

The Discharge of CleanOxide into Sea Water (Technical Explanation)

CleanOxide is designed to produce a solution of pure chlorine dioxide in water i.e. free from chlorine and other hazardous chlorinated compounds. Sodium salts, primarily sodium sulphate and sodium chloride, are also formed as by-products but are not regarded as hazardous. There is a small amount of residual sodium chlorite and sodium chlorate present in CleanOxide; typically, the amount of chlorite is about 1% of the amount of chlorine dioxide present. Sodium chlorate is left over from the manufacture of the raw materials and is typically present at about the same concentration as chlorite.

Unlike chlorine or hypochlorite, chlorine dioxide does not have the potential to form persistent organochlorine compounds. In aqueous solution, chlorine dioxide reacts rapidly with oxidisable materials (both organic and inorganic). The principle by-product of these reactions is chloride (Cl^-). Chlorine dioxide can also degrade to chlorite (ClO_2^-) and to a lesser extent chlorate (ClO_3^-). In addition to the presence of oxidisable materials many other factors influence the exact composition of the degradation products from chlorine dioxide including exposure to sunlight, pH, temperature and contact time.

Chlorine dioxide itself is so susceptible to degradation in aqueous media it is considered highly unlikely that any chlorine dioxide would survive the proposed treatment process. If any were present in the discharge stream, reaction with oxidisable material in untreated water would be expected to rapidly degrade the residual chlorine dioxide.

Chlorate once formed is relatively stable to chemical degradation. It is also regarded as of low acute and chronic toxicity (Reference 1). Envirogulf Consulting in their report prepared on behalf of Gunns (Reference 2) argued that there is strong evidence for biological pathways for the degradation of chlorate. In the proposed system, any chlorate present would be diluted in the treatment process, further diluted with untreated waste before being diluted by discharge into the ocean. The dilution factors, together with the relatively low toxicity of chlorate and the biodegradation pathways that may exist are considered sufficient to minimize any risk from discharge of chlorate.

Chlorite is of high acute and chronic toxicity and therefore of greater concern as a potential pollutant. Only limited data is available for chlorite toxicity in sea water; available data indicates it to be of moderate to low acute toxicity in this environment. Chlorite is not a stable ion and like chlorine dioxide reacts readily with oxidisable material and is thereby reduced to chloride. It is also susceptible to degradation by sunlight which converts chlorite to chlorine and oxygen. These two mechanisms are the principle degradation pathways for chlorite. Biodegradation of chlorite to chloride also occurs in the marine environment.

Residual chlorate can be reduced by introducing an anaerobic or anoxic stage to the treatment process. According to the EnviroGulf Consulting report (Reference 2) “...an anoxic selector, which is anticipated to reduce chlorate levels by a minimum of 98% for an hydraulic retention time (HRT) of between 1 and 3 hours (with a design HRT of 2.3 hours). This proposed secondary biological treatment system (anoxic selector) will reduce chlorate

concentrations to environmentally safe levels for discharge.” Given that the proposed treatment system includes a holding tank and recycling/treatment tank, this offers a chance to include an anaerobic stage adequate to minimize the presence of chlorate.

Chlorite can be removed by dosing the discharge water with a reducing agent such as sulphite or ferrous iron (Reference 3). Addition of ferrous iron as ferrous chloride or ferrous sulphate is a relatively cheap, rapid method of reducing chlorite and does not introduce any harmful substance to the effluent stream.

Estimating the possible concentration of undesirable by-products in the discharge stream is fraught with difficulties in view of the number of variables in the system. What we can say with certainty is that:

- the use of chlorine dioxide will not result in the formation of hazardous chlorinated compounds that occur with the use of chlorine or hypochlorite
- chlorine dioxide is not likely to survive the treatment process or, if any is present in the discharge stream, will be rapidly degraded on contact with untreated water
- chlorite and chlorate levels in CleanOxide are low and do not contribute significantly to the overall load of these contaminants
- the main undesirable by-products resulting from the use of chlorine dioxide is chlorite and to a lesser extent chlorate

The total molar concentration of by-product chloride, chlorite and chlorate combined must equal the total molar concentration of chlorine dioxide. If we make the assumption that 50% of the chlorine dioxide used is converted to chloride, and that the ratio of chlorite to chlorate is 4:1 then we can estimate the concentration of these contaminants in the waste stream. These assumptions are based on limited experience with other treatment systems using CleanOxide.

At a dose rate of 30ppm, the residual chlorite level would be 12 ppm ($0.5 \times 30 \times 0.8$) and the residual chlorate level would be 2.4 ppm ($0.5 \times 30 \times 0.2 \times 0.81$). After dilution with untreated sea water, these levels would fall to 10.2 and 2ppm respectively. These are worst case scenarios as they take no account of any degradation during the treatment and holding tanks and take no account of degradation of chlorite on contact with untreated sea water. In practice, we believe the levels would be substantially lower for both contaminants.

At very high dose levels (200ppm chlorine dioxide) residual chlorite and chlorate levels using the same assumptions are approximately 70 and 14ppm respectively and could be higher since proportionally less chlorine dioxide is likely to be consumed by oxidation. However, as these high dose rates are only planned for short (2 hour) spells the total increase in chlorite and chlorate is relatively small and could be ignored.

In our opinion, there would be no need to treat the effluent stream to reduce residual chlorate when dosing at 30ppm or less. Short periods of treatment at 200ppm chlorine dioxide would not raise the total level of chlorate sufficiently to warrant any special treatment (estimated maximum level is 3.4ppm over a 24hour period. Treatment to reduce chlorite appears advisable at both 30ppm and 200ppm chlorine dioxide. The recommended dose rate for ferrous sulphate is 100mg/L treated water. In the event of high (200ppm) chlorine dioxide dose rates being used; this should be increased to 150mg/L.

These estimates could be refined with further information on the dilution factors and treatment regime during the holding period.

References

1. K L Bates, W Young and A J Sutton, Proposed Environmental Quality Standards for Chlorine Dioxide in Water, WRc plc, R&D Technical Report P80, published 2002
2. EnviroGulf Consulting, Gunns Limited, Bell Bay Pulp Mill Project, Review of the Toxicity and Fate of Chlorate in the Effluent Discharge, CR 001/3, July 2007
3. Enric Palacios Doñaque, Aleix Martorell Cebrian, Pedro Javier Miranda Luján, CHLORINE DIOXIDE AS DISINFECTANT FOR PRETREATMENT IN SEAWATER DESALINATION PLANTS, AWWA Conference Paper, March 2015

Regards,

Roger

Dr Roger Franklin