OPTICAL DIAGNOSTICS OF METALS IN HIGH TEMPERATURE ENVIRONMENTS

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Preface

The documentation is the demonstration of many years of study and submitted for the award of the Doctoral of Philosophy. The topic of research is "Optical Diagnostics of Metals in High Temperature Environments". Alkali metals released from combustion of solid-fuel particles (Loy Yang Brown coal and pine wood) in premixed methane flat flame and iron in the plasma cloud generated by gas tungsten arc welding were investigated using optical diagnostic techniques. The consumption of renewable energy resources increasingly grows owing to the issues of global climate change and rapidly diminishing reserves of energy resources. Understanding of alkali metals released during combustion is important for the industrial interests to maintain and to improve the equipment for power generation. To apply the comprehensive laser diagnostic techniques extensively in extreme environments, the studying of iron in the welding plasma could favour the understanding of dynamic chemistry and the dispersion of chemical species in the plasma fumes.

The intention of this work is to assess techniques enabling the quantitative measure of sodium (Na) and potassium (K) released during the different stages of solid-fuel combustion so that industrial concerns can be satisfied. An understanding of the behaviour of iron (Fe) in atmospheric plasma would help reduce the hazard that it poses to operators.

Li-Jen Hsu

Declaration

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Abstract

The thesis presents results for the detection of metal species in high temperature environments using optical techniques. Three optical techniques, namely laser Polarisation Spectroscopy (PS), Atomic Emission Spectroscopy (AES) and Laser-Induced Breakdown Spectroscopy (LIBS) have been employed. Each technique possesses some unique characteristics to achieve the aims of this work.

The PS technique has been employed to detect atomic sodium (Na) in the seeded flames and plume of burning solid-fuel particles and to investigate atomic iron (Fe) in the welding fume plume. A mathematical equation has been developed to describe the lineshape of the target metal using PS technique in the high temperature environments, as follows:

$$I_{PS\_FIT}(\omega) = I_{baseline} + I_{PS} \times \left\{ \cfrac{1}{1 + \left[\cfrac{2 \times (\Delta\omega - \Delta\omega_{shift})}{\Delta\omega_{PS}} \right]^2} \right\}^n \times exp \left[\cfrac{-\alpha_0 \cdot L_{abs}}{1 + \left(\cfrac{2 \times \Delta\omega}{\Delta\omega_{abs}} \right)^2} \right]$$

Eq. 3-5

The capability of PS technique employed for the quantitative measurement has been assessed. Due to the nonlinear measurement, the quantitative measurement using PS is not applicable in this work. In particular, the atomic Na released from burning solid-fuel particles. However, the qualitative analysis of atomic Na and Fe has been demonstrated. The time-resolved records of atomic Na released from the burning solid-fuel particles and the Stark shift of atomic Fe in the welding fume have been observed.

The AES technique has been used to record the temporal atomic Na and K released from burning solid-fuel particles. The qualitative analysis of the simultaneous release of atomic Na

and K using AES has been demonstrated. However, the quantitative analysis is not applicable in the present experimental arrangement. The temporal records of atomic Na and K were associated with the instantaneous shrinkage of burning solid-fuel particles. This implies that the release of atomic Na and K is related to the burning particle size. It was observed that the peak release of atomic Na and K released from the burning solid-fuel particles occurred at the end of char phase simultaneously.

The quantitative measurement of atomic Na and K released from burning solid-fuel particles using LIBS has been achieved. The time-resolved histories of atomic Na and K released from burning solid-fuel particles are consistent with those measured using PS and AES. Unlike conventional quantitative measurement using LIBS, a particular absorption, termed as signal trapping to the calibration process, caused by the atomic Na or K in the outer seeded flames has been indentified.

The overall comparison among three optical techniques summarizes the advantages and disadvantages of the metal detection in high temperature environments. The PS technique is capable of being applied to detect metal species in strong background environments. The AES possesses the capability of multi-element detection in flames with the characteristics of low cost, good sensitivity and simple experimental arrangement. However, the quantitative analysis of target metal species is not eligible for both techniques. The LIBS technique demonstrates the quantitative analysis with an appropriate calibration curve.

