

# Electrochemical Destruction of Toxic Organic Industrial Waste

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A recent report by the House of Commons Environment Committee on toxic waste drew attention to the fact that no new technology for the treatment of industrial waste had emerged in the United Kingdom during the last decade (1). The majority of wastes continued to be disposed of by burial in landfill sites, sometimes after chemical treatment—for example, neutralisation—or solidification. A further, smaller proportion was incinerated, with the most toxic and persistent materials, such as chlorinated solvents and polychlorinated biphenyls, being dealt with by a few specialist operators in plants subject to stringent controls on combustion conditions and on the levels of emissions of substances like 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

Public and media concern about the siting and operation of such plants has led to some being closed down, and to planning consent for new plants being the subject of an almost inevitable protracted and expensive Public Enquiry.

This article describes a novel electrochemical

process, developed by AEA Technology at their Dounreay site, for the safe destruction of a wide variety of organic waste types.

The new process involves the electrolytic production of highly oxidising species in an electrolyte consisting of a silver salt, usually silver nitrate, in nitric acid. These oxidising species in turn attack the organic waste material, ultimately converting it to carbon dioxide, carbon monoxide and water, along with inorganic compounds arising from any hetero-atoms, such as phosphorus or sulphur, which are converted to phosphate and sulphate, respectively.

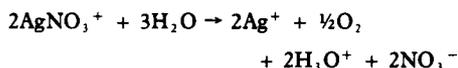
This process is made possible by the unique characteristics of the platinum group metals as electrode materials. At the heart of the system is an electrochemical cell, consisting of an anode compartment, a cathode compartment and a membrane separator. Cells of this type are widely used in the chemical industry for the production of chlorine by the electrolysis of brine, and a typical cell, manufactured by Imperial Chemical Industries, is shown in Figure 1. The anode of the cell consists of a titanium



**Fig. 1** This electrolyser manufactured by ICI for the production of chlorine shows a typical modern compact cell which could be used at the heart of the process for the destruction of industrial organic waste materials

substrate coated with a material which is appropriate for the particular cell application, this being ruthenium dioxide in the case of chlorine manufacture. However, for the electrochemical oxidation of wastes, the coating material of choice to date has been platinum, on account of its useful overvoltage behaviour with respect to oxygen evolution. This property of platinum, allied with its resistance to very highly oxidising conditions, allows the efficient production of highly oxidising silver(II) from silver(I) ( $E^\circ$  of Ag(II)/Ag(I) couple = +1.98 volts versus S.H.E.) at electrode potentials considerably higher than the reversible oxygen evolution potential ( $E^\circ$  of  $O_2/H_2O$  couple = +1.23 volts versus S.H.E.).

Silver(II) is one of the strongest oxidants known, being exceeded in its oxidising power only by such species as persulphate, ozone and fluorine. Solutions of silver(II) in nitric acid are an intense brown colour, due to the presence of the complex ion  $AgNO_3^+$  (2), but the colour fades at a rate dependant upon the temperature of the solution, due to the destruction of the silver(II), and is accompanied by oxygen from the oxidation of water:



It is this reaction of the silver(II) with water which is the key to the electrochemical oxidation of organic wastes. The water oxidation is not a single step reaction but proceeds via a number of intermediate processes, some of which involve very highly reactive species, including OH radicals (3). These radicals tend to react indiscriminately with organic compounds and ultimately oxidise the waste to carbon monoxide, carbon dioxide and water.

### Platinum Anode

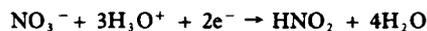
There is no net consumption of silver in the anolyte. The silver functions as a "coupler" between the electric power being fed into the cell and the organic wastes being destroyed. The concentration of silver(II) in the anolyte when the process is operating at steady state is actually very low, as silver(II) has very rapid kinetics

and reacts as fast as it is formed. This fast reaction in the solution, coupled with the facile production of silver(II) on a platinum electrode (the activation energy for the  $Ag(I) \rightarrow Ag(II)$  oxidation on platinum is approximately zero, and the rate of silver(II) production is controlled almost entirely by the rate of transport of silver(I) from the bulk solution to the anode surface (4)) results in the process running at almost the theoretical electrochemical efficiency, even at high current density.

