

Influence of Dust on High Temperature Desulfurization of Iron Oxide Sorbent

ZHAO Jiantao*, HUANG Jiejie, WU Jinhua, ZHANG Jianming, WANG Yang
(*Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, China*)
(*E-mail: Zhaojt@sxicc.ac.cn, Tel: +86-351-2021137, Fax: +86-351-4041153*)

Abstract The understanding of influence of deposited dust on desulfurization performance of sorbent is of significance for developing combined processes for simultaneous desulfurization and dust removal in hot gas cleanup. In this paper, the influence of dust from a fluidized-bed coal gasifier on iron oxide desulfurization sorbent made by a kind of waste material containing iron oxide was systemically evaluated at different temperatures (400°C---550°C) and at different quantity of dust (0.5%---5%) in a fixed-bed reactor. The result showed that dust could interact with sorbent and adversely influenced sulfur capacity and sulfidation rate of sorbent. The influence was promoted with increasing sulfidation temperature and quantity of dust. But below 450°C, the interaction could be neglected. Kinetic studies were also conducted using the grain model. Deposition of dust on the surface of the sorbent could cause the deterioration of mass transfer and the decrease of the effective diffusivities.

Key Words: High temperature gas cleaning, Desulfurization, Dust, Iron oxide sorbent, The grain model

1. Objectives & Approach

Hot gas cleanup is a key technique in advanced coal-based power generation systems, such as integrated gasification combined cycle (IGCC) and molten carbonated fuel cells, because it offers the potential of significantly improving the process thermal efficiency and environmental performance. Fuel gas generated from gasifier contains a lot of contaminants, primarily dust and sulfur gases (H₂S, COS), which must be removed for protecting downstream equipments. So desulfurization and dust removal are two main subsystems of hot gas cleanup. Generally, the two subsystems are designed as independent unit operation process. Fuel gas first goes through dust removal process before entering desulfurization process, and after desulfurization fuel gas passes through a filter once again to remove dust generated in the process of desulfurization. In order to simplify the processes of hot gas cleanup, combined processes have been developed, especially the process based on moving granular bed filters being considered as the most promising one, in which sulfur gases and dust are simultaneously removed with chemically reactive sorbent⁽¹⁾. Obviously, the combined process has the advantages of more compact process and lower cost in comparison to conventional processes. However, in this case dust in fuel gas may deposit on the surface of sorbents and may influence the reaction of sulfur gases with metal oxide based sorbents. Peukert W. et al⁽²⁾ has reviewed this subject in detail and reported the studies of the influence of inert quartz dust on desulfurization with limestone pellets. It was found that there was no decay of desulfurization performance of limestone. But so far, Studies on this subject are scarce although they are of

significance for developing combined processes. Especially, few basic studies have been conducted on the influence of dust from gasifier on desulfurization of regenerable sorbents in hot gas cleanup.

Regenerable sorbents based on iron oxide are currently the leading candidates and have been developed for coal-derived gas desulfurization at moderate temperature below 550 °C due to their higher sulfur capacity, superior regenerability and lower cost. Furthermore, besides reagent-grade iron oxide as regenerable and durable sorbents, iron-containing waste materials including coal ash, taconite, illmenite, red and brown “muds” from metal refining residues can be used for desulfurization more economically. It offers a viable solution between once-through Ca-based sorbents and expensive polishing sorbents⁽³⁻⁶⁾.

The objective of the present work is to investigate the influence of dust from gasifier on desulfurization performance of iron oxide based sorbents made by waste material containing iron oxide.

2. Experimental Section

2.1 Materials

The iron oxide sorbent was supplied by Taiyuan University of Technology. Before experiment the original cylindrical pellets were crushed and sieved to the diameter of 1~2 mm. The composition and properties of sorbent are listed in Table 1. Dust in the experiment was obtained from a pressured fluidized-bed gasifier (200 mm i.d.), which was collected by a sintered metal screen filter after the second cyclone. The dust sample was semi-coke with high carbon content. The composition and particle size analysis of samples are listed in Table 2 and 3, respectively.

