DEVELOPMENT AND OPERATING EXPERIENCE OF ADVANCED PLATE TYPE CATALYST FOR SCR SYSTEM

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Abstract

So far, Hitachi Ltd.(HTC)/Babcock-Hitachi K.K.(BHK) have supplied their own plate type catalyst to more than 200 SCR systems for various stationary combustion sources since 1970. In U.S.A, NOx emission standards became stringent at West Coast area in mid of 1980's, and we have supplied the plate type catalyst for 40 SCR systems for gas fired plants, mainly gas turbines since 1986. The catalyst has been in service satisfactorily and its long life has been proven.
Recently, however, from the RACT (Reasonably Available Control Technology) point of view, reducing cost of SCR system is most desirable by users. As a result of investigation, we finally developed the advanced (Cross-Undulated(CU)) plate type catalyst which has a considerably higher performance than the conventional plate type catalyst, and applied it to several commercial SCR systems.

Introduction

Selective Catalytic Reduction(SCR),which is the most reliable and effective technology for reducing nitrogen oxide (NOx) with ammonia from stationary sources has been widely applied in Japan, Europe and U.S.A. Hitachi Ltd.(HTC)/Babcock-Hitachi K.K.(BHK) started study for developing SCR catalyst in 1963,

and then began to install pilot plants in 1973. HTC/BHK developed the plate type catalyst and have applied it to more than two hundred SCR plants for various fuels such as gas, oil and coal. Especially, in high dust application for coal fired plants, plate type catalyst has been appreciated owing to the high erosion resistance to dust. Besides plate type catalyst has a merit of low pressure loss, compared with honeycomb type catalyst, therefore, it can reduce the operation cost of SCR system(1).
HTC/BHK have supplied this proprietary plate type catalyst for 40 SCR systems of gas fired plants, mainly gas turbines in U.S.A since 1986. The catalyst has been in service satisfactorily and its long life has been proven.
Recently, from RACT(Reasonably Available Control Technology) point of view, reducing cost of SCR system is desired by users. In response to this, HTC developed Cross-Undulated (CU) plate type catalyst which has a higher performance than the conventional plate type catalyst. Consequently, it reduces the cost of SCR system considerably. CU catalyst causes turbulent flow intentionally in it to increase the mass transfer so as to promote the NOx removal reaction on the catalyst surface. The CU catalyst has already been applied to several commercial SCR systems.
This paper describes the features and characteristics of the CU catalyst with test results and study on the kinetic mechanism in comparison with conventional plate type catalyst and honeycomb catalyst.
In addition, the operating experience with CU catalyst is also described.

Conventional Plate Type Catalyst and Operating Experience

Plate type catalyst based on TiO_2, developed by HTC/BHK has high DeNOx performance and durability for SOx in the flue gas(2). The catalyst shape was selected according to design requirements for the catalyst. In high dust application for coal fired plant, it is desirable to minimize dust accumulation on catalyst surface to prevent catalyst plugging and it is appreciated to lower the pressure loss of catalyst layer from a viewpoint to reduce operational cost.
Plate type catalyst consists of several catalyst elements which are coated with catalyst material on the surface of expanded metal plate and pressed to the undulation lines regularly so as to make flue gas channels. It is possible to change the pitch between catalyst elements corresponding to flue gas condition. Generally, we apply 6mm pitch (P) plate type catalyst for high dust application of coal firing and 4mmP for gas firing.
Plate type catalyst has features in comparison with honeycomb type catalyst as follows.

① Lower pressure loss through catalyst layer
② No accumulation and plugging of dust
③ High-erosion resistance to dust

The features of plate type catalyst has been proven by successful operational experience in various kinds of flue gas sources(3).

Effect of catalyst shape on mass transfer characteristics
(Background of CU catalyst development)

It is well known that the mass transfer can be improved by turbulence in the flow. At the beginning of development of the plate type catalyst, we had already confirmed that the catalyst activity was considerably increased by disturbing the gas flow in parallel flow channels. That is an idea of CU catalyst. However, the idea was not adopted at that time because of considerable increase of pressure loss compared with the present plate type catalyst. Since then, the activity and deterioration of the catalyst have been improved so much compared with the early product. As the result of high performance catalyst, we could reduce the required catalyst volume. Consequently, we can design the catalyst at low pressure loss and it allows CU catalyst application. Figure 1 shows the background for developing CU catalyst.

