

CALCIUM SILICATE CEMENTS FOR DESULFURIZATION OF COMBUSTION GASES

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INTRODUCTION

Fluidized-Bed Combustion (FBC) is a relatively new technique for burning high sulfur coals cleanly, at a projected cost comparable to conventional combustion systems. In a typical fluidized-bed design, sized and dried sorbent is blended with the feed coal and fed to the fluidized-bed combustor. Fluidization of the bed is effected by passing air up through the bed material, i.e., mixture of coal and sorbent. Sulfur dioxide formed by the oxidation of the sulfur contained in the feed coal reacts with and remains an integral part of the sorbent, thus reducing the quantity of sulfur emitted to the atmosphere by the combustor flue gases.

Limestone is known as a sorbent for desulfurizing combustion gases in fluidized-bed combustors. It has a moderate sulfur capture capacity of 30 to 40% (based on CaO) at temperatures of 800° to 850°C at a reasonable reaction rate. Also it is cheap and naturally abundant. However, limestone has several serious drawbacks. The sorption capacity decreases markedly above 850°C. It cannot be easily regenerated economically even at a temperature of 1000°C. It has serious attrition loss problems in fluidized-bed reactors. The reactivity is highly variable depending on the type of natural limestone. Because of these unfavorable properties, limestone is currently used only on a once-through basis. A potential problem in commercialization of fluidized-bed combustion with a once-through sorbent is that vast amounts of spent sorbent will be generated by this system, especially if high sulfur coals are burned and if air pollution emission limits continue to become increasingly stringent. Thus it may become necessary, particularly if a large number of FBC plants are built, to regenerate and recycle the sorbent. In this respect, for the last several years the Process Sciences Division of the Department of Energy and Environment at Brookhaven National Laboratory has been searching for a better sorbent and has identified calcium silicate bearing Portland Cement as a regenerative sorbent for FBC application (1-2).

The objective of this work is to develop an SO₂ sorbent, using commercial calcium silicate bearing Portland Cement, for desulfurizing fluidized-bed combustion gases. For this we have concentrated our development efforts on preparing and evaluating Portland Cement Type III (PC III) pellets for fluidized-bed combustion service, since earlier studies (3) showed that PC III was intrinsically the most reactive towards SO₂.

1. SORBENT PREPARATION

The PC III pellets used in this experiment were prepared at Brookhaven National Laboratory using a drum pelletizer 18 inches in diameter. The agglomerating procedure is not energy intensive and is used in the metal ore preparation industry and thus equipment for preparing production quantities of PC III pellets is commercially available.

The cement powder (Portland Cement Type III) is loaded into the screw feeder via hopper and fed into the drum of the drum pelletizer rotating at a predetermined speed. At the same time the water spray nozzle in the drum pelletizer is opened to moisten the powder in the pelletizing drum with a fine spray of water. The rate of water spray is predetermined to bring the moisture content of the product (i.e., cement pellets) to a desired value. The continuous rolling and tumbling of moistened powder in the inclined drum results in seed pellets, which

then continue to grow as they roll on the bed of moistened cement powder. Note that it is a continuous operation and thus the pellets growing in the rotating drum have a wide range of size distribution, with their sizes depending on the residence time of the individual pellet. However, the inclined rotating drum inherently classifies the pellets in the drum in such a way that the larger ones manage to move to the surface and then to the edge of the drum, where they fall into the pellet receiving drum via the guiding chute. The size of the pellet is mainly controlled by the inclined angle of the drum pelletizer, which in fact determines the residence time of the pellet in the drum. Other process variables affecting the pellet size and its quality are the rotating speed of the drum pelletizer, cement feed rate and location, and water spray rate and location.

