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(54) Electrochemical regeneration of metal oxide after use for oxidative treatment of waste

(57) In a method of oxidation of a substance such as polychlorinated biphenyl waste by treatment with a metal oxide selected from the group consisting of ruthenium, osmium, iridium, and rhodium in the higher valency state, after oxidation of the substance the metal oxide is regenerated to the higher valency state by electrochemical means.

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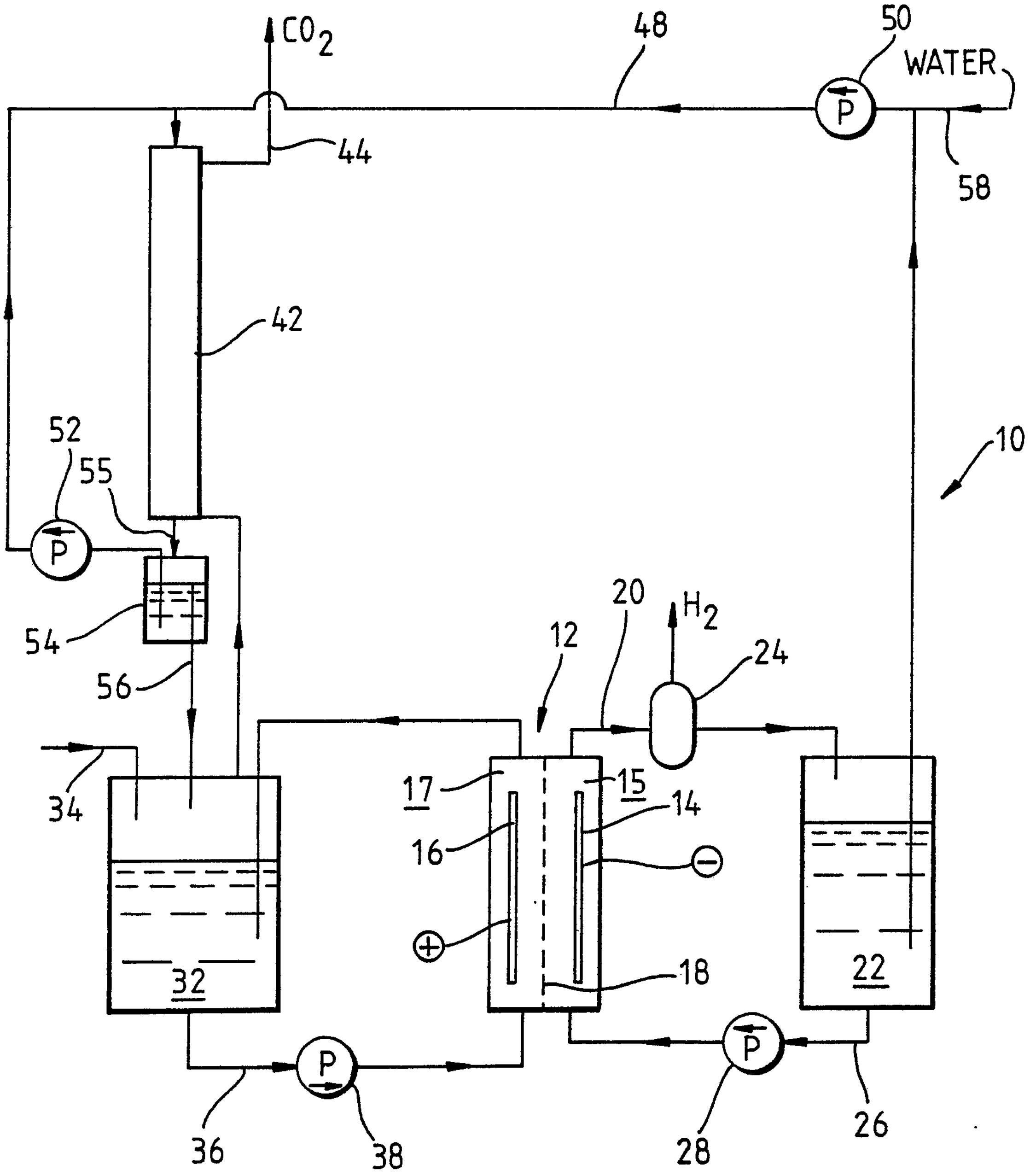

CO$_2$
48
50
WATER
44
58
42
10
52
55
P
54
56
20
H$_2$
24
12
34
17
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32
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P
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36
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A method of oxidation

This invention relates to a method of oxidation, and is more particularly but not exclusively concerned with the oxidative treatment of polychlorinated biphenyl (hereinafter referred to as "PCB") waste matter.

