

**ACUTE ECOTOXICITY OF THE  
SIXTEEN MOST USUALLY FOUND  
CHEMICALS IN BLEACHING  
PLANT EFFLUENTS**



**BRAZIL**

**By**

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## **OBJECTIVES OF THE STUDY**

- 1. IN THE FIRST PART OF THE PAPER, THE AUTHORS HAVE EVALUATED THE IMPACT OF SOME BLEACHING SEQUENCES, INCLUDING ECF, TCF AND CONVENTIONAL BLEACHING WITH ELEMENTAL CHLORINE**

**AS A RESULT OF THE BLEACHING STUDIES, AN IMPORTANT CONCLUSION WAS DRAWN:**

**BLEACHING CHEMICAL RESIDUALS SHOW A FUNDAMENTAL ROLE IN EFFLUENT TOXICITY**

**THEN, THE SECOND OBJECTIVE WAS:**

- 2. TO EVALUATE THE ACUTE TOXICITY OF THE MOST USUALLY FOUND CHEMICALS IN BLEACHING PLANT EFFLUENTS.**

**MICROTOX AND *Ceriodaphnia dubia* ACUTE ECOTOXICITY METHODS WERE USED TO DETECT THE TOXIC CONCENTRATION LEVELS**

**BOTH TESTS HAVE AS LIMITATION THE OBLIGATION TO CORRECT THE pH TO NEUTRAL USING HNO<sub>3</sub> OR NaOH**

## **BLEACHING EXPERIMENTS**

**PULP: KRAFT PULP**  
*Eucalyptus* AS RAW MATERIAL

## **OXYGEN DELIGNIFICATION**

**% NaOH = 1.5%**  
**TEMPERATURE = 95°C**  
**PRESSURE = 7 kgf/cm<sup>2</sup>**  
**CONSISTENCY = 10%**

## O<sub>2</sub> DELIGNIFICATION RESULTS

	UNBLEACHED PULP	AFTER O <sub>2</sub>
BRIGHTNESS (% ISO)	42.9	53.4
INTRINSIC VISCOSITY (cm <sup>3</sup> /g)	1020	860
KAPPA NUMBER	15.4	10.5

## D<sub>c</sub> E<sub>o</sub> D BLEACHING

**D<sub>c</sub>**  
ACTIVE CHLORINE = 0.15 x KAPPA  
TIME = 30 minutes  
TEMPERATURE = 65°C  
CONSISTENCY = 10%

### CHLORINE / CHLORINE DIOXIDE RATIOS

100 : 0  
50 : 50  
25 : 75  
0 : 100

**Dc Eo D BLEACHING**

**Eo**

**% NaOH = 1.6%**

**TIME = 60 minutes**

**TEMPERATURE = 90°C**

**PRESSURE = 3 kgf/cm<sup>2</sup>**

**Dc Eo D BLEACHING**

**D**

**% ACTIVE CHLORINE = 3.45%**

**TIME = 180 minutes**

**TEMPERATURE = 75°C**

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**TOTAL ACTIVE CHLORINE: 4.25%**

**TCF BLEACHING**

**SEQUENCES AZQP and AZX<sub>0</sub>P**

**A**

**H<sub>2</sub>SO<sub>4</sub> = 1%**

**TIME = 15 minutes**

**TEMPERATURE = 40°C**

**CONSISTENCY = 10%**

**TCF BLEACHING**

**Z**

**% O<sub>3</sub> = 0.85%**

**TEMPERATURE = 35°C**

**CONSISTENCY = 40%**

## TCF BLEACHING

### Q or X<sub>Q</sub>

XYLANASE = 0 or 4 u/g  
DTPA = 0.15%  
TIME = 90 minutes  
TEMPERATURE = 60°C  
pH = 8.0  
CONSISTENCY = 10%


## TCF BLEACHING

### P

% H<sub>2</sub>O<sub>2</sub> = 1.25  
% NaOH = 1.5  
% SILICATE = 1.0  
TIME = 120 minutes  
TEMPERATURE = 75°C  
CONSISTENCY = 10%  
INITIAL pH = 11.5

