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Pilot plant performance of a SO_2 to SO_3 oxidation catalyst for flue-gas conditioning

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Abstract

A honeycomb catalyst for the oxidation of endogenous SO_2 from a coal-fired power-station flue-gas has been developed. The catalyst reached a SO_2 to SO_3 conversion of 60 vol.% after 200 h in operation at the pilot plant. When this catalyst is further treated for another 100 h at lab scale to complete its activation, a stable 80 vol.% conversion is obtained. The results have been used to design an industrial unit for flue-gas conditioning to improve the fly ash collection by the electrostatic precipitator in a 220 MW coal-fired power plant. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Monolith; Sulfur dioxide oxidation; Flue-gas conditioning; SO_2 abatement

1. Introduction

Emissions control techniques are some of the main environmental concerns of energy supply based on coal-fired power plants. As it is known, the sulfur oxides emitted from coal-fire combustion stations are currently controlled by wet lime/limestone scrubbers and spray dryers where the disposal of the waste products is a major problem due to the lack of suitable disposal sites.

Latterly, catalytic oxidation of sulfur dioxide to sulfur trioxide has emerged as one alternative to the above mentioned processes. In these catalytic systems, a useful SO_3 by-product is obtained from which various commercial products may be produced, such as sulfuric acid and ammonium sulfate [1–3]. Another promising application of the SO_2 to SO_3 catalytic oxidation, in coal-fired power stations, is flue-gas conditioning to improve the performance of the particulate electrostatic precipitator (ESP). Modern ESPs reach fly ash removal efficiencies of 99.9% complying with the particulate current emission standards. However when low-sulfur coal is used in order to fulfill the sulfur oxide emission regulations, inefficient operation of these ESP unit arises, since in this situation, the SO_3 concentration in the flue-gas is not enough to adjust the fly ash resistivity. Although the amount of the required SO_3 to increase the ESP's efficiency depends on various factors such as gas temperature or coal ash content, the typical values for SO_3 concentration usually vary within the range of 20–50 ppmv [4]. Most SO_3 flue-gas conditioning systems currently used, are based on catalytic conversion of SO_2, supplied in liquid form or obtained by burning sulfur. The drawbacks of these units, besides the economical and environmental issues, comprise the storage and handling of those hazardous materials.

An original flue-gas conditioning method, which overcomes these problems, has been proposed [5,6], where endogenous SO_2catalytic oxidation to SO_3

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takes place in such a way that the ESP requirements are fulfilled. The design of an adequate installation varies with the operational parameters of each specific industrial plant to be retrofitted. The percentage of oxidized SO_2 could be managed in a broad range of values depending on the portion of the flue-gas to be treated. In the case of total flue-gas conditioning, Unland et al. [5] reported that a 75 MW power plant would only need 6 vol.% of SO_2 conversion. Whereas, according to the Epricon technology [6], in a 250 MW power plant where around 3% of the total flue-gas is treated, about 70 vol.% conversion would be required. In both cases, the catalysts were conformed as a parallel channel-type or honeycomb structure to avoid plugging by the fly ash, but as they were prepared by impregnation, their deactivation due to abrasion could be expected.

In the present study, an industrial-scale monolithic catalyst based on vanadium pentoxide, potassium sulfates and diatomaceous earth has been tested at pilot plant scale for the endogenous SO_2 oxidation to SO_3. The catalyst with honeycomb configuration has been produced by extrusion in order to minimize the abrasion effect observed when impregnated catalysts are used. A 60 vol.% conversion of the SO_2 to SO_3 would allow the conditioning of a flue-gas, which contains 700 ppmv of SO_2 by treatment of about 3% of the total flue-gas from a coal-fired power plant.

2. Experimental

2.1. Catalyst preparation

The honeycomb catalyst was based on diatomaceous earth with potassium sulfate and ammonium metavanadate as active-phase precursors. The components were intimately mixed before extrusion in order to obtain a homogeneous paste following the method reported elsewhere [7]. The catalyst was manufactured by extrusion of a paste comprising all the components. The diatomaceous earth and potassium sulfate powders were kneaded after adding the vanadium salt aqueous solution. The V/K atomic ratio was 3.5 with 7.5 wt.% V_2O_5. The square-cell monoliths, after activation, had a cell density of 5 cells cm^{-2}, pitch of 0.38 cm, wall thickness of 0.08 cm, geometric surface area of 720 $m^2\,m^{-3}$, bulk density of 0.7 $g\,cm^{-3}$ and a crushing strength of around 750 $kg\,cm^{-2}$. The external monolithic dimensions were $95\times95\times500\,cm^3$.