According to the present invention, there is provided a method of oxidation of a substance by treatment with a metal oxide in the higher valency state thereof and selected from the group consisting of ruthenium osmium, iridium, and rhodium, the metal oxide after said oxidation treatment being regenerated to the higher valency state thereof by electrochemical means.

Preferably, the electrochemical means comprises an electrochemical cell comprising an anolyte comprising an aqueous solution comprising an alkali metal chloride, hydroxyl ions, and said oxide, a catholyte comprising an aqueous alkali solution, and a cation exchange membrane for separating the anolyte and the catholyte.

The metal may comprise a soluble salt thereof, and the membrane may comprise a sulphonated fluoropolymer. The anode of the cell may comprise platinum or a platinum coated substrate, for example titanium. The cathode may comprise a steel preferably a stainless steel.

Preferably, the method includes transferring a portion of the catholyte back to the anolyte, and desirably includes passing said portion of the catholyte through a caustic scrubbing means.

Advantageously, the anolyte comprises an alkaline or a neutral buffered brine.

In one form of the invention, the substance comprising PCB waste matter is added to the anolyte and is oxidised by higher valency ruthenium oxide in the anolyte.

In another form of the invention, the metal oxide in the higher valency state thereof may be withdrawn from the anolyte so as to oxidise the substance outside the cell, the reduced metal oxide subsequently being recycled to the anolyte in the cell for regeneration to said higher valency state.

In one use of the invention, waste matter to be oxidised such as PCB may be fed into the anolyte. An electric current passing through the cell generates chlorine at the anode:

$$2Cl^- \longrightarrow Cl_2 + 2e^- \qquad (1)$$

The chlorine reacts with OH^- ions in the anolyte to form OCl^-:

$$Cl_2 + 2OH^- \longrightarrow OCl^- + Cl^- + H_2O \qquad (2)$$

The OCl^- oxidises the Ru salt or oxide to RuO_4:

$$\text{eg } RuO_2 + 2OCl^- \longrightarrow RuO_4 + 2Cl^- \qquad (3)$$

The RuO_4 oxidises the PCB waste matter to carbon dioxide, water and the chloride ion and is itself reduced to RuO_2. The RuO_2 and chloride ions from the PCB and those formed in reaction (3) are then re-oxidised as shown above.

The current flowing through the cell is carried by Na^+ ions crossing the membrane, which is selectively permeable to cationic species. Some water molecules also cross the membrane in association with the Na^+ ions. The Ru-containing species in the anolyte, which are anionic or neutral are prevented from crossing the membrane into the catholyte, where they would otherwise be deposited on the cathode as RuO_2 and rendered unavailable for further reaction.

At the cathode, H_2 is produced:

$$2H_2O + 2e^- \dashrightarrow H_2 + 2OH^- \qquad (4)$$

The overall reaction in the cell is, for a typical PCB ($C_{12}H_5Cl_5$):

$$C_{12}H_5Cl_5 + 24\ H_2O \dashrightarrow 12CO_2 + 26.5\ H_2 + 5Cl^- \qquad (5)$$

Overall, there is a net <u>consumption</u> of water as the O atoms in the CO_2 produced come from water molecules or OH^- ions in the anolyte, and hydrogen is evolved from the cathode. The consumption of OH^- in the anolyte to form OCl^-, the transfer of Na^+ across the membrane and the formation of OH^- in the catholyte is equivalent to the transfer of NaOH from anolyte to catholyte. If this was not countered, the anolyte would become less and less alkaline and eventually become acid, at which stage there would be evolution of Cl_2. This is not necessarily a problem, as RuO_4 can be formed by Cl_2

oxidation but it may be inconvenient and may not be as efficient as the oxidation via OCl^-.

The catholyte alkalinity would increase at the same rate as the anolyte alkalinity decreased if no remedial measures were taken. However, by simply transferring catholyte back to the anolyte at the appropriate rate, with an addition of water to replace that consumed to form CO_2 and H_2, the anolyte and catholyte alkalinities can be held substantially constant. Further, this ensures that any Cl^- or anionic Ru species which manage to cross the membrane do not build up in the catholyte but are continuously returned to the anolyte. Another advantage which accrues from this catholyte to anolyte transfer is that the flow of alkaline liquor can be used in a scrubber before it is returned to the anolyte. The scrubber would be used to remove any Cl_2 (as OCl^-), or RuO_4 escaping from the anolyte since RuO_4 boils at 127° C and has a considerable vapour pressure at the cell operating temperature.

