Clean Diesel Technologies, Inc.

CARB – International Diesel Retrofit Advisory Committee

Part II – Use of Metal Additives; What Are the Issues?

February, 2002

Use of Metal Additives What are the Issues?

- How much of the metal is emitted?
- Are emissions of "nano-particles" increased?
- What is the environmental impact?
- What is the human toxicity impact?
- What is the benefit?

Comparative Emissions of Metals and their Oxides from Use of Metallic FBC's in Diesel Fuel

	No Filter		With Filter	
	Pt	**Ce**	**Pt**	**Ce**
SwRI[1]				
Cummins N-14				
Pt/Ce @ 0.5/7.5 ppm				
Emissions µg/bhp-hr	**4.8**	**128**	**1.1**	**4.7**
Retention %	94%	92%	98.6%	99.7%
VERT (VSET)[2]				
Liebherr 6.1 liter				
Pt/Ce @ 0.5/7.5 ppm				
Emissions µg/bhp-hr	**1.8**	**101**	**0.12**	**6.0**
Retention %	98%	92%	99.8%	99.5%
Heeb 1998[2]				
Liebherr 6.6 liter				
Cerium @ 64 ppm				
Emissions µg/bhp-hr	-	**13,500**	-	**75[3]** **1,800[4]**
Retention %	-	-	-	(99%) (87%)

1 Following 1,000 hours at 1/15; FTP Transient Test
2 ISO cycle 8178 for construction equipment; 8 modes 100 minutes
3 Sintered Metal DPF
4 Fiber DPF

Clean Diesel Technologies, Inc.

Data On Platinum And Cerium Emissions

From Engine With And Without Aftertreatment

FBC Dosing In Fuel @ 0.5 ppm Pt + 7.5 ppm Ce
(After 1000hrs @1/15ppm)

	Brake Specific Emissions FTP Composite Test		
	Platinum µg/bhp-hr	Cerium µg/bhp-hr	PM µg/bhp-hr
Baseline	-	-	100,000
FBC - No Aftertreatment	4.8	128	90,000
FBC - With Diesel Oxidizer	4.4	133	70,000
FBC - With Filter	1.1	4.7	20,000

Engine: Cummins 1998 NIA 370E 14.OL
Certified @ 0.1 g/bhp-hr (100,000 ug/bhp-hr)
SwRI; June, 1999

Clean Diesel Technologies, Inc.

Comparison Of Platinum Emissions

From Autocatalyst And Light Duty And Heavy Duty Diesels Using A Platinum Fuel Catalyst (PFC)

Platinum Emissions From Current Autocatalyst (Industry Estimate)	1.3 µg/mile
Light Duty Diesel with PFC (30 mpg, 15,000 miles/yr @ 0.15 ppm PFC)	
Platinum Consumption	0.25 grams/yr
Platinum Emissions @ 6% (No Filter)	1.0 µg/mile
Platinum Emissions @ 1.4% (with Filter)	0.2 µg/mile
Heavy Duty Diesel with PFC (6 mpg, 50,000 miles/yr @ 0.15 ppm PFC)	
Platinum Consumption	4.0 grams/yr
Platinum Emissions @ 6% (No Filter)	4.8 µg/mile
Platinum Emissions @ 1.4% (with Filter)	1.1 µg/mile

Note: Platinum emissions measured at 0.5/7.5 ppm platinum and cerium treatment rate following 1000 hours of engine durability at 1.0/15 ppm treatment rate as reported in SwRI letter report of June 3, 1999. Platinum Emissions at 0.15 ppm are expected to be less due to higher retention in engine and exhaust.

Clean Diesel Technologies, Inc.

Comparison of Emissions of Cerium/Cerium Oxide Reported by Various Sources

- Samaras: Predicted ambient concentrations of **1.2µg/m³** based on 8 ppm Ce emitted after a 92% efficient filter in an urban canyon model.
- Health Effects Institute: Reported "cerium oxide appears to have low toxicity and might not present a concern when inhaled or ingested for some period of time at the low levels caused by Eolys additive (**estimated to be in low µg/m³**)."
- CDT cerium input level is 7.5 ppm (max.) and retention is 92% without filters and 99% with filter. (SwRI; VSET tests).
  - Predicted ambient concentration based on Samaras model are **0.1 µg/m³** without filter and **0.01 µg/m³** with filter; one to two orders of magnitude lower than levels evaluated by HEI.
  - Ambient concentrations based on Radian Urban Canyon Model are **0.02 µg/m³** without filter and **0.003 µg/m³** with filter.
- OSHA and NIOSH list cerium as a nuisance dust; with limits of 15mg/m^3 and 5 mg/m^3. Safety factor is 220,000 – 1,600,000

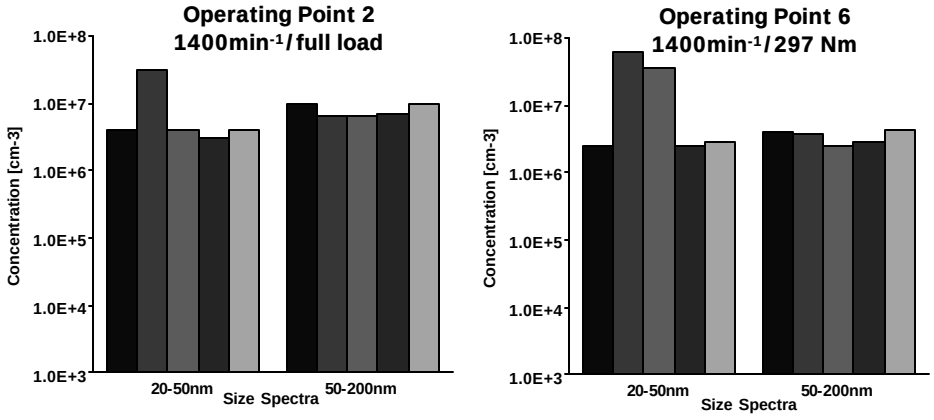
Clean Diesel Technologies, Inc.

Use of Metal Additives What are the Issues?

- How much of the metal is emitted?
- Are emissions of “nano-particles” increased?
- What is the environmental impact?
- What is the human toxicity impact?
- What is the benefit?

Clean Diesel Technologies, Inc.

No Increase in Ultra Fine Particles at Normal Dose Rates of Platinum Plus



Clean Diesel Technologies, Inc.

VERT (VSET) Tests
Tests of Platinum (0.5ppm) + Cerium (7.5ppm) Additive Without Filter

- Conclusion:
  "Additive particles do not show up as a separate peak in the size distribution nor do they increase submicron particle number"

- Particle analysis by NanoMet:
  "Comparing the PAS (signal) clearly shows that the additive reduces the total surface of emitted particles substantially – in some operating points up to 30% which **proves the catalytic activity for the oxidation of submicron soot particles even without trap"**
  "...DC (signal) proves that there are **no additional non soot particles created** while soot particles are oxidized"

Clean Diesel Technologies, Inc.

Use of Metal Additives
What are the Issues?

- How much of the metal is emitted?
- Are emissions of "nano-particles" increased?
- What is the environmental impact?
- What is the human toxicity impact?
- What is the benefit?

Clean Diesel Technologies, Inc.

Environmental Impact of Platinum Based FBC Summary of Findings

- There is a background of platinum from natural sources
- Use of PGM in auto catalyst results in emissions of PGM finely dispersed particles on ceria and alumina or mixed oxides with ceria and/or alumina
- Road side levels are increasing on major roads – not on minor roads
- Platinum is taken up by certain plants
- Platinum is not retained in the human body and is not bioaccumulated
- Allergenic response is limited to soluble halogenated ionic platinum species
- There are no known human health effects of platinum metal or platinum oxide
- Use of platinum and cerium FBC results in platinum particles finely dispersed on ceria or as a mixed oxide with ceria
- Measured emissions of platinum from FBC are 1,000,000 times below workplace standards (2000-5000 in worst case scenario)

References: "Platinum Group Metals in the Environment" Imperial College of Science and Technology – London, 1995
"Impact of Platinum in Diesel Exhaust on Human Health" Radian International LLC, 1997
"Particulate Emissions Containing PGM from Motor Vehicles" G.J. K. Acres, 2002

Clean Diesel Technologies, Inc.

Comparison Of Ambient Platinum Concentrations

From Use Of A Platinum Fuel Additive To Workplace Standards Based On A Dispersion Model

Maximum Ambient Concentration for a Generic Metallic Additive @ 1 ppm; 100% Emitted(1)	0.037µg/m^3
Platinum Exposure Limits	Platinum – Metal
TLV - TWA	1000µg/m^3
Percent of Platinum in Fuel Emitted From Engine Exhaust @ 0.5 ppm(2)	
Without filter	< 6%
With Filter	< 2%
Maximum Ambient Concentration of Platinum @ 0.5 ppm in Fuel	
Without Filter	0.0011µg/m^3
With Filter	0.00037µg/m^3

(1) Air Quality Impacts in an Urban Street Canyon from a Generic Atypical Fuel Additive Prepared for CMA by Radian; August, 1996.
(2) Letter Report from Testing by SwRI; June, 1999.

Clean Diesel Technologies, Inc.

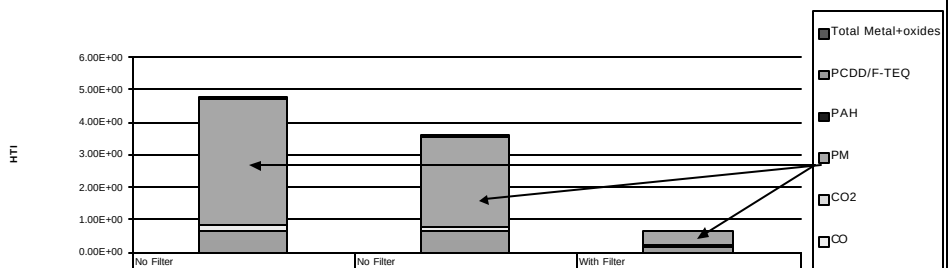
Use of Metal Additives What are the Issues?

- How much of the metal is emitted?
- Are emissions of “nano-particles” increased?
- What is the environmental impact?
- What is the human toxicity impact?
- What is the benefit?

Clean Diesel Technologies, Inc.

Human Toxicity Impact (HTI) by SAEFL (1998) Method NOx Omitted

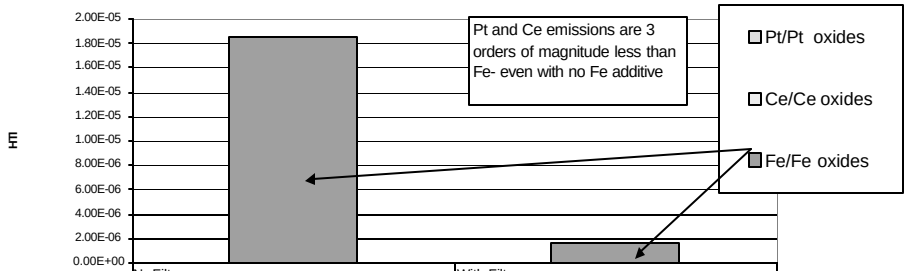
Source: INFRAS



	No Filter No Additive	No Filter 0.5Pt+7.5Ce	With Filter 0.5Pt+7.5Ce
Total Metal+oxides	8.71E-06	1.85E-05	1.74E-06
PCDD/F-TEQ	5.64E-05	6.57E-05	5.08E-05
PAH	8.08E-02	7.80E-02	3.75E-03
PM	3.90E+00	2.76E+00	3.90E-01
CO2	0	0	0
CO	1.43E-01	1.25E-01	4.68E-02
HC	6.65E-01	6.26E-01	1.96E-01

Clean Diesel Technologies, Inc.

Human Toxicity Impact (HTI) by SAEFL (1998) Method From metal and metal oxide emissions Source: INFRAS - 2001

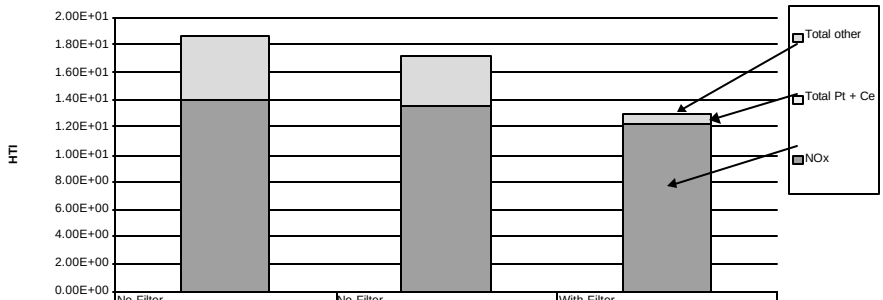


	No Filter 0.5Pt+7.5Ce	With Filter 0.5Pt+7.5Ce
Pt/Pt oxides	3.16E-09	7.24E-10
Ce/Ce oxides	1.74E-08	6.38E-10
Fe/Fe oxides	1.85E-05	1.74E-06

Clean Diesel Technologies, Inc.

Human Toxicity Impact (HTI) of Emissions From Diesel Engines by SAEFL (1998) Method

Source: INFRAS - 2001



	No Filter No Additive	No Filter 0.5Pt+7.5Ce	With Filter 0.5Pt+7.5Ce
Total other	4.79E+00	3.59E+00	6.37E-01
Total Pt + Ce	1.02E-09	2.06E-08	1.36E-09
NOx	1.39E+01	1.36E+01	1.23E+01

Clean Diesel Technologies, Inc.

Use of Metal Additives What are the Issues?

- How much of the metal is emitted?
- Are emissions of "nano-particles" increased?
- What is the environmental impact?
- What is the human toxicity impact?
- What is the benefit?


Clean Diesel Technologies, Inc.

Benefits of Using Platinum + Cerium at Ultra Low Dose Rates (<8 ppm in fuel)

- Reduction "engine out" of:
  - PM – both elemental and organic carbon
  - CO
  - HC
  - Fuel Consumption
- Used with Filters:
  - Improved regeneration
  - Reduced PAH
  - Reduced NOx
- Reduction in Human Toxicity Impact (HTI)
  - Without Filters of 25%
  - With Filters of 85%


Clean Diesel Technologies, Inc.

Summary

- Emissions of Pt + Ce used at ultra low dose rate < 8 ppm – measured by SwRI and VERT without a filter – are at the same level as emissions of cerium used at 64 ppm with a filter (measured by Heeb EMPA – Zurich) and similar to platinum attrition from auto three way catalyst
- Pt + Ce gives reductions in all regulated emissions with and without a filter and it reduces PAH's – these reductions result in significant reductions in Human Toxicity Impact (HTI) with and without a filter
- HTI due to Pt + Ce emissions is 9 orders of magnitude less than the HTI of diesel regulated emissions + PAH's
- Pt + Ce emissions with or without a filter are 3 to 4 orders of magnitude less toxic than Iron (Fe) emissions due to engine wear
- Pt + Ce used at dose rate of 8 ppm reduces carbon soot by 30% and does not increase ultrafine particle emissions

Clean Diesel Technologies, Inc.