Procedure concerning the Mercury Removal from Municipal Waste Combustion Flue Gases

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Since the climatic changes are more and more attesting that humanity is causing additional man made pollution, the concept of sustainable development imposes the necessity of selecting and applying the most appropriate and available novel energy resources, including application of technologies focusing on waste incineration. Municipal solid wastes contain manufactured and natural materials, including paper, plastics, food wastes, etc., as well as inorganic materials such as glass and metals residues. Approximately all of these solid wastes also contain in more or less significant quantity heavy metals (e.g. mercury, chromium, lead, etc.). After combustion, these metals are to be found both in bottom and fly ash, but also in the flue gas, as particulate or vapour. Once discharged and dispersed into the atmosphere the flue gases represent a risk for human health and generally for the natural eco-system. One of the most harmful for human health is the emission of mercury. This paper focuses on mercury removal from waste combustion exhaust gases accomplished on a lab facility. The composition of the municipal waste combustion flue gases is physically simulated in order to correspond to real waste flue gases, by using natural gas combustion and injection of different known rates of pollutants, such as NO\textsubscript{x}, SO\textsubscript{2}, particles and heavy metals, including mercury, into the resulted gases, previous to the point where the proposed technology is applied. Several comparative tests and key-solution in order to clean up the municipal waste flue gases are presented, with results comprised in tables and diagrams. As conclusion, one draws the general idea, that the procedure proposed by the authors is efficient and acts effective for the mercury reduction in flue gases, according to the maximum admitted limits indicated by Romanian and European legislation, and determines also the simultaneous reduction of other pollutant components.

Keywords: waste incineration, heavy metals, mercury, flue gas cleaning technologies, environmental pollution.

Since the climatic changes are more and more attesting that humanity is causing additional man made pollution, the concept of sustainable development determines the necessity to operate more and more with new energy resources. One of the approaches in meeting this goal is the use of municipal wastes for energy production [1-3]. Municipal solid wastes contain manufactured and natural materials, including paper, plastics, food wastes, etc., as well as inorganic materials such as glass and metals residues. Approximately all of these solid wastes also contain in more or less significant quantity heavy metals (e.g. mercury, chromium, lead, etc.). After combustion, these metals are to be found both in bottom and fly ash, but also in the flue gas, as particulate or vapour. Once discharged and dispersed into the atmosphere the flue gases represent a risk for human health and generally for the natural eco-system. One of the most harmful for human health is the emission of mercury [2-9]. Around 5000 t of mercury are emitted annually from different sources, ca. one third of them being of anthropogenic origin. 80% of anthropogenic mercury comes from the combustion of fossil fuels, wastes and other sources [10-12]. Due to the enormous quantities of municipal wastes, in the last decades, it was started a world program for ecological wastes incineration [13, 14]. The European Environmental Laws emission limitation brings a new challenge for advanced flue gas cleaning by different methods using high performance technologies [2, 15, 16].

This research focuses especially on mercury removal from waste combustion exhaust gases. The experimental tests were carried out on a lab facility with a 5 m\textsuperscript{3}/h flow rate. The composition of the gases was simulated in order to correspond to real waste flue gases, by using natural gas combustion and injection of different known rates of pollutants, such as oxides of nitrogen, sulphur dioxide, particles and heavy metals, including mercury [17-19]. Emissions of SO\textsubscript{2}, NO\textsubscript{x} were removed simultaneously during the process, indicating that the proposed technology acts efficiently and non-selective.

Experimental part

The removal process of mercury from the flue gas has been achieved on an experimental lab facility (flue gases flow rate 5 m\textsuperscript{3}/h). A schematic of this procedure and a view of the lab facility are shown in figure 1. Most significant components of the proposed facility are: reactor, flue gas cooling system, cyclone, bag filters, and flue gas cleaning system. Also, it is important to note that the lab facility was fitted with a digital dosing pump, which permits the dosage of the specific pollutants to the system, as for example Hg and HCl at desired concentrations. Details of this complex device are described in previous studies [20-25].

In order to simulate different compositions of the flue gas, under optimal conditions in order to correspond to real flue gases, a number of preliminary tests were approached and accepted [4, 6, 12, 20, 24, 26]. Table 1 indicates the composition of flue gases as a result of the injection of specific pollutant components into the experimental combustion chamber [6].

