Detection of rare earth elements in Powder River Basin sub-bituminous coal ash using laser-induced breakdown spectroscopy (LIBS)

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Abstract

We reported our preliminary results on the use of laser-induced breakdown spectroscopy to analyze the rare earth elements contained in ash samples from Powder River Basin sub-bituminous coal (PRB-coal). We have identified many elements in the Lanthanide series (cerium, europium, holmium, lanthanum, lutetium, praseodymium, promethium, samarium, terbium, ytterbium) and some elements in the actinide series (actinium, thorium, uranium, plutonium, berkelium, californium) in the ash samples. In addition, various metals were also seen to present in the ash samples.

Key words: Rare earth elements, LIBS, coal ash

Introduction

Rare earth elements are the chemical elements in group 3 of the periodic table. They are grouped into two series: the Lanthanide series (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium) and the Actinide series (Actinium, Thorium, Protactinium, Uranium, Neptunium, Plutonium, Americium Curium, Berkelium, Californium, Einsteinium, Fermium, Fm, Mendelevium, Nobelium, Lawrencium). Due to their unique magnetic, phosphorescent, and catalytic properties, these elements are the critical and irreplaceable materials in modern technologies (TVs, cellular phones, computers, permanent magnet motors for wind turbines and disk drives, hybrid car batteries, compact fluorescent lighting, catalysts for refining heavier crude oil, automobile catalytic converters, etc.).

Traditionally, rare-earth elements are extracted from natural mineral deposits (carbonatite and weather-cut elution-deposited ores). Recently, however, it has been reported that many rare earth elements were found in coal samples from certain regions in Germany and in the United Sates [1-5] in Bulgaria [6], in Bangladesh [7], and in United Kingdom and Poland [8]. Since the combustion of coal for energy generation results in highly concentrated non-volatile minerals in the coal ash wastes, the concentrations of rare-earth elements in coal ash could be enriched up to within the range of mineral ore deposits [1, 4, 8, 9]. For example, as reported by Seredin and Dai [1], Mayfield and Lewis [9] the total rare earth concentrations in a Kentucky coal were about 54.9 mg/kg while in coal ash from a Kentucky power plant they were from 1312.6 – 1667 mg/kg in fly ash and 1202.5 mg/kg in bottom ash. Zhang et al. [4] reported that germanium content in Illinois coal from 4 to 42 ppm and it was enriched to 1810 ppm in fly ash. Therefore, it is necessary to analyze rare earth concentrations in ash wastes produced from coal power plants in order for identifying and evaluating the ash sources that are viable for rare earth recovery.

For that reason, we report in this short communication our preliminary results on the characterization of various elements in ash samples produced from Powder River Basin sub-bituminous coal. Many techniques such as X-ray fluorescence (XRF) [4], inductively coupled plasma–mass spectrometry (ICP-MS) [4], neutron activation [6], and LIBS [7, 10-15] have been used for coal and coal ash elemental composition analysis. We, however, use the LIBS technique because this is the fast, simple, reagent-free, low-ppm level detection technique for many different situations. The LIBS technique also provide better data correlations [15] and has an important advantage in that the neutron activation method, because it requires a strong radioactive/neutron source, is bulky and presents potential health hazards [7, 10, 15].

Experiment

For this work, rare earth elements content in sub-bituminous coal from Powder River Basin and its ash are spectroscopically characterized using the LIBS technique. Small coal pellets of 10 mm in diameter and about 2.5 mm thick were made for our LIBS measurements. To do so, we first ground the supplied coal powder and shook it through a 150 μm sieving machine. Each pellet was made by pouring about 1.5 g of the prepared powder into a pellet die and compressed with a pressure of 15000 psi for 5 minutes. Ash samples were prepared by drying, devolatilizing and burning the prepared coal powders in a TGA (Leco TGA-601). The drying and devolatilization processes were carried out under N_2 atmosphere at 107 ^oC and 950 ^oC, respectively. The devolatilized samples were cooled to 600 ^oC then burned at 750^oC under air environment until the weight of the remaining ash became unchanged indicating that all the moisture content in the coal has been removed and all the volatile gases and fix carbon have been completely burned. The resulting ash was cooled down, collected and stored in a desiccator. Ash pellets were prepared using the same procedure described above.