2.2 Apparatus and Procedure

A fixed-bed reactor, made of stainless steel tube, 2.1 cm i.d., was employed to evaluate the influence of dust on iron oxide sorbent. The reactant gas composition was 15% H₂, 0.6% H₂S and N₂ as the balance. The total gas flow rate was 600 cm³/min. The concentration of H₂S was measured by an iodine method (Chinese Standard GB12211-90).

In the evaluation of desulfurization performance, 10 g of sorbent and quantitative dust were placed into in a glass utensil and blended thoroughly so that dust was adhered to the surface of sorbent as possible as it could to simulate the process of dust deposition on the surface of sorbent. They were placed into the fixed-bed and N₂ was fed into the reactor. In N₂ atmosphere, the reactor was heated up to experimental temperature and kept for 0.5 h. Then reactant gas containing H₂S was switched to the reactor. The H₂S concentration of outlet was measured every 20 min. When the H₂S concentration in outlet gas was higher than 5 g/m³, the reactor was switched to N₂ atmosphere and it was cooled down to room temperature.

In kinetic studies, the amount of sample was about 0.3 g. In order to eliminate exterior diffusion, the gas flow rate was increased to 1500 ml/min. Sulfur content of sulfided sorbent was measured by sulfur and carbon analyzer (LECO SC-444).

BET surface area was measured by adsorbing and desorbing N₂ at 77 K with ASPN 2000. Pore volume, average pore diameter and pore size distribution were

detected by Hg intrusion porosimetry with Autoscan 60 up to a final pressure of 4.14×10^5 KPa which allows filling of pores down to 2 nm diameter.

3. Results and discussion

3.1. Influence of dust on desulfurization performance

In order to describe the result clearly, two indices are defined. One is the effective sulfur capacity of the sorbent, which is defined as the weight ratio of the absorbed H₂S before breakthrough and the sorbent in absorption bed.

$$S_c = \frac{\int_0^t (C_{in} - C_{out}) V dt}{W_0} \quad (1)$$

S_c —the effective sulfur capacity of the sorbent. C_{in} —the H₂S concentration of reactor inlet, g/Nm³. C_{out} —the H₂S concentration of reactor outlet, g/Nm³. V —the total gas flow rate, m³/min. W_0 —the weight of sorbents in absorption bed, g. t —the breakthrough time of absorption bed, min.

The other is the influence index of dust on desulfurization of the sorbent, which is defined as the ratio of effective sulfur capacity of the sorbent without dust and with dust.

$$\beta = \frac{S_c}{S_{c,d}} \quad (2)$$

β —the influence index of dust on the sorbent. S_c —the effective sulfur capacity of the sorbent without dust. $S_{c,d}$ —the effective sulfur capacity of the sorbent with dust.

3.1.1. Influence of dust at different sulfidation temperatures

The experimental temperature range was selected from 400°C to 550°C. This temperature interval covers the more interesting temperatures for desulfurization process of iron oxide based sorbents. Figure 1 shows the breakthrough curves of absorption bed with 2% dust and without dust at different temperatures. From the figure, it can be seen that the H₂S breakthrough time is closely related to sulfidation temperature. When there is no dust added into the absorption bed, the breakthrough time is promoted slightly by higher temperature. Namely, S_c becomes greater at higher temperature. However, when dust is added in absorption bed, with increasing temperature the breakthrough time decreases obviously. This indicates influence of dust on desulfurization become more and more serious. At 450°C the breakthrough curve of absorption bed with dust has little difference from that of absorption bed without dust. But at 550°C the breakthrough time of absorption bed with dust decreases greatly. So it can be concluded that the influence becomes slight and can be neglected below 450 °C.

