169

The nominal residence time in the equalization basin is 13 hours. In reality this time is less since there is chemical sludge deposit on the bottom. One remarkable difference between samplings was the amount of chemical sludge. In the second sampling, mill A workers had cleaned the pool, decreasing the amount of sludge accumulated. In the first sampling the pool bottom was covered with sludge, while in the second sampling, there was only a little amount of chemical sludge in the middle of the basin. Nonetheless, the chlorate is removed in the basin (completely removed in the first sampling and almost completely in the second). The low oxygen content conditions achieved in the basin (oxygen level lower than 2 mg/L in the entire basin) and the normal absence of nitrate in pulp mill wastewaters could induce that chlorate acts as electron acceptor in the basin and is reduced to chlorine due to microorganism action. In addition the fact of not achieving complete chlorate removal in the second sampling could indicate that the microorganism system was altered when the basin was cleaned and still not in its maximum efficiency when the samples were taken.

Mill B.

The results obtained are presented in Table 2.

Table 2. Physical and chemical properties in different parts of mill B wastewater treatment plant. n/d: dissolved oxygen was not possible to be determined in this point because the sensor cannot operate at high temperature. DO, ClO_3^- , COD and TOC are in mg/L.

	pH	Temp (°C)	ORP (mV)	DO (mgO ₂ /L)	ClO_3^- (mg/L)	COD (mg O ₂ /L)	TOC (mg /L)
Alkaline Filtrate	10.5	59	217	n/d	142	---	1825
Acid Filtrate	3.1	45	436	4.6	210	---	935
Before Primary clarifier	7.0	32	296	6.0	63	3820	680
Anoxic selector inlet	7.0	28	116	0.5	35	3290	520
Clarifier Water	7.6	30	297	3.9	0	1020	175

Considering the chlorate content in the acidic and alkaline streams, the flows of these streams and the flow in the primary clarifier could indicate that the decrease of chlorate concentration before the primary clarifier is mainly for the dilution (assuming that no chlorate is coming in from the paper mill wastewater stream or the urban wastewater stream). The retention time in the primary clarifier is about 3 hours, but no measurements were taken from the interior of this clarifier, so it could not be concluded whether the system can achieve the conditions to remove chlorate. Regardless, the chlorate concentration in the final clarifier is zero, which means that in some part of the system between the activated sludge treatment and the outlet of the system there are given the conditions to remove chlorate. Unfortunately, it was not possible to measure more points in the treatment system, especially before the secondary clarifiers. This plant has three secondary clarifiers working in parallel with

retention time of 9 hours each. It may be possible that suitable conditions for chlorate removal are achieved in the secondary clarifiers but this could not be verified due to lack/not enough sampling points.

Mill C.

In this mill chlorate is measured weekly in three sampling points: WAL (stream with high solids content, mainly coming from woodyard area), WAB (stream with low solid content, mainly from bleaching area) and final clarifier. According to data published in (Ecometrix, 2008) the chlorate concentration in the final clarifier became zero after the third month of the plant operation. By personal communication with mill engineers they confirmed that this behaviour continues until nowadays.

In order to determine chlorate behaviour in the wastewater treatment and the causes of this behaviour, more sample points in the treatment system were analysed. The results are shown in Table 3.

Table 3. Physical and chemical properties in different parts of mill C wastewater treatment plant.

	Temp (°C)	ORP (mV)	DO (mgO ₂ /L)	ClO ₃ ⁻ (mg/L)	COD (mg/L)
WAL	46	267	5.8	2.0	170
WAB	64	229	4.5	95	266
EQ Basin 1. OUT	45	214	6.1	0	400
EQ Basin 2. IN	52	486	4.4	67	900
EQ Basin 2. OUT	45	112	1.0	1.0	740
Final Clarifier	29	333	5.0	0	210

The redox potential difference between the inlet and the outlet points of equalization basin 2 (the basin was being filled at the time of sampling) was about 400 mV, which is almost the same level as observed in the anaerobic trials done at laboratory (Cabrera, 2010). In addition, the dissolved oxygen in the outlet section of this basin is 1.0 mgO₂/L. The chlorate is almost completely removed in that basin. The conditions in the end part of the basin are appropriate for the growth of anoxic microorganism capable to use chlorate as an electron acceptor (almost no oxygen and no nitrate in the media, and a reductive media). On the other hand, the conditions of the equalization basin 1 in the outlet section (the basin which was emptied at the time of the sampling) were much different than equalization basin 2; the dissolved oxygen was about 6, the redox potential increased. However the chlorate content in this sampling point was zero.

After the first set of experiments and according to the data obtained in this work and the data obtained by the mill personnel, the engineers of Mill C decided to eliminate the anoxic selector (installing air diffusers and then increasing the aerobic section). After this change in the mill, the chlorate level in the clarified water remains in the zero level.

CONCLUSIONS

From the assays done at mill scale it could be concluded that chlorate is in the bleaching lines in a concentration from 100 mg/L (the newest plant, processing hardwood) to nearly 350 mg/L (the oldest plant, processing softwood). In all the cases studied, chlorate was removed in zones of the treatment system where low oxygen conditions and reductive media were reached. Normally these conditions are achieved in the equalization basins or in the clarifiers.

More assays are needed, but it could be suggested that the chlorate removal in this system is by biochemical ways. Some microorganisms are capable of using chlorate as electron acceptor in absence of nitrate and oxygen in the media.

