

Degradation Resistance of Cordierite Diesel Particulate Filters to Diesel Fuel Ash Deposits

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The thermochemical degradation resistance of a typical cordierite diesel particulate filter (DPF) material by synthetic ashes typical of those arising in practice has been investigated over the temperature range 950°C-1250°C. Differential thermal analyses and heat treatment of pressed pellets were used to characterize the melting/transformation behavior of ashes representative of typical diesel fuel (ash A) and those typical of when the catalysts ferrocene (ash FeA) and cerium carboxylate (ash CeA) were present in the fuel and to study the interaction chemistry between powdered cordierite and the ash compositions. Additional experiments involved the application of surface coverings of ash to DPF specimens. The results obtained showed that filter performance would not be compromised by ash liquefaction/sintering as long as temperatures did not exceed 900°C for ash A, 970°C for ash FeA and 1100°C for ash CeA. For long time periods, compared to the expected application durations, liquid phosphates dissolve cordierite leading to the formation of Zn and Fe aluminate spinels. Overall, the results clearly indicate that thermochemical degradation of cordierite by ashes under conditions representative of typical diesel engine systems is highly unlikely at temperatures of 1100°C and below.

I. Introduction

NVIRONMENTAL friendly light (car) and heavy (truck) duty E diesel engines are required to have diesel particulate filters (DPFs) fitted to the exhaust train to remove unburnt carbon particulates from exhaust emissions. Typically, such particulate filters are of the honeycomb wall-flow type comprising ceramic honeycomb structures, which have a checkerboard pattern of open and closed cells at the entry face and at the exit face. Open cells at the entry face are blocked at the exit face and the blocking of alternate cells forces the exhaust gas to flow through the porous walls trapping the particulate matter in the pores and on the surfaces of the open channels.¹ Foamed ceramics and fiber mats as well as sintered ceramics are used as DPFs. Materials' requirements for honeycomb wall-flow filters are typically: low coefficient of thermal expansion, high thermal shock resistance, and thermal stability.² Adler² has also listed suitable materials which possess these properties as cordierite, aluminum titanate, silicon carbide, silicon nitride, and mullite.

Cordierite (Mg₂Al₄Si₅O₁₈) ceramic bodies exhibit excellent thermal shock resistance, making cordierite a good material choice for the diesel particulate filter application. The orthorhombic cordierite crystal structure contains six-member coplanar rings (four SiO₄ groups and two AlO₄ groups) with the corner-sharing tetrahedra allowing for an open channel parallel to {00l}.³ These rings are cross-linked by (Si,Al)O₄ tetrahedra and MgO₆ octahedra. The large expansion of the Mg–O bonds and lower expansion of the Si–O and Al–O bonds result in a crystal having a low, anisotropic thermal expansion.⁴ Cordierite DPF systems have been commercially available for nearly 2 decades.⁵ The principal function of the filter is to capture solid carbon particles with high efficiency (up to 99%).

The carbon particulates captured by wall-flow filters are intimately mixed with unburnt hydrocarbons as well as contaminants, such as calcium, zinc, phosphorous, and sulfur compounds which arise from engine lubrication. Iron-containing particles arising from engine abrasion can also be captured. This composite solid fluid admixture comprises the particulate matter requiring filtration. Clearly as time progresses, then carbon builds up on filter walls and if not removed contributes to significant increases in backpressure. Regeneration of the filter occurs by carbon particle combustion at temperatures of 600°C and above,² with typical temperatures up to 890°C.⁶ Ferrocene ($(C_5H_5)_2Fe$) and cerium carboxylate (Ce(COOH)₄) are both useful fuel additives for diesel because they reduce carbon buildup in DPFs by lowering the light-off temperature of the carbon particulates. Particulate matter burn-off temperatures can be reduced by as much as 250°C by the use of such catalytic fuel additives.^{2,7} The use of these additives results in the deposition of Fe₂O₃ or CeO_2 in the diesel particulate filter.

Particulate matter combustion is, of course, a highly exothermic reaction, and if uncontrolled, can cause local temperature increases well above 1000° C.⁸ As a result of multiple regenerations, a residual ash comprising the contaminant oxides from the lubricating oil, iron from engine abrasion, and oxides from catalytic fuel additives, will remain on and in the wall of the filter. At elevated temperatures (>1100°C), which may be generated during *in situ* incineration, this residual ash may react with the ceramic structure. Such reactions may cause premature mechanical or chemomechanical failures through formation of low eutectic surface liquids as well as crystalline and vitreous phases of incompatible thermal expansion with the diesel particulate filter ceramic matrix.

