Development of a Semi-Quantitative Method for the Determination of Silicon Carbide in Recycled Automotive Catalyst Feedstocks

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Introduction

- The recycling of catalytic converters is an important source of platinum-group metals (PGMs) for the precious metals industry.
- Converters from small cars may contain a few grams of precious metals (PM), whereas converters from large trucks may contain up to ten times or even more.
- For this reason, some collectors may blend Diesel Oxidation Catalysts (DOC) with higher PM loading into their standard Three-way Catalyst (TWC) lots to maximize their returns.
- The presence of silicon carbide (SiC) from DOC incorporated in TWC lots presents a unique challenge to refiners using pyrometallurgical extraction.
- **In order to minimize the potential for these effects, we have developed a semi-quantitative method for determining the SiC content in recycled automotive catalyst materials**.

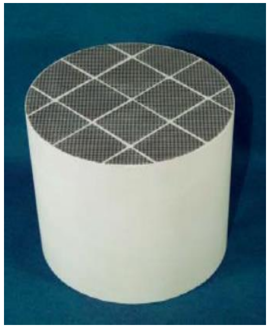
Where does SiC come from?

- Silicon Carbide in the recycle streams of “spent” emission control catalysts only comes from diesel vehicles.
- For Light Duty Diesel (LDD) Passenger Car Vehicles
  - SiC DPF first appeared in Europe in 2000
  - Alternatves to SiC exist but not in widespread use
  - SiC will remain the material of choice in LDD DPFs
- For Heavy Duty Diesel (HDD) Trucks
  - Filters first appeared in 2007 (US) and 2013 (EU)
  - Cordierite is the material of choice
- Other Applications
  - Cordierite filters (perhaps without PGM) may appear on future gasoline cars in Europe, to meet particulate number standards
  - Some medium duty vehicles in US and Europe use SiC filters
- Appearance of SiC in future “spent catalyst” recycle streams will be determined by mix of LDD diesel/gasoline vehicles sold.

Typical LDD Catalysts

Type	Substrate	PGM Type	PGM wt% Range
DOC	Cordierite	Pt:Pd	0.4 – 1.5
CSF	SiC	Pt:Pd	0.01 – 0.23
LNT	Cordierite	Pt:Pd:Rh	0.4 – 0.6
SCR	Cordierite	None	0
AMOx	Not Used		

Cordierite



SiC

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Properties of SiC compared to Cordierite

Property	Cordierite (200/12)	SiC (200/18)	AT (300/13)
Intrinsic material properties			
Melting point (°C)	~1,460	~2,400	~1,600
Density (g/cm^3)	2.51	3.24	3.40
Specific heat @ 500°C (J/g°C)	1.11	1.12	1.06
DPF material properties			
CTE (22° to 1,000°C) (10^{-7}/°C)	7	45	9
Wall porosity (%)	50	43	50
Mean pore size (μm)	12	9	16
Permeability (10^{-12} m^2)	0.61	1.24	
Axial E-modulus (10^6 psi)	0.68	4.83	0.21
Axial MOR (psi)	410	2,700	290
Thermal conductivity (W/m K)	<2	~20	<2
Thermal shock index (°C)	860	125	1,535
Weight density (g/cm^3)	0.46	0.85	0.72
Heat capacity per unit volume of filter @ 500°C (J/cm^3°C)	0.51	0.95	

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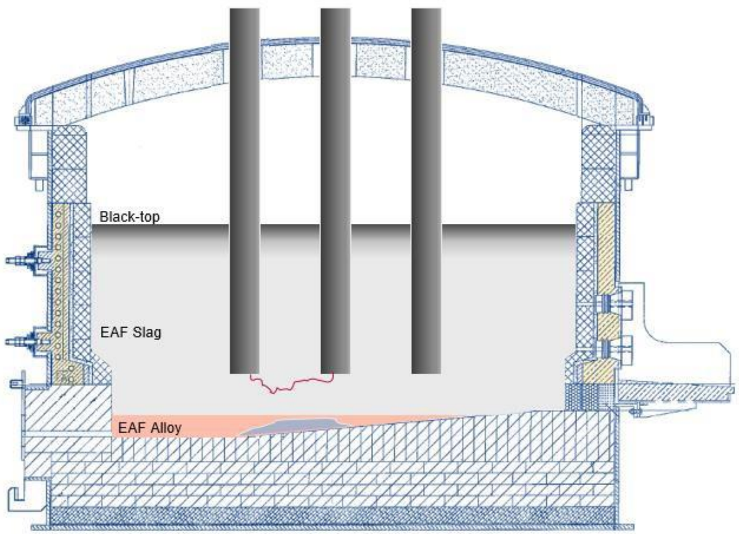
Effect of SiC on EAF Operation



SiC can only be accommodated in small quantities in the feed without causing operational problems. Even then, a significant portion of the PGM contained in the SiC-matrix may not be recoverable, but lost through the slag.

- During melting, slag components dissolve and PGM is released as alloy droplets in the slag. These droplets will slowly sink to the bottom of the furnace and collect as EAF alloy.
- SiC requires more energy to melt than cordierite; decomposition temperature of SiC is 2730°C, compared to 1460°C for cordierite and 1900-2100°C for the furnace refractories. This temperature is only reached in the electric arc.
- SiC has a higher density than cordierite; (3.24 compared to 2.51 g/cm^3, which means it will sink to the bottom of the furnace.

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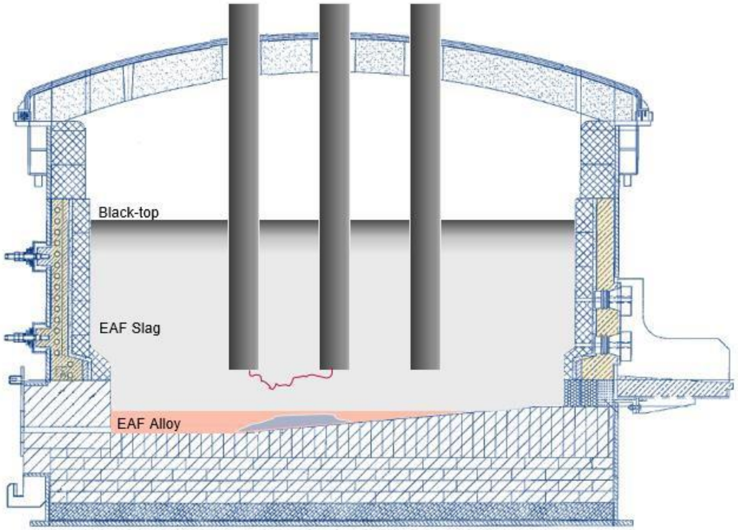

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- Since SiC will be present as solid phase particle in the slag, it will increase the slag viscosity.
- SiC has a higher electrical conductivity than typical slag – the presence of SiC will reduce the resistance of the slag, allowing current to flow between electrodes, rather than through the alloy pool, resulting in build-up on the furnace floor, potentially allowing the alloy level to reach the water-cooled copper panels.
- Solid SiC that have not been in direct contact with the electric arc could leave the furnace entrained in the slag, potentially without the PGM being recovered.

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Analytical Challenge

- Due to the potential issues with feeding mixed SiC/Cordierite lots into the EAF, the refinery came to BASF Analytical Expert Team to develop a rapid, semi-quantitative method for determining the amount of SiC in recycled autocat lots.
- Analytical needs:
  - Rapid – completed during typical autocat analysis (≤ 3 days)
  - Cost effective – using existing equipment
  - Accurate and reproducible
- Potential methods:
  - X-ray diffraction (too slow, but phase specific)
  - X-ray fluorescence (fast, but not as accurate)
  - Raman or FTIR Spectroscopy (too slow, required CAPEX)

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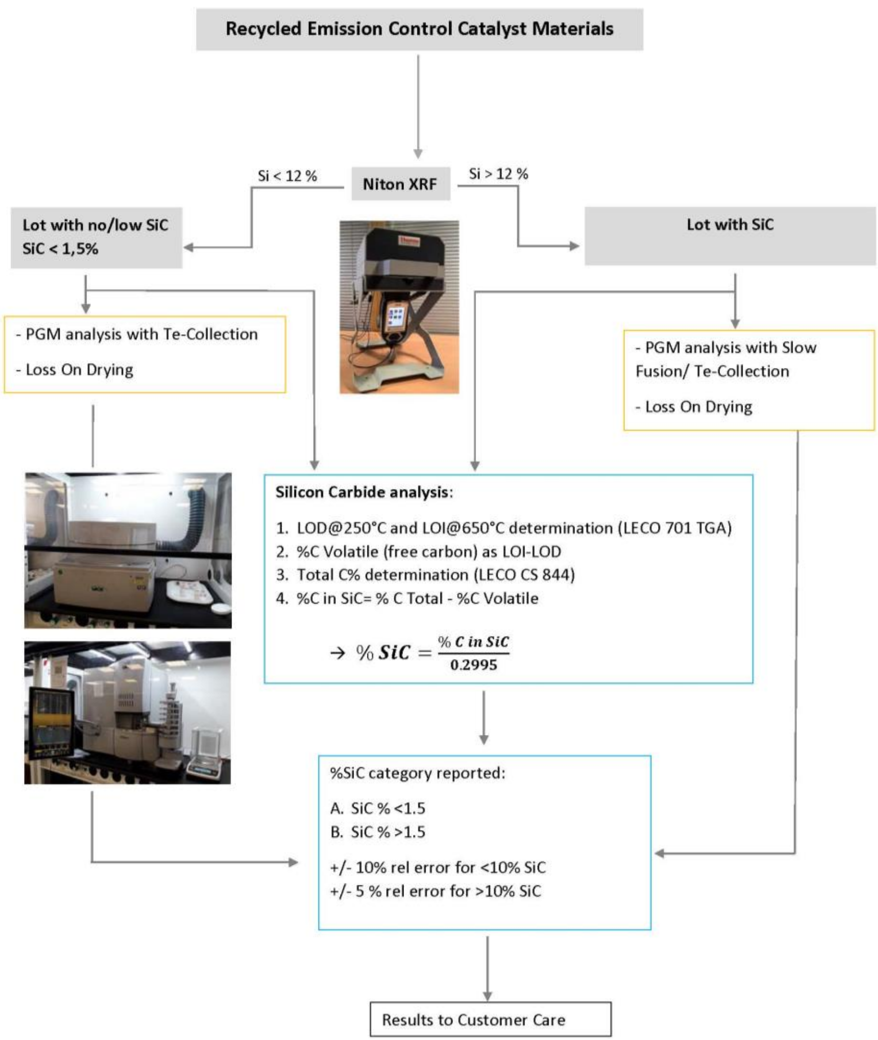
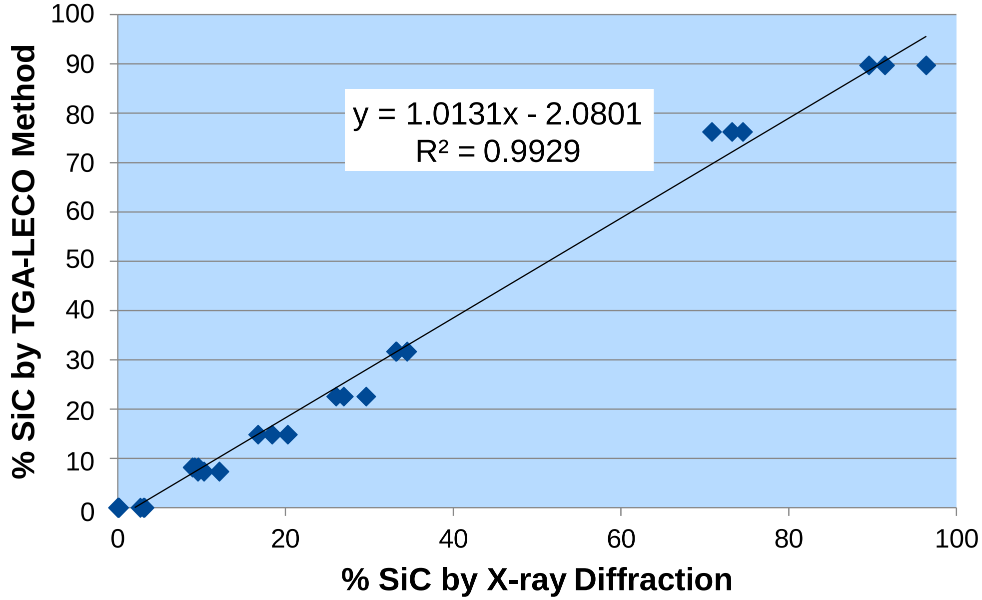
SiC Testing Method



- The method developed in Union lab (NJ-USA) was based on a published standard method (Ref No. ISO 21068-2:2008)
- Samples are prescreened by X-ray fluorescence; samples containing SiC have over 12 % Si
  - LOD, LOI, and LECO C (total carbon) determined to approximate SiC content
- Technology employed:
  - Thermo Niton XRF
  - LECO 701 TGA
  - LECO CS 844

Method Correlation



- Pure cordierite and SiC initially blended to test the method
- Quantitative XRD was completed by our R&D analytics group

Conclusions

- Use of this method allows for more efficient operation of an EAF – which increases PGM recovery.
- The method is
  - Accurate – validated with a XRD method,
  - Low cost – uses existing lab equipment,
  - Fast – analysis can be completed within the time it takes to complete an autocatalyst assay.
- Is expected to be used more in the future as more diesel vehicles with DPF's reach end of life.

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