

Ruthenium-Mediated Electrochemical Destruction of Organic Wastes

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No industrial process is 100 per cent efficient and the generation of waste, both organic and inorganic, is an unavoidable reality. The recycling of waste is becoming increasingly important as concerns about the environment and the availability of resources come more to the fore, but there remain many waste streams which are not yet suitable for recovery of their reusable content, on the grounds of cost or practicality. Historically, the disposal of such wastes has been either via incineration or release into the environment after neutralisation or immobilisation, in a landfill site or into a drain or sewer, or the like. These options are becoming more restricted as regulations tighten and public perception of any but the most benign discharges worsens. This paper sets out reasons for using electrochemical oxidation with a ruthenium electrocatalyst to provide an effective and environmentally friendly alternative to other technologies. Electrochemical oxidation can effect mineralisation of toxic organic species with minimal generation of secondary waste and efficient recovery of the ruthenium mediator and is particularly suited for the treatment of highly chlorinated and aromatic compounds.

Organic wastes, of the types which cannot be converted into benign biodegradable species, are often treated by oxidation, usually incineration, although other chemical treatments are sometimes used. Many of the oxidants which could be used are ruled out by cost or toxicity.

The use of air for such oxidations, normally by high temperature incineration, is the cheapest in terms of reagents. The current best-available technology is capable of achieving essentially complete destruction of even refractory materials. However, the combustion products from many organic materials, in particular chlorinated species, contain acidic gases (for example, hydrogen chloride, sulphur oxides and nitrogen oxides) which must be scrubbed to very low levels before discharge. As excess air is always used, the volumes of gases for treatment tend to be large, leading to large scrubbers and other related equipment, and associated increased costs. Incomplete combustion, possibly due to maloperation, can lead to the production of secondary species, such as dioxins and dibenzo-

furans which are highly toxic and limited, by Regulatory bodies, to low ppb levels in the discharges. Toxic waste incineration has thus tended to become very 'high-tech' in recent years, with only a few highly specialised facilities treating most of the waste destined for combustion. Public perception of incinerators, particularly those treating toxic wastes, is poor or hostile, and the licensing of new facilities in most countries in the developed world is becoming very difficult and sometimes almost impossible.

Table I
Comparison of Oxidation Costs*

Oxidant	Cost/mole of [O] equivalent, £
Electron	0.01
Hydrogen peroxide	0.058
Potassium dichromate (Cr ^{VI})	0.18
Ceric nitrate (Ce ^{IV})	8.68

