Time-lapse Visualization of Ash Deposition in Diesel Particulate Filter

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ABSTRACT: The ash deposition process on the wall surface of a diesel particulate filter was investigated through time-lapse visualization utilizing a field-emission scanning electron microscope. The components of zinc and phosphorus included in the primary particles of particulate matter (PM), as well as other large ash particles consisting of calcium, zinc, sulfur, and phosphorus in a PM cake layer, were sintered as an ash layer. These ash components were deposited locally around the perimeters of surface pores during a regeneration process. The pressure drop in the filter was reduced by the growth of the ash layer.

KEY WORDS: Heat engine, Particulate filter, Emissions gas, Ash deposition, Time-lapse visualization [A1]

1. Introduction

Diesel engines have become increasingly sophisticated based on continuous increases in output power, output torque, and thermal efficiency. However, still there are many significant issues regarding after-treatment systems, such as diesel oxidation catalyzers (DOCs), diesel particulate filters (DPFs), selective catalyst reduction, and ammonium slip catalyzers for reducing the emission of unburnt components, particulate matter (PM), nitrogen oxides, and trace components of ammonium. Among these issues, the emission control of PM, including soot particles (mainly carbon), soluble organic fractions (SOFs), and ash components, is the most significant issue. DPFs are utilized to reduce the emission of PM. However, performance factors related to filtration efficiency and pressure drop are strongly dependent on ash deposition. There are two types of ash deposition: wall ash deposited on the DPF wall surface 1) and other plug ash stacked at the ends of inlet channels 2, 3, 4). Wall ash acts as a membrane filter covering the main DPF wall, resulting in high filtration efficiency. In contrast, plug ash reduces the wall flow area of DPFs, resulting in significant pressure drop. Therefore, the ash deposition process should be investigated in parallel with the trapping and oxidation processes of PM.

Recently, the mechanism for the increase in the pressure drop upon the soot loading was investigated by the authors through time-lapse visualization utilizing a field-emission scanning electron microscope (FESEM) 5, 6), where ash components were not included. From this visualization, it was determined that at the beginning of soot deposition, soot is trapped on the surfaces of grains of silicon carbide (SiC) DPFs. Based on dendrite-structured deposition, a bridging structure is formed by soot at a depth of 10–20 microns from the surface of the DPF wall. After the bridging structure is completely formed, soot is stacked inside the surface pores that are opened to the inlet channel below the surface. In this phase of trapping, the pressure increases dramatically. After the surface pores are completely filled with soot, a soot cake layer is formed. However, if there is wall ash on the surface of the DPF wall, it is expected that the trapping process will change significantly.

Fluid dynamics around ash aggregated on the wall surface are also a significant issue. Depending on its size, it is predicted that wall ash may be removed by the fluid-dynamical shear force caused by the velocity gradient around the wall surface. The ash would then move and deposit at the ends of inlet channels as plug ash 4, 7). However, because wall ash has a porous structure (otherwise, there could be no soot deposition), the velocity gradient becomes smaller when there is suction flow into the porous structure.

The initial conditions of the ash introduced into DPFs are not well known. Therefore, the elements and components of the ash were investigated. It was determined that the components are mainly oxide materials, including elements of calcium (Ca), sulfur (S), zinc (Zn) and phosphorus (P).

In this study, by utilizing time-lapse visualization, the ash deposition process on the surface of a DPF wall was investigated through the repeated trapping and oxidation of PM with a high concentration of ash elements for accelerated experimentation.

2. Experiments

2.1. Experimental setup

Figure 1 presents a schematic of a small DPF sample and holder for visualization, while detail information about the DPF is described in Table 1. The sample was comprised of a 7×7 channel matrix, where cells were alternately plugged at each end by a ceramic paste. To visualize the cross section of the vertical wall of the DPF, the horizontal outer wall was removed from the sample 5, 6).
The DPF sample was set into the holder, which is made of stainless steel. The top surfaces of the vertical walls and the holder were polished uniformly utilizing abrasive papers with grit sizes ranging from P400 to P4000. Next, the open channels were covered by a quartz glass plate in place of the removed horizontal wall during the trapping and oxidation processes. After repeated trapping and oxidation, cross-sectional images of the vertical wall between the open channels were obtained by utilizing an FE-SEM (JEOL, JSM-6301F) with resolution limit of 1.5 nm and acceleration voltage of 2.0 kV.