Additionally there were used simultaneously two main measuring systems, one dedicated to the mercury detecting, in all its complex forms, and the other for other pollutions, e.g. NO\textsubscript{x}, SO\textsubscript{2}, CO. In addition to thermodynamic parameters of the process. The thermal regimes, the pressure levels and mass flows were strictly controlled and monitored.

The complete measuring system of the emissions of mercury involves two main components:
- a flue gas processing device Hg-PPS
Hg-PPS includes a catalytic converter that transforms ionic compounds of mercury (Hg\(^{2+}\)) into elemental mercury (Hg\(^0\)), under condition of being heated up to 610°C. The concentrations of other heavy metals were recorded as well, using: Varian SpecrAA 110 - spectrometer, Varian Pro Star - chromatograph for fluids and a chromatograph for gases, etc.

At a flue gas temperatures of 300°C recorded at the exhaust of reactor, the injection of aqueous mercuric chloride (HgCl\(_2\)) has started. Its concentration was calculated in advance in order to achieve a value of 300 \(\mu g/\text{m}^3\) flue gases. Also, simultaneously, there were proportioned other pollutants such as sulphur dioxide, other heavy metals and hydrogen chloride.

For producing SO\(_2\), there were used some chemical methods [28], characterized by the following reactions:

\[
\begin{align*}
\text{HCl} & \rightarrow 2\text{H} + \text{Cl}, \\
\text{Na}_2\text{SO}_3 + \text{H} \rightarrow \text{Na}_2\text{SO}_4 \quad (1) \\
\text{Na}_2\text{SO}_4 + 1/2\text{O}_2 & \rightarrow \text{Na}_2\text{SO}_3, \quad (2) \\
\text{Na}_2\text{SO}_3 + \text{O}_2 & \rightarrow \text{Na}_2\text{SO}_4, \quad (3) \\
\text{Na}_2\text{SO}_4 + 1/2\text{O}_2 & \rightarrow \text{Na}_2\text{SO}_3, \quad (4)
\end{align*}
\]

As shown in the flow chart, the flue gases after cooling are passed through a complex flue gas cleaning system for:

- a device for mercury monitoring - Hg-MONITOR 3000 [27].

Pollutants that have been dosed to the facility, using a dosing pump, are: mercury, sulphur dioxide, hydrogen chloride, directly or in form of a sprayed in solution. For ex., the pump injected the aqueous solution of hydrogen chloride at pH 1-1,5 and hydrogen peroxide (H\(_2\)O\(_2\), 30 %), by means of spraying nozzles, with an internal diameter of 0,3 mm.

In respect to the hydrogen chloride, two situations have been noted:

- HCl was not sprayed into the flue gas channel and the pH of the solution was around 6, with not efficient results meaning that the mercury was not retained, as only small amounts of it were absorbed;

Results and discussions

- removal of ash and dust that occur in a cyclone and in filters respectively;
- a washing out procedure in a washing unit, with the purpose of retaining other liquid and gaseous pollutants. Washing unit comprises: a spraying scrubber to convert metallic Hg to ionic Hg; and, a bubbling scrubber used to retain the ionic Hg into the liquid washing solution. The combination between both scrubber systems is presented in figure 2.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>IS Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>g/m(^3)_H</td>
<td>1</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>mg/m(^3)_N</td>
<td>100-800</td>
</tr>
<tr>
<td>NO(_x)</td>
<td>mg/m(^3)_N</td>
<td>200-500</td>
</tr>
<tr>
<td>Hg</td>
<td>(\mu g/m^3)_N</td>
<td>100-300</td>
</tr>
<tr>
<td>CO</td>
<td>mg/m(^3)_N</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>O(_2)</td>
<td>% vol.</td>
<td>10-11</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>g/m(^3)_N</td>
<td>100-150</td>
</tr>
<tr>
<td>C(_6)H(_6)</td>
<td>mg/m(^3)_N</td>
<td>2</td>
</tr>
</tbody>
</table>
- spraying of HCl and maintaining a pH of 1-1.5 determines more adequate conditions that determined rapidly and efficient the removal of Hg, reaching an overall efficiency of 80 %.

After the flue gas cleaning, the concentration of mercury in the exhaust gas was below 50 μg/m³, that meant, that the results are corresponding to existing environmental legislations. A special remark is given concerning the composition of the flue gases. Thus it was mentioned that during the whole experimental procedure the main combustion parameters have been regulated at appropriate extend to assure and maintain the contents of oxygen in the exhaust gases not more than 10 % (vol).

