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自動車 廢觸媒로부터 白金族 回收를 위한 어트리션 스크러빙의 效果[†]

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Effect of Attrition Scrubbing on the Recovery of Platinum Group Metals from Spent Automobile Catalytic Converters[†]

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요 약

자동차 폐촉매로부터 백금족 금속(PGMs)의 회수를 위한 어트리션 스크러빙의 효과를 조사하였다. 자동차 폐촉매를 2 mm 이하로 분쇄한 후 60분 범위내에서 어트리션 스크러빙하였으며 이를 체가름하였다. 스크러빙을 통해 촉매층은 촉매 지지체 표면으로부터 탈리되어 45 μm 이하의 미립자로 분리되었다. 45 μm 이하 미립자의 양은 스크러빙 시간이 증가함에 따라 증가하였으며, 스크러빙 시간 40분에서 미립자의 유가물 함량은 CeO_2 19.3%, ZrO_2 1.9%, PGMs 419 ppm을 나타내었다. 미립자에서 감마 알루미나의 회수율은 스크러빙 시간이 증가함에 따라 증가하였으며, 동시에 CeO_2, ZrO_2 및 PGMs의 회수율도 CeO_2 82.9%, ZrO_2 78.7%, PGMs 78.9%로 증가하였다. 시료의 고액비 및 초기 투입 입자 크기가 증가할 때 미립자의 양 및 감마알루미나의 회수율은 증가하였다. 어트리션 스크러빙은 분쇄 및 분리 기술로서 스크러빙 용기내에서 입자들 사이의 충격 및 전단 운동에 의해 코디어라이트 촉매 지지체로부터 감마알루미나의 분리에 효과적임을 알 수 있었다.

주제어 : 어트리션 스크러빙, 백금족 금속, 회수, 폐촉매

Abstract

The effect of attrition scrubbing on the recovery of platinum group metals (PGMs) from automobile catalytic converters has been investigated. Catalytic converters were first crushed into particles less than 2 mm and attrition scrubbed in the range of 60 min, and then they were sieved with several screens. The catalyst layer, γ-alumina, was dislodged from the surface of the supporting matrix into fine particles less than 45 μm by attrition scrubbing. The fraction of fine particles less than 45 μm increased as the residence time for attrition scrubbing increased. The composition of the fine fraction obtained at a residence time of 40 min was CeO_2 19.3%, ZrO_2 1.9% and PGMs 419 ppm. In the fine fraction, the recovery of γ-alumina increased proportionally to the residence time. Simultaneously, the recovery rates of CeO_2, ZrO_2 and PGMs increased to 82.9%, 78.7% and 78.9%, respectively. The production of the fine fraction less than 45 μm and the recovery of γ-alumina increased when the solid concentration and initial feed size increased. Therefore, the attrition scrubbing as the comminution and separation process was concerned to be effective for the recovery of catalyst layer from ceramic supporting matrix by physical impact and shearing action between particles in the scrubbing vessel.

Key words : Attrition Scrubbing, Platinum Group Metal, Recovery, Catalytic Converter

1. Introduction

Currently, several million tons of used catalytic

converters are annually disposed of worldwide. An automobile catalytic converter generally contains 1~2 g of all types of PGMs, including 0.5~1 g of platinum.[1]

The recovery technologies of PGMs from spent catalytic converters have been reviewed by numerous

researchers in the last few decades. Two types of process, wet and dry methods, have been commercially operated. In a wet process, PGMs on the spent catalytic converters were dissolved mostly in the form of chloro-complex, MCl_6^{2-}, by contacting them in aqueous solutions. Subsequently the resulting solutions are concentrated and then the precious metal ions are cemented by metals such as Al, Fe or Zn in the concentrated system.[2] In a dry process, spent catalytic converters are melted, for example, with CaO at elevated temperatures to produce a slag with low viscosity. PGMs in the melt are separated by allowing them to adsorb on Fe or Cu having high specific gravity.[3] Although highly-pure precious metals could be obtained, the current recovery technologies of PGMs do not seem to be cost-effective since PGMs embedded in these types of catalytic converters are present in very small quantities.

