Characterization of combusted syngas contaminants

Serges Tatsinkou & Matthew Cavalli
Department of Mechanical Engineering
John P. Hurley
Energy & Environmental Research Center

The University of North Dakota Grand Forks

EERC

Project Objectives

The objectives are to 1) characterize microcontaminants in combusted syngas and 2) determine their corrosive effects on the mechanical properties of three superalloys (Rene80, CM247LC, and APMT) used for gas turbine parts.

Background & Method

Syngas samples are collected from a combusted syngas created in a pilot-scale gasifier. The University of North Dakota (UND) Energy & Environmental Research Center (EERC) has several pilot-scale gasifiers that are used in a variety of test configurations. Samples analyzed in this work are taken from the entrained-flow gasifier (EFG) shown in Figure 1 and from the fluidized-bed gasifier (FBG). The analysis is aimed to determine what types of trace contaminants may occur in cleaned syngas that could lead to corrosion issues in turbines firing syngas. Once the sampling process is complete, samples are analyzed to determine the nature, the composition and the size distribution of different syngas microcontaminants.

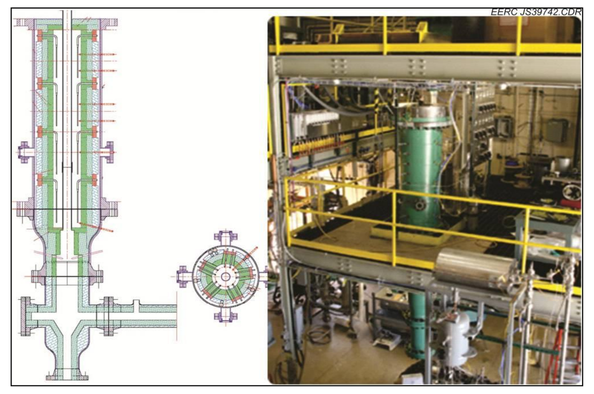

Figure 1: Entrained-flow gasifier

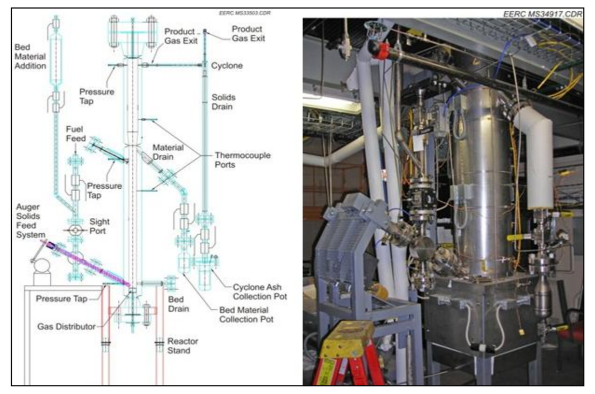

Figure 2: Fluidized-bed gasifier

The EFG fired a blend of Powder River Basin coal and ground wood while the FBG fired the Montana Subbituminous Rosebud coal. During those tests, we collected particulate and trace element samples from the thermal oxidizer used to burn the syngas produced. The sampling train used is shown in Figure 3 and was designed for EPA Methods 29 and 26-A samplings, although the typical glass fiber prefilter was replaced with a Nucleopore polycarbonate membrane filter with etched 0.1-micron-diameter pores.