* The Appendix contains more details of comparative costs

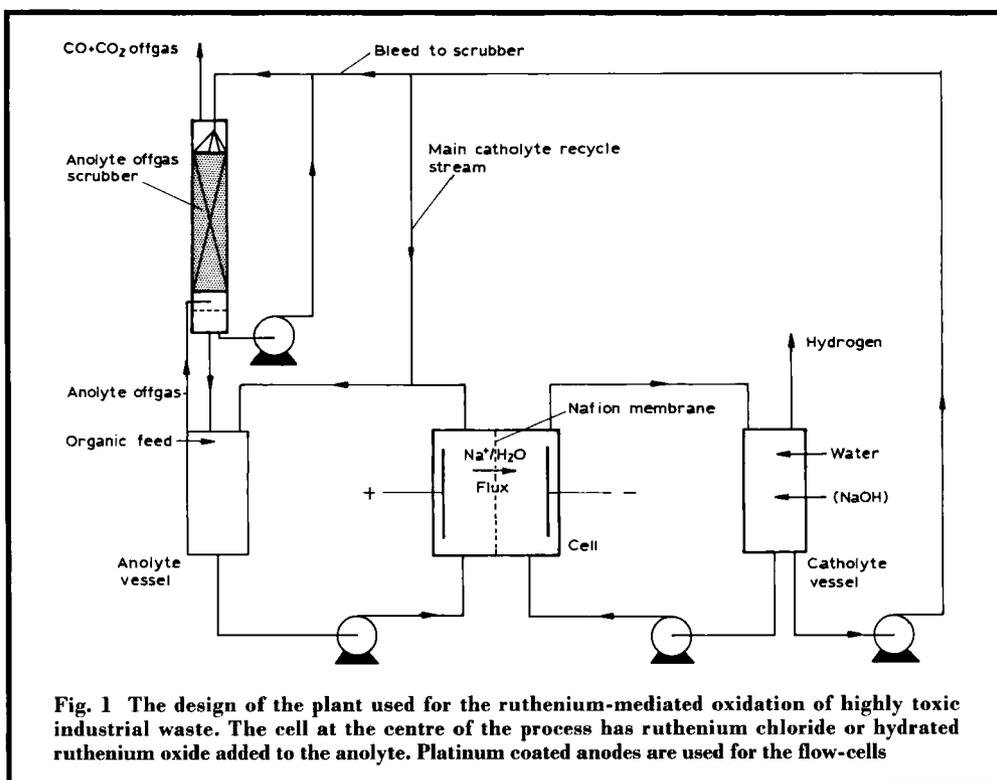


Fig. 1 The design of the plant used for the ruthenium-mediated oxidation of highly toxic industrial waste. The cell at the centre of the process has ruthenium chloride or hydrated ruthenium oxide added to the anolyte. Platinum coated anodes are used for the flow-cells

However, the use of electrochemical oxidation to treat organic industrial waste gives a cheaper, cleaner and renewable alternative: the 'electron'. The 'electron' is also cheaper than chemical oxidants on a per/mole basis, see Table I.

In principle, electrochemical oxidation has a number of advantages over oxidation using conventional oxidising agents. In practice, however, direct electrochemical oxidation of organic species is often difficult due to mass transfer and kinetic restraints at the electrode surface and competing reactions with the electrolyte. Many of the restrictions can be overcome by the use of a mediator which is easily oxidised at the anode surface to a species which then reacts in the bulk solution with the organic substrate. The mediator can be re-oxidised at the anode for further use and can thus be termed an electrocatalyst as it is not consumed in the overall reaction.

The silver-mediated electrochemical oxidation of organics (SILVER II™) has been under

development by AEA Technology for some time as a possible process for the complete oxidation of a number of types of organic waste or the organic waste component in a mixed waste. However, in the silver-mediated system, the presence of significant amounts of halogen (usually chlorine) in the organics being oxidised can result in the formation of substantial amounts of insoluble silver halide(s), which are, at best, a nuisance.

Here an alternative, ruthenium-mediated electrochemical system is described, see Figure 1, which has many similarities to the SILVER II™ system but which is not affected by the presence of halogen, and in particular by chlorine.

Chemical Considerations

In order to understand the internal workings of the ruthenium-mediated oxidation system, it is necessary to consider some aspects of the aqueous chemistry of ruthenium. Ruthenium can form compounds with a multiplicity of

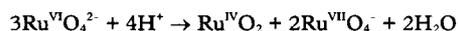
oxidation states, ranging from -2 to +8. Its chemistry in aqueous solution mainly relates to the +3, +4, +6, +7 and +8 oxidation states, with the +3 and +4 states being the most stable. Ruthenium is normally supplied as the trichloride, "RuCl₃·(H₂O)_n" (n = 2 or 3), a very soluble dark red-brown solid which contains a complex mixture of chloro and chlorohydroxo complexes, many of which are polymeric and contain mainly Ru(IV) (1).

Although "ruthenium(III) trichloride" is the form in which ruthenium is initially added to the ruthenium-mediated electrolytic system, Ru(IV), in the form of hydrated RuO₂ is of much greater significance. The great insolubility of this oxide in water ensures that its production is favoured when ruthenium oxo-anions in high valent states are reduced (in a similar manner to the easy formation of insoluble MnO₂ when MnO₄⁻ is used as an oxidant).

