The Treatment of Mercury-Bearing Activated Carbon from a Gas Cleaning System by Electro-Oxidation. The Ultimate Solution.

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Abstract

This study aimed at extracting the adsorbed mercury from the mercury loaded activated carbon so as to recycling both, the elemental mercury and the carbon, after being reactivated. The process used in this study was the electro-oxidation of the mercury in a reaction system where the loaded carbon is acting as an anode, during the electrolysis of brine, the electrolyte of the cell.

Key words: electrolytic treatment, activated carbon, electro-oxidation

I) Introduction

Compared to other fuels, the natural gas detains an excellent reputation as a clean source of energy at a low cost, being, thus, the most used fuel worldwide. Therefore, it is very important to the gas industry to keep such image. However, the gas exploitation is a powerful source of pollution representing a potential impact to the environment on different compartments (air, soil and water) and to the human being as such. On the other hand, the gas quality depends on different parameters that have to be assured for a proper utilization by the consumers. Low composition changes can cause several problems, in particular when using it as a vehicular fuel [1].

Several contaminants are present in natural gas and related products such as condensates or residual water. They can have dramatic effects on the gas quality, on the gas prospecting operation and on the environment. The nature and concentration of such impurities, having an environmental and material impacts while transported, distributed and used as a fuel were already determined [2].

Among the several constituents of natural gas, some of those, such as mercury and arsenic, are present as trace elements (<0.01% molar). The presence of mercury was detected, for the first time, back to 76 [3], as being 180 ng/L, but its real impact was evidenced back to 75 at Skikda (Algeria) [4], where severe damages have been detected on the aluminium heat exchanger, causing the production process to stop and, therefore, strong economic losses.

The mercury is an element that can be detected in the environment as elemental mercury (Hgo), as inorganic species (HgX₂, HgO), organic species (RHgR’) or as mixed compounds (RHgX), where R and R’ stand for alkyl groups and X a halogen. The mercury emissions to the environment, from the human being activities are of great concern as it is very toxic to a great deal of living species. It is well known that the toxicity of the mercury species is a function of the chemical structure under consideration. The organic structures are the most toxic, the methyl-mercury in particular, which caused the accidental death of hundreds of people in Japan back to the 50’s [5].
The total mercury concentration in natural gas varies dramatically according to the exploitation place[6], as shown in table 1.

Table 1: mercury concentration on natural gas from different deposits all around the world.

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Mercury Content (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Netherlands (North Sea)</td>
<td>180</td>
</tr>
<tr>
<td>Middle East</td>
<td>1 – 9</td>
</tr>
<tr>
<td>Algeria</td>
<td>59 – 193</td>
</tr>
<tr>
<td>United States (pipeline)</td>
<td>0.019 – 0.4</td>
</tr>
<tr>
<td>North America</td>
<td>0.005 – 0.04</td>
</tr>
<tr>
<td>Indonesia</td>
<td>0.1 – 150</td>
</tr>
<tr>
<td>Canada</td>
<td>0.2 – 150</td>
</tr>
<tr>
<td>Germany</td>
<td>Up to 11000</td>
</tr>
<tr>
<td>Venezuela</td>
<td>0.01 - 2</td>
</tr>
</tbody>
</table>

Regarding the mercury speciation on natural gas and condensate, few studies have been undertaken. The different possible forms of mercury are shown on table 2 with their respective boiling points.

Table 2- Chemical forms of mercury and arsenic and their boiling temperatures under atmospheric pressure.

<table>
<thead>
<tr>
<th>Mercury Species</th>
<th>Boiling Temperature (°C)</th>
<th>Arsenic Species</th>
<th>Boiling Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg°</td>
<td>357</td>
<td>AsH₃</td>
<td>-55</td>
</tr>
<tr>
<td>(CH₃)₂Hg</td>
<td>96</td>
<td>CH₃AsH</td>
<td>2</td>
</tr>
<tr>
<td>(C₂H₅)₂Hg</td>
<td>170</td>
<td>(CH₃)₂AsH</td>
<td>36</td>
</tr>
<tr>
<td>(iC₃H₇)₂Hg</td>
<td>190</td>
<td>C₂H₅AsH₂</td>
<td>36</td>
</tr>
<tr>
<td>(C₄H₉)₂Hg</td>
<td>206</td>
<td>(CH₃)₂As</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C₂H₅)₃As</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C₆H₅)₂As</td>
<td>360</td>
</tr>
</tbody>
</table>

The environment pollution from metals through the human industrial activities is assuming a more and more remarkable importance. To such intention, intense studies are been undertaken to evaluate the effect of those metal on the living organisms, to monitor the heavy metals concentration in the environment, and to prevent and eliminate the pollution.