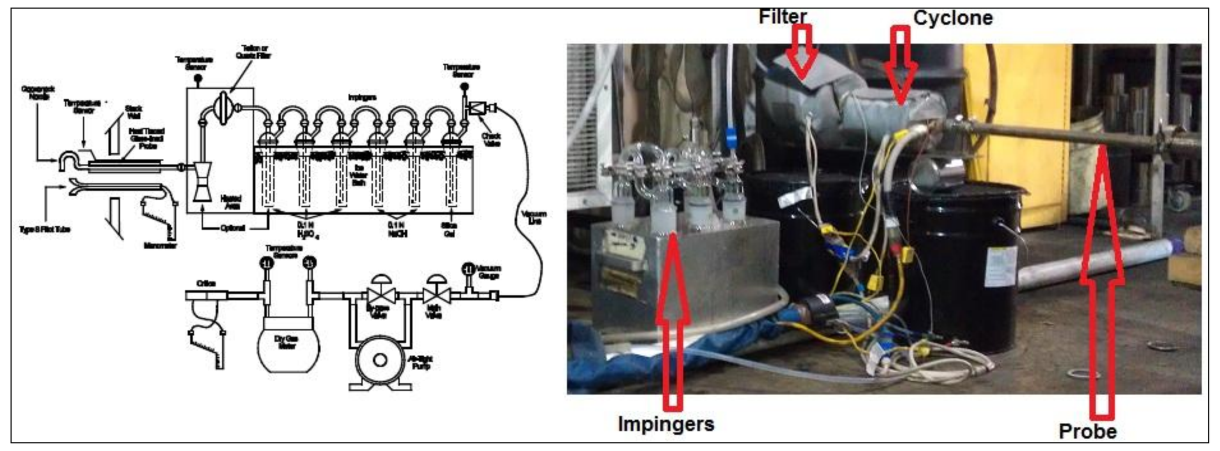

Figure 3: Sampling train used

The thermal oxidizer contains a premixed air-syngas burner at the top of a refractory-lined chamber. The sampling occurs at the bottom of the downfired oxidizer. The gas being sampled is at approximately 750°C and it is quenched as it is pulled through the glass sampling tube to approximately 100°C before reaching the filter. The EFG is a dry-feed, downfired system. The reactor tube is vertically housed in a pressure vessel approximately 24 in. in diameter and 7 ft in length. The EFG fires nominally 8 lb/h of coal and produces up to 20 scfm of fuel gas. The maximum allowable working pressure is 300 psig. The reactor has the capability to run in oxygen- or air-blown mode. The supplemental electrical heating system is capable of reaching a nominal temperature of 1500°C and is separated into four independent zones so that a consistent temperature can be maintained throughout the length of the furnace.

The radially spaced heating elements provide the initial heat for the centrally located alumina reactor tube, and refractory walls outside the heating elements provide insulation. Type S thermocouples are used to monitor and control the temperatures of the heating zones and reactor tube. All of the gasification reactions occur inside the reactor tube, and slag is able to flow on the tube walls. Pressure inside the alumina reactor tube is balanced with a slightly positive N_2 pressure outside. The pressurized FBG (Figure 2) reactor is designed with the capability to operate at 1000 psig at an operational temperature of 843°C , 650 psig at an operational temperature of 917°C , and 300 psig at an operational temperature of 1800°F. It is capable of feeding up to 9.0 kg/hr of pulverized coal or biomass at pressures up to absolute 1000 psig. The externally heated bed is initially charged from an independent hopper with silica sand, but through time the bed converts to coal ash. Independent mass flow controllers meter the flow of nitrogen, oxygen, steam, and recycled syngas into the bottom of the fluid bed. Various safety interlocks prevent the inadvertent flow of pure oxygen into the bed or reverse flow into the coal feeder. Recycled syngas is injected several inches above the bottom distributor plate, which prevents direct combustion of syngas with oxygen entering at the bottom of the bed. Sixteen thermocouple ports are spaced every 4 to 5 inches up the bed to monitor for loss of fluidization, solids agglomeration, and localized combustion zones.

Results & Discussion

The sampling period went from March 2012 to July 2012. Samples were collected on March 27 (natural gas only), March 28 (coal), March 30 (natural gas), April 11 (coal), and April 18 (syngas), July 10 (coal), 2012 respectively. The complete analysis of the April 11 sampling is presented below. For this sampling, a water gas shift reactor was used and the Montana Subbituminous Rosebud coal was fed into the FBG.

Analysis of impinger samples

Impinger solution samples were analyzed by Ion Chromatography (IC) for halides and halogens detection, cold vapor atomic absorption spectrometry (CVAAS) for Hg detection, and inductively coupled plasma mass spectrometry (ICP-MS) for the remaining trace metals. A total of 21 trace metals were found in solution and their respective concentrations are shown in the tables below.

Trace Metal	As	Be	Cd	Co	Cr	Mn	Ni	Pb	Sb	Se	Hg
LLQ (µg/L)	0.5	0.1	0.1	0.5	0.1	0.1	0.2	0.1	0.1	1.0	0.02
Conc.(µg/L)	0.4	0.2	0.2	0.4	8.2	63.80	7.53	0.76	0	1.1	0.99
Conc.(µg/m³)	0.12	0.06	0.06	0.12	2.39	18.58	2.19	0.22	0	0.32	0.29

Trace Metal	K	Mg	Ca	Na	Fe	Ti	V	Mo	Zn	Ge
LLQ (µg/L)	20	20	20	20	20	20	20	20	20	20
Conc.(µg/L)	140	128.8	670.4	243.5	354.6	15.84	0.777	3.959	13.42	1.881

Analysis of filter samples

Filter samples were analyzed by scanning electron microscopy (SEM). A JEOL 5800 SEM equipped with oxford Instruments INCA EDS system and a silicon drift x-ray detector was used. A total of 3089 particles were analyzed and spectra acquired for 20s using a 2-nA beam current at 20-kV accelerating voltage. Fe, S, Cr, Si and some traces of Na, Mg, Al, K, Mn and Ni were found on the filter . Below are presented the SEM images of the filter at different magnifications and the spectral values of five particles choses at random.

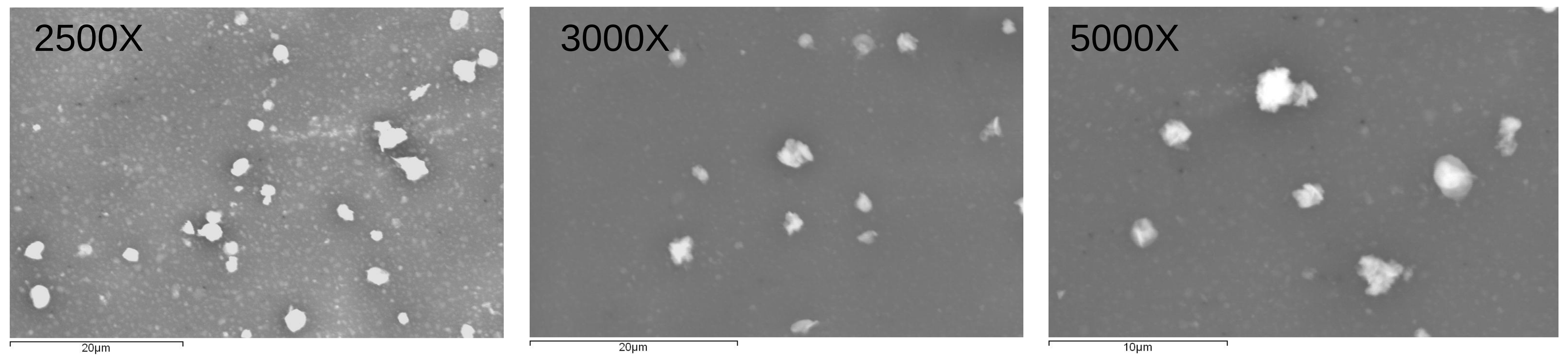

Figure 4: SEM images of the filter particles obtained at different magnifications