This thermochemical durability of cordierite and other DPF materials has been studied to a degree by reacting oxides with them. Thus, cordierite has been reacted with sodium, lead, iron, calcium, zinc, and vanadium oxides^{9–11} and been shown to be degraded to slight extents by each of the oxides. Sodium and lead oxides were observed to cause

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greatest damage to cordierite.⁹ Del Pin *et al.*¹² examined the degradation of DPF candidate material zircon with respect to sodium, calcium, lead, zinc, iron (III), vanadium, and cerium oxides over the temperature range 700°C–1000°C. Results showed again that only sodium and lead oxides induced significant chemical interaction by the formation of sodium and lead zirconates. Maeir *et al.*¹³ have investigated the chemical interaction between single crystal cordierite and a soda–silica mixture of composition Na₄Si₃O₈ with a lowest liquidus of 830°C. As might be expected, the cordierite reacted rapidly with the liquid alkali–silicate at temperatures of 900°C and 1000°C allowing cordierite dissolution. After a certain period of time, however, a protective nepheline corrosion deposit formed on the cordierite, slowing down the degradation process.

While the above chemical durability experiments were of benefit in assessing the durability of cordierite to potential diesel ash impurities, lead and sodium impurity levels in diesel fuels are miniscule (typically 2 ppm for sodium,¹⁴ although sodium levels may increase as Biodiesel becomes more commonly used).¹³ O'Sullivan *et al.*¹⁵ studied the interaction of silicon carbide with a calcium–zinc phosphate–sulfate mixture based on analyses obtained for ash removed from a DPF which had been operating for the equivalent of 160 000 km. While this ash composition alone may sinter to damage the filtration efficiency of the SiC filter, no such damage or chemical degradation of the filter material was observed when the ash chemistry was adjusted to take into account iron or cerium additions arising from the catalytic additives referred to above.

With respect to cordierite, Maier *et al.*¹³ have investigated degradation of single crystal material by an equimolar mixture of $Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$, and $Zn_3(PO_4)_2$. They observed that single crystal cordierite was severely corroded by the equimolar phosphate at 1050°C. Earlier preliminary work^{15,16} (J. Kracklauer, Econalytic Systems Inc., private communication (1998)) has indicated that cordierite filter elements have withstood corrosion in this temperature range by a calcium-zinc phosphate-sulfate ash composition based on ash recovered from a DPF used in engine tests for durations equivalent to 160 000 km service. This article reports the results of the effect of particulate matter ash constituents on the chemical stability of cordierite filter materials as a function of the DPF temperature environment.

II. Experimental Procedure

As indicated above and determined from data obtained from engine tests for the authors¹⁶ (J. Kracklauer, Econalytic Systems Inc., private communication (1998)), lubricant and fuel impurities being deposited on diesel particulate filters are typically ZnO, CaO, P₂O₅, and SO₃ with relative mass ratios of 1:1.75:2:2.25, respectively. In addition, it was decided to recreate the conditions when the one filter regeneration cycle was missed, i.e. there was double the maximum expected carbon load on the filter prior to burn off. Based on this rationale, various ash compositions were derived for the baseline ash (A), and two other ashes derived from the combustion of diesel containing either ferrocene (FeA) or cerium carboxylate (CeA) as combustion catalysts. For these ashes, the catalysts decompose to their base oxides, Fe₂O₃ or CeO₂.

Table I details the ash compositions studied and in addition, relates compositions reflecting an ash loading on a 152mm long, 144-mm diameter DPF representative of 160 000 km (100 000 miles) operation. Ash compositions were prepared by dry ball milling relevant weighed powder mixtures of CaSO₄·2H₂O (Alfa/98% min), CaO (BDH/99% min), ZnSO₄·7H₂O (Alfa/98% min), ZnO (BDH/99% min), P₂O₅ (BDH/97% min), Fe₂O₃ (Alfa/99.99%), CeO₂ (Alfa/ 99.9%), and graphite (BDH/99% min) for 1 h using sialon milling media. The 50 mg portions of uniaxially pressed compacts of the three ash compositions were subjected to simultaneous Differential Thermal Analysis/Thermogravimetric Analysis (DTA/TGA) (Stanton Redcroft STA1640; Polymer Labs Rheometric Scientific, Epsom, U.K.). These analyses were carried out using a heating rate of 10°C/min to 1400°C in air + 200 ppm SO₂ flowing through the system at 70 cm³/ min. This quantity of sulfur dioxide was added to simulate the presence of this gas in the exhaust train of a diesel engine. Pressed pellets, typically 8-mm diameter and 5-mm high were subjected to heat treatment in the same gas environment for 24 h at temperatures selected on the basis of the thermal analysis studies (900°C, 970°C, 1100°C, and 1250°C). A heating rate of 50°C/min and furnace cooling were used for all heat treatments. The dimensions of the pressed and heat-treated pellets were measured using Vernier callipers and radial shrinkages calculated. X-ray diffraction (XRD) of heat-treated pellets ground to powder was carried out with CuK_{α} radiation in a Philips X'Pert system.

