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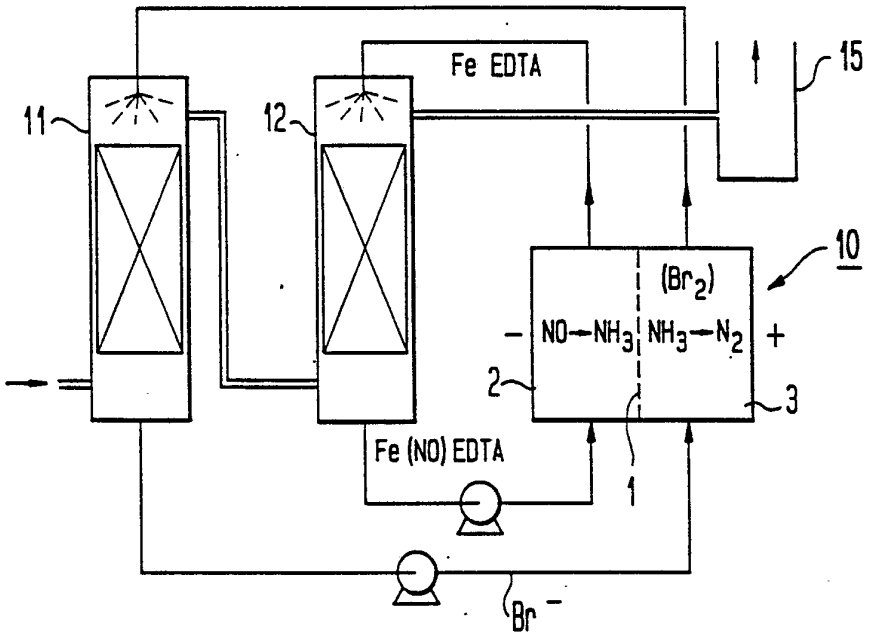

(57) Abstract

The invention concerns a device and a method for removing nitrogen compounds from an aqueous liquid containing nitrogen oxides (NO_x) and/or nitrates (NO_3^-). It comprises an electrochemical cell (10) with a cathode and an anode and a current source applied thereto. According to the invention, the cell is divided by a cation selective membrane into a cathode compartment (2) to be filled with said liquid, and an anode compartment (3) to be filled with an anolyte containing an aqueous solution of an alkali or hydrogen halide such as sodium bromide or sodium chloride, and the membrane (1) is constituted by a microporous fabric of PTFE.

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A DEVICE AND A METHOD FOR REMOVING NITROGEN COMPOUNDS FROM A LIQUID

The invention concerns a device and a method for removing nitrogen compounds from an aqueous liquid containing nitrogen oxides NO_x and/or nitrates NO_3^-, the device comprising an electrolytical cell with a cathode and an anode and a current source applicable thereto.

Environmental protection requires a considerable reduction of the emission of nitrogen oxides in waste gases. As an example, the present limit set by the European Community directives require a reduction of the content of nitrogen oxides to a maximum of 200 mg/m^3 (calculated as $NO_{2)}$ in flue gases from large scale power stations. These low concentrations cannot be obtained only by special measures during the combustion process (so-called primary measures) but require the application of special processes for the removal of nitrogen oxides from waste gases, i.e. denoxing processes.

The process for the removal of nitrogen oxides consists in the reduction of the compound to nitrogen. For flue gases, several industrial processes are already known (Chem. Ing. Techn. 57, 1985, page 717 to 727).

The presence of nitrates in waste waters is also a growing problem. The intensive use of natural manure and fertilizers in agriculture leads to an increasing content of nitrates in subsoil water. In many places in Europe, drinking water producers have difficulties in maintaining the limit below 50 mg/m^3 of nitrates in their final product.

The usual way of removing nitrates from waste waters is by biological processes which are slow and expensive.