The PC III pellets freshly prepared in the drum pelletizer are extremely fragile. They cannot be picked up or touched but must be left in the pellet receiving drum for 16-18 hrs at room temperature at which point they have become sufficiently strong so that water can be flowed into the drum to soak the pellets for hydration. This initial cure continues for about 20 hrs at room temperature. At the end of this period, when the pellets are strong enough to handle, they are removed from the drum in order to separate them into individual pellets. The pellets are then wet sieved and stored in a container under 100% humidity for final cure. The PC III pellet prepared and cured for 28 days under 100% humidity is rigid and spherical in shape. It contains 25-35% by weight of water, depending on the initial water content used which ranges from 7 to 12% by weight, and has a density of about 2 gm/cc. The pellet size ranges from 100 to 4000 microns with the average size of about 800-1000 microns.

The PC III pellets prepared by low energy agglomeration techniques have a number of advantages in physical properties over natural limestone or dolomite as an SO₂ sorbent for desulfurizing fluidized-bed combustion gases. First of all, since the pellets (agglomerates) are formed from very fine cement powders, they are of uniform quality, which is not the case with natural limestone or dolomite. Furthermore, the agglomeration process is an established technology which offers good control of external particle size as well as internal structure. The pelletizing conditions, namely powder feed rate, water spray rate, and the speed and angle of the pelletizing drum, can be easily controlled to give an optimal internal pore structure, as well as pellet size, for use in fluidized-bed combustors of different designs. For example, an increase in water content during agglomeration gives rise to a pellet of high strength and thus high resistance to attrition. On the other hand, as the water content is decreased, the pellet becomes more porous and has a higher sulfur capture capacity.

2. SORBENT CHARACTERIZATION

Chemical/physical properties of PC III sorbent pellets were determined in order to have a better understanding of the characteristics of sorbent pellets prepared by the agglomeration technique described previously. These include sulfation/regeneration capacities, water content, surface area, and pore size and its distribution. These properties are believed to vary with sorbent preparation conditions and affect sorbent performance in fluidized bed combustors. For this we used thermogravimetric analysis (TGA), surface area analysis, mercury porosimetry and scanning electron microscopy (SEM).

Sulfation/Regeneration Capacities

Sulfation/regeneration capacities of PC III sorbent pellets (20/200 US mesh) were determined for five cycles via TGA (DuPont 951). Sulfation was carried out at 958°C using a simulated combustion gas (i.e., 0.25% SO₂, 5% O₂, 15% CO₂, and balance N₂) at a total pressure of 1 atmosphere. The sulfation temperature of 958°C was chosen because preliminary tests showed that PC III sorbent was most reactive at this temperature. The sulfation period utilized was 2 hours.

Regeneration of the sulfated sample was accomplished at 958°C by flowing a reducing gas (i.e., 5% CO, 20% CO₂, and balance N₂) over the sample until no weight loss is observed. The gas containing 15% CO₂ and 85% N₂ was then passed through the sample. This was done to convert all the sulfide remaining after the CO treatment to the oxide form by the following reaction mechanism:



The results of TGA measurements for cyclic sulfation/regeneration capacities are presented in Table 1. It can be seen in Table 1 that the PC III sorbent has a two-hour sulfation capacity of 45% or better and that it does not deteriorate with cycling. The small variation in sulfation capacities with different batches is not clearly understood at the present time. Note that Batches 9-12 were prepared under more or less same conditions. It is, however, speculated that the variation may be due either to unknown variables in preparation conditions or to non-uniformity of the PC III pellets. Table 1 also shows that the regeneration of PC III pellets is almost complete (above 95%) during cyclic use. The data indicates that PC III pellets can be successfully used as a regenerative sorbent without any loss of reactive sites caused by poor regeneration. No change in sulfation capacities and complete regeneration after repeated cycling of the same material show that the PC III sorbent pellets are not subject to sintering and pore destruction during cyclic sulfation and regeneration, which is the case with limestone.

