

Analysis of Ca in Cement using Laser-Induced Breakdown Spectroscopy

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Abstract: The major element of Ca directly affects the quality of the cement, so how to obtain its concentration fastly and accurately becomes especially significant. In this study, all the objects we chose to analyze were the powder cement without any pre-treatment. Firstly, We got the spectrum data on the surface of the cement samples by using Laser-induced breakdown spectroscopy technique, then we built the multivariate quantitative analysis models which were based on the partial least squares(PLS) after the data had been pre-processed. Experimental results showed the feasibility of the LIBS technique within a certain accepted range, and indicated that LIBS will have great potential to be applied more extensive in the future.

Key Words: Laser-induced breakdown spectroscopy, PLS, cement analysis

1. INTRODUCTION

Cement act a important role as a kind of construction materials, and widely used in the construction such as roads, bridges, buildings and so on. The quality of the cement is depending on the components especially the main element Ca, so it is essential to detect the concentration of Ca accurately for the cement production. There are several conventional analysis methods of concentration, chemical method, which is timing-consuming and complex, affecting the process of industrial production, neutron analysis and X-ray fluorescence spectrometry^[1](XRF) have the radioactive source, so they are harmful to human body and not conducive to the sustainable development of society. As a result, there is an urgent need for a technology which can detect the concentration accurately and quickly.

Laser-induced breakdown spectroscopy (LIBS) technique^[2] is a method of generating plasma by using high-energy laser pulse to excitation materials, and collecting plasma spectral information to analyze the composition of materials. LIBS can achieve qualitative and quantitative analysis of matters, and can detect almost all elemental content, which is a distinct advantage, besides, this technique also has the advantages such as fast speed for analysis, no sample preparation, and can be reach the on-line detection, so the method has been widely popular since its inception, the most important is it has no pollution

to the environment. In recent years, Industry research and application are more and more extensive, covering metallurgical analysis, space exploration, environmental testing, biomedical, industrial applications^{[3]-[6]} areas, so LIBS technique will have a broad prospects for development in the future. In the field of cement composition analysis, many scholars at home and abroad carried out different research experts, foreign A. Mansoori et al^[7] used LIBS technology to analyze some of the experimental parameters on the cement study; N. Taefi^[8] did the quantitative analysis of the powder cement samples through the EDM induced breakdown; domestic professor Zhang Lei^[9] also carried out some research and application of cement components using LIBS. To sum up, the technology can be used for rapid analysis of cement components.

The univariate model based the corresponding relationship between the true concentration of the element and the intensity of the characteristic line cannot achieve a satisfying result due to the influence of factors such as matrix effect, self-priming phenomenon, element interference and spectral fluctuation, so in this experiment, we used a multivariate model to establish the model of Ca. Compared with the univariate model, the multivariate model chooses multiple variables from the spectral data to establish the model together, which has higher adaptability and precision. Therefore, the multivariate model is more suitable for analysis of the main elements. We chose the partial least squares(PLS) to analyze Ca in cement which is one of multivariate methods, because PLS is the combination of multiple linear regression(MLR) and principal component analysis (PCA). And has advantages

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to process high-dimensional data. At present, many experts have used PLS method to analyze materials in biomedical, pharmacy and social science and other fields. Such as professor Wang Zhe^{[10]-[12]} established the PLS models of coal under different environmental gases using LIBS; doctor Tian Ye^[12] of China Ocean University improved PLS model to the analysis of cuttings; Yan Shunchun, a professor of South China University of Technology^[13], applied the PLS model to the ash content analysis of coal and confirmed the feasibility of the method. In this paper, we chose the original powder cement without any pre-processing as the analysis objects. The spectral data were collected directly on the surface of the powdery sample using LIBS. The PLS model of the main element of Ca in cement was established based on the spectral data, and proved the feasibility of the PLS model in the application of Ca in cement.

