# Gas purification by removal of atomic mercury using electrochemical cells

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## Abstract

Electrochemical cells are described, which allow the oxidative removal of gaseous atomic mercury from gas streams. The gas stream is fed into an electrochemical cell containing an electrolyte solution and a three-dimensional anode with a large surface. The results can be explained by assuming that the atomic mercury is first transferred from the gas to the electrolyte solution followed by oxidation to mercury(II) ions at the electrode surface. Once mercury(II) has reached a sufficient concentration, it reacts with the atomic mercury to form mercury(I). The dissolved mercury(I) is than oxidized to mercury(II) at the electrodes. Therefore the efficiency of mercury removal from the gas stream can be enhanced by adding mercury(II) to the electrolyte at the very beginning of the process.

## 1. Introduction

A number of electrochemical cells have been described for the purification of flue gases. Most operate as multiphase reactors where gaseous components are transferred into a liquid electrolyte and then converted to ionic species at a solid electrode surface. The requirements for an effective electrochemical absorption, the intimate contact between the gas and the absorbing liquid and a large electrode surface can be realized in fluidized beds, packed beds or membrane cells [1–3]. These cells have been optimized to achieve efficient removal of impurities from a gas stream, for example, as chlorine and sulphur dioxide.

Atomic mercury is a constituent of various flue gases, such as those from waste incinerators, alkali chloride electrolysis, fossil fuel combustion. Because of its toxic properties it attracts much concern and various techniques have been developed for its removal. Chemical extraction and absorption processes are well established to remove mercury from gases by transforming it into nonvolatile species like mercury sulfide or by immobilizing it by adsorption on charcoal [4, 5]. The oxidation of atomic mercury by ozone, known as the major route for the conversion of $Hg^0$ into Hg(II) in the atmosphere, has also been investigated for this purpose [6–8].

Because atomic mercury is fairly easy to oxidize ($E^{\circ}_{Hg_{atomic}/Hg^{2+}} = 0.661$ V vs SHE [9]) the idea evolved to use an electrolysis cell for the purpose of gas purification. It is important to note that all tabulated values of standard potential relate to metallic mercury, whereas here it is necessary to take into account the redox couple (atomic mercury dissolved in water)/(ionic mercury dissolved in water). We have shown already how this value can be calculated [10]. However, there are only a few studies devoted to the decontamination of mercury by the application of electricity [11, 12].

## 2. Experimental details

### 2.1. Chemicals

All chemicals used were of the highest available purity. Aqueous solutions were prepared in bidistilled water. The concentration of the electrolyte solution was 0.2 mol $L^{-1}$ $K_2SO_4$ or $NaClO_4$, respectively. Because of a probable content of mercury(I) ions in commercial mercury(II) salts, a $10^{-3}$ M $Hg(ClO_4)_2$ solution was freshly prepared using stoichiometric quantities of HgO and $HClO_4$. The $NaBH_4$ solution was prepared by dissolving 1.5 g NaOH in 250 mL bidistilled water followed by the addition of 1.5 g $NaBH_4$. The 5 M HCl was prepared by dilution of 37% HCl with bidistilled water.

The mercury loaded gas stream was achieved by mixing of two separate gas streams with controlled mass flow rates. The nitrogen (1–20 L $h^{-1}$) flowed through a thermostated mercury reservoir before being added to the air stream (150–200 L $h^{-1}$). This assembly allowed mercury concentrations up to 600 $\mu$g $m^{-3}$ in the gas to be established.

The reservoir was a 2 L round bottom flask filled up to a level of 2 cm with high purity mercury. The nitrogen gas stream was led in through a glass tube almost touching the mercury surface to make sure that the gas was saturated with mercury vapour.

## 2.2. Analytical measurements

The content of atomic mercury in the gas stream was detected with a portable cold-vapour atomic absorption (CV-AAS) spectrometer (Hg-MAK monitor 1200, Seefelder Messtechnik SMT, Germany). The arrangement of the complete experimental system allows the measurement of the mercury content in the spiked and in the purified gas stream during the treatment.

The determination of the total mercury content in the electrolyte solution was performed by CV-AAS with a SpectrAA 400 spectrometer (Varian, Australia). The ionic mercury species in the solution were all reduced to the atomic state by $NaBH_4/HCl$. Both techniques make use of the specific absorption of atomic mercury at 254 nm.