EP-A-0 243 889 discloses a process for the electrolytic denoxing of flue gases. The nitrogen oxides are absorbed in a iron-ethylene diamine-tetraacetic acid (Fe-EDTA) complex. The reduction occurs then according to the following reaction equation:

$$2\ Fe(NO)EDTA + 2H^+ + 2e \longrightarrow 2Fe(EDTA) + N_2 + H_2O \qquad (1)$$

However, in practice it has been found, that the electrolytic reduction of this complex leads to the formation of ammonia and, as an intermediate product, of hydroxylamine according to the following reaction equations:

$$Fe(NO)EDTA + 3\ H^+ + 3\ e \longrightarrow Fe(EDTA) + NH_2OH \qquad (2)$$

$$Fe(NO)EDTA + 5\ H^+ + 5\ e \longrightarrow Fe(EDTA) + NH_3 + H_2O \qquad (3)$$

For the development of an attractive denoxing process, the formation of ammonia in the catholyte is not desired since the removal of the ammonia from this liquid presents new problems. Therefore it would be highly desirable that the nitrogen oxides could be converted into gaseous nitrogen.

It is already known that NH_3 can be oxidized to nitrogen by chemical oxidation with hypobromides and hypochlorides according to the following reactions:

$$3BrO^- + 2NH_3 \longrightarrow N_2 + 3Br^- + 3H_2O \qquad (4)$$

If a solution containing ammonia and bromide ions is submitted to electrolysis, primarily bromine will be formed at the anode:

$$2Br^- \longrightarrow Br_2 + 2\ e \qquad (5)$$

It is further known from French Patent 1 493 735 to produce

bromine by electrolysis in a cell which is devided by a microporous fabric into two reaction chambers. Bromine production in an electrolytic cell is also mentioned in the first quoted document EP-A 0 243 889.

As bromine is unstable in alkaline solutions, the following disproportionation reaction occurs:

$$Br_2 + 2OH^- \longrightarrow Br^- + BrO^- + H_2O \qquad (6)$$

Subsequently, the formed hypobromide oxidizes ammonia to nitrogen according to reaction (4).

In acidic solutions, bromine is stable and oxydizes ammonia according to the following reaction:

$$3Br_2 + 8NH_3 \longrightarrow N_2 + 6NH_4^+ + 6Br^- \qquad (7)$$

It thus follows that the presence of bromine in alkaline or acid solutions in the anodic compartment leads to the chemical oxidation of ammonia and the formation of gaseous nitrogen. However, it must be noted that during the electrolysis reduction, ammonia is formed in the cathodic compartment.

The object of the present invention is to provide a simple, compact and reliable process which is apt to be realized on an industrial scale for removing from an aqueous liquid considerable amounts of nitrogen oxides, i.e. either NO_x and/or NO_3^-.

This problem is solved by the device as defined in claim 1. As far as preferred embodiments of this device and methods for using this device are concerned, reference is made to the dependent claims.

The invention will now be described in detail with reference

to two preferred embodiments thereof and with the drawings.

Figure 1 shows schematically an electrolytic cell of the device according to the invention.

Figure 2 shows the application of this invention to a flue gas purification plant where NO_x is removed from the flue gas.

Figure 3 represents schematically the application of this invention to the purification of liquids, in particular waste water including nitrates (NO_3^-).

The main feature of the present invention is the reduction of nitrogen oxides to ammonia or hydroxylamine and the subsequent oxidation of these compounds to gaseous nitrogen. Both steps can be carried out in one single electrolytic cell. The cathode compartment of this cell is used for the reduction of nitrogen oxides and the anode compartment is used for the oxidation of ammonia and hydroxylamine, respectively to gaseous nitrogen. The two compartments are separated by a cation selective membrane or diaphragm. Surprisingly, it has been observed that the ammonia formed in the cathode compartment of the cell is transported through the membrane to the anode and immediately reacts electrolytically with the bromine formed in the anode compartment.

Such a cell is schematically shown in figure 1. The cell is divided by a cation selective membrane 1 into a cathode compartment 2 and an anode compartment 3. The membrane is a microporous fabric, especially of polytetrafluorethylene fibers or of fibers containing carbon fluorine backbone chains with perfluoro side chains having sulphuric or carboxylic acid groups. The thickness of the membrane is between 10 and 80 µm, preferably between 20 and 40 µm. Both compartments are provided with inlets 4, 5 and outlets 6, 7 respectively, and

electrodes 8, 9 are provided in each of the compartments. The electrodes may be connected to a DC current source (not shown). The current polarity is such that the compartment 2 constitutes the cathode compartment and the compartment 3 constitutes the anode compartment.

According to a first aspect, the inventive method concerns the denoxing of the above mentioned Fe-EDTA complex in the frame of a flue gas purification plant. Such a plant is partly indicated in figure 2 and contains a cell 10 in accordance with figure 1. The flue gases pass subsequently through a washing column 11 and an absorption column 12. They are then conveyed to a chimney 15. These columns are located at the outlet of a flue gas desulphurizing plant as disclosed in the above quoted document EP-A-0 243 889.