3.1.2. Influence of the quantity of dust

In the experiment, the quantity of dust was selected from 0.5% to 5% of weight of sorbent. Figure 2 shows the breakthrough curves of the absorption bed with different quantity of dust at 550°C. It shows that the breakthrough time becomes shorter with the increase of the quantity of dust. It indicates that the influence of dust

on sorbent become more serious in the case of the greater quantity of dust.

Table 4 lists the influence indices of dust on desulfurization sorbent. As it is shown, the value of β increases with rising temperature and the quantity of dust. Furthermore, temperature is a more important factor. At 400°C β is about 1 when 5% dust was added into absorption bed. However, at 550°C β is about 1.5 although only 0.5% dust was added in absorption bed.

3.2 Influence of dust on sulfidation kinetics

Figure 3 shows conversion of sorbent vs. reaction time. From the comparison between Figure 3a and figure 3b, it can be seen that conversion decreases in the case of dust existence. It means that sulfidation rate decreases due to the interaction of dust with sorbent.

The reaction between iron oxide sorbent with hydrogen sulfide is a typical non-catalytic gas-solid reaction. The grain model has been used to correlate the data on the sulfidation reaction^(6,7). According to Sohn and Szekely⁽⁸⁾, for an isothermal, first order-reaction system in which the structure changes may be neglected, the model can be given by the following equation:

$$t = AG(x) + BF(x) \quad (3)$$

$$A = \frac{\rho_s r_g}{bk_s C_{A0}} \quad (4)$$

$$B = \frac{\rho_s R_s^2}{6bD_e C_{A0}} \quad (5)$$

t —reaction time, min; x —conversion of sorbent; b —stoichiometric coefficient; ρ_s — Fe_2O_3 concentration in sorbent, g/m³; r_g —grain radius, m; k_s —apparent chemical reaction rate constant; C_{A0} —concentration of H₂S in bulk phase, g/m³; R_s —pellet radius, m; D_e —effective diffusion coefficient

For a spherical pellet made up of a spherical grain, $G(x)$ and $F(x)$ are defined as follows:

$$G(x) = 1 - (1 - x)^{1/3} \quad (6)$$

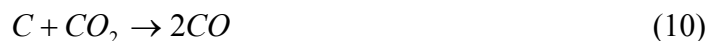
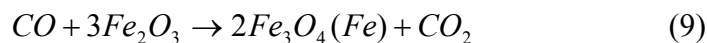
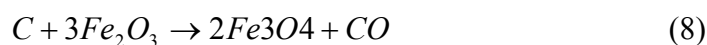
$$F(x) = 1 - 3(1 - x)^{2/3} + 2(1 - x) \quad (7)$$

Since sulfidation of sorbent is in the interior diffusion-controlled region except initial sulfidation stage, equation (7) was only considered and the effective diffusivities were estimated in the studies.

Figure 4 and 5 depict the graphs of $F(x)$ vs. t derived from Figure 3. The good linear relationship indicates that equation (7) is suitable for fitting the experimental data. Figure 6 shows effective diffusive coefficients of sorbent with and without dust. From this figure, it can be seen that effective diffusive coefficients (D_e) decrease in the presence of dust at higher temperature. It can be inferred that the influence of dust can promote mass transfer resistance to hinder reactant gaseous molecule diffusion in sorbent.

From the experiments, dust from gasifier has serious interaction iron oxide sorbent at higher temperature. In general, the size of dust was much larger than the pore size of sorbents so dust can't enter the interior of sorbents. However, if dust only adheres to the surface of sorbents physically, they may cover the surface and form a porous dust layer, but reaction and diffusion in the sorbent interior remain unchanged. Because diffusion through the porous dust layer is much faster than that through interior product layers of sorbents, mass transfer almost keep constant⁽²⁾. So there might be complicated chemical changes.