2.2. Catalytic activity test: pilot plant scale experiments

A schematic diagram of the pilot plant is shown in Fig. 1. The main body of the system was a catalytic reactor that contained a basket for the vertically arranged monolith package. The pilot plant operated using combustion gases from a gas–oil burner with a well-defined composition and operating temperature. The head unit was a gas generator designed to operate between 200 and 650 STP $m^3\,h^{-1}$ of flue-gas in the range of 350–500°C. These operational conditions were reached by setting the air–fuel ratio and the air-cooling water-recirculated device. A fly ash doser and a solid–gas mixer were placed upstream of the catalytic reactor. Two heated lined probes were connected up and downstream of the reactor in order to withdraw aliquots for SO_x analysis. A centrifugal fan located downstream of the bag-filter composed the tail unit. The pressure and temperature in the inlet/outlet of the reactor were monitored by a PC-program, along with the unburned hydrocarbons, SO_2 and O_2 levels. An additional thermocouple was installed at 15 cm depth inside a selected centered monolith channel in order to check the catalyst temperature. The required SO_2 inlet concentrations were obtained by sulfur carbide doping of the gas–oil. The catalytic reactor design and coupling accessories assured the isokinetic gas flow conditions at the entrance of the reactor.

2.3. Catalytic activity test: lab scale experiments

Catalytic activity measurements were carried out in a reactor working close to the isothermal axial profile, where carborundum fixed and isolated the monolith. A 98 wt.% sulfuric acid solution was placed at the reactor exit in order to avoid corrosion problems inside the SO_2 analyzer. Temperature and flow rate were controlled by two PID inlet/outlet reactor located and massflow controllers, respectively. The gas suppliers were cylinders without significant percentages of impurities and no fly ash dosage was added. The operating pressure was maintained at 120 kPa and SO_x analysis was continuously performed.

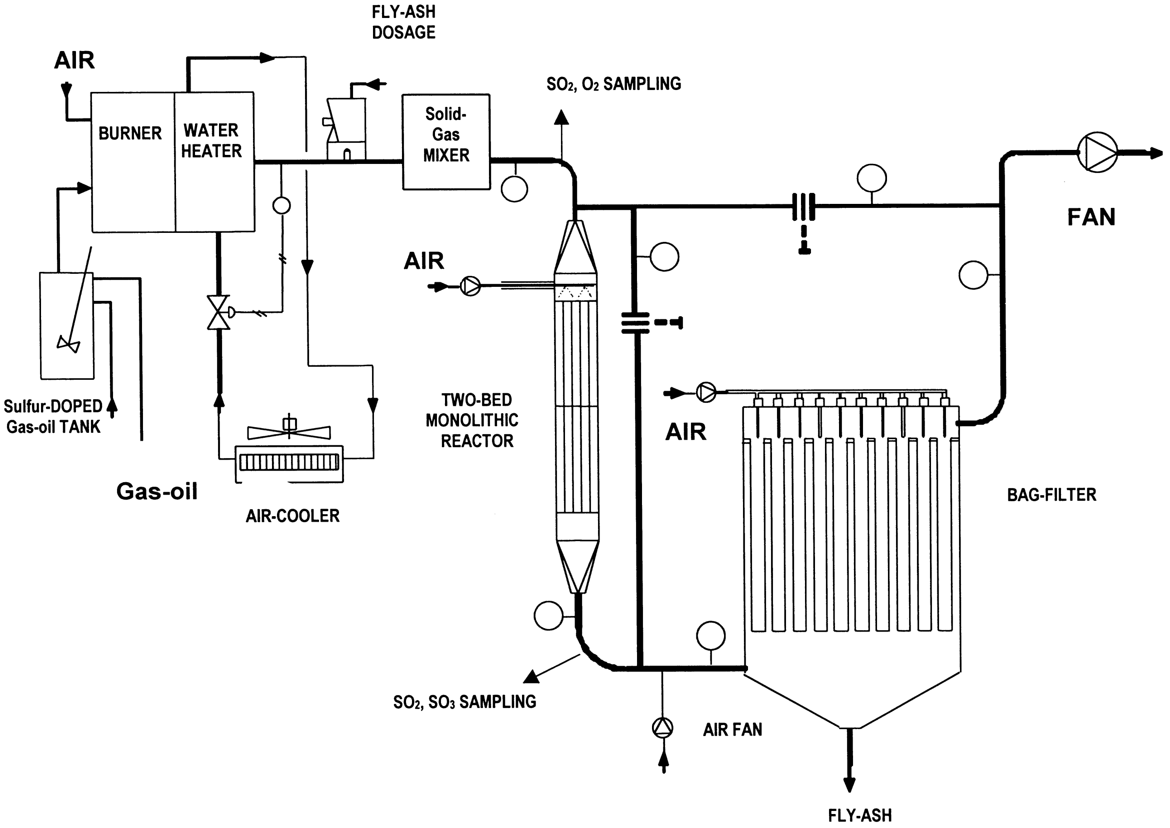

Fig. 1. Pilot plant scheme.