2.2. Experimental procedure

Figure 2 presents a schematic of the diesel particulate generator (DPG) that was utilized to produce PM containing ash components. The total flow and PM/ash loading ratio was controlled by the main combustor based on the primary, secondary, and tertiary air supplies. Figure 3 presents a schematic of the bypass line of the small DPF for time-lapse visualization. The flow rate of the bypass line was controlled and measured by a suction pump and mass flow meter, respectively, on the downstream side of the DPF. The small DPF was kept at a constant temperature of 150 °C for PM loading. In this case, the space velocity ratios for both DPFs were fixed at 60,000 h⁻¹ and the superficial velocities for wall flows in the full- and small-size DPFs were 26.4 and 28.2 mm/s, respectively.

As a result, the mass loadings of soot (mainly carbon) and ash were nearly the same for both DPFs, as shown in Table 1. Regarding the oxidation of PM, the working gas was switched from the combustion gas from the DPG to ambient air. The PM was oxidized at 650 °C. After the trapping and oxidation processes for PM were repeated several times, the cross-sectional area of the vertical wall was visualized by utilizing an FESEM. This constitutes the first time-lapse visualization. By utilizing the same open-channel DPF, these processes were repeated to create a time-lapse video.

3. Results and discussion

3.1. Elemental analysis of precursors for ash layer

Figure 4 presents FESEM images of the ash precursors in the PM and a large ash particle in a soot cake layer. Elemental analysis results are also shown. In the top-left image, one can see that fine particles (white dots) were observed in the PM sampled from a soot cake just after the trapping process. The signals of Zn (1.01 and 8.63 keV) and P (2.01 keV) were detected via elemental analysis, as shown in the bottom-left intensity results, but there were no signals for Ca (3.69 keV) or S (2.31 keV). There were some large particles (diameters of 700~800 nm) in the soot cake layer, as shown in the top-right image.
The signals of all the introduced elements (Ca, S, Zn, and P) were detected in the large particles, as shown in bottom-right intensity results. Although it is unclear how the fine particles of Zn and P and the large particles of all elements were formed during combustion in the DPG and reaction in the DOC, the initial components of the ash layer deposited on the DPF were characterized as fine particles containing Zn and P from the PM and large particles containing all introduced components.

3.2. Time-lapse visualization of ash deposition

Figure 5 presents FESEM images (cross-sectional view) after the fourth lapse and ninth lapse of repeated trapping and oxidation of PM on the left and right, respectively. As shown in the fourth lapse image (left), the ash was deposited around the surface pores. One pore is entirely covered by the ash layer, while the other is only partially covered. After trapping and oxidizing PM five more times, from a comparison between the fourth lapse (left) and ninth lapse (right) images, one can see that a new ash layer was deposited on top of the previous ash layer. Additionally, the ash layer expanded in the horizontal direction to cover the neighboring surface pore.

Figure 6 presents time-lapse FESEM images (surface view) of the bare DPF (before deposition, top-left), first lapse (top-right), second lapse (bottom-left), and third lapse (bottom-right) of ash deposition after each regeneration of the DPF. In the first lapse image (top-right), one can clearly see that the ash was deposited around the perimeters of some surface pores, as indicated by the yellow dotted circles. In contrast, the surface pores indicated by yellow arrows have no deposition of ash. As time passed from the first lapse to the third lapse, the ash agglomerate grew via accumulation of ash layers at the same location. However, we observed that some ash was completely removed or moved to another location by comparing the second lapse and third lapse. As shown in Fig. 4, ash elements were contained in the PM cake layer and primary particles. During the oxidation (regeneration) process, the PM cake layer and primary particles should shrink and the PM cake should break down. The separated PM cake islands are continuously oxidized at each location. As a result, the ash elements in the PM cake islands are concentrated in local areas that are consistent between each time lapse. However, it is unclear why the ash was deposited around the perimeters of the surface pores through shrinkage of the PM cake layer. Also, as shown in Fig. 6 (second and third lapses), the ash layer island may occasionally be removed by movement of the PM cake islands during shrinkage via oxidation.