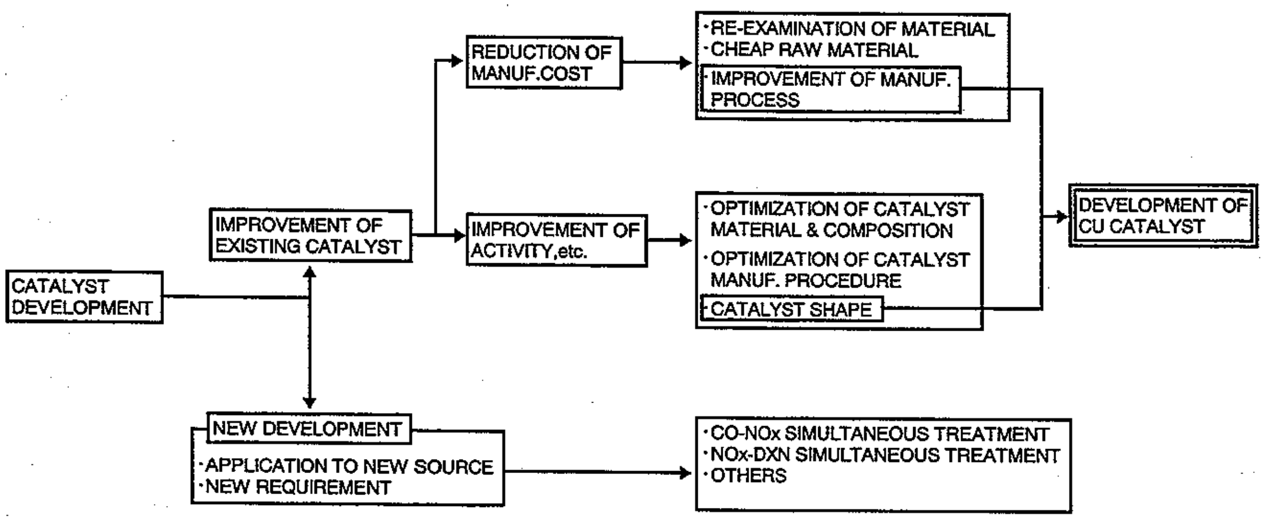


Fig.1
Background for developing CU catalyst

1. Influence factor on catalyst performance

The overall reaction rate constant (K) in catalyst reaction, that is, activity of catalyst can be shown in the following equation(1).

$$1/K=1/K_r+1/K_f \qquad (1)$$

K : overall reaction rate constant(m/h)

Kr: reaction rate constant based on catalyst surface(m/h)

Kf: mass transfer coefficient(m/h)

(Kf: Large / Kf has a large effect on K.)

Pellet type catalyst

(Kf: Small / Kf has a small effect on K.)

Parallel type catalyst

Fig.2

Influence of catalyst shape on K f

From the equation (1), it can be seen that the overall reaction rate constant (K),that is, activity of catalyst depends on both reaction rate constant based on catalyst surface (Kr) and mass transfer coefficient (Kf).And then, high activity of catalyst can be obtained by increasing Kr and / or Kf values. As shown in Figure 2 , the mass transfer coefficient (Kf) of pellet type catalyst is quite large in comparison with the reaction rate constant of the catalyst (Kr) due to turbulence in the flow. Accordingly, Kr is the dominant factor of the overall reaction rate of the catalyst (K). Meanwhile, the mass transfer coefficient of parallel flow type catalyst (Kf) is small due to the laminar flow. Accordingly, Kf has a large effect on the overall reaction rate of the catalyst (K).In CU catalyst, Kf value is large due to the turbulent flow, as a result, K value is large.

2. Shape of CU catalyst.

The original CU catalyst of HTC/BHK is shown in Figure 3. The CU catalyst consists of many catalyst elements in the shape of same undulated plate as conventional catalyst, but they are assembled as different from the conventional ones. As shown in Figure 3, CU catalyst is assembled with two kinds of element alternately, one of which has undulated lines in parallel with the direction of gas flow, and the other has undulated lines at right angle to the direction of gas flow. Table 1 shows the flow pattern and supposed mechanism of CU catalyst compared with conventional plate type catalyst.