It may be preferable to use a $Na_2CO_3/NaCl$ alkaline or neutral buffered brine as the anolyte. This brine may in fact be the final compositon of a caustic anolyte, since CO_2 generated from the destruction of the PCB will be absorbed into the caustic solution with the formation of Na_2CO_3. The use of a carbonate electrolyte may be beneficial as there should be no problem with CO_2 absorption. Also, the electrolyte has buffer properties and will resist acidification by the formation of HCO_3^- or CO_2. The electrolyte is preferably held at a mildly alkaline pH, which is beneficial as far as the generation of OCl^- is concerned. The catholyte may be either NaOH or Na_2CO_3.

The invention will now be further described by way of example only with reference to the Examples, and the accompanying Figure in the drawing in which a diagrammatic representation of a system including an electrochemical cell is shown for the treatment of waste matter.

EXAMPLE 1

An electrochemical cell with 100 mls of 2M Na_2CO_3/0.1M NaOH/1M NaCl/0.24M Ru solution as anolyte, 10M NaOH as catholyte and separated by a proprietary sulphonated fluoropolymer ion exchange membrane (Nafion 324) was set up. A platinum anode was placed in the anolyte compartment, a stainless steel cathode was placed in the catholyte compartment, and the cell was heated to 60°C.1 ml of trichlorobenzene (a simulant for and frequent component of commercial PCB mixtures) was placed in the anolyte which was stirred vigorously while a current of 2 amps was passed. A solution of 10M NaOH was fed into the anolyte at the correct rate to replace the Na^+ and OH^- ions which were being removed therefrom. A yellow colour developed above the anolyte, followed by a black deposit of RuO_2, confirming that RuO_4 was being generated. Examination of the offgas by IR spectroscopy showed no carbon dioxide, but this is not surprising as the anolyte was alkaline for the duration of the Example. Extraction of the anolyte with methylene chloride after the current had been passed for 4 hours showed only a trace amount of trichlorobenzene remained (gas chromatography analysis).

EXAMPLE II

The cell was set up as in Example 1, but this time with 5M NaCl as both anolyte and cathloyte. 1 ml of chlorobenzene was added to the anolyte and a current of 1 amp was passed for 6 hours. There was an immediate evolution of Cl_2 from the anolyte. Analysis of the offgas by IR spectroscopy showed the presence of carbon dioxide, which could only have arisen from the chlorobenzene. At the end of the Example, the anolyte was extracted with methylene chloride and the extract was shown by gas chromatography analysis to contain no chlorobenzene and small amounts of 1,2- and 1,3-dichlorobenzene.

Referring now to the Figure, a system 10 is shown and comprises an electrochemical cell 12 having a stainless steel cathode 14 in a cathode compartment 15, a platinum anode 16 in an anode compartment 17, and a sulphonated fluoropolymer (Nafion 324) ion exchange membrane 18 separating the cathode compartment 15 and the anode compartment 17. The cathode compartment 15 is connected by a duct 20 to a catholyte reservoir 22, and a gas/liquid separator 24 in the duct 20 removes hydrogen from the catholyte. A return duct 26 from the reservoir 22 is connected to a pump 28 which is connected to the cathode compartment 15. An outlet duct 30 from the anode compartment 17 extends to an anolyte reservoir 32 which has an inlet 34 for waste material (eg PCB). A return duct 36 from the anolyte reservoir 32 connects through a pump 38 to the anode compartment 17.

A gas vent 40 from the anolyte reservoir 32 connects to a scrubber column 42 with an outlet 44 for carbon dioxide and an inlet from a circulation duct 48. The circulation duct 48 extends from the catholyte reservoir 22, through a transfer pump 50 and a scrubber pump 52 to a scrubber reservoir 54, the reservoir 54 having a duct 55 to the bottom of the scrubber column 42, and a discharge pipe 56 such as to maintain a preselected level of scrubbed liquid in the scrubber reservoir 54. A water feed inlet 58 is connected to the circulation duct 48 between the catholyte reservoir 22 and the transfer pump 50.

