New Temperature and Metals Emissions Monitoring Technologies for Furnaces

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ABSTRACT

New technologies have been successfully tested for continuous real time monitoring of temperature and hazardous metals emissions in a DC graphite electrode arc furnace that is being evaluated for mixed waste processing. An active millimeter-wave pyrometer with rotatable graphite waveguide/mirror optics inside the furnace has proven to be a robust, spatially resolved temperature monitor of the molten slag and refractory surfaces even during waste feeding operations when dense smoke is present. The active probe beam provides additional information on surface emissivities. A microwave plasma torch constructed of refractory materials has been implemented as part of the furnace exhaust duct up stream of the scrubbers to sample high temperature, $> 500 \, ^\circ\text{C}$, undiluted exhaust gases. It has proven to be a robust gas excitation device for sensitive \textit{in situ} atomic emission spectroscopy (in the part per billion range) of metals entrained in the exhaust emissions.

INTRODUCTION

Cleaning up past pollution and maintaining the quality of our environment has become an important societal goal. As part of this goal new technologies are being sought to cleanup hazardous waste sites and to treat on going waste streams. A 1 MW pilot scale DC graphite electrode plasma arc furnace (Mark II) is being used at the MIT Plasma Fusion Center for studies of waste processing for the DOE Buried Waste Integrated Demonstration (Surma et al. 1993). A key part of this program is the development of new and improved diagnostics to study, monitor, and control the entire waste remediation process for the optimization of this furnace technology and to prevent air pollution. In particular, we have developed new diagnostic technologies for the reliable measurement of internal furnace temperature profiles and for continuous monitoring of hazardous metals emission in the off-gas exhaust.

Accurate temperature measurements inside the hot and dirty furnace environment are a fundamental necessity for controlling the furnace process. However,

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conventional temperature measurement instrumentation is not always adequate. Thermocouples require direct surface contact and are limited to temperatures $< 1700^\circ$C. Infrared pyrometers require clear, direct lines of sight that are frequently unavailable or become obscured during operations. Furthermore, the surface emissivity, which can vary during the process, must be known.

We have developed an active millimeter-wave pyrometer which overcomes all these limitations (Woskov et al. 1995). Pyrometry at millimeter wavelengths has the unique advantage that these wavelengths are long enough to penetrate smoke and visibly obscure coatings on window and mirror surfaces, yet short enough to provide useful spatial resolution. Efficient waveguides and mirrors in this wavelength range can be fabricated from refractory materials such as graphite. Another advantage is that heterodyne receivers used for millimeter-wave pyrometry naturally leak a millimeter-wave beam that can be used for probing surface emissivity.

The second furnace process diagnostic we have developed is for continuous emissions monitoring of hazardous metals in the furnace exhaust gas. Strictly controlling such emissions is an important task because they can pose an unacceptable safety and health risk on local communities and the environment. In order to make such control practical and enforceable, a need exists for continuous emission diagnostics of vapors and particulates in the off gas stream of furnaces. Currently, the Environmental Protection Agency has determined a need for monitoring the emissions of twelve metals (Ag, As, Ba, Be, Cd, Cr, Hg, Ni, Pb, Sb, Se, Tl).

To meet this need we have successfully tested the use of a microwave plasma in the Mark II furnace exhaust stream for atomic emission spectroscopy. Plasmas such as inductively coupled plasmas (ICP) and microwave induced plasmas are in routine use in the laboratory for trace element analysis (Blades et al. 1991). We have adapted a microwave plasma to in situ use on a furnace. The waveguide device, constructed of refractory materials and using fused quartz fiber optics, was located as part of the furnace exhaust duct structure within one meter of the furnace. The exhaust stream was sampled undiluted and at high temperature. Robust microwave plasma performance was observed and real time continuous monitoring of metals emissions was demonstrated during soil loading operations.

**ACTIVE MILLIMETER-WAVE PYROMETER**

The active millimeter-wave pyrometer used a heterodyne receiver with a local oscillator (LO) frequency of 135.4 GHz. Thermal emission was collected in the two sidebands at 133.9 - 135.0 GHz and 135.8 - 136.9 GHz and down shifted to 0.4 - 1.5 GHz for detection. The leaked LO beam was used as the active probe and its detected reflection produced a DC signal. In this wavelength range the radiated thermal power from a surface is linearly related to the surface temperature by the relation:

$$P_s = k_B \Delta f \varepsilon_s T_s$$  \hspace{1cm} (1)
where $k_B$ is Boltzmann’s constant, $\Delta f$ is the frequency bandwidth over which the signal is detected, $\varepsilon_s$ is the surface emissivity, and $T_s$ is the surface temperature. This is in contrast to conventional infrared pyrometers which operate near the peak of the black-body curve and therefore the relationship between emission and temperature can be a high power of temperature, limiting instrument dynamic range.