Nomenclature

A	Pre-factor (experimentally determined), 1/concentration
	Empirical Pre-factor Coefficient, dimensionless
AFR_{exp}	Experimental AFR, dimensionless
AFR_{stoi}	Stoichiometric AFR, dimensionless
A_{21}	Spontaneous Emission, s^{-1}
A_r	Surface Area of a Sphere, m^2
a_1	Pre-factor, 1/concentration
a_2	Pre-factor Constant, dimensionless
a_m	Molar Ratio, dimensionless
B_{12}/B_{21}	Einstein Coefficient of Absorption / Stimulated Emission, $m^3 \cdot J^{-1} \cdot s^{-2}$
b	Absorption Coefficient, dimensionless
c	Specific Heat, $J \cdot kg^{-1} \cdot K^{-1}$
	Light Speed, $m \cdot s^{-1}$
C_s	Concentration of Alkali Salt, $g \cdot L^{-1}$
$C_{species}$	Concentration of Atomic Na or K in the flame, ppm
C_{Na}	Concentration of Na, ppm
C_K	Concentration of K, ppm
D_0	Diameter of Pump Beam, m
D_P	Diameter of Focused Pump Beam, m
D_{SD}	Diameter of Nebulised Salt Droplet, μm
ΔE	Energy Difference between Two Allowable Transition States, J
E_{BS}	Systematic Error Caused by Beam Steering, dimensionless
$F_{pump\text{-}probe\_geometry}(\gamma, \chi)$	Dependence of the I_{PS} on the Geometrical Polarisation Status of the

Probe and Probe Beams

f_B	Boltzmann Fraction of Target Species, dimensionless
f_i	Boltzmann Distribution at the Energy State i, dimensionless
f_L	Focal Length of a Lens, mm
$G(\omega)$	Normalized Lineshape of the Target Species Absorption Function, dimensionless
g_i	Degeneracy of Energy State i, dimensionless
h	Planck's Constant (= 6.626×10^{-34}), J·s
	Surface Convection Coefficient, W·K^{-1}·m^{-2}
$\hbar$	Planck's Constant Divided by 2π, J·s
I_{abs}	Intensity of Absorption in PS Measurement, arbitrary unit
$I_{baseline}$	Intensity of Background in PS Measurement, arbitrary unit
I_{exp}	Experimental Radiation Intensity of Atomic Na or K, arbitrary unit
I_{act}	Actual Radiation Intensity of Atomic Na or K, arbitrary unit
I_{PS}	Intensity of PS Signal, arbitrary unit
I_{LIBS}	Intensity of Radiation using LIBS, dimensionless
$I_{PS\_FIT}(\omega)$	Simulation of PS Lineshape
I_{probe}	Intensity of Probe Beam in PS, arbitrary unit
I_{pump}	Intensity of Pump Beam in PS, arbitrary unit
$k \,/\, k_p$	Thermal Conductivity Coefficient, W·K^{-1}·m^{-1}
k	Boltzmann Constant, J·K^{-1}
$[\text{K}]_{total}$	Total Concentration of K, ppm
$[\text{K}]_{total}^{max}$	Maximum Concentration of total K, ppm
L_{PS}	Probe Beam Path, m
M	Molar Mass, g·mol^{-1}
ml$_\text{n}$	Normal Litre per Minute, L/min