The photometric speciation of mercury(I) in the electrolyte solution was measured with a u.v.-spectrometer Spectronic 601 (Milton Roy, Belgium) at a wavelength of 236 nm using 1 cm quartz cells.

The differential-pulse voltammetric measurements of ionic mercury were performed with an Autolab (ECO Chemie, Utrecht, Netherlands) combined with an electrode stand VA 663 (Metrohm, Switzerland). Glassy carbon electrodes (Tokay, Japan) were used as working electrode (disc) and as auxiliary electrodes (rod). As reference electrode (Metrohm, Switzerland) a Ag/AgCl electrode with 3 M KCl ($E = 0.208$ V vs SHE) was used. After purging the sample solutions with high-purity nitrogen for 300 s the measurements were performed with the following parameters: pulse amplitude 35 mV, step potential 3.2 mV, modulation time 0.07 s and interval time 0.5 s.

## 2.3. Apparatus

After preparing a gas stream with a defined mercury content, as described above, the spiked gas passed a three-way tap to enter the electrochemical cell (Figure 1). The oxidation unit was then followed by a droplet separator and an optional permeation gas dryer. The gas was finally exhausted through a second three-way tap. The taps enabled the separation of a gas stream of 90 L h$^{-1}$ from the main gas stream (150 to 200 L h$^{-1}$), necessary for the measurements with the Hg-MAK Monitor in a bypass.

## 2.4. Electrode design

Figure 2 depicts the general design of the electrochemical absorber used for the removal of atomic mercury from the gas stream. It was a three-chamber acrylic cell. The system operated in inner-cell mode to allow the simulta-
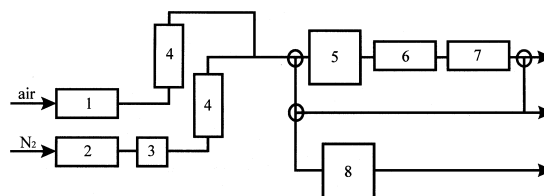


Fig. 1. Flow scheme of experimental set-up for electrochemical purification of gas mixtures containing atomic mercury: (1) membrane-pump; (2) electronic mass flow controller; (3) Hg reserve; (4) rotameter; (5) electrochemical cell; (6) droplet separator; (7) permeation gas dryer; (8) CV-AAS (Hg-MAK monitor).
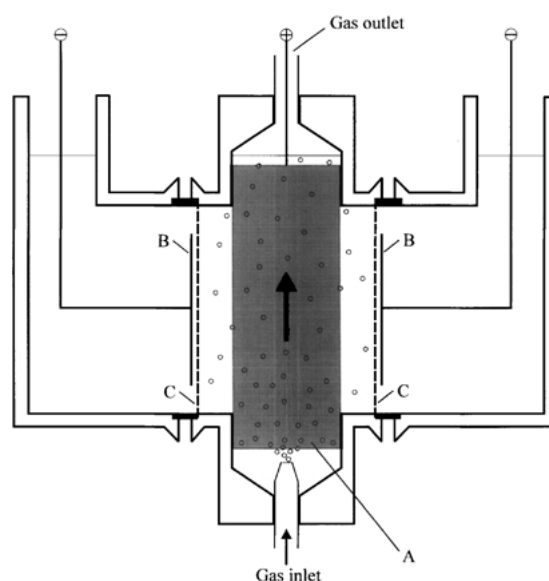


Fig. 2. Front-view of the electrochemical absorption cell. (A) anode; (B) cathode; (C) ion exchange membrane.

neous absorption and electrochemical reaction. The central chamber, containing a fixed bed of either graphite rod electrodes or a dimensional stable titanium supported $RuO_2$–$TiO_2$ anode (DSA, Chemische Werke Bitterfeld, Germany), was separated by cation exchange membranes (Ionac MC 3470, Sybron Chemicals, USA) from the outer chambers containing the lead cathodes. These membranes ensured the generated mercury ions remained in the anode compartment and allowed independent filling levels of the electrolyte solution in the chambers.

The graphite anode (Figure 3) consisted of paraffin impregnated graphite rods of a diameter 5 mm stuck into the rear wall of the cell. The distance between the electrode rods was 2 mm. The whole anode was contacted by a copper plate glued onto the rear plate with a silver contact glue. The graphite rods were impregnated with paraffin according to a published procedure [13] to prevent a creeping of the electrolyte into the graphite rods to avoid memory effects by contamination.