The present instrument had the capability to make linear temperature measurements over the range from room temperature up to 15,000 °C (limited by the electronics linearity) with a relative temperature resolution of 0.3 °C for signal integration times of one second. Absolute calibration was achieved by using a liquid nitrogen cooled black-body at 77 K (response of this system to relative temperatures hotter or cooler than room temperature is equivalent). It was estimated that the absolute calibration had an accuracy of better than 5% throughout the furnace runs.

Figure 1 illustrates the active pyrometer setup on the Mark II furnace. The temperature measurements are all relative to the room temperature black-body surfaces on the blades of a chopper which periodically block the pyrometer view into the furnace. A lock-in amplifier referenced to the chopper frequency produces this temperature difference signal. The chopper also modulates the reflection signal and another lock-in amplifier detects this modulated DC signal which is proportional to surface reflectivity and round trip losses in the waveguide and mirror. Thus the one pyrometer instrument simultaneously provides at surface emission and surface reflectivity measurement to determine $T_s$ and $\varepsilon_s$.

Figure 1. Active millimeter-wave pyrometer setup on the Mark II furnace.
A 3.8 cm i.d. by 1.23 m long graphite waveguide transmits the pyrometer field-of-view and probe beam into the furnace through the thick refractory wall (Woskov and Titus 1995). This waveguide is sealed with a Teflon window and purged with nitrogen gas flow to prevent burning of the waveguide. A miter graphite mirror on the end of the guide directs the pyrometer view sideways. Rotation of the waveguide allowed complete vertical temperature profiles to be taken with approximately a 5 cm spatial resolution.

**PYROMETER MEASUREMENTS**

At the time of this writing the active millimeter-wave pyrometer was used in six Mark II furnace runs. Table 1 summarizes the length of these runs and the maximum temperatures achieved. The pyrometer was operated 24 hours a day throughout these runs plus an additional two to four day cool down period after furnace shut down. The first four runs were refractory conditioning and furnace shake down runs. In Runs #5 and #6 clean Idaho Falls soil with a 10% mix by weight of calcium carbonate was loaded, melted, and poured. The active millimeter-wave pyrometer performed reliably throughout all these runs. It was used as the primary furnace power control diagnostic.

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Run Length (Days)</th>
<th>Maximum Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>11</td>
<td>960</td>
</tr>
<tr>
<td>#2</td>
<td>10</td>
<td>2200</td>
</tr>
<tr>
<td>#3</td>
<td>5</td>
<td>1450</td>
</tr>
<tr>
<td>#4</td>
<td>1</td>
<td>725</td>
</tr>
<tr>
<td>#5</td>
<td>3</td>
<td>1640</td>
</tr>
<tr>
<td>#6</td>
<td>4</td>
<td>1710</td>
</tr>
</tbody>
</table>

Typical signals from the active millimeter-wave pyrometer are shown in Figure 2. The temperature and reflection signal records are for the 4th day of Run #6 from 1:00 am to 1:00 am the next day. Each signal was recorded once every six seconds. Ten 40 pound bags of soil were fed into the furnace in the middle of this day as shown. The view of the pyrometer was down into the hearth rotated slightly toward the section under the loading port. The decrease in slag surface temperature as each soil bag was dropped in is clearly recorded. However the reflection signal does not show corresponding signal decreases, confirming that the millimeter-wave signals are not significantly affected by the dense smoke present during soil loading.

The pyrometer provided rapid indications of surface temperatures inside the furnace. On a number of occasions, during arcing, rapid temperature rises of hundreds of degrees centigrade on time scales of a few seconds were observed as illustrated by the temperature spike in Figure 2 when the furnace was briefly restarted. Slight changes in arc power and length were observed to control large, rapid swings in surface temperature. The exponential temperature decrease after a rapid upward temperature spike indicates that these are true surface temperatures in a very thin surface layer and not just reflection of millimeter-wave arc emission. Thermocouples
would not only not have the time response to follow such transients, but would be destroyed by the elevated temperatures.