$Mole_{oxy}$	Molar Ratio of Fed Oxidizer, mol
$Mole_{fuel}$	Molar Ratio of Fed Fuel, mol
$Mass_{oxy}$	Mass of Fed Oxidizer, g
$Mass_{fuel}$	Mass of Fed Fuel, g
$Mole_{stoi\text{-}oxy}$	Stoichiometric Molar Ratio of Oxidizer, dimensionless
$Mole_{stoi\text{-}fuel}$	Stoichiometric Molar Ratio of Fuel, dimensionless
$Mole_{exp\text{-}oxy}$	Experimental Molar Ratio of Oxidizer, dimensionless
$Mole_{exp\text{-}fuel}$	Experimental Molar Ratio of Fuel, dimensionless
$N_{species}$	Population of Target Species, atom·m^{-3}
n	Refractive Index, dimensionless
	Power of a Lorentzian function, dimensionless
	(3: Lorentzian-cubed; 1: Lorentzian)
n_s	Number Density of Target Species, atoms·m^{-3}
$[Na]_{total}$	Total Concentration of Na, ppm
$[Na]_{total}^{max}$	Maximum Concentration of total Na, ppm
P	Atmospheric Pressure, atm
Q	Hear Transfer, J
q	Partition Function, dimensionless
r	Radial Distance, m
r_c	Radii of Unconsumed Core, m
R	Radius of a Virgin Particle, m
	Gas Constant, J·g^{-1}·mol^{-1}·K^{-1}
$R_{K/Na}$	Release Ratio of K-to-Na, dimensionless
R_{coal}	First Order Reaction Rate of coal, s^{-1}
$R_{K\_char/de}$	Ratio of Peak Intensities of Atomic K at the Char and Devolatilisation Phases using AES, dimensionless
$R_{K\_total\_char/de}$	Ratio of Peak Intensities of Atomic K at the Char and

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Devolatilisation Phases using Quantitative LIBS, dimensionless

$R_{Na\_char/de}$	Ratio of Peak Intensities of Atomic Na at the Char and Devolatilisation Phases using AES, dimensionless
$R_{Na\_total\_char/de}$	Ratio of Peak Intensities of Atomic Na at the Char and Devolatilisation Phases using quantitative LIBS, dimensionless
S	Slope of Calibration Curve of LIBS Measurement, dimensionless
T	Local Particle Temperature, K
ΔT	Temperature Variation between Two Locations, K
T_0	Initial Particle Temperature, K
T_c	Temperature at Core Surface, K
T_f	Flame Temperature, K
T_g	Gas Temperature, K
T_P	Temperature of Coal Particle, K
T_s	Temperature at Particle Surface, K
T_r	Room Temperature, K (298 K)
υ_a	Air Flowrate, $L \cdot s^{-1}$
υ_f	Total Gas Flowrate, $L \cdot s^{-1}$
υ_g	Methane Flowrate, $L \cdot s^{-1}$
υ_m	Mass flowrate of seeding salt solution, $g \cdot s^{-1}$
υ_{mf}	Molar Flowrate of Total Gas, $mol \cdot s^{-1}$
υ_{ms}	Molar flowrate of seeded salt in the flame, $mol \cdot s^{-1}$
υ_s	Consumption Rate of Salt Solution, $L \cdot s^{-1}$
Δx	Shrinking Layer, m
x	Absorption Length, m
$[X]_{species}$	Concentration of target species, $atom \cdot m^{-3}$ or ppm

Greek Letters

Φ	Equivalence Ratio, dimensionless
$\alpha(\omega)$	Absorption Coefficient at Angular Frequency, m^{-1}
$\Delta\alpha_0(\omega)$	Induced Dichroism
$\sigma_a(\omega)$	Absorption Cross-Section at angular frequency, m^2
$\sigma_{J_f \leftarrow J_i}$	Absorption Cross-Section from the Initial to Final Rotational State, J
σ	Stefan-Boltzmann Constant, $W \cdot K^{-2} \cdot m^{-2}$
	Mean Relative Standard Deviation, dimensionless
θ	Angular Offset of the Two Polarisers, radians
λ	Wavelength, nm
ϕ	Phase of the Wave ($= k \cdot L_{PS}$)
δ	FWHM of the Lineshape of Wavelength Scan Measurement, cm^{-1}
ξ	Fractional Light Leakage, dimensionless
ρ	Particle Solid Density, $kg \cdot m^{-3}$
γ	Angle between the Polarisation Axis of the Probe Beam and the Vertical Axis, radians
κ	An Integral Constant, dimensionless
χ	Angle between the Pump and Probe Beam in the Horizontal Plane, Radians
$\zeta_{J_f \leftarrow J_i}$	Polarisation Dependent Numerical Factor, dimensionless
τ_{pump}	Laser Pulse Duration, ns
τ_d	Duration of the Devolatilisation Phase, *sec*
τ_c	Duration of the Char Phase, *sec*
τ_a	Duration of the Ash Cooking Phase, *sec*
ω_{12}/ω_{21}	Angular Frequency of the Transition, s^{-1}
ω	Chosen Angular Frequency, cm^{-1}
ω_0	Transition of Target Species, cm^{-1}

