

# Electrochemical Destruction of Organic Hazardous Wastes

THE CERIUM OXIDATION CEROX™ PROCESS ELECTROCHEMICAL CELL

By Norvell Nelson

CerOx Corporation, 2602 Airpark Drive, Santa Maria, CA 93455, U.S.A.

*The destruction of hazardous organic waste produced as waste products in chemical processes has become an industry in itself, regulated by environmental agencies and government bodies. The environmentally harmful waste has been incinerated at high temperature with the aim of forming less harmful and less complex compounds, but this may lead to dioxin formation in the presence of chlorine-containing waste. It may also be treated electrochemically to result in carbon dioxide and water. One on-site electrochemical method, described here, which uses platinum-plated titanium electrodes, can treat most organic waste materials very effectively at low temperatures.*

Destroying the hazardous organic waste products from chemical and industrial operations, laboratory waste, pesticides, military waste materials and organic waste management in general is an acknowledged problem, and government bodies and environmental agencies worldwide are concerned over its regulation. In the U.S.A., the Environmental Protection Agency (EPA) monitors and advises industry and individuals about the safe disposal of hazardous waste, and a system of laws and regulations are in place for tackling waste produced. In particular, the 'Resource Conservation and Recovery Act' (RCRA) is designed to ensure that hazardous waste, from time of creation to time of disposal, is properly managed. The RCRA establishes sets of rules for dealing with hazardous wastes. The rules define which hazardous wastes require regulation and also identify the responsibilities for those who generate, transport, store, treat, dispose of, or otherwise manage them.

Additionally, there is a 'Part B Permit' for the generators of hazardous waste. The EPA requires waste generators to obtain this Permit before they can treat their hazardous waste by incineration. It may take several years to obtain a Part B Permit and can be a costly procedure, so any effective procedure which can avoid this is attractive. Further, several states, including California, will no longer license new hazardous waste incinerators.

With any waste destruction process there are always concerns that the processes themselves could be polluting. Common methods for dealing with hazardous waste disposal include container storage, incineration and electrochemical treatment, the latter releasing carbon dioxide and water. Any one process may not be able to treat all hazardous waste successfully. The electrochemical process described here, the CerOx™ (1) Process, can be used to treat most organic waste materials, and can do so non-thermally on-site. The hazardous materials to be treated present a much greater danger to the environment than the relatively small amounts of carbon dioxide that are released by the process. In fact, compared to a hazardous waste incinerator destroying the same amount of waste materials, the CerOx Process releases about 25 per cent less carbon dioxide (a value that includes the generation of the needed electricity from a fossil fuel fired generation station).

## The CerOx Process

A cerium-catalysed electrochemical oxidation process, the CerOx Process, is one electrochemical means of destroying waste organic material. Cerium, as the oxidised Ce(IV), is a very powerful oxidising agent which will remove electrons from virtually any organic compound with which it

*CerOx™ is a registered trademark of CerOx Corporation*



*Fig. 1 Four welded CerOx electrochemical T-Cells manufactured for the System 4 delivered to the University of California at Irvine to be used for organic waste destruction. Each T-Cell has 10 platinum-plated electrodes which are electrically connected in series*

comes in contact (except fluorocarbon materials). The process uses Ce(IV) which is produced in electrochemical cells that utilise platinum-plated titanium electrodes. Operating at atmospheric pressure, the process can convert organic hazardous waste materials into carbon dioxide and water.

The CerOx Process will treat most organic waste materials. Pretreatment of the organic waste materials, in general, is not needed as long as the materials are pumpable fluids. As the process works best on 'concentrated' organic materials, the organic content of the waste stream should preferably be greater than 15–20%. Electrochemical cells for a CerOx System 4 are shown in Figure 1. The CerOx System 4 is designed to process approximately one drum of waste per day. The process throughput scales with the number of electrochemical cells in the system.

The process has been designed so that it never attains the reaction conditions, in particular the high temperatures which result in the unwanted synthesis of highly dangerous dioxins from the chlorocarbon feed materials. In effect, this process can be used to destroy dioxins, and not generate them. Indeed, the unwanted production of dioxins is a constant problem for thermal processes,

such as incineration, when treating similar waste materials.