## ECF SEQUENCE WITH OZONE

SEQUENCE = A Z E<sub>OP</sub> D<sub>1</sub> D<sub>2</sub>

A → SIMILAR TO  AZQP  
AZXQP

Z → % O<sub>3</sub> = 0.55%

E<sub>OP</sub> → % H<sub>2</sub>O<sub>2</sub> = 0.3%

## ECF SEQUENCE WITH OZONE

**D<sub>1</sub>**  
% ACTIVE CHLORINE = 2.2%  
TIME = 90 minutes  
TEMPERATURE = 75°C  
CONSISTENCY = 10%

**D<sub>2</sub>**  
% ACTIVE CHLORINE = 0.5%



## BLEACHING RESULTS

SEQUENCE	% ACTIVE CHLORINE	% 03	BRIGHTNESS % ISO	VISCOSITY cm <sup>3</sup> /g	POST COLOR NUMBER
D100 EOD	4.25	-	88.4	736	1.12
D75 EOD	4.25	-	89.4	719	1.29
D50 EOD	4.25	-	89.8	681	0.76
C EOD	4.25	-	90.2	687	0.95
A Z Q P	-	0.85	86.4	519	0.81
A Z XQ P	-	0.85	86.9	495	0.87
A Z EOP D1 D2	2.70	0.55	91.4	600	0.77

## TOXICITY AND EFFLUENT CHARACTERISTICS

### OXYGEN DELIGNIFICATION EFFLUENT

COLOR	28.18 kg/adt
COD	19.68 kg/adt
CONDUCTIVITY	5 390 $\mu$ S/cm
pH	12.10
TOXIC UNITS <i>Ceriodaphnia dubia</i>	2.49
TOXIC UNITS MICROTOX	4.35

## TOXICITY AND EFFLUENT CHARACTERISTICS

### SEQUENCES WITH CHLORINE AND CHLORINE DIOXIDE

AFTER STAGES	TOXIC UNITS		pH	COLOR kg/adt	CHLORIDES kg/adt	CONDUCTIVITY $\mu$ S/cm	COD kg/adt	AOX kg/adt
	C. dubia	MICRO-TOX						
D 100	4.49	6.59	2.5	7.98	2.78	2 200	5.70	0.46
D 75	7.14	6.89	2.3	13.63	6.80	3 750	6.10	0.50
D 50	4.62	11.52	2.0	13.23	11.60	4 400	8.22	0.76
C	5.19	13.78	1.8	15.30	13.53	6 500	9.59	1.01

kg/adt bleached pulp

## TOXICITY AND EFFLUENT CHARACTERISTICS

### SEQUENCES WITH CHLORINE AND CHLORINE DIOXIDE

AFTER STAGES	TOXIC UNITS		pH	COLOR kg/adt	CHLORIDES kg/adt	CONDUCTIVITY $\mu$ S/cm	COD kg/adt	AOX kg/adt
	C. dubia	MICRO-TOX						
D100 Eo	3.15	3.52	12.6	12.71	0.13	6 000	5.51	0.053
D75 Eo	3.35	6.65	12.5	14.54	0.34	5 700	4.73	0.074
D50 Eo	7.34	5.66	12.4	16.17	0.51	5 000	7.29	0.123
C Eo	7.54	5.90	12.3	22.50	1.00	4 700	6.70	0.194

kg/adt bleached pulp

## TOXICITY AND EFFLUENT CHARACTERISTICS

### SEQUENCES WITH CHLORINE AND CHLORINE DIOXIDE

AFTER STAGES	TOXIC UNITS		pH	COLOR kg/adt	CHLORIDES kg/adt	CONDUCTIVITY $\mu$ S/cm	COD kg/adt	AOX kg/adt
	<i>C. dubia</i>	MICROTOX						
D100 EoD	33.16	29.44	3.5	1.21	4.64	2 500	2.75	0.150
D75 EoD	27.79	33.19	3.8	0.80	3.65	2 300	2.49	0.160
D50 EoD	495.05	43.97	3.5	6.89	3.51	2 100	2.01	0.058
C EoD	1785.70	95.21	3.9	7.30	2.95	1 800	1.01	0.052