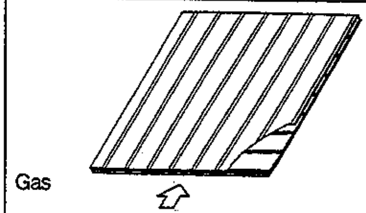
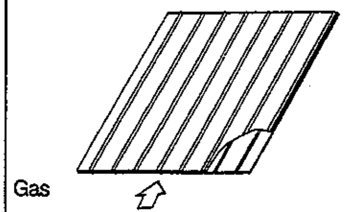
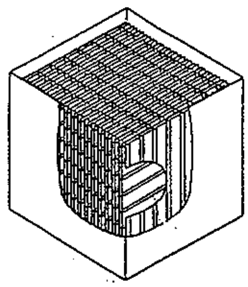
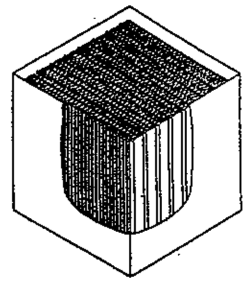
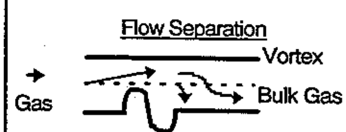
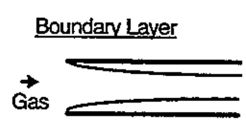
Type	CU Plate Catalyst	Parallel Flow Type Catalyst
Catalyst Element		
Unit Configuration		

Fig.3

CU90 catalyst configuration in comparison with conventional 4mm pitch plate type catalyst

Table 1

Comparison of flow pattern between CU and parallel flow type catalyst

Type	CU Plate Catalyst	Parallel Flow Type
Flow Pattern		
	Turbulent Flow	Laminar Flow
Supposed Mechanism	CU Plate Catalyst Structure ↓ Flow Separation ↓ Destroy The Boundary Layer ↓ Promotion of the Diffusion of Bulk Gas to Catalyst Surface (Increase of Reaction Rate)	Parallel Flow Structure ↓ Formation of Boundary Layer (Boundary Layer is Major Determining Factor of Reaction Rate)

The reason why CU catalyst has higher DeNOx performance than conventional parallel flow type catalyst is explained as follows.

The parallel flow type catalyst such as conventional plate type or honeycomb type causes laminar gas flow through catalyst elements which limits mass transfer effect(4). On the contrary, the mass transfer coefficient of NOx in CU catalyst is larger due to turbulence in the flow which is caused by the undulations of the catalyst. In this case, the undulated lines in CU catalyst are playing the role of turbulence promoters. Owing to it, the overall reaction rate constant of CU catalyst (K) becomes large and it results in a high DeNOx performance. The reality of the afore-mentioned mechanism of CU catalyst is supported by reports of researches(5). Thus, CU catalyst can achieve the high performance at smaller catalyst surface. It means that it can reduce the required catalyst surface to meet the required DeNOx performance. Consequently, it can reduce the cost of catalyst and SCR system.

Investigation of catalyst shapes

As mentioned before, the overall reaction rate constant (K) of CU catalyst is increased with the undulation lines which works as turbulence promoters. On the contrary, it results in undesirable higher pressure loss of catalyst layer. For the optimization, we set the target for development of CU catalyst as shown in Table 2.

Table 2

Target for development of CU catalyst

DeNOx Activity	Pressure Loss of catalyst
More than conventional plate type catalyst(4mmP) / unit volume	Less than 3.5mmP honeycomb type catalyst

To reach the target, it is required to investigate suitable shape of CU catalyst with increasing mass transfer coefficient of NOx while decreasing pressure loss.

At first, we confirmed the relation between DeNOx efficiency and pressure loss of the catalyst which is assembled with the undulated elements set at right angle to the direction of gas flow and another in parallel with the direction of gas flow (hereinafter as CU90),compared with conventional 4mmP plate type catalyst as shown in Figure 3. Figure 4 shows the applied bench scale pilot facility using 150mm square catalyst unit and test condition.