The electrolytes used in the CerOx Process are strong nitric acid solutions, ~ 20% acid. Alkaline solutions need to be neutralised before treatment to avoid excessive heat generation. The process has successfully treated organic solutions containing in excess of 50% triethanolamine. However, the process will not destroy or degrade fluorocarbon materials such as Teflon or its derivatives. This exception is fortunate because it allows these materials to be used in the construction of the CerOx Process equipment.

### Equipment and Procedure

The oxidation process is performed in a series of tanks and pipes, and is thus classified as a 'tank system'. A tank system is one where processes occur in closed containers, in contrast with an 'open' system, such as an incinerator. In an incinerator the materials treated are fed through the process in a single pass operation.

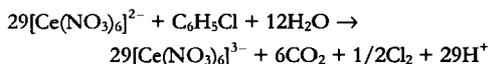
In general, tank systems retain the in-process waste materials until the process is run to completion. The classification of the CerOx Process as a tank system exempts the process from RCRA regulation. However, the primary requirement is that

the user may only process his own waste materials. As the generator will have a record of the waste materials by identity and quantity, no pretreatment analyses are required.

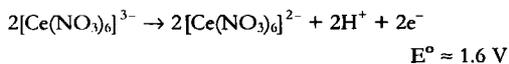
## The Chemical Process

The CerOx Process is comprised of four distinct chemical reactions which are temporally and physically separate. These are:

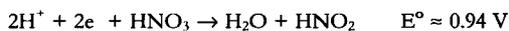
(i) Organic destruction of organic hazardous waste material through oxidation by Ce(IV). For example, the destruction of chlorobenzene is a 29 electron [29 Ce(IV)] process:



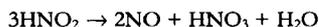
(ii) Electrochemical regeneration of the Ce(IV) oxidant at the platinum coated anode:



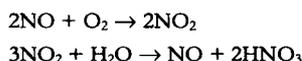
(iii) The corresponding cathode reaction, that is, the reduction of nitric acid to nitrous acid:



(iv) and the recovery of nitric acid from the cathode reduction product:



Then recovery by the oxidation of NO and capture in water:



Since the cerium is not consumed in the process, it acts as a catalyst which is electrochemically regenerated. As the electrochemical oxidation involves the use of platinum-plated titanium electrodes, it is the operating unit of interest here and will be examined in more detail.

### Electrochemical Waste Destruction

The electrochemical part of the process is a very necessary component of the operation. It comprises the most straightforward of the unit operations involved in the waste destruction process and is the best characterised part of the

operation. The economics of waste destruction are burdened by the fact that in industry, waste management is not considered to be a part of production. The money spent on waste treatment is not available for manufacturing. Thus, to gain acceptance, waste destruction equipment must be provided at the lowest possible cost for the waste generators. In responding to this, CerOx Corporation has designed and is producing an electrochemical cell that is considerably less costly than traditional 'plate and frame' designs.

Standard, commercially available, electrochemical equipment is constructed from precision-machined metal parts. This results in equipment that is often prohibitively expensive. To reduce the capital cost for the process, CerOx has designed and developed an electrochemical cell with key components that can be manufactured in high volume, and are easy to maintain (2). The material of construction is poly(vinylidene fluoride), (PVDF), an injectable and weldable fluorocarbon plastic material.

## The CerOx Process Electrochemical Cell

The basic building block of the electrochemical cell comprises an anode and cathode separated by a membrane. Cells are assembled in series, much like a car battery, to form the CerOx electrochemical cell. The electrodes in the interior of the stack are bipolar and support the cathode reaction on one side and the anode reaction on the other side. A schematic of the cell construction is shown for one bipolar plate in Figure 2 (1).

### Electrodes

The electrodes are made of titanium, one of the few metals stable in the highly reactive environment of the Ce(IV)/nitric acid anolyte solutions. The anode surfaces of the electrodes are covered with a layer of electroplated platinum. The platinum is critical to the performance of the electrochemical process, playing two key functions: [1] Although, titanium is an electropositive metal, it has stability in the strongly oxidising solutions used here because it is able to form a strongly adherent native oxide, TiO<sub>2</sub>, which passivates the