kg/adt bleached pulp

## TOXICITY AND EFFLUENT CHARACTERISTICS

### TCF SEQUENCE = A Z XQ P

AFTER STAGE	TOXIC UNITS		COLOR kg/adt	COD kg/adt	CONDUCTIVITY $\mu$ S/cm	pH
	<i>C. dubia</i>	MICROTOX				
A	5.90	5.63	0.96	-	1 900	1.75
Z	AT	1.34	6.54	6.82	1 000	2.21
XQ	2.95	NT	6.62	10.86	1 200	7.19
P	141.44	15.90	1.45	14.26	2 200	11.24
$\Sigma$	150.29	22.87	15.57	31.94	-	-

AT = almost no toxic

NT = no toxic

## TOXICITY AND EFFLUENT CHARACTERISTICS

### TCF SEQUENCE - A Z Q P

AFTER STAGE	TOXIC UNITS		COLOR	COD	CONDUCTIVITY	pH
	<i>C. dubia</i>	MICROTOX	kg/adt	kg/adt	µS/cm	
A	5.90	5.63	0.96	-	1 900	1.75
Z	AT	1.34	6.54	6.82	1 000	2.21
Q	3.40	NT	8.39	8.96	1 000	7.55
P	214.13	27.78	0.61	15.38	1 800	11.98
Σ	223.43	34.75	16.50	31.16	-	-

AT = almost no toxic

NT = no toxic

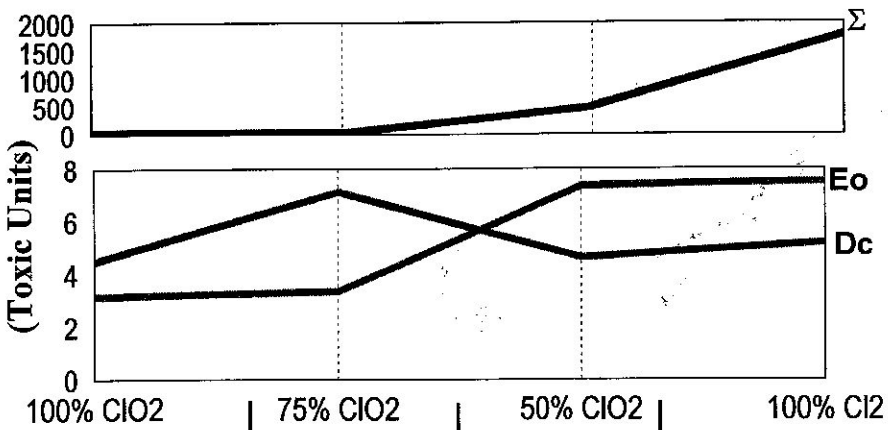
## TOXICITY AND EFFLUENT CHARACTERISTICS

### ECF SEQUENCE WITH OZONE

AFTER STAGE	TOXIC UNITS		COLOR	CHLO- RIDES	COD	AOX	CONDUCTIVITY	pH
	<i>C. dubia</i>	MICRO- TOX	kg/adt	kg/adt	kg/adt	kg/adt	mS/cm	
A	5.90	5.63	0.96	-	-	-	1 900	1.75
Z	NT	1.71	8.39	-	5.65	-	470	2.85
EOP	32.10	3.17	9.96	-	10.60	-	1 300	11.56
D1	186.57	27.10	1.45	3.37	1.90	0.085	1 850	3.73
D2	85.54	4.44	1.12	0.65	0.47	0.013	1 500	4.03
Σ	310.11	42.05	21.88	4.02	18.62	0.098	-	-

