ELECTROCHEMICAL GENERATION OF HIGH-CONCENTRATION OZONE IN COMPACT INTEGRATED MEMBRANE SYSTEMS

Final Report

to the

Water Research Commission of South Africa

by

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I. EXECUTIVE SUMMARY

Background and motivation for conducting research

Ozone has been used for almost 100 years in water treatment in Europe where it is largely used for disinfection, control of taste and odour, and for the removal of colour. The role of ozone in the treatment of potable water supplies and wastewater is as a disinfectant and a powerful oxidant. As a disinfectant, ozone successfully inactivates enteric bacteria, viruses, amoebic cysts and spores. As an oxidant, ozone oxidises many inorganic materials completely and rapidly, for example, sulphides to sulphates, nitrites to nitrates, etc. Ozone also oxidises organic materials such as unsaturated and aromatic compounds which are oxidised and cleaved at the double bonds; humates and fulvates which are commonly found in potable water supplies are effectively bleached, and foul tasting phenol materials are readily destroyed.

In addition to the direct reactions of molecular ozone described above, ozone can also react indirectly via the radical species formed when ozone decomposes in water. The production of hydroxyl radicals (•OH) could be enhanced by increasing pH, addition of hydrogen peroxide or irradiation with ultra-violet light.

Ozone competes with chlorine-based technologies on the water treatment market. Safety of ozone treatment plants is an advantage over chlorine plants.

Ozone has an important role to play in the treatment of water and wastewater, which can be summarised as follows:

POTABLE WATER TREATMENT
- Improvement of organoleptic qualities (colour and taste)
- Disinfection of bacteria and viruses
- Oxidation of organic matter, micropollutants and metal salts in solution
- Improvement in biodegradability of water contaminants prior to other treatment
- Avoiding chlorinated by-products

INDUSTRIAL EFFLUENT TREATMENT
- Oxidation of many types of industrial effluents
- Bleaching of coloured effluents such as from dye houses and food manufacturers
- Deodorization
- Improvement in biodegradability prior to bio-treatment

MUNICIPAL WASTEWATER
- Disinfection of treated water
- Deodorization, particularly used for treatment of sludge

SWIMMING POOL WATER
- Improvement of visual qualities
- Degradation of certain amine substances present in swimming pool water
- Disinfection action in regeneration circuit
- Avoiding chlorinated by-products

There are many other applications of ozone such as in cooling tower waters, synthesis of specialised organic and inorganic materials, and in such areas as cleaning printed circuit boards and removing photoresists.

In most water treatment applications, reactions with ozone occur in the aqueous phase. Typically, reactions in the aqueous phase obey first order kinetics, and the rate of oxidation is thus dependent on aqueous ozone concentration. It is, therefore, important that as much ozone as possible is transferred rapidly into the water. Higher dissolved ozone concentrations could thus lead to faster rates of reaction. Ultimately this could lead to greater degrees of oxidation.

Ozone can be produced using pure oxygen or air by means of the corona discharge method. Ozone can not be transported and has to be produced on site. Ozone production by means of the corona discharge method requires a permanent source of oxygen. An additional requirement is a low dew point of the oxygen to be used for ozone generation.

Technological developments over the last decade have led to corona discharge generators capable of producing concentrations of up to 15 % w/w when oxygen is used as the feed gas. More recent developments in electrochemical ozone generation have led to high concentration ozone (HCO), with concentrations as high as 40 % w/w.

The electrochemical method of ozone generation is based on the reaction of anodic oxidation of water:

$$9H_2O \rightarrow 6H_3O^+ + 6e^- + O_3$$

In the electrochemical ozone generation process only two components are consumed, namely, electricity and water.

However, commercialisation of the technology is hampered by the relatively high power consumption involved. A lack of reliable data in the field of HCO applications also holds back development of the technology.

It is for these reasons that a project dealing with the development of a compact, simple to use, low-cost electrolytic generator capable of delivering high-concentration ozone was undertaken by DINAX Technologies cc in co-operation with the University of Stellenbosch in South Africa.

Objectives

A general aim was to develop a South African-made cost-effective unit capable of producing ozone with concentrations six-fold higher than currently available units. More specifically, an objective was to develop an efficient, inexpensive system, which is easy to operate, maintain and scale-up. Such a system would be able to produce ozone at high concentration for industries, such as textile, pulp, paper, as well as for pre-treatment of wastewater prior to the bio-treatment. Another objective was to identify the best niches for the application of the novel technology in various water and effluents treatment processes. Finally, an objective was to combine electrochemical ozone generation with electrochemical generation of hydrogen peroxide to improve water treatment efficiency.

Results

Titanium-based anodes containing a beta (β) crystalline form of PbO_2 were prepared and tested for ozone generation. The anodes were studied by means of the X-Ray Diffraction (XRD) technique. It was shown that the developed method enabled to obtain anodes with a predominant β-PbO_2 phase.

Proton-exchange membranes (PEM) containing Pt particles were prepared. Such catalytic membranes minimise power consumption during electrocatalytic ozone generation due to the superiority of Pt as a cathodic catalyst during the discharge of hydroxonium ions into gaseous hydrogen in the membrane cell.

An electrochemical PEM-based plate-and-frame membrane reactor with a variable active anode area to study ozone generation has been constructed and tested. An active anodic area of the reactor varied from ≈ 50 to ≈ 200 cm^2.

A tubular glassy carbon-based ozone generator was also built and tested. The ozone generator consisted of the following main components:

- Electrolyser
- Power supply
- Control system and instrumentation
- Refrigeration
- Liquid and gas flow systems
- Separation systems

The ozone generator was able to deliver ozone at 25 wt% concentration and higher.

