Mercury Retrieval from Flue Gas by Monolithic Adsorbents Based on Sulfurized Sepiolite

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The current sulfur-impregnated activated carbons are extremely costly sorbents in mercury control technologies. In this regard, the present study offers a cheaper alternative by using a natural silicate, sepiolite, as sulfur substrate. Sepiolite is a fibrous hydrated magnesium silicate clay that is very cheap (around $100/t of the 0.6–0.8-mm fraction) and abundant with unique textural and structural characteristics: S_{BET}, 150–350 m² g⁻¹; pore volume, 0.3–0.8 cm³ g⁻¹; density, ~0.8 g cm⁻³. Samples of 10% S supported on monolithic sepiolite have been used to retain 90 ppm mercury in air at 320 K and ambient pressure. The experiment has been effected in a dynamic system at fluid velocities in the 4.7–18.8 cm s⁻¹ range. A comparative study of the performance of three different monoliths against a fixed-bed reactor of powders of 0.026-cm size is made. Under the work conditions, the process is governed by mass transfer, which on fresh solids fits the expression Sh = 0.075Re⁴/₃ for powders and Sh = 0.766 (Re Sc d⁻¹)⁴/₃ for monoliths. In the work, the importance of the adsorbents texture and, consequently, of the monoliths preparative method is demonstrated: the capacity per mass unity of the samples is better when impregnation is the last preparation step because porosity is better preserved and sulfur is more uniformly distributed.

Introduction

Global emissions of mercury resulting from human activities are quite important for human safety, at least at the local level. Worldwide mining of mercury is estimated to yield about 10 000 t per year, the related activities leading to some losses of mercury and direct discharges into the atmosphere. Other important sources are chlor-alkali industries, metal sulfide ore smelting, gold refining, cement production, and sulfur is more uniformly distributed. ostatements of 1990 have required the U.S. EPA to perform a study of mercury emissions from several sources to establish the corresponding safety levels.

Currently the best technology developed for mercury abatement is the use of dry lime scrubbing followed by fabric filters, which gave removal efficiencies of 97% (2). To achieve the high removal efficiencies required, adsorption-based technologies seem promising. In this regard, solids with a high surface area to be used either as a direct adsorbent or as a support for a disperse active phase are necessary (4). In previous works (4–6), sulfurized sepiolite has proven to be useful as much less expensive alternative than the currently used activated carbon to retain mercury vapors. Sepiolite is an abundant and cheap, naturally occurring silicate with surface areas between 150 and 300 m² g⁻¹ depending on the mineral history.

Concerning the high volumetric rates involved in the incineration of sewage sludge or a combustion of fossil fuels for thermic and electric utilities, the use of monolithic structured reactors seems profitable (7, 8). The main advantages of a monolithic substrate are due to its large external surface and its low-pressure drop, 2 or 3 orders of magnitude lower than for a bed of spherical particles with a particle diameter of the same order of magnitude as the channel width of the monolith (9); in contrast, mass and heat transfer in monoliths are in general somewhat lower than in conventional fixed-bed reactors.

This paper presents experimental data on mercury retrieval from gas streams using different types of reactors. With it, we pretend on one hand to compare the performance of a fixed bed of spherical particles against that of a monolithic structure, both made from sulfurized sepiolite, and on the other hand to search for the appropriate mass transfer correlation to be used in the performance estimation of both types of solids. Finally, we use it to study the effect of varying the method of active phase incorporation to the substrate in the adsorbent efficiency.

Experimental Section

Surface area of the samples was calculated from N₂ adsorption isotherms built in a Micromeritics ASAP 2000 at 76 K using 0.162 nm² as a cross-section of the adsorbed N₂ molecule. From the isotherms, pore size distributions were also evaluated by the BJH method. The study of porosity was completed by mercury intrusion in a Poresizer 9310, also evaluated by the BJH method. The study of porosity was completed by mercury intrusion in a Poresizer 9310, also from Micromeritics, using 140° as the contact angle and 485 dyn cm⁻¹ as mercury surface tension.

The content of sulfur in the adsorbents was monitored by sulfur burnout to SO₂ in 50 mL min⁻¹ flowing air in a TGS-2 Thermobalance from Perkin-Elmer rated at 10K min⁻¹. The percent weight loss at around 513 K was evaluated, and the average of a series of measures from various spots along the samples length is given as % S in the sample.
The mercury removal activity was tested in the dynamic system described elsewhere (6) (Figure 1). Mercury concentration at the inlet was maintained at 90 \( \times 10 \text{ mg m}^{-3} \). The total setup and heating was designed to use high concentrations of Hg in order to shorten the experimentation time.

