Adsorption and oxidation of sulfur dioxide by active carbons

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Sulfur dioxide is adsorbed by active carbons in an oxidized form when adsorption takes place in presence of oxygen and water vapor, and the adsorbate can be removed as sulfuric acid by extraction with water or dilute sulfuric acid . These reactions can be used as the basis of an industrial process for the desulfurization of flue gases. It has an important advantage over processes in which the carbon is regenerated by high temperature desorption, since extraction is a regeneration procedure that does not cause deterioration of the carbon.

The economics are largely determined by the quality of the adsorbent used, which must meet simultaneously the three following requirements:(a) High capacity and high rate for the adsorption of sulfur dioxide. (b) High catalytic activity for the oxidation of sulfur dioxide to sulfuric acid, (c) Weak adsorption energy for sulfuric acid, resulting in high and rapid extractability. Quality (a) largely determines the purity of the treated gas and the size of the adsorption bed, and qualities (b) and (c) determine the concentration of the sulfuric acid obtained, the duration of the desorption cycle, and the stability and long term performance of the adsorbent. The concentration of the sulfuric acid obtained has a crucial economic importance as it determines whether this acid is a usable product or a waste.

The present research shows that carbons with high efficiency for this particular process, can be obtained by introducing acidic surface groups with oxidizing properties. The three above mentioned required properties are improved, specially the extractability of the sulfuric acid formed. A simple way of introducing acidic oxidizing surface groups is by treating the carbon with nitric acid at controlled conditions.

The effect of the oxidizing power and acidity of the surface groups on the transformation of sulfur dioxide into sulfuric acid and on the extractability of this acid is easily understood. Their effect on the enhancement of the adsorption of sulfur dioxide can be explained by a mechanism involving promotion of the condensation of water vapor in the pores and interaction of the condensed water with the sulfur dioxide.

Experimental

The behavior of treated carbon samples (C2) is compared with that of untreated samples (C1) in two types of experiments:

a) Performance tests in which a stream of simulated flue gas flows through a fixed bed of adsorbent. They include: Measurement of the adsorption capacity for sulfur dioxide of various carbon samples with feeds of various compositions, flowing at various space velocities. Estimation of the fraction of the adsorbed sulfur extractable as sulfuric acid, and concentration of the extracted acid, at various operation conditions . Test of the performance of the carbons after repeated cycles of adsorption and extraction

b) Determination of the kinetics of adsorption and the equilibrium adsorption of sulfur dioxide on carbon samples preheated at various temperatures up to 1000^0 C . Adsorption was performed by allowing helium containing a small concentration of sulfur dioxide to flow through the carbon sample. Adsorption runs were followed by desorption runs performed by flushing helium at the adsorption temperature. Measurements were performed by using a Cahn balance.

Results

Adsorption and extraction in fixed beds of carbon:
In all the tests and with all the types of carbon examined, the performance of a treated carbon was superior to that of an untreated one at the same operating conditions .

Example :
Adsorption experiment: Bed volume 3 litres. Feed 0.2% SO_2 in nitrogen. Space velocity 0.47 sec^{-1}. Temperature 80^0C. Point at which average concentration of SO_2 in effluent is 0.02% taken as breakthrough point Results: SO_2 content in carbon bed at breakthrough point (in moles. kg^{-1}): Sample C1, 1.34, Sample C2, 1.93.
Extraction of sulfuric acid following adsorption: 1.6 liter 2N solution of sulfuric acid allowed to percolate through the carbon bed. Results: Concentration of sulfuric acid in effluent: Sample C1, 2.3 N, Sample C2, 3.8 N.

Cahn balance experiments:
Preheating of the carbon causes increase of adsorption and decrease of desorption. The effects are more important in carbons C2 than in carbons C1. The results indicate adsorption by an acid base mechanism different from the mechanism that prevails when the carbon is not preheated .