During the tests using also activated carbon, the removal efficiency of mercury was around 90-95 %, regardless of the form of state of the mercury: metallic or cationic. Simultaneously, one achieved to retain the captions of other heavy metals, as well. The removal capacity of activated carbon was large enough, even at higher concentrations of pollutants. Using the washing activated carbon one attends best results, meaning that a small content of pollutants has been detected in the scrubbing liquid, while the rest of pollutants were chemically fixed by carbon. By washing it with strong acids, i.e. with HCl 31 % or H₂SO₄, one achieved the extraction of these pollutants additionally.

In order to fully protect the environment and avoiding passing the pollution from air into soil or water, one tested several possibilities for the removal of heavy metals from the washing liquid of activated carbon in steps, as follows:

- precipitation with a very concentrated solution sodium sulphide (Na₂S). The consumption was very high and accompanied by evolving of hydrogen sulphide. As result a mixture of insoluble sulphides of the heavy metals was formed. The reaction route is as follows:

\[
2\text{HCl} + \text{Na}_2\text{S} \rightarrow \text{H}_2\text{S}_2(\text{g}) + 2\text{NaCl} \tag{5}
\]

\[
[\text{Me}]\text{Cl}_2 + \text{Na}_2\text{S} \rightarrow [\text{Me}]\text{S}_2(\text{precipitate}) + 2\text{NaCl} \tag{6}
\]

where [Me] means one of the metals: mercury, iron, chromium, nickel, molybdenum.

- circulation of washing liquid through an ion exchange resins Purolite S-330. The achieved removal efficiency for this quality of resins is very high, up to 526 g Hg/l. The operating temperature is about 80°C and the pH is in average 1-13. After the saturation of the resins it is indicated to accomplish a regeneration procedure with sulphuric acid (4 %).

- precipitated into alkaline method. Once regenerated, heavy metals are expected to be precipitated into alkaline medium at pH 8.9-9: (excepting amounts of Hg which remain in solution), according to following reaction:

\[
[\text{Me}]\text{Cl}_2 + 2\text{NaOH} \rightarrow [\text{Me}]\text{OH} + [\text{Me}]\text{S}_2(\text{precipitate}) + 2\text{NaCl} \tag{7}
\]

After filtration of the precipitate, two options were tested for the mercury separation from solution:
- by means of precipitation with sodium sulphide,
- through electrolysis of the solution with salts content of mercury.

For the first option it was achieved the precipitation with Na₂S at approximately stoichiometric consumption, having already alkaline medium. Later the filtration of HgS, and metallurgical processed for extraction of metallic mercury have been realised. The reaction of precipitation and the oxidation of HgS:

\[
\text{HgCl}_2 + \text{Na}_2\text{S} \rightarrow \text{HgS}_{(\text{precipitate})} + 2\text{NaCl} \tag{8}
\]

\[
\text{HgS} + \text{O}_2 \rightarrow \text{Hg}_{(\text{metallic})} + \text{SO}_2(\text{g}) \tag{9}
\]

As second option: electrolysis of the solution with mercury chloride (HgCl₂) or with mercury sulphate (HgSO₄) has been applied. During electrolysis alkali/alkaline earth metals, e.g. sodium, potassium, calcium, magnesium, react with water by resulting hydrogen, according to the following situations:

- in case of potassium and sodium,

\[
[\text{Me}] + \text{H}_2\text{O} \rightarrow [\text{Me}]\text{OH} + \frac{1}{2}\text{H}_2 \tag{10}
\]

- in case of calcium and magnesium,

\[
[\text{Me}] + 2\text{H}_2\text{O} \rightarrow [\text{Me}]\text{OH}_2 + \text{H}_2 \tag{11}
\]

It has been noticed that during the electrolysis the pH of the solution decreased from 8.5-9 to almost neutral values such as 6.5-7. Under the circumstances that the electrolysis takes place into acid medium (HCl, H₂SO₄, HNO₃) one achieves conditions that lead to a solubility of Hg into H₂SO₄ and HNO₃, and formation of HgSO₄, Hg(NO₃)₂ which is a completely undesirable process.