Experimental conditions are as follows: volumetric flow rate, \( Q \), 0.036–0.22 m\(^3\) h\(^{-1}\); linear velocity, \( U \), 4.7–18.8 cm s\(^{-1}\); temperature, 320 \( \pm 2 \text{ K} \); W/F, 0.04–3 g of adsorbent mg\(_{Hg}\)\(^{-1}\) h; \( W \) is the mass of adsorbent in g, and \( F \) is the mercury feed, QC\(_0\), in mg h\(^{-1}\).

The retained mass of mercury was evaluated by raising breakthrough curves of the packed bed, representing the mercury concentration, at the outlet against time. From them, conversion, \( X \), at any time \( t \) is defined as

\[
X = \frac{C_0 - C_s}{C_0}
\]

in which \( C_0 \) and \( C_s \) are respectively the mercury concentration at the inlet and outlet at time \( t \).

The retained mass of mercury at any time \( t \) was obtained from

\[
q = \frac{Q}{W/F} \int_0^t (C_0 - C_s) \, dt
\]

To compare the performance of different materials, \( C_{min} \), minimum mercury concentration in the effluent gas in mg m\(^{-3}\), and material maximum capacity, total mercury uptake by the exhausted adsorbent in mg g\(^{-1}\), have been evaluated.

Mercury concentrations in air at the inlet and outlet of the system were monitored by a gold film mercury vapor analyzer, Jerome 411, through a rubber portion in the tubing (S). The equipment is periodically calibrated against the tabulated values of mercury vapor pressure at a stable temperature. The gold film is selective to elemental mercury, and no other mercury compound (HgS or HgO), water vapor, particulate, etc. interferes with the lecture, which is directly read in mg m\(^{-3}\) after calibration.

Sensitivity is 1 \( \mu \text{g m}^{-3}\), and deviation on clean sensor surfaces is less than ±5%.

The reaction of Hg(0)g with O\(_2\)(g) proceeds at 298 K at the slow rate of \(< 1 \times 10^{-23} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) (10), and then, no HgO formation along the reactor is expected. On the other hand, the possible catalytic effect of the sepiolite support has been discarded through a blank test under the same work conditions on which lectures at the inlet and outlet of the experimental system do coincide within the experimental error.

Eventually, the samples were post-test examined by a scanning electron microscope ISI DS 130 equipped with an EDX analyzer. The elemental analysis of the two main components, S and Hg, was carried out using the lines K\(_R\) and L\(_R\), respectively. In the analysis, around 25 spots through a vector across the monoliths walls were examined, and the corresponding composition is given as a percent of the total elements present.

**Adsorbents**

Sulfurized monoliths have been prepared:

- (a) By mass extrusion of sepiolite powders previously sulfurized by either surface reaction between H\(_2\)S and SO\(_2\) following a super-Claus process at around 373 K temperature, sepiolite acting as a catalyst (powder PP), or impregnation with 0.5 M sulfur solution in CS\(_2\) (11) at 318 K (powder IP).

- (b) By impregnation of sepiolite monoliths with the same 0.5 M S solution in CS\(_2\) said above.

To manufacture the monoliths, powders in the 0.020–0.032-cm size range, sulfurized or not, were mixed with water in a 1:1 proportion, kneaded 1 h, and finally extruded through the corresponding die in a Bonnot extruder. The obtained monoliths are square channeled with the geometrical dimensions and cell densities, after being dried at 373 K and controlled humidity, as shown in Table 1. They give rise to samples PPCM and IPCM from sulfurized powders PP and IP, respectively, and sample CPIM from fresh sepiolite followed by impregnation. All samples were designed to have 10% S. The pressure drop corresponding to both types of samples at various \( U \) values has also been incorporated into the table.

The physicochemical characteristics of the samples are gathered in Table 2.
Results and Discussion

As has been reported elsewhere \(^5\), sulfur reacts with mercury to give HgS, black metacinnabar \((\text{F}, 7, 7, 3\text{gc m})\), with an equilibrium constant at the reaction conditions of \(1.93 \times 10^{-38}\), equivalent to the total conversion of the sulfur present; the theoretical capacity of the adsorbent (in mg g\(^{-1}\)) is, as a consequence, 62.5 times its percent content of sulfur.