The hydrated oxide can be dissolved oxidatively (for example, using oxygen, persulfate or permanganate) in alkaline solution (pH > 12) to yield a solution of the orange ruthenate ion, RuO₄²⁻ (Ru(VI)):



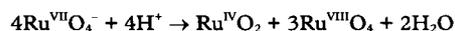
Ruthenate is only stable at high pH and in the absence of reducing agents. If the pH is lowered, RuO₄²⁻ disproportionates to give hydrated Ru(IV)O₂ and green perruthenate, Ru(VII)O₄⁻:



Perruthenate solutions are unstable and decompose, either with the formation of O₂ and RuO₂:



or, if the pH is below ~7.5, the decomposition can produce RuO₄:



Important points to note from the above are:

- (i) The favoured reduced form of uncomplexed ruthenium in near-neutral aqueous solution is Ru(IV)O₂.
- (ii) Uncomplexed ruthenium exists in aqueous solution as neutral or anionic species.

(iii) Partial oxidation of Ru(IV) in neutral or acid solution, followed by disproportionation, forms ruthenium tetroxide.

Ruthenium Tetroxide

Volatile RuO₄ (b.p. ~130°C), like isostructural OsO₄, is a powerful and unstable oxidising agent. It may be prepared from an acidic solution or suspension of any one of a number of ruthenium salts or hydrated RuO₂ by treatment with a powerful oxidant, such as MnO₄⁻, Cl₂, IO₄⁻, Ce⁴⁺ or NaOCl (bleach). Pure RuO₄ is not particularly stable in either the liquid or vapour phase and tends to decompose, eventually forming RuO₂. It is freely soluble in organic solvents, although its reactivity limits the solvents which can be used (typically CCl₄ or CHCl₃, plus some polar solvents with little nucleophilic character). These solutions of RuO₄ are reasonably stable if kept in the dark and with a slight excess of the oxidant which formed the tetroxide. It is not normally prepared in bulk quantities, but is generated for immediate use.

Organic Oxidation by Ruthenium Oxo-Species

Ruthenate, perruthenate and, in particular, ruthenium tetroxide have all been studied as oxidants for organic synthesis. RuO₄ has been studied fairly comprehensively and preparative oxidations in both the aqueous and organic phases (mainly in unreactive solvents like CHCl₃ and CCl₄) have been described (2, 3), with the exact conditions being tailored to suit the particular synthesis.

One of the first investigations of organic oxidations using RuO₄ included the following description using only 10 mg of tetroxide with some common solvents:

"Benzene – vigorous explosion; pyridine – no explosion, only flame; anhydrous ether – small explosion, followed by yellow flame" (4).

Of particular interest in the context of destructive, rather than synthetic, oxidation by RuO₄ are the following properties:

- The solubility of RuO₄ in both polar and non-polar organic solvents, allows oxidation to take

place within an immiscible organic phase rather than only at the aqueous/organic interface.

- RuO₄ cleaves many C=C bonds, usually yielding carbonyl compounds in the first instance.
- RuO₄ is able to oxidise saturated hydrocarbons under mild conditions (5).
- The complete oxidation of the highly toxic and relatively unreactive polychlorodibenzo-*p*-dioxins (6) and polychlorinated biphenyls (7) by RuO₄ has been reported.
- Aromatic nuclei are attacked and are completely degraded.

Destruction of Organics by Mediated Oxidation

Direct electrochemical oxidation is in principle easily capable of oxidising any organic species to carbon dioxide, and other inorganic products, based on thermodynamic, electrode potential considerations alone. However, in practice this is usually ruled out by a combination of slow electrode kinetics, difficult mass transfer of substrate to the electrode and competition from side reactions, such as oxygen evolution, so that mediated oxidation must be used. A suitable electro-active mediator must:

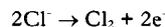
- be soluble in the electrolyte to an extent which minimises any restrictions on mass transfer to the anode;
- have fast electrode kinetics to minimise activation overpotential at the anode;
- react rapidly in the bulk solution with a wide range of organic substrates, forming a reduced species which is easy to re-oxidise at the anode;
- form no insoluble or complex species which remove the mediator irreversibly from solution.