The wet scrubber technique used in the tests utilizes hydrogen peroxide to oxidize elemental mercury to a water soluble form. In the scrubber Hg, SO₂ and NOx are oxidized by the hydrogen peroxide. The oxidation and absorption are performed in a scrubber with tower packing. The flue gas is passed in counter current to the scrubber liquid. The oxidized mercury could either be precipitated either collected for safe deposit or recycled as Hg⁰. Chemical reactions occurred as follows, both in a gaseous medium as well in a scrubbing liquid:

![Fig. 3. Evolution of the pollutants concentration and thermodynamic parameters, before and after application of the technology. Measure points (p.m.) are shown in figure 2](image-url)
\[ Hg^2+ + H_2O_2 \rightarrow Hg^3+ \]  
(12)

\[ SO_2 + H_2O \rightarrow H_2SO_4 \]  
(13)

\[ 2NO + 3H_2O \rightarrow 2HNO_3 + 2H_2O \]  
(14)

\[ CO + H_2O \rightarrow CO_2 + H_2O \]  
(15)

Besides these reactions, there are oxidative processes of the hydrocarbon traces, such as methane (CH₄), present in combustion gases, the global reaction being:

\[ CH_4 + 4H_2O \rightarrow CO_2 + 6H_2O \]  
(16)

For chemical oxidation, some peroxides (Na₂O₂) could be used with the same effect, but a supplementary charge with Na⁺ of the washing fluid and an important rising of the pH occurs. In the presence of water, a high exothermic reaction is produced, with NaOH forming:

\[ Na_2O_2 + H_2O \rightarrow 2NaOH + 1/2O_2 \]  
(17)

The results of the tests are shown in figure 3.

**Conclusions**

As result of municipal waste incineration huge amounts of emission pollutants are discharged into the atmosphere, including mercury. The technology proposed in this study reduces by removing, at an acceptable rate, the mercury contents in the exhaust flue gases. Other emissions can be mitigated as well using a specific concentration of the removal additive solutions. The technical methodology consists of an easy removal of mercury, of mercury compounds and other heavy metals, by direct removal of mercury as metal or electrochemically removal from a solution [26]. The used solution is active for other compounds as well.

The advantages of the proposed method are:

- simultaneous removal of other heavy metals such as copper, cadmium, nickel, zinc, chromium, with an attested elimination efficiency achieved of over 90 %;
- decrease in the emission amounts of sulphur dioxide and nitrogen oxide concentrations, effectiveness of 90 %;
- low energy requirements for the total flue gas cleaning procedure;
- possibility of recovering the mercury, by a special technology, characterised by the retaining heavy metals on the resin from the cationic filter are supposed to be passed through a regeneration solution, washing with HCl 8 %;
- using a bed of Raschig rings assures a good contact between the flue gas and liquid, resulting in a suitable efficiency at low cost.

- using many possibilities of producing SO₂, a good method being the injection in proportioned solution of Na₂S₂O₃ or Na₂S₂O₅.

The main advantage of this technology is the possibility of coupling the waste incinerator with a steam generator working on coal (or another fossil fuel), by introducing the combustion gasses from the incinerator in the generator - the UPSWING system [6].

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**Review**

**ORGANIC CHEMISTRY**

**SIXTH EDITION**

**AUTHOR: MIRCEA IOVU**

**PRINTING HOUSE: “MONITORUL OFICIAL”, BUCHAREST, ROMANIA, 2008, 1,147 PG.**

A CONTEMPORARY APPROACH TO ORGANIC CHEMISTRY

The Printing House of the “Monitorul Oficial” of Romania has recently published the 6th edition of Organic Chemistry. The first five editions have appeared in Romanian since 1978. The author and editor of the book is Professor Mircea Iovu, who started his academic career and research activity at the Department of Organic Chemistry of Bucharest University and pursued it at “Carol Davila” University of Medicine and Pharmacy for over half a century.

Each of the previous five editions allowed the author to confront the reader’s expectations and update the summary, taking into account the rapid evolution of research methods and new applications and the amazing growth of the number of organic compounds, which demand a better systematization of the material and even giving up information that has become less important.

In ORGANIC CHEMISTRY, the author manages to present, in a relatively small number of pages (1,100) all the essential theoretic and practical issues of Organic Chemistry that are prerequisites for advanced courses. In American universities, such textbooks are compulsory in the introductory years of study of Chemistry majors, but also for further instruction in other academic areas: Biology, Medicine, Agricultural Science etc.

The book adheres to the classification of compounds according to functional group and not to the division between aliphatic vs. aromatic series.

The book consists of 23 chapters. The first chapter presents a brief history of Organic Chemistry, the structure of atoms and molecules, reaction mechanisms (in general) and the theory of acids and bases.

The following three chapters are devoted to a synthetic presentation of the isolation, purification, analysis (including chromatographic methods) and physical properties of organic compounds.

