Influence of particle size and mineral phase in the analysis of iron ore slurries by Laser-Induced Breakdown Spectroscopy ☆

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Abstract

Laser-Induced Breakdown Spectroscopy (LIBS) was applied to the analysis of iron ore concentrates. The objective was to determine the influence of particle size and mineral phase on the LIBS signal. The LIBS spectra of hematite and magnetite ore concentrates were qualitatively indistinguishable from each other but magnetite yielded systematically less than hematite. This behavior could be set into an empirical equation to correct the iron peak intensities according to the level of magnetite in the analyzed sample. Similarly, an increase of the LIBS signal was observed as the particle size of the ore samples decreased. Again, an equation could be written down to correct the intensity of either iron or silicon in response to a variation of the average particle size of the ore concentrate. Using these corrections, proper response of the silicon signal against the concentration of silica in the samples was restored. The observed dependence of the strength of the iron signal upon the mineral phase is attributed to oxidation of magnetite into hematite.
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1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) has long been recognized as a potential on-line process analyzer for the chemical characterization of various materials [1,2]. Many studies have been published with this objective in mind [3–9] but few industrial implementations have been reported [10–13]. As the result of a lengthy effort [14–17], a LIBS analyzer was installed in an iron ore pelletizing plant, in 2005, for monitoring the composition of the end product [18]. The instrument turned out to be a sensitive tool to study the process and, indeed, through the accumulation of data, some insight was gained about the practical influence of the variables which effectively affect the measurements.

The influential variables likely to perturb the LIBS signal when analyzing ore slurries were discussed in previous papers

[14,15,19]. These are the slurry density, the particle size and the possible mineralogical or matrix effects. The slurry density is a minor issue since the weight percentage of solids in the liquid suspension is user defined and easily controlled in ore processing plants. Grinding the ore with ball mills or rod mills determines the mean size and the size distribution of the end product. This distribution can be quite large, e.g. from 10 to 200 μm in particle diameter. Finer particles suspended in slurries were found to yield stronger LIBS signals [19]. Further, particle size and size distribution are also linked to mineralogical properties and to the original grain size in the raw ore. The effect of particle size on the LIBS intensities must thus be examined with care.

Matrix effects are a particular matter of concern for the LIBS method in general [20,21]. In discrete cases, these have been circumvented by specific calibrations and/or special data analyses [22,23] with different levels of success. Applying dedicated calibration curves remains the general practice especially for on-line and industrial applications. Some indications pointing to a matrix effect induced by magnetite relative to hematite during the analysis of iron ore slurries have been collected in previous papers [15,19]. In cases where the magnetite content of an ore should be high or subject to significant variations, some provision to

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Table 1
Sample data

Variable	BMD	FC	MagC	Fine MagC	Coarse MagC	Reground BMD	Reground FC	Dilute BMD	Dilute MagC
% SiO_2	4.72	1.37	3.96	1.17	5.64	4.73	0.88	3.95	4.70
% Fe_2O_3	93.5	96.8	97.7	98.6	96.1	93.8	97.6	94.3	96.3
% MgO	0.28	0.35	0.09	0.06	0.11	0.28	0.27	0.30	0.16
% magnetite	23.5	25.9	81.8	84.4	76.3	23.7	26.5	24.1	65.2
% <45 μm	57	62	69	88	58	75	76	60	59

Analytical methods used: SiO_2, MgO, Fe_2O_3=XRF; %magnetite=FeO titration; % <45 μm=Microtrac.
Total oxides may exceed 100% because magnetite is a heavier molecule than hematite but is expressed and included in the %Fe_2O_3 equivalent concentration reported here.

account for its effect will be needed. Establishing in a more definite way the influence of magnetite on the LIBS signal was the main objective of this work.

2. Experimental

2.1. Materials

Ore samples were taken directly from the process of an iron ore plant treating ores containing typically 25% magnetite (the range seating between 10% and 40%). The samples are, namely, the discharge from a ball mill (BMD), the concentrated material from a magnetic separator (MagC) and the concentrated product from a flotation circuit (FC). These samples vary in composition, in magnetite content and in particle size as shown in Table 1. Additional samples were prepared through modifications of the original samples, either by sieving, grinding, diluting or blending. The main mineral phases found in the samples are: hematite (Fe_2O_3), magnetite ($Fe_2O_3 \cdot FeO$) and quartz (SiO_2). To replicate industrial practice, the subject material was put in slurry form by wetting with tap water to attain a solids concentration of 70% by weight.

2.2. Set-up

The set-up adopted a classical geometry for LIBS analyses in single pulse mode. An Nd:YAG laser (CFR200, Big Sky Laser Technologies) was aimed at a column of free falling slurry (6 mm in diameter) following the procedure described elsewhere [19].

Plasma emission was captured at an angle of 45° with a pair of lenses and focused in a fiber optic bundle coupled to a Czerny-Turner-type spectrometer (Triax 550, Jobin-Yvon) fitted at its exit port with an ICCD camera (DH501, Andor Technologies). Typical analytical conditions were as follows: laser wavelength 1064 nm; pulse duration 10 ns; pulse energy 150 mJ; focused spot size 0.5 mm^2; repetition rate 2 Hz; gate delay 2 μs; integration time 10 μs. The average of 100 laser shots was considered as a measurement; each data point was replicated 6 times. The wavelength span of the acquisition window was set from 278 to 290 nm, encompassing the peaks Fe I 278.81 nm and Si I 288.16 nm used for the quantitative analysis. All data treatment was performed using in-house-developed software.

2.3. Method

The three variables: %SiO_2, %magnetite and particle size, define a three-dimensional space and the samples listed in Table 1 occupy a discrete location in this space. The testing strategy consisted in constructing blend curves between pairs of these samples in order to cover as much as possible of the enclosed volume. For example, progressive additions (usually in 5 steps) of BMD material to FC material yielded a blend curve where, practically, only the silica equivalent concentration varied. A total of 14 blend curves were drawn in this manner, and the number of variables left free to vary in each test was decided a priori. In this way, the behavior of each variable and its influence on the LIBS signal could be isolated and understood. Particle size is represented here by the percentage
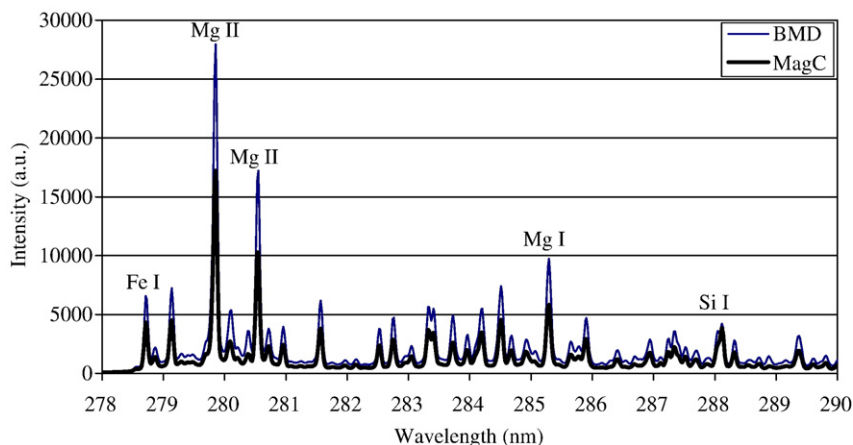

Fig. 1. Spectra of hematite-rich (BMD) and magnetite-rich (MagC) iron ores.