Based on electrode potential considerations alone, a number of possible electrochemical couples may be suitable, but most are ruled out by one or more of the above criteria. However, the simple oxidation of chloride can be used to regenerate RuO₄ in a *double*-mediated, continuous system.

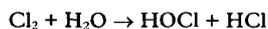
The electrolysis of sodium chloride, NaCl, solution to produce chlorine, Cl₂, and sodium hydroxide, NaOH, is one of the best understood electrochemical processes. This electrolysis is carried out industrially in a variety of cell types

and is the basis for a worldwide industry with a capacity of millions of tonnes/year (8).

The principal process at the anode surface is oxidation of chloride ions (with very minor oxidation of water to form oxygen):



At the low pH normally encountered in chlorine cells, the product is gaseous chlorine. As the pH is raised, the hydrolysis of the chlorine to form HOCl begins to predominate and at pH 5.5 HOCl is the sole product, from hydrolysis of the Cl₂ formed at the anode:



The hypochlorite (HOCl or OCl⁻, depending on the pH of the solution) generated electrochemically can be used to drive mediated organic oxidations and replace the continuous additions of, for example, NaOCl solution. As a mediating couple, the chloride/hypochlorite system has a number of advantages:

- NaCl is soluble up to ~5M in water, so there is little mass transfer limitation on the anode reaction.
- The production of chlorine at a suitable anode is a fast reaction and the overpotential, even at high current density, is only a few tens of mV.
- The reaction of the chlorine either directly with Ru(IV) or with water to form HOCl is a fast reaction and the reduced product (Cl⁻) is easily re-oxidised.
- The complexation or reaction of Cl⁻ to form species which cannot be re-oxidised is unlikely.

The anodic production of chlorine in a NaCl anolyte containing a small amount of dissolved ruthenium or hydrated RuO₂ thus produces highly reactive RuO₄ as long as current is passed. The RuO₄ in turn attacks organic material fed to the anolyte, ultimately oxidising it to carbon dioxide, carbon monoxide and water (plus sulfate, phosphate or nitrate from heteroatoms such as S, P and N, for example).

It is this continuous coupling of electric power with oxidation which makes the ruthenium oxidation system so useful for the treatment of organic wastes, in particular wastes with a high

chlorine content, which are often toxic and difficult to dispose of. The integration of the ruthenium-mediated oxidation into a complete system is described next.

Process Description

At the heart of the ruthenium-mediated oxidation process, see Figure 1, is an electrochemical cell, very similar to the type used for chlorine manufacture. The anode, where chloride is oxidised, has to favour the production of chlorine over oxygen and in practice this restricts the material (or the coating) to platinum or platinum/iridium (or RuO₂, but not the hydrated form). Modern cell designs have a titanium anode which is coated with a few microns of the noble metal or oxide (9). Development trials of the ruthenium process have employed anodes consisting of either platinum mesh (lab-cell scale) or 2.5 µm platinum coated on titanium (flow-cell scale).

As the anolyte and catholyte chemistries are very different, the cell is divided with a Nafion™ cation exchange membrane which permits the passage of cations to carry the cell current but prevents bulk mixing of the two solutions. Nafion™ is a sulfonated perfluoropolymer which combines extreme chemical resistance with selective permeability to cations and is widely used industrially in cells for chlorine production. The selective permeability has a further advantage in that it prevents migration of soluble ruthenium species (which tend to be anionic under operating conditions) from anolyte to catholyte.

A number of materials can be used for the cathode – stainless steel has been used during development trials, but nickel, or one of the proprietary types of chlor-alkali cathode, would be a better choice for a full-scale plant.