In contrast to the graphite anode, the DSA consisted of a package of 2 mm thick gratings with asymmetric hexagonal meshes (6 mm × 3 mm). These gratings were contacted by a graphite rod pressing them together from the top of the cell.

To obtain an effective gas distribution the incoming gas stream passed an optional G2-frit at the bottom of the central chamber. The gas bubbled through the electrolyte solution and the gaps in the three-dimensional anode and finally left the cell at the top of the chamber. The gas pressure at the inlet maintained the electrolyte in the anode compartment of the cell.

## 3. Results and discussion

The performance of the cell was studied with respect to the removal of atomic mercury from the gas and its conversion to ionic mercury. Parameters like voltage or potential and components like the anode material and the composition of the electrolyte solution were varied to find the optimal configuration of the system.

First experiments with graphite anodes and neutral 0.2 M potassium sulfate under variation of the voltage showed that only voltages above 3 V (corresponding to $I > 100$ mA) ensured a decrease of contaminant in the gas. A cell voltage of 3 V corresponded to an anode potential of about 1 V vs SHE. The minimum potential necessary for the oxidation of atomic mercury to ionic mercury(II) is 0.661 V vs SHE [9]. Hence, the applied voltages are all assumed to be sufficient for a quantitative oxidation of the atomic mercury. However, no sudden decrease in the contaminant was observed. The application of a 6 V voltage resulted in an almost complete removal after 20 min (Figure 4).

Parallel measurements showed that the pH declined from about 7 to less than 2 within 2 h due to the anodic generation of protons.

$$2\,H_2O \rightarrow 4\,H^+ + O_2 + 4\,e^- \tag{1}$$
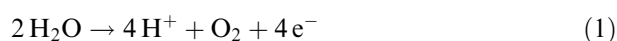
The initially rather slow decrease of the contaminant in the gas indicates that the purification process is not exclusively effected by the single process of electrochemical oxidation to ionic mercury. Hence, additional processes must contribute to the purification.
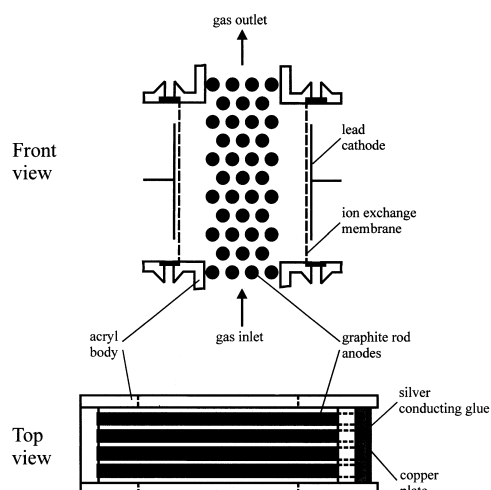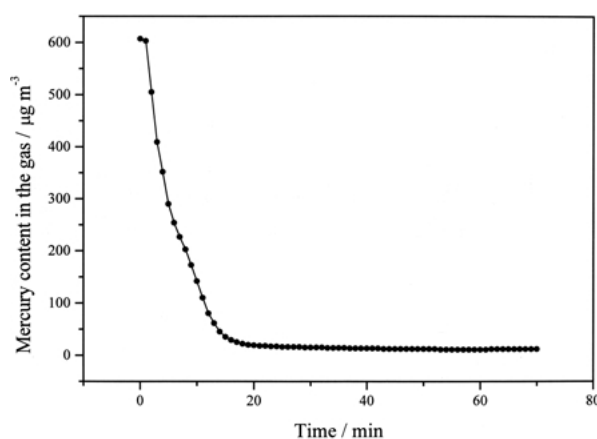


Fig. 4. Electrochemical purification with graphite anode in 0.2 M K$_2$SO$_4$ (250 mL) at 6 V without any further additives.

The chemical synproportionation of dissolved atomic mercury with mercury(II) can contribute to the purification:

$$Hg + Hg^{2+} \rightarrow Hg_2^{2+} \tag{2}$$

Figure 5 shows the effect of the deliberate addition of mercury(II) ions to the electrolyte on the removal of the contaminant in a common gas washing bottle without electrical power input. To avoid the precipitation of basic mercury(II) salts, a low pH value was necessary. A pH of about 2 should ensure that all added or anodically generated mercury(II) ions are available for the synproportionation with atomic mercury.