Figure 1 shows the effect of temperature on the two-hour sulfation capacity of PC III pellets. As one can see, the sulfation rate is very much dependent upon the reaction temperature. For example, below 800°C the reaction rate is quite slow. As the temperature is increased, the reaction rate increases sharply, reaches its maximum around 950-1000°C, and then start to decrease with further increase in temperature. The higher optimum temperature, 950-1000°C, for sulfation of PC III sorbent than that of limestone, which is around 815-875°C, is an advantage in that combustion and power cycle efficiencies tend to increase as bed temperature increases.

Effect of Pellet Size on Sulfation Rate

Figure 2 shows TGA sulfation experiments on various sizes of PC III pellets. One can see from Figure 2 that the rate of sulfation reaction as well as the sulfur capture capacity increases as the pellet size becomes smaller. For example, for the pellet of 200/230 mesh size the two-hour sulfation capacity is 66% whereas it is 44% for the pellet of 6/10 mesh size. It is worth mentioning at this point, that the cement powder itself has a two-hour sulfation capacity of 53%, which is much lower than that of 200/230 mesh size PC III pellet. It indicates that the enhanced sorbent capacity with smaller pellets is not due to the increase in surface area associated with the pellet size. It may be attributed to the internal structural change accompanied by hydration during curing. In this respect, measurements were carried out on the internal pore structure of PC III pellets using a mercury porosimeter. Figure 3 shows the result of pore measurements on PC III pellets of various sizes, where the total pore volume is plotted against the pore diameter. It is seen in Fig. 3 that the total pore volume increases with a decrease in pellet size. For example, the total pore volume of 200/230 mesh size PC III pellet is 1.46 cc/gm compared to 0.32 cc/gm for 6/10 mesh size. It has been known that sulfation reactions between SO₂ gas and the sorbents, which are currently under investigation by many researchers, are diffusion controlled and that the internal pores of the sorbent provide most of the reactive sites for the gas-solid reaction. In other words, an increase in the pore volume of the sorbent will give rise to an increase in its sulfur capture capacity. Therefore, it can be said that the increase in the sulfation capacity of PC III pellets with smaller pellet size, as shown in Figure 2, is due to an increase in the total pore volume associated with the pellet size. It is also seen in Fig. 3 that the pore size distribution shifts to larger size as the pellet

becomes smaller. For example, for the 200/230 mesh size, the pores in the size range of 10 to 60 microns account for about 75% of the total pore volume whereas in the case of 6/10 mesh size the same pore volume is due to the pores in the size range of 0.1 to 1.0 micron. It is noted that the rate of diffusion of SO_2 gas into the pellet depends very much on the size of the pores. In other words, as the pore size is decreased, the diffusion rate of SO_2 gas into the pore becomes lower and thus the rate of sulfation reaction is decreased. This is what one can see in Fig. 2, where the sulfation rate of the larger pellets is much smaller than that of smaller pellets. Therefore, it can be concluded that the pore size and its distribution of PC III pellets have a profound influence on its sulfation rate and sulfur capture capacity.

Sulfation/Regeneration Characteristics by SEM

A scanning electron microscope (SEM) was used to study the sulfation/regeneration characteristics of the PC III sorbent pellet. Figure 4(a) shows a sulfur scan across the cross-section of the fully sulfated PC III pellet. As one can see from Figure 4(a), the sulfur (white dots in the picture) is distributed fairly uniformly throughout the sulfated pellet. This can be more clearly seen from Figure 4(b), which shows the line scan of sulfur along the axis of the same pellet as in Figure 4(a). In Figure 4(b) the height of the scan is proportional to sulfur concentration at that particular location along the axis. This scan clearly shows uniform sulfur concentration from the outer surface to the center. This indicates that SO_2 gas actually penetrates all the way into the center of the pellet, probably due to its favorable pore size distribution for gas-solid reaction. This is a quite striking result since for limestone the sulfation reaction has been known to take place only near the outer surface, leaving the sorbent unutilized around the center.

