TECHNICAL NOTE

Oxidative separation of nitrogen oxides from off-gases by electrochemical mediators

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Received 4 July 1996; revised 18 November 1996

1. Introduction

Electrochemical mediators such as Ag(II)/ Ag(I) are powerful agents for the oxidative removal of biogically persistent highly chlorinated organic substances (Equation 1,2) for example, pentachlorophenol or lindane (γ- hexachlorocyclohexane) [1,2]. Unfortunately, Ag(II) must be generated electrochemically in nitric acid so that the following reactions occur in the cathodic compartment (Equations 3,4):

anodic compartment:

$$x\,\mathrm{Ag(I)} \xrightarrow{\text{anode}} x\,\mathrm{Ag(II)} + x\,\mathrm{e}^- \qquad (1)$$

$$x\,\mathrm{Ag(II)} + \text{organic substance} \longrightarrow x\,\mathrm{Ag(I)} + y\,\mathrm{CO_2} \qquad (2)$$

cathodic compartment:

$$\mathrm{HNO_3 + 2\,H^+ + 2e^-} \xrightarrow{\text{cathode}} \mathrm{H_2O + HNO_2} \qquad (3)$$

$$\mathrm{3\,HNO_2 \longrightarrow HNO_3 + H_2O + 2\,NO} \qquad (4)$$

The cathodic generated NO (Equation 4) can be oxidized by oxygen to NO_2 and then be absorbed by water or dilute nitric acid [3]:

$$\mathrm{6\,NO + 3\,O_2 \rightleftharpoons 6\,NO_2} \qquad (5)$$

$$\mathrm{6\,NO_2 \rightleftharpoons 3\,N_2O_4} \qquad (6)$$

$$\mathrm{3\,N_2O_4 + 3\,H_2O \longrightarrow 3\,HNO_3 + 3\,HNO_2} \qquad (7)$$

$$\mathrm{3\,HNO_2 \longrightarrow HNO_3 + 2\,NO + H_2O} \qquad (8)$$

$$\mathrm{(2\,NO + O_2 \rightleftharpoons N_2O_4)} \qquad (9)$$

$$\mathrm{4\,NO + 2H_2O + 3\,O_2 \longrightarrow 4\,HNO_3} \qquad (10)$$

For this purpose the overall process has to be carried out in a device consisting of an oxidation- and absorption-column. Increasing the pressure favours the rate of chemical absorption and a minimal threshold of 4 bar is generally admitted [3–5]. The goal of the present investigation is to simplify the procedure for oxidation and absorption of NO and NO_2.

For this purpose NO and NO_2 are oxidized to HNO_3 under normal pressure in an individual column in the presence of an electrochemically generated oxidation mediator metal $M^{(n+1)+}$

$$\mathrm{3\,M^{(n+1)+} + 2\,H_2O + NO \longrightarrow 3\,M^{n+} + 3\,H^+ + HNO_3} \qquad (11)$$

$$\mathrm{M^{(n+1)+} + H_2O + NO_2 \longrightarrow M^{n+} + H^+ + HNO_3} \qquad (12)$$

After reaction the circulating mediator M^{n+} is regenerated at the anode to $M^{(n+1)+}$.

As electrolyte for the electrochemical generation of the mediators an aqueous mineral acid is used whose anions cannot be reduced at the cathode. The oxidation potential of the Co(III)/Co(II)– ($E_o = 1.82$ V vs NHE) and the Mn(III)/Mn(II)– ($E_0 = 1.51$ V vs NHE) system in H_2SO_4 is high enough to oxidize the nitrogen oxides directly to nitric acid and the cathodic deposition of Me^0 does not occur. In an electrochemical cell, divided by an anion selective membrane, the following reactions take place:

anodic compartment:

$$\mathrm{Mn(II) \longrightarrow Mn(III) + e^-} \qquad (13)$$

bubble column:

$$\mathrm{3\,Mn(III) + 2H_2O + NO \longrightarrow 3\,Mn(II) + 3H^+ + HNO_3}$$

cathodic compartment:

