Analysis of blockage material at the Sellafield High-Level Waste (HLW) vitrification plant (2011 onwards)

Overview of application

An unknown material had been found to be causing blockages in cell ventilation pipework at the Sellafield High-Level Waste vitrification plant. A sample of this blockage material had been collected within one of the hot cells at the plant and placed inside a “paint can” within the cell and within the viewing region of one of the lead-glass shield windows.

Location:	High-Level Waste Vitrification Plant
Inspection task:	Elemental characterisation of Highly Active materials
Environment:	High Active (HA) Hot Cell (dose rates up to 3,000 Sv/hr). 2-metre thick shield walls, lead-glass shield windows
Location of material:	On floor of hot cell
Access:	Fibre-optic probe umbilical inserted into hot cell via a traversee port in shield wall. Master-Slave Manipulator (MSM) used to position FO-LIBS probe on sample while viewed through lead-glass shield window

FO-LIBS instrument design

This FO-LIBS instrument was of the compact, single-fibre design described earlier in this report. The FO-LIBS instrument (LIBSProbe 100S) was used to analyse a sample of the blockage material and consisted of the following main components:

- A miniature stainless steel LIBS probe of approximate dimensions 24 mm diameter and 80 mm length.
- A 10-metre length of flexible stainless-steel umbilical housing an optical-fibre cable.
- A Q-switched Nd:YAG laser operating at 1064 nm.
- A fibre launching / plasma light collection module.
- A six-channel, time-gated optical spectrometer covering the wavelength range approximately 185 nm to 900 nm with a data gap between approximately 680 nm and 710 nm. Resolving power typically 4,000 (ie. medium resolution)
- A laptop computer for controlling and acquiring data from the six-channel optical spectrometer.
- A 10-litre bottle of high-purity argon for supplying low-pressure (< 5 psi) argon to the LIBS probe.

The probe and connected umbilical were manually inserted into the HA cell via a traversee port in the shield wall. Once the probe entered the cell, a Master-Slave Manipulator (MSM) was used pick up the probe and position it where required. Less than 4 metres of the flexible umbilical entered the traversee port and so there remained approximately 6 metres of umbilical on the outside of the HA cell.

High-Level Waste Vitrification Plant, Sellafield, UK

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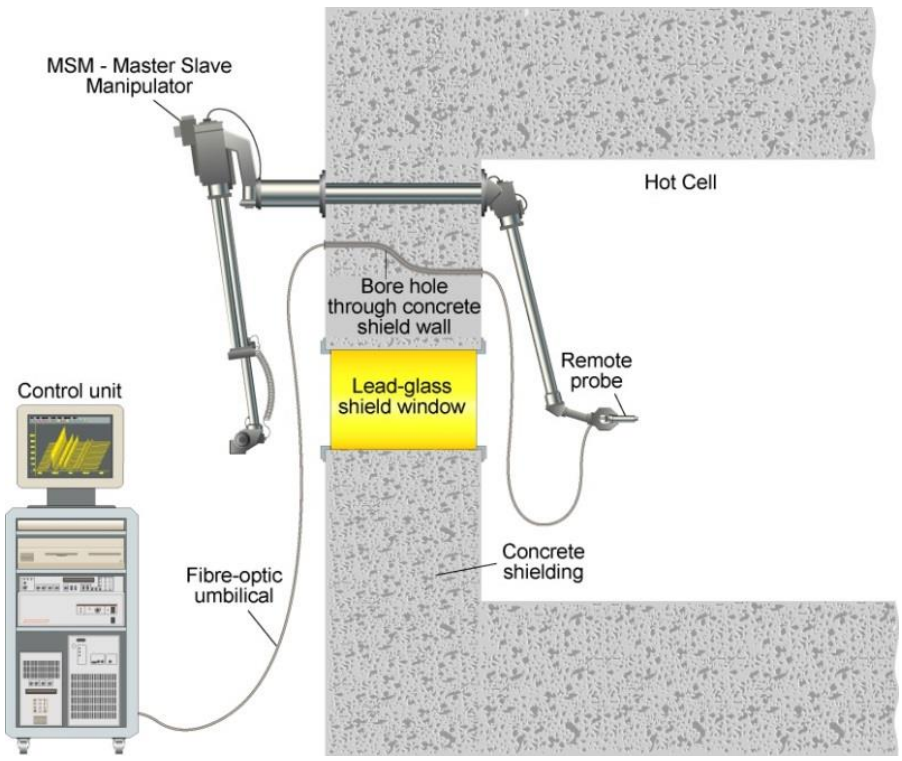

Schematic diagram illustrating the deployment of the FO-LIBS instrument within a hot cell at the HLW Vitrification Plant

Data analysis

The sample of blockage material was located inside a "paint can" inside the HA cell but prior to LIBS analysis the sample was removed from the can and placed on the cell floor in order to facilitate viewing of the sample (through the shield wall window) and positioning of the LIBS probe on the sample surface.