NT = no toxic

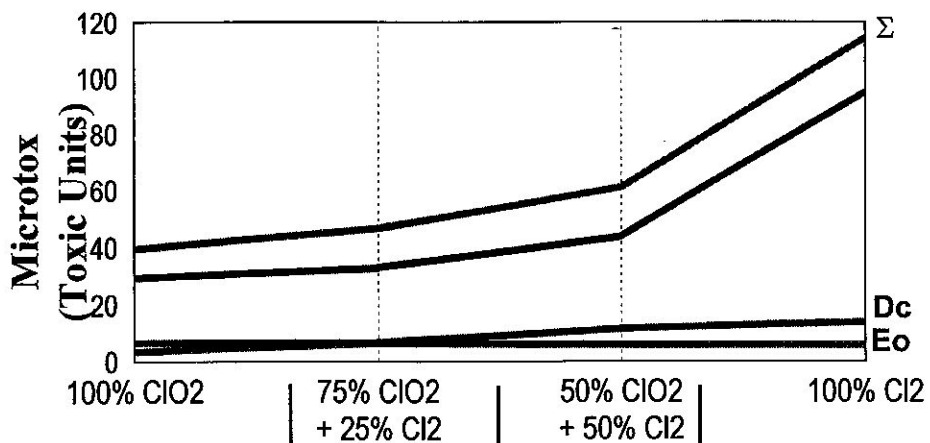
**ACUTE TOXICITY**  
*Ceriodaphnia dubia*



SUBSTITUTION RATES IN Dc

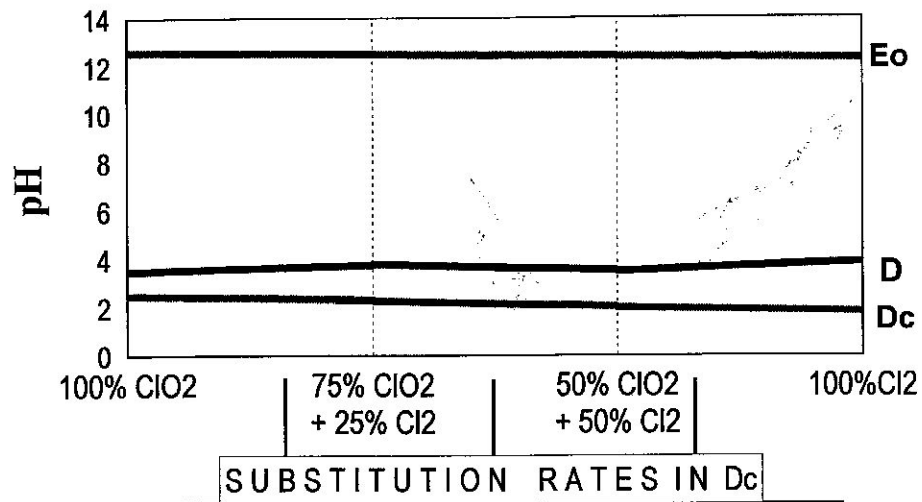
<b>Dc</b>	<b>4.49</b>	<b>7.14</b>	<b>4.62</b>	<b>5.19</b>
<b>Eo</b>	<b>3.15</b>	<b>3.35</b>	<b>7.34</b>	<b>7.54</b>
<b>D</b>	<b>33.16</b>	<b>27.79</b>	<b>495.05</b>	<b>1 785.70</b>
<b>Σ Stages</b>	<b>40.80</b>	<b>38.28</b>	<b>507.01</b>	<b>1 798.43</b>

