Application note | 41711

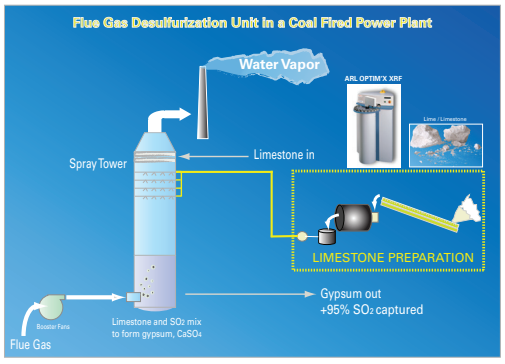
X-ray fluorescence

Analysis of limestone for flue gas desulfurization in a power plant

ARL OPTIM'X Simultaneous-Sequential Wavelength Dispersive X-ray Fluorescence Spectrometer

Keywords

ARL OPTIM'X, lime/limestone, power plant, WDXRF, X-Ray fluorescence



Industry background

What is flue gas desulfurization?

Power plants burning sulfur-containing coal or oil emit sulfur dioxide (SO2). A flue gas desulfurization (FGD) processing unit, commonly referred to as a scrubber, removes the SO_2 from the exhaust flue gases and prevents the SO_2 from entering the atmosphere, where it contributes to acid rain formation. As environmental emissions regulations for sulfur dioxide tighten worldwide, technologies for SO_2 removal and associated analysis continue to advance.

How does a scrubber work?

During the combustion process the sulfur in the coal combines with oxygen in the air to form SO_2. To remove the SO_2, the flue exhaust from a coal-fired power plant is commonly bubbled through a mixture of lime or limestone and water. The resultant reaction typically captures 95 % or more of the SO_2. Approximately 80-85 % of worldwide FGD units installed in power plants use wet limestone scrubbing vs. other technologies.

What happens to the SO_2 captured in a scrubber?

The captured SO_2 combines with the lime or limestone slurry ($Ca(OH)_2$ or $CaCO_3$) to form several byproducts, primarily calcium sulfate ($CaSO_4$) commonly called gypsum. Gypsum is recyclable or marketable for many industrial uses. The gypsum created by a power plant that is not reused is disposed of in permitted landfills along with scrubber byproducts that are not reusable.

Element/ Oxide	Concentration	Required Std. Dev
$CaCO_3$	> 95.0 %	0.12
SiO_2	< 3.0 %	0.05
$MgCO_3$	< 2.0 %	0.05
Al_2O_3	< 1.5 %	0.05
Fe_2O_3	< 3.0 %	0.03

XRF application

The acceptability of the lime or limestone used for scrubbing may be determined through element/oxide analysis, a perfect application for XRF. Typical ranges and reproducibility of interest for limestone are shown to the left.

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Instrument

A Thermo Scientific ARL OPTIM'X XRF spectrometer has been used to derive limits of detection and precision for the analysis of lime/limestone. The ARL OPTIM'X is a WDXRF system which provides superior resolution and light elements capability. It is fitted with an air-cooled Rh end window tube with thin Be window (0.075 mm) and has a maximum power of 50 Watts. Thanks to close coupling between the X-ray tube anode and the sample, the performance of the ARL OPTIM'X is equivalent to a 200 W conventional WDXRF instrument. The instrument can be equipped with the unique SmartGonio™, a series of monochromators or both for various elements.

Instrument configuration

- ARL OPTIM'X analyzer – vacuum chamber, SmartGonio™, element range F to U
- 12-position sample changer
- OXSAS XRF analytical software

With an analysis time of only 10-40 seconds per element of interest, the ARL OPTIM'X can easily satisfy the required repeatability with standard deviations as low as 0.001 to 0.03 depending on the element. Longer analysis times provide further improved results.

Calibration and repeatability

A standard calibration curve has been developed on the ARL OPTIM'X for the five elements (Ca, Si, Mg, Al, Fe) in limestone as a pressed powder. The resulting calibrations for lime, magnesia, iron oxide and silica are illustrated in Figures 1, 2, 3 and 4.

A repeatability test was carried out by running a sample for ten repeat analyses with a counting time of two minutes per element. The results are summarized in Table 1.

Run #	$CaCO_3$ %	SiO_2 %	$MgCO_3$ %	Al_2O_3 %	Fe_2O_3 %
Run 1	95.56	2.10	1.60	0.49	0.26
Run 2	95.35	2.11	1.60	0.49	0.26
Run 3	95.59	2.10	1.60	0.50	0.26
Run 4	95.67	2.09	1.61	0.50	0.26
Run 5	95.31	2.12	1.58	0.50	0.26
Run 6	95.43	2.10	1.60	0.50	0.26
Run 7	95.57	2.12	1.59	0.50	0.26
Run 8	95.41	2.10	1.61	0.49	0.26
Run 9	95.48	2.08	1.59	0.50	0.26
Run 10	95.47	2.10	1.59	0.50	0.26
Avg.	**95.49**	**2.10**	**1.60**	**0.50**	**0.26**
Std. Dev.	**0.114**	**0.012**	**0.011**	**0.005**	**0.002**

Table 1. Repeatability for element oxides in pressed limestone powder.

Conclusion

Excellent calibration curves and repeatability can be achieved with the ARL OPTIM'X to determine the suitability of limestone minerals for use in power plant scrubbers. The technique is both rapid and suitable for multiple oxides of interest at both high levels (approaching 100 %) and low levels (less than 0.25 %) of inclusion.

Furthermore, operation is made easy through the state-of-the-art Thermo Scientific OXSAS software which operates with the latest Microsoft Windows® 10 packages.

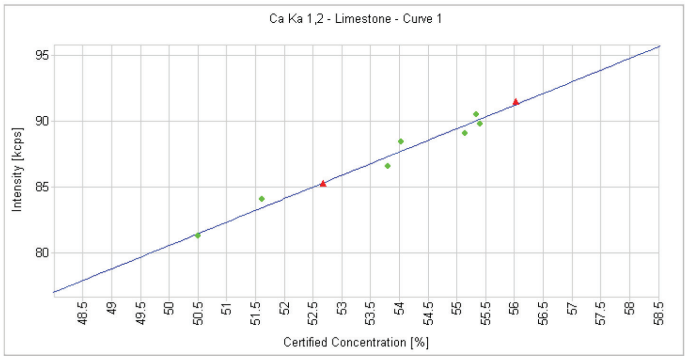

Figure 1. Calibration curve for $CaCO_3$ in limestone.

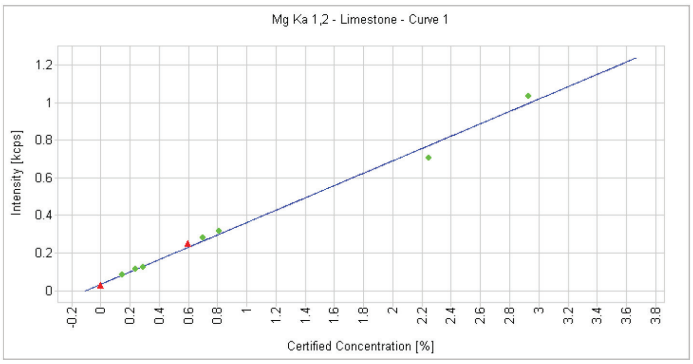

Figure 2. Calibration curve for $MgCO_3$ in limestone.

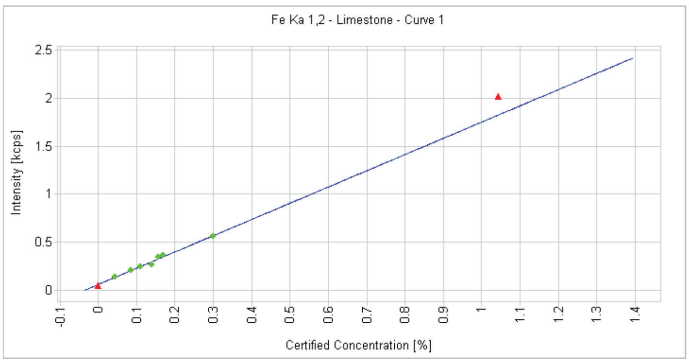

Figure 3. Calibration curve for iron oxide in limestone.

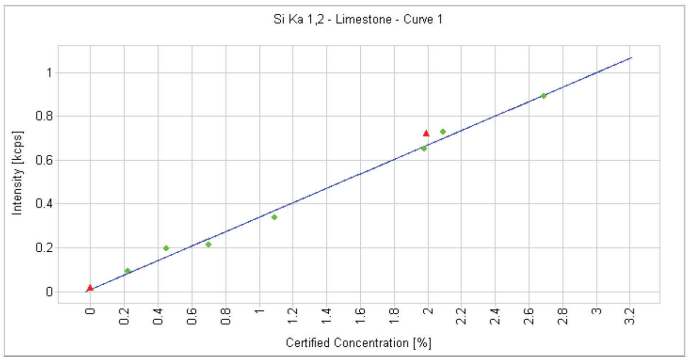

Figure 4. Calibration curve for silica in limestone.

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