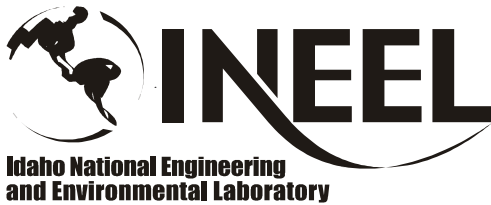


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Cermet Filters To Reduce Diesel Engine Emissions

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Abstract

Pollution from diesel engines is a significant part of our nation's air-quality problem. Even under the more stringent standards for heavy-duty engines set to take effect in 2004, these engines will continue to emit large amounts of nitrogen oxides and particulate matter, both of which affect public health. To address this problem, the Idaho National Engineering and Environmental Laboratory (INEEL) invented a self-cleaning, high temperature, cermet filter that reduces heavy-duty diesel engine emissions. The main advantage of the INEEL cermet filter, compared to current technology, is its ability to destroy carbon particles and NO_x in diesel engine exhaust. As a result, this technology is expected to improve our nation's environmental quality by meeting the need for heavy-duty diesel engine emissions control. This paper describes the cermet filter technology and the initial research and development effort.

Introduction

Diesel engines currently emit soot and NO_x that pollute our air. It is expected that the U.S. Environmental Protection Agency (EPA) will begin tightening the regulatory requirements to control these emissions. The INEEL's self-cleaning, high temperature cermet filter provides a technology to clean heavy-duty diesel engine emissions. Under high engine exhaust temperatures, the cermet filter simultaneously removes carbon particles and NO_x from the exhaust gas.

The cermet filter is made from inexpensive starting materials, via net shape bulk forming and a single-step combustion synthesis process, and can be brazed to existing structures. It is self-cleaning, lightweight, mechanically strong, thermal shock resistant, and has a high melting temperature, high heat capacity, and controllable thermal expansion coefficient. The filter's porosity is controlled to provide high removal efficiency for carbon particulate. It can be made catalytic to oxidize CO, H₂, and hydrocarbons, and reduce NO_x. When activated by engine exhaust, the filter produces NH₃ and light hydrocarbon gases that can effectively destroy the NO_x in the exhaust.

The following sections describe cermet filter technology and properties of the INEEL filter.

The Technology

A cermet is a composite material consisting of interdispersed ceramic and metallic phases. The ceramic component may be oxides or non-oxides; the metallic phase may be a single metal or an intermetallic compound. The INEEL cermet filter is made by mixing low-cost metal and ceramic powders with sacrificial filler materials to form a near-net-shape compact. The compact is fired at high temperatures to initiate synthesis, which is complete when all the metal components are reacted,

forming the filter. Our cermet filter technology uses an intermetallic aluminide compound¹ as the primary metallic phase so that the net-shape filter can be manufactured by combustion synthesis.² The cost of producing this cermet filter is low.

To illustrate, one aluminide that can be used in combustion synthesis is nickel aluminide³. A ceramic phase that could be used is alumina. The Al and Ni powders, in 1:1 atomic ratio, could be mixed well with alumina powder and a sacrificial filler material, such as polystyrene spheres, in a mixer. The reactant mixture would be placed in a structurally configured mold and pressed into discs, cylinders, or any chosen shape. The compact in the mold would be fired in a furnace between 600 and 700°C to set off the combustion synthesis process. At 660°C Al melts, and liquid Al is extremely reactive. Molten Al reacts with the Ni powder and set off a “solid flame”². The “solid flame” is an intensely luminous combustion front separating the initial reactant mixture and the solid combustion product. In a pure metallic combustion synthesis process the combustion front is white-hot and the temperature is extremely high. However, in a cermet system the combustion synthesis is moderated by the refractory ceramics. Although the combustion front luminosity is less intense, the combustion temperature remains so high that partial fusion of the particles occurs, giving rise to the high mechanical strength of the final product. The combustion process continues until the entire powder compact has been reacted. The intense heat during combustion burns out the sacrificial filler materials, leaving behind residual pores reminiscent of the starting material shapes. The final product retains the net shape of the mold and has a porous structure with ceramic powders dispersed in a metal matrix. The porous structure provides high internal surface area for material retention and/or reactions. The ceramic constituent of the cermet is refractory, allowing very high service temperatures. The composition of the cermet can be tailored to achieve desired functional characteristics, e.g., catalysts may be incorporated to perform selected catalysis.

The INEEL cermet filters possess the following desirable properties:

- High melting temperatures (> 1500°C)
- High thermal shock resistant (fracture toughness up to 22 mPa·m^{1/2})
- High temperature oxidation resistant
- Controlled porosity (pore size, shape, and structure manageable)
- Inexpensive starting materials
- Any material compositions possible
- Net shape bulk forming by a solid state combustion synthesis process
- Electrically conducting (internal heating capability)
- Light weight (density of porous cermet <3 g/cm³)
- Mechanically strong
- High heat capacities
- Thermal expansion coefficient controllable
- Catalytic to steam reforming or partial oxidation of hydrocarbon
- NO_x reduction under reducing conditions
- Generate ammonia and light hydrocarbon gases when activated by engine exhaust
- High particulate filtration efficiency

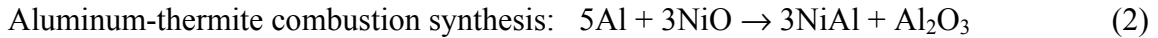
¹ Y. Kaieda, M. Otaguchi, and N. Oguro, *Combustion and Plasma Synthesis of High-temperature Materials*, ed. By Z. A. Munir and J. B. Holt, p106 (1990).]

² A. G. Merzhanov, *Combustion and Plasma Synthesis of High-temperature Materials*, ed. By Z. A. Munir and J. B. Holt, p1 (1990).]

³ B. H. Rabin, A. Bose, and R. M. German, *Combustion and Plasma Synthesis of High-temperature Materials*, ed. By Z. A. Munir and J. B. Holt, p114 (1990).]

Combustion Synthesis

There are two combustion synthesis reactions related to the manufacture of NiAl·Al₂O₃ cermets:



The first reaction only involves combustion of aluminum. The reaction starts at the melting temperature of aluminum when the Al forms a molten phase and spreads over the surface of nickel particles by capillary force. Molten Al reacts with Ni particles in a highly exothermic solid state reaction to form NiAl. The alumina in the system is not involved in the reaction, and it moderates the Al combustion reaction. In the second reaction, aluminum-thermite, the molten aluminum reduces NiO to Ni. During this reduction step the Al reacts with the oxygen to form Al₂O₃, and the remaining molten Al combusts with Ni to form NiAl. The energy released by Al₂O₃ and NiAl formation is tremendous and raises the overall reaction temperature. Examining the thermodynamics of these two reactions, one can conclude that the aluminum-thermite reaction is much more exothermic than the aluminum reaction, and that the aluminum-thermite reaction temperature is also higher. Therefore, net shape bulk products formed by the aluminum-thermite reaction would achieve higher densities.

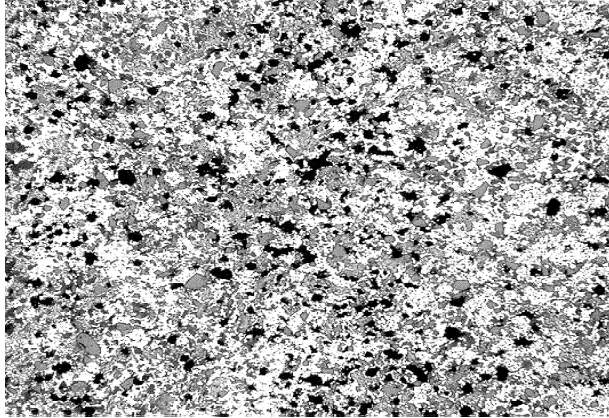
Cermet Porosity Engineering

A highly efficient filter to remove very fine particles entrained in a gas stream must have very fine porosity and irregular, nonlinear pore channels. However, to maintain a very low-pressure drop across a fixed cross-sectional area the filter must also have a high porosity. Pore phase engineering becomes important to achieve low-pressure drop across the filter while maintaining high particulate filtration efficiency.

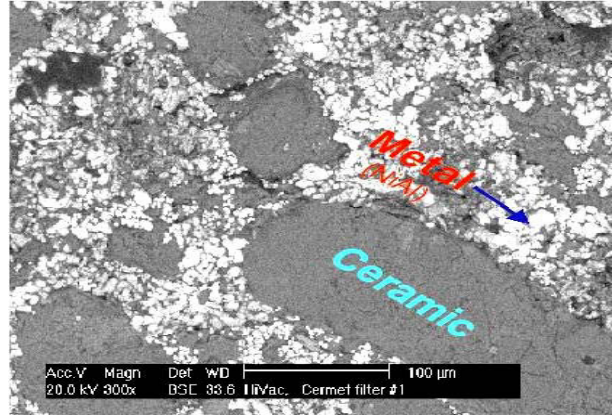
Pore phase engineering addresses percent porosity increase, pore size distribution, and pore shape control. Using sacrificial materials in the powder compact produces residue pores in the product after firing. The size, shape, and volume of the filler material control the pore size, shape, and volume in the final product. Spherical and fiber materials produce highly porous cermet filters with nonlinear pore channels. The powder consolidation pressure also affects the porosity development. At higher compacting pressures, higher density green compacts will be produced. To a much lesser extent, the sizes and shapes of the ceramic particles also affect the geometry of porosity in the cermet filter. Figure 1 shows the porosity geometry using fine and coarse ceramic particles to manufacture the cermet filter. These two specimens were synthesized without sacrificial filler materials. The specimen represented in Figure 1a had an average ceramic particle size of 5-10 μm and its average porosity is <10 μm. The coarse ceramic particles showed in Figure 1b are 100-200 μm and the smaller ceramic particle is <44 μm; the porosity size in this specimen varied from submicron to >50 μm.

Some sacrificial filler materials used to engineer pores and nonlinear pore channels are polystyrene and styrofoam particles, sugar, corn starch, hair, and organic long thin fibers. Nonlinear pore channels are produced with hair and organic fibers. Figure 2 is the cross-section of a cermet filter manufactured with sugar filler particles. The pore sizes range from submicron to over 150 μm.

Sodium carbonate is a leachable phase used to produce additional residue porosity after combustion synthesis. Sodium carbonate decomposes to CO₂ and Na₂O during combustion synthesis. Carbon dioxide escaping from the compact during combustion synthesis produced a first



a. Fine ceramic phase



b. Coarse ceramic phase

Figure 1. Cermet filters.

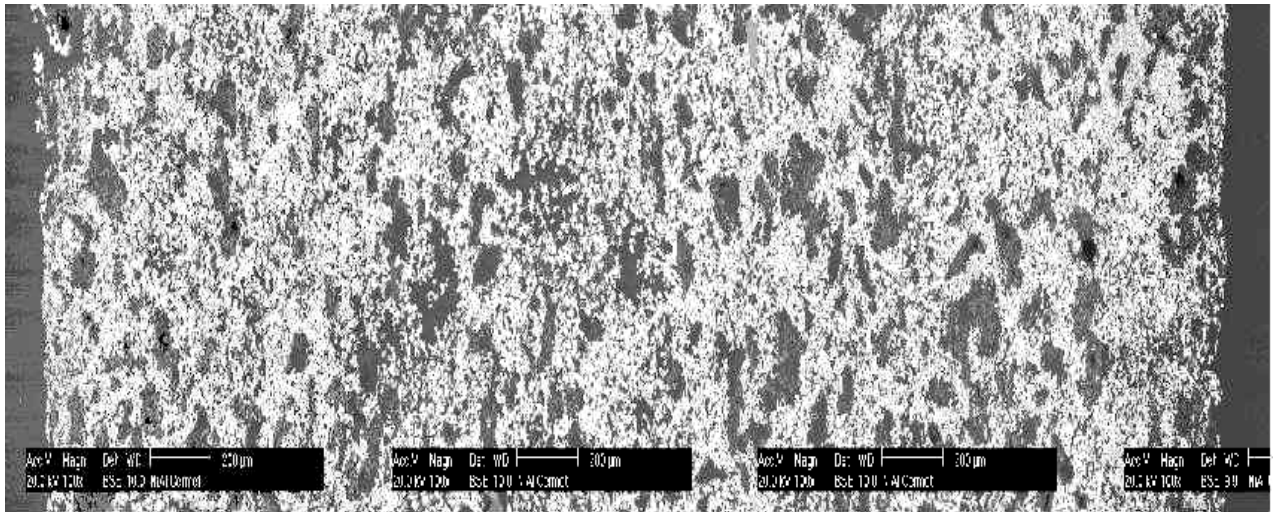


Figure 2. Cross-section of a cermet filter manufactured with sugar filler materials.

stage porosity in the filter. Post combustion synthesis leaching of the cermet filter dissolved the Na_2O particles and further increases the porosity of the final cermet filter.

Graded porosity in the cermet filter can be produced by sequential layering of small and large sacrificial filler materials in the powder mix in the mold prior to powder consolidation and firing. After combustion synthesis, the internal structure of the bulk will retain layers of pores reminiscent of the initial sacrificial material size.

The efficiency of the INEEL cermet filter for fine carbon particle filtration was tested under a cold flow condition. The as-produced porosity for this cermet filter was approximately 30% and no filler materials were used in this specimen. Carbon particles used in this test were generated by thermal plasma decomposition of methane; their agglomerated particle size was approximately 0.5 – 1.0 μm . The airflow rate was 60 L/min under high pressure (56 psi). The test lasted 60 min. The carbon fine particle filtration efficiency for this moderately low porosity filter was almost 100%; results are listed in Table 1.

Table 1. Fine Carbon Particulate Filtration Tests

• Initial wt of cermet filter = 3.3073g	• Wt of carbon before filtering = 1.3846g
• Final wt of cermet filter = 3.3070g	• Wt of carbon after filtering = 1.3826g
• No clogging of the filter observed	• Carbon filtration efficiency = 99.86%
• Effective cermet filter area = 0.448 in. ² .	• Filter porosity ~ 30%

Cermet Filter Heating

The relatively good electrical conductivity in cermet lends itself to a bulk heating capability. Operating with a hot cermet filter continuously burns out condensed carbon particles to prevent clogging. Continuous burnout of trapped carbon particles also assists in fuel NO_x reduction—as NO_x oxidizes the fine carbon particles to CO₂, it is reduced to N₂. Therefore, the cermet filter can remove carbon particles and NO_x from the exhaust gas simultaneously. Headspace fuel vapor from the fuel tank could also be injected into the cermet filter for NO_x reduction.

There are two methods of cermet filter bulk heating, direct internal self-heating and auxiliary internal heating. Direct internal self-heating is achieved by directly passing a current through the metallic phase of the cermet filter to cause joule heating. This method requires uniform continuity of the metallic phase throughout the cermet filter so that the average electrical resistance is constant throughout. To achieve this, the Al and Ni powders must be uniformly dispersed in the green compact and the electrode must be fabricated directly on the surface of the cermet filter.

A combustion synthesis method has been successfully developed to ‘burn-in’ the electrodes directly on both ends of the cermet filter. In Figure 3, the electrode is directly ‘burnt in’ onto both faces of the cermet filter. During compaction the powder mixture was sandwiched between the electrodes inside the mold. To enhance bonding of the electrode to the cermet material, Ni and Al fine powders were painted on the underside of the electrodes using Ag paint. The combustion synthesis of Ag, Al and Ni permanently bonded the electrode to the cermet filter in one operation.

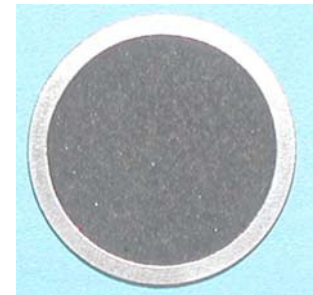


Figure 3. Cermet filter with direct ‘burn-in’ electrode

For auxiliary internal heating, a high temperature resistive heating element is incorporated in the filter’s green compact. During combustion synthesis the heating element is permanently embedded in the cermet filter. Incorporating an internal heating element also strengthens the cermet filter.

Figure 4 shows a heating element in a cermet filter. To prevent shorting between the heating element and the filter’s intermetallic phase, the heating element was dip-coated with a thin layer of ceramic material before assembly with the precursor powders. In auxiliary internal heating the filter is heated by the heating element, the electrical current does not pass through the filter to cause direct joule heating of the material. The temperature achieved by the cermet filter is controlled by the size of the applied current; the temperature of the filter shown in Figure 4c was about 600°C.

The advantages of cermet heating are continuous self-cleaning of the filter and NO_x reduction. Two cermet filter compositions and a pure intermetallic were tested for NO conversion. The metal phases, nickel aluminide, in the cermets were identical; the ceramic in cermet 1 is alumina and in cermet 2 is iron (III) oxide. Table 2 shows some of the initial test results for the cermet filter reduction of nitric oxide (NO) under a reducing condition.



a. Internal heating element b. Frontal view c. Heated filter

Figure 4. Cermet filter with indirect internal heating.

The results showed that the nickel aluminide in the cermet filter has marginal function for NO reduction to nitrogen under a reducing atmosphere. However, the oxide phase in cermet 2 showed a significant activity to NO reduction to nitrogen under a reducing atmosphere. The third test used a pure intermetallic, MoSi₂, as a comparison for the activity of nickel aluminide. This test showed MoSi₂ had no measurable activity for NO reduction even under a reducing atmosphere. The enhanced performance for cermet filter 2 for NO reduction may be due to combined properties of nickel aluminide and the iron (III) oxide.

Table 2. Cermet Filter Reduction of NO under Reducing Condition

Cermet Filter Temperature, °C	% NO conversion to N ₂ under reducing atmosphere		
	Cermet 1	Cermet 2	Intermetallic
300	0	0	0
400	0	2.5	0
475	0	2.6	2
550	0	4.7	2
623	3.8	13.3	2
696	11.3	43.1	3
797	38.7	98.3	7
904		100	

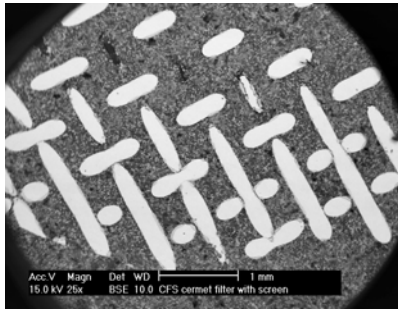
Diesel exhaust also contains incomplete combustion products, light hydrocarbons and CO. The cermet filter also destroyed hydrocarbon and CO. Table 3 shows that more than half of the propylene and CO have been destroyed while methane needs a higher temperature for destruction.

Cermet Filter Strength Enhancement

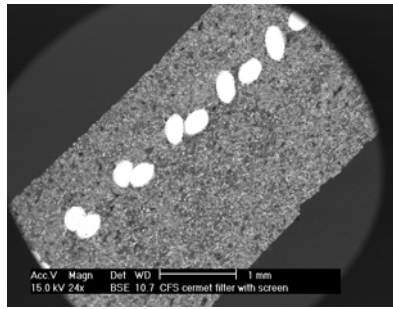
A highly porous system may have considerably weaker mechanical strength. Enhanced structural development is necessary to increase the fracture toughness of a highly porous cermet filter. Structural enhancement could be accomplished by incorporating long thin metal fibers or metal screens into the structure during green powder consolidation. At combustion synthesis the reinforcement materials would fuse with the cermet components to enhance the cermet strength. Figure 5 shows the cross sections of cermet filters that have been partially reinforced by either a single metal screen or the heating element.