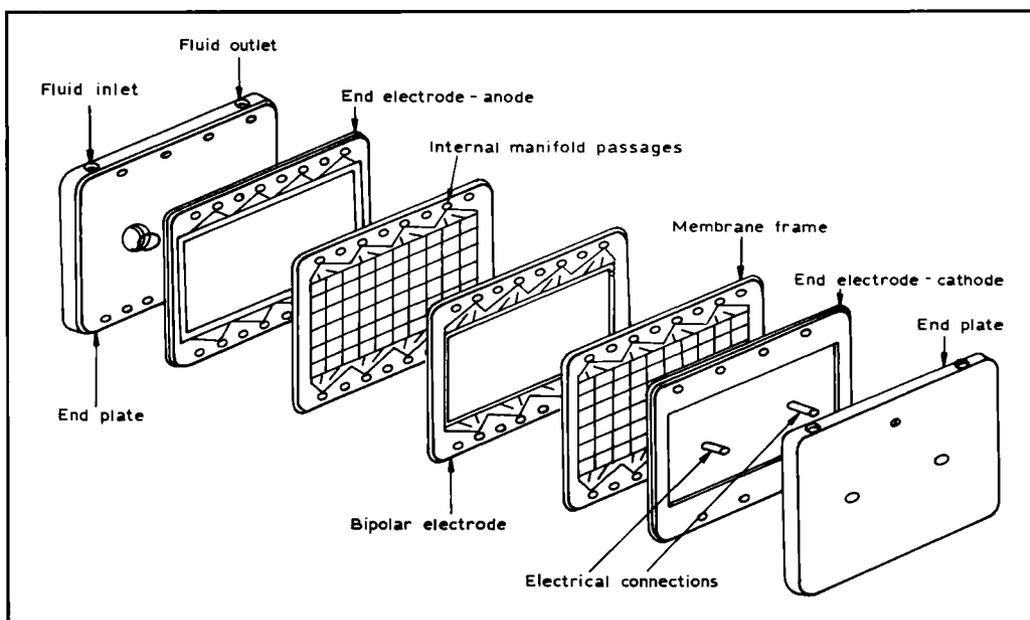
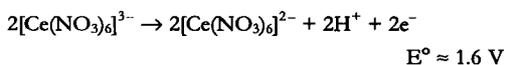


Fig. 2 In the CerOx electrochemical cell the basic building block of the electrode stack (the bipolar electrode) is a titanium electrode welded into a plastic carrier making one half of the cellpack module. The other half is an identical plastic carrier with a Nafion membrane separator that acts as the internal flow distribution manifold and the separator of the two electrolytes. The construction allows hydraulic and gaseous connections to be internal via moulded manifolds

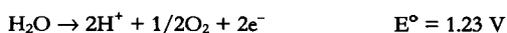
surface.  $\text{TiO}_2$  is an *n*-type semiconductor, passing electrons and functioning as the cathode surface in the bipolar cell. However,  $\text{TiO}_2$  covered titanium could not function as an anode without having a platinum coating.

[2] The oxidation of Ce(III) to Ce(IV) in nitric acid occurs around 1.62 V which is  $\sim 0.4$  V above the potential needed to oxidise water to oxygen,  $\sim 1.23$  V. The platinum coating also functions as an electrocatalyst which selectively inhibits the energetically favoured water oxidation reaction in preference to the oxidation of Ce(III) to Ce(IV) at the higher potential.

There are two predominant anode reactions, the oxidation of Ce(III) to Ce(IV):



and the parasitic reaction, the oxidation of water to oxygen:



It is desirable to maximise the ratio of Ce(III) oxidation to water oxidation. This percentage of the

total current used for Ce(III) oxidation is termed the coulombic efficiency for this reaction. The selectivity (coulombic efficiency) for the oxidation of Ce(III) over the oxidation of water can approach 90 per cent in the commercial electrochemical cell (called the T-Cell by CerOx), see Figure 1. Figure 3 shows a plot of three operational parameters recorded during a 24-hour test run with the CerOx T-Cell. In operation, the organic feed rate is balanced with the Ce(IV) generation rate so that the in-process concentration of Ce(IV) remains invariant. The feed rate of  $2.34 \text{ kg hour}^{-1}$  in Figure 3 is supported by a coulombic efficiency for Ce(III) oxidation of 88.9%.