As the worldwide environmental legislation is becoming more and more restrictive, it is necessary new studies to get higher purification levels to an acceptable cost and to develop easier applicable technologies.

Among the harmful metals, that cause severe impact on ecosystems and, therefore, to the human being, the mercury causes serious environmental problems. The mercury remains in the environment and, when exposed to the atmosphere, it is metabolised by bacteria that introduce it in the biological cycle and further reaching the man. The mercury is accumulated in the human organism provoking damages particularly to the digestive, nervous and breathing systems.
The elemental mercury is still used in different industries for different purposes causing damages to the environment. Among them, one can mention the chlor-alkali industry, that uses, during the electrolysis of brine, mercury cathode, and in gold prospecting areas for amalgamating gold from gravity concentrates. Regarding the chlor-alkali industry, nowadays, many facilities are using cation exchange membranes, that does not require the use of elemental mercury.

As far as the gold extraction is concerned, there are available technologies either to avoid the mercury volatilisation, during the thermal decomposition of the gold amalgam, or to treat the residues from the elutriation operation, providing the recovery and reuse of it and avoiding its dispersion in the environment.

In recent years, the increasing concern about the severe impact of toxic and persistent elements, such as mercury, on ecosystems has become an important issue in environmental legislation.

The mercury content in gases varies broadly (from \(1 \times 10^{-8} \text{ g m}^{-3}\) to \(14 \text{ mg m}^{-3}\)). Mercury in the hydrocarbon gases occurs in Precambrian, Caledonian and Hercynian tectonic structures and young folded belts of gas-oil and gas deposits. Mercury-bearing gases are localized in practically all the stratigraphic deposits of the Paleozoic, Mesozoic and Cen where gas deposit exist. The lithological composition of the rock-collectors differs greatly, so there is no stratigraphic or even lithologic control for gases with higher mercury component in the oil-gas area.

All these data infer the conclusion that the mercury content in natural gases is stipulated by rising of mercury-containing fluid fluxes from the Earth’s mantle along the deep fault zones during their activization.

The gas-fire power plant is a widely used technique for energy production, supplying heat and power in several east-European countries. However, during the gas prospecting operation, in deep wells, a considerable mercury concentration is being detected taking part of the gas mixture implying that the straight combustion of such gas is a considerable source of mercury emission. Therefore, in this case, a flue gas cleaning system or emission control measurements has to be strongly considered, or, even better, to pass such gas mixture through an activated carbon column so as to grab the elemental mercury vapours and releasing a mercury-free gas stream. However, once reaching the loading capacity of such carbons another environment problem is introduced. The loaded carbon contains up to 20% of mercury with high conditioning cost.

**The Generation of Mercury-Bearing Activated Carbon**

The sulphur impregnated activated carbon has been used for cleaning natural gas from deep wells. Such carbon is produced by contacting the carbon, previously activated, with elemental sulphur, as fine particles, and proceeding with an increase in temperature up to the sulphur melting point (120 oC). As the sulphur melts down, it penetrates in the carbon pores homogeneously producing the proper environment for reacting with elemental mercury vapours. Therefore, after loading it with mercury and some other metals, also carried by the gas stream, the coalesced elemental mercury acts as metals absorber by amalgamating them. Therefore, the carbon under consideration in this study, contains elemental mercury, HgS, and some other amalgams. For the
sake of mercury removal from the mercury loaded carbon, it should be mentioned that either elemental mercury or mercury sulphide are conductive and, thus, being dissolved anodically to produce the quite soluble mercury species (HgCl$_2^-$).

The Figure 1, as follows, shows a SEM (scanning electron microscopy) photograph of an activated carbon loaded with elemental mercury.

![Figure 1 - A SEM photograph of an activated carbon loaded with elemental mercury.](image)

The grey spots means elemental mercury covered with other metals amalgams being accumulated during the adsorption process.

In general, there are different ways to treat mercury bearing residues, such as:

- biological methods\[7,8\]
- physical treatments (mineral processing techniques)\[9,10\]
- chemical-physical treatments (reagents addition and precipitation)\[11-15\]
- electrochemical treatments\[11\]

The electrochemical method is becoming more and more important, as it provides low processing costs, and, in addition, the possibility of recovering the metals under consideration.

In this study the electrolytic process was used for removing the elemental mercury from the carbon structure by using it as an anode in a reaction system that can be seen later in the electrolytic experimental procedure.

Before going any further, a brief voltammetric study had to be carried out so as to better explain the behaviour of elemental mercury during the decontamination process.

**Experimental**
The present study uses a steady state linear sweep technique to investigate the mercury electrodeposition process at a vitreous carbon solid electrode from a $10^{-3}$ mol dm$^{-3}$ Hg$^{2+}$ solution, 1.0M NaCl as supporting electrolyte. The supporting electrolyte is present (a) to increase the conductivity of the solution and hence to reduce the resistance between the working and counter electrodes (to avoid undue Joule heating, to help maintain a uniform current and potential distribution and reduce the power requirement of the potentiostat) and (b) to effectively eliminate migration as a mode of mass transport for the electroactive species; transport numbers are proportional to concentration, and since the ions of the supporting electrolyte are present in large excess over the electroactive species, they will transport a large majority of the charge through the solution.

Since cyclic polarograms are observed at quiet electrodes and the time interval between reverse sweeps is relatively short, products of say, a cathodic reduction, are available at and near the electrode surface for re-oxidation on the anodic-going segment of the cycle. Ideally, CV should employ strictly linear diffusion conditions.

Intuitively it is easy to see that a rapid charge-transfer process (reversible system) will show that the anodic and cathodic peaks are not at exactly the same potential, but a separation is predicted. It is verified that $E_{p,c}$ for a reduction is 0.029/nV more cathodic than $E_{1/2}$. Correspondingly, $E_{p,a}$ for the oxidation of the same system will be 0.029/nV more anodic than $E_{1/2}$. The potential increment between the peaks for a reversible system will be:

$$E_{p,a} - E_{p,c} \equiv 2(0.029 / n) = \frac{0.058}{n}$$

The solutions were made up using deionised distilled water and were de-aerated with oxygen-free nitrogen before steady state polarisation curves were recorded.

This study was carried out using a rotating vitreous carbon electrode (area = 1.26 x 10$^{-5}$ m$^2$) embedded in a PTFE holder and attached to a rotating disc assembly. The electrode was polished to a mirror finish with diamond lapping compound (1-5 µm particle size - Hyprez Five Star Engis Ltd.) using a silk cloth and water soluble lubricant liquid (hyprez Fluid Type W). A conventional Pyrex cell assembly (Figure 2) was used, incorporating a saturated calomel reference electrode separated from the bulk solution by a Luggin capillary; a large platinum foil in a separate compartment served as a counter electrode.
The cyclic voltammogram of Figure 3, shows important features:

i) a peak at -0.47 V(SCE) resulting from reduction of HgCl$_4^{2-}$ ions to elemental mercury, and

ii) a peak at 0.060 V(SCE) resulting from the elemental mercury oxidation back to HgCl$_4^{2-}$ ions, as depicted in the following reaction:

\[
HgCl_4^{2-} + 2e \leftrightarrow Hg + 4Cl^- \tag{1}
\]
Fig. 3- Steady state sweep profile of $1 \times 10^{-3}$ mol dm$^{-3}$ HgCl$_2$, in 0.5 mol dm$^{-3}$ NaCl supporting electrolyte. Sweep rate 0.050 V s$^{-1}$ and the potential scan program was: initial potential = 0.00 V(SCE), lower limit = -1.00 V(SCE), upper limit = +1.00 V(SCE) and final potential = 0.00 V(SCE).