Electrolyte Chemistry

The following processes occur in the anolyte:

- (a) Cl₂ production at the anode,
- (b) Cl₂ hydrolysis to HOCl,
- (c) RuO₄ production (with reduction of the HOCl to Cl⁻, which is available for further oxidation to Cl₂ at the anode),
- (d) The reaction of the RuO₄ with the organic wastes fed to the anolyte (with the formation of

insoluble hydrated RuO₂) forming CO and (mainly) CO₂, plus inorganic anions from, for example, S and P,

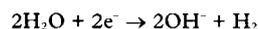
(e) RuO₂ re-oxidation to RuO₄ by further HOCl.

The overall process thus consists of two linked cycles, (a)–(c) and (c)–(e). The oxygen which ultimately appears as CO+CO₂ is derived from water molecules in the anolyte, via the formation and reduction of HOCl and RuO₄. The overall anode/anolyte reaction thus becomes:

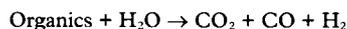


with the electrons passing to the external cell circuit.

Current through the cell is carried by Na⁺ ions which cross the membrane to the catholyte, usually in association with 1 to 3 molecules of water per Na⁺ ion. The Na⁺ ions do not react at the cathode, but merely transport charge to the catholyte (NaOH solution) while the cathode reaction is hydrogen evolution:



The transfer of Na⁺ ions and water to the catholyte and the formation of hydroxyl ions produces NaOH solution, exactly as in a chlor-alkali cell. The catholyte thus becomes more alkaline while the production of hydrogen ions in the anolyte causes a shift to a more acid pH. These changes are controlled by returning NaOH solution from the catholyte to the anolyte at the same rate as Na⁺ transfers from the anolyte. The overall reaction across the cell then becomes:



The process is thus a net *consumer* of water, rather than a producer as is the case with most organic oxidations, and the organic hydrogen fed to the anolyte appears from the cathode as hydrogen, rather than as water. A water feed is thus needed to replace that lost as H₂ and CO+CO₂ or, alternatively, dilute organic streams can be treated with equal ease. Combustion of the hydrogen can be used to recover about 30 per cent of the power fed to the cell as useful heat, if this is deemed cost-effective and/or necessary.

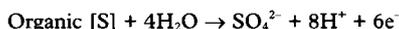
Table II
Summary of Substrates Oxidised and Offgas Compositions

Substrate	Temperature, °C	Carbon dioxide (2), maximum per cent	Carbon monoxide (2), maximum per cent
(2-Chloroethyl)ethyl sulphide (1)	50	73-95	2.6-6.7
Tributyl phosphate	50	93	2.6
Dodecane	80	93	2.9
Chlorobenzene	80	85.5	11.8
Trichlorobenzene (1)	95	68-83	0.8-1.2
PCBs (Aroclor 54)	90	67.6	1.2
Pentachlorophenol	85	91.7	7.7
2,4-Dinitrotoluene	85	76.5	2.3
Hexachlorobutadiene	95	84.8	16.9
Tetrachloroethylene	60	96.1	21.6

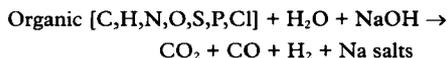
(1) Results from repeat runs

(2) The maximum percentages of CO₂ and CO observed during run(s) are not necessarily observed simultaneously

If heteroatoms, such as Cl, S or P, are present in the organic feed additional NaOH has to be fed to the system (usually to the recycle stream from the catholyte) to balance the additional formation of H⁺ in the anolyte, for instance:



The net product from organic heteroatoms is the appropriate sodium salt (sulfate or phosphate, for instance). Note that organic chlorine produces chloride, which is one of the process reagents. When heteroatoms are present the overall reaction becomes:



Offgas Treatment

Electrolysis of chloride-containing solutions, like the ruthenium process anolyte, can lead to chlorine evolution if the pH is allowed to fall. Also, RuO₄ is volatile and could be flushed from the anolyte along with the CO₂ and CO formed from organic oxidation. In order to prevent either species from escaping, some of the recycle stream of NaOH is used to maintain alkaline conditions in a scrubber through which the off-gases from the anolyte pass. Any Cl₂ is absorbed as NaOCl while the RuO₄ is absorbed as "hyper-ruthenic acid" (H₂RuO₅) or its sodium salt. In

this manner, the oxidising power of both the Cl₂ and the RuO₄ is returned to the anolyte and the escape of valuable ruthenium is prevented.

