



Labscale testing and economic environmental aspects of Oxicide Treatment

Executive Summary

Hydrogen peroxide is an oxidising compound and can be produced in-situ by means of an electrochemical conversion of dissolved oxygen. This new process, the Oxicide process, is carried out in an especially designed and patented electrochemical reactor. H_2O_2 destructs plankton and micro-organisms in the ballast water. Hydrogen peroxide is known to be of limited risk to humans, especially at low concentrations. It decays within a period of days or a few weeks, resulting in harmless compounds: water and oxygen. Hydrogen peroxide has various applications, among others treatment of swimming pool water, as alternative to chlorine based disinfectants.

A first design of the Oxicide cell has been build and tested under laboratory conditions at a scale of 100 dm^3 water per hour. It contained three Oxicide cells in series, each with contactors for supplying oxygen to the seawater, the source of which is either pure oxygen or air. The seawater runs along a 3 dimensional electrode (cathode), where the oxygen is transformed to hydrogen peroxide. The anode compartment is fully separated from the seawater compartment by means of a conducting membrane. It was found that the maximum achievable concentration of hydrogen peroxide in seawater is determined by kinetics and depends on the concentration of dissolved oxygen, temperature, electrical current and cell voltage. The H_2O_2 concentration follows a logarithmic trend in batch operation. The highest concentration of H_2O_2 achieved at ambient condiments is approx. 400 mg per litre (using pure oxygen gas) or 150-180 mg per litre (using air). The initial current efficiency (CE) is 70-80%. The pH of the seawater decreases because of some migration of H^+ ions from the anode compartment through the membrane. The maximum observed pH drop in a batch operated Oxicide cell was from pH 8.4 to pH 6.5. The 3-dimensional electrode of the Oxicide module showed no plugging or irreversible retention of particles in tests with kaolin, wheat flour and algae, i.e. particles $< 100 \mu\text{m}$.

The Oxicide process is a promising treatment technology for ballast water. The tests at the premises of UNEW show that H_2O_2 is efficient against selected organisms: 100% of *Nereis virens* and $\geq 90\%$ of *Acartia tonsa* were removed in all experiments at 10-15 $\text{mg } H_2O_2/\text{dm}^3$. *Tisbe battagliai* proved more difficult, but was also removed by at least 85% at higher concentrations of H_2O_2 ($> 28 \text{ mg}/\text{dm}^3$). Furthermore, at least 50% of the phytoplankton is removed by Oxicide treatment at 10-15 mg/dm^3 , although some of the other test results with phytoplankton were inexplicable. Elevated temperature (up to 35°C) seems to improve the efficiency of H_2O_2 , especially zooplankton. A literature study and additional tests revealed that some organisms need much larger concentrations ($>100 \text{ mg } H_2O_2/\text{dm}^3$) to be destructed or inactivated; this especially holds for large organisms.

Electrochemically produced H_2O_2 had the same efficiency in killing *Skeletonema* sp. algae as a technical solution. This indirectly shows that probably no significant amounts of byproducts (e.g. chlorine) are formed.

In summary, various organisms are destructed or inactivated at relatively low concentrations of hydrogen peroxide (10-30 $\text{mg } H_2O_2/\text{dm}^3$). A treatment time of at least 24 hrs is required for H_2O_2 to take full effect. However, a combination of Oxicide with other techniques should be considered, because of the relative high resistance of some organisms to hydrogen peroxide.

In terms of corrosion assessment, the production of H_2O_2 and the significant increase of the Redox potential of the water (several hours to a few days) may have consequences for the metal corrosion, coatings and gaskets. In addition, it is recommended to pay attention to the electric isolation of the DC equipment, because of the risk of unexpected current return paths and significant local metal corrosion.