# Retention and Emissions of Inorganic Species from a Molten Salt Processing Unit Measured using Laser-Induced Breakdown Spectroscopy


[A]Jaya Kumar P. Patil, [B]Jerry S. Salan, and [A]Steven G. Buckley

[A]Department of Mechanical Engineering, University of Maryland, College Park, MD

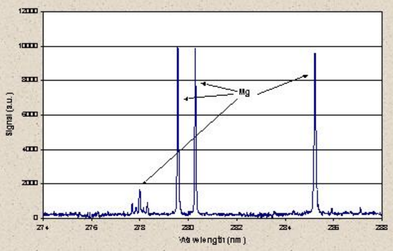
[B]Naval Surface Warfare Center, Indian Head Division, Indian Head, MD



**Abstract**

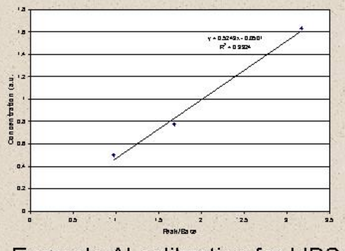
Molten salt oxidation is under consideration as a treatment process for waste and demilitarized propellants, mixed wastes, and hazardous wastes. In this process, a salt such as sodium carbonate is heated above its melting point, and the waste is introduced into the molten salt bath, where it oxidizes. Benefits to this technology include the high thermal mass of the salt, which enhances the stability of the oxidation process in comparison with traditional combustion processes, the controllable residence time in the salt bath, and the chemical and physical characteristics of the salt. Salts such as sodium carbonate tend to bind chlorine ($Na_2CO_3$ + 2Cl => 2NaCl + $CO_2$ + 0.5$O_2$), significantly reducing acid gas emissions. In addition, the high surface area of the bubbles formed during the oxidation process may trap particulate matter, reducing particulate and toxic metal emissions.

This investigation focuses capture of inorganic material from metal-containing waste in a laboratory scale molten salt reactor. Mg and Al are injected into the reactor to assess their retention in the salt. The retention of metals in the salt is assessed using Laser-Induced Breakdown Spectroscopy (LIBS), an analytical technique that can measure many toxic metals at the parts-per-billion level. In addition, using LIBS we assess the impact of salt vaporization / mobilization as a loss mechanism for salt in these reactors.

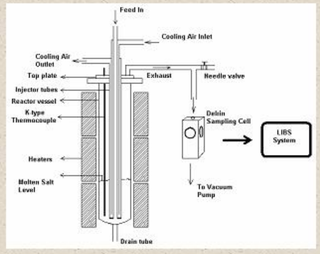




**200-shot average LIBS signal showing Mg peaks corresponding to 3.25 mg/m$^3$.**

**Calibration**: LIBS systems exhibit a linear calibration for all species investigated. Limits of detection are defined as three times the signal-to-noise value determined from the RMS fluctuation in the respective spectra.




Example Al calibration for LIBS



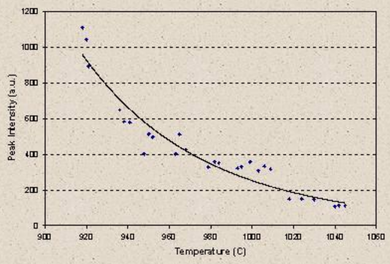

Experimental Setup:

The MSO reactor vessel is a 3.5 inch OD, 3 inch ID and 3 foot long circular cylinder, with a tapered base plate welded on the bottom. This base plate has a ½-inch NPT port, to which is affixed a 6-inch long drain tube. The top of the vessel is an approximately 15-lb detachable plate with a sealing groove but no hard seal, designed to prevent overpressure of the reactor by simply lifting up freely. In the center of this plate is a 0.75 inch through hole for the air-cooled injector. Additional ports on the center plate are used for a pressure transducer, a ¼-inch type-K shielded thermocouple for measurement of the molten salt bath temperature, and a gas sample port. The entire reactor is supported on a Unistrut frame, enclosed by steel doors, and has secondary containment to protect the laboratory and the operator(s) from any potential spill of molten salt.