Bench Test Condition

Item	Unit	Condition
Gas Flow Rate	m3N/h	240
Gas Temperature	℃	350
O2 Conc.	%	14
NOx Conc.	ppm	80
H2O Conc.	%	6
NH3/NO	-	1.2

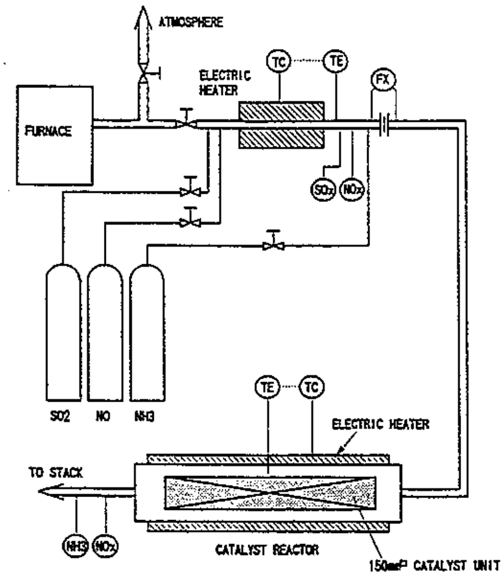
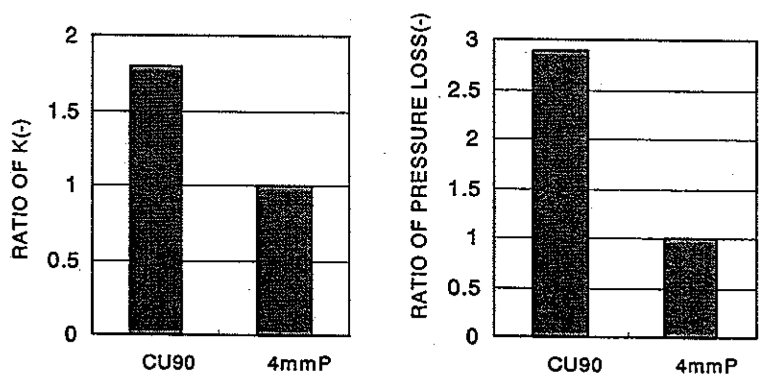


Fig.4

Bench scale pilot facility and test condition

Figure 5 shows the test results of CU90. The overall reaction rate constant (K) of CU90 is about 1.8 times than that of 4mmP plate type catalyst whereas the pressure loss of CU90 is about 3 times of 4mmP plate which is larger than 3.5mmP honeycomb catalyst on this condition. However, we also confirmed CU90 catalyst has higher performance with smaller catalyst surface as shown in Figure 5.



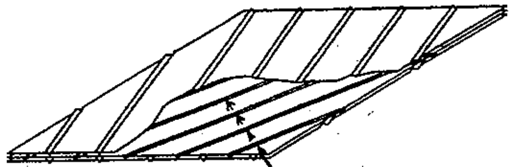
	CU90	4mmP Plate
Catalyst Surface(m2)	3.2	5.3

Catalyst surface areas are based on the 150 mm square units which were tested in bench scale test facility.

Fig.5

DeNOx activity and pressure loss of CU90 catalyst

Then, we prepared the catalyst elements which have some undulated lines at an angle of θ with the direction of gas flow, and assembled these elements turning back one after another as shown in Figure 6.

<table>
<tr><th>Item</th><th>CU(Cross-Undulated) Plate Catalyst</th></tr>
<tr><td>Element</td><td>
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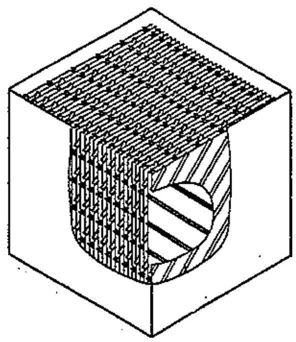
<tr><td>Unit Configuration</td><td>
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Fig.6
Plate configuration of CU catalyst

In the bench scale test, the catalyst should be evaluated as SV (Space Velocity) activity because the activity of plate type catalyst can be influenced by catalyst configuration so much and SV activity is directly related with the catalyst volume. Figure 7 shows SV activity with the cross angle of undulated lines to gas flow. The SV activity of CU catalyst is higher than that of conventional plate type catalyst at the range of the large cross angle. It means that CU configuration of the plate can achieve equal or more activity with the smaller catalyst volume than the conventional one as described before. For easy understanding, this SV activity can be converted to the AV (Area Velocity) activity using the following specific surface area.

