APPLICATION NOTE

Analysis of limestone for flue gas desulfurization in a power plant with ARL QUANT'X EDXRF Spectrometer

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Abstract

The Thermo Scientific™ ARL™ QUANT'X Energy-Dispersive X-ray Fluorescence (EDXRF) Spectrometer is used to control the quality of limestone used for flue gas desulfurization (FGD) in coal-fired power plants. After a short introduction to FGD, the application note focuses on sample preparation, measurement conditions as well as accuracy and precision of EDXRF for the quantification of major and minor components in limestone.

Industry background

What is flue gas desulfurization?

A flue gas desulfurization (FGD) processing unit, commonly referred to as a scrubber, removes sulfur dioxide (SO_2) from the exhaust flue gases in power plants that burn coal; airborne SO_2 oxidizes within airborne water droplets to form sulfuric acid (H_2SO_4) forming "acid rain". As environmental emissions regulations for SO_2 tighten in countries worldwide, technologies for SO_2 removal and associated analysis continue to advance.

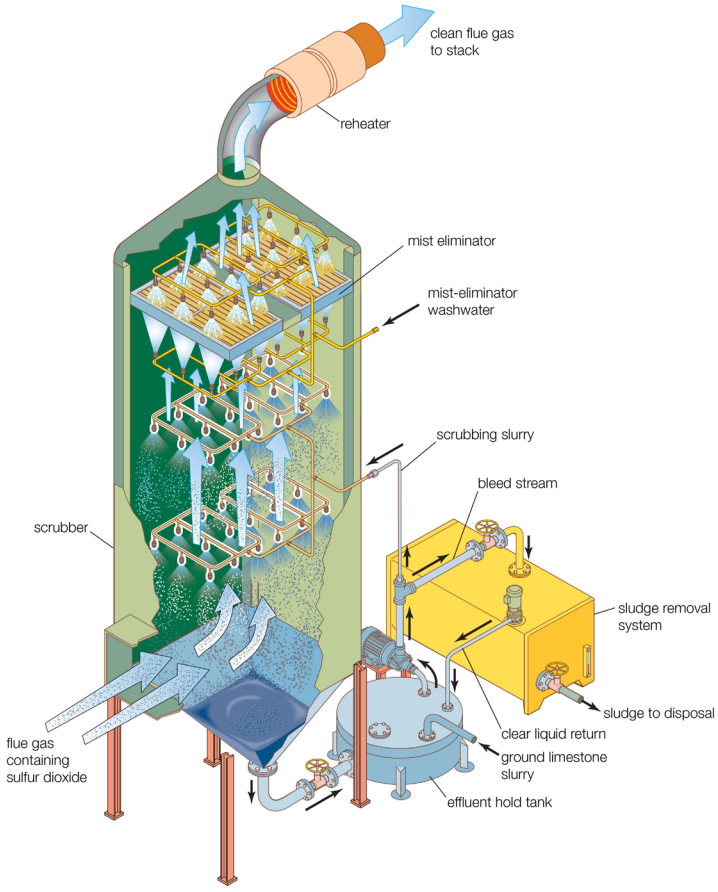
How does a scrubber work?

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 gases from a coal-fired power plant are commonly led through a spray of limestone slurry in a so-called scrubber. The resultant reaction typically captures 90% 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 limestone slurry to form $CaSO_3$ (and CO_2) which is further oxidized to the

Figure 1: Wet scrubber using a limestone slurry to remove sulfur dioxide from flue gas.



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main byproduct; 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.

Table 1: Concentration ranges and required reproducibility.

Element/Oxide	Concentration	Required Std. Dev
$CaCO_3$	> 95.0 %	0.10
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

X-ray Fluorescence (XRF) application

The quality of the limestone used for scrubbing may be determined through element/oxide analysis; a perfect application for XRF. Typical ranges and reproducibilities of interest for limestone analysis are shown in Table 1.

Instrumentation

An ARL QUANT'X XRF Spectrometer has been used to derive limits of detection and precision for the analysis of limestone. The ARL QUANT'X Spectrometer is an EDXRF system which provides a fast and cost-effective analytical capability. It is fitted with an air-cooled Rh end-window tube with thin Be window (0.05 mm) and has a maximum power of 50 Watts. The ARL QUANT'X Spectrometer is equipped with an electrically cooled silicon drift detector (SDD) with an area of 30 mm^2. The instrument features a total of nine primary beam filters ensuring that an optimal excitation condition is always found. An optional 10-position sample changer allows for unattended analysis.

Sample preparation and analytical conditions

Sample preparation consists of grinding the powder to achieve a particle size of ~325 mesh followed by pressing the sample into a pellet with a diameter of 40 mm using a pressure of 200 kN.

Two excitation conditions are used which are shown in Table 2 below. A first condition focuses on the lightest elements Mg, Al and Si while a second condition excites Ca and Fe. The current is adjusted per sample to ensure a maximum count rate without saturating the detector. We used a total live measurement time of 150 s. All measurements are done in vacuum.

Table 2: Excitation conditions used for limestone analysis.

Condition	Voltage (kV)	Filter	Atmosphere	Live Time (s)	Elements
Low Za	4	None	Vacuum	120	Mg, Al, Si
Mid Za	18	Thin Pd	Vacuum	30	Ca, Fe

Calibration and repeatability

Calibration curves have been developed for the five elements of interest (Ca, Si, Mg, Al, Fe) in limestone using certified reference materials. The resulting calibrations for magnesium, calcium and iron are shown in Figures 1, 2 and 3.

Figure 2: Calibration curve for magnesium in limestone.

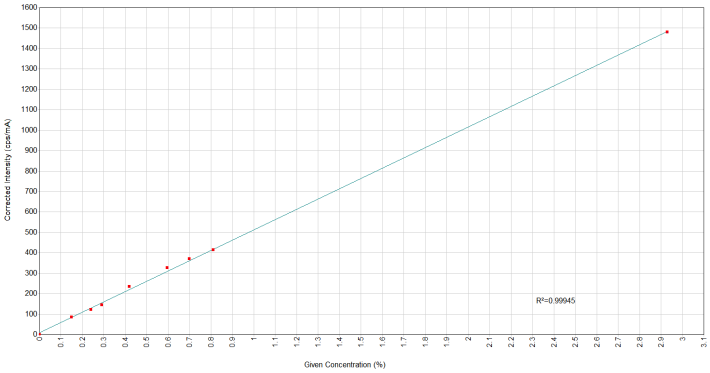


Figure 3: Calibration curve for calcium in limestone.

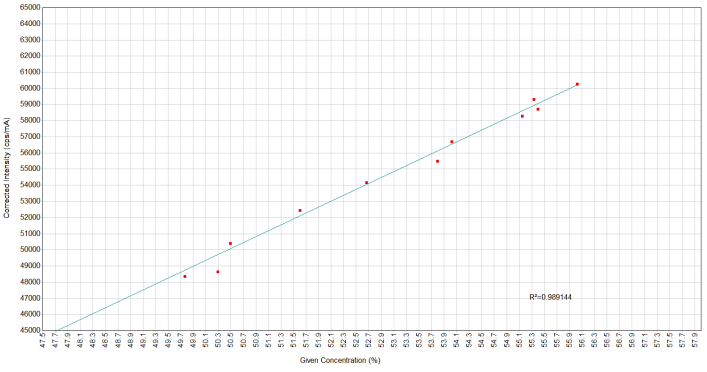
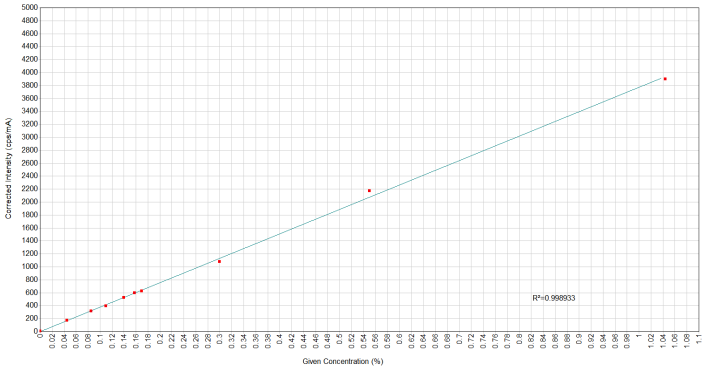


Figure 4: Calibration curve for iron in limestone.



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An instrument repeatability test was carried out by running a sample for ten repeat analyses without sample replacement. The results are summarized in Table 3.

Table 3: Repeatability for element oxides in pressed limestone powder.

Run #	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3
	% w/w	*% w/w*	*% w/w*	*% w/w*	*% w/w*
Run 1	0.789	0.2014	0.977	53.89	0.1045
Run 2	0.795	0.2015	0.978	53.96	0.1048
Run 3	0.798	0.2020	0.985	54.00	0.1034
Run 4	0.799	0.2016	0.986	54.01	0.1044
Run 5	0.798	0.2008	0.982	54.04	0.1050
Run 6	0.793	0.1990	0.983	54.07	0.1052
Run 7	0.801	0.2005	0.982	54.07	0.1037
Run 8	0.795	0.2024	0.981	54.12	0.1050
Run 9	0.807	0.2010	0.985	54.15	0.1048
Run 10	0.795	0.2004	0.984	54.09	0.1037
Average	0.797	0.2010	0.982	54.04	0.1045
SD	0.005	0.0009	0.003	0.08	0.0006
RSD (%)	0.62	0.47	0.30	0.15	0.61

Conclusion

Excellent calibration curves and repeatabilities can be achieved with the ARL QUANT'X Spectrometer 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 (approaching 100%) and low (less than 0.25%) concentration levels.

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