After getting the cathodic peak of HgCl$_4^{2-}$ reduction the potential scanning goes until -1.0 V(SCE) without any hydrogen evolution since its cathodic overpotential on the mercury cathodic surface, just generated, is greater than that of any other metal.

The large separation ($\sim 0.5$ V) of peaks may be due to the irreversibility of HgCl$_4^{2-}$ ions, generated during the dissolution of mercuric chloride (HgCl$_2$), in dissociating before the reduction reaction takes place. This means that a slower charge-transfer process is occurring.

**The Electroleaching Process**

The treatment of the mercury bearing activated carbon comprises different processes and unit operations. Initially, the electroleaching of such carbon takes place where we got elemental mercury at the cathode surface and, as a result of this treatment, a mercury-free carbon. This carbon needs to be reactivated and further re-impregnated with elemental sulphur to be used back to the gas cleaning system. The flow diagram of the Figure 4, as follows, gives a brief idea of the whole treatment.
The reaction system depicted in Figure 5, was used for the electroleaching of the mercury loaded activated carbon. It is a batch recycle mode reactor where the mercury bearing activated carbon is used as anode. As a cathode, a titanium foil was used, in the first place, and the elemental mercury being deposited, during the electrolytic process, was eventually collected at the bottom of the cathodic compartment.

The electrolyte used, in the electro-oxidation tests, was a 1M sodium chloride solution, which pH was adjusted to pH 4, using hydrochloric acid or sodium hydroxide in the case of lower or higher pH respectively. The mercury loaded carbon was used as anode, as shown in the Figure 6, being the current fed, initially, through a graphite rod.

To maximise the use of the available sections of reticulate electrode material, a three compartment flow cell was designed along expected commercial lines, i.e., the current flow and the electrolyte flow directions were orthogonal in a side-by-side arrangement. The three compartment cell is rectangular and made out of Perspex glass (PMMA); the compartments are separated by a porous polypropylene separator (Polypropylene filter – Z10,425-6 – Aldrich), located between the cathode compartments and the anode compartment, so as to keep the carbon particles accommodated without short circuiting with the cathodes.
This process, for treating residues with high mercury content, promotes the dissolution of mercury as HgCl$_4^{2-}$, a quite stable mercury species, that is, immediately, deposited on the cathode surface. The success of this process will depend, to some extent, on how effective is the chlorine reaction with the aqueous solution, generating the oxidising agent (ClO$^-$), which promotes the chemical dissolution of mercury according to the following reaction:

$$Hg + 2ClO^- + 4Cl^- + 2H_2O \Leftrightarrow Cl_2 + HgCl_4^{2-} + 4OH^-$$  \hspace{1cm} (2)
Mercury compounds are highly soluble in aqueous chloride solutions because of the complexation of mercuric ions. The following equilibrium reactions must be considered:

\[ Hg^{2+} + Cl^- \rightleftharpoons HgCl^+ \quad K_1 = 5.6 \times 10^6 \]  
\[ Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_{2(aq)} \quad K_2 = 1.7 \times 10^{13} \]  
\[ Hg^{2+} + 3Cl^- \rightleftharpoons HgCl_3^- \quad K_3 = 1.2 \times 10^{14} \]  
\[ Hg^{2+} + 4Cl^- \rightleftharpoons HgCl_4^{2-} \quad K_4 = 1.2 \times 10^{15} \]

The total mercury concentration in the solution is given by:

\[ C = [Hg^{2+}] + [HgCl^+] + [HgCl_{2(aq)}] + [HgCl_3^-] + [HgCl_4^{2-}] \]  

By substituting into Equation 6 the concentrations of \( HgCl^+ \), \( HgCl_2 \), \( HgCl_3^- \) and \( Hg^{2+} \) ions from the equilibrium expressions (3)-(4), respectively, and rearranging, the relationship between the concentration of \( HgCl_4^{2-} \) species and the total mercury concentration can be obtained:

\[ \frac{[HgCl_4^{2-}]}{C} = \frac{K_4[Cl^-]^4}{1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3 + K_4[Cl^-]^4} \]  