Dust from gasifier contains carbon and various minerals, which can interact with iron oxide sorbent. Extensive studies have been reported in the literatures on the reaction of iron oxide with graphite, due to its importance in the steel industry⁽⁸⁾. It can be expressed as follows:



In the experimental conditions, these reactions may occur at high temperature. Additionally, iron oxide also can be reduced by H₂, form metallic iron. CO may be decomposed according to equation (11) with metallic iron as catalyst⁽⁹⁾.



The reaction may cause carbon transfer into the interior of sorbent. Formed carbon may deposit on the surface of reactive site, or cover and block up the pore causing the decrease of pore size and pore volume, hindering reactant molecule diffusion in sorbent. Moreover, It is possible to form iron carbide causing the deactivation of sorbents⁽⁹⁻¹⁰⁾.

In addition, the sintering of minerals in coal has been extensively studied in literatures and the initial sintering temperature of coal ash in the range of 500-1000°C had been reported^(11,12). According to the experiment above 500°C the influence of dust on desulfurization performance of sorbents became serious. It can be inferred that minerals sinter each other or with components of sorbent at high temperature. On the other hand, the Tammann temperature of FeS is only about 733K so it is possible that the sintering of production of sulfidation with minerals occurs. The layer of sintering on the surface of sorbents deteriorates mass transfer leading to the decay of sorbents.

As shown in Table 5, BET surface area, pore volume and average pore diameter of the sulfided sorbent are different at different temperatures in the presence of dust. BET surface area, pore volume of the sulfided sorbent decrease obviously while average pore size increases at 550°C. However, all of these become reverse trend at 450°C. It indicates that the interaction of dust with iron oxide sorbent may take place at higher temperature but it can't take place at lower temperature. The increase of BET surface area and pore volume below 450°C is resulted from those of dust

adhered to the surface of sorbents, which have large surface area and pore volume.

4. Conclusions

1. Dust from a fluidized bed gasifier has obvious influence on sulfur capacity and sulfidation rate of sorbent with the increase of temperature and the quantity of dust. The influence becomes more serious when sulfidation temperature is higher than 500°C. However, when sulfidation temperature is lower than 450°C, the influence becomes slight and can be neglected.

2. The interaction of dust with iron oxide sorbent deteriorates interior mass transfer of sorbent. According to the grain model, interior diffusion coefficients become small at higher temperature in the presence of dust.

3. Carbon in dust can react with iron oxide to produce interior carbon in sorbent even iron carbide, which can cover the active site or block up the pore of sorbent causing loss of reactive site and deterioration of interior mass transfer. Minerals in dust can sinter with components of sorbent to form compact layer causing the increase of mass transfer resistance and result in the decay of sorbent.

Acknowledgement

The authors gratefully acknowledge the financial support by the Special Funds for Major State Basic Research Projects—Basic Research in Coal Pyrolysis, Gasification and Hot Gas Cleaning (G1999022104, G1999022105).

References

(1) Ishikawa, K.; Kamei, K.; Shindo, K. Development of a Simultaneous Sulfur and Dust Removal Process for IGCC Power Generation Systems, In 3rd International High Temperature Gas Cleaning; Schmidt, E., Ed.; Karlsruhe: Institut für Mechanische Verfahrenstechnik und Mechanik, 1996; pp316-327.

(2) Peukert, W.; Lofler, F. A. Combined Process for High Temperature Gas Cleaning. In 3rd International High Temperature Gas Cleaning; Schmidt E., Ed.; Karlsruhe: Institut für Mechanische Verfahrenstechnik und Mechanik, 1996; pp247-266.

(3) Rachid, B. Slimane; Javad Abbasian. Utilization of metal oxide-containing Waste Materials for Hot Coal Gas desulfurization. Fuel process. Technol. 2001, 70, 97-113.

(4) Eiji Sasaoka; Masayo Sakamoto; Tomoo Ichio; et al. Reactivity and Durability of Iron Oxide High Temperature Desulfurization Sorbents. Energy Fuels 1993, 7, 632-638.