As stated above, the electrolytic cell 10 is divided, into two compartments, and the two compartments are respectively integrated into two different liquid conveying loops. The cathode compartment 2 is fed with an aqueous solution containing Fe(NO)EDTA from the absorption column 12 and supplies to this column an aqueous solution containing Fe(EDTA).

The anode compartment 3 is fed with a scrubber liquid from the washing column containing between 0.1 and 0.5% by weight of HBr and between 0.1 and 0.5% by weight of sulphuric acid H_2SO_4. The scrubber liquid leaving this compartment 3 is again supplied to the washing column 11.

The liquid containing NOx is passed through the cathode compartment, where the complex is decomposed into ammonia NH_3 and Fe(EDTA) according to reaction (3). The ammonia formed in the cathode compartment diffuses through the cell membrane and is oxidized in the anode compartment to nitrogen N_2 and hydrogen H_2. In the anode compartment, also Br_2 is formed (reaction N°

5), which can be recirculated either to the washing column 11, as is shown in figure 2, or else to the reactor of the desulphurization process (not shown).

The following table I shows laboratory results of the reactions proceeding in the two compartments of the electrolytical cell.

The cell used in this laboratory scale experiment is equipped with an anode consisting of a 4 cm^2 graphite cylinder, a cathode consisting of a 10 cm^2 Pt cylinder and a membrane consisting of a PTFE fabric with an surface area of 20 cm^2 and a thickness of 0.02 mm. The initial composition of the catholyte is shown in the first column of table I. The test temperature is 25°C and the current applied to the cell is 500 mA. The second column of table I shows the composition of the catholyte after four hours of operation. It can be seen that the contents of nitrogen oxides and ammonia are substantially reduced.

TABLE I

	Cathode initial conc. (mmol/l)	Cathode final conc. (mmol/l)	Anode initial conc. (mmol/l)	Anode final conc. (mmol/l)
EDTA	100	100	--	--
NO	50	10	--	--
NH_3	345	314	--	--
Br^-	600	600	1000	740
Br_2	--	--	--	170
pH	7.0	11.5	10.0	2.4

In the anolyte, (initial composition in column 3, final composition shown in column 4) there are no nitrogen compounds, the nitrogen having escaped in gaseous form (N_2).

A similar experiment is shown by table II. In this case, the experiment is carried out at 60°C and, due to the presence of 100 mmol/l of H_2SO_4, the initial pH value of the anolyte is as low as 1,0. A current of 340 mA is applied to the cell and the experiment is proceeded for three hours. The substantial decrease of the ammonia and NO concentration in the catholyte is again very clearly demonstrated. However, in this experiment the ammonia conversion in the anolyte is not complete. In fact, there remains a small equilibrium concentration (27 mmol/l) due to the less favorable chemical equilibrium.

TABLE II

	Cathode initial conc. (mmol/l)	Cathode final conc. (mmol/l)	Anode initial conc. (mmol/l)	Anode final conc. (mmol/l)
EDTA	100	100	--	2
NO	40	10	--	--
NH_3	338	319	--	27
Br^-	---	10	330	184
Br_2	--	--	--	80
pH	6.8	6.5	1.0	1.0

This second experiment is well adapted to a desulphurization process in which the anolyte contains a relatively high amount of sulphuric acid and the pH value is low.

It should be noted that the Fe(EDTA) complex cited above can

be replaced by other members of the EDTA family such as nitrilotriacetic acid (NTA) or N(hydroxyethyl)ethylene diaminetriacetic (FeII-HEDTA).

Another application of the inventive method concerns the removal of nitrates from waste waters. The corresponding device is shown in figure 3, and it is a very simple device, as it almost exclusively consists of the cell 10. The cathode compartment is included in a waste water loop, waste water with nitrates being fed to this compartment and purified waste water without nitrates being collected at the outlet of this compartment. The corresponding reaction equation is as follows:

$$NO_3^- + 9H^+ + 8e \rightarrow NH_3 + 3H_2O \qquad (8)$$

The anodic loop conveys an anolyte consisting of a bromide or chloride solution, for example 0.5% by weight HBr or NaBr. The anodic loop further contains a recirculation pump 13 and a gas separator vessel 14 from which N_2 may escape.