It is, therefore, worth separating the catalyst layer mainly composed of γ-alumina (Al_2O_3) which contains cerium and zirconium oxides and PGMs (Pd, Pt and Rh) from the ceramic catalyst supporting matrix, cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$), prior to any wet or dry recovery process. The main purpose of this work is to provide information about the effect of attrition scrubbing, one of the viable pre-treatment methods, on the recovery of these precious metals from spent automobile catalytic converters. The process variables that influence the efficiency of attrition scrubbing such as residence time, solid/liquid ratio and initial feed size of the catalyst sample have been explored in this study.

2. Experimental

Fig. 1 illustrates a typical catalytic converter installed in the engine exhaust system of an automobile. The ceramic supporting matrix which is of honeycomb structure controls the volume of the converter and the catalyst layer covers the surface of the supporting matrix to increase the effective surface area of catalyst[4].

Several spent catalytic converters were collected from a local auto junkyard. The spent catalytic converters were crushed to pass a laboratory standard sieve of 2 mm prior to experiments. The scrubbing vessel made of acrylate with a total volume of 1.5 L
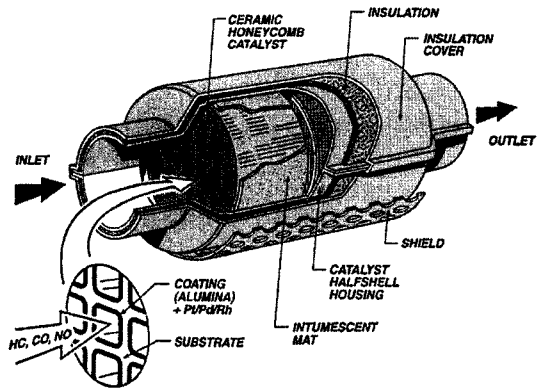

Fig. 1. Catalytic converter including honeycomb support and mounting canister.

was used. The attrition scrubbing was carried out with an aqueous suspension. A laboratory mechanical overhead stirrer, which was attached to a single axis with a two-bladed impeller, was used for the attrition scrubbing. The impeller in the scrubbing vessel was fixed in such way that it was just above the bottom of the vessel. The rotation speed of the impeller was fixed at 1100 rpm throughout the experiment.

X-ray diffraction (XRD, RINT-2000, Rigaku) analysis was carried out in order to evaluate the mineralogical phases of the sample. The chemical compositions of the samples were analyzed using an X-ray spectrometer (PW2404, Philips).

3. Results and Discussion

Table 1 shows the chemical composition of the spent automobile catalytic converter particles less than 2 mm used in this work. The table indicates that the sample mainly consists of SiO_2, Al_2O_3 and MgO. It also contains other metal oxides such as CeO_2, ZrO_2 and minor CaO. These oxides are used as promoters or stabilizers to increase the catalytic activities or to stabilize the structure of catalyst.[5] It also reveals that the sample contains appreciable quantities of PGMs.

The crushed catalytic converter particles were subsequently wet sieved. Table 2 shows the chemical composition of the different size fractions. It is noted that as the size of the fractions decreased, the contents of SiO_2 and MgO decreased, whereas those of other constituents increased. Furthermore, the increment was

Table 1. Chemical composition of the spent automobile catalytic converter particles

Oxides (wt%)						PGMs (ppm)		
SiO_2	Al_2O_3	MgO	CaO	CeO_2	ZrO_2	Pd	Pt	Rh
32.9	42.0	8.2	0.6	6.9	0.7	62	56	19

Table 2. Chemical composition of the different size fractions

Size (μm)	Oxides (wt%)						PGMs (ppm)		
	SiO_2	Al_2O_3	MgO	CaO	CeO_2	ZrO_2	Pd	Pt	Rh
+1000	39.4	38.8	9.8	0.1	4.0	0.5	49	35	12
−1000+600	39.5	38.8	9.9	0.2	4.0	0.5	41	39	14
−600+300	41.0	38.6	10.3	0.2	3.5	0.4	36	30	11
−300+212	22.3	48.1	5.4	0.5	10.9	1.6	116	60	26
−212+106	7.9	57.3	1.8	1.5	17.5	1.7	125	132	43
−106+45	11.4	50.5	2.7	3.6	15.9	1.5	129	138	48
−45	7.5	49.8	1.7	2.4	20.4	1.3	136	146	59

Table 3. Yield of the fractions obtained by attrition scrubbing at different times

Size (μm)	Attrition scrubbing time (min)					
	0 (raw)	5	10	20	40	60
+1000	33.1	32.6	27.6	25.5	18.4	18.9
−1000+600	28.6	28.1	29.0	28.4	27.8	29.2
−600+300	14.1	13.0	14.2	14.0	15.3	15.1
−300+212	4.8	2.7	2.7	2.8	3.0	2.9
−212+106	8.5	5.4	5.3	4.3	4.5	3.4
−106+45	5.7	4.4	4.5	4.0	4.6	3.1
−45	5.2	13.8	16.7	21.0	26.4	27.4
Total	100.0	100.0	100.0	100.0	100.0	100.0

significant in the fraction less than 300 μm. Fig. 2 shows the X-ray diffraction patterns of three fractions. The main peaks of the coarse fraction (A) were exactly matched with those of cordierite (JCPDS 13-0029) although weak peaks of CeO_2 (JCPDS 43-1002) were also detected in the XRD pattern. On the other hand, the peaks of CeO_2 were predominant in the pattern of the particle less than 45 μm. Although the peaks of γ-Al_2O_3 are not observable in the patterns owing to its very poor crystallinity, the γ-Al_2O_3 content should be high based on its chemical analysis. These results indicate that the catalyst layer rather than supporting matrix tends to be easily broken into fine particles less than 300 μm. In addition, it can be also expected that the contents of PGMs and other metal oxides increased simultaneously as the particle size decreased since they are mostly imbedded in the catalyst layer which is mainly composed of γ-Al_2O_3.
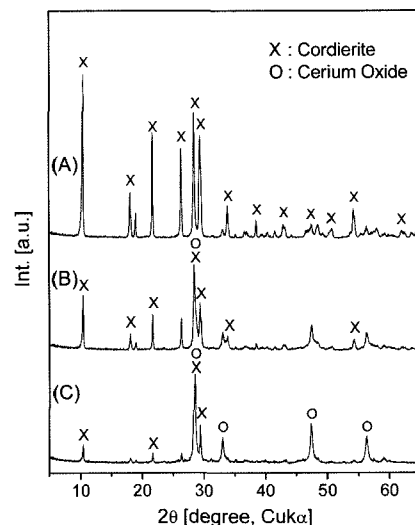
Fig. 2. X-ray diffraction patterns of three fractions, A: −600+300 μm, B: −300+212 μm, C: −45 μm.
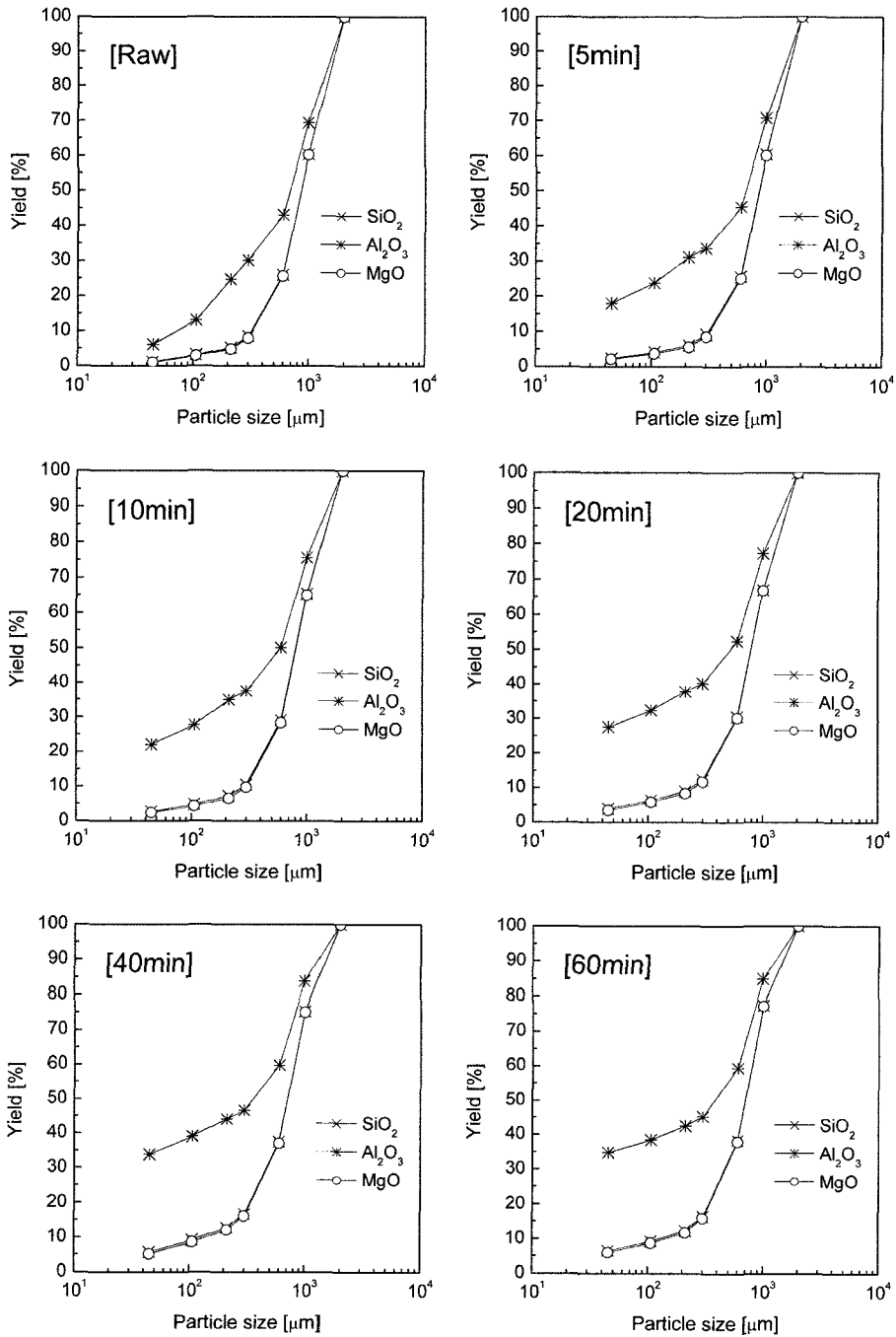
Fig. 3. Yield of SiO_2, Al_2O_3 and MgO at different times.

Table 3 shows the yield of the fractions obtained by attrition scrubbing at different times. It is worth mentioning that the process seems to be quite effective for the production of fine particles less than 45 μm. As the residence time increased, the yield of the fraction less than 45 μm increased by 22.2 wt%, whereas the total fractions larger than 300 μm decreased only by 12.6 wt%. Fig. 3 shows the yield of SiO_2, Al_2O_3 and
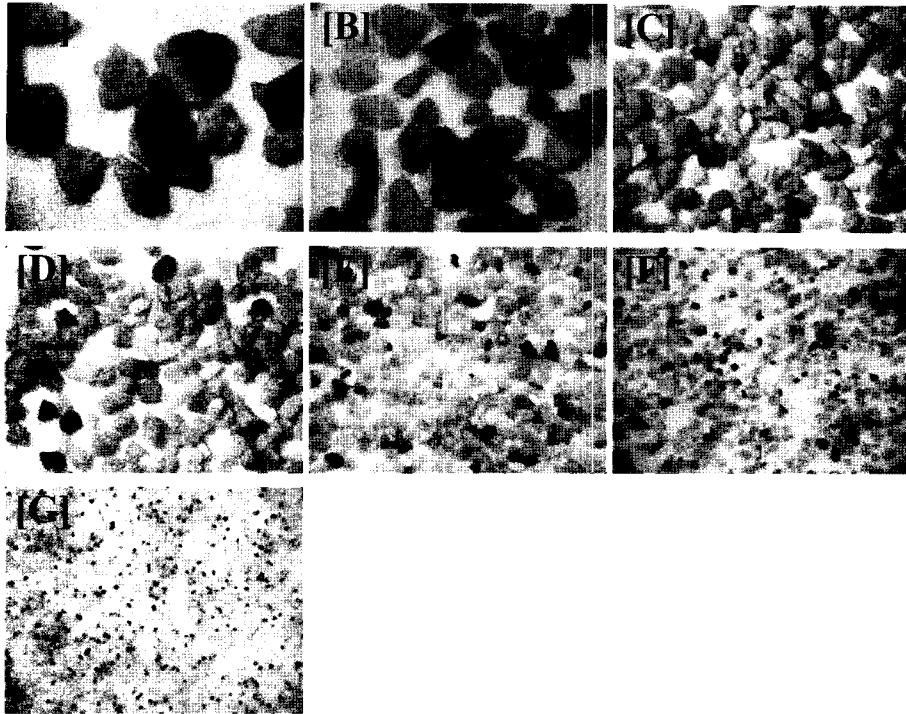
Fig. 4. Microscopic images of the fractions obtained by attrition scrubbing for 40 min, A: −2000 + 1000 μm, B: −1000 + 600 μm, C: −600 + 300 μm, D: −300 + 212 μm, E: −212 + 106 μm, F: −106 + 45 μm, G: −45 + 25 μm.

MgO at different times. In the case of the particles less than 45 μm, as the residence time increased from zero to 40 min, the yield of Al_2O_3 increased from 6.2 wt% to 33.8 wt%. The most of Al_2O_3 in the fractions less than 45 mm is believed to be originated from the catalyst layer rather than the supporting matrix. In strongly bonding matrix material with a catalytic layer for manufacturing catalytic converters, the thermal expansion coefficient of the two materials has to be similar each other to prevent a delamination between them. Therefore, thermal shock or chemical leaching is considered insufficient to separate catalyst layer from supporting matrix. In this work, it is noted that the process of attrition scrubbing seems to be effective for the separation of the catalyst layer from the supporting matrix.

Fig. 4 shows the microscopic images of the fractions obtained by attrition scrubbing for 40 min. The images of the particles larger than 300 μm, (A), (B) and (C), indicate that most particles (light gray) consisting of the catalyst layer seem to be delaminated from the supporting matrix while a small amount of particles
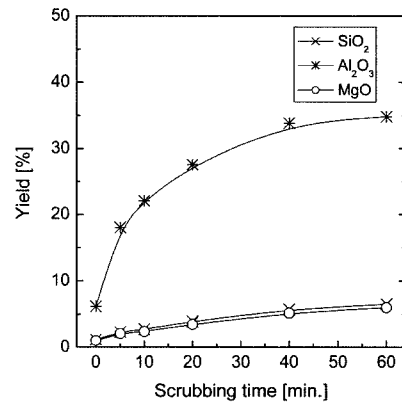

Fig. 5. Yield of SiO_2, Al_2O_3 and MgO in the fraction less than 45 μm according to residence time.

(black) still remains unchanged. However, we conclude that the fine particles less than 45 μm be originated from the catalyst layer although the degree and manner of particle delamination are not clearly understood in review of Fig. 4.

Fig. 5 shows the yield of the main constituents, SiO_2, Al_2O_3 and MgO, in the fraction less than 45 μm

Table 4. Variation of γ-alumina and cordierite contents in different particle sizes as a function of attrition scrubbing time

Size (μm)	γ-alumina (wt%)					
	Raw	5min.	10min.	20min.	40min.	60min.
+1000	20.3	16.6	12.7	9.9	6.6	5.9
−1000+600	17.3	13.8	13.0	10.8	9.2	9.4
−600+300	7.7	5.7	5.6	4.8	4.5	5.0
−300+212	8.1	2.0	1.7	1.4	1.2	1.1
−212+106	22.4	13.9	12.7	8.8	6.6	5.0
−106+45	12.4	10.7	10.0	7.8	7.1	4.8
−45	11.8	37.3	44.3	56.5	64.8	68.8
Total	100.0	100.0	100.0	100.0	100.0	100.0
Size (μm)	Cordierite (wt%)					
	Raw	5min.	10min.	20min.	40min.	60min.
+1000	39.6	39.6	34.7	33.1	24.8	22.6
−1000+600	34.4	34.9	36.3	36.3	37.7	39.0
−600+300	17.5	16.5	18.7	18.3	20.9	22.0
−300+212	3.2	3.0	3.2	3.4	4.0	4.1
−212+106	2.0	2.0	2.4	2.6	3.5	3.1
−106+45	2.1	1.7	2.0	2.4	3.5	2.8
−45	1.2	2.3	2.7	3.9	5.6	6.4
Total	100.0	100.0	100.0	100.0	100.0	100.0

Table 5. Yield and chemical composition of the fraction less than 45 μm at different S/L ratios at a scrubbing time of 40 min

S/L ratio	Yield (wt%)	Oxides (wt%)					PGM (ppm)
		SiO_2	Al_2O_3	MgO	CeO_2	ZrO_2	
0.33	24.2	7.1	54.6	1.6	19.3	1.9	419
0.55	24.6	8.1	54.6	1.9	19.4	1.9	421
0.65	25.5	8.2	54.7	2.0	20.0	2.0	429

according to residence time. It can be seen that the yield of Al_2O_3 increased by 34.8 wt% at a scrubbing time of 60 min, whereas the increments for SiO_2 and MgO during the same period were mere 5∼6 wt%.