**ACUTE TOXICITY**  
Microtox

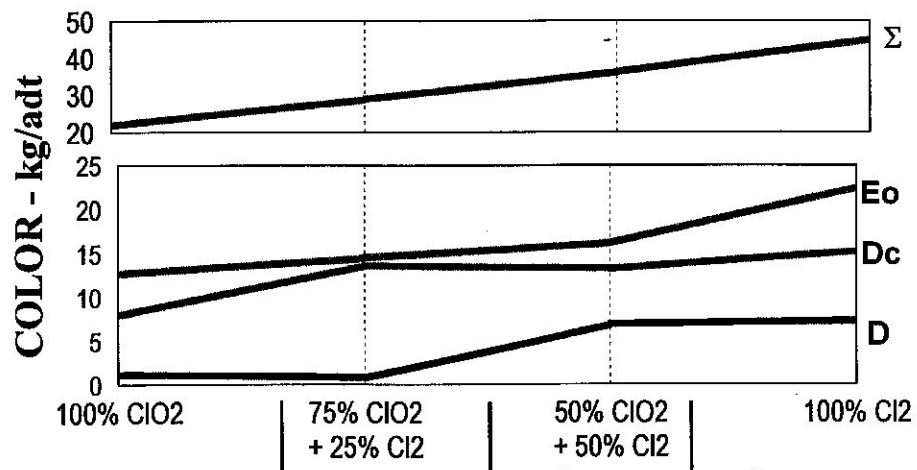


SUBSTITUTION RATES IN Dc

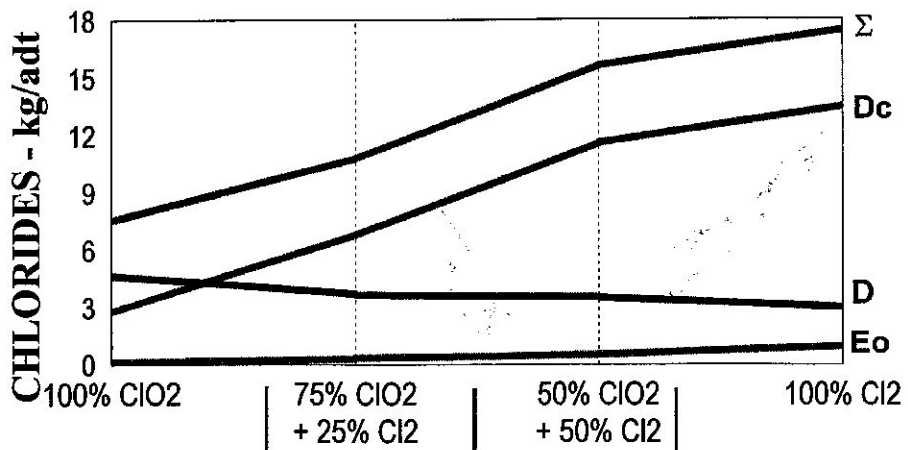
<b>Dc</b>	<b>6.59</b>	<b>6.89</b>	<b>11.52</b>	<b>3.78</b>
<b>Eo</b>	<b>3.52</b>	<b>6.65</b>	<b>5.66</b>	<b>5.90</b>
<b>D</b>	<b>29.44</b>	<b>33.19</b>	<b>43.97</b>	<b>95.21</b>
<b>Σ Stages</b>	<b>39.55</b>	<b>46.73</b>	<b>61.15</b>	<b>114.89</b>



	100% ClO2	75% ClO2 + 25% Cl2	50% ClO2 + 50% Cl2	100% Cl2
<b>Dc</b>	2.5	2.3	2.0	1.8
<b>Eo</b>	12.6	12.5	12.4	12.3
<b>D</b>	3.5	3.8	3.5	3.9

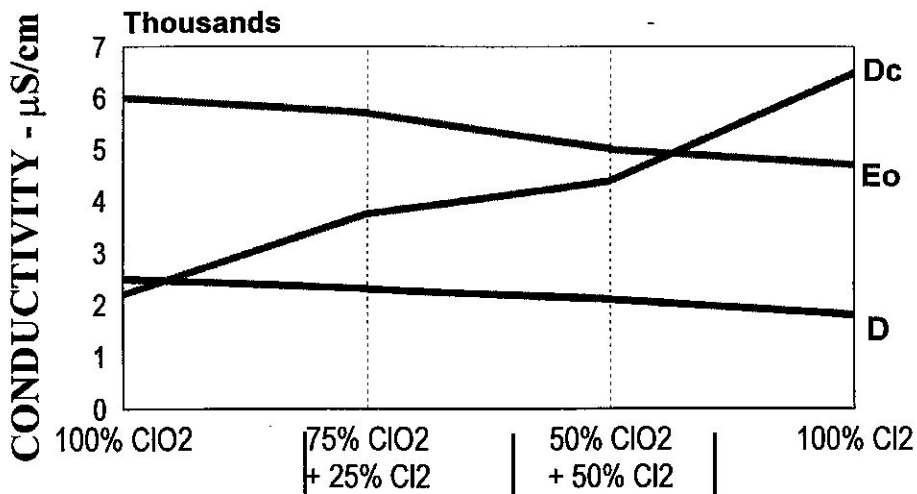


	100% ClO2	75% ClO2 + 25% Cl2	50% ClO2 + 50% Cl2	100% Cl2
<b>Dc</b>	7.98	13.63	13.23	15.30
<b>Eo</b>	12.71	14.54	16.17	22.50
<b>D</b>	1.21	0.80	6.89	7.30
<b>Σ Stages</b>	21.90	28.97	36.29	45.10