Operating Conditions

The process is typically operated with an electrolyte temperature of 50 to 80°C. The anolyte consists of a NaCl solution held near neutral pH and usually buffered to limit pH changes. The catholyte consists of NaOH solution, typically 35 wt.% NaOH or less (the limit being set by the properties of the membrane – the process will operate chemically at up to 50 wt.%). Conditions in the anolyte are highly aggressive to materials like stainless steel, so titanium or polymers, such as PTFE or PVDF, must be used there. The catholyte is much less aggressive and cheaper materials, such as polypropylene can be used.

Organic Substrates

The ruthenium-mediated system is surprisingly reactive compared to literature reports of organic oxidations using RuO₄. This may be because the oxidation is carried out in the aqueous phase rather than in an inert solvent, and thus the formation of reactive radicals from water, for example, OH[•], is possible.

In Table II is shown some of the compounds which have been successfully oxidised during

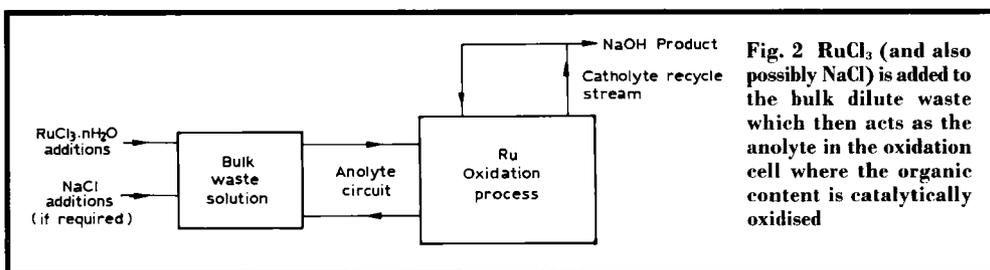


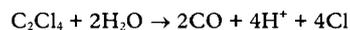
Fig. 2 RuCl₃ (and also possibly NaCl) is added to the bulk dilute waste which then acts as the anolyte in the oxidation cell where the organic content is catalytically oxidised

development trials, together with the composition of the gases leaving the anolyte. The percentage of CO+CO₂ in the anolyte offgas gives a good indication of the electrochemical efficiency (that is the percentage of the current flowing which is driving useful oxidation, rather than oxygen evolution, at the anode).

The amount of current which has to flow per mole of organic material oxidised is very dependent on the chemical nature of the organic material and the composition of the offgases. For instance, in the slightly extreme case of tetrachloroethylene, C₂Cl₄, oxidation to CO₂ requires 4 faradays/mole:



while production of CO is actually hydrolysis rather than oxidation:



Oxidation to CO always requires less current to flow than oxidation to CO₂, with a consequent saving in the power consumed by the cell.

The ruthenium process is thus able to oxidise highly chlorinated substrates, such as arise as waste from pesticide and herbicide manufacture, organophosphates (insecticides) and aromatic nitro-compounds (explosives manufacture) and can do so when these are in association with chloride ion or other salts in an aqueous stream. The ruthenium process is therefore seen as complementary to the related SILVER IITM electrochemical oxidation process in terms of feeds.