2. EXPERIMENT

2.1 Experimental system

The instruments used for our experiments as shown in Fig1. The laser source employed was a Q-switched Nd : YAG laser with a wavelength of 1064nm, and the maximum energy of 200mJ per pulse. The laser source was focused on the sample through a 750mm focal lens. The detection system was composed of the Avantes spectrometer which cover the spectral range from 238-360nm, giving a nominal resolution of 0.06nm. Besides, the way plasma spectra was coaxial collected with the laser excitation. Using the self-made delay generator to control the series of laser excitation and spectra collection. The samples were placed in an auto-controlled X-Y translation stage.

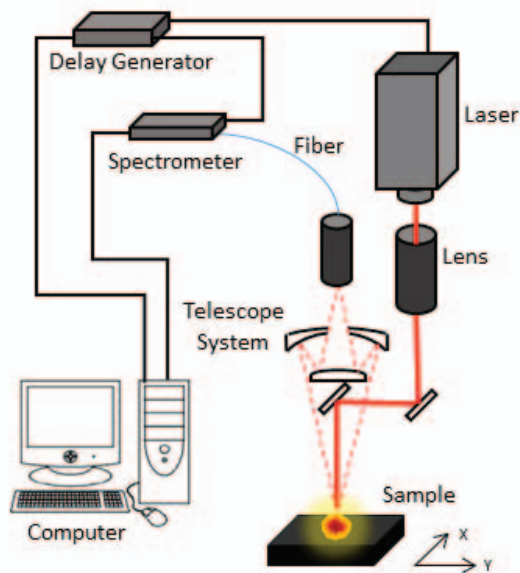


Fig 1. Diagram of the integrated LIBS system

2.2 Preparation of samples

In our experiments, all 32 powder samples were made up on the basis of the raw materials from 6 cement production, which had differences in the trace elements composition.

The concentration of some elements in cement are shown as bellows Table1.

Table1. The major elemental concentration of the samples

Sample No.	Ca(%)	Si(%)	Al(%)	Fe(%)	Mg(%)
C301	47	10	1.07	1.01	0.6
C302	45.92	14.11	1.07	1.44	0.56
C303	41.27	14.45	3.9	3.3	1.57
C304	39	15.5	4.7	2.5	0.5
C305	43.55	13.7	3.04	2.1	1.2
C306	45.24	11.65	2.25	0.1	1
C307	42.52	16.5	0.14	1.01	1.8
GH1	37.18	17.49	4.26	2.48	3
GH2	39.54	10.91	1.98	3.15	4.06
GH3	42.15	13.48	2.99	1.99	2.01
GH4	44.79	15.43	0.5	0.49	1.49
GH5	46.85	7.96	0.99	1.27	1.17
HK1	53.73	1.14	0.09	0.05	1.33
HK2	37.32	17.71	2.95	1.6	4.44
HK3	48.1	7.73	1.28	0.5	1.78
HK4	43.54	13.86	0.5	1.21	2.58
HK5	40.98	5.97	2.28	0.8	6.43
SN1	40.23	35.32	3.29	7.04	5.03
SN2	45.75	24.24	10.05	5.77	3.9
SN3	51.13	31.47	8.35	2.54	1.35
SN4	55.74	27.09	4.04	3.84	2.03
SN5	63.65	21.25	4.6	2.92	1.54
SYS1	28.59	30.6	5.12	0.2	2
SYS2	34.47	21.7	3.94	4.02	3.27
SYS3	39.2	9.85	2.45	2.22	4.91
SYS4	44.85	14.96	1	0.97	1.3
SYS5	49.89	3.51	2	0.45	1.5
JG1	39.57	18.07	3.61	1.5	0.99
JG2	40.4	11.08	4.14	3.24	3.57
JG3	42.87	13.04	2.47	2.26	2.08
JG4	45.26	14.63	0.6	0.99	1.3
JG5	46.25	9.47	1.99	0.48	1.5

We chose the best experimental condition through continually test the parameters, which the laser energy, the frequency of the laser pulse and spectral acquisition delay time, was 82mJ, 5Hz and 1us, respectively. When we did experiments, we put the sample into the container without any processing, and every sample was stimulated 1000 times on the surface of different positions. One of the samples is shown in Fig 2.