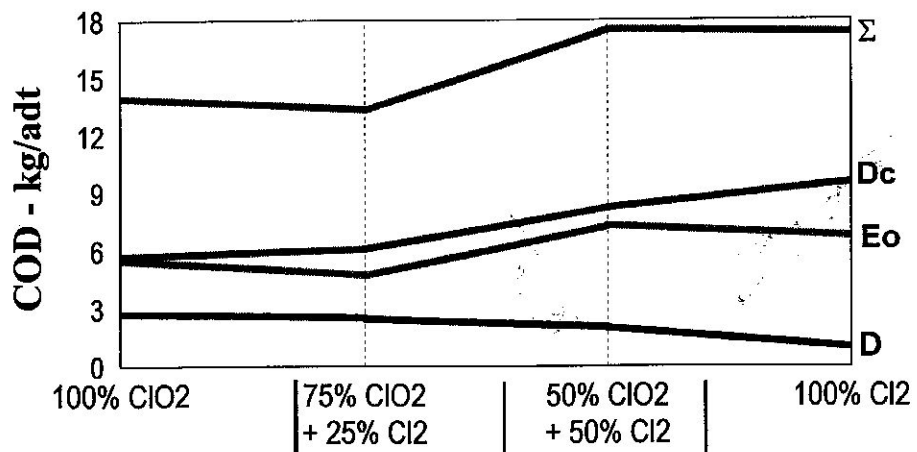
SUBSTITUTION RATES IN Dc

Dc	2.78	6.80	11.60	13.53
Eo	0.13	0.34	0.51	1.00
D	4.64	3.65	3.51	2.95
Σ Stages	7.55	10.79	15.62	17.48



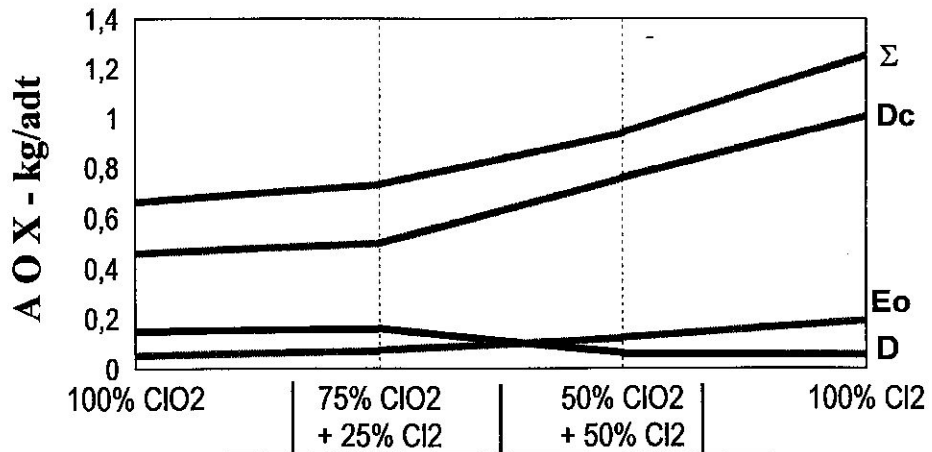
SUBSTITUTION RATES IN Dc

Dc	2 200	3 750	4 400	6 500
Eo	6 000	5 700	5 000	4 700
D	2 500	2 300	2 100	1 800



**SUBSTITUTION RATES IN Dc**

<b>Dc</b>	<b>5.70</b>	<b>6.10</b>	<b>8.22</b>	<b>9.59</b>
<b>Eo</b>	<b>5.51</b>	<b>4.73</b>	<b>7.29</b>	<b>6.70</b>
<b>D</b>	<b>2.75</b>	<b>2.49</b>	<b>2.01</b>	<b>1.01</b>
<b>Σ Stages</b>	<b>13.96</b>	<b>13.32</b>	<b>17.52</b>	<b>17.30</b>