747

Interaction chemistry between cordierite and ash mixtures was evaluated by DTA/TGA and heat-treatment analysis of intimately mixed and uniaxially pressed cordierite–ash couples. Accordingly, cordierite filters supplied by Corning Inc. were crushed and ground to <90 μ m powder and dry ball mill mixed for 1 h with each of the three ashes. Cordierite–ash compositions corresponded to the loadings given in Table I. The 50 mg portions of these pellets were subjected to DTA/TGA in the same way as the ash samples and 8 mm × 5 mm pellets were heat-treated in the same manner as the ash pellets.

To evaluate the surface interaction of cordierite with the ashes and thus simulate more likely thermochemical conditions in an operating filter, samples of cordierite filter were coated with each of the ash mixtures. Thus, surface coatings of each ash (A, FeA and CeA) were deposited on flat coupons (6.25 cm^2 area and two cells thick) sectioned from a cordierite filter. The coatings were applied by spraying the coupon surfaces, preheated to ~200°C, with a solution of nitrates of the metallic (Ca, Zn, Fe, Ce) constituents of the ash, as well as P2O5 and H2SO4. The target ash loading after spraying and drying corresponded to an in-service lifetime of 80 000 km. The coated specimens were heat-treated at the same temperatures used for the powder compacts (900°C, 1000°C, 1100°C, and 1250°C). The heat-treatment times were chosen to reflect the total estimated time that a diesel particulate filter would experience at the particular temperature as a result of repeated regenerations during its in-service lifetime. Thus, heat treatment at 900°C was carried out for 24 h and at the other temperatures for 30 min. The heat-treated sprayed surfaces were analyzed by XRD and scanning electron microscopy (SEM) examination using a JEOL JSM840 (Tokyo, Japan). Compositional variations were analyzed using energy dispersive X-ray analysis (EDS). Selected speci-

Table I. Ash Compositions and Loadings (% by Weight)

Ash Code	$CaSO_4 \cdot 2H_2O$	CaO	$ZnSO_4$	ZnO	P_2O_5	Fe ₂ O ₃	CeO ₂	С	Ash loading $(\%)^{\dagger}$
A	35.424	8.553	19.064	1.869	23.054	0.000	0.000	12.036	24.0
FeA	25.705	4.306	8.716	2.891	14.477	36.240	0.000	7.664	33.8
CeA	20.083	1.889	2.998	3.279	9.676	0.000	56.999	5.077	43.8

[†]As a percentage of filter + ash weights

mens were fractured and the resulting cross-sections were also examined using SEM and EDS.

III. Results

(1) Ash Characterization

For each of the ashes, large exotherms at ~800°C, associated with carbon burnout were observed. Associated weight losses corresponded well with those expected from complete combustion of the carbon. For the baseline ash, endotherms occurred at 954°C and 996°C, which were associated with weight losses. These weight losses totaled some 7-8 wt%. Radial shrinkage and XRD analyses of sintered pellets showed that while little change in ash character occurred after heat treatment at 900°C, significant shrinkage (16%) occurred after heat treatment at 970°C and this was associated with the disappearance of CaSO₄ from the phase assemblage. These results indicate two factors: (i) that CaSO₄ decomposition gives rise to the weight losses observed during DTA and (ii) as the measured weight losses only account for about 25% of the total SO₃ content, that CaSO₄ is incorporated into a liquid phase which facilitates shrinkage through liquid phase sintering. After heat treatment at 1100°C, complete melting of pellets was observed as was the case at 1250°C. The XRD analyses (Table II) showed that calcium phosphate $(Ca_3(PO_4)_2)$ and calcium zinc phosphate $(CaZn_2(PO_4)_2)$ occurred after heat treatment at 970°C and 1100°C. After heat treatment at 1250°C, $(Ca_3(PO_4)_2)$ was the only crystalline phase present. In addition to the crystalline phases present in samples heat-treated at 1100°C and 1250°C, a significant amorphous halo, consistent with the presence of much glass, was observed. As CaSO₄ and the mixed Ca, Zn phosphate disappeared from the phase assemblage as temperatures increased, it appears that the liquid phase comprises Ca, Zn, P, S, and O.