Economic and Practical Aspects

Like most electrochemical processes, the economics of ruthenium-mediated oxidation are closely tied to the cost of the electric power

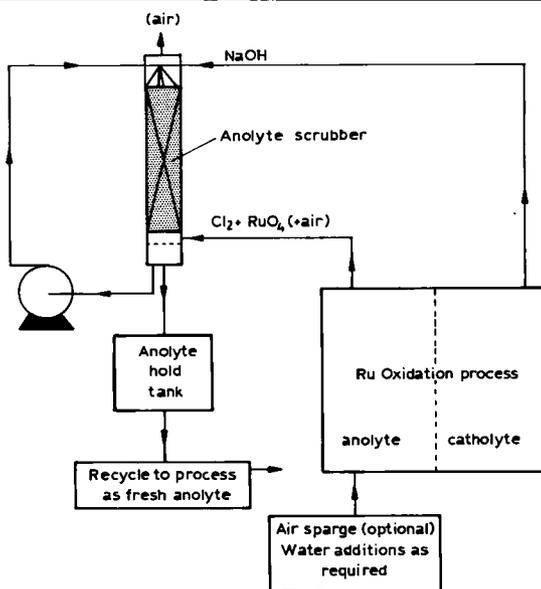
supplied to the cell. Electrochemical cells and DC power supplies are also expensive items of equipment and cells suffer from a relatively poor economy of scale compared to many process plant items (doubling the plant throughput requires twice as many cathode-anode pairs, while pipework and tankage would only have to be increased by a factor of ~2^{0.6}). The treatment of bulk quantities of relatively benign organic wastes is therefore not likely to be very economic unless driven by environmental and regulatory pressures which eliminates incineration, for instance.

When organic wastes arise in conjunction with salts and water, as is the case with many industrial processes, particularly the manufacture of pharmaceuticals, dyestuffs and explosives, ruthenium-mediated oxidation becomes a much more attractive prospect. The incineration of salty wastes is often not very practical and the toxicity/salinity of the waste may rule out more 'aqueous' treatments such as reed beds and biodegradation. The dilution of the organic in the water is not a particularly limiting factor.

The 'ideal' feed for the process shown in Figure 1 would consist of a mixture containing the correct amount of water to replace that consumed to form the CO+CO₂ and H₂. However, more dilute feeds can be treated on a batch recycle basis, and the waste stream itself functions as the anolyte with additions of ruthenium (and possibly NaCl if it is not already present) being made, see Figure 2. If Na⁺ ions are already present in the waste liquor, a 'product' of catholyte NaOH solution can be withdrawn for recycle/reuse, if desired.

The ruthenium is only required at low concentrations as its role is principally catalytic, but

Fig. 3 One method for recovering the ruthenium after catalytic oxidation of the various organic wastes in the cell is to allow the pH to fall, thereby forming chlorine along with the RuO_4 . The chlorine gas and volatile RuO_4 are swept from the anolyte by an air sparge and absorbed (as hypochlorite and perruthenate) in the offgas scrubber which is fed with catholyte NaOH . The Ru - and hypochlorite-containing liquor is then used to prepare the anolyte for treatment of the next batch of waste



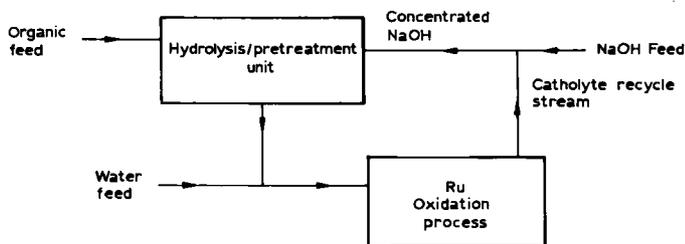
its cost probably precludes its disposal, albeit as insoluble and inert RuO_2 , with the treated waste. However, the low solubility of the RuO_2 , which is the form the ruthenium takes when the cell is switched off and the electrolyte is allowed to stand, means that simple filtration can be used for recovery.

Alternatively, the ruthenium can be swept from the anolyte by allowing the pH to fall so that some chlorine is evolved. This (possibly assisted by an air sparge) sweeps the ruthenium from the anolyte as RuO_4 , which is then absorbed into NaOH (formed simultaneously at the cathode) using the anolyte offgas scrubber. In this way a fresh batch of anolyte or reagent is effectively reformed, and can be used for dosing the next

batch of waste liquor requiring treatment, see Figure 3.