$$\mathrm{H^+ + e^- \longrightarrow 1/2\,H_2} \qquad (14)$$

2. Experimental details

2.1. *Electrochemical cells and equipment*

The apparatus for destruction of pollutants and gas cleaning consisted of two electrochemical reactors and a simple bubble column (length, $l = 50$ cm; diam., $d = 3$ cm, filled with Raschig rings). With respect to the gas absorption efficiency the column was not optimized. The first electrochemical reactor was filled with 0.5 M $AgNO_3$ and 7 M HNO_3. Chlorinated organic substances are destroyed by Ag(II) in the anodic compartment, whereas NO is generated in the cathodic compartment. A recent paper [1] gives a detailed description of the arrangement. The cathodically formed NO (0.6–0.7 vol %) was mixed with a carrier gas stream of air to oxidize NO to NO_2. The gas mixture streamed from the bottom through the thermostated ($T = 20\,°C$) bubble column. At the top of the column Co(III)/Co(II) in 3 M H_2SO_4 or Mn(III)/ Mn(II) in 6 M H_2SO_4 was fed. Mn(III) or Co(III) was generated in the second electrochemical reactor divided by a Nafion® 450 anion selective membrane (DuPont). The anodic mediator solution was continuously circulated so that at any time an excess of oxidation mediator was present in the bubble

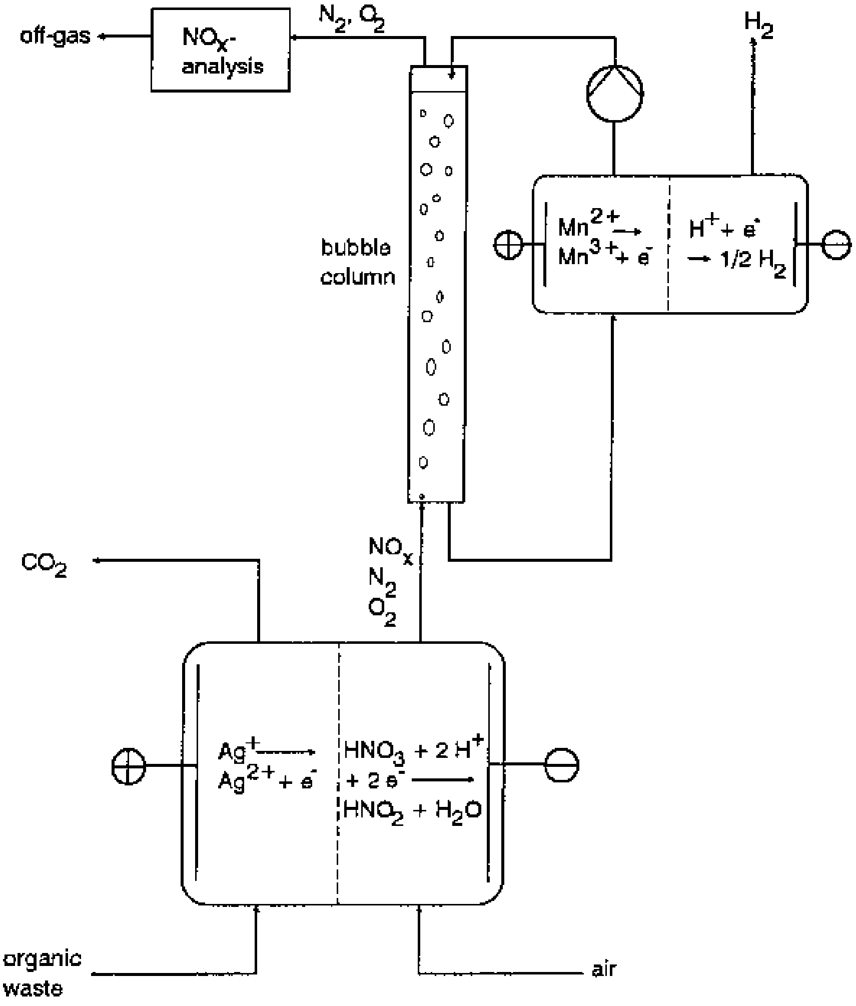

Fig. 1. Experimental arrangement of the electrochemical NO_x oxidation.

column. During the anodic Mn(III) generation only small amounts of brown MnO_2 were formed:

$$2\,Mn^{3+} + 2\,H_2O \rightleftarrows Mn^{2+} + MnO_2 + 4\,H^+ \qquad (15)$$

which does not disturb the overall process. Figure 1 shows the experimental arrangement. Table 1 gives a detailed description of the reaction conditions.

