1. Introduction

The elemental mercury has a lifetime in the atmosphere up to one year and can be transported. The EU strategy on mercury endorses the objective of reducing mercury emissions from large power plants by the application of the IPPC Directive and LCP Directive. The Commission will assess the co-benefit effect of these rules on mercury and will consider if further actions are needed, by the end of 2010. ENEL is focusing on mercury emission reduction by enhancing its removal in the already available APCD. Previous work has shown that SCR catalysts can oxidise elemental mercury to its ionic form that can be removed in a wet FGD plant. The mechanisms of homogenous and heterogeneous and catalytically driven oxidation of mercury are not clear. ENEL activity is involved in:
- evaluating the mercury emissions on the production units
- evaluating the effect of catalyst on the oxidation of mercury with 150 Nm3/h side-stream SCR reactor
- studying the possibility of removing mercury by using sorbents.

In order to measure the sorption capacity of the commercial sorbents a lab-scale device was set-up where it is possible to make tests using synthetic gas mixture similar to the combustion gas and mercury can be added in its elemental and oxidised form. The final purpose of this activity is to evaluate the capacity of fly ash and sorbents to absorb mercury; the tested substrate are ash from an ESP and a FF and commercial sorbents as Norit FGD and HOK. The relative importance of the main gas components (water, sulphur dioxide, nitrogen dioxide, hydrogen chloride) was tested in the mercury oxidation process.

2. Reactor description

The reactor has three main parts:
- the gaseous fluxes mixer
- the oven containing the fixed bed section
- the \( \text{Hg}_0 \) e \( \text{Hg}^{++} \) speciation system

The general reactor scheme is shown in Figure 1. The gas used as carrier is nitrogen. A flux of nitrogen (some ml/min) passes through two small reservoirs in series which contain elemental and ionic mercury. The reservoirs are warmed at different temperatures since they are in two ovens. Another nitrogen line transports the vapours generated by a dilute solution of HCl. Two lines are dedicated to two standardised gas mixture containing SO2 and NO in nitrogen. After the addition of the necessary amount of air the overall flow rate was set at 3.5 l/min with nitrogen. The sorbent fixed bed to test is put in a special glass cell which has a capacity of about 1.5 g of bed. The cell is in an oven in order to control the reactor temperature. All the tests were run at 150°C. Before each test the bed is equilibrated at the oven conditions for about 1 h. During this phase the gas is by-passed. In order to measure elemental (\( \text{Hg}_0 \)) and
ionic (Hg2+) mercury a specific system was developed by ENEL [4]. The system consists of two parts, a commercial instrument (FIMS 400) for the mercury determination by Cold Vapour Atomic Absorption Spectroscopy (CVAAS) in liquids, and a device that captures the vapour-phase mercury through the absorption in two solutions; this system was modified to allow the sampling and the analysis of the two different solutions every 20 seconds.

Figure 1. Reactor scheme

3. Experimental Plan

It is well known that mercury can be absorbed by carbonaceous particles and a big effort was made in order to formulate sorbents that should be able to remove this element from gases. The combustion of coal produces itself carbonaceous particles which can absorb mercury too. The substrate used for the absorbing tests are

- fly ash sampled at an experimental test rig which include an experimental electrostatic precipitator (ESP), a fabric filter (FF) and a fabric filter compact (FFC)
- two commercial activated carbon named FGD and HOKp
- a fly ash obtained mixing the ash of different hopper of an electrostatic precipitator ESPA.

The ESP ash was separated in 4 sized fractions in order to evaluate the influence of particle size on mercury absorption.

The same unseparated ESP ash was used for the experiments at different gas composition. Finally the sorbents FGD and HOK are added at different concentration to a fly ash produced by a 640 MWe boiler and named ESPA. For each experiment the standardised procedure was the following:

- place the sorbent layer in the cell (diameter 33 mm, depth 2mm, about 1.5 grams)
- build-up of gas mix as stated by the experimental matrix,
- turn on the oven and leave to stabilise the system for at least one hour, during this phase the gas mixture is by-passed by the cell containing the sorbent and the Hg levels are recorded as baseline
- switch the gas to the cell and record the concentration of the elemental and oxidised mercury at its exit
- record the end of the test at the break through-out point, when the system is stabilised again and the sorbent is saturated by mercury.
The gas velocity cross the substrate layer was fixed at 3-4 m/min, about 3 times more than a conventional fabric filter.