Fig 2. Cement sample

3. RESULTS

3.1 Data pre-processing

Due to the serious fluctuation of the pulse-to-pulse data obtained from the surface of loose powder samples, which resulted a poor reproducibility and accuracy, so we used the average value for every 50 excitation from different positions to improve it. Finally we got 640 groups of data for 32 samples (each sample with 20 groups), then used formula (1) to pre-process each group.

$$X_i = x_i / \bar{x}_i \quad (1)$$

Where x_i is a group of data, \bar{x}_i is the average of the data x_i , then X_i is the processed data.

3.2 PLS Model

PLS is a method of modeling a linear relationship between a set of output variables and a set of input variables, and generates a regression model that correlates the input and output, the LIBS spectra data (X) and the elemental concentrations (Y) as described by formula (2).

$$Y = XB \quad (2)$$

As a result, the PLS analysis obtains a linear combination of values to correlate the spectral intensities with the concentration as follow formula (3).

$$C = b_0 + b_1 I_1 + \dots + b_n I_n \quad (3)$$

Where C is the concentration of Ca, I_n is the spectral intensities at different wavelengths, b_n is the regression coefficient. As seen above, the PLS model utilize the full spectral information, so there is more variables for the calibration and prediction, and it is more flexible to compensate for the fluctuations than the traditional univariate methods.

Based on the above description of the PLS model, we built the analysis model of Ca.

3.3 Results analysis

In order to analyze the adaptability of the model entirety, we used the following 3 indicators as reference.

- R^2 -Coefficient of determination, used to assess the performance of the calibration and validation qualities of the model, and the closer to 1 of the R^2 , the better performs of the model.
- RSD-Relative standard deviation, the repeatability of the model will be better if the RSD is closer to 0.

- ARE-Average relative error, also, the model will has a higher precision when the ARE is close to 0.

The experimental results were obtained through two different patterns of models.

As mentioned above, there are a total of 6 categories samples, respectively, C30, GH, HK, JG, SN and SYS. We divided the data of each sample to 15 groups and 5 groups, which the 15 ones were used for the calibration set to build the PLS model and the 5 ones were used for the validation set to predict the results.

Firstly we analyzed each category individually, so we built 6 PLS models, and the results of the separate models is shown in Fig 3 to Fig 8 and the details in Table 2.