In a second experimental step the electrochemical reactor for total oxidation of organic waste was replaced by a NO pressured cylinder bottle. The NO was mixed with air in a glass vessel (empty volume $V_e = 1000\ cm^3$) to adjust the desired NO_x content (2.14–9.48 vol%) and fed to the bubble column.

2.2. *Analytical procedure*

After the off-gas stream had left the bubble column, it was led to a NO–NO_2–converter **CGO-K** (Hartmann & Braun) to convert NO_2 to NO. The conversion to NO is necessary because only NO can be

Table 1. Reaction conditions of the electrochemical NO_x oxidation

	Electrochemical cell for organic waste oxidation	*Electrochemical cell for NO_x oxidation*	*Bubble column*
Electrolyte	0.5 M $AgNO_3$ / 7 M HNO_3	0.1 M $MnSO_4$ / 6 M H_2SO_4 0.1 M $CoSO_4$ / 3 M H_2SO_4	
V_e / cm^3	1000	1000	353
T / °C	70	20	20
I / mA	6000 maximum	5000 maximum	
A / cm^2	anode:60 cathode:60	anode:120 cathode:24	
p / mbar	970–1030	970–1030	970–1030
carrier gas / ml min^{-3}	200–1800 air		200–1800 air

All chemicals used were Merck products. The solutions were prepared with triply distilled water.

Table 2. Conversion rates of the reactive NO_x absorption with Co(III) and Mn(III)

Mediator	*Electrolyte*	*NO_x content before treatment / vol%*	*NO_x content while treatment / vol%*	*Rate of conversion /%*	*Overall gasflow / ml min^{-1}*
Co(III)	3 M H_2SO_4	0.66	0.42	36	300
Mn(III)	6 M H_2SO_4	0.60	0.06	90	300
Mn(III)	6 M H_2SO_4	0.70	0.10	86	760
Mn(III)	6 M H_2SO_4	2.14	0.24	89	760
Mn(III)	6 M H_2SO_4	3.54	0.50	86	760
Mn(III)	6 M H_2SO_4	9.48	0.30	97	760
Mn(III)	6 M H_2SO_4	2.60	0.26	90	1800

detected quantitatively by ultraviolet flow spectrometer **RADAS 2** (Hartmann & Braun). In all experiments the sum of NO- and NO_2-content in the off-gas was measured.

3. Results and discussion

A first experiment using Co(III) as mediator in 3 M H_2SO_4 produced a small conversion from NO_x to HNO_3. It is evident that the small conversion rate is caused by kinetic inhibition because the oxidation potential of Co(III) (E_0 = 1.82 V vs NHE) is thermodynamically sufficient to oxidize NO_x to HNO_3:

$$NO + 2\,H_2O \longrightarrow HNO_3 + 3H^+ + 3\,e^- \qquad E_0 = 0.957 \text{ V vs NHE} \qquad (16)$$

$$NO_2 + H_2O \longrightarrow HNO_3 + H^+ + e^- \qquad E_0 = 0.803 \text{ V vs NHE} \qquad (17)$$

In this context it should be noted that the results of experiments using Co(III) to oxidize chlorinated organic substances were likewise not satisfactory [1, 2, 6, 7]. Possibly the chemical absorption of NO_x by Co(III) / 3 M H_2SO_4 might be inhibited by the high acid concentration, as observed for the oxidation of nitrous acid by Ce(IV) [8].

In contrast to Co(III) the experiments with Mn(III) as mediator were successful. Table 2 shows the results of the reactive NO_x absorption with Co(III) and Mn(III). The experiments show that Mn(III) in H_2SO_4 is a suitable mediator to oxidize NO_x to HNO_3 yielding up to 97%. Advantages of the described method are the small size of the single absorption column and the operation under normal pressure. Short gas/liquid contact times of about 7 to 15 s are sufficient for the reaction. An increase in the contact time does not cause a noticeable increase in the conversion rate.

An unequivocal connection between NO_x content before treatment and the rate of conversion for a constant overall gas flow was not observed (Table 2, line 3, 4, 5 and 6, overall gas flow 760 ml min^{-1}.

To decrease the current consumption of Mn(III) generation NO should be oxidized as much as possible to NO_2 using atmospheric air.

The process described will be integrated into a pilot plant for electrochemical oxidation of highly chlorinated organic waste at the Forschungsungszentrum Karlsruhe after scale up and further investigation.

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