4. Results

The chemical characteristics of fly ash and sorbents used in the experimentation are summarised in table 1

<table>
<thead>
<tr>
<th>Ash</th>
<th>D 50% μm</th>
<th>Surf. Area m²/g</th>
<th>C %</th>
<th>Hg μg/g</th>
<th>Fe2O3 %</th>
<th>CaO %</th>
<th>K2O %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESP</td>
<td>17.2</td>
<td>4</td>
<td>5.3</td>
<td>0.46</td>
<td>4.99</td>
<td>8.99</td>
<td>0.89</td>
</tr>
<tr>
<td>FF</td>
<td>15.4</td>
<td>6.3</td>
<td>8.4</td>
<td>1.29</td>
<td>11.99</td>
<td>8.54</td>
<td>1.39</td>
</tr>
<tr>
<td>FFC</td>
<td>9.8</td>
<td>3.5</td>
<td>5.3</td>
<td>0.46</td>
<td>10.21</td>
<td>7.44</td>
<td>2.79</td>
</tr>
<tr>
<td>CA FGD</td>
<td>24.8</td>
<td>670</td>
<td>64.7</td>
<td>&lt;0.01</td>
<td>11.57</td>
<td>38.16</td>
<td>1.68</td>
</tr>
</tbody>
</table>

*Table 1 Chemical characteristics of the tests sorbents*

The ESP ash is similar to the FF ash even if the particle mean diameter is a little bit higher and the surface area a little bit lower. The surface area of the activated carbon is about two order of magnitude bigger than that of fly ash. The ash of the Fabric Filter Compact shows a particle diameter lower about 10 microns and a surface area lower than all the sorbents used.

**4.1. Effect of substrate**

Figure 3 shows the result of the first test made on the ESP ash. The elemental mercury (pink) when the gas is shifted to the absorbing cell drops to zero. After about two hours the signal of oxidised mercury (blue) increases up to the same level of the elemental mercury fed to the cell. The absorbing capacity of the ash can be evaluated by the saturation time at the half concentration point.

The relevant fact is that all the mercury is oxidised by the gas and that this reaction is catalysed by the fly ash. For this experiments the chloride concentration was relatively higher than that commonly found in the coal combustion gas since in the hypothesis of a participation of chloride to the mercury oxidation and absorption we added a large excess of this reagent.

<table>
<thead>
<tr>
<th>Ash</th>
<th>Gas Composition</th>
<th>Hg tot in</th>
<th>Hg tot out</th>
<th>Hg final</th>
<th>Hg initial</th>
<th>Sat. time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO (mg/Nm³)</td>
<td>SO2 (mg/Nm³)</td>
<td>HCl (ppm)</td>
<td>gas μg/Nm³</td>
<td>μg/Nm3</td>
<td>ash μg/g</td>
</tr>
<tr>
<td>ESP</td>
<td>955</td>
<td>1358</td>
<td>108</td>
<td>21.8</td>
<td>21.5</td>
<td>2.13</td>
</tr>
<tr>
<td>FF</td>
<td>955</td>
<td>1358</td>
<td>108</td>
<td>18.1</td>
<td>17.8</td>
<td>1.87</td>
</tr>
<tr>
<td>FFC</td>
<td>955</td>
<td>1358</td>
<td>108</td>
<td>17.3</td>
<td>16.8</td>
<td>0.54</td>
</tr>
</tbody>
</table>

*Table 2. Mercury oxidation on ESP, FF, and FFC ash*

The ash collected at the fabric filter shows properties similar to those of ESP (Figure 3 and Figure 4). The same test made with the fabric filter compact ash which shows a saturation time lower than ESPA but the starting mercury level for this substrate is higher and consequently it can be understood that the total absorbing capacity is lower.

