Application Note 41305

Analysis of clinker phases with the Thermo Scientific ARL 9900 Total Cement Analyzer X-ray fluorescence system with compact XRD

Jairo Rueda, Henry Santamaria, Jorge Montana, Nestor Bernal and Renan Jaimes, *Cementos Paz del Rio S.A., Columbia*
Bertrand Jequier and Felix Torres, *Symtek, Columbia*

Key Words
Cement, ARL 9900, XRD, XRF, Clinker phases

Goal

On-line quantification of clinker phases using an integrated XRF-XRD instrument.

Introduction

Quantitative analysis of clinker phases is a very interesting challenge faced by the cement industry. Apart from conventional chemical analysis using XRF techniques, the role of XRD has been increasingly solicited to perform the analysis of phases or minerals.

Analysis of phases such as free lime in clinkers and limestone additions in cement by XRD has been extremely useful in controlling the kiln process and the quality of the end product respectively. Indeed, XRD has replaced traditional wet chemical or other methods in many cement laboratories over the past 10 years.

A study was undertaken to introduce reliable, cost effective and rapid analytical methods to address clinker phase analysis. This study focused on the analysis of clinker phases in real time kiln conditions, and examined the potential use of XRD as a substitute for microscopy or other indirect methods of calculation.

Instrument and sample preparation

A Thermo Scientific ARL 9900 Series was used for the purposes of this study. This instrument is equipped with a series of XRF fixed channels (monochromators), an XRF goniometer, and an XRD goniometer integrated in such a manner that both XRF and XRD measurements can be carried out on the same sample with the same tube conditions and under vacuum.

A series of 30 clinker samples were collected over a period of production time. Microscopy measurements were carried out in parallel on the 30 samples to obtain quantitative data for

C_3S, C_2S, C_3A and C_4AF phases. A set of samples were then selected with a view to getting a reasonable dynamic range (working range) for concentrations of the four clinker phases. These clinker granules were ground and pressed into pellets before being measured by the ARL 9900 Series Total Cement Analyzer.

In usual microscopic observation of clinkers, the biggest limitation resides in the presence of a vitreous interstitial phase which makes it difficult to differentiate the ferrite and the aluminium oxide. This is not the case with the samples in this study, since the clinker samples are cooled slowly allowing C_3A crystallisation.

On the other hand, the microscopically determined interstitial phase (alumina and ferrite) is always smaller than that calculated by Bogue formulæ, as they assume that all of the Al_2O_3 and Fe_2O_3 contributes to the formation of C_3A and C_4AF without considering the possibility that part of those oxides can form solid solutions with silicates.

The total analysis time taken by the Compact Integrated XRD system for free lime and the four clinker phases is less than 4 minutes. Peak intensities are used directly without corrections.

Thermo
SCIENTIFIC

Identification	XRF analysis of oxides										
Clinker sample	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Na_2O	K_2O	P_2O_5	TiO_2	Mn_2O_3	Total
1	66.62	23.73	5.16	3.17	0.75	0.65	0.14	0.73	0.36	0.29	0.02	**101.6**
2	66.36	21.77	4.99	3.2	0.75	0.84	0.14	1.01	0.36	0.29	0.02	**99.73**
3	66.64	23.56	5.22	3.41	0.77	0.53	0.14	0.52	0.36	0.3	0.03	**101.45**
4	66.57	22.52	5.13	3.34	0.75	0.66	0.14	0.87	0.36	0.3	0.03	**100.65**
5	66.47	23.86	5.38	3.69	0.76	0.45	0.13	0.42	0.36	0.31	0.03	**101.83**
6	66.56	23.15	5.08	3.21	0.75	0.6	0.14	0.7	0.35	0.3	0.03	**100.85**
7	66.55	23.66	5.33	3.47	0.75	0.56	0.14	0.62	0.36	0.3	0.02	**101.74**
8	66.51	23.37	5.14	3.55	0.75	0.62	0.14	0.73	0.36	0.3	0.03	**101.49**
9	66.73	23.58	5.24	3.25	0.75	0.53	0.14	0.53	0.35	0.31	0.02	**101.41**
10	66.66	23.11	5.1	3.25	0.75	0.72	0.14	0.68	0.36	0.3	0.03	**101.07**
11	66.64	23.33	5.13	3.25	0.75	0.59	0.14	0.61	0.36	0.3	0.03	**101.11**
12	66.71	22.91	5.15	3.35	0.75	0.5	0.13	0.57	0.36	0.29	0.02	**100.72**
13	66.62	22.82	5.19	3.43	0.75	0.57	0.14	0.72	0.36	0.3	0.02	**100.89**

Table 1: XRF analysis of clinkers

Results and discussion

Table 1 shows the results of chemical analysis (total oxide concentration) obtained by the XRF part of the instrument. These concentrations are used to calculate the equivalent concentrations of clinker phases using Bogue formulæ:

$$\%C_3S = (\%CaO - \%CaO\ free) \times 4.07 - (\%SiO_2 \times 7.6 + \%Fe_2O_3 \times 1.43 + \%Al_2O_3 \times 6.72)$$

$$\%C_2S = \%SiO_2 \times 2.87 - C_3S \times 0.75$$

$$\%C_4AF = \%Fe_2O_3 \times 3.04$$

$$\%C_3A = \%Al_2O_3 \times 2.65 - \%Fe_2O_3 \times 1.69$$

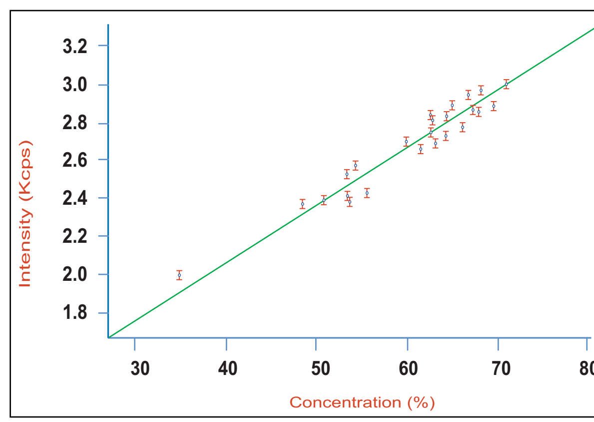

Figure 1: Calibration curve for alite (C_3S) in a series of industrial clinker samples using the Integrated XRD system

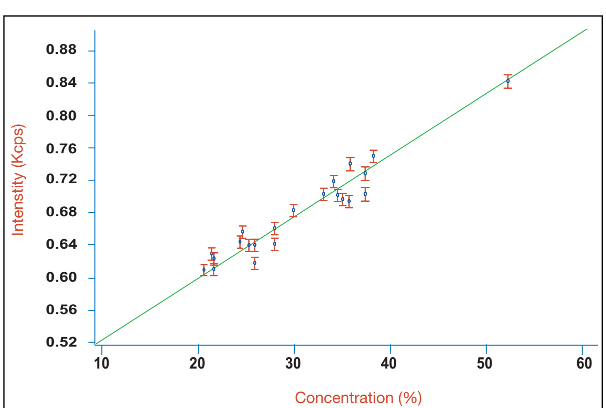

Figure 2: Calibration curve for belite (C_2S) in a series of industrial clinker samples using the integrated XRD system

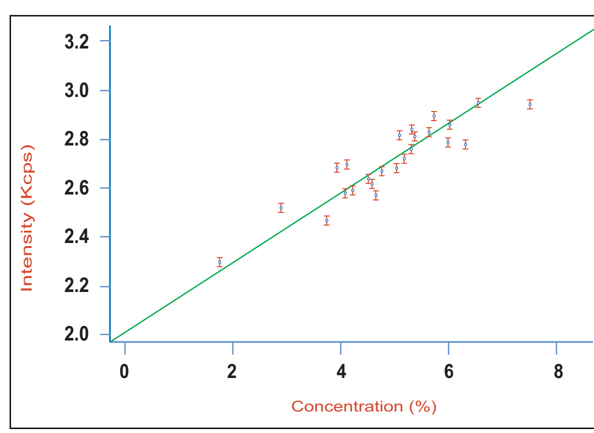

Figure 3: Calibration curve for aluminate (C_3A) in a series of industrial clinker samples using the Integrated XRD system

Identification	Phases measured with integ. XRD of TCA					Bogue's calculation				Microscopy			
Clinker sample	CaO free	C_2S	C_3A	C_3S	C_4AF	C_2S	C_3A	C_3S	C_4AF	C_2S	C_3A	C_3S	C_4AF
1	1.53	30.55	4.06	61.34	3.48	34.09	8.32	45.36	9.64	29.91	4.56	60.19	3.61
2	3.29	53.87	1.79	38.87	4.46	22.63	7.82	53.13	9.73	52.33	1.77	35.08	4.04
3	1.21	25.36	4.41	63.18	3.81	32.15	8.07	47.29	10.37	24.32	4.75	66.32	3.73
4	2.97	41.07	4.76	50.15	4.2	28.29	7.95	48.45	10.15	38.27	4.12	48.67	4.06
5	1.25	32.95	5.27	51.73	4.29	36.47	8.02	42.68	11.22	35.68	6	53.68	4.48
6	1.74	33.96	4.28	55.8	3.84	29.58	8.04	49.15	9.76	33.05	4.5	53.44	4.65
7	1.14	27.78	5.81	62.08	3.91	33.69	8.26	45.62	10.55	24.68	6.02	64.54	4.14
8	2.17	38.52	3.48	51.94	4.13	33.60	7.62	44.63	10.79	35.92	2.9	53.87	4.06
9	1.27	23.22	5.71	67.1	3.52	32.16	8.39	47.35	9.88	21.68	5.33	69.7	2.98
10	1.47	23.4	4.56	70.44	3.61	28.40	8.10	50.57	9.88	21.48	5.04	68.28	4.03
11	1.4	25.71	3.92	64.23	3.66	30.13	8.10	49.10	9.88	27.86	4.09	62.92	3.03
12	1.73	25.55	5.58	62.84	3.89	27.54	7.99	50.95	10.18	25.89	5.08	62.79	3.38
13	1.42	21.67	6.04	69.3	3.76	26.38	7.96	52.15	10.43	20.62	5.74	66.99	4.14

Table 2: Quantitative XRD analysis of free lime and clinker phases in comparison with microscopy and Bogue calculations

It is clear that Bogue's formulæ do not produce accurate results, fundamentally due to the fact that the conditions of the process are not taken into account. For example, the effects of very coarse raw mineral grains, temperature profile, time spent in the kiln, cooling speed have a significant bearing on the formation of clinker phases.

The concentrations determined by microscopy counting have been used as 'nominal concentrations' to establish a quantitative analysis program using the integrated XRD system. The peak intensities of C_3S, C_2S, C_3A and C_4AF are correlated with these concentrations to obtain calibration curves.

Figures 1, 2 and 3 show the calibration curves obtained for C_3S, C_2S and C_3A respectively. Similar calibration curve has been obtained for C_4AF phase.

Table 2 compiles the results of the clinker phases obtained with the Compact XRD system integrated in the ARL 9900 in comparison with the values obtained from microscopy and the Bogue calculations.

It is clear that microscopy values and XRD results obtained with the ARL 9900 TCA correlate well (Figure 4) while the Bogue data can be seriously in error compared to microscopy. Figure 5 shows the very poor correlation between microscopy as a reference and Bogue calculation for C_3S obtained with the data of Table 2.

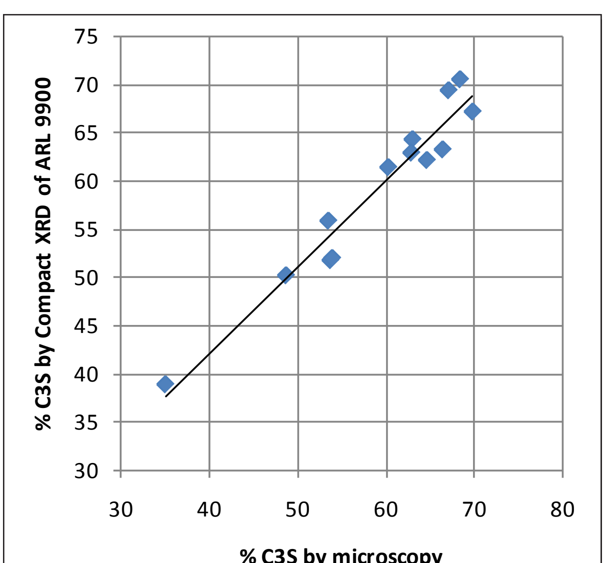

Figure 4: Microscopy vs Compact XRD for C_3S: good correlation

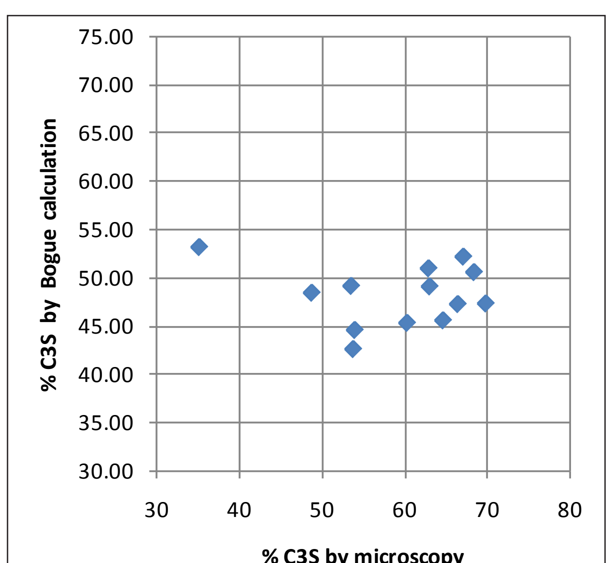

Figