DEACTIVATION OF SCR CATALYSTS ON THE REMOVAL OF DIOXINS

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Abstract
The dioxin removal abilities of the used selective catalytic reduction (SCR) catalyst samples in plate-type form, obtained from the sinter plant in different time periods, were measured and the cause of deactivation was investigated in this work. The catalytic activity was measured at a reaction temperature of 250℃ and gas hour space velocity (GHSV) of 5,000 hr^{-1} in the laboratory. Compared with the fresh SCR catalyst, the dioxin removal abilities over the used SCR catalysts decreased with the time period in the sinter plant from 90% to 73%, with a slow reduction of 19% within 3 years operation. The deactivation was found for the polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs) and the sparsely and the highly chlorinated PCDD/Fs species of the dioxin-like congeners over the used catalysts. The deactivation correlated well with the ratio of alkali metals concentration to the vanadium (V) concentration, adjusted by the surface area of the used SCR catalysts. The loss of ability was recovered by water treatment, which resulted in an increase of the removal ability back to 82%. It indicates that the deactivation of the SCR catalysts is mainly caused by the physical blocking of pores by the alkali metal salts carried over from fly ash.

Introduction
To meet the new dioxin emissions standard set by the Environmental Protection Agency (EPA) in Taiwan, the sinter plant in China Steel Corporation (China Steel) has been urged to adopt a pipe-end dioxin reduction plan. At the outlet of sintering process, the flue gas is treated via a SCR process and the dioxin concentration is reduced to 0.5ng-TEQ/Nm^3. Due to the high electrostatic precipitator (ESP) ash concentrations contained in the flue gas, China Steel uses the plate-type SCR catalyst to remove both dioxins and NOx at the same time. The ESP ash contains high concentrations of alkali metal salts, especially potassium (K).
In a previous study[1], the dioxin removal ability was shown to deteriorate substantially with the addition of ESP ash and the degree of deterioration became more prominent at higher temperatures, with a 31% reduction at 320℃. Furthermore, K has been proposed as a major element for the deactivation of SCR catalysts on the removal ability of NOx[2]. The deactivation is caused mainly by the chemical poisoning of active sites and the physical blocking of the surface area. K in ultra fine particles (＜100nm) in the flue gas diffused into the catalysts can react with the V-OH group and turns the active sites to V-O-K；this chemical poisoning renders the NOx removal ability inactive[3]. However, the effect of the alkali metals on the dioxin removal activity has seldom been reported in the use of the SCR catalysts operated at the plant sites.
In this paper we report on the traced results of the dioxin removal ability over a series of TiO_2-based SCR catalyst samples, obtained over different time periods during the operation of the sinter plant, and correlate the deactivation with the alkali metals accumulated in the SCR catalysts.

Materials and Methods
The four SCR catalyst samples in a plate-type form obtained from different time periods during the operation of the sinter plant were commercial type V_2O_5-WO_3-TiO_2 catalysts. The time periods for the four used catalyst were taken 12 months, 21 months, 27 months and 33 months, denoted as UC(12), UC(21), UC(27) and UC(33), respectively, after the installation of the SCR catalyst in the sinter plant. The catalyst was used in a pelletized form for the reaction tests. The major components contained in the SCR catalysts were obtained by ICP-AES (Arl 3580) and the BET surface areas were measured from N_2 absorption isotherms at 77K using a Micromeritics ASAP 2000 apparatus.
The dioxin source was generated by extracting the fly ash obtained from the ESP of the sinter plant with n-hexane. The n-hexane solution was injected into the reaction system by a high precision micro pump and the n-hexane was decomposed at 500~550℃ before the dioxins were transported with air into the glass flow reactor. The generated dioxin concentration was around 5ng-TEQ/Nm^3. The dioxin removal reactions were tested in a glass flow reactor whose catalytic bed was 34mm in height and 12mm in diameter. Catalyst weighing 0.4g was

mixed with quartz sand in the reactor and the particle sizes of catalyst were around 1mm in diameter. The reaction temperature was maintained at 250℃, and the inlet total flow rate of the carrier gas, comprising 15%O_2 with N_2, was 320 mL/min. The GHSV of the reaction flow was controlled at around 5000hr^{-1}.
The gas stream sampling was located at the outlet of the reactor. PCDD/Fs sampling, clean up and quantification were conducted in accordance with the USEPA Method 23A. Analysis of the 17 dioxin-like congeners was performed with high resolution gas chromatography (HRGC) (HP6890 plus) and a high resolution mass spectrometer (HRMS) (JEOL JMS-700) equipped with a fused silica capillary column DB-5 MS.
In the analysis of alkali metals and sulfate concentrations trapped in the used SCR catalysts, a catalyst sample of 0.12g was boiled in deionized water for 2hrs. The aqueous solution obtained was then measured by ion chromatography (Dionex 4500i) and the columns used were CG12A and AS4A-SC, respectively.

Results and Discussion

Catalytic Activity The plate-type catalysts tested in this study were taken from the sinter plant during the regular maintenance period which occurs in every quarter of the year. It is to be noted that a soot blower is installed at the top of each layer of the catalyst module in the sinter plant's reactor. The blower is designed to move back and forth every 8 hrs to remove the fly ash deposited on the surface of SCR catalysts. The size of the catalyst sample cut from plate-type catalyst was around 30×30cm, which was cleansed of fly ash by blowing N_2 on the surface.
The catalytic activity of the used SCR plate-type catalysts was tested at the temperature of 250℃ with an inlet dioxin concentration of 5ng-TEQ/Nm^3, and the results of the dioxins removal ability are shown in Figure 1. Figure 1 shows that the dioxin removal ability decreased with time period with the removal ability decreasing from 90% for a fresh SCR catalyst to 73~78% for a used catalyst, depending on the length of the period. These results indicate that the deactivation occurrs with a reduction of 19% in dioxin removal ability within 33 months operation. Comparing the dioxin removal abilities of the PCDDs and PCDFs for both fresh and used SCR catalysts, a similar deactivation was observed for both sets of congeners, as shown in Figure 2. The removal ability of the PCDDs dropped from 89% to 72~77% and that of the PCDFs from 89% to 73~78%, and the loss in the removal ability was inversely proportional to the operation period of time. There was only a slight difference between the two sets of congeners with PCDFs being the more favorable. The comparable ability for the removal of PCDDs and PCDFs was also reported by Liljelined et.al.[4] in a study with V_2O_5/TiO_2 as the catalyst.
From the test results of their dioxin removal abilities, selected PCDDs (7 species) and PCDFs (10 species) congeners were further investigated and the results of each species in both congeners for both fresh and used SCR catalysts are compared in Figure 3. Among the dioxin-like congeners, the sparsely chlorinated PCDD/Fs species (with 4~5 chlorine atoms) showed slightly better removal ability than the highly chlorinated PCDD/Fs species (with 6~8 chlorine atoms). This finding is consistent with the common characteristic for the decomposition of chlorine-containing aromatic compounds, in which the removal ability decreases with the increase in the number of chlorine atoms. The same deactivation was also observed for each species in both congeners. The longer the operation period, the greater the deactivation for the used SCR catalysts.
Characterization The major V content in the used SCR catalysts ranged from 1.6wt% to 1.8 wt% and was comparable with the 1.8wt% of the fresh SCR catalyst. Correspondingly, the BET surface areas (SA) of the used SCR catalysts decreased from 55m^2/g for the fresh SCR catalyst to a range of 22 to 33m^2/g for the used catalysts. This decrease was inversely proportional to the time period that the catalyst operated in the plant site's reactor. The longer the operation time, the less the BET surface area.
From the IC analysis results, two alkali metal cations (sodium (Na) and K) were observed in the used SCR catalysts, with K the predominant one ranging from 1.0 to 2.1wt%. In contrast, the major anion appeared in the used SCR catalysts was sulfate ($SO_4^=$) and its concentration ranged from 4.9wt% to 14.7wt%. This finding indicates that the major alkali metal salt was K_2SO_4 with Na_2SO_4 as the minor, accumulated on the used SCR catalysts. Both K_2SO_4 and Na_2SO_4 were carried over by the fly ash from the sintering process.
Deactivation In order to investigate the cause of the deactivation of the used SCR catalysts with regard to their dioxin removal ability, it was attempted to correlate the catalytic activities with the concentrations of alkali metals. The correlation investigation was undertaken by calculating the K/V molar ratio for each used SCR catalyst, which was adopted by Zheng et al. in the study of deactivation over the SCR catalysts caused by the KCl or K_2SO_4 aerosols for the NOx removal ability at 350℃. The deNOx catalytic activity was only 10% after a