(5) Schrodt, J.T.; Hilton, G. B.; Rogge, C. A. High-temperature desulfurization of Low-CV Fuel Gas. Fuel 1975, 54, 269-272.

(6) Yan-xu Li Characterization and Kinetics Studies of Iron-Calcium Oxides in High Temperature Desulfurization Processes: [Ph. D. Thesis]: Institute of Coal Chemistry, Chinese Academy of Science, 1998.

(7) Tamhankar, S.S.; Hasatani, M.; Wen, C.Y. Kinetic Studies on the Reactions Involved in the Hot Gas Desulfurization Using a Regenerable Iron Oxide Sorbent-1. Chem. Eng. Sci. 1981, 36(7), 1181-1191.

(8) Szekely, J.; Evans, J. W.; Sohn, H. Y. Gas—solid Reactions, Academic Press, New York 1976.

(9) Weng Sihao; Wu Youqing Study on the high Temperature Desulfurization of Fuel Gas—the Mechanisms of Desulfurization, Deactivation and Regeneration of Ferric Oxide Sorbent. Chinese Journal of Chemical Physics 1994, 7(2), 147-151.

(10) Gangwal, S. K.; Harkins, J. M.; Stogner, M. C.; Roger, T. N. Bench-scale Testing of Noval High-temperature Desulfurization Sorbents, Final Report. DOE/MC?23126-2662, NTIS/DE89000935, 1988.

(11) Al-Otoom, A.Y.; Bryant G.W.; Elliott L.K. Experimental Options for Determining the Temperature for the Onset of Sintering of Coal Ash. Energy Fuels 2000, 14, 227-233..

(12) Bengt-Johan Skrifvars; Mikko Hupa; Rainer Backman; Matti Hiltunem. Sintering Mechanisms of FBC Ashes. Fuel 1994, 73, 171-175.

Table 1. Physical properties of iron oxide sorbent

Fe ₂ O ₃	39.76%
Surface area	6.184 m ² /g
Pore volume	0.258 cm ³ /g
Average pore diameter	116.6 nm
Density	1.72 g/cm ³

Table 2. Composition of dust

C	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O	Others
70.27	12.87	4.14	5.92	3.35	0.18	0.25	3.02

Table 3. Particle size distribution of dust

Size (μm)	<2.50	2.50~5.00	5.00~7.50	7.50~10.00	>10.00
V%	6.18	59.37	19.11	12.39	2.95

Table 4. Influence indices of dust on desulfurization sorbent

Temp. /°C	Influence indices of dust (β)		
	Sorbent+0.5%dust	Sorbent+2%dust	Sorbent+5%dust
400	—	—	1.0
450	—	1.0	1.2
500	1.1	1.8	2.1
550	1.5	2.1	2.8