2.4. Analysis and characterization techniques

Textural properties of monolithic samples were analyzed in terms of total pore volume, mean pore diameter and BET surface area. These measures corresponded to the fresh and used catalyst from the pilot plant performance. Total pore volume and mean diameter were determined using a CE Instrument Pascal 140/240 porosimeter. The BET surface area was determined from the N_2 adsorption/desorption isotherms at 77 K, which were carried out in a Carlo-Erba Sorptomatic Series 1800. In both techniques, samples were outgassed overnight at 140°C. In the case of N_2 isotherm technique, samples were also outgassed to vacuum below 10^{-4} Torr to ensure a dry clean surface.

The mechanical strength of the fresh and used monolithic channel wall was determined using a Chatillon LTCM Universal Tensile Compression and Spring Tester with a cylinder test head of 1 mm diameter.

A Varian 3400 model GC coupled to a FPD was used to monitor the inlet/outlet SO_2 concentration at lab scale experiments.

The inlet/outlet SO_2, O_2 and unburned hydrocarbons measures at the pilot plant scale were performed using an ESSA ML9850 model ultraviolet fluorescence analyzer.

The EPA Method 8 [8] was selected for SO_3 sampling at the reactor outlet; the condensed sulfuric acid mist was measured by the barium–thorine titration method.

3. Results and discussion

3.1. Pilot plant scale experiment

The green catalyst must undergo an activation step, which requires SO_2 and SO_3 enrichment. In this activation process, which has been previously studied [7], the SO_x sorption gives rise to eutetic VK pyrosulfate complexes that were liquid under reaction conditions. The activation step could last from 60 to 100 h depending on the SO_2 and O_2 concentration in the flue-gas. This activation step has been shown to be a crucial factor to achieve satisfactory catalytic performance.

Moreover, interesting studies about the nature of the molten liquid active-phase have been carried out in order to identify which species were responsible for the catalytic activity [9].

In the pilot plant experiment, the activation of the catalyst was carried out using the flue-gas according to the conditions previously selected [7]. The operating conditions at the pilot plant are summarized in Table 1.

The concentration of unburned hydrocarbons was constant at 750 ppm (by vol.) and ca. 300 ppm for CO_2, CO and NO_x. Particulate matter was added in a concentration of about 15 g N m^{-3}. The monolithic pieces were distributed in two beds of 50 cm height each, with a total catalyst volume of 180 l. The pressure drop through the catalytic bed was in the range of 22–26 mm of H_2O m^{-1}.

In Fig. 2, the outlet concentration of SO_2, SO_3 and SO_2+SO_3 against time in operation is plotted. As can be observed, different physico-chemical processes took place during the course of the experiment.

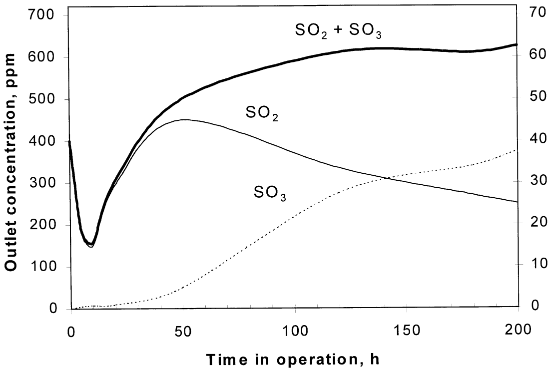

Fig. 2. Outlet concentration of SO_2, SO_3 and SO_2+SO_3 as a function of time in operation of the monolithic catalyst for the pilot plant experiment.

Table 1
Operational conditions (NTP) for the pilot plant scale test[a]

Average temperature (°C)	470
Pressure (kPa)	120
GHSV (h^{-1})	3200
LV (m s^{-1})	1.4
AV (m h^{-1})	4.4
Gas composition (by vol.)	
SO_2	700 ppm
O_2	3%
H_2O	7.5%
N_2	Balance

[a] GHSV: gas hourly space velocity; LV: linear velocity; AV: area velocity.