The ash mixture containing Fe_2O_3 showed endothermic activity at temperatures of 935°C and 996°C, suggesting that iron oxide lowered the temperature of the lower endotherm. However, negligible radial shrinkage occurred after heat treatment of pellets at 970°C suggesting that the appreciable liquid phase sintering of the baseline ash was suppressed by the presence of the 42 wt% Fe₂O₃. After heat treatment at 1100°C, 9% radial shrinkage occurred and at 1250°C, complete melting of the FeA ash was observed. The phase assemblages (see Table II) showed that the same phases were present as for the baseline ash. However, $ZnFe_2O_4$ was present at all temperatures as well as Fe_2O_3 . The formation of $ZnFe_2O_4$ at all temperatures would remove ZnO from the system and suppress liquid formation. The presence of residual Fe₂O₃ in the phase assemblages also indicates that it fulfills a dilution effect, thus reducing the amount of liquid formed compared to the baseline ash. Such dilution effects were even more prominent for the CeA ash where the presence of nearly 63 wt% CeO₂ suppressed endothermic events at temperatures less than 1000°C. Radial shrinkages of heattreated pellets were negligible until a temperature of 1250°C was reached when 13% was observed. The phase assemblages of the heat-treated ceria containing ashes, shown in Table II, comprised those of the baseline ash (i.e. Ca and Zn phosphates and sulfates) plus ceria.

(2) Cordierite-Ash Interactions

Figure 1 shows DTA/TGA data for 50 mg samples of pressed cordierite and cordierite-ash mixtures. It is seen that no thermal events arise for the cordierite and no weight changes occur [Fig. 1(a)]. For each of the cordierite-ash mixtures, carbon burnout exotherms can be observed at temperatures of the order of 800°C [Figs. 1(b)-(d)]. For the cordierite-baseline ash system, weak endotherms arise at 979°C, 998°C, and 1310°C, whereas a stronger endotherm is observed at 1186°C [Fig. 1(b)]. From Fig. 1(c), it can be seen that the incorporation of Fe_2O_3 into the system induces lower temperature endothermic events at 927°C and 968°C, although these are again weak in character. Two stronger endotherms arise at 1168°C and 1305°C, which appear to correspond reasonably well with those observed for the cordierite-baseline ash system. Figure 1(d) shows the DTA/ TGA data for the cordierite-CeA system. It is seen that the only significant endothermic event due to melting occurs at 1291°C. At lower temperatures, low intensity endotherms arise at 995°C and 1209°C, with the latter being more pronounced. At temperatures in excess of 1300°C, a series of exothermic peaks arise which are thought to be associated with phase transitions.

Heat treatment of the pressed pellets of cordierite and cordierite-ash mixtures at 900°C, 1000°C, and 1100°C for 24 h in flowing air—200 ppm SO₂, caused little change in the physical character of the pellets. However, at 1250°C, the cordierite-baseline ash and cordierite–FeA ash pellets showed complete slumping, while the cordierite–CeA ash pellets showed partial slumping. The XRD data for the heat-treated pellets are shown in Table III. It is seen that no change in the crystallographic character of the cordierite occurs. For the cordierite–baseline ash system, phases arising from the ash are CaSO₄ and Ca₃(PO₄)₂ at 900°C and 1000°C, with the relative intensity of reflections becoming more intense with increasing temperature. At 1100°C, the CaSO₄ reflections disappear and at 1250°C, the Ca₃(PO₄)₂ reflections disappear and at 1250°C, the Ca₃(PO₄)₂ reflections disappear and at no be replaced by an amorphous halo associated

	Heat-treatment temperature				
	900°C	970°C	1100°C	1250°C	
Ash A	$\begin{array}{c} Ca_3(PO_4)_2\\ CaZn_2(PO_4)_2\\ CaSO_4 \end{array}$	$\begin{array}{c} Ca_3(PO_4)_2\\ CaZn_2(PO_4)_2 \end{array}$	$\begin{array}{c} Ca_3(PO_4)_2\\ CaZn_2(PO_4)_2 \end{array}$	Ca ₃ (PO ₄) ₂ Glassy phase	
Ash FeA	Fe_2O_3 $Ca_3(PO_4)_2$ $ZnFe_2O_4$ $CaZn_2(PO_4)_2$ $CaSO_4$	$\begin{array}{c} Fe_2O_3\\ ZnFe_2O_4\\ Ca_3(PO_4)_2\\ CaZn_2(PO_4)_2 \end{array}$	$\begin{array}{c} ZnFe_2O_4\\ Ca_3(PO_4)_2\\ Fe_2O_3 \end{array}$	$\begin{array}{c} ZnFe_2O_4\\ Ca_3(PO_4)_2\\ Fe_2O_3 \end{array}$	
Ash CeA	$CeO_2 Ca_3(PO_4)_2 CaZn_2(PO_4)_2 CaSO_4$	$\begin{array}{c} CeO_2\\ Ca_3(PO_4)_2\\ CaZn_2(PO_4)_2 \end{array}$	CeO ₂ Ca ₃ (PO ₄) ₂	CeO ₂ Ca ₃ (PO ₄) ₂	

 Table II.
 Phase Assemblages for Ash Pellets Heat-Treated in Air—200 ppm SO₂ Gas Mixture for 24 h at Different Temperatures (Phases Listed in Order Of Decreasing X-Ray Intensities)



Fig. 1. Thermal analysis data for (a) cordierite, (b) cordierite + ash A, (c) cordierite + ash FeA and (d) cordierite + ash CeA.

Table III.	Phase Assemblages Following Heat Treatment of Cordierite and Cordierite-Ash Pellets in Air-200 ppm SO ₂ Gas
	Mixture for 24 h at Different Temperatures (Phases Listed in Order of Decreasing X-Ray Intensities)

	Heat-treatment temperature				
	900°C	1000°C	1100°C	1250°C	
Cordierite	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	
Cordierite + ash A	$Mg_2Al_4Si_5O_{18}$	$Mg_2Al_4Si_5O_{18}$	$Mg_2Al_4Si_5O_{18}$	Mg ₂ Al ₄ Si ₅ O ₁₈	
	CaSO ₄	$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2$	$ZnAl_2O_4$	
	$Ca_3(PO_4)_2$	CaSO ₄	$ZnAl_2O_4$	Glassy phase	
	$ZnAl_2O_4$	$ZnAl_2O_4$		• •	
Cordierite + ash FeA	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	
	Fe_2O_3	Fe_2O_3	Fe_2O_3	Fe_2O_3	
	$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2$	FeAl ₂ O ₄	
	$ZnAl_2O_4$	$ZnAl_2O_4$	$ZnAl_2O_4$	Glassy phase	
	CaSO ₄	2 .	FeAl ₂ O ₄		
Cordierite + ash CeA	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	$Mg_2 \tilde{A} l_4 Si_5 O_{18}$	Mg2Al4Si5O18	
	CeO ₂	CeO ₂	CeO ₂	CeO ₂	
	$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2$	
	$ZnAl_2O_4$	$ZnAl_2O_4$	$ZnAl_2O_4$	$ZnAl_2O_4$	
	CaSO ₄	CaSO ₄	$CaSO_4$	CePO ₄	
	-1	-	CePO ₄	Glassy phase	

with a glassy phase. For all temperatures, zinc in the ash appears to remove aluminum from the cordierite to form the $ZnAl_2O_4$ spinel and it appears to be a relatively abundant phase at all temperatures examined. The consumption of zinc in the formation of this spinel presumably accounts for the absence of the mixed Zn, Ca phosphate present for the heat-treated ash (see Table II).

The incorporation of Fe_2O_3 into the system (cordierite– FeA) gives rise to a similar phase assemblage as for the cordierite-baseline ash system, except, of course, the presence of Fe_2O_3 in the phase assemblage after heat treatment at 900°C. It should also be noted that the relative intensities of the CaSO₄ and Ca₃(PO₄)₂ phases are reversed. After heat treatment at 1000°C, CaSO₄ reflections disappeared, while after heat treatment at 1100°C, the iron analogue of the ZnAl₂O₄ spinel, FeAl₂O₄, had formed. After heat treatment at 1250°C, the resulting phase assemblage was cordierite plus Fe₂O₃ plus FeAl₂O₄ plus glass. When ceria is

	Heat-treatment temperatures and times				
	900°C 24 h	1000°C 30 min	1100°C 30 min	1250°C 30 min	
Cordierite	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	
Cordierite coated with A	$Mg_2Al_4Si_5O_{18}$	$Mg_2Al_4Si_5O_{18}$	$Mg_2Al_4Si_5O_{18}$	Mg2Al4Si5O18	
	$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2$	$Ca_3(PO_4)_2$	$ZnAl_2O_4$	
	$ZnAl_2O_4$	$ZnAl_2O_4$	$ZnAl_2O_4$		
	$CaSO_4$	$CaSO_4$			
Cordierite coated with FeA	$Mg_2Al_4Si_5O_{18}$	$Mg_2Al_4Si_5O_{18}$	$Mg_2Al_4Si_5O_{18}$	Mg ₂ Al ₄ Si ₅ O ₁₈	
	Fe_2O_3	Fe_2O_3	Fe_2O_3		
	$CaSO_4$				
Cordierite coated with CeA	Mg ₂ Al ₄ Si ₅ O ₁₈	Mg ₂ Al ₄ Si ₅ O ₁₈	$Mg_2Al_4Si_5O_{18}$	Mg ₂ Al ₄ Si ₅ O ₁₈	
	CeO ₂	CeO_2	CeO ₂	CeO ₂	

 Table IV.
 XRD Phase Assemblages for Cordierite Test Pieces, Sprayed with Ash Constituents and Heat-Treated in Air—200 ppm SO₂ (Phases Listed in Order of Decreasing X-Ray Intensities)

added to the cordierite–ash system (cordierite–CeA), the phase assemblages after heat treatment at 900°C and 1000° C are the same as for the cordierite–baseline ash system excepting, of course, the presence of CeO₂. After heat treatment at 1100°C, CePO₄ arises in the phase assemblage, and in contrast to the cordierite–baseline ash system, CaSO₄ remains present. After heat treatment at 1250°C, the phases present include both Ca₃(PO₄)₂ and CePO₄, in contrast to the other two systems where no phosphates are present. In contrast to the two other ash types, the relative intensity of the ZnAl₂O₄ spinel in the reaction products is less.

(3) Surface Interactions of Cordierite with Ashes

Table IV shows XRD results for the phases present on the surfaces of coupons of cordierite spray coated with each of the ash compositions and heat-treated in air—200 ppm SO_2 . It is seen that the phase assemblages for cordierite coupons coated with baseline ash are similar to those observed for heat-treated pellets (see Table III). Thus, as heat-treatment temperatures increase, $CaSO_4$ and $Ca_3(PO_4)_2$

reflections disappear. There remains a phase assemblage of cordierite plus $ZnAl_2O_4$ spinel after heat treatment at the highest temperature. However, in contrast to the data given in Table III, Table IV does not indicate the presence of a glass phase. In the other two cordierite–ash systems, the significant dilution effects of Fe₂O₃ and CeO₂ reduce other phases to levels where they are undetectable, except for the cordierite–FeA system at 900°C where CaSO₄ is observed.

The SEM observations of the surface of cordierite coupons after heat treatment showed that the temperature of heat treatment had little effect on surface morphology. Figure 2(a) details the surface morphology of a coupon heat-treated at 900°C for 24 h and shows the characteristic prismatic cordierite grain structure surrounding deliberately induced porosity. Figure 2(b) shows the development of an apparently friable particulate layer developed by the representative sprayed coating of baseline ash. The surface applied FeA ash appears to have interacted more with the cordierite surface giving rise to what appears to be a matrix glaze in which prismatic cordierite grains are visible [Fig. 2(c)]. For the CeA ash coating [Fig. 2(d)], the cordie-



Fig. 2. Surface topography of cordierite samples after heat treatment in air—200 ppm SO₂ for 24 h at 900°C (a) cordierite only, (b) cordierite–baseline ash deposit, (c) cordierite– Fe_2O_3 containing ash deposit, (d) cordierite–ceria containing ash deposit (width of scale bar is 10 μ m).



Fig. 3. Surface topography of cordierite samples after heat treatment in air—200 ppm SO₂ for 30 min at 1250°C (a) cordierite only, (b) cordierite–baseline ash deposit, (c) cordierite–Fe₂O₃ containing ash deposit, (d) cordierite–ceria containing ash deposit (width of scale bar is 10 μ m)

rite coupon surface appears little affected. Indeed, the prismatic cordierite structure of the uncoated cordierite is clearly apparent indicating a lack of interaction with the ash and thus poor adhesion. Figure 3 shows the appearance of the corresponding surfaces after heat treatment at 1250°C for 30 min. The cordierite coupon surface [Fig. 3(a)] was very similar in appearance to the one heat-treated at 900°C for 24 h. The surface topographies of coupons coated with ashes A and FeA after heat treatment at 1250°C for 30 min [Figs. 3(b) and (c)] took on a glazed appearance with the surface glaze appearing to contain particulates which would be expected on the basis of XRD to be zinc aluminate and Fe_2O_3 , respectively. While the surface morphology after heat treatment at 1250°C did have certain features in common with those for the other ashes, the extent of glazing appeared less as indicated in Fig. 3(d). For the coupons heat-treated at 1000°C for 30 min, the coupons coated with A, FeA, and CeA ash all had similar appearances to their 900°C counterparts. For those coupons heat-treated at 1100°C, the coupon coated with baseline ash A, was similar in appearance to the coupon heat-treated at 1250°C, while the cordierite surfaces coated with the other two ashes looked very similar to the images collected for the 900°C equivalents.

IV. Discussion

(1) Ash Properties

From the DTA/TGA studies, it is evident that in addition to weight losses occurring at temperatures of the order of 800°C due to carbon burnout, further weight losses occur at temperatures in excess of 950°C for the baseline ash and these are associated with endothermic processes. The SO₃ loss from calcium sulfate is one process which would account for such thermal behavior and investigation of the necessary thermodynamic data¹⁷ shows that in an atmosphere of air containing 200 ppm SO₂, calcium sulfate should begin to decompose at temperatures of the order of 920°C. Accordingly, these decomposition effects should arise and would explain the weight losses, endothermic behavior, and the disappearance of CaSO₄ reflections from the phase assemblage of heat-treated pellets at temperatures of 1100°C and 1250°C. The resulting CaO, formed from the decomposition of CaSO₄, would then be capable of reacting with P_2O_5 according to the reaction scheme:

$$3CaSO_4 \rightarrow 3SO_3 + 3CaO$$
 (1)

$$3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_3 \tag{2}$$

A similar reaction scheme could be envisaged for zinc sulfate decomposition and reaction:

$$3ZnSO_4 \rightarrow 3SO_3 + 3ZnO$$
 (3)

$$3ZnO + P_2O_5 \rightarrow Zn_3(PO_4)_2 \tag{4}$$

Such reactions would provide $Ca_3(PO_4)_3$ and $Zn_3(PO_4)_3$ which can react to form a mixed phosphate, which has a lowest liquidus at zinc rich compositions of 1048°C.¹⁸ This chemistry does not, however, explain the significant sintering (16% radial shrinkage) which arises when pressed pellets of the baseline ash are heat-treated at 1000°C. It is important to note that TGA weight losses of only about 25% SO₃ arise, which would tend to suggest that the residual SO₃ could suppress the lowest liquidus temperature in the $Ca_3(PO_4)_3$ and $Zn_3(PO_4)_3$ system and thus account for the significant shrinkage noted at 1000°C.

The addition of iron (III) oxide to the ash system might be expected to cause two effects. On one hand, it might be expected to induce liquid formation through reaction with P_2O_5 as a lowest liquidus temperature of 960°C arises in the Fe–P–O system for compositions where P_2O_5 is not stable.¹⁹ On the other hand, if reasonably inert, the replacement of nearly 40% by weight of the baseline ash composition by Fe₂O₃ would reduce liquid volumes significantly as well as the observed formation of ZnFe₂O₄ which would reduce the amount of zinc available for liquid formation. Given the retardation of sintering by the addition of Fe_2O_3 , it appears that a reduction in the amount of liquid phase is more likely. In the case of ceria replacement of 60% by weight of the baseline ash, an even greater reduction in liquid volume would be expected and this would be in agreement with the observed results. However, it appears that the action of ceria as a diluent is not its only function as $CePO_4$ is formed when ceria is present in the ash. The gettering of phosphorus from the ash system in such a way by cerium would also decrease liquid volume and accordingly reduce the sinterability of the CeA ash system compared to both A and FeA ash systems.

The sintering and liquefaction characteristics of the ash are important with respect to the degradation of cordierite filter elements from two standpoints. One effect that significant sintering of an ash covering on the filter surface may have is to increase the pressure drop across the filter walls, with negative consequences for the efficient operation of the engine to which the filter is attached. Based upon the information collected in this work, it is quite clear that such effects are unlikely unless temperatures rise above 900°C for the baseline ash, 970°C for ash derived from diesel containing the ferrocene additive, and 1100°C for ash derived from diesel containing cerium carboxylate. These temperatures can thus be used as guideline temperatures in assessing undue increases in pressure drop which are not due to the mecha-nisms indicated by Adler.² It can thus be concluded that the representative ash compositions studied herein could induce poorer filter performance due to liquefaction/sintering effects if temperatures exceed 900°C for the baseline ash, 970°C for the Fe₂O₃ containing ash, and 1100°C for the ceria containing ash. The other significant effect of ash sintering and liquefaction is catastrophic thermochemical degradation of the cordierite filter material which was not observed at any temperature or with any of the ashes. Interactions between the cordierite and the various ashes were, however, observed and these are now discussed.