Surface roughness studies of membranes, anodes and cathodes were carried out using atomic force microscopy (AFM).

The economics of the process was studied by generating HCO under different conditions (e.g., various electrical current densities were applied). Data on the relationship between power consumption and ozone yield were produced.

The HCO generator was tested in batch experiments with textile effluents, SAPPI effluents, and wastewater received from the food industry. It was shown that HCO has much higher oxidation efficiency in comparison with low-concentration ozone available from commercial oxygen-fed ozone generators.

Electrolytic generation of hydrogen peroxide was carried out in the PEM-based ozone generator. It was found that the efficiency of the process was low, making it impractical to combine it with the system developed. The combination would increase capital costs of the system with no visible improvement in the efficiency.

Conclusions

A. An electrochemical ozone generator comprising proton-exchange membranes, platinum cathodes, and lead dioxide anodes was built and tested.

Anodic generation of ozone using a PEM-supported lead dioxide catalyst suffers from the relatively fast irreversible degradation of the catalyst. The method could be

suitable for generation of ozone of very low concentration when relatively low current densities are used (less then 0.1 A/sm^2) competing with traditional technologies (such as UV-based generation) for the production of low-concentration ozone at a small scale.

Further research is needed to optimise operational conditions of PEM-based electrochemical ozone generation and to improve stability of the metal-oxide-based anodic catalysts. This could be a separate project in the field of the PEM-based electrochemical ozone generation technology provided there is enough economic drive behind the technology itself.

B. An electrochemical ozone generator comprising glassy carbon electrodes and a water-soluble electrolyte was built and tested. In theory the electrochemical processes, which are used for ozone generation by means of DINAX generators, are capable of producing ozone very efficiently. However, in practice the theoretical efficiency can not be easily achieved, and the electric current consumption in the generators is higher than that in large corona-discharge units. That is why it is expected that such a system could be used for small-scale applications.

Current research was also aimed at reducing power consumption. This was achieved by various means such as efficient design of the ozone generator and forced mixing of the electrolyte.

Another important issue that should be taken into consideration is that ozone of high concentration produced electrochemically could be used more efficiently than lower-concentration ozone produced by corona discharge systems and, therefore, a true cost comparison between the different systems should take into account the efficiency of ozone use.

It is also important to remember that ozone generation in a DINAX generator occurs along with generation of hydrogen gas. This hydrogen can potentially be used in fuel cells to recover partially costs associated with high power consumption.

Optimisation of the design of the generator is required to ensure optimum efficiency and ease of use in various applications. This could be addressed in a separate project.

Industrial prospects and recommendations for future research

In South Africa, DINAX Technologies, cc, in co-operation with Chemistry Department of the University of Stellenbosch and the Water Research Commission of South Africa are involved in the development of small electrocatalytic high-concentration ozone generators for water treatment, medical, electronical and petrochemical applications.

Based on the results of the current project it is clear that the electrolytic HCO technology could successfully compete with the traditional ozone generation technology on the market of small-scale applications, such as mobile medical sterilisation units, colour removal systems, odour removal systems, mobile rescue disinfecting units and mobile systems for destruction of chemical weapons. In other

words, the HCO technology could be useful in cases when the cost of ozone generation is of less concern than immediate solution to a localised environment-related problem.

Further research in this field is believed to be feasible. For example, it could also include a comparative study of the efficiency of HCO and LCO in treatment of *Cryptosporidium* and *Giardia.*

Costs

Cost related to the electrolytic generation of ozone using glassy carbon electrodes.

Operational current density, (amps/cm^2)	**Ozone concentration, (wt %, O_2/O_3)**	**Ozone productivity, (g/h)**	**Power consumption, (kWh/kg O_3)**
0.05	8.0	0.36	155.6
0.075	11.2	0.71	119.7
0.1	13.4	1.20	108.3
0.125	15.2	1.66	99.6
0.15	19	2.22	98.5
0.2	21.7	3.37	96.3
0.225	23	4.10	92.2

It is seen that with an increase in the current density the efficiency of ozone generation also increases.

II. ACKNOWLEDGEMENTS

The results of the research in this report emanated from the project No K5/852 funded by the Water Research Commission of South Africa and entitled "Electrochemical generation of high-concentration ozone in compact integrated membrane systems". The project leader, Dr DG Bessarabov (D.G.B.), is thankful to the members of the project steering committee for their constructive suggestions made in the course of the project.

D.G.B. is very grateful to Dr. G. Offringa for his continuous interest in the project and support, as well as for letting me finalise the project report in Canada, where I am working in my new capacity[1].

Dr. Z. Twardowski of Kvaerner Chemetics (Canada) for valuable advice in the field of electrochemistry and for letting me finish the report at his department.

D.G.B. thanks Prof. Ron Sanderson for his support during the project. The assistance of the Institute for Polymer Science and Chemistry Department of the University of Stellenbosch is also greatly appreciated.

D.G.B. thanks Dr. J. Mellor of SASOL for his enthusiastic and useful advise in the field of fuel cell technology.

Assistance of Prof. G. Wolfaardt (Department of Microbiology, University of Stellenbosch) is appreciated.

D.G.B. thanks Dr Yu.M. Popkov from Karpov Institute of Physical Chemistry, Moscow, Russia, for interesting discussions in the course of the project.

D.G.B. thanks postgraduate students, Mss. W. Michaels and V. Jackson for their contributions.

D.G.B. thanks Mr. Cliff Thomson from AEC of South Africa for his efforts in fluorination of electrode samples.

This work was also supported by the National Research Foundation of South Africa through bursaries for students involved in the project.

And, finally, I would like to thank my wife Natasha for her endless love and support in the course of the project.

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