During the first 10 h, a steeply decreasing value of the outlet SO_2 was observed, but SO_3 was not observed. The SO_2 was transformed into SO_3 and retained in the molten active-phase, starting the formation of VK-pyrosulfates, the active-phase. The SO_2 sorption/oxidation phenomena and negligible SO_3 desorption during this period merely corresponded to the activation step of the green catalyst.

During the next 40 h in continuous operation, the rate of the activation process slowed down and the outlet SO_2 concentration started to increase until a maximum value of about 440 ppm was reached. Meanwhile, the SO_3 desorption was slightly taking place. Therefore, as SO_2 increased, only a small amount of SO_3 started to be released from the SO_3 saturated molten active-phase.

After 50 h in operation, the SO_2 catalytic oxidation started to be the main process in progress as the active-phase is more developed and less SO_3 was needed to be transformed into VK-pyrosulfates. During this period the SO_2+SO_3 outlet concentration was getting closer to the inlet SO_2 value. Therefore, the oxidation reaction rate increased as further active-phase was formed from the simultaneous SO_x absorption process.

After 200 h in operation, most of the active-phase had been formed although the outlet SO_2+SO_3 value was lower than 700 ppm, indicating that the activation process had not been accomplished. However, the SO_2 to SO_3 conversion achieved the required range of 60 vol.% and the pilot plant experiment was stopped. The analysis of the textural properties of the fresh and used catalyst showed significant changes. The S_{BET} decreased from 26 in the fresh sample to 2 $m^2\,g^{-1}$ in the used one. A reduction of the total pore volume was also observed from 0.27 to 0.18 $cm^3\,g^{-1}$. Drastic change of the mean pore diameter was recorded: the 65 nm diameter in the fresh sample shifted to 200 nm after reaction. The mechanical strength of the used catalyst steeply increased to 750 from the value of 114 $kg\,cm^{-2}$ of the brittle fresh sample.

Data from this physical analysis did not inform about the actual situation when SO_2 oxidation reaction was proceeding. As mentioned before, this type of catalyst — denominated supported liquid phase (SLP) — presents the characteristics of having a molten active-phase under reaction conditions. When the reactor was cooling down, the VK molten compounds precipitated and therefore, the porous structure changed. Nevertheless, a general evaluation could be drawn from the textural characterization results. As a consequence of the SO_x uptaking and simultaneous melting processes during the activation step, the smaller pores were filled up. Chemical changes of the VK-bearing species also produced variations on mechanical properties.

3.2. Lab scale experiment

As the activation process had not been completed during the pilot plant run, because the SO_x inlet/outlet balance was not closed, the catalyst activation was continued for a further 150 h at lab scale. The experiment was carried out using a 28 cm length 4 channel monolith taken from that used in the pilot plant. In this run, neither fly ash nor water vapor was added. The remaining operational conditions were as similar to those used in pilot scale as the scaling-down procedure allowed. The operating parameters are shown in Table 2.

Table 2
Operational conditions (NTP) for the lab scale test

Average temperature (°C)	470
Pressure (kPa)	120
GHSV (h^{-1})	3200
LV ($m\,s^{-1}$)	0.4
AV ($m\,h^{-1}$)	4.4
Gas composition (by vol.)	
SO_2	700 ppm
O_2	3%
N_2	Balance

The evaluation of the outlet SO_2, SO_3 and SO_2+SO_3 concentrations with time in operation is shown in Fig. 3. After 70 h, the SO_x reached steady state values of 175 ppm for SO_2 and 540 ppm for SO_3, indicating that the activation process was concluded. At this point, 80 vol.% SO_2 to SO_3 conversion was obtained, which remained constant until the reaction system was shut down 80 h later.

The textural and mechanical properties were also analyzed. The S_{BET} and total pore volume did not change from 2 $m^2\,g^{-1}$ and 0.18 $cm^3\,g^{-1}$, respectively, for the used catalyst at the pilot plant scale experiment. Nevertheless, the mean pore diameter increased from 200 to 600 nm. As the activation process had not finished after the 200 h in operation at the pilot plant experiment, the small increase in SO_x uptake during the lab scale run was thought to cause the alteration in the porous structure of the catalyst.