The simultaneous reflection signal provides a wealth of additional information. The detection of the return signal confirms that the pyrometer has a view of the internal furnace surfaces. When viewing a flat surface at normal incidence the surface emissivity can be determined by reflection signal strength. In this way it was observed that the millimeter-wave emissivity of the high alumina content refractory wall surface inside Mark II has decrease from about 0.88 when the surfaces were new to the range of 0.71-0.76 since they have acquired a glass coating. Also, turbulence in the slag melt surface is clearly observed as shown in Figure 2. This turbulence is correlated with temperature, being more rapid a higher temperatures. Note that hours after the arc has been turned off the turbulence continues until the temperature drops below approximately 1000 °C. With more study this could be useful for monitoring the chemistry in the melt.

The ability to make continuous surface profile temperature measurements inside a furnace with one small penetration is another important capability of the millimeter-wave pyrometer. Temperature gradients were found to exist inside the Mark II furnace throughout a run. Profiles taken in Run #5 during arcing and when the furnace was up at melt temperatures are shown in Figure 3. The horizontal axis gives the view direction of the pyrometer where 0° corresponds to looking straight up and 180° to
looking straight down. The trace for day 3 was made after the hearth was filled for the first time. A higher arc voltage made the hearth significantly hotter than the rest of the furnace. The off center appearance of the hot spot in the hearth is most likely due to a slight upward drift in arc voltage during the scan across the hearth which took about 15 to 20 minutes to complete. Overnight the arc voltage was reduced and by next morning the profile scan shows a relatively uniform temperature across the entire melt surface. The furnace in general has also come up to a higher temperature. The capability of the pyrometer to determine the melt surface temperature uniformity was useful to confirm the readiness of the furnace for soil loading.

Figure 3. Temperature profiles inside Mark II at the highest temperatures for Run #5.

MICROWAVE PLASMA CONTINUOUS EMISSIONS MONITOR
The microwave plasma device for atomic emission spectroscopy of the furnace exhaust emissions used a 1.5 kW, 2.45 GHz magnetron source. The main features of the waveguide device, which was mounted to the side of the Mark II furnace exhaust duct, are illustrated in Figure 4. The plasma was induced inside a shorted graphite waveguide which also propagated the microwave power to the plasma from the magnetron. The waveguide internal cross-sectional dimensions were 7.21 x 3.40 cm (WR284 band) with a 3.5 cm diameter hole through the wider sides of the guide 1/4 wavelength back from the short. This hole was lined with a boron nitride tube with an internal diameter of 2.86 cm which confined the plasma and gas flow through the waveguide.
The furnace exhaust stream was intercepted by a 2.86 cm diameter stainless steel tube which was bent into the center of the furnace exhaust duct. The total length of this exhaust pick off tube was 48 cm. A Penberthy jet pump was used as a suction pump down stream of the plasma to insure an adequate gas flow was maintained through the waveguide. The nominal gas flow through the waveguide was in the range $10 - 30$ l/m ($20 - 60$ scfh). After passing through the plasma the exhaust gas was returned to the furnace exhaust duct.

An alumina dielectric tube penetrates the exhaust pick off tube to the waveguide wall, centered in the hole through the guide. The end of this alumina tube provides a thermal source of electrons when heated by the plasma to keep the plasma centered in the gas flow through the guide. This tube also provides a way to introduce a starter and calibration samples into the plasma.

Fused quartz fiber guides with high temperature gold cladding from Fiberguide Industries were used to transmit the plasma light to the spectrometers. These fibers were embedded inside the graphite waveguide wall in an alumina tube and could be readily replaced during furnace operation. The fibers penetrated the boron nitride liner...
so that the fiber ends were in close proximity to the inside wall of the boron nitride tube. The radiated plasma heat and the rapid gas flow kept the viewing ends of these fibers clean. After two days of continuous operation during Run #6, including the soil loading campaign, only one fiber of the three used was observed to have degraded light transmission.

Two spectrometers were used to analyze the plasma light in the 183 - 690 nm wavelength range. A low resolution Ocean Optics Model SD1000 instrument provided complete instantaneous surveys of this entire wavelength range on time scales of less than one second with about 1 nm resolution. High resolution spectra were obtained with a SPEX Model THR-640, 0.64 m Czerny-Turner spectrometer having a 2400 g/mm grating and a 512 silicon diode array from Princeton Instruments. The high resolution spectrometer had a resolution of approximately 0.01 nm and an instantaneous wavelength range of approximately 6.5 nm. Though instantaneous spectra as fast as once every 17 ms could be obtained with the high resolution spectrometer system, data acquisition generally was limited to once every 0.5 seconds during the furnace run to conserve computer storage memory.

Laboratory tests of this microwave plasma device have demonstrated plasma robustness and high sensitivity to trace elements. Using nitrogen as the gas flow medium (nitrogen is the purge gas for Mark II) and SPEX calibration powered mixes inserted directly into the plasma flame, detection limits for the metals: Ag, Ba, Be, Cd, Ni, Sb, Cr, Pb, Hg, and As were determined to range from 0.01 ppb for Ag to 1 ppb for As. In addition, plasma temperatures in the range of 5000 to 6000 K have been spectroscopically determined which is hot enough to vaporize particulates, decompose oxides, and excite all metal species in the exhaust. For example, when refractory zirconium oxide particles were introduced atomic zirconium was observed in the emission spectrum. Therefore, this microwave plasma device promises to be a sensitive and comprehensive monitor for all metals in whatever form or compound that they exist in the furnace exhaust.

EMISSIONS MEASUREMENTS

The continuous microwave emissions plasma monitor was installed as part of the Mark II furnace exhaust duct with the input of the exhaust pick-off pipe about 1 meter back from the inside furnace wall. This pick-off directed undiluted hot furnace exhaust directly into the microwave plasma well up stream of the scrubbers. By sampling up stream of the scrubbers the sensitivity to actual emissions into the air is increased by the efficiency of the scrubbers to remove metals. So far, one furnace test with this microwave device has been conducted, Run #6. The maximum temperature measured with a thermocouple installed on the exhaust pick-off pipe was 660 °C. It was observed that plasma robustness improved with temperature. There was no evidence of the plasma extinguishing with the maximum particulate loadings encountered during soil feeding into Mark II. These initial measurements have established this technology for furnace exhaust emissions monitoring.

A representative exhaust spectrum taken with the high resolution spectrometer just prior to soil loading during Mark II, Run #6 is shown in Figure 5. The spectrometer was tuned to a region of the spectrum where prominent lines of chromium are known to emit. Chromium was the only hazardous metal in the list given above
which was continually present in the furnace emissions of this run. Other metals evident in the furnace emissions just prior to soil loading are manganese and iron. The relative ratios of these metals emissions did evolve during the 48 hour monitoring period as the chemistry of the slag changed. All these metals are present in the original soil fill of the hearth.

These signal levels are not yet absolutely calibrated. A major task that is in progress is to develop a technique to introduce calibration samples into the plasma during furnace operation for in situ calibration. However, preliminary calibrations of this device with well characterized soil dust prior to furnace turn on have approximately reproduced the threshold detection limit for chromium (0.3 ppb for the 359.349 nm transition) established in the laboratory with SPEX powder. Assuming the plasma properties have not changed significantly with temperature, then an order of magnitude estimate for the concentrations corresponding to the chromium signals shown in Figure 5 is in the 3 - 30 ppb range.

Another interesting observation to point out in the spectrum of Figure 5 is for what is not seen. There is no interference from N$_2^+$ or CN molecules which have been observed in the laboratory tests of this device in this wavelength range. This is surprising since Mark II is arcing to graphite electrodes in a nitrogen purge, a condition that would seem likely to create the gas matrix for these interfering species to
be present in the microwave plasma. For whatever reasons, the relatively clean background observed in the emission spectrum of actual furnace exhaust gas suggests that laboratory sensitivities could be achieved in situ.

Figure 6 shows the record of the real time chromium emissions and slag temperature during a 33 minute period of Run #6 when three soil bags were dropped into the hearth. Again the chromium signal levels are shown as relative levels, but the peak levels are estimated to be less than 100 ppb. The chromium emissions first increase rapidly when a soil bag is dropped into the melt followed by a sudden decrease as the slag is cooled slightly by the new soil. There is also bursting and decrease in chromium emissions between bag 2 and 3 which could be related to the assimilation of the first few bags into the slag. This figure demonstrates for the first time a capability for rapid real time monitoring of hazardous metals emissions which could be used for furnace control to minimize air pollution.

Figure 6. Partial time record of chromium emissions and slag temperature in the Mark II furnace during soil loading.

ACKNOWLEDGMENTS

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