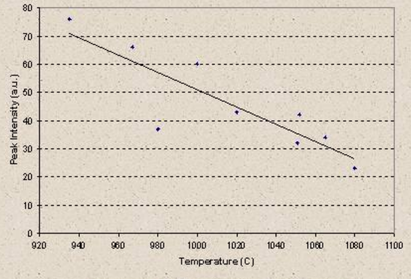
The entire reactor is constructed of Inconel 600, a chromium-nickel alloy, to withstand both high temperatures (900 - 1100 °C) and chorine attack. The high nickel content of the alloy provides considerable resistance under reducing conditions and makes it resistant to corrosion by a number of organic and inorganic compounds.

Sierra Instruments Mass-Trak™ flow controllers are used to control the reactor air flow and the cooling air to the injector. Liquid solutions were fed using a calibrated syringe pump, and metal solutions may also be introduced using a standard medical nebulizer to create an aerosol. The reactor operation is entirely controlled using an in-house program written in National Instruments' LABVIEW™ software. A schematic of the reactor is shown in Figure 1.

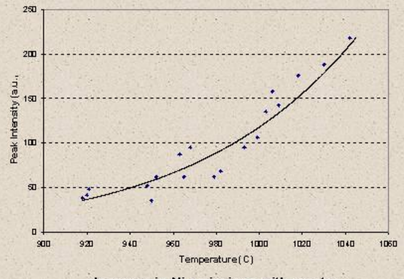
Analysis of gas-phase products was performed with a Bio-Rad Excalibur Fourier Transform Infra-Red (FTIR) spectrometer at 0.1 cm$^{-1}$ resolution. This was coupled to a ½-liter long path gas cell (Infrared Analysis) configured for 1.2-meter (4-pass) operation. Samples were transferred from the MSO reactor to the cell in a heated line. Elemental analysis of reaction products was performed using an in-house Laser-Induced Breakdown Spectroscopy (LIBS) unit, consisting of a Quantel Brilliant Nd:YAG laser (up to 300 mJ / pulse, operated at 1064 nm), a Multichannel Instruments echelle spectrometer (Mechelle 7500), and transfer optics. Samples were sampled from the MSO unit through heated sample lines, and interrogated in a Delrin flow cell.