The experimental results for both pilot plant and lab scale runs, which summarize the catalytic activity performance, are plotted in Fig. 4. The SO_2 to SO_3 conversion versus time in operation is represented and

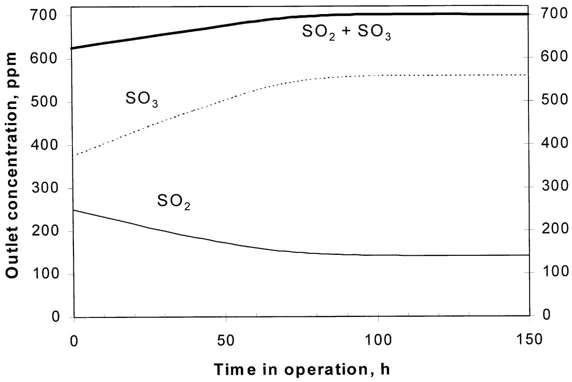

Fig. 3. Outlet concentration of SO_2, SO_3 and SO_2+SO_3 as a function of time in operation of the monolithic catalyst for the lab scale experiment.

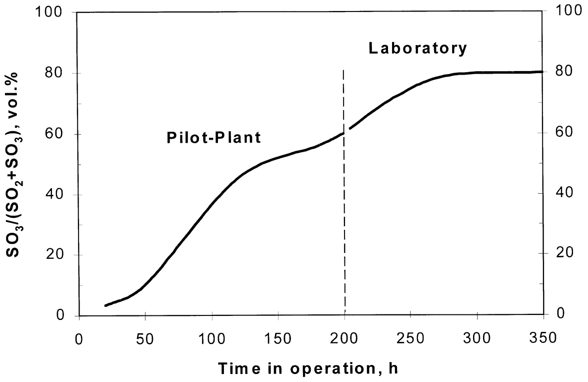

Fig. 4. Catalytic activity in terms of SO_3 percentage as a function of time in operation for both pilot plant and laboratory experiments.

the dotted line indicated the break point between the different operating-scale systems. In spite of variations in some of the operational parameters, such as linear velocity and the absence of fly ash and water vapor at lab scale conditions, a continuity of the catalyst performance was observed. In Fig. 4, at least three different steps can be distinguished:

1. In the first 50 h, the SO_2 to SO_3 conversion smoothly increased along with the formation of the active-phase through capturing the SO_x by the starting VK compounds. Moreover, these newly formed compounds must also be transformed into a molten material.
2. Between 50 and 300 h, the outlet SO_3 concentration steeply increased at different rates. In this step, the amount of the molten VK-pyrosulfates was augmented on the support and consequently, the SO_2 to SO_3 catalytic reaction increased. The phase transformation, which accompanied the chemical change, might also alter the porous structure because the liquid layer in motion was occupying the inter and intraparticulate space. Due to this movement, the starting VK compounds would be exposed to further activation processes. This fact might explain why the released SO_3 did not have a linear trend.
3. The steady state condition for the catalytic activity was achieved after 300 h in operation, where the active-phase was completely formed and neither SO_2 nor SO_3 was retained in the catalyst.

4. Conclusions

An industrial-scale honeycomb catalyst based on vanadium–potassium–diatomaceous earth was manufactured. A pilot plant was designed and built to simulate the real conditions of a coal-fired power plant.

The catalytic activity in the pilot plant scale experiment showed satisfactory results. The 60 vol.% requirement of SO_2 to SO_3 conversion was achieved after 200 h in operation.

A further experiment carried out at lab scale conditions showed a residual catalytic activity and when the activation process finished, a stable 80 vol.% SO_2 to SO_3 conversion was achieved.

The results have been used to design an industrial unit for flue-gas conditioning to improve the performance of the electrostatic precipitators in the 220 MW coal-fired power plant at Puertollano (Spain) run by Compañía Sevillana de Electricidad-Endesa Company.

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References

[1] D.C. Borio, W.H. Kingston, Processing and Utilization of High-Sulfur 5 (1993) 451.
[2] S. Blumrich, B. Engler, Catal. Today 17 (1993) 301.
[3] J. Blanco, A. Bahamonde, E. Alvarez, P. Avila, Catal. Today 42 (1998) 85.
[4] P. Gelfand, Electrical World (November 1984) 75.
[5] M.L. Unland, A. Vavere, R.A. Wright, Proc. Am. Power Conf. 58 (1) (1996) 326.
[6] P.P. Bibbo, Proc. Am. Power Conf. 57 (1995) 32.
[7] E. Alvarez, J. Blanco, P. Avila, C. Knapp, Catal. Today 53 (1999) 557.
[8] Environmental Protection Agency, Pt. 60, App. A Method 8, 40 CFR Ch. I (7-1-90 Ed.).
[9] G.E. Folkmann, K.M. Eriksen, R. Fehrmann, M. Gaune-Escard, G. Hatem, O.B. Lapina, V. Terskikh, J. Phys. Chem. B 102 (1998) 24.