Table 4 shows the variation of γ-alumina and cordierite contents in different particle sizes as a function of attrition scrubbing time. It is noticeable that the attrition scrubbing leads to make the γ-alumina concentrated into fine particles less than 45 μm, while cordierite remains in the coarse particles larger than 300 μm although the cordierite was also comminuted into fine particles.

The raw catalytic converter particles less than 2 mm were attrition scrubbed as a function of time and then the product was sieved with a 300 μm. Fig. 6 shows the recovery and content of each constituent in the 300 μm-fraction according to the time. As expected, the recovery of the main constituents increased by 16.4%

SiO_2, 45.2% Al_2O_3 and 15.9% MgO at 40 min. It is important to note that the recovery increased markedly by 82.9% CeO_2, 78.7% ZrO_2 and 78.9% PGMs although their contents slightly decreased as the attrition scrubbing progressed.

Table 5 shows the yield and chemical composition of the fraction less than 45 μm at different solid liquid (S/L) ratios at a scrubbing time of 40 min. The yield and chemical composition of the fraction were found to be little affected by the S/L ratio although the yield and the PGMs content slightly increased. The efficiency of attrition scrubbing generally increases as the S/L ratio increases owing to more effective scrubbing actions.[6]

Three different feed sizes of the catalytic converters, 2000, 1000 and 600 μm, were prepared in an effort to improve the recovery of γ-alumina during attrition scrubbing. Table 6 shows the variation in the yield of
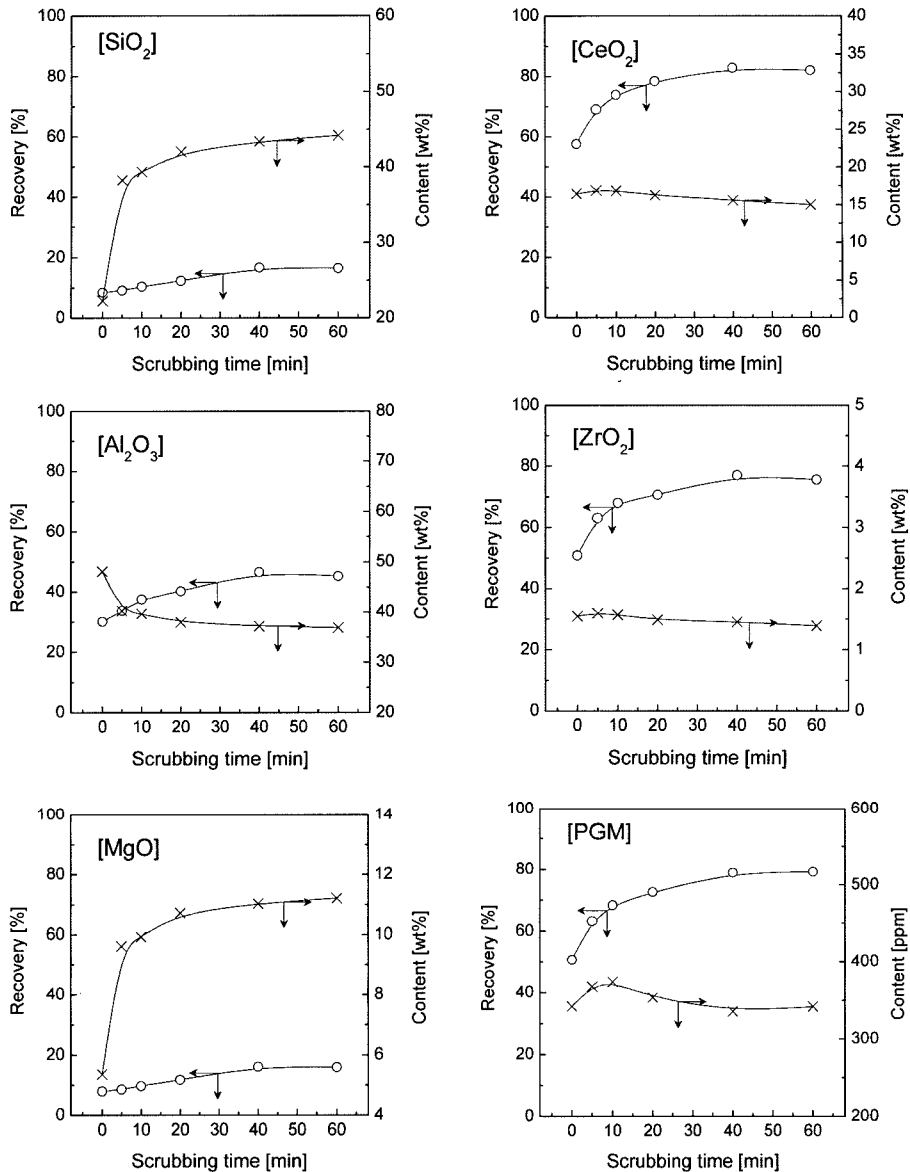
Fig. 6. Recovery and content of each constituent in the 300-μm fraction as a function of time.

fractions with the 3 feed sizes at an attrition scrubbing time of 40 min. It can be seen that the amount of the fine particles less than 45 μm decreased from 26.4 wt% to 20.4 wt% when the feed size decreased. The chances of contacting catalyst layers each other is likely to become small as feed size decreases due to the increase of surface area. On the contrary, particle-particle scrubbing action is believed to become dominant as initial feed size increases.

4. Conclusions

1. The spent automobile catalytic converters are mainly composed of 32.9% SiO_2, 42.0% Al_2O_3 and 8.2% MgO, which are the main constituents of catalyst layer (γ-alumina) and catalyst supporting matrix (cordierite) in the form of oxides. The feed also contains 6.9% CeO_2, 0.7% ZrO_2 and 0.6% CaO in the form of oxides as well as 62 ppm Pd, 56 ppm Pt, 19

Table 6. Variation in the yield of fractions with the 3 feed sizes at an attrition scrubbing time of 40 min

Size (μm)	Initial feed size (μm)					
	600		1000		2000	
	Feed	Product	Feed	Product	Feed	Product
+1000	-	-	-	-	33.1	18.4
−1000+600	-	-	43.7	32.1	28.6	27.9
−600+300	51.6	51.1	24.9	29.2	14.1	15.3
−300+212	12.2	10.2	7.5	4.6	4.8	2.9
−212+106	14.2	10.8	11.1	5.7	8.5	4.5
−106+45	9.9	7.5	6.3	4.3	5.7	4.6
−45	12.1	20.4	6.5	24.1	5.2	26.4
Total	100.0	100.0	100.0	100.0	100.0	100.0

ppm Rh in the form of metals.

2. The contents of SiO_2 and MgO in the feed decrease as the particle size decreases during the attrition scrubbing, whereas the Al_2O_3 content increases. The contents of metal oxides and PGMs also increase as the Al_2O_3 content increases since they are mostly imbedded in the catalyst layer.

3. Attrition scrubbing as a comminution and separation process is determined to be a viable route to recover the catalyst layer from the supporting matrix. Physical impact and shearing action between particles in the scrubbing vessel causes the PGMs-containing catalyst layer to delaminate from the supporting matrix. The particles obtained at the residence time of 40 min contain 7.1% SiO_2, 54.6% Al_2O_3, 1.6% MgO, 19.3% CeO_2, 1.9% ZrO_2 and 419 ppm PGMs.

4. The recovery of γ-alumina, in the fraction less than 300 μm increases as the residence time increases. The recoveries of CeO_2, ZrO_2 and PGMs increase simultaneously by 82.9% CeO_2, 78.7% ZrO_2 and 78.9% PGMs at a residence time of 40 min. However, there seems practically no relationship between solid concentration and γ-Al_2O_3 recovery in the present work although the yield and PGMs content in the fraction less than 45 μm slightly increase with increasing the solid concentration.

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