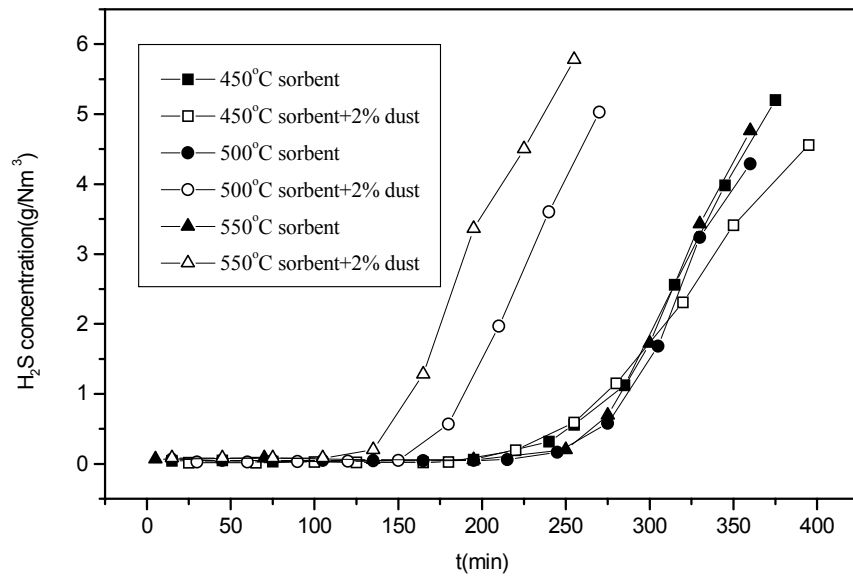


Figure 1 Influence of temperature on the breakthrough curves of absorption bed

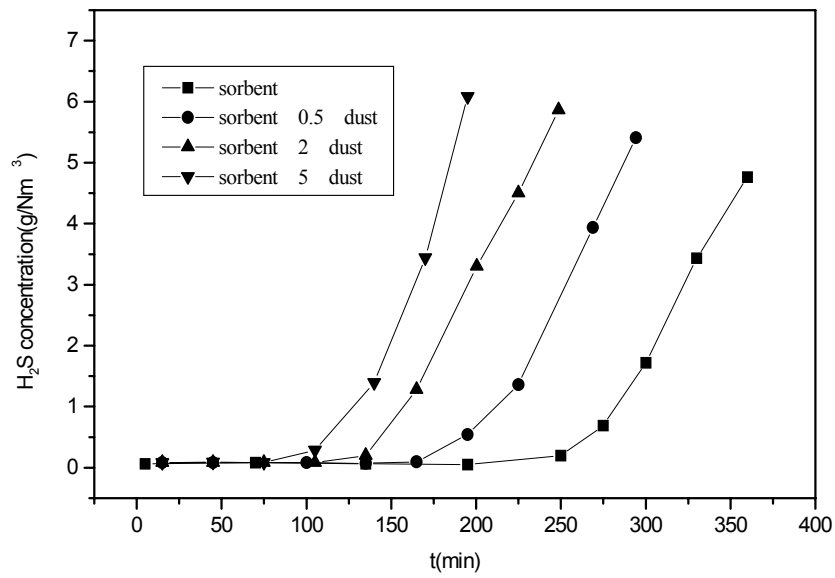


Figure 2 Influence of the quantity of dust on the breakthrough curves of absorption bed (T=550°C)

Table 5. Textural properties of samples

Samples	BET surface area	Pore volume	Pore diameter
	A (m ² /g)	V (ml/g)	D (nm)
FC450	4.50	0.19	167.02
FC450D	5.86	0.20	135.57
FC550	7.59	0.24	126.48
FC550D01	5.52	0.20	143.77
FC550D02	4.01	0.19	190.82

FC450—sulfided sorbent at 450°C; FC450D—sulfided sorbent with 5% dust at 450°C; FC550—sulfided sorbent at 550°C; FC550D01—sulfided sorbent with 0.5% dust at 550°C; FC550D02—sulfided sorbent with 2% dust at 550°C

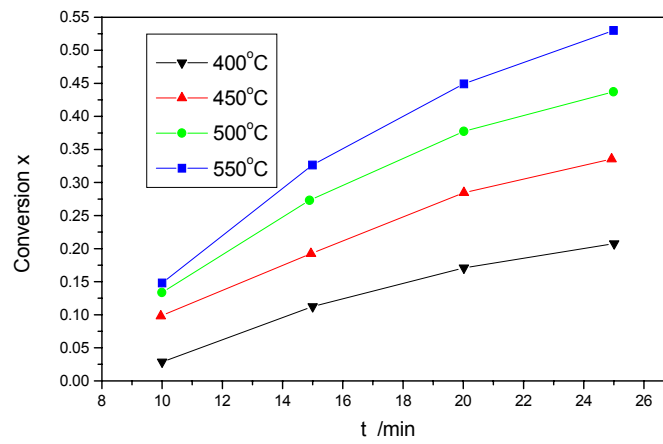


Figure 3a. Conversion x vs. t (sorbent)

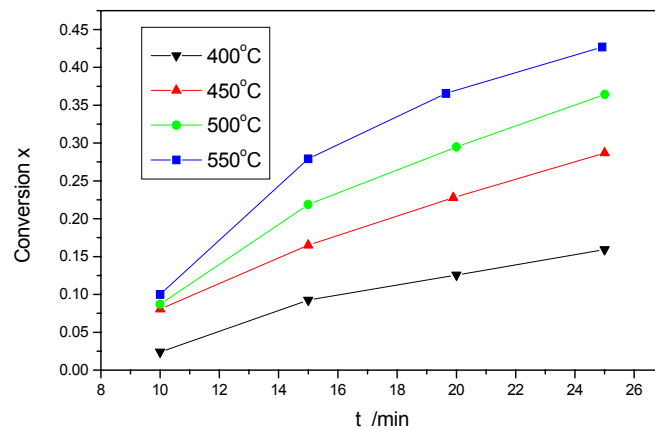


Figure 3b. Conversion x vs. t (sorbent with 2% dust)

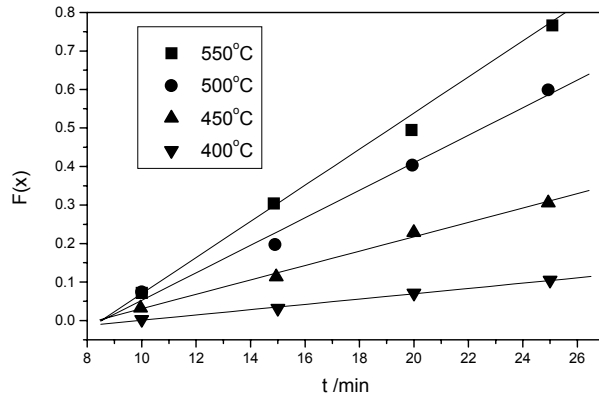


Figure 4. Relationship of $F(x)$ - t for sorbent

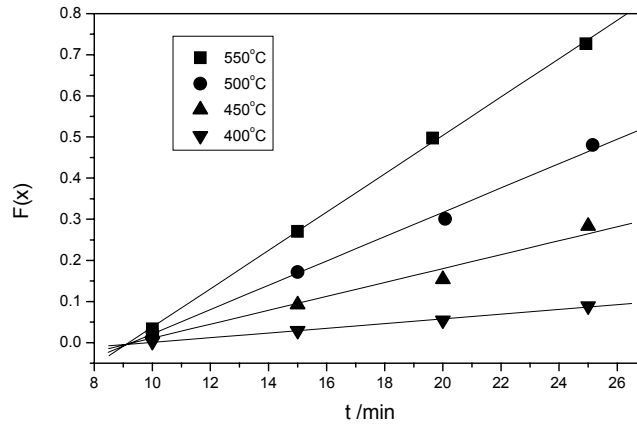


Figure 5. Relationship of $F(x)$ - t for sorbent with dust

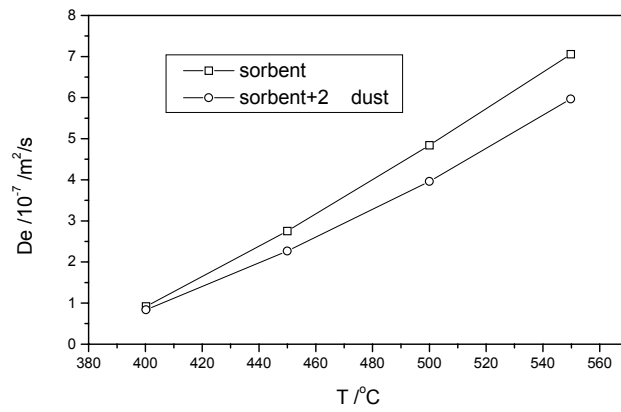


Figure 6. Effect of dust on effective diffusive coefficient