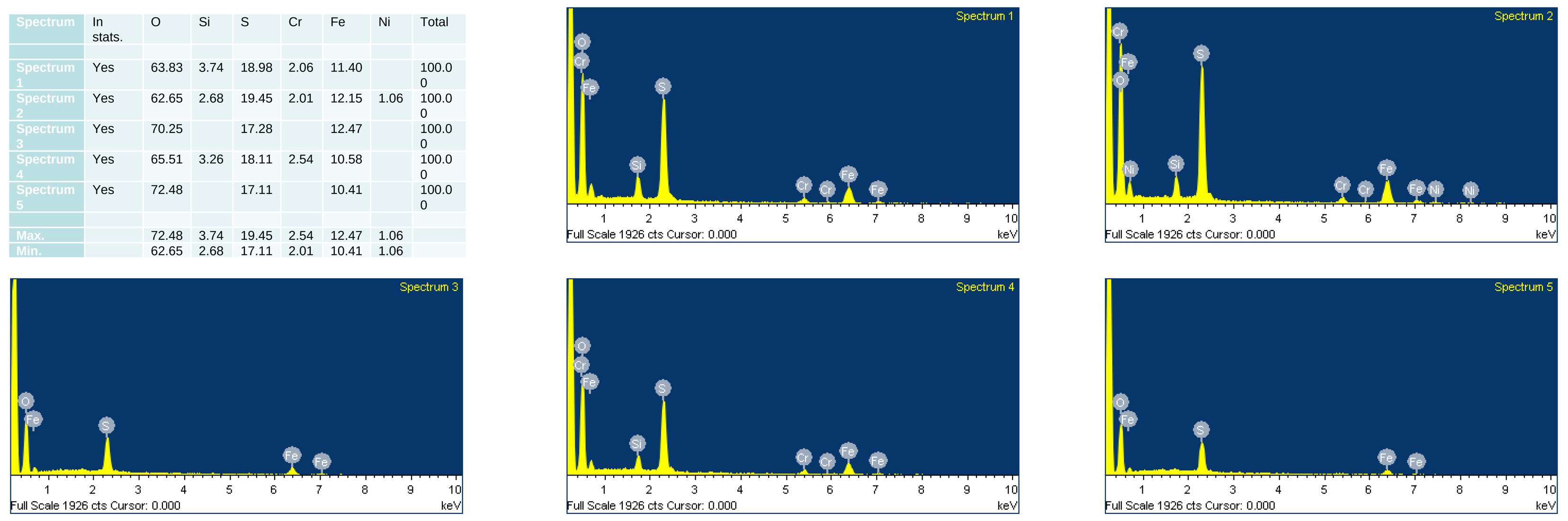

Figure 5: SEM spectral values and peaks of filter particles

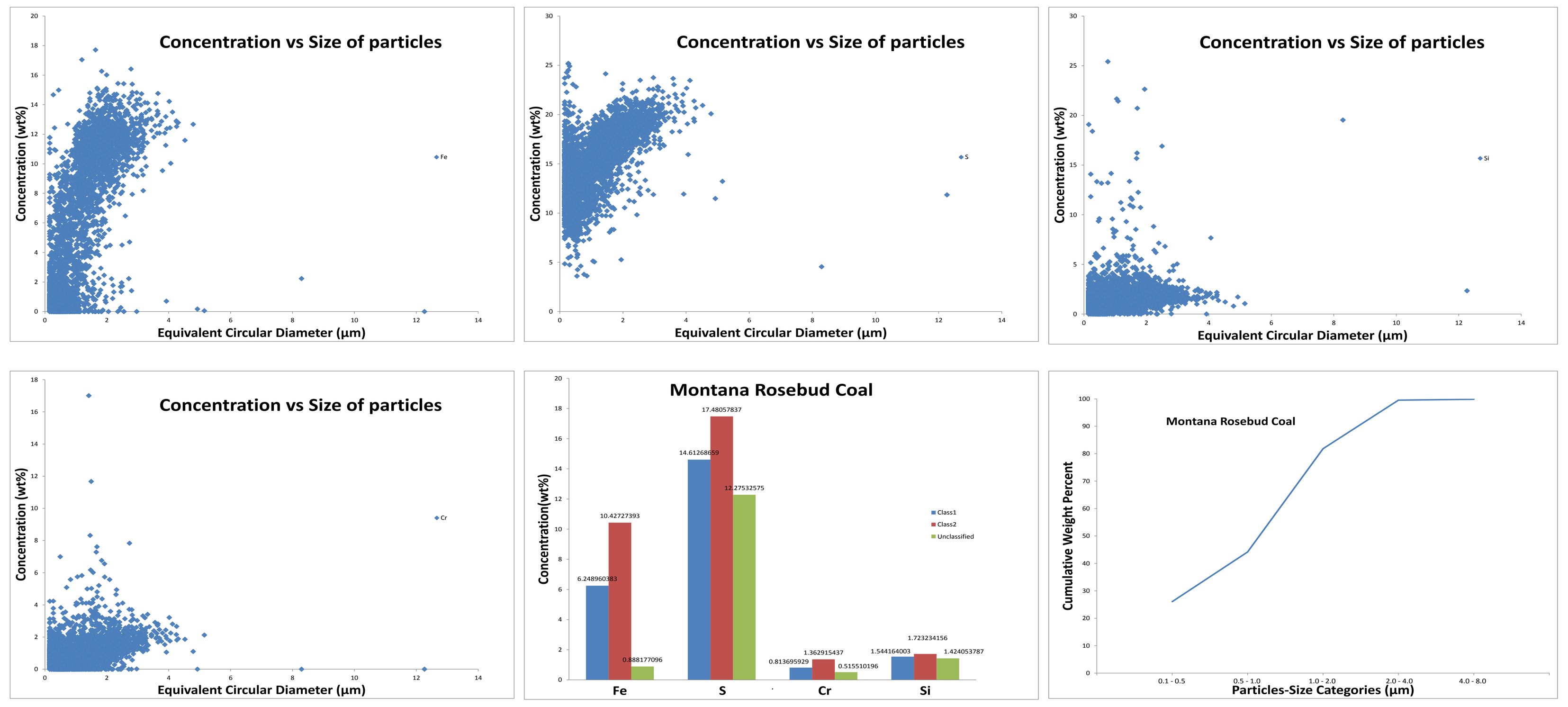

Figure 6: Composition vs Size of the filter particles.

Discussion

It is believed that the high values of Fe, Ni, Mn and Cr, observed on the filter and in solution, come from the interaction of the syngas with the stainless steel pipes used to transport both the coal and the syngas. They probably reached the thermal oxidizer as vapor phase carbonyls formed from the interaction of the CO in the gas stream with the 316L stainless steel tubing in the system. In the thermal oxidizer they were oxidized and reacted with the sulfur in the gas to form some non-stoichiometric sulfate particles.

Conclusion

- Elements such as As, Sb, K, Mg, Ca, Na, Fe, Ti, Mo, Zn, Pb, Ni, Mn, Hg, Se, Cd, Co, Be, Cr were found in impinger solution samples.
- Elements such as Fe, S, Cr, Si and some traces of Na, Ni, Al, Mg, K, Ca, Mn were found on the filter surface.
- Most particles are spherical as the average shape factor is less than 1.2 µm.
- Two chemical classes were detected: class1 which is iron-rich and class2 which is sulfur-rich.

Acknowledgment

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