(2) Cordierite-Ash Interactions

Examination of the X-ray phase assemblage data for heattreated cordierite-ash mixture pellets clearly shows that the only reaction products arising that contain elements from the cordierite are the zinc or iron aluminate spinels. For these species to form, aluminum must be extracted from the cordierite with the result that the cordierite–ash interface should become richer in Mg and Si. Maier *et al.*¹³ have observed a similar effect for the interaction of single crystal cordierite with an equimolar mixture of Mg, Ca, and Zn phosphates. They envisage the degradation process occurring via the solution of cordierite by a liquid phosphate with subsequent formation of a zinc aluminate spinel and silica. This reaction type could certainly be the cause of ZnAl₂O₄ formation at the temperatures examined herein for the baseline ash and presumably the iron oxide-containing ash, although there is little evidence of major liquefaction from either shrinkage or DTA analyses at 900°C to support the solution reaction mechanism. However, the enrichment of Mg and Si in the corrosion product may reduce liquidus temperatures to facilitate this as the process goes on. Given the findings reported herein and those reported by Maier et al.,13 it is clear that cordierite degradation to form a ZnAl₂O₄ spinel is due to solution by phosphate-based liquids. The gettering of phosphorus from the ash system by ceria, as discussed above, reduces the probability of liquid phase formation and this is why the zinc aluminate spinel occurs in less significant amounts in the X-ray phase assemblage.

In addition to the formation of the $ZnAl_2O_4$ spinel, a corresponding FeAl₂O₄ spinel is formed by the interaction of cordierite with the Fe₂O₃ containing ash at temperatures of 1100°C and 1250°C. It would therefore appear that if this were an additional degradation mechanism, it would only be likely to augment cordierite degradation at these tempera-

tures which are extreme for a DPF system. A similar reaction mechanism to the formation of the zinc aluminate would be expected and accordingly, the activity of iron in the liquid would be important. Given that the studies of the ash alone indicates the diluent effect Fe_2O_3 has on the amount of liquid phase formed, then it is expected that while $FeAl_2O_4$ forms at 1100°C and 1250°C, its formation does not really affect the amount of cordierite degradation as much as that of zinc aluminate.

(3) Surface Interactions of Cordierite with Ashes

The XRD phase assemblage and the surface topographies reported above are consistent with the analyses of the results discussed above in subsections A and B. For the baseline ash, the same phase assemblages arise for both the reacted pellets and the ash deposit-filter interaction. For the iron and cerium containing ashes, the phase assemblages effectively comprise cordierite and Fe₂O₃ or CeO₂. This information together with the SEM image information endorses the argument that the cordierite DPF material does not significantly degrade in the presence of ash containing the combustion catalysts. While the same cannot be said for the situation when the catalysts are absent (baseline ash), significant surface glazing/liquefaction would only appear to arise at temperatures of 1250°C. Based on the observations made for the surface degradation tests, it seems that cordierite DPFs could be used without fear of thermochemical degradation at temperatures of 1100°C or less. Of course, thermochemical degradation is a kinetic process and will depend on times at temperature. Data obtained by Corning²⁰ indicate that the total time a DPF spends at temperatures in excess of 900°C is about 30 min over the warranted DPF life, 48 times less time than that investigated herein. Ten minutes would be the apparent maximum duration at 1000°C (three times the time investigated herein) and excursions to higher temperatures have not been recorded in the working systems examined. Based on these observations, then it could be fairly safely concluded that interactions between cordierite and the three representative ashes examined herein would not be expected to cause thermochemically induced failure of cordierite DPFs.

V. Conclusions

- The representative ash compositions studied herein do not lead to liquefaction/sintering effects unless the temperatures exceed 900°C for the Ca, Zn, S, P containing baseline ash, 970°C for the Fe₂O₃ containing ash, and 1100°C for the ceria containing ash. Accordingly, ash agglomeration effects would not be expected during normal cordierite filter lifetimes.
- 2. The baseline ash and iron oxide containing ash cause cordierite to degrade by extracting aluminum from it via a solution mechanism involving molten phosphate-based liquids. The presence of ceria in the ash results in phosphorus being removed from the ash, causing less liquid formation and accordingly, with less ZnAl₂O₄ formation.
- At temperatures of 1100°C and 1250°C, FeAl₂O₄ formation occurs via a similar solution mechanism to the formation of ZnAl₂O₄. In contrast, however, Fe₂O₃ acts as a diluent in the iron containing ash and reduces the amount of liquid available for the degradation process.
- 4. The interaction of DPF surfaces with the ashes studied herein strongly indicates that thermochemical degradation of cordierite by ashes representative of typical diesel engine systems is unlikely.
- 5. As the interaction times for a specific temperature used in the experiments conducted in this work were at least three times longer than that which might arise in an actual DPF, it can be fairly safely concluded that

interactions between cordierite and the three representative ashes examined herein would not be expected to cause thermochemically induced failure of cordierite DPFs over a 160 000 km (100 000 mile) warranted life span.

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