The behaviour of the fly ash collected by the fabric filter compact is quite different, only a part of the elemental mercury passing trough the ash layer is oxidised (Figure 5), this fact
indicates that the oxidation sites are in a less amount for this substrate. The fabric filter compact collects the fly ash leaving a reduced ESP section where about 95% of fly ash is removed from gas. The mass median diameter of the FFC ash is one half but the surface area is lower than the other ash samples. Probably the FFC ash contains an higher fraction of vitreous particles less reactive. At lower SO2 concentration in the gas the mercury absorption capacity of this ash increases. Averaging all the tests made on the three types of fly ash the best substrate in terms of mercury absorption capacity is the ESP ash (table 2)

![Figure 3](attachment:espa.png)  
*Figure 3 Elemental mercury oxidation on ESP fly ash*

![Figure 4](attachment:ffpa.png)  
*Figure 4. Elemental mercury oxidation on Fabric Filter ash*
4.2. **Effect of the gas composition**

The mechanism of mercury oxidation is not completely clear. It was postulated the existence of free chlorine in the flue gas or some other oxidising species. In the present work they are evaluated the separate effects of the main syntetic gas components. The observed effects are quite strong. In absence of SO2 the absorption capacity of fly ash increases strongly so that the saturation time is more than doubled (Figure 6).

![Figure 6. Absorption of mercury on ESP ash in absence of HCl](image)

In absence of HCl (Figure 7 and table 3) mercury is still oxidised but not completely and the sorption capacity of the fly ash decreases respect to test with the complete gas mixture.

<table>
<thead>
<tr>
<th>Ash</th>
<th>Gas Composition</th>
<th>NO (mg/Nm³)</th>
<th>SO2 (mg/Nm³)</th>
<th>HCl (ppm)</th>
<th>Hg tot in</th>
<th>Hg tot out</th>
<th>Hg final</th>
<th>Hg initial</th>
<th>Sat.</th>
<th>time</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESP</td>
<td>955</td>
<td>1358</td>
<td>0</td>
<td>Hg gas</td>
<td>Hg gas</td>
<td>Hg ash</td>
<td>Hg ash</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ESP</td>
<td>955</td>
<td>0</td>
<td>108</td>
<td>15.4</td>
<td>16.8</td>
<td>21.7</td>
<td>0.54</td>
<td>0.47</td>
<td></td>
<td>39</td>
</tr>
<tr>
<td>ESP</td>
<td>0</td>
<td>1358</td>
<td>108</td>
<td>14.83</td>
<td>16.7</td>
<td>18.1</td>
<td>2.74</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 3. Mercury oxidation on different composition gas*
In absence of NO mercury is not oxidised at all. This is a particular aspect of the entire experimentation: the chemical species which seems to be responsible of elemental mercury oxidation is NO. After that mercury is oxidised it can react with chloride and released as HgCl₂ or it can be released as HgO. The continuous mercury analyser in effect is not able to distinguish between HgCl₂ or HgO.

5. Conclusions

In a lab-scale device a series of tests were performed in order to evaluate the Hg oxidation mechanisms. The fly ash mercury absorption capacity is strongly affected by the ash origin. The ESP ash has a strong tendency to absorb mercury in its oxidised form. The tests were performed in a medium which simulated the system fly ash-combustion gases as in a pulverised coal generated combustion gas. SO₂, NO and HCl seems to play an active role in the mercury oxidation mechanism, but the oxidation by NO is probably the first stage in this reaction. The analytical and instrumental set-up was reliable and allows to study all the sorbents and all the effects on mercury oxidation.

6. References

1. COM(2005) 20 final – Communication from the Commission to the Council and the European Parliament, 28.01.05 – Community strategy Concerning Mercury;
4. Bianchi A., La Marca C., Cioni M. Joint Meeting of the Scandinavian Nordic and Italian Sectors of Combustion Institute, Napoli, September 18-21, 2003;