3.3. Pressure drop in DPF with ash

Figure 7 presents the increase in pressure drop with PM loading time for a bare DPF (initial trapping denoted by blue line) and that for the DPF after the first, second, and third lapse of regeneration, denoted by orange, gray, and yellow lines, respectively.
In the case of the first trapping (blue line), the pressure drop increases from the beginning of trapping, following a slight S-curve. The pressure drop profile can be divided into three phases: the first phase is bridge formation by PM at a depth of 10-20 microns from the entrances of the surface pores, which can be defined as the point when the pressure-drop increase rate attained the maximum. The second phase is surface pore filtration. Then, the third phase is PM cake filtration, which can be defined as a moment when the pressure-drop increase rate becomes constant. After the trapped PM was oxidized, additional PM with ash elements was introduced and trapped by the same DPF, which constitutes the second trapping (orange line). From a comparison between the first and second trappings, one can see that the bridge formation and surface pore filtration in the case of the second trapping were completed in a shorter period of time compared to the first trapping. With a further increase in ash deposition, as shown in the cases of the third and fourth trappings, the pressure drop during surface pore filtration also decreased. Therefore, the pressure drop during the final phase of PM cake filtration was reduced by an increase in ash deposition (i.e., repeated trapping and oxidation processes). The chance of creating bridge formations is increased around the perimeters of surface pores, but some PM still enters into the surface pores. As a result, the pressure drop increase following an S-curve shifted to an earlier time and is reduced in amplitude by ash deposition. After the ash layer covers the surface pores completely, the pressure drop increases linearly based on PM cake layer filtration.

3.4. Time-lapse visualization of ash and PM deposition

Figure 8 presents time-lapse FESEM images of PM deposition (trapping) and ash deposition. In the case of the first deposition of PM, as shown in the top-right image, the surface pore was entirely covered by PM, which contributed to the drastic increase in pressure drop shown in Fig. 7. After the first regeneration in the same DPF, as shown in the bottom-left image, we observed that one of the surface pores was entirely covered by ash. After repeated trapping and oxidation of PM (four cycles), as shown in the bottom-right image, the PM was trapped on the ash layer. Based on the ash layer filtration of PM, the pressure drop at the start of trapping was reduced, as shown in Fig. 7, because the surface pore filtration causing the drastic increase in pressure drop was slightly reduced, but not completely.

3.5. Elemental analysis of ash deposited on DPF

Figure 9 presents the elemental analysis results of the deposited ash and PM cake layer on the Si-C DPF. A FESEM image is also presented in the top-left. The red or yellow arrows indicate the ash layer. This figure represents the fourth time lapse after repeated processes of trapping and oxidation of PM. Energy-dispersive X-ray spectroscopy (EDX) element mapping is also shown for the components of Si, C, S, P, Ca, and Zn. The structure of the DPF can be clearly confirmed from the Si mapping in the top-middle of Fig. 9. The PM layer is represented by the C mapping in the top-right. In this case, some PM was trapped inside the surface pore because the ash layer did not completely cover the entrances of all surface pores in the fourth lapse of trapping and oxidation of PM with ash components. However, one can clearly see that the ash was not deposited inside the surface pores, but was mainly layered on the DPF outer grains, as shown in the S, P, Ca, and Zn mappings in the center and bottom rows in Fig. 9, where each component was detected at nearly the same location. However, these components are not necessarily homogeneous because the signal intensity profiles for S, P, Ca, and Zn are not the same.