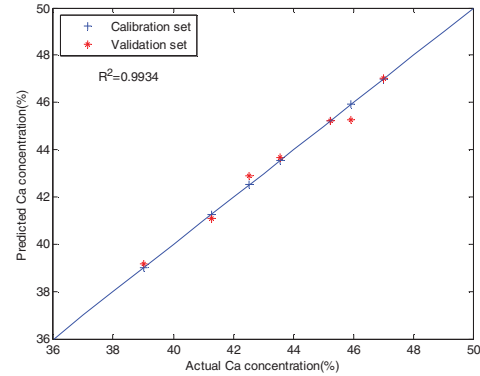


Fig 3. The calibration results of model C30 based on PLS

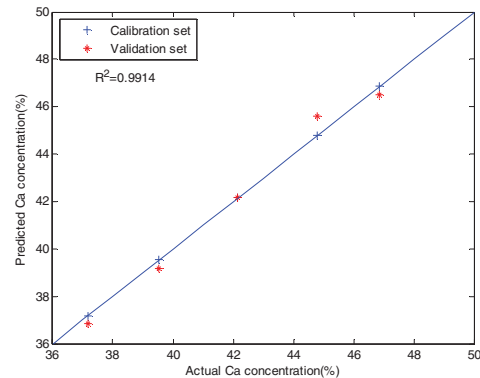


Fig 4. The calibration results of model GH based on PLS

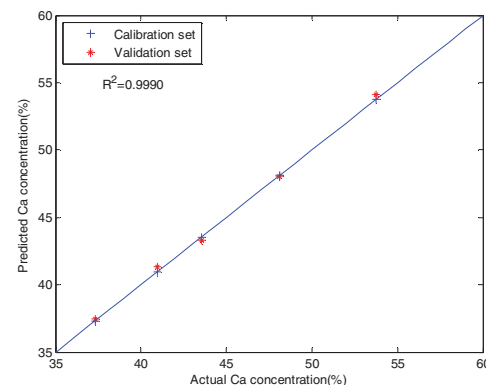


Fig 5. The calibration results of model HK based on PLS

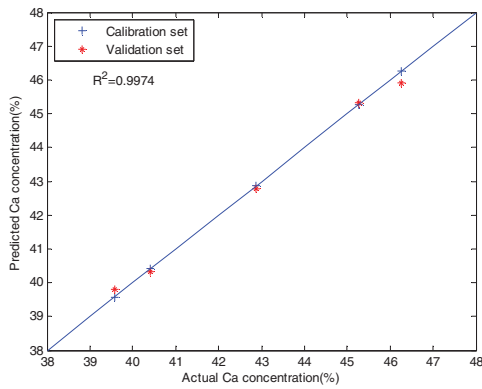


Fig 6. The calibration results of model JG based on PLS

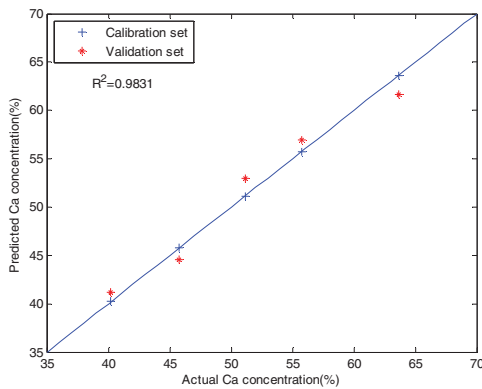


Fig 7. The calibration results of model SN based on PLS

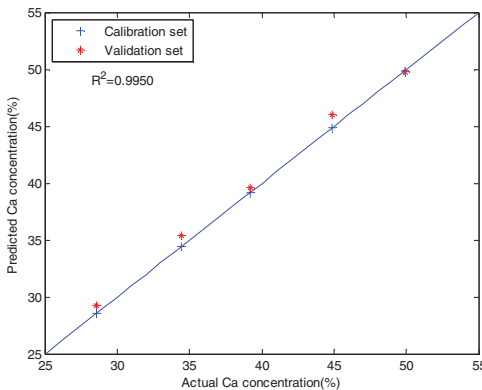


Fig 8. The calibration results of model SYS based on PLS

Table2. The indicators of separate models

Category No.	Indicator	Calibration set(%)	Validation set(%)
C30	RSD	0.0720	0.8513
	ARE	0.0023	0.5012
GH	RSD	0.0369	0.9439
	ARE	0.0020	0.8881
HK	RSD	0.0153	0.9982
	ARE	0.0003	0.5101
JG	RSD	0.0137	0.4500
	ARE	0.0004	0.3581
SN	RSD	0.0164	2.9675
	ARE	0.0006	2.7466

SYS	RSD	0.0828	1.5990
	ARE	0.0024	1.7567

The indicator RSD in Table2 is the average of all RSD from calibration set or validation set of each category (each sample in calibration set had a RSD of 15 groups results, and each sample in validation set had a RSD of 5 groups results), besides, the ARE is the average of all relative errors from calibration set or validation set (each calibration set or validation set had a relative error which is the average of 15 or 5 relative errors of prediction).

From the above results in Fig3-Fig8, the average R^2 is about 0.99, besides, the RSD and ARE are relatively satisfactory. We think the reason of this phenomenon is that the samples of each category had a part of data for the established of the model, moreover, the nature of samples in the same category is similar. Then, we built a PLS model based on the total samples of 6 categories for whole analysis. The method to choose the calibration set and validation set was the same as the way used in the above, so we got 480 groups data for calibration, 160 groups for validation. and the results of the whole model is shown in Fig 9 and Table3.