According to Equation 1, when the chloride concentration is 0.86 mol dm\(^{-3}\), approximately 90% of the total mercuric ions conform to the \( HgCl_4^{2-} \) species. The calculation procedure, based on the above equations, is only an approximate one, as the activity coefficients were not taken into account. However, it is useful because of its simplicity and it allows us to propose the following reaction:

\[ HgCl_4^{2-} + 2e \rightleftharpoons Hg^{0} + 4Cl^- \]  

as the predominant reaction during the deposition of mercury from a solution containing chloride ions in high concentration. Reaction 9 has a reversible electrode potential, under standard conditions, of 0.4033 V(SHE). This potential was calculated from standard Gibbs energy data.

The electrolytic process start, once the current is supplied, with the oxidation of the chloride ions to chlorine at the anode surface:

\[ 2Cl^- \rightleftharpoons Cl_2 + 2e \]  

While at the cathode the water is, initially, reduced producing hydroxyl ions and hydrogen:

\[ 2H_2O + 2e \rightleftharpoons H_2 + 2OH^- \]
Simultaneously, hypochlorous acid is generated, in the bulk, by the chemical reaction of chlorine, being formed at the anode, with the aqueous phase:

\[ \text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HClO} + \text{H}^+ + \text{Cl}^- \]  

which dissociates into hypochlorite and hydrogen ions, reaction directly dependent on the pH, and the oxidation power increases as the pH goes down since the generation of HClO is favoured as depicted in the thermodynamic stability diagram of Figure 6, which can be confirmed observing the speciation diagram of Figure 7. As the pH goes down below 5 one generates nearly 100% of HClO.

\[ \text{HClO} \leftrightarrow \text{ClO}^- + \text{H}^+ \]

These hydrogen ions react with the hydroxyl ions, product of the cathodic reaction, to form water:

\[ \text{H}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O} \]

During the electrolysis, after a while, the production of hypochlorite ions does not increase as expected, which is attributed to the generation of chlorate ions, either chemically:

\[ 2\text{HClO} + \text{ClO}^- \leftrightarrow \text{ClO}_3^- + 2\text{H}^+ + 2\text{Cl}^- \]

or electrochemically:

\[ 6\text{ClO}^- + 3\text{H}_2\text{O} \leftrightarrow 2\text{ClO}_3^- + 6\text{H}^+ + 4\text{Cl}^- + 3 / 2\text{O}_2 + 6e \]

This kind of reactions does not constitute a drawback to the process but improve the chemical oxidation of mercury species as the chlorate ions are even more oxidant than hypochlorite ions and hypochlorous acid.
Once producing those chlorine species (HClO and ClO⁻), the oxidation of elemental mercury takes place, according to the following reaction:

$$Hg + 2ClO^- + 4Cl^- + 2H_2O \leftrightarrow Cl_2 + HgCl_4^{2-} + 4OH^- \quad (16)$$

Once produced, the $HgCl_4^{2-}$ are reduced at the cathode surface:

$$HgCl_4^{2-} + 2e \leftrightarrow Hg^0 + 4Cl^- \quad (17)$$

The mercury deposition from chloride solutions, at the cathodes surfaces, where no reaction occurs among the elemental mercury and the electrode material, mercury droplets lost from the electrode cause calomel precipitation on the bottom of the cell by the following reaction:

$$Hg^0 + Hg^{2+} + 2Cl^- \leftrightarrow Hg_2Cl_2(s) \quad (18)$$

As can be seen, in the reaction (18), a very insoluble mercurous compound ($Hg_2Cl_2$) is formed which remains in the residue after the electroleaching process. Thus, is imperative to use mechanical devices to collect those mercury drops, falling down from the cathode surface, extracting them from the reaction system.

In the early stage of the electroleaching process, hydrogen evolution occurs according to the reaction (17). This reaction is in charge of a pH rise. Subsequently, this pH rise occurs through the mercury dissolution reaction, reaction (2).

During the electroleaching process, the solution pH had to be controlled in a safe range, between 4 and 6. When the solution pH goes down below 4, mercurous chloride ($Hg_2Cl_2$) is formed, which is very insoluble in chloride solution. On the other hand, if the solution pH goes up above 9 causes precipitation of a large amount of mercury oxide (HgO), as insoluble as mercurous chloride, and will remain in the residue as such. In addition, it is recommended to keep the pH below 6 where one has the formation of HClO, a stronger oxidizing agent, rather than ClO⁻.

For tracing the mercury concentration down, during the electro-oxidation process, the electrolyte and carbon were sampled for every set of experiment and analysed for mercury by atomic absorption spectrometry, before and after the electro-oxidation process, in addition, following the same procedure, the sulphur and the sulphate concentrations were also analysed in the carbon and electrolyte, respectively.
During the electroleaching process the mercury-bearing activated carbon was used as the anode of the electrolytic cell. However, such carbon is used as particles, ranging from 3 to 5 mm, implying that it is necessary to use a sort of inert current feeder so as to make the electrolysis to take place. Two different current feeders were used during the experimental work: a) graphite bar and b) titanium gore covered with iridium oxide (IrO₂), the so-called DSA® (dimensionally stable anode) electrode, which in this case was produced by De Nora do Brasil Ltda.

It is well known that conventional electrochemical reactors with two-dimensional electrodes suffer from low space-time yields and consequently high specific investment costs. Attempts to overcome this handicap were made with the introduction of three-dimensional electrodes (fluidised bed\textsuperscript{[23]} or packed beds\textsuperscript{[24]}, which, by means of increased electrode surface area per unit volume and high mass transfer coefficients, give higher specific capacities. The behaviour of packed bed and fluidised bed electrodes for a range of reactions has been widely reported\textsuperscript{[25-29]}

Nickel foam electrodes were used for pollution control using dilute synthetic and industrial effluents\textsuperscript{[30-32]}. More recently, a copper foam electrode was used in electroorganic synthesis\textsuperscript{[33]}, while reticulated vitreous carbon or RVC began to be commercially available in 1976\textsuperscript{[34]}, and started to be applied, at least on laboratory scale, to remove, for example, mercury from contaminated brine solutions\textsuperscript{[35]}. Nickel foam which also have a reticulated structure, are now produced industrially; their performance as flow-through porous electrodes was reported by Marracino \textit{et al.}\textsuperscript{[36]}, who used the limiting diffusion current technique.

Before considering the application of the foams as porous electrodes percolated by electrolyte in forced flow (flow-through or flow-by porous electrodes), some parameters must be known, \textit{e.g.}:

- geometrical properties such as porosity, specific surface area, pore diameter distribution, isotropy of the texture, tortuosity, surface state etc.;
- Physical properties such as hydraulic diameter, permeability, electrical conductivity, mechanical strength etc.

The cathode used was the reticulated nickel foam as shown in Figure 8.
Results and Discussions

During the electroleaching tests the cell voltage and the cathode and anode potentials were monitored, while keeping constant the current intensity, which means that the tests were accomplished galvanostatically. The current intensity and brine flow rate were varied so as to evaluate the performance of the reaction system in terms of current efficiency (%) and specific energy consumption (kWh ton⁻¹) of carbon treated.

The current efficiency measures how much of the available current is used for the main reaction to take place, affecting, directly, the power consumption of the whole process. In this study, the current efficiency, related to the mercury removal from the carbon, which will always consider the mercury content of the carbon before and after each test, can be worked out by using the following expression [20]:

$$CE(\%) = \frac{100}{nF} \frac{V(C_i - C_f)}{\int_0^t I(t) dt}$$  \hspace{1cm} (19)

where \( F \) stands for the Faraday’s constant (Coulomb/mol-1), \( n \) for number of electrons in the electrochemical reaction, which in the case of the mercury oxidation from elemental mercury to \( \text{Hg}^{2+} \) is 2. However, in the case of mercury sulphide, which means the oxidation of the mercury sulphide (HgS) into sulphate (SO₄²⁻), \( n \) is 8. \( C_i \) and \( C_f \) is the mercury content of the carbon in the beginning and after finishing each electrolysis test, respectively, and finally, \( I \) is the current intensity used during the electrolysis time.
The specific energy consumption, a major portion of the operating cost of an electrowinning process, is calculated using the following equation\textsuperscript{[20]}:

\[
S.E.C = E \frac{nF}{M \cdot CE} \frac{100}{3600} \quad (\text{kWht.kg}^{-1})
\]  

(20)

where \(E\) is the cell voltage (V), \(M\) the molar mass, \(n\) the number of electrons in the electrochemical reaction, as above mentioned, \(F\) stands for the Faraday’s constant (Coulomb.mol\(^{-1}\)), and \(CE\) the current efficiency (\%).