![Fig. 7 Pressure drop during two hours of PM loading. The blue, orange, gray, and yellow lines represent the first (bare DPF), second, third, and fourth trappings by the DPF, respectively.](image)

![Fig. 8 Time-lapse FESEM images (cross section) of a bare DPF and the first deposition (trapping) of PM with ash elements, as well as the first regenerated DPF and fourth deposition (trapping) of PM with ash elements.](image)
In this study, the source elements and their concentrations in the oil for producing ash were specified and the initial conditions of the ash in the PM cake layer were characterized, as shown in Fig. 4. Additionally, as shown in Table 2, the elemental composition of the ash generated by the DPG utilized in this study was analyzed by an inductively coupled plasma analyzer. However, the process of ash layer production during regeneration is not well understood. Additionally, there are many possibilities of chemical composition of ash components, as shown in Table 3. During the regeneration process, fine particles consisting of Zn and P, and relatively large particles consisting of all the initial elements are gathered and sintered to produce many types of components, as shown in Table 3. These components are partially localized in the ash layer. Consequently, the signal intensity shown in Fig. 9 depends on the elemental composition.

3.6. Process of ash layer production

Figure 10 presents a schematic diagram of the production process of the ash layer at the start of regeneration. In the PM cake layer, initial ash particles consisting of Ca, S, Zn, and P, or mainly consisting of Zn and P are contained. During the regeneration process, combustible components, such as SOFs and soot (mainly carbon), are oxidized. Next, the PM cake layer shrinks, keeping its structure similar, while the size of the ash particles is the same as that at the beginning of regeneration, as shown in Fig. 10. When the fine ash particles contact each other and relatively large ash particles, they are sintered to produce large-scale ash particles under a regeneration temperature of 650 °C.

Table 2 Elemental composition of ash generated by the DPG

| Element | S  | P  | Ca | Zn |
|---------|----|----|----|----|
| Composition [wt%] | 6.3 | 10.7 | 20.4 | 23.3 |

Table 3 Predicted ash components and melting points

| Component | Composition | Melting Point [°C] |
|-----------|-------------|--------------------|
| ZnP4O10 | ZnSO4·H2O, ZnO, Zn3(PO4)2 | 680, 900, 1975 |
| CaSO4·Ca3(PO4)2·CaO | CaZn(PO4)2 | 1394, 1460, 2572 |
| CaZn2(PO4)2 | Tmelt = NA |

Fig. 9 Elemental analysis of deposited ash on DPF after four cycles of PM deposition and oxidation. The ash layer is indicated by the red and yellow arrows.

Fig. 10 Schematic diagram of the process of ash layer production. The PM cake layer shrinks via oxidation, whereas the size of the ash particles is constant prior to sintering.

Fig. 11 FESEM image of ash after regeneration and elemental analysis via EDX.
This spherical structure has been reported previously (9). Additionally, it was observed that there was a cavity in the spherical ash particle by utilizing a focused ion beam SEM. Although there were some particles with a size similar to the initial particle, they were aggregated together.

4. Conclusions

The ash deposition process on the wall surface of a DPF was investigated through time-lapse visualization utilizing an FESEM. It was clarified that ash was deposited locally (not uniformly) around the perimeters of surface pores in a DPF consisting of SiC under small ash loading conditions. However, there was no ash layer stacking or accumulation inside the surface pores. PM was mainly trapped between the deposited ash and SiC grains. This means that bridge formation by PM was established from the beginning of the trapping process and only a small amount of PM was trapped inside surface pores, which contributed to the reduction in pressure drop during the trapping process. When the surface pore was completely covered by ash layer after several lapses of regeneration, the PM is deposited on the ash layer as a cake layer. Components of S, P, Ca, and Zn were observed nearly uniformly in the ash layer. During the regeneration process (i.e., oxidation process), all components were sintered in the ash layer around the perimeters of the surface pores.

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