Table III shows the initial and final compositions of the catholyte and the anolyte obtained in an experiment similar to those referred to in tables I and II and concerning the purification of NO_3^- containing waste water. The experiment is carried out at a temperature of 60°C, the anode consists of a 4 cm^2 graphite electrode and the cathode of a 210 cm^2 copper cathode.

As in the above quoted experiments, this table shows that the nitrates are reduced to ammonia in the cathode compartment and subsequently oxidized to nitrogen in the anode compartment.

TABLE III

	Cathode initial conc. (mmol/l)	Cathode final conc. (mmol/l)	Anode initial conc. (mmol/l)	Anode final conc. (mmol/l)
NO_3^-	120	77	--	5
NH_3	---	28	--	--
Br^-	633	650	595	210
Br_2	--	--	--	165
pH	1.6	12.0	5.4	2.3

In the frame of this invention, the anolyte may contain chlorine or iodine instead of bromine.

CLAIMS

1. A device for removing nitrogen compounds from an aqueous liquid containing nitrogen oxides (NO_x) and/or nitrates (NO_3^-), comprising an electrolytical cell (10) with a cathode (8) and an anode (9) and a current source applicable thereto, characterized in that the cell is divided by a cation selective membrane (1) into a cathode compartment (2) to be filled with said liquid, and an anode compartment (3) to be filled with an anolyte containing an aqueous solution of an alkali or hydrogen halide, in particular of sodium bromide or sodium chloride, and that the membrane (1) is constituted by a microporous fabric.

2. A device according to claim 1, characterized in that the membrane thickness is chosen between 10 µm and 80 µm, preferably between 20 and 40 µm.

3. A device according to claim 1 or 2, characterized in that the microporous fabric is made from synthetic fibers selected from the group consisting of polytetrafluorethylene (PTFE) and carbon fluorine backbone chains with perfluoro side chains containing sulphuric or carboxylic acid groups.

4. A device according to anyone of claims 1 to 3, characterized in that the anolyte is circulated in a loop comprising said anode compartment (3), a recirculation pump (13) and a gas separator vessel (14), the upper part of said vessel being provided with a gas outlet.

5. A method for removing nitrogen compounds from an aqueous liquid containing nitrogen oxides (NO_x) and/or nitrates (NO_3^-), using a device according to one of claims 1 to 4, characterized in that said liquid is fed to the cathode compartment,

said anolyte is circulated through said anode compartment and a current is applied to the cell.

6. A method according to claim 5, characterized in that said anolyte is an aqueous solution containing between 250 and 600 mmol/l of NaBr, preferably between 300 and 500 mmol/l of NaBr.

7. A method according to claim 5, characterized in that said anolyte is an aqueous solution containing between 250 and 600 mmol/l of NaCl.

8. A method according to any one of claims 5 to 7, characterized in that the anolyte has an initial pH value of at least 7, preferably of 10.

9. A method according to any one of claims 5 to 8, characterized in that said liquid fed to the cathode compartment contains an iron-ethylene diamine tetraacetic acid complex (Fe-EDTA) or an iron-trinitrilo acetic acid complex (Fe-NTA) or a N(hydroxyethyl)ethylene diaminetriacetic acid (FeII-HEDTA) complex with nitrogen oxide (NO) absorbed thereto.