Table 3. Cermet Destruction of Hydrocarbon and CO

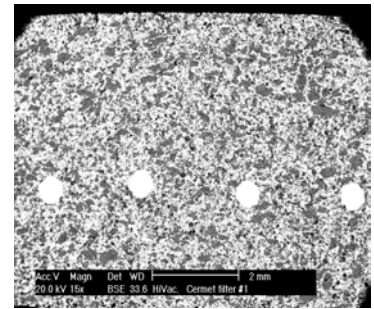
Cermet Filter Temperature, °C	C ₃ H ₆	CH ₄	CO
25	0	0	0
101	0	0	0
203	2.1	0	5.3
302	1.4	0	6.1
403	0	0	8.9
478	11.3	15.9	24
553	47.8	23.3	81.2
627	93.8	25.2	97.0
702	100	36.0	100
797	100	52	100



a. Polished top section showing woven screen



b. Cross-section showing woven screen



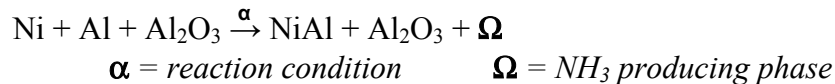
c. Cross-section of heating element

Figure 5. Cermet filters reinforced with woven screen (a & b) and heating element (c).

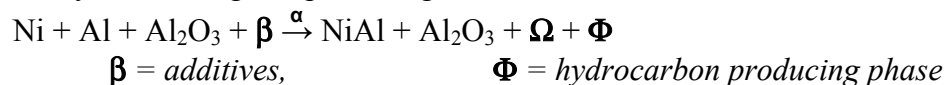
Ammonia and Hydrocarbon Generating Cermet Filters

In another combustion synthesis method, the cermet filter is manufactured under a specific condition, α . The cermet filter emits ammonia after activation. During ammonia emission the cermet filter generates a significant amount of heat. The reaction indicates that some new phases formed in the cermet filter during combustion synthesis. When a sacrificial filler material, β , is added to the cermet composition and the combustion synthesis is carried out under the same specific condition, the resulting cermet filter contains additional new phases. These additional new phases generate light hydrocarbon gases when activated. However, the compositions of the ammonia and hydrocarbon gas-generating phases have not been fully identified. The general combustion synthesis reactions for the ammonia and hydrocarbon generating cermet filters are represented by the reactions below.

1. Ammonia producing cermet filter:



2. Ammonia and hydrocarbon gases producing cermet filter:



Ammonia and hydrocarbon gases are reducing agents for NO_x in the diesel exhaust gas. The internal generation capability of reducing agents has significant implications for on-board destruction of exhaust NO_x . Figure 6 shows the gas chromatography (GC) analysis of the ammonia standard and the ammonia generated from the cermet filter after activation. Ammonia generation from the cermet filter is also evident from hydriion paper tests. Figure 7 shows the pH paper test results. The pH papers in petri dishes X&Y (Fig. 7b) turned dark blue after the cermet filters were activated.

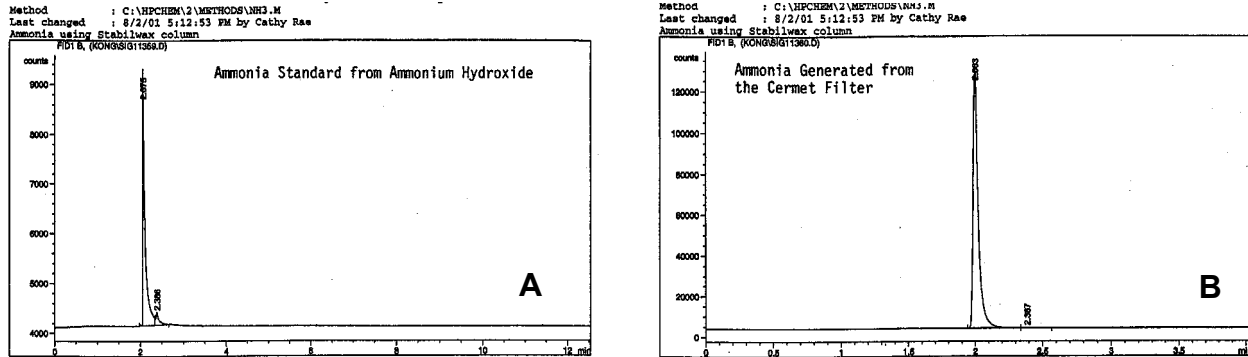


Figure 6. GC profile of (A) NH_3 standard and (B) NH_3 generated by cermet filter.