The reaction in the anolyte overall is the same as if the organics had been oxidised directly at the anode. Using benzene as an example:



In fact this reaction can be carried out directly at a platinum anode, but only at very low current density. The  $H_3O^+$  ions cross the membrane to the catholyte under the influence of the voltage being applied to the cell, typically 2–3 volts, and thereby carry the current from anode to cathode. At the cathode, nitric acid is reduced to (primarily) nitrous acid:

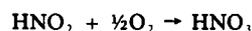


Some further reduction to nitric oxide and nitrogen dioxide also occurs if the nitrous acid concentration is allowed to rise.

### Platinised Cathode

The material of choice for the cathode is also platinum as it shows the lowest overvoltage for the nitric acid reduction reaction. This results in a saving of approximately 0.15 volts in the cell voltage, which is about 7 per cent. However, this saving must be offset against the greater cost of a platinised cathode compared to alternative materials such as stainless steel which perform satisfactorily, although at the expense of a higher cell voltage.

The catholyte is circulated between the cathode compartment and a regeneration system where air or oxygen is used to re-oxidise the nitrous acid and nitrogen oxides to nitric acid:

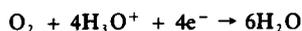


Apart from minor unavoidable losses, there is no net consumption of nitric acid in the



**Fig. 2 The pilot plant built at Dounreay for the destruction of organic waste is being used to establish the chemical engineering parameters that are required for a full scale plant**

catholyte. The reaction across the cathode/regeneration part of the process simplifies to:



which is, of course, the cathode reaction in a fuel cell. In both systems the oxidising power of oxygen is beneficially coupled into the process, although the oxidation of organics is being driven by electric power in one case and is driving electric power in the other.

Again using benzene oxidation as an example, the reaction across the whole process may be considered as:



(some carbon monoxide is also formed) which is stoichiometrically identical to combustion.

The initial interest in the work arose from the

need to destroy the organic component of some types of combustible radioactive waste before it was conditioned for final disposal. Early trials demonstrated that materials like cellulose tissue, rubber gloves, some plastics, ion exchange resins, lubricating oils, hydraulic fluids and waste process solvent (tributyl phosphate/odourless kerosene mixture) could all be converted to carbon dioxide, carbon monoxide and inorganic products. There was an additional bonus in that the activity associated with the waste ended up in nitric acid solution, the usual form in which the waste streams from reprocessing operations arise. The acid can be removed by distillation and the residues solidified into glass or concrete before final disposal into a repository.

The wide range of materials which could be

destroyed led to the extension of the process to deal with organic wastes of industrial origin. To date trials have shown that phenols, chlorinated phenols, chlorinated aliphatic and aromatic solvents, organophosphorus compounds, organosulphur compounds and polychlorinated biphenyls can be destroyed, and the list is continually growing. A pilot scale rig, shown in Figure 2, has been built at Dounreay to derive the chemical engineering parameters required to build a full scale plant.

### Priority Pollutants

The United Kingdom Department of the Environment has recently published a provisional "Red List" of chemicals, for which it is intended to set strict environmental standards for the quality of water into which they have been discharged. This "Red List" is shown in the Table, and the 26 chemicals are accompanied

by a further 23 candidates which are under investigation pending their possible inclusion. The United Kingdom list falls well short of the European Economic Community list which contains 129 chemicals. Note that all but two of the entries in the Table are organic chemicals, many of which would require well controlled incineration to effect their safe disposal. It is proposed to require processes responsible for significant point source discharges of "Red List" substances, and this would probably include toxic waste incinerators, to be authorised by Her Majesty's Inspectorate of Pollution using standards based on the "batneec" (best available technology not entailing excessive costs) concept.

### Conclusions

This article has described a novel process for the safe low-temperature destruction of organic

Priority Pollutants	
Provisional red list	Priority candidate list
Mercury	2-Amino-4-chlorophenol
Cadmium	Anthracene
Lindane	Azinphos-ethyl
DDT	Biphenyl
Pentachlorophenol	Chloroacetic acid
Hexachlorobenzene	2-Chloroethanol
Hexachlorobutadiene	4-Chloro-2-nitrotoluene
Aldrin	Cyanuric chloride
Dieldrin	2, 4-D
Endrin	Demeton-O
Chloroprene	1,4-Dichlorobenzene
3-Chlorotoluene	1,1-Dichloroethylene
PCBs	1,3-Dichloropropan-2-ol
Triorganotins	1,3-Dichloroprene
Dichlorvos	Dimethoate
Trifluoralin	Ethylbenzene
Chloroform	Fenthion
Carbon tetrachloride	Hexachloroethane
1,2-Dichloroethane	Linuron
Trichlorobenzene	Mevinphos
Azinphos-methyl	Parathion
Fenitrothion	Pyrazon (Chloridazon)
Malathion	1,1,1-Trichloroethane
Endosulfan	
Atrazine	
Simazine	