Figure 2a–c depicts the breakthrough curves for mercury retention as outlet concentration against time corresponding respectively to powders (a), PPCM monolith at two different gas velocities (b), and monoliths PPCM, IPCM, and CPIM under identical external conditions (c). All curves show the three different stages reported by Otani for activated sulfur on alumina and zeolites \(^1\): activation, reaction, and exhaustion. The extension of every step is related to the design parameters but also to the physicochemical characteristics of the samples \(^6\). In Table 3, the performance of the samples is summarized.

From the curves, it can be inferred first that sulfurized sepiolite is able to retain mercury; second, that the time necessary for activation, i.e., the time to reach the maximum in conversion, is slightly lower on samples prepared by reaction/deposit and the same for monoliths conforming after sulfurization; and third, inferable from Table 3, that the capacity of the adsorbents per unit mass differs from sample to sample, being much smaller on monoliths than on powders. It must be emphasized that an increase in linear velocity from 4.7 to 18.8 cm s\(^{-1}\) (gas–solid contact time from 2 to 0.5 s, respectively) provokes on sample PPCM a decrease in conversion from 0.997 to only 0.944, which means that external mass transfer is deeply affecting the process.

The mass balance for plug-flow conditions can be written as

\[
\frac{\partial (C_{\text{Hg}})_{\text{b}}}{\partial z} = r_{w,P} + \epsilon \frac{\partial (C_{\text{Hg}})_{\text{b}}}{\partial t}
\]

where \((C_{\text{Hg}})_{\text{b}}\) is the mercury concentration in the bulk, \(r_{w,P}\) is the global rate per unit volume of the reactor at time \(t\), \(\epsilon\) is the external fraction of voids in the bed, and \(U\) is the linear velocity in direction of flow.

The gas–solid contact time \((U/z)\) is 0.5–2 s, and given the experimentation extent, some hours should be needed before

\[
\Delta P (\text{cm of water m}^{-1} ) = \frac{\alpha}{U (\text{cm s}^{-1} )}
\]

\(\Delta P\) is the pressure drop across the bed.

In a previous work, Guijarro \(^13\) has reported first-order kinetics \((K (C_{\text{Hg}}))\) for the reaction on fresh solid. Under such conditions, the integrated form of eq 4 is

\[
\ln \frac{1}{1 - x_{\text{max}}} = KW/Q
\]

\(x_{\text{max}}\) is the maximum conversion.
TABLE 4. Evaluation of Mass Transfer Coefficients

<table>
<thead>
<tr>
<th>sample</th>
<th>U (cm s⁻¹)</th>
<th>K (cm² g⁻¹ s⁻¹)</th>
<th>Ka⁻¹ (cm s⁻¹)</th>
<th>Re</th>
<th>Sh</th>
<th>kc (cm s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>9.4</td>
<td>127</td>
<td>0.50</td>
<td>1.4</td>
<td>0.12</td>
<td>0.52</td>
</tr>
<tr>
<td>IP</td>
<td>9.4</td>
<td>114</td>
<td>0.45</td>
<td>1.5</td>
<td>0.12</td>
<td>0.52</td>
</tr>
<tr>
<td>PPCM</td>
<td>4.7</td>
<td>7.3</td>
<td>0.31</td>
<td>3.4</td>
<td>0.22</td>
<td>0.19</td>
</tr>
<tr>
<td>PPCM</td>
<td>18.8</td>
<td>13.4</td>
<td>0.42</td>
<td>13.5</td>
<td>0.38</td>
<td>0.41</td>
</tr>
<tr>
<td>IPCM</td>
<td>18.8</td>
<td>20.6</td>
<td>0.28</td>
<td>13.5</td>
<td>0.38</td>
<td>0.41</td>
</tr>
<tr>
<td>CIPM</td>
<td>18.8</td>
<td>14.3</td>
<td>0.38</td>
<td>13.5</td>
<td>0.38</td>
<td>0.41</td>
</tr>
</tbody>
</table>

Then, the capacity of the samples is related to their geometric surface area but also to their porosity. In Table 3, the capacity per area unity has been included. As can be seen, it is of the same order of magnitude in all samples independent of size and shape, which confirms the external mass transfer as addressing the process but also shows slight differences among samples that should be related to the porosity of the solid. Incidentally, from the data, a similar reactivity of the sulfur incorporated to the samples, despite their different origin and method of incorporation, is inferred.

Every sulfur atom after reacting with mercury to form HgS occupies 1.6 times its original volume; the retained mercury not only will affect the pore diameter by a factor proportional to the fraction of sulfur entering in the reaction but also will form an increasingly thicker layer of product, which will hinder the progression of the reactive gases toward the active sulfur, decreasing the effectiveness factor of the solid. As a consequence, the reaction takes place only on a part of the solid, and the efficiency of the adsorbent will depend on the portion of the solid that can be penetrated by the reactant.

Pore volume in all samples is high enough (Table 2) to accommodate all the mercury stoichiometrically corresponding to the sulfur present (assuming a density for the formed metacinnabar of 7.73 cm³ g⁻¹), but, because of the fouling of the solid, the actual capacity of the samples is far from its theoretic value (column 7 in Table 3) and will also depend on pore size distribution and even connectivity of the pore system.

Mercury profile inside the samples of monoliths, built by scanning microscopy, is nearly homogeneous throughout their length, no matter the preparative method used: entrance effect does not exist, and neither axial nor radial dispersion are apparent. However, the cross-section of the monolith walls shows a different distribution of both elements, sulfur and mercury, depending on the samples. Post-test line profiles corresponding to S and Hg across the walls of samples PPCM and CIPM are shown in Figure 3a,b, respectively, on which the X-axis denotes the distance (in μm) from the external surface within the solid walls. Sulfur exhibits a heterogeneous distribution piling up near the external surface in PPCM, whereas it is almost uniformly distributed on CIPM; mercury, on its turn, qualitatively adopts the same tendency as sulfur, although at lower values, and shows a higher concentration on CIPM than on PPCM from a certain distance, about 24 μm, from the surface, that should be related to the smaller sulfur concentration on the outer surface of CIPM and justifies its higher capacity in the dynamic test. In the figure, also the mercury line profile corresponding to sample PPCM exposed to 4.7 cm s⁻¹ fluid velocity has been included: a smaller incoming of the reactant, a consequence of a poorer mass transfer, results also in the accumulation of mercury on the outer surface of...
the adsorbent but in a profile within the solid at slightly lower level than above denoting the influence of the external conditions in the efficiency of the solid.

Those differences in sulfur distribution that ultimately determine the capacity of the solids should be related to the preparative method which, in that sense, is of utmost importance. In the case of powders, sample PP sulfurized by reaction deposit has around 17% of the total sulfur on its external surface, 8 × 10⁻³ times the internal one (24), which means that it offers to mercury a thick layer of sulfur difficult to penetrate, thus limiting its efficiency. In contrast, sample IP with the active phase uniformly distributed throughout the sample by impregnation, facilitates mercury diffusion and leads to a capacity slightly better than above. In the case of monoliths, the differences in sulfur distribution arise from using sulfurized against fresh powders as raw material because in the first case the extrusion procedure results in an accumulation of sulfur on the outer surface of the solid, whereas in the second, impregnation after conformation, the distribution of sulfur throughout the solid is nearly uniform (Figure 3a).

The preparative method also plays a role in the time necessary to reach the maximum in conversion (the activation time detected in the breakthrough curves), because sulfur is more accessible on the outer surface than inside the solid to the gaseous reactant and can create through the heat evolved in the reaction with mercury (ΔH₂⁰ = 92 kcal mol⁻¹) a larger number of S radicals, the active phase in the reaction with mercury (24), by breakdown of S−S bonds on which 52 kcal mol⁻¹ are involved (25).

As a consequence, powders PP and monoliths PPCM coming from them are the most active at zero time, despite offering the lower capacity of all samples and in the opposite sense do powders IP and monoliths CPIM.

From the above, the retention of mercury by sulfurized sepiolite takes place mainly on the external surface of the solid and progresses inside the bulk up to a depth whose extension depends on the operational parameters but also, and especially, on the texture of the solid and the active phase distribution, both of them deeply related to the preparative method. The V:S ratio as much as the appropriate amount of sulfur to avoid the accumulation of product in the porous system of the solid are two more variables to have in mind in order to optimize the efficiency of the adsorbent.

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