3wt% V_2O_5 SCR catalyst doped with pure KCl aerosols with a K/V molar ratio of 0.8, indicating that a significant chemical poisoning had occurred[3]. In this study, for the used SCR catalysts after operation between 1 year to 3 years at 300℃ in the sinter plant's reactor, the BET surface areas were found to reduce from 55m^2/g for the fresh catalyst to 22~32m^2/g for the used catalyst. Therefore adjustments were made by considering two factors: firstly, that the BET surface area changes, and, secondly, that the Na to alkali metal concentration besides K should be included into the K/V molar ratios. Accordingly, a new (K+Na)/(V×SA) ratio was adopted in the correlation with the dioxin removal ability. The correlation result of dioxin removal ability to (K+Na)/(V×SA) ratio for both fresh and used SCR catalysts is shown in Figure 4. Figure 4 shows that the dioxin removal ability decreases quickly initially and then reduces slowly with the increase of the (K+Na)/(V×SA) ratio.

In contrast, the calculated (K+Na)/V molar ratios for the used SCR catalysts were 1.1~2.2, which was much larger than the average K/V molar ratios of 0.5~0.75 shown in Zheng et al.'s report[3]. Despite the larger (K+Na)/V molar ratios, these did not result in a significant deactivation of the dioxin removal ability. In this study, the loss of dioxin removal ability for SCR catalysts was about 19% within 3years operation in the sinter plant. This loss occurred because the alkali metal salts were carried along with the fly ash in sinter plant but not with the pure K aerosols which resulted in the large loss of NOx removal ability reported in Zheng et al.'s study[3]. On the contrary, in the other case also reported by Zheng et al. with SCR catalyst exposing to the fly ash (consisting of KCl and K_2SO_4), no deactivation was found for NOx removal ability after 2970hrs (about 4 months) operation, which is more similar to the results obtained in here. Thus, the main cause for the deactivation of the SCR catalysts may be traced to the plugging of the pores by alkali metal salts in the used catalysts.

To further support the postulation of deactivation, the plate-type used SCR catalyst of UC(27) was further treated with deionized water at mild temperature for 1 hr in order to wash away the major alkali metal salts, i.e. K_2SO_4 with Na_2SO_4, trapped in the catalysts (denoted as UCW(27)). Both K_2SO_4 and Na_2SO_4 have high solubility in water and hence can be removed by water treatment. From the IC analysis results, about 96% and 95% of the K and Na, respectively, were removed from the UC(27) used SCR catalyst and only about 0.08 and 0.02wt% of K and Na, respectively, remained in the catalyst. This IC result shows that most of the alkali metal salts were removed from the catalyst and no substantial alkali metal salts would foul or plug the catalyst. In such a case, the measured dioxin removal ability was found to increase with some extent from 74% to 82%. Although the correlation result of the dioxin removal ability to (K+Na)/(V×SA) ratio for UCW(27), as presented in Figure 4, fits well on the depicted curve, the cause of deactivation still mainly come from the physical plugging of the pores in the SCR catalysts by alkali metal salts.

From the cause of deactivation shown in this study, the dioxin removal ability can be further improved if the soot blower installed inside the reactor is operated as efficiently as possible by raising the injection pressure in order to prevent the alkali metal salts contained in fly ash from physical blocking the pores of the SCR catalyst.

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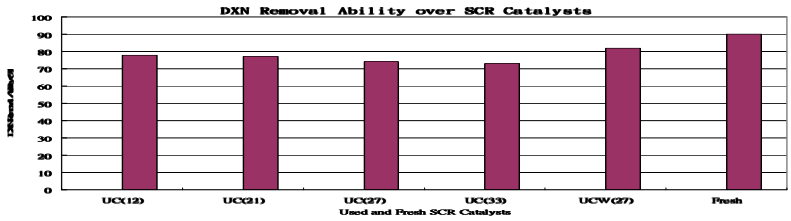

Fig.1. Dioxin removal ability of the used SCR catalysts

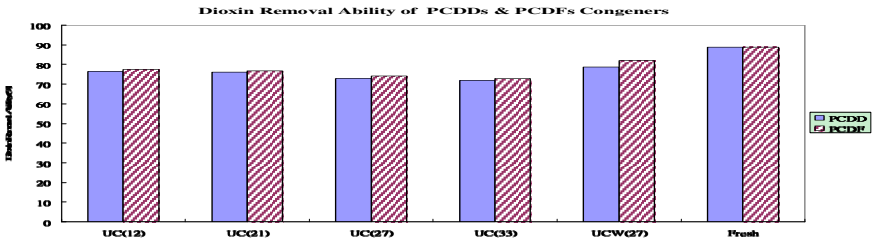

Fig.2. Dioxin removal ability of PCDDs and PCDFs congeners over the used SCR Catalysts.

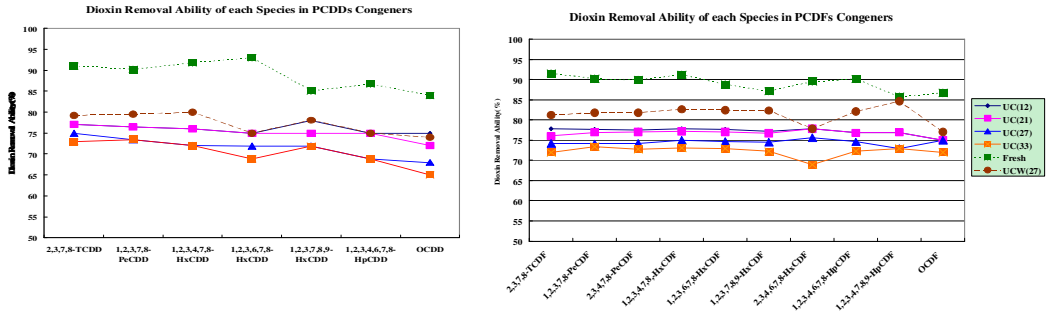

Fig.3. Dioxin removal ability of each species included in PCDDs and PCDFs congeners over the used SCR catalysts.

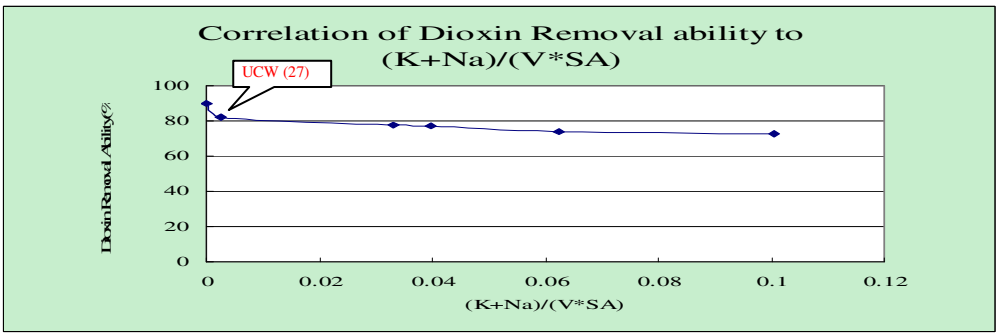

Fig.4. Correlation of dioxin removal ability with (K+Na)/(V×SA) over the used SCR catalysts.