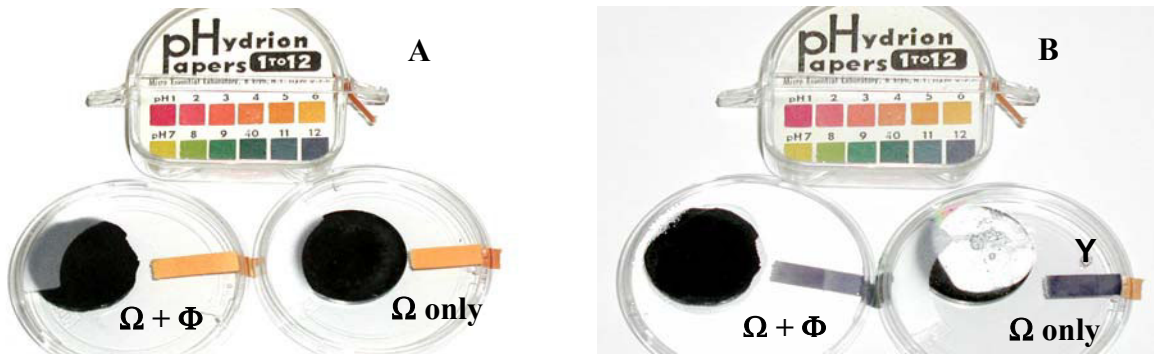


Figure 7. pH paper test for ammonia gas. (A) Before generation (B) After.

Co-generation of hydrocarbon gases was also detected when the cermet filters were activated. The primary hydrocarbon produced is methane with minor amounts of other higher hydrocarbon gases ($\text{C}_1 - \text{C}_4$). These gases are also useful for on-board NO_x destruction. Figure 8 shows the GC analysis of a methane standard and the methane generated from the cermet filter.

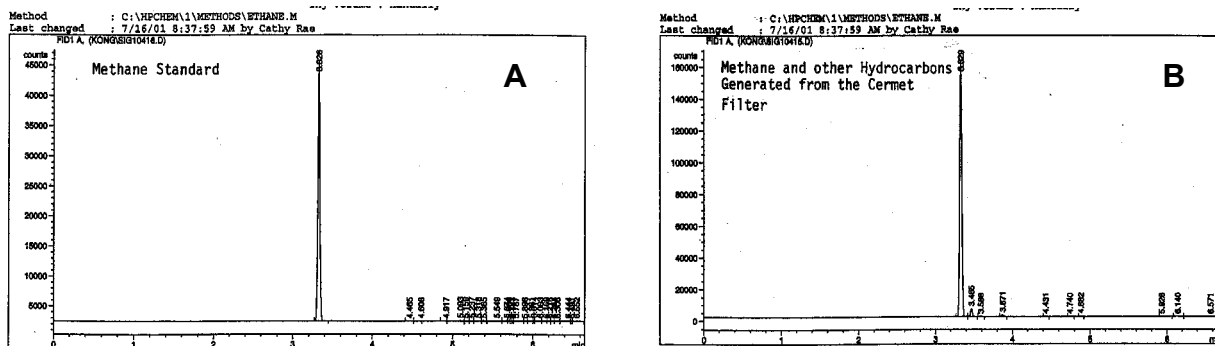


Figure 8. GC profile of (A) CH_4 standard and (B) CH_4 generated by a cermet filter.

Conclusion

A new cermet filter technology for controlling diesel engine emissions is being developed at the Idaho National Engineering and Environmental Laboratory. A single-step combustion synthesis process forms the cermet filter. Various sacrificial filler materials are used for porosity engineering. Continuous heating of the filter burns off condensed fine carbon particles. The filter's strength is enhanced by incorporating a metal screen, metal fibers, or a heating element. Initial tests of the cermet filter showed high removal efficiency for fine carbon particles, catalytic functions for NO_x and CO, and hydrocarbon destruction. The material also displays unusual properties of ammonia and light hydrocarbon gases generation for NO_x destruction.

Acknowledgment

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