3. BENCH SCALE FLUIDIZED-BED EXPERIMENT

A 40mm I.D. small fluidized-bed reactor was constructed of quartz and used for both sulfation and regeneration tests of PC III sorbent. The purposes of this experiment are to obtain data for PC III sorbent pellets on: 1) sulfur removal efficiency, 2) attrition resistance, and 3) SO_2 content in the off gas stream during regeneration.

Experimental Apparatus and Its Procedure

The apparatus used in this test consists of a 40mm I.D. fluidized-bed reactor, an air preheater, flow meters, temperature indicators, and SO_2 IR analyzer (Beckman) and recorder. The reactor and air preheater were constructed of quartz, which is capable of withstanding temperatures up to 1100°C , and equipped with external electric heaters. Note that the fluidized-bed reactor is not a type of coal-model but for batchwise operations with simulated combustion gases. A schematic diagram of the layout of the apparatus is shown in Figure 5.

About 150 gm of 20/200 US mesh PC III sorbent pellets was placed in the bed and fluidized with air. This smaller size pellet was chosen because it could be fluidized reasonably well in the 40mm I.D. small fluidized-bed reactor used in the present study. The bed and the air preheater were heated with electric heaters at a rate of $20^\circ\text{C}/\text{min}$ until the bed temperature reached about 800°C . Propane as fuel gas was then introduced to the bed through a distributor plate for the purpose of simulating the coal-fired fluid bed combustor and served as a main source of maintaining the desired bed temperature ($950\text{--}1000^\circ\text{C}$). When the bed temperature reached a desired value, SO_2 gas was introduced to the bed to carry out the sulfation test, and at the same time the SO_2 analyzer was activated to monitor the SO_2 concentration in the off gases from the bed. The sulfation cycle continued until the SO_2 concentration in the flue gases reached the steady value of SO_2 feed concentration. At the completion of the sulfation cycle the SO_2 feed gas was shut

off, and the propane feed rate was increased to produce a propane rich mixture. Note that the partial combustion of propane produces CO and H₂, which act as reducing agents. The regeneration cycle continued until no SO₂ was detected in the off gas stream.

Result and Discussion

Figure 6 shows the sulfur removal efficiency of PC III sorbent, where the SO₂ content in the off gas stream is plotted against time. As one can see from Figure 6, most of the sulfation (more than 90%) is completed within the first 70 minutes and no SO₂ is detected in the flue gas for the first 50 minutes at which point about 45% of sulfation is achieved. This result clearly shows that with PC III sorbent 90% or more of sulfur removal is obtained until 45% of the sorbent is utilized, at least under the process conditions used in this test. Note that the input SO₂ content used in the test, i.e., 2.7%, is much higher than the one usually encountered in the coal-fired fluid bed combustor, i.e., less than 0.5%. Therefore it can be expected that the sulfur removal efficiency of PC III sorbent will be even better in the fluid bed combustors of practical interest.

Figure 7 shows the SO₂ concentration in the off gas stream during the regeneration of fully sulfated (sulfation capacity of 60%) PC III sorbent. It is seen in Figure 7 that the SO₂ concentration during the regeneration cycle strongly depends on the regeneration temperature. For example at a temperature of 850°C the SO₂ concentration is 0.15% whereas at 1000°C it is 5.0%. This indicates that the rate of regeneration of sulfated PC III sorbent increases drastically as the regeneration temperature is increased. It is noted that the theoretical SO₂ concentration equivalent to complete utilization of test propane (i.e., 25% excess) is 8.0%, which indicates that only part of feed propane is utilized during the regeneration cycle. This may be attributed either to the short gas residence time (i.e., about 0.5 sec) employed in the present study or to the incomplete utilization of CO, produced by partial combustion of propane, due to its slow reaction with the sulfated sorbent.