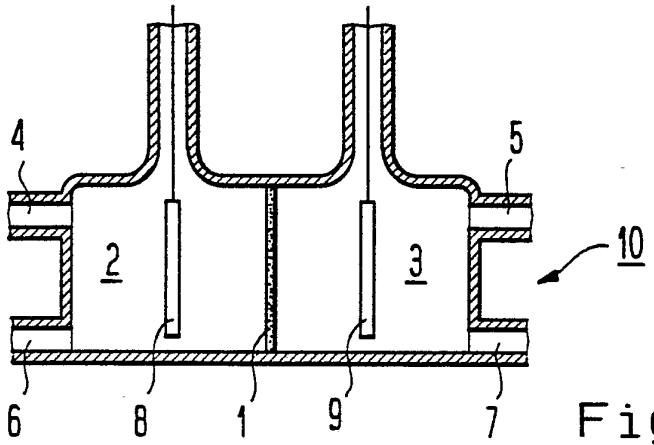

Fig. 1

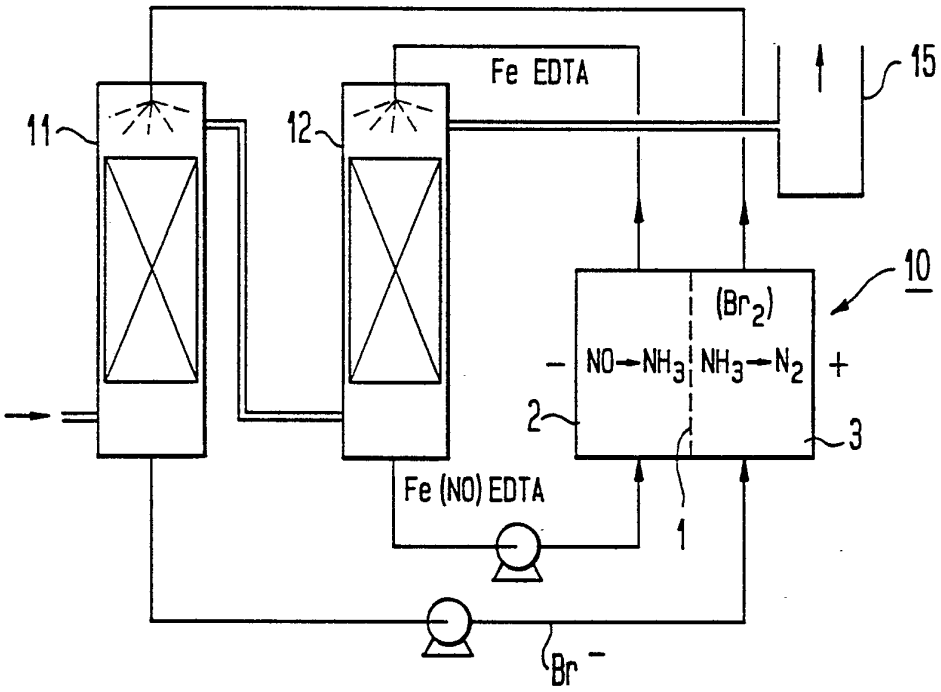

Fig. 2

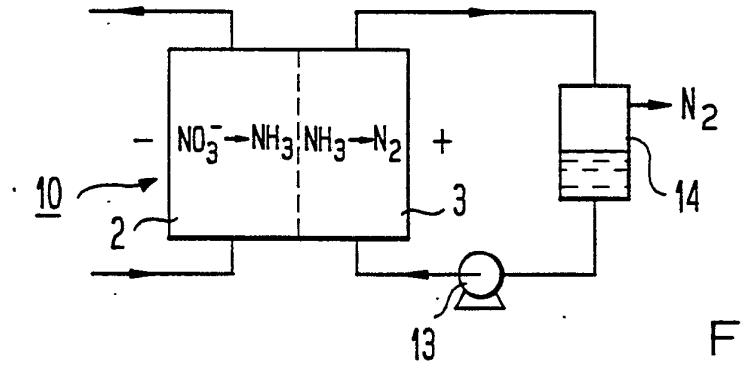

Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 90/01285

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C02F1/76 ; C02F1/46 ; C25B1/24

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C02F ; C25B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X Y	EP,A,0243889 (EURATOM) 04 November 1987 see pages 1 - 4; figure 2 (cited in the application)	1, 4-6, 9 3
Y	FR,A,1493735 (S.A. AQUITAINE-ORGANICO) 01 September 1967 see page 2 (cited in the application)	1, 3
A	FR,A,2470093 (ANVAR) 29 May 1981 see pages 2 - 6	1-9
A	US,A,3574084 (R.A. BRUCE) 06 April 1971 see the whole document	1-9
A	US,A,3669857 (T.A. KIRKHAM ET AL.) 13 June 1972 see the whole document	2, 3

° Special categories of cited documents : [10]

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
22 OCTOBER 1990	08 NOV 1990
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Mme N. KUIPER

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

EP 9001285
SA 39403

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0243889	04-11-87	LU-A- 86407 AU-A- 7481887 WO-A- 8706493 JP-T- 1500572	02-09-86 24-11-87 05-11-87 01-03-89
FR-A-1493735		None	
FR-A-2470093	29-05-81	None	
US-A-3574084	06-04-71	None	
US-A-3669857	13-06-72	None	