Conventional plate type catalyst(4mmP);500m2/m3
CU catalyst 315m2/m3

As shown in Figure 8, the AV activity is considerably improved with CU configuration. It increases with the cross angle and saturated over the certain degree θ. Meanwhile, the CU configuration increases the pressure loss as shown in Figure 9. In Figure 9, the pressure loss per 1m(meter) is presented and it increases with cross angle. Considering the activity and pressure loss, CU catalyst at the certain degree θ can satisfy the target for development of CU catalyst. The characteristics of CU θ are described in the following.

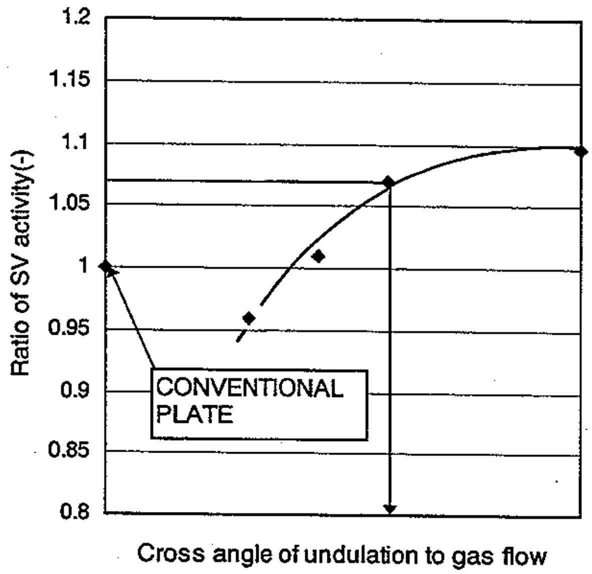

Fig.7

SV activity vs.cross angle of CU catalyst

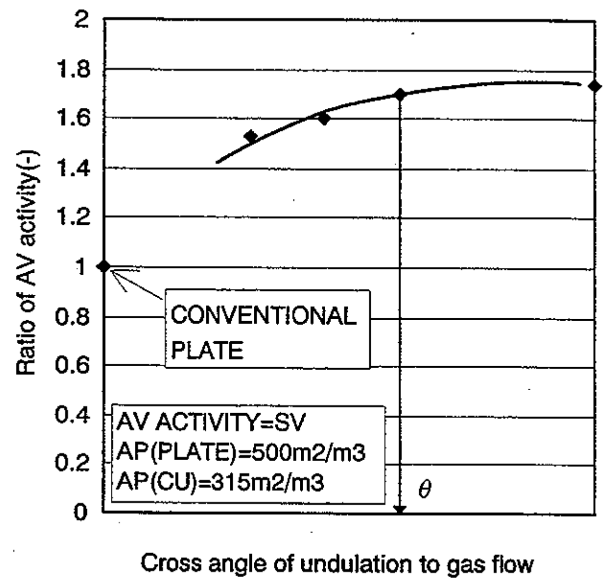

Fig.8

AV activity vs. cross angle of CU catalyst

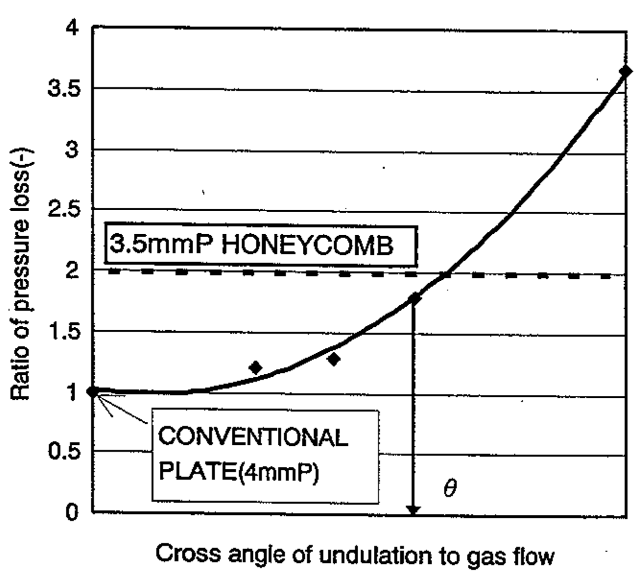

Fig.9

Pressure loss of CU catalyst

Characteristics of CU catalyst

It is necessary to confirm the DeNOx performance of a newly developed catalyst before applying it to actual plant .In case of CU catalyst, it is produced with the same materials of the present catalyst whose performance has been proven in commercial plants. The difference from the present catalyst is only the flow condition in the catalyst. Accordingly, the investigation required for CU catalyst is limited as shown in Table 3.

Table 3

Investigation items for CU catalyst

Investigation	Test	Test Item	CU catalyst
Catalyst screening	Laboratory test	Activity, Physical property, Mechanical property, Durability	Not required
↓ If good catalyst is found,			
Check for productivity	Semi-commercial scale production		Not required
↓ If there is no problem on productivity,			