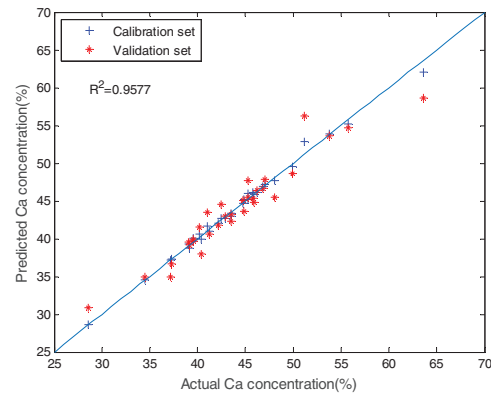


Fig 9. The calibration results of whole model 1 based on PLS
Table3. The indicators of whole PLS model 1

	Calibration set(%)	Validation set(%)
RSD	1.9555	3.0910
ARE	0.7794	3.1398
R^2	0.9577	

The indicators in Table3 and Table2 were obtained by the same method of calculation. We find that all the predicting values from calibration set still maintain a high accuracy because of the model was based on the calibration set. In addition, for the results of validation set, one will have better perform when the concentration of Ca is in the range of 40%-50% , where the most samples concentrated here, so the individual samples maybe performs a bit poor when the concentration of Ca were belongs the both ends of the overall concentration scope, but look at the overall results, the model had a adaptability in a certain error range.

To further analyze the Ca in cement, we built a whole model which was different from the above one, we used the data of C305, GH3, HK4, JG3, SN3, and SYS3 as the validation set, the remaining 26 samples were used for building the PLS model, the reason we chose the 6 samples were that they were all not belongs the both ends of the concentration of Ca in their categories. Then we built

another whole model, we called it model 2, and the results are shown in Fig 10 and Table4.

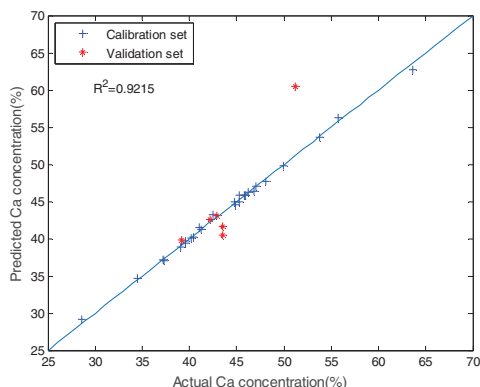


Fig 10. The calibration results of whole model 2 based on PLS

Table4. The indicators of whole PLS model 2

	Calibration set(%)	Validation set(%)
RSD	2.2509	3.7768
ARE	0.6469	5.3820
R ²	0.9215	

The difference of RSD and ARE between Table4 and the above is that each sample in validation set or calibration set were based on 20 groups results, It can be seen that the ability of prediction for the calibration set is still relatively satisfactory compared with the above models, and most of the predictions of the six samples in validation set showed the acceptable results except sample SN3, which had the highest content of Ca in validation set, and this sample had the highest Si element content, which might cause the influence of excitation of the plasma, then the characteristic lines of the Ca element were disturbed. In addition, average of RSD could remain the range within 4%, therefore, we believe that when the model is further optimized, the result of prediction will be better.

4. CONCLUSION

From the experiment in our study, the cement samples we chose were without any pre-processed, we got the spectral data using LIBS technology, and built the PLS multivariate analysis models of Ca after pre-processing the raw data. The validation results showed that when a part of groups data in one sample were used to build the model, then the predicted results of the other data in the sample were more accurate, the reason is that the model had known the information of the sample. However, in our final test, we found that the prediction values of SN3 performed poor. Because of the different characteristics among samples in 6 categories, which performed the unlike features though the samples with a similar concentration of Ca, then resulted a

undesirable effect. Compared to the experiment in laboratory, these results were not satisfied, but the way we performing experiment could be a good reference for a broader application by using LIBS technique. As for how to improve the accuracy and the repeatability, also the optimization of the model and data processing, is the focus of the next step.

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