Figure 8 shows the effect of the reducing gas (i.e., propane) flow rate on the SO₂ concentration during the regeneration step at 1000°C. It is seen in Figure 8 that the concentration of regenerated SO₂ is increased from 5% to as much as 24% as the propane flow rate is increased from 25% excess to 160% excess. This is a significant result confirming the earlier thermodynamic calculations on calcium silicates (3) and indicates that the regeneration process is not equilibrium limited, which is the case with limestone. Note that the concentration of SO₂ in the product gases from the regenerator is a critical factor for economic operation of the downstream sulfur plant. Thus the regeneration gases from the sulfated PC III sorbent can reach concentration levels which adequately exceed the economical minimum concentration of an SO₂ feed gas (~8%) needed to design an economically viable process for the production of either sulfuric acid, if desired, or sulfur which is a more suitable product for market or disposal.

Table 2 shows the attrition loss of PC III sorbent pellets during sulfation/regeneration cycles. It is seen in Table 2 that the attrition loss of PC III sorbent is about 3-4% per cycle (i.e., 6 hrs) except for the first cycle. The high sorbent loss during the first cycle is probably due to the elutriation of fine cement powders originally present in the virgin sorbent. This initial loss may be recovered and recycled in an industrial operation for preparation of pellets. This result clearly indicates that the PC III pellet is highly superior in its resistance to attrition than either natural limestone or dolomite which have serious loss problems in fluidized bed reactors. Table 3 shows the result of another set of attrition tests performed under the same conditions as the one in Table 2, except that in this case 15 gm (or 10% of the initial weight of the sorbent) of new undried sorbent was added to the bed at the beginning of the second and the following cycles, for the purpose of simulating the fluid bed of

continuous operation. It should be noted that the additional sorbent was poured into the hot (i.e., at 950-1000°C) bed. It is seen in Table 3 that the attrition loss is almost the same as the one in Table 2. This is significant in that rapid heating of the virgin undried pellets does not lead to the destruction of the sorbent pellets so that the virgin sorbent may be directly added to the hot fluid bed without predrying it under controlled conditions.

ACKNOWLEDGEMENTS

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Table 1. Cyclic Sulfation/Regeneration Capacities* of PC III Sorbent Pellets

Batch Cycle No.	9		10		11		12	
	S1	R2	S	R	S	R	S	R
1	56.5	100.0	49.3	100.0	63.9	100.0	54.5	100.0
2	56.5	95.9	48.3	94.9	63.9	100.0	54.5	100.0
3	54.2	100.0	46.8	100.0	63.5	100.0	54.5	100.0
4	54.2	98.2	46.8	100.0	63.4	100.0	54.0	99.0
5	53.2	100.0	46.8	100.0	63.2	100.0	54.0	100.0

1) Sulfation capacity (%) at 958°C

2) Regeneration capacity (%) at 958°C

* Sulfation capacities are based on available CaO in PC III sorbent.

Table 2. Attrition Loss of PC III Sorbent Pellets

Cycle No.	Attrition Loss (wt%)
1st	21.0
2nd	3.3
3rd	3.6
4th	2.1
5th	3.7

Table 3. Attrition Loss of PC III Sorbent Pellets

Cycle No.	Attrition Loss (wt%)
1st	17.6
2nd	2.8
3rd	4.0
4th	—
5th	3.5

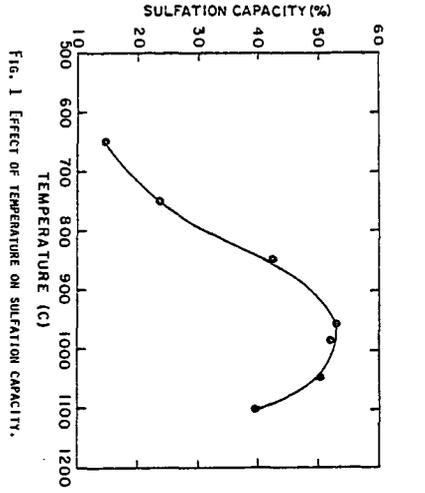


Fig. 1. Effect of temperature on sulfation capacity.