In operation, waste material is fed into the anolyte reservoir 32 and circulated with anolyte through the anode compartment 17 where the afore-described electro-chemical reactions take place when ruthenium is included in the anode compartment 17. Catholyte from the catholyte reservoir 22 is circulated through the cathode compartment 15. At the same time catholyte from the catholyte reservoir 22 is circulated through the circulation duct 48 by the transfer pump 50 and through the inlet into the top of the scrubber column 42 into which the scrubber pump 52 also discharges from the scrubber reservoir 54, with water being injected through the feed inlet 58. Off-gases from the anolyte reservoir 32 are passed through the gas vent 40 into the scrubber column 42, and CO_2 escapes through the outlet 44. The scrubbed catholyte from the scrubber column 42 discharges into the scrubber reservoir 54 and overflows through the discharge pipe 56.

The system 10 produces RuO_4 on a continous basis for oxidation reactions in the cell 12 or the anolyte reservoir 32. Alternatively the RuO_4 could be removed from the anolyte by extraction, distillation, or possibly by sparging for oxidation reactions elsewhere. For example, RuO_4 is soluble and stable in organic solvents such as chloroform and can be extracted from the anolyte to effect an oxidation in the organic phase. The resulting ruthenium product (RuO_2) after the oxidation could be separated from the organic product by known techniques and subsequently recycled through the cell 12 to regenerate RuO_4 again. The water which will need to be added to the anolyte may be used in this application, since this may provide a suitable interface with the extractant subsequent to the oxidation reaction at which solid dioxides can collect, and can also act as a vehicle for the solids after they have been separated, for example by centrifugal separation.

It will be understood that alternative metal salts and oxides may be used in the invention, such salts and oxides being selected from the group consisting of ruthenium, osmium, iridium, and rhodium, with appropriate changes being made where necessary to the reagents used and the techniques involved.

It can be seen that one advantage of the invention, is that it enables expensive metal oxides such as RuO_4 to be used for oxidative reactions with subsequent regeneration of the higher valency metal oxide from the RuO_2 after oxidative treatment. This is a major advantage when the metal oxide is to be used outside the electrochemical cell.

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Claims

1. A method of oxidation of a substance by treatment with a metal oxide in the higher valency state thereof and selected from the group consisting of ruthenium osmium, iridium, and rhodium, the metal oxide after said oxidation treatment being regenerated to the higher valency state thereof by electrochemical means.

2. A method as claimed in Claim 1, wherein the electrochemical means comprises an electrochemical cell comprising an anolyte comprising an aqueous solution comprising an alkali metal chloride, hydroxyl ions, and said oxide, a catholyte comprising an aqueous alkali solution, and a cation exchange membrane for separating the anolyte and the catholyte.

3. A method as claimed in Claim 1 or Claim 2, wherein the metal comprises a soluble salt thereof.

4. A method as claimed in Claim 2, wherein the membrane comprises a sulphonated fluoropolymer.

5. A method as claimed in any one of the preceding Claims, wherein the anolyte comprises an alkaline or a neutral buffered brine.

6. A method as claimed in any one of the preceding Claims, including transferring a portion of the catholyte back to the anolyte.

7. A method as claimed in Claim 6, including passing said portion of the catholyte through a caustic scrubbing means.

8. A method as claimed in any one of Claims 2 to 4, wherein the substance is added to the anolyte in the cell, and an electric current passed through the cell.

9. A method as claimed in any one of Claims 2 to 4, wherein the metal oxide in the higher valency state thereof is withdrawn from the anolyte so as to oxidise the substance outside the cell.

10. A system for performing the method as claimed in Claim 1, and comprising an electrochemical cell having a cation exchange membrane for separating an anolyte from a catholyte, an anolyte reservoir, duct means connected to the anolyte reservoir for cycling anolyte to and from the cell, a catholyte reservoir, duct means connected to the catholyte reservoir for cycling catholyte to and from the cell, and a return duct means connecting the catholyte reservoir to the anolyte reservoir for returning a portion of the catholyte from the catholyte reservoir to the anolyte reservoir.

11. A system as claimed in Claim 10, wherein caustic scrubber means are connected in series in the return duct means, and a duct for off-gases from the anolyte reservoir is connected to the scrubber means.

12. A system as claimed in Claim 11, wherein a scrubbed catholyte reservoir is in series in the return duct means for receiving catholyte scrubbed by the scrubber means.

13. A method of oxidation substantially as hereinbefore described with reference to Example I or Example II.

14. A method of oxidation substantially as hereinbefore described with reference to the Figure in the accompanying drawing.

15. A method as claimed in any one of Claims 1 to 9, or 13 or 14, wherein the substance comprises polychlorinated biphenyl.

16. A system for performing the method as claimed in Claim 1, and substantially as hereinbefore described with reference to the Figure in the accompanying drawing.

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