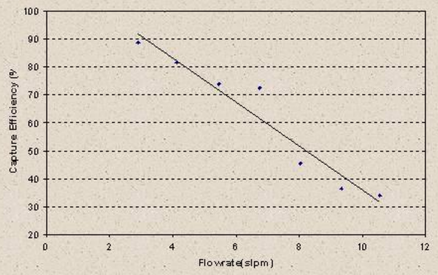

**Decrease in Mg emissions with reactor temperature at a fixed flow rate and a constant injection rate.**



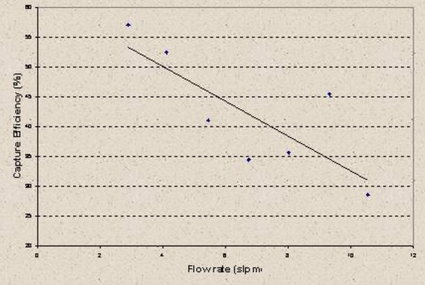

**Decrease in Zn emissions with reactor temperature at a fixed flow rate and a constant injection rate.**




**Increase in Ni emissions with reactor temperature at a fixed flow rate and a constant injection rate.**



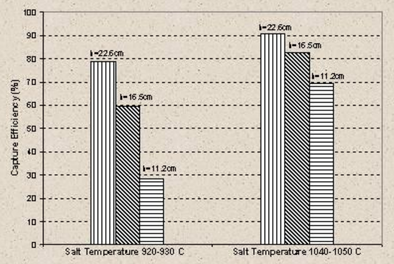

**Al Capture Efficiencies vs. Flow rate at h=22.6 cm, T= 1040-1050 ºC**

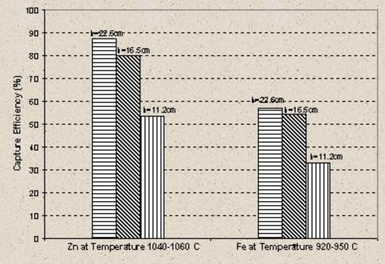



**Fe Capture Efficiencies vs. Flow rate at h=22.6 cm, T= 930 ºC**

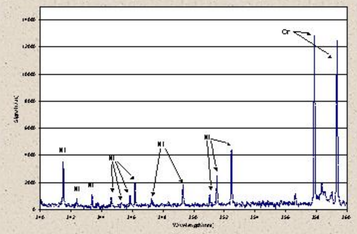
**Inorganic Measurement Results Using LIBS**: LIBS has been used to quantify capture and emissions of several inorganic species in the MSO reactor. Averaged LIBS spectra were acquired at known reactor conditions with metal-containing aerosol injected into the reactor. Capture efficiencies were quantified on the basis of percent of input feed. In all cases the feed amount was very low (parts-per-million by mass) and the quantities of any metal captured in the salt remained extremely dilute. Decreases in emissions of injected aerosols with increasing reactor temperature point to variations in surface characteristics of the MSO interface with increasing temperature.

Several other elements were routinely observed in the MSO reactor exhaust. The $Na_2CO_3$ salt begins to decompose into $Na_2O$ between 1000 and 1050 °C. At even lower temperatures there is still significant Na emission, as for example NaCl has a vapor pressure of 83 ppm at 1000 °C. Averaged measurements of sodium concentration during steady reactor operation revealed outlet concentrations of 8.1 mg/m$^3$ at 973 °C, and 10.0 mg/m$^3$ at 1045°C. However, of more concern than Na emissions were the Cr and Ni (and Fe) emissions that were observed due to decomposition of the Inconel 600 alloy of which the reactor is constructed. The figure above (right) illustrates spectra of Ni. The estimated peak Cr concentration in the effluent is 17.5 mg/m$^3$, and the estimated Ni concentration is 6.5 mg/m$^3$, with the reactor at 1020 °C.




**Capture efficiency as a function of salt bed height for Mg (left figure), Zr and Fe (right figure). Trends for other metals were the same.**




**Ni and Cr emissions from decomposition of the Inconel reactor suggests that materials choice for MSO reactors is very important.**

**Discussion and Conclusions**

This study, in conjunction with a parallel study of MSO reactor performance, has suggested the need for detailed studies of emissions for specific applications of MSO. Traditional reactor parameters such as temperature and superficial velocity may not be sufficient for predicting metals capture. In this study, injection of metal aerosols provided a worst-case scenario of metal emissions from an MSO reactor. Typical waste feeds such as energetic materials have metals embedded in the material, hence capture is more likely.

In terms of metals capture, several trends are noted. First, some metals, such as Mg, Al, and Zn exhibit decreasing emissions with increasing reactor temperature. In addition, lower carrier gas flow rates and greater salt bed heights contributed to decreasing emissions for all metals studied.

However, metals associated with reactor construction, Fe, Ni, and Cr, all exhibit increasing emissions with increasing reactor temperatures. Inconel leached Cr and Ni into the salt in measureable quantities, and were emitted at 17.5 mg/m$^3$ and 6.5 mg/m$^3$, respectively. This points to decomposition of the reactor, even at temperatures (900 ºC) typically considered acceptable for MSO reactor operation. As Ni and Cr are toxic metals, this emission rate would be a cause for concern. In addition, Na from the salt was emitted at measurable levels. The potential for capturing toxic or radioactive metals in the salt for future disposal at a hazardous waste landfill remains attractive, but it is clear that for each inorganic component of waste, study must be performed to determine the conditions leading to sufficient capture of inorganics.