The LIBS apparatus is shown in Fig.1. It consists mainly of a laser system, a spectrometer unit, a beam-delivery optics, and a sample holder. The laser system uses a single-mode, Q-switched Nd-Yag laser that is able to produce a laser pulse up to 100 mJ either at 1064 nm or 532 nm with a pulse duration of 5.5 ns and it delivered to the sample using a 75 mm focal length lens. The spectrometer (OceanOptics, LIBS2500) permits real-time, qualitative measurements of elements in solids. It provides spectral analysis across the 200-980 nm range at a resolution of ~0.1 nm (FWHM). During each experiment, LIBS sample was glued on the sample holder which was mounted on xyz translator so that it can be manually and continuously moved around the focal point. In our experiment, laser pulse energy of 25 mJ was focused onto the sample to create a spot size of about 200 μm using a 100 mm focal lens. The laser intensity was approximated to be about 14.5 GW/cm^2 at the spot. A delay of 1.5 μs between the firing of the laser and the acquisition of the LIBS spectra was applied. In order to reduce errors due to laser fluctuation and sample heterogeneity, a total of about 3 ash pellets and 3 coal pellets were tested and, for each pellet, we created about 10 spectra.

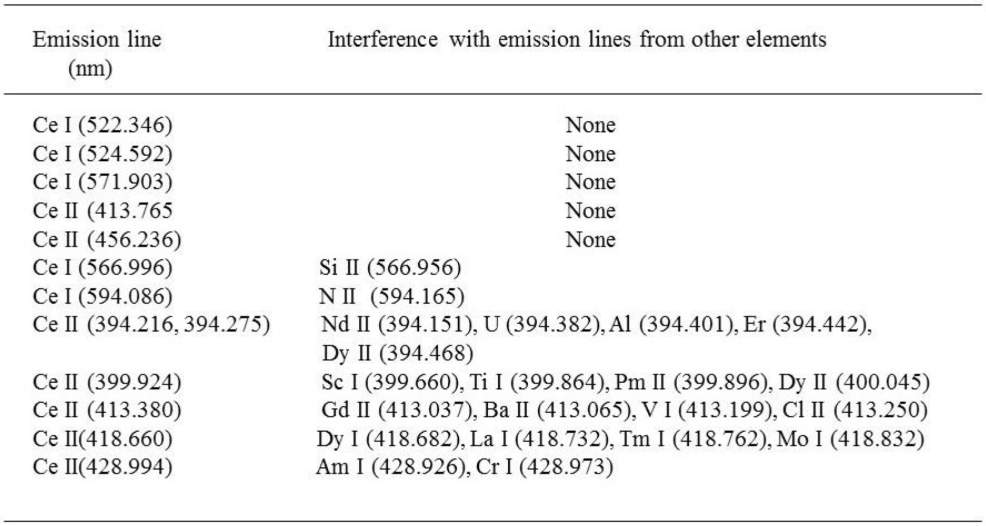
Results and Discussions

Figure 2 shows a typical LIBS spectrum spreading from 200 to 900 nm for coal and coal ash obtained by our present experiments. Our general observation indicates that the wavelengths of the observed emission lines were independent of the laser intensity. Their intensities, however, increased with the laser intensity. For all of these elements, their emission lines were more significantly pronounced and many of them became saturated in the ash samples than in the coal samples.

By comparing the wavelengths of the emission lines of the spectra in Fig. 2 with those from the online NIST Atomic Spectra Database, we obtained a spectrum of numerous strong emission lines emitted by both neutral and single-ionized states of the various metals and rare earth elements in lanthanide and actinide series present in our PRB-coal and coal ash samples. Many rare earth elements detected in ash samples were not detectable in the coal samples due to their low concentrations. We also observed that the wavelengths of the emission lines from neutral elements were mainly in the visible range (from about 450 to 700 nm) and the wavelengths of the emission lines by single-ionized elements were mostly in the UV range (from 250 nm to about 420 nm).

Because many of the emission lines from an element interfered significantly with those from others, in our present experiments, an element was considered to be identified if it had three or more emission lines that were unambiguous and did not interfere with those from other elements. As an example, by analyzing the ash spectrum in Fig. 1 against the online NIST data on cerium (Ce), we obtained a total of thirteen strong emission lines assigned for cerium (Ce). The results are shown in Table 1. Among these lines, emission lines from Ce I (522.346), Ce I (524.592), Ce I (571.903), Ce II (413.765), and Ce II (456.236) were unambiguous and they were used for Ce identification. The other emission lines: Ce I (566.996), Ce I (594.086), Ce II (394.216, 394.275), Ce II (399.924), Ce II (413.380), Ce II (418.660), and Ce II (428.994) were discarded because they interfered with many emission lines from other elements.