$\Delta\omega_{abs}$	FWHM of Absorption, cm^{-1}
$\Delta\omega_{collision}$	Collisional Broadening, cm^{-1}
$\Delta\omega^H$	Homogenous Line Broadening, cm^{-1}
$\Delta\omega_n$	Natural Linewidth, cm^{-1}
$\Delta\omega_{PS}$	FWHM of PS Signal, cm^{-1}
$\Delta\omega_{self}$	Self-broadening, cm^{-1}
ν	Frequency of Radiation, Hz
ε	Emissivity, dimensionless
	Ratio between Atomic Species and Total Amount of the Species, dimensionless
ψ	Surface Tension of Liquid, Water in This Work, $mN{\cdot}m^{-1}$
Λ	Total Electronic Orbital Angular Momentum Quantum Number
$\Sigma, \Pi, \Delta, \Phi$	Electronic Energy State corresponding to Λ = 0, 1, 2, 3, dimensionless

Subscripts

0	initial
a	air, area
abs	absorption
act	actual
c	core
$cone$	effective volume of the cone shape
exp	experimental
f	flame
g	gas
m	molar

max   maximum

probe   probe beam

PS   Polarisation Spectroscopy

pump   pump beam

r   room

s   salt

species   target species, such Na, K or Fe

total   total

Acronym

AES	Atomic Emission Spectroscopy
AFR	Air-Fuel Ratio
CNT	Carbon Nanotube
EDX or EDS	Energy-Dispersive X-Ray Spectroscopy
FTIR	Fourier Transform Infrared spectrometry
FWHM	Full Width at Half Maximum
GTAW	Gas Tungsten Arc Welding
HDP	High Density Plasma
HV	Heating Value
ICCD	Intensified Charge-Coupled Device
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
LIBS	Laser-Induced Breakdown Spectroscopy
LIPS	Laser-Induced Plasma Spectroscopy
LOD	Limit of Detection
IRPS	Infrared PS
IRLIF	Infrared LIF
LTE	Local Thermodynamic Equilibrium
MFC	Mass Flow Controller
MS	Mass Spectroscopy
ND filter	Neutral Density filter
NMR	Nuclear Magnetic Resonance
PLIF	Planar Laser-Induced Fluorescence
PS	Polarisation Spectroscopy

ppm	Part per Million
ppb	Part per Billion
SAES	Simultaneous Atomic Emission Spectroscopy
SEM	Scanning Electron Microscopy
SNR	Signal-to-Noise Ratio
TGA	Thermogravimetric Analysis
XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction

Chemical Expression

Element

Aluminium	Al
Barium	Ba
Beryllium	Be
Carbon	C
Calcium	Ca
Chlorine	Cl
Chromium	Cr
Copper	Cu
Fluorine	F
Hydrogen	H
Iron	Fe
Lead	Pb
Manganese	Mn
Nickel	Ni
Nitrogen	N
Oxygen	O
Potassium	K

Silicon	Si
Sodium	Na
Strontium	Sr
Sulfur	S

Compounds

Acetylene	C_2H_2
Ammonia	NH_3
Carbon Radical	C_2
Carbon Monoxide	CO
Carbon Dioxide	CO_2
Cyanide	CN
Methylidyne	CH
Ethane	C_2H_6
Formaldehyde	H_2CO
Hydrogen Cyanide	HCN
Hydroxyl Radical	OH
Methane	CH_4
Methyl	CH_3
Nitrogen Monohydride	NH
Nitric Acid	HNO_3
Nitric Oxide	NO
Nitrogen Oxides	NO_x
Potassium Chloride	KCl
Potassium Sulphate	K_2SO_4
Sodium Chloride	$NaCl$
Sodium sulphite	Na_2SO_3

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