The current intensity of 10, 12 and 20 Amperes were used and the flow rate varying from 1.96 x 10\(^{-2}\) to 3.61 x 10\(^{-2}\) m\(^3\) s\(^{-1}\), using about 1.4 kg of the carbon for each test.

Before starting the experimental electroleaching work, a sample of the so-called sulphur impregnated activated carbon was analyzed so as to find out the presence of elemental sulphur on the surface of such carbon particles. The Figure 14, as follows, shows the EDS (energy dispersing spectrometry) spectrum of the carbon surface evidencing the presence of sulphur associated to aluminium, oxygen, silicon and iron but not as free sulphur.

![Fig. 9 – EDS analysis of the sulphur impregnated activated carbon.](image)

The Figure 10 shows an x-ray diffraction diagram of the mercury-bearing activated carbon showing the presence of two different mercury compounds the cinnabar and meta-cinnabar, both with the same formula (HgS), and elemental mercury.
Fig. 10 – X-ray diffraction of the mercury-bearing activated carbon.

The Figure 11 confirm the presence of sulphur and mercury in the same spectrum emphasizing that mercury sulphide was generated during the gas cleaning operation.

Fig. 11 – EDS analysis of the mercury bearing carbon particle.

The Figure 12 shows, in detail, the previous photograph of the mercury-bearing activated carbon. It is clear, observing that photo, that the carbon particles are completely covered with mercury compounds.
The reticulate nickel foam, a kind of three-dimensional electrode, was used, apart from decrease, dramatically, the current density, for the same current range used in this study, due to the increase of the specific surface area, the mercury species reduction efficiency also increases. As a result of that, a very smooth mercury deposit could be observed on the whole foam surface, which means a high mercury loading capacity and, consequently, less residue in the bottom of the cell. However, one has to mention that once loaded with elemental mercury the metallic sponge has to be mechanically freed of it, either using compressed air or even vibrating it. The Figure 13, as follows, shows the nickel foam cathode loaded with mercury.

The Figure 14 shows the results of current efficiency changes with time and, as a consequence, the specific energy consumption. The results quoted in this figure show that the current efficiency reach, at
the beginning of the process, higher values but drops down faster reaching lower values more quickly causing, consequently, an increase in the power consumption.

![Graph showing the current efficiency (C.E) and specific energy consumption (S.E.C) changes with time for higher current intensity.](image)

**Fig. 15-** The current efficiency and specific energy consumption changes with time for higher current intensity.

**Conclusions**

The experimental results permit to conclude that:

The Hg concentration can be reduced from 15g/kg of carbon down to <50ppm, with high extraction efficiencies, which will, actually, depend on how the electrolysis is extended;

The remaining Hg concentration in the carbon is not low enough to be considered as suitable for being recycled, neither as activated carbon nor as energy source, being necessary to extend the electrolysis time; or use it back to the gas cleaning process;

The final leaching solution should not be released, as it contains high salinity and [Hg\(^{+2}\)] not suitable for being discharged. It should be reused for further carbon treatments;

It is recommended to perform the electroleaching process in an acidic pH range (between 4 and 6) so as to enhance the mercury dissolution.

We do suggest to use a three-dimensional cathode, such as the nickel foam used, so as to speed up the mercury deposition as we can use higher current intensities without increasing, to some extent, the current density; although, this can result in low current efficiencies.

The use of a three-dimensional electrode is also convenient as it keeps more elemental mercury on its surface, avoiding the mercury to drop down to the cell bottom, which would generate calomel (Hg\(_2\)Cl\(_2\));
References


[10] For example, Chem. Abs., 81, 82126e.


[34] The Electrosynthesis Co., PO Box 16, East Amherst, New York 14050, USA.