REFERENCES

- Alm, A., (1990), "Elimination of chlorate emissions in an aerated pond", EUCEPA International Symposium, Barcelona, 22-24 October, pp 74-84.
- Basta J., Wäne G., Meuller L., Herstad-Svärd S., Birath L., (1995), "New aspect of ECF bleaching on eucalyptus pulps", 28th Pulp and Paper Annual Meeting, ABCTP, Sao Paulo, Brazil, November 6-10, pp 115-132.
- Basta J., Wäne G., Herstad-Svärd S., Lundgren P., (1996), "Partial Closure in modern bleaching sequences", Tappi Int. Pulp Bleaching Conference, Washington, USA, pp 341-346.
- Cabrera, M.N., (2010), Master Thesis "Chemical composition and treatment of filtrates from A-Ep-DnD and A-Ep-D-P bleaching sequences", Universidad de la República, Uruguay
- Coates J.D., Michaelidou U., Bruce R.A., O'Connor S., Crespi J., Achenbach I.A. (1999), "Ubiquity and diversity of dissimilatory (Per)chlorate-reducing bacteria", Applied and Environmental Microbiology, V 65 (12), pp 5234-5241.
- Ecometrix Inc., (2008), "Orion Pulp Mill, Uruguay Independent Performance Monitoring as required by the International Finance Corporation Phase 2: Six-Month Environmental Performance Review",
http://www.ifc.org/ifcext/lac.nsf/AttachmentsByTitle/Uruguay_Orion_EcoMetrix
- Germgård U., (1989), "Chlorate discharges from bleach plants – how to handle a potential environmental problem", Paperi ja Puu, V3, pp 255-260.
- Gordon G. and Rosenblatt A. (2005) "Chlorine Dioxide: The Current State of the Art" Ozone: Science and Engineering, V27 pp 203-207.
- Joncourt M., Froment P., Lachenal D., Chirat C., (2000), "Reduction of AOX formation during chlorine dioxide bleaching", Tappi Journal, V 83 (1), pp 144-148.
- Lachenal D., Joncourt M., Froment P., Chirat C., (1998) "Reduction of formation of AOX during chlorine dioxide bleaching", Journal of Pulp and Paper Science, V 28 (8), pp 274-279.
- Lehtinen K., Axelsson B., Kringstad K., Strömberg L., (1991), Characterization of pulp mill effluents by the model ecosystem technique", Nordic Pulp and Paper Res. J., V2, pp 81-88
- Logan B.E., (1998a), "A Review of Chlorate- and Perchlorate-Respiring Microorganisms", Bioremediation Journal V 2 (2), pp 69-79.
- Logan B.E., Bliven A.R., Olsen S.R., Patnaik R., (1998b), "Growth kinetics of mixed cultures under chlorate reducing conditions", J. Environmental Eng., V 124 (10), pp 1008-1011.
- Malmqvist A., Welander T., Gunnarsson L., (1991), "Anaerobic growth of microorganism with chlorate as an electron acceptor", Applied and Environmental Microbiology, V 57 (8), pp 2229-2232.
- Malmqvist A., Welander T. (1992), "Anaerobic removal of chlorate from bleach effluents", Water Science and Technology, V 25 (7), pp 237-242.

Malmqvist A., Gunnarsson L., (1993), "Biological removal of chlorate from Kraft bleach plant effluent- A pilot plant study", *Nordic Pulp and Paper Research*, V 8 (3), pp 303-306, 337.

Ni Y., Kubes G., Van Heiningen A. (1993), "Mechanism of Chlorate Formation During Bleaching of Kraft Pulp with Chlorine Dioxide", *J. Pulp and Paper Science*, V 19 (1), pp 1-6.

Rosemarin, A., Mattsson J., Lehtinen K., Notini M., Nylen E., (1990), "Effects of treated and untreated Softwood Pulp Mill Effluents on Baltic Sea Algae and Invertebrates in model Ecosystems." *Nord. Pulp Pap. Res. J.* V 103(2), pp 83-87.

Rosemarin, A., Mattsson J., Lehtinen K., Notini M., Nylen E., (1994), "Effects of Pulp Mill Chlorate on Baltic Sea Algae." *Environmental Pollution*, V85(1), pp3-13.

Stauber J. (1998), "Toxicity of chlorate to marine microalgae", *Aquatic Toxicology*, V 41, pp 213-227.

van Ginke C.G., Plugge C.M., Strooa C.A., (1995), "Reduction of chlorate with various energy substrates and inocula under anaerobic conditions", *Chemosphere*, 31(9), 4057-4066.

Wartiovaara I., (1982), "The influence of pH on the D1 stage of a D/CED1 bleaching sequence", *Paperi ja Puu*, 64(9), pp 539-40, 545.

Yoon B., Wang L., Kim Y., Choi K., (1999), "Reduction of the formation of Chlorate in chlorine dioxide pulp bleaching", *10th International Symposium on Wood and Pulping Chemistry*, Yokohama, Japan, June 7 – 10, Book2, pp 434-437.

Yu P., Welander T., (1990), "Biological removal of chlorinated organics from Kraft bleach effluent", *24th EUCEPA Conference: Control, Maintenance, Environment* Stockholm, Sweden, May 8-9, pp 490-495.

ACKNOWLEDGMENTS

The authors thank the laboratory personnel at the mills for their kind assistance during this work. A special thank you to UPM Fray Bentos laboratory personnel and G. Gonzalez from UPM Fray Bentos for his valuable support.