Chapter 5 is devoted to spectroscopic methods, including UV-Vis and IR molecular absorption, nuclear magnetic resonance spectrometry and mass spectrometry. The chapter presents the phenomena involved and the equipment used for such methods. Each group of compounds in the chapters to follow will be characterized by physical constants, especially spectral ones.

Starting with Chapter 6, titled Hydrocarbons, presents the main classes of organic compounds. "Hydrocarbons”, the longest chapter of the book (130 pages), includes alkanes, cycloalkanes, polycyclic alkanes, alkenes, alkynes, alkadienes, mono- and polycyclic aromatic hydrocarbons, charge transfer complexes and free radicals of hydrocarbons. Types of isomerism are mentioned for various classes of hydrocarbons.

Chapter 7 deals with Organic halides, alkyl, allyl, benzyl, vinyl and aryl halides. The mechanisms of nucleophilic substitution reactions are also discussed.

Hydroxyl compounds are presented in Chapter 8, which includes monohydroxyl and polyhydroxylic alcohols, enols, monohydroxylic and polyhydroxylic phenols, mixed ethers and esters of inorganic acids. This chapter also mentions phenomers, many of which have hydroxyl groups or derivatives.

The presentation of Carbonyl compounds is the topic of Chapter 9. The chapter deals independently with monocarbonyl compounds, saturated or unsaturated dicarbonyl compounds.

Chapter 10 presents Carboxylic compounds divided into subgroups: saturated monocarboxylic acids, dicarboxylic acids, unsaturated monocarboxylic and aromatic acids. The chapter also presents the derivatives of carboxylic acids such as acyl halides, anhydrides, esters, soaps, acyl peracids and peroxides, orthoesters, amides, hydroxamic acids, hidrazides and azides, nitriles and isonitriles.

Chapter 11, titled Carbonic acid and its derivatives, presents carbonyl chloride and carbonic acid amides, urea, urethanes, ureides, melamine and guanidine.

Carboxyl and other functional groups, such as halogenated acids, hydroxy acids, prostaglandines, carboxy aldehydes and ketones are discussed in Chapter 12.

Chapter 13 is devoted to Stereochimistry, chirality, enantiomers, the R-S conventional system, diastereoisomers and asymmetric synthesis. Chapter 12 also contains a discussion of chiral drugs, less usual in Organic Chemistry textbooks.

Chapter 14 presents Nitrogen containing compounds, nitroderivatives, nitrosoderivatives, amines, phase transfer catalysts, diazonium salts, azo derivatives, aryldiazines, oximes and carcinogenic nitrogen containing compounds.

Chapter 15 is devoted to Bilfunctional compounds with two different functional groups. One of these groups is amino, as in amino acids, amino alcohols and amino phenols. This chapter also discusses proteins, and in relation to them, Combinatorial chemistry.

Sulfur containing compounds are the topic of Chapter 16. Phosphorous and silicon compounds are discussed in the same chapter, 17.

Chapter 18 of the book deals with Organometalic compounds. Such compounds are usually included in inorganic chemistry books, as numerous methods of synthesis have been devised for organic compounds using organometallic compounds as intermediaries.

Carbohydrates, including monosaccharide, disaccharides and polysaccharides (with a presentation of glycogen and heparin) are discussed in Chapter 19.

Chapter 20 extensively presents Heterocyclic aromatic compounds. Alongside pentaatomic and hexaatomic compounds, this chapter is concerned with nucleic acids, whose molecular structure includes nitrogen-containing bases.

Chapter 21, Polyisoprenic natural compounds, includes terpenoids, carotenoids and steroids.

Dyes are devoted a separate chapter, 22, which includes the classification and description of the main classes of dyes, a feature less frequently encountered in a foreign book on Organic Chemistry. In a separate sub-chapter non-conventional dyes are mentioned: macromolecular dyes, photochronic dyes, thermochromic dyes and liquid crystal dyes.

The last chapter, 23, refers to Macromolecular compounds. This chapter deals with the classification, preparation, molecular structure and physical and chemical properties of such compounds, after which there is a presentation of the main classes of polymers.

There is a separate discussion of biodegradable and technological polymers of a special importance today, as well as polymeric composite materials.

Each chapter is followed by exercises and applications.

A separate chapter, 24, contains 54 Complex review problems that include physical and chemical data.

The Glossary includes brief definitions of the terms (compounds, phenomena, reactions) that allow the reader to understand and continue to read the material.

The book ends with a rich index, annexes and references.