The incoming waste liquor may contain metal ions which would precipitate in the membrane and these could therefore be usefully removed from the waste before the oxidative step, for separation and disposal. The continuous production of NaOH at the cell cathode provides a convenient source of caustic with which many metals can be precipitated as their insoluble hydroxides. An alternative use for the catholyte NaOH is that refractory materials (such as highly chlorinated, hydrophobic solids, for example hexachlorobenzene) may be partially hydrolysed using the catholyte recycle stream (10). Figure 4 shows how the additional NaOH that must

Fig. 4 The NaOH used to balance organic Cl , S , P , etc., can be added to the catholyte recycle stream to give a highly concentrated solution for pretreatment of the waste feed, for example to precipitate metals or hydrolyse refractory organics in the feed



be added to balance the halogen content of the organics, may be added to the recycle stream to give the highest practical concentration for the hydrolysis.

Conclusions

Double mediated electrochemical oxidation using the Cl(-I)/Cl(I) and Ru(IV)/Ru(VIII) couples in a cell very similar to a chlor-alkali cell has been shown to have promise for the treatment of organic waste streams, particularly halogenated or dilute, salty liquors. Currently, studies are concentrating on optimising the core process and examining the application of the system to a variety of 'real' wastes with an industrial origin.

Appendix

In a cell (193000Cb, 54 Ah) in which oxidation occurs, with cell voltage of 3V, 2 moles of electrons carry out the oxidation process, equivalent to one mole of [O] and costs ~ 1p. The same amount of oxidation delivered using hydrogen peroxide (one of the cheapest chemical oxidants) at a nominal cost of £600/te for a 35 wt.% solution (£1700/te H₂O₂, 29411 moles [O]) costs ~ 5.8 p. High-valent metal-based oxidants such as Cr^{VI} and Ce^{IV} are much more expensive. Bulk K₂Cr₂O₇ costs £1835/te (3400 moles, 10200 moles [O]) while Ce^{IV} nitrate ~ £10000/te (2300 moles Ce^{IV}, equivalent to 1150 moles [O]) and the equivalent oxidation, carried out using this reagent costs £8.68 (all costs assume 100 per cent efficiency for simplicity). Like peroxide, the electron (the oxidant itself) leaves no residues which are toxic or difficult to dispose of, while oxidants like Cr^{VI} and Ce^{IV} leave large quantities of spent oxidant for disposal.

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Direct Methane Oxidation by Platinum Catalyst

The conversion of natural gases into more useful alcohols is usually achieved by changing the alkane component of the natural gas into a combination of carbon monoxide and hydrogen (synthesis gas) which is then converted to higher order alkanes by the Fischer-Tropsch reaction (1). These processes require a lot of energy, so it would be less costly if the alkane component, usually methane, could be directly converted into alcohols, by selective oxidation; the main difficulty being the low reactivity of the C-H bond. One such method, from Catalytica Advanced Technologies Inc., California, used toxic mercury(II) salts, and resulted in methane being converted into a methanol ester in an approximately 43 per cent yield.

Now, however, the same group has reported the development of a successful, stable platinum catalyst (2). Platinum salts were already known to be more efficient for the oxidation of methane in strong oxidising acids, but were not stable in hot (>100°C) acid. By utilising stabilising ligands, catalysts of greater stability were devel-

oped. They found that the addition of a bidiazine ligand to a platinum(II) salt gave high stability to strong acids and oxidising conditions. One of the most effective catalysts was dichloro(η-2-{2,2'-bipyrimidyl})platinum(II), [(bpym)PtCl₂]. Three key steps were proposed for the conversion of methane: C-H activation, oxidation and functionalisation.

The present reaction, which takes place at 220°C, converts ~ 72 per cent of the methane to methyl bisulfate, and is thought to proceed via the formation of a methyl-platinum species. The authors state that the mechanism of the C-H reaction needs more investigation as the factors controlling its reactivity could lead to greater control of the reaction selectivity.

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