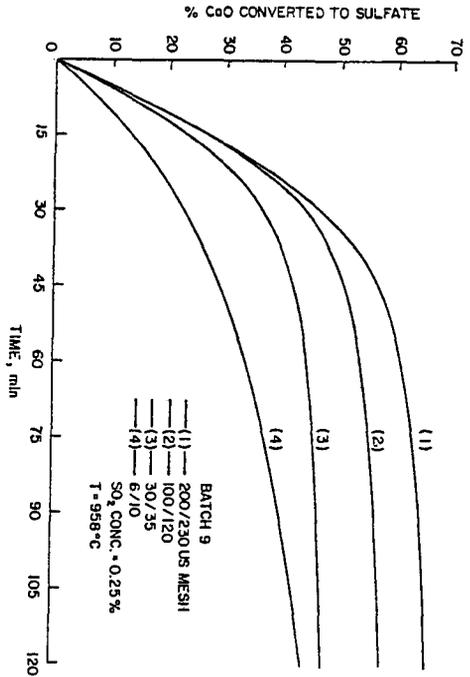


Fig. 2. Effect of pellet size on sulfation rate.

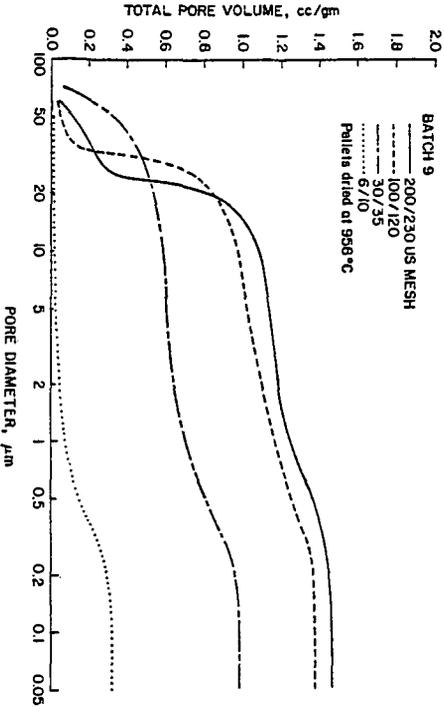
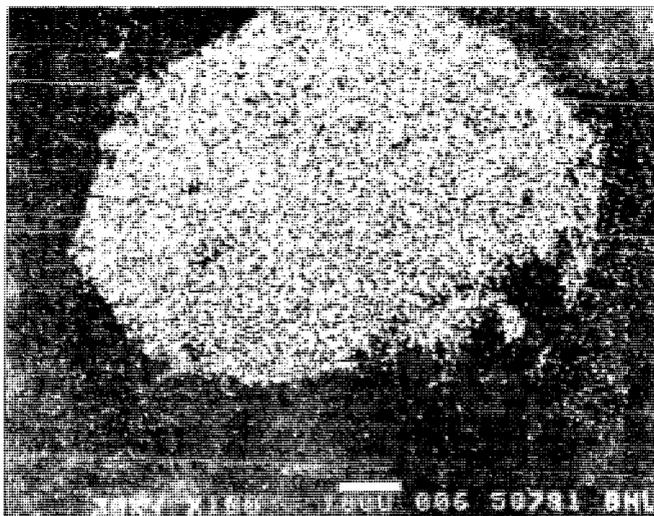
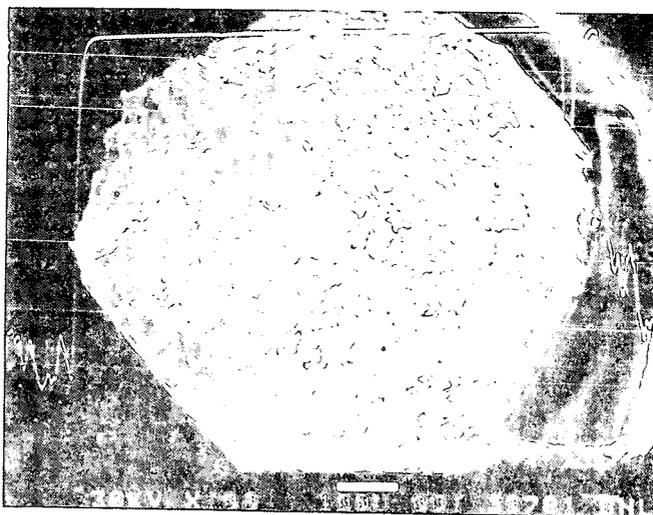