waste materials. Current understanding of the process is such that it can be stated with some confidence that all of the entries in the Table, apart from mercury and cadmium, would be amenable to destruction. Although it has not yet been developed beyond pilot rig scale, appraisal of the process suggests that it may be both "bat" and "neec" for categories of both radioactive and non-radioactive organic waste which are troublesome to dispose of safely by any other acceptable means.

## The Faraday Lecture on Platinum

On 22nd February, 1861 Michael Faraday delivered a Friday Evening Discourse on platinum to the members of the Royal Institution, London. Faraday's talks were highly popular, and his "Lecture on Platinum" came to be regarded as a classic. However, the meeting did not take the form that he had originally intended. In France, Henri Sainte-Claire Deville and Jules Henri Debray had devised a lime-block furnace fired by a mixture of oxygen and coal gas in which platinum could be melted and refined. This was a major advance in technology, and when the French and British patents were filed in 1857 the British rights to the process were at once acquired by George Matthey; indeed after a lengthy period of development this method became the first by which platinum could be successfully melted commercially on a large scale. In view of the great interest in it, Faraday invited Deville to demonstrate the process at the Royal Institution, and the

"intention was to have fused here some thirty or forty pounds of platinum, and so to have made manifest, through my mouth and my statement, the principles of a new process in metallurgy in relation to this beautiful, magnificent, and valuable metal".

However, in early February, 1861 it was decided that the time was not right for the process to be carried out in front of a public audience. Thus at short notice Faraday, drawing on his wide knowledge of the platinum metals, had to prepare and deliver a lecture of his own (1), and an abridged version of this historic address was reprinted here in 1961 (2).

Following tradition, on Friday, 13th October 1989, Professor John M. Thomas, F.R.S., Director of the Royal Institution, and also an internationally recognised authority on

- ### References
- 1 House of Commons Environment Committee on Toxic Waste, Volume 1 (Report with Appendices), H.M.S.O., March 1989
  - 2 H. Mishima, T. Iwasita, V. A. Macagno and M. C. Giordano, *Electrochim. Acta*, 1973, 18, (4), 287
  - 3 H. N. Po, J. H. Swinehart and T. L. Allen, *Inorg. Chem.*, 1968, 7, (2), 244
  - 4 M. Fleischmann, D. Pletcher and A. Rafinski, *J. Appl. Electrochem.*, 1971, 1, (1), 1
  - 5 "Inputs of dangerous substances to water : Proposals for unified systems of control", Department of the Environment, 1988

heterogeneous catalysis, delighted Members and their guests when he presented the Faraday Lecture of the Royal Society of Chemistry, choosing to pay homage to the scientific genius of Michael Faraday during a most informative and interesting discourse on "Platinum". As is customary at the Royal Institution, Professor Thomas carried out a wide range of experiments which demonstrated in a most entertaining way some of the remarkable properties of platinum, including a number which are the basis of many important industrial, medical and scientific processes and others which have not yet been commercially exploited.

When concluding his presentation he thanked Johnson Matthey for their help with the demonstrations, and in particular the loan of the platinum exhibited. Again he was following the example of Faraday, who in 1861 recorded his indebtedness to "Messrs. Johnson and Matthey.... for these ingots, and for the valuable assistance in the illustrations".

The spectacular nature of Professor Thomas's performance, his respect for Michael Faraday—both as a person and as a scientific investigator—and his wide knowledge of the science and technology of platinum, cannot be adequately conveyed in the written word.

Fortunately the Royal Institution made an audio-visual tape recording of the events of the evening, and plans are in hand to make copies of this available. Details may be obtained from: The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS.

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- 1 M. Faraday, in "A Course of Six Lectures on the Chemical History of a Candle, to which is added A Lecture on Platinum", ed. W. Crookes, Charles Griffin, London, 1865, pp. 173-204
  - 2 *Platinum Metals Rev.*, 1961, 5, (1), 26-29