Because of the observable corrosion of the graphite anode, substitution by a package of gratings consisting of titanium supported RuO$_2$–TiO$_2$ anodes was tested. These DSA (dimensional stable anodes) ensured dimensional stability and provided a simple assembling. Even the purification was slightly accelerated by this anode material.

To obtain faster decontamination rates, even at lower voltages, the addition of an acidic mercury(II)-solution at
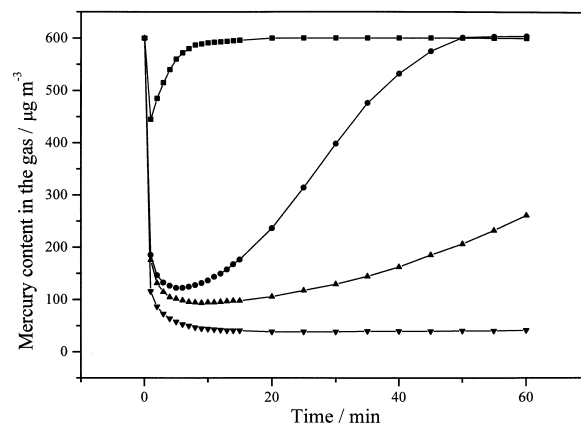


Fig. 3. Electrode arrangement with graphite rod anodes.



Fig. 5. Effect of Hg(II) addition and pH of the electrolyte solution (50 ml of 0.2 M K$_2$SO$_4$); (■) $5 \times 10^{-6}$ mol HgSO$_4$ (neutral pH); (●) $5 \times 10^{-7}$ mol HgSO$_4$ (pH 2); (▲) $1 \times 10^{-6}$ mol HgSO$_4$ (pH 2); (▼) $5 \times 10^{-6}$ mol HgSO$_4$ (pH 2).
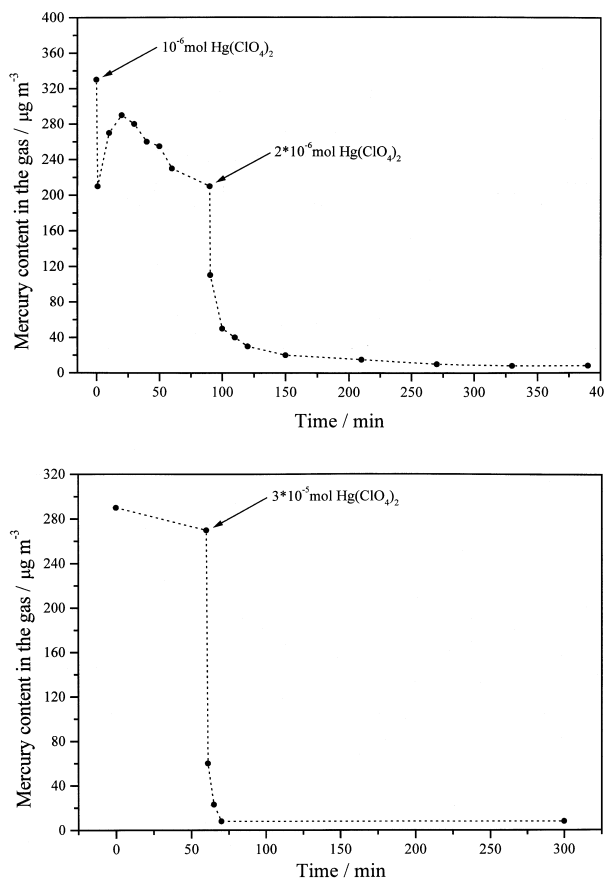
Fig. 6. Electrochemical gas purification with titanium supported $RuO_2$–$TiO_2$ anode in 0.2 M $KClO_4$ (250 mL) and addition of acidic $Hg(ClO_4)_2$-solution at 3 V.

the beginning of the treatment was introduced. Depending on the quantities added, rapid decontamination was observed. As illustrated in Figure 6, the addition of dissolved $Hg(ClO_4)_2$ and a 3 V voltage resulted in an almost immediately complete removal of the contaminant. These Figures show that a concentration of $10^{-4}$ mol $L^{-1}$ of Hg(II) is necessary for rapid decontamination, if there is a supply of $2 \times 10^{-7}$ mol $h^{-1}$ $Hg^0$.

An explanation of the mechanism of the purification process required further investigation. Unfortunately the spectrophotometric analysis of mercury(I) at 236 nm was corrupted by species generated during the electrolysis. Both, $K_2SO_4$ and $KClO_4$ formed species absorb at this wavelength. Hence, a spectrophotometric Hg(I) speciation analysis in the electrolyte solution was impossible. Only the total concentration of mercury in the solution was measurable by CV-AAS.

From the results, the following mechanism can be proposed (Figure 7). The atomic mercury is first transferred from the gas to the electrolyte solution followed by oxidation to mercury(II) at the electrode surface. As soon as mercury(II) has reached a sufficient concentration, it reacts with the atomic mercury to form mercury(I). The dissolved mercury(I) is than oxidized to mercury(II) at the electrode. This model also explains why the mercury(0) removal is much faster once there is a certain mercury(II) concentration in the electrolyte,
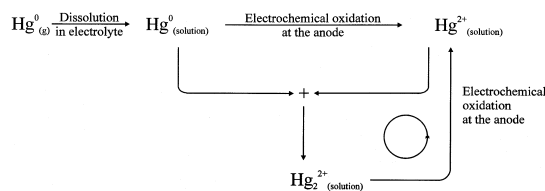


Fig. 7. Proposed mechanism of mercury(0) oxidation in the electrochemical cell.

because the electrochemical oxidation of Hg(0) to Hg(II) at the anode is a heterogeneous reaction at a relative small electrode surface area, whereas the chemical oxidation of Hg(0) by dissolved Hg(II) is a heterogeneous reaction at the surface of the gas bubbles, that is, at a relatively large moving gas–liquid interface.

## 4. Conclusions

The feasibility of electrochemical decontamination of atomic mercury in flue gas was experimentally demonstrated in a laboratory scale fixed-bed reactor. The experiments show that contents of several hundreds $\mu g\ m^{-3}$ of $Hg^0$ can be gradually removed by more than 90% from the gas flowing through the cell at 150 to 200 L $h^{-1}$ at voltages higher than 3 V and a current density of 3 A $m^{-2}$. To achieve a rapid decrease at the beginning of the treatment a deliberate addition of mercury(II) ions is recommended. Low pH ensures that the mercury(II) ions do not precipitate in the form of basic salts. Anodes of titanium supported $RuO_2$–$TiO_2$ (DSA) ensure dimensional stability and simple cell assembling.

## References

1. G. Kreysa and H.J. Külps, *Chem.-Ing.-Tech.* **55** (1983) 58.
2. G. Kreysa and K. Jüttner, *in* F. Lapicque, A. Storck and A.A. Wragg (Eds), 'Electrochemical Engineering and Energy' (Plenum, New York, 1994), p. 255.
3. K. Sundmacher and U. Hoffmann, *Chem. Eng. Sci.* **54** (1999) 2937.
4. P. Neumann and G. Schmidt, *Umwelt* **22** (1992) 574.
5. R. Kubisa, R. Holste and R. Hillen, Lecture presented at IUTA Duisburg (1994).
6. A. Iverfeldt and O. Linquist, *Atmos. Env.* **20** (1986) 1567.
7. G. Petersen, A. Iverfeldt and J. Munthe, *Atmos. Env.* **29** (1995) 47.
8. G.Ya. Gerasimov, *High Energy Chem.* **34** (2000) 13.
9. F. Scholz and M. Lovric, *Electroanal.* **8** (1996) 1075.
10. F. Scholz and M. Lovric, *Electroanal.* **9** (1997) 1189.
11. H.K. Hansen, L.M. Ottosen, B.K. Kleim and A. Villumsen, *J. Chem. Tech. Biotechnol.* **70** (1997) 67.
12. W. Yong-Fu, C. Wie-Lung and Y. Shi-Chern, *J. Environ. Sci. Health* **A35** (2000) 1153.
13. F. Scholz and B. Meyer, *in* A.J. Bard and I. Rubinstein (Eds), 'Electroanalytical Chemistry, A Series of Advances' (Marcel Dekker, New York) **20** (1998) 1.