Fig. 3. Pore size and its distribution of PC III pellets.



(A) SULFUR SCAN ACROSS THE CROSS-SECTION.



(B) SULFUR LINE SCAN ALONG THE AXIS.

FIG. 4 SEM PHOTOGRAPHS OF SULFATED PC III PELLETS.

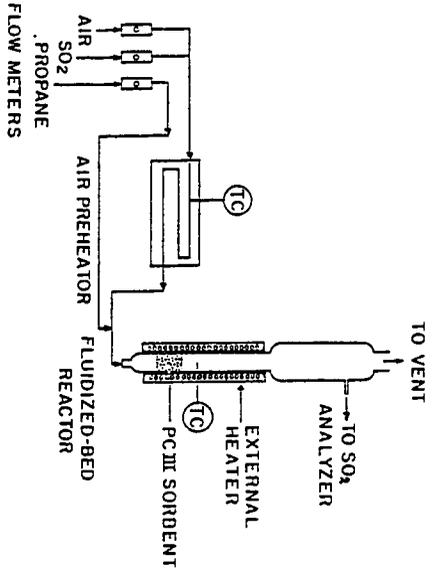


Fig. 5. A SCHEMATIC DIAGRAM OF THE LAYOUT OF THE APPARATUS.

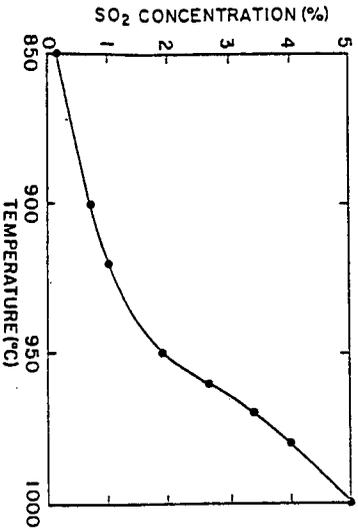


Fig. 7 EFFECT OF TEMPERATURE ON CONCENTRATION OF REGENERATED SO₂.

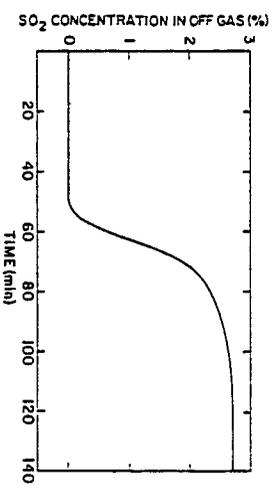


Fig. 6 SULFUR REMOVAL EFFICIENCY OF PC III PELLETS.

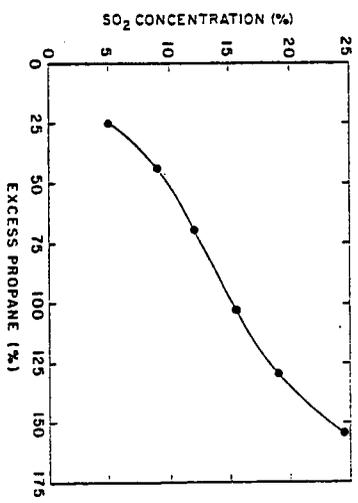


Fig. 8 EFFECT OF REDUCING GAS FLOW RATE ON CONCENTRATION OF REGENERATED SO₂ AT 1300°C.