Design data	Bench scale test	SV,Temp,Mole ratio, ΔP, etc.,	Required
↓ If it is a new development or by customer's request,			
Further requirement	Sample catalyst test	Catalyst deterioration	Not required
	Large scale pilot test	Catalyst deterioration and system	Not required
	Others	Erosion, thermal resistance,	Not required

1. LV characteristics

The CU catalyst has a higher activity than the conventional plate type catalyst by mass transfer effect with turbulent flow. Then the influence of gas velocity on CU catalyst is larger than the conventional one. Figure 10 shows the LV characteristics of CU catalyst which is indicated based on the activity as 1.0 at gas velocity of 6.9m/s , compared with conventional one. From figure 10, it is clear that the activity of CU catalyst is less than conventional one , especially in lower LV region. This can be explained as the result of decreasing mass transfer effect due to lower LV. Then, it is important for CU catalyst to keep high LV in the application in order to achieve good performance.

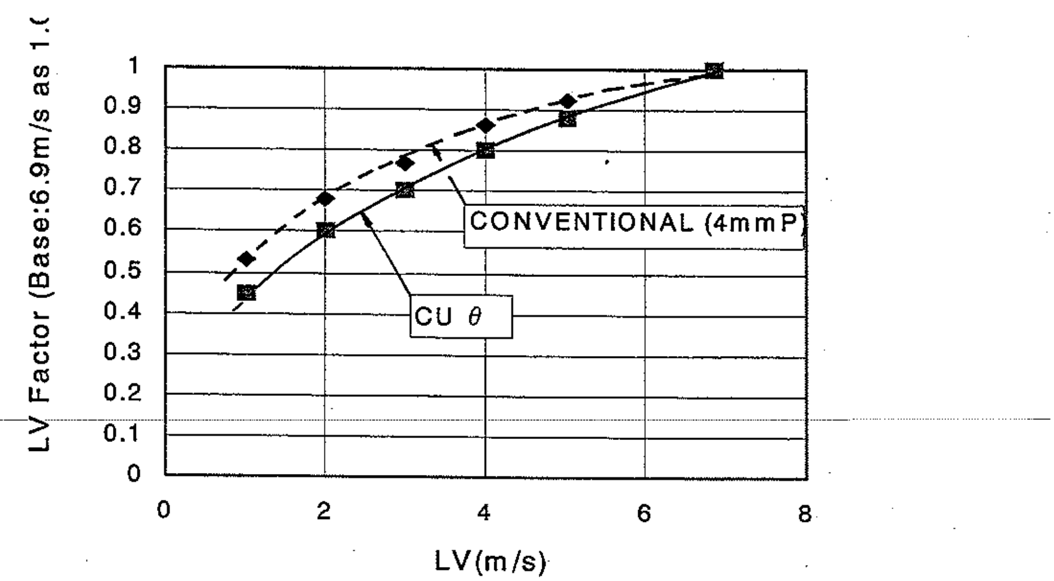

Fig.10

LV characteristics of CU catalyst

2. Pressure loss

The mass transfer effect of CU catalyst becomes higher with larger LV value. In the same manner , the pressure loss becomes higher with larger LV. Therefore, it needs to evaluate not only DeNOx efficiency but also pressure loss of CU catalyst in the application to actual plants. Then, we prepared 450mm square catalyst unit as used at actual plants to investigate pressure loss characteristics on cold condition exactly. Figure 11 shows the relation between friction factor and Reynolds number (Re) for the pressure loss.