Spectra were recorded from several positions on the sample. Each spectrum was acquired using 100 laser pulses at a pulse repetition rate of 10 Hz. During the last measurement, the laser energy was increased from ~21 mJ to ~25 mJ (as measured at the probe) in order to improve the signal-to-noise ratio of the recorded spectrum. It was this spectrum that was used in the subsequent analysis.

In order to identify the more intense of the numerous emission lines observed in the recorded spectra, the following procedure was adopted. Firstly an initial identification of the emission lines was conducted using a software program called SpecLine by Plasus (www.plasus.de). This software has an extensive database of atomic and ionic emission lines allowing a semi-automated identification of spectral emission lines to be conducted. In addition to the SpecLine database, the NIST database available online (http://physics.nist.gov/PhysRefData/ASD/lines_form.html) was referred to for technetium. The relatively low wavelength resolution of the six-channel optical spectrometer used to record the LIBS spectra made the task of uniquely identifying each emission line rather more difficult since for many lines it was possible to attribute several elements. Reducing the number of candidate elements used in the database search will obviously help matters and so this was done by limiting the elements to those known to exist in relatively high abundance in the process materials (calcine, glass feedstock). After this initial identification was completed, spectra of a number of inactive reference materials (Zr, Mo, Sr, Mg, Al, Si, etc) were analysed using the same type of LIBS instrument used at the plant. The resulting spectra were then compared with the spectra of the active HA sample in order to confirm or deny the presence of that particular reference material subject to the limit-of-detection of the LIBS instrument (ie. typically 1 – 1000 ppm, depending upon the analyte).

It is important to be clear that the fibre-optic LIBS probe instrument used to analyse the active HA sample was not calibrated for quantitative measurements since suitable matrix-matched calibration reference materials were not available. Furthermore, the detection limits for this type of LIBS instrument are typically 1 to 1000 ppm depending upon the element concerned. The relative intensities of the various emission lines together with past experience with interpreting LIBS spectra may be used to provide a rough estimate of the composition of the sample, the caveat being that this approach is not always reliable and so the

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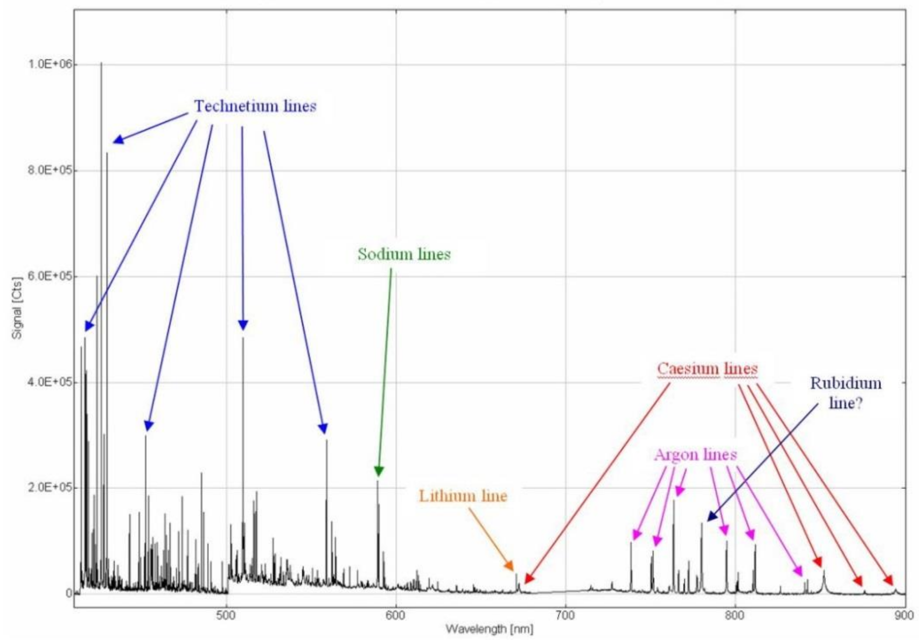
conclusions should be treated with an appropriate degree of caution. With that said, we conclude that the blockage material consists primarily of Cs, Tc and O with other elements such as Li, K, Na, and possibly Rb being detected at lower concentrations. We could not detect Zr, Mo, Al, Mg, Cr, Sr, Si, Fe, Gd. On discussing the matter with the customer a candidate material for the blockage material is caesium pertechnetate (CsO_4Tc) mixed with other materials which include Na, Li and K at levels above the detection limits of the FO-LIBS instrument used.



Example of a spectrum acquired from the blockage material using APL's FO-LIBS instrument

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