The thickness of the platinum coating on the electrodes is important in two respects. The coating must be thick enough to provide for several years of operation before attrition depletes the coating to the point of inoperability, yet it must be 'thin' enough to remain adherent to the electrode during operation. Coating thicknesses in the 200–400 micro-inch range can meet these criteria. The combination of platinum upon titanium in the electrodes is stable to the process conditions, with

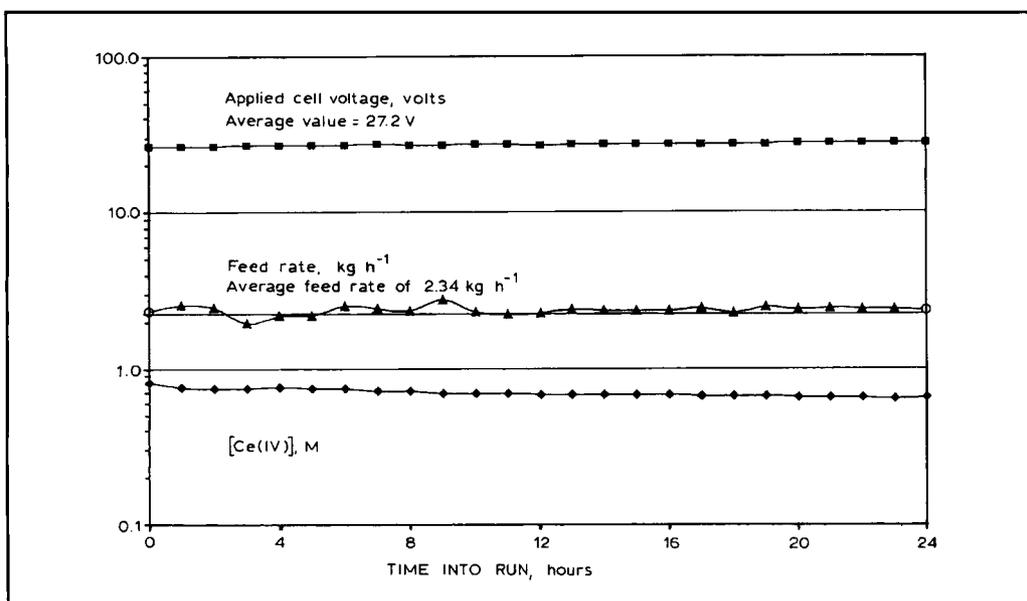


Fig. 3 Operating parameters for a CerOx T-Cell during steady state operation over 24 hours showing applied potential, volts; process feed rate, kg hour<sup>-1</sup>; and steady state Ce(IV) concentration, M

life expectancy for the electrodes exceeding 2 to 3 years of operation. CerOx designs and manufactures the electrodes to conform to the geometrical requirements of the material. PVDF is used for the carriers. The carriers for the electrodes and membranes are identical in design and construction.

This process has been designed such that the majority of organic destruction occurs in the liquid-phase organic reactor and not in the electrochemical cell. In this way exposure of the cell and its components to constituents of the waste stream is minimised.

The anolyte and catholyte solutions need to be kept separate, and this is the function of the Nafion membrane. However, the membrane allows the free passage of hydrogen ions (protons) between these two solutions to maintain current flow. (Nafion is a sulfonated Teflon-like material, stable to the highly reactive anolyte.)

Having identical PVDF carriers for the electrodes and membranes, greatly reduces the cost of the electrochemical cell and eliminates the leak potential associated with 'plate and frame' designs. The design of a standard size cellpack allows for modular units of the process systems and for easy maintenance. A cellpack is fabricated by welding

10 electrode pairs in series and is the basic electrochemical module for the process, providing leak-proof containment for the hazardous waste materials, the electrolyte supply-and-return and off-gases. Figure 1 shows four new cellpacks.

### Electrochemical Cell Performance

The bipolar cell is nominally operated at an applied current of 500 A. This gives a current density of  $\sim 4000 \text{ A m}^{-2}$ . The nominal electrolyte concentrations are  $\sim 1.0 \text{ M}$  total dissolved cerium in  $\sim 3.5 \text{ M}$  nitric acid for the anolyte and  $\sim 4 \text{ M}$  nitric acid for the catholyte. These electrolyte compositions form a workable compromise between electrolyte cost, electricity consumption and electrochemical performance.