**SUBSTITUTION RATES IN Dc**

<b>Dc</b>	<b>0.460</b>	<b>0.500</b>	<b>0.760</b>	<b>1.010</b>
<b>Eo</b>	<b>0.053</b>	<b>0.074</b>	<b>0.123</b>	<b>0.194</b>
<b>D</b>	<b>0.150</b>	<b>0.160</b>	<b>0.058</b>	<b>0.052</b>
<b>Σ Stages</b>	<b>0.663</b>	<b>0.734</b>	<b>0.941</b>	<b>1.256</b>



## BLEACHING CHEMICAL RESIDUALS

### MICROTOX TOXICITY RESULTS IN PPM

CHEMICALS	IC50	IC20	IC10	IC01	NO TOXICITY AT CONCENTRATIONS UP TO
<b>- OXIDANTS</b>					
O <sub>3</sub>	3.2	2.0	1.5	0.6	-
Cl <sub>2</sub>	1.1	0.4	0.2	0.03	-
NaClO	1.2	0.3	0.2	0.01	-
ClO <sub>2</sub>	1.6	1.0	0.7	0.3	-
H <sub>2</sub> O <sub>2</sub>	16.0	7.0	4.5	1.5	-

## BLEACHING CHEMICAL RESIDUALS

### MICROTOX TOXICITY RESULTS IN PPM

CHEMICALS	IC50	IC20	IC10	IC01	NO TOXICITY AT CONCENTRATIONS UP TO
<b>- SALTS</b>					
NaClO <sub>3</sub>	9 605	3 279	1 748	272	-
NaCl	7 434	4 972	3 929	1 960	-
Na <sub>2</sub> CO <sub>3</sub>	-	-	-	-	4 500
MgSO <sub>4</sub>	-	-	-	-	13 500
Na <sub>2</sub> SiO <sub>3</sub> . 5H <sub>2</sub> O	-	-	-	-	9 000

## BLEACHING CHEMICAL RESIDUALS

### MICROTOX TOXICITY RESULTS IN PPM

CHEMICALS	IC50	IC20	IC10	IC01	NO TOXICITY AT CONCENTRATIONS UP TO
<b>- CHELANTS</b>					
DTPA	15 764	3 624	1 533	120	-
EDTA	10 813	1 360	105	5	-
<b>- ACIDS / BASIS</b>					
HCl	-	-	-	-	9 000
H <sub>2</sub> SO <sub>4</sub>	-	-	-	-	9 000
NaOH	-	-	-	-	9 000
H <sub>2</sub> SO <sub>3</sub>	28	8	3	1	-

## BLEACHING CHEMICAL RESIDUALS

### *Ceriodaphnia dubia* TOXICITY RESULTS IN PPM

CHEMICALS	LC50	NO TOXICITY AT CONCENTRATIONS UP TO
<b>- OXIDANTS</b>		
O <sub>3</sub>	1.9	-
Cl <sub>2</sub>	0.12	-
NaClO	0.13	-
ClO <sub>2</sub>	1.12	-
H <sub>2</sub> O <sub>2</sub>	10.7	-

## BLEACHING CHEMICAL RESIDUALS

### *Ceriodaphnia dubia* TOXICITY RESULTS IN PPM

CHEMICALS	LC50	NO TOXICITY AT CONCENTRATIONS UP TO
- SALTS		
NaClO3	189	-
NaCl	1 338	-
Na2CO3	148	-
MgSO4	697	-
Na2SiO3 . 5H2O	443	-

## BLEACHING CHEMICAL RESIDUALS

### *Ceriodaphnia dubia* TOXICITY RESULTS IN PPM

CHEMICALS	LC50	NO TOXICITY AT CONCENTRATIONS UP TO
- CHELANTS		
DTPA	64	-
EDTA	68	-
- ACIDS / BASIS		
HCl	54	-
H2SO4	224	-
NaOH	590	-
H2SO3	46	-