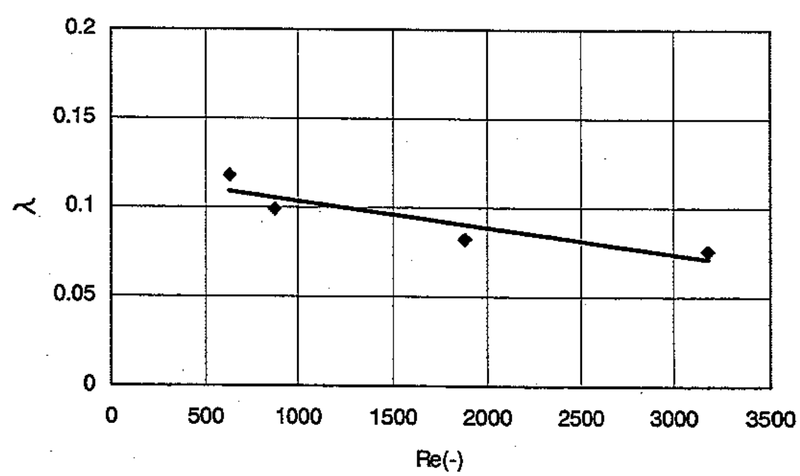

Fig.11

Friction factor of CU θ catalyst vs. Reynolds number

3. SO2 to SO3 conversion rate

The SO2 to SO3 conversion rate is decreased in proportion to reduction of the catalyst surface. However, the conversion rate is hardly influenced by mass transfer effect of CU configuration. Figure 12 shows SO2 to SO3 conversion rate of CU θ catalyst. It is clear that the conversion rate of CU θ catalyst is lower, in proportion to the decreased catalyst surface area compared with conventional 4mmP plate type catalyst. It means the mass transfer effect is only useful for DeNOx performance since the reaction rate of SO2 oxidation is too small to increase the overall reaction rate by mass transfer.

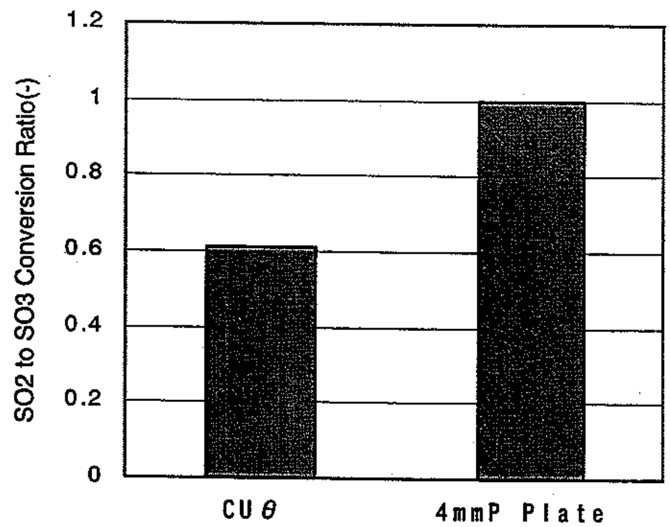

Fig.12

SO2 to SO3Conversion rate of CU catalyst

4. Other characteristics.

SV, temperature, mole ratio and deterioration characteristics of CU catalyst are the same as those of conventional plate type catalyst because CU catalyst is made of same materials as conventional plate type catalyst whose performance has already been proven.

First application to actual plant and operating result

CU catalyst was first applied to the SCR plant for Drever steel mill plant of National steel company located in Illinois state in U.S.A. The SCR system was supplied by Babcock & Wilcox Co. under license of HTC/BHK. The design condition for the plant and operating result are shown in Table 4 .The SCR system treats the flue gas from the gas fired furnace and the required DeNOx efficiency is 90.2% or more.

Table-4

Design condition of SCR plant for DREVER of National Steel Co.