### Organic Destruction Reaction

The purpose of the electrochemical operation is to produce Ce(IV) for use in the oxidation of waste organic material. The organic destruction reactions occur in a tandem set of reactor vessels. The process starts by metering the organic waste materials into a liquid-phase reactor to mix with the Ce(IV) reactant solution. The addition rate of the organic materials is controlled by monitoring the

in-process concentration of Ce(IV). The addition rate is set to maintain a steady state concentration of Ce(IV) in the system. All the gaseous products from this reactor are vented into a second reactor – a packed bed reactor – in which the exhaust gases are contacted with a downflow of Ce(IV) anolyte. This reactor destroys any adventitious VOC materials that may have been volatilised from low boiling materials passed into the liquid-phase reactor.

Hydrocarbon materials and oxygenates, such as alcohols and ketones, are converted to carbon dioxide and water. Organic materials that contain other heteroatoms, such as chlorine, nitrogen, sulfur, phosphorus and many other members of the Periodic Table, are also broken down to carbon dioxide, water and an oxidised species containing the heteroatom. Carbon-bound Cl is converted to Cl<sub>2</sub> (chlorine gas), and N to nitric acid. The volatile products, such as Cl<sub>2</sub>, separate from the reactor along with the carbon dioxide and are removed from the exhaust stream before venting. Sulfur species are oxidised to sulfate and phosphorus species are oxidised to phosphate.

As stated previously the CerOx Process does not destroy or degrade fluorocarbon materials, such as Teflon, or its derivatives. These materials can therefore be used for the construction of the processing equipment. The carbon-fluorine bonds are not degraded during the process as they are stable to the chemical environment of the anolyte. Any inorganic fluoride added to the system is strongly bound to Ce forming an insoluble

fluoride. This sequestering of fluoride by Ce(III) prevents fluoride-promoted corrosion of the Ti electrodes.

## Conclusions

Using this electrode/membrane carrier construction system, it is possible to manufacture more simply and easily key components for the catalytic destruction of hazardous organic waste. These can be manufactured in high volume and are easy to maintain. The CerOx Process may be regarded as a solution to the problem of the total treatment of hazardous organic waste materials. It is the only non-thermal alternative to incineration that is both technically and economically viable for on-site treatment and destruction of organic wastes, to comply with current U.S. environmental regulations.

## References

- 1 The CerOx™ Process was originally developed by the Pacific Northwest National Laboratory (PNNL). J. E. Surma, G. H. Bryan, J. G. H. Geeting and R. S. Butner, *U.S. Patent* 5,707,508; 1998
- 2 The CerOx™ Process has been commercialised by CerOx Corporation under an exclusive license from the PNNL. G. A. Steward, *U.S. Patent* 5,756,874; 1998

### The Author

Norvell Nelson is the Chief Technology Officer (and co-founder) of CerOx Corp. He holds a PhD in organic chemistry from Stanford University and has been a Postdoctoral Fellow and Instructor at Northwestern University in inorganic chemistry. He worked at Eastman Kodak, Varian Associates and Catalytica before co-founding CerOx. His interests are in the application of novel chemistries for solving organic waste management problems. Information about CerOx can be found at [www.cerox.com](http://www.cerox.com).

## Modern Organic Catalytic Reactions

CATALYSIS OF ORGANIC REACTIONS, Chemical Industries Series, Vol. 82

EDITED BY MICHAEL E. FORD, Marcel Dekker, Inc., New York, 2001, 629 pages, ISBN 0-8247-0486-X, U.S. \$195.00

This book contains papers given at the 18th Conference on Catalysis of Organic Reactions, in Charleston, U.S.A., in 2000. Papers cover a wide range of material including the latest industrial and academic research. Platinum group metals (pgms) remain important and several themes emerge.

Pgms continue to replace base metal catalysts for environmental and cost reasons. In fat hardening (a multi-million tonne industry using base metal catalysts) superior catalytic processes would result in

economic, quality and environmental benefits.

Supported homogeneous pgm catalysts continue as a favourite topic, many based on well-known technologies. Pgms are now more widely used in selective oxidation reactions and industrial interest is growing. The work of industrial groups and collaborations looking at 'real' problems, besides more fundamental work, is of particular interest.

D. R. KELL

Darren Kell is Business Projects Manager at Avecia, Scotland. His interests are in the commercialisation of inkjet printing materials.