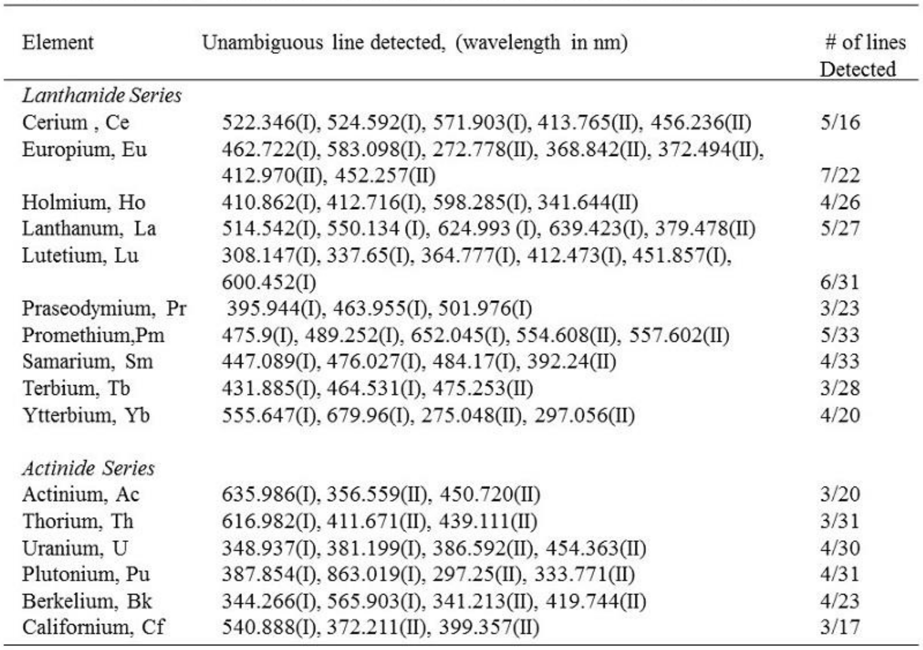
Table 1. Emission lines from Ce and their interferences with the emission lines from other elements



Emission line (nm)	Interference with emission lines from other elements
Ce I (522.346)	None
Ce I (524.592)	None
Ce I (571.903)	None
Ce II (413.765	None
Ce II (456.236)	None
Ce I (566.996)	Si II (566.956)
Ce I (594.086)	N II (594.165)
Ce II (394.216, 394.275)	Nd II (394.151), U (394.382), Al (394.401), Er (394.442), Dy II (394.468)
Ce II (399.924)	Sc I (399.660), Ti I (399.864), Pm II (399.896), Dy II (400.045)
Ce II (413.380)	Gd II (413.037), Ba II (413.065), V I (413.199), Cl II (413.250)
Ce II(418.660)	Dy I (418.682), La I (418.732), Tm I (418.762), Mo I (418.832)
Ce II(428.994)	Am I (428.926), Cr I (428.973)

With the identification criterion described above, elements that were identified with 3 or more unambiguous emission lines are tabulated in the following Tables 2 and 3. Other rare earth elements such as Dy, Er, Gd, Nd， Tm, Pa, Am, Cm, Es and numerous metal elements (Ag, Au, Al, Cr, Ga, Ge, Hf, Hg, Mn, Mo, Na, Nb, Os, Pb, Pt, Ra, Rb, Ru, Sc, Si, Sn, Ta, Tc, Zn, Y) were also detected but were not included in these tables simply because the number of the unambiguous detected emission lines for these elements did not meet the identification criterion. We, however, did not detect Cd, Cu, Ni, Pd, Rh and the remaining elements of the actinide series (Neptunium, fermium, mendelevium, nobelium, lawrencium). This might be possible that our ash samples contain these elements at the concentration levels that our present experiment could not detect.

Table 2. Summary of the rare-earth elements identified in PRB-coal ash



Element	Unambiguous line detected, (wavelength in nm)	# of lines Detected
Lanthanide Series		
Cerium , Ce	522.346(I), 524.592(I), 571.903(I), 413.765(II), 456.236(II)	5/16
Europium, Eu	462.722(I), 583.098(I), 272.778(II), 368.842(II), 372.494(II), 412.970(II), 452.257(II)	7/22
Holmium, Ho	410.862(I), 412.716(I), 598.285(I), 341.644(II)	4/26
Lanthanum, La	514.542(I), 550.134 (I), 624.993 (I), 639.423(I), 379.478(II)	5/27
Lutetium, Lu	308.147(I), 337.65(I), 364.777(I), 412.473(I), 451.857(I), 600.452(I)	6/31
Praseodymium, Pr	395.944(I), 463.955(I), 501.976(I)	3/23
Promethium,Pm	475.9(I), 489.252(I), 652.045(I), 554.608(II), 557.602(II)	5/33
Samarium, Sm	447.089(I), 476.027(I), 484.17(I), 392.24(II)	4/33
Terbium, Tb	431.885(I), 464.531(I), 475.253(II)	3/28
Ytterbium, Yb	555.647(I), 679.96(I), 275.048(II), 297.056(II)	4/20
Actinide Series		
Actinium, Ac	635.986(I), 356.559(II), 450.720(II)	3/20
Thorium, Th	616.982(I), 411.671(II), 439.111(II)	3/31
Uranium, U	348.937(I), 381.199(I), 386.592(II), 454.363(II)	4/30
Plutonium, Pu	387.854(I), 863.019(I), 297.25(II), 333.771(II)	4/31
Berkelium, Bk	344.266(I), 565.903(I), 341.213(II), 419.744(II)	4/23
Californium, Cf	540.888(I), 372.211(II), 399.357(II)	3/17

Conclusions

We have conducted a simple LIBS experiment for identifying various metal and rare earth elements in PRB-coal ash samples. Our preliminary results indicated that PRB-coal ash contains a number of rare earth elements in both the Lanthanide series and the Actinide series. Various metal elements were also detected. Although some rare earth elements in the lanthanide series have been identified for some coals and coal ash samples [2, 6-8], rare earth elements of both actinide and lanthanide series in PRB-coal ash are reported here for the first time. Comparisons with other detection techniques, therefore, could not be made at present. To quantify the concentrations of the detected elements requires that (a) the plasma spectrum must have all the emission lines by all the elements of the sample and (b) spectroscopic data for all emitting species must be available and reliable. The first requirement is fulfilled because the spectrometer used by our present experiments permits a sensitive detection of a spectrum from 200 to 900 nm range, which is typically required to record all the emission lines by the elements in coal and ash samples. The second requirement, however, is difficult to fulfill at present due to the scarcity of the spectroscopic data. We, therefore, report here only the various elements that were identified from PRB sub-bituminous ash samples, work on quantifying their concentrations is continued and the results will be reported in due course.

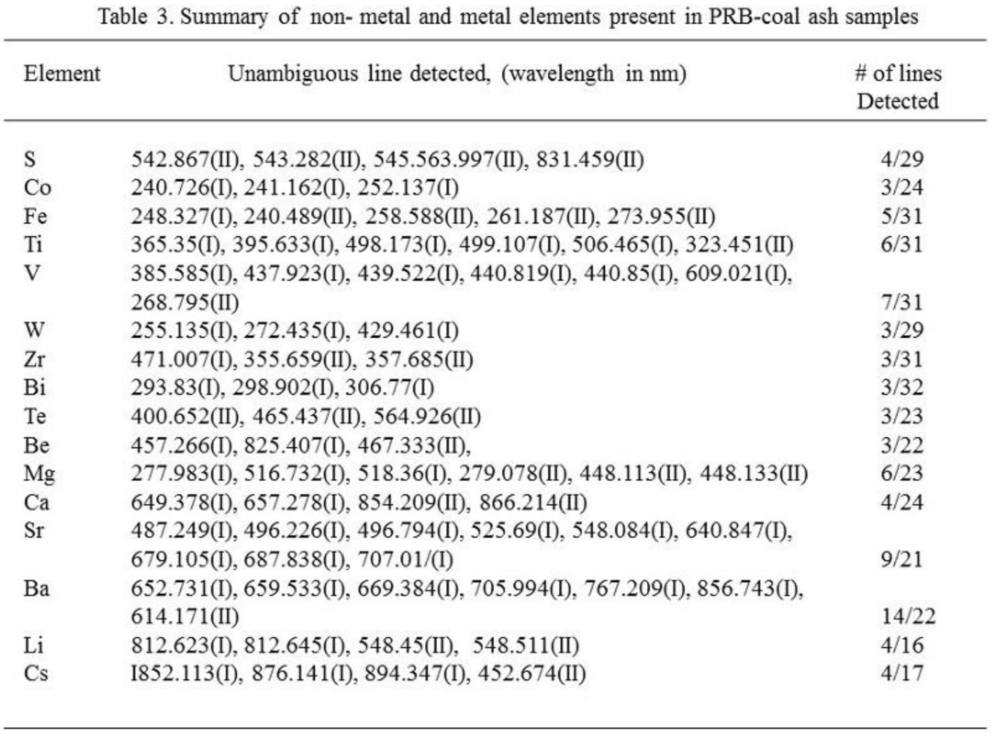


Table 3. Summary of non- metal and metal elements present in PRB-coal ash samples

Element	Unambiguous line detected, (wavelength in nm)	# of lines Detected
S	542.867(II), 543.282(II), 545.563.997(II), 831.459(II)	4/29
Co	240.726(I), 241.162(I), 252.137(I)	3/24
Fe	248.327(I), 240.489(II), 258.588(II), 261.187(II), 273.955(II)	5/31
Ti	365.35(I), 395.633(I), 498.173(I), 499.107(I), 506.465(I), 323.451(II)	6/31
V	385.585(I), 437.923(I), 439.522(I), 440.819(I), 440.85(I), 609.021(I), 268.795(II)	7/31
W	255.135(I), 272.435(I), 429.461(I)	3/29
Zr	471.007(I), 355.659(II), 357.685(II)	3/31
Bi	293.83(I), 298.902(I), 306.77(I)	3/32
Te	400.652(II), 465.437(II), 564.926(II)	3/23
Be	457.266(I), 825.407(I), 467.333(II),	3/22
Mg	277.983(I), 516.732(I), 518.36(I), 279.078(II), 448.113(II), 448.133(II)	6/23
Ca	649.378(I), 657.278(I), 854.209(II), 866.214(II)	4/24
Sr	487.249(I), 496.226(I), 496.794(I), 525.69(I), 548.084(I), 640.847(I), 679.105(I), 687.838(I), 707.01/(I)	9/21
Ba	652.731(I), 659.533(I), 669.384(I), 705.994(I), 767.209(I), 856.743(I), 614.171(II)	14/22
Li	812.623(I), 812.645(I), 548.45(II), 548.511(II)	4/16
Cs	I852.113(I), 876.141(I), 894.347(I), 452.674(II)	4/17

Disclaimer:

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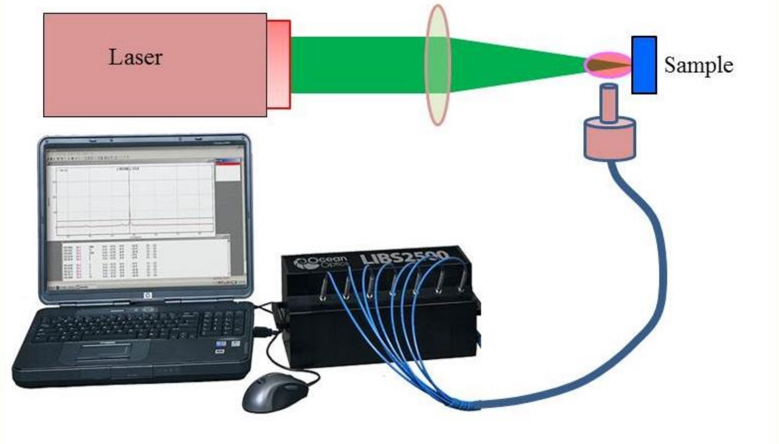
Figure 1. Schematic set up of the LIBS for REE profiling



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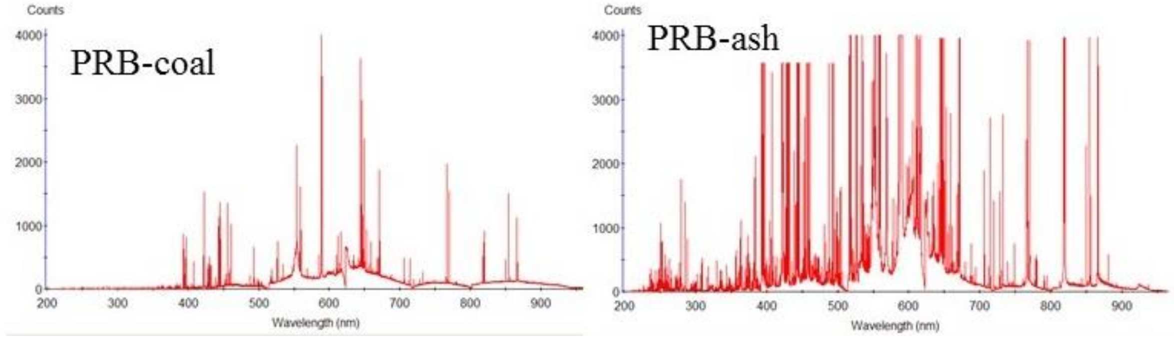

Figure 2. Typical LIBS spectrum observed for PRB-coal and PRB-coal ash

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