Item		Unit	Design data	Operating Result (At initial operation)
Process		-	Selective Catalytic Reduction	→
Flue Gas Source		-	Furnace	→
Fuel		-	Natural Gas(NG)	→
Flue Gas Flow Rate		m3N/h	49,572(30,842 SCFM)	41,790
Flue Gas Temperature		℃	371(700 F)	→
Inlet Flue Gas Composition	CO2	(%)	3.2	
	H2O	(%)	6.2	
	N2	(%)	76.6	
	O2	(%)	14.0	
	NOx	(ppm;15%O2)	95.8(20.42 lb/h)	→
Outlet Flue Gas Composition	NOx	(ppm;15%O2)	9.4(2.0 lb/h)	4.2(0.89)
	NH3	(ppm;15%O2)	10	
Required DeNOx Efficiency		(%)	90.2 or more	95.6
Allowable Pressure Loss		(mmAq)	76.2(3 in H20)	63.5
Guarantee Period		Year	3	-

As shown in Table 4, it was confirmed that the required DeNOx efficiency and pressure loss across the catalyst well satisfied the requirements. This SCR system is now in operation successfully.

Application to CO/NOx simultaneous removal

Recently, the catalyst for simultaneous removal of NOx and CO from gas turbine flue gas has been applied in U.S.A. In response to this, HTC/BHK developed a dual function catalyst, which exhibits high activity for not only NOx removal with NH3 but also CO oxidation. The normal TiO2 based catalyst has no activity for CO oxidation. Then, a dual function catalyst of HTC/BHK is prepared adding precious metal to the TiO2 based catalyst (6).CU catalyst also can be applied to the plants which need both NOx and CO removal, since the reaction rate of CO oxidation is very high as same as that of NOx reduction. Namely, in CO oxidation reaction, diffusion of CO from bulk to catalyst surface is major determining factor of the overall reaction rate as same as NOx .In CU configuration, CO in the flue gas can be diffused to catalyst surface by disturbed gas flow and reacts with oxygen on the surface of catalyst to form harmless CO2. Figure 13 shows NOx/CO removal efficiencies of NOx/CO- CU catalyst. High performance of simultaneous removal of NOx and CO is obtained with CU catalyst.

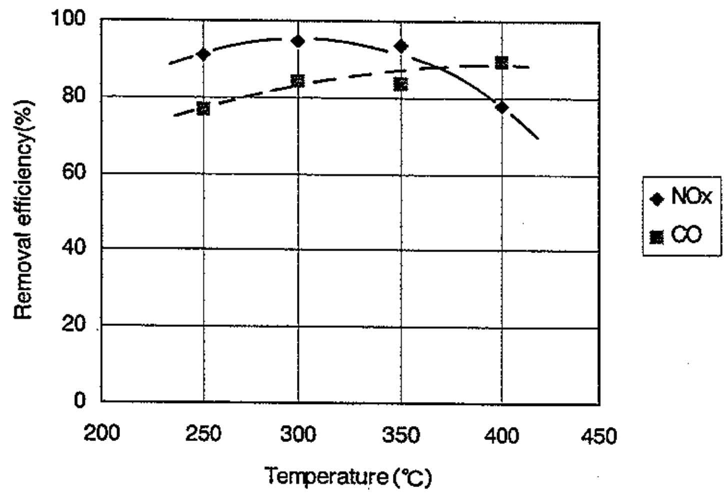

Fig.13

Simultaneous removal of NOx and CO by dual-function CU catalyst

Conclusion

Regarding SCR system incorporated with CU catalyst for gas fired plants, the followings were confirmed.

(1)CU catalyst has high DeNOx performance at it's smaller catalyst surface than the conventional plate type catalyst and the pressure loss of CU θ catalyst is lower than 3.5mmP honeycomb type catalyst.

(2)CU catalyst enables to reduce the cost of SCR system considerably, because the required catalyst surface of CU catalyst for NOx reduction is considerably lower than that of conventional plate type catalyst.

(3)CU catalyst which was first applied to the actual plant satisfied the required DeNOx efficiency and pressure loss across the catalyst layer.

(4)Dual-function CU catalyst can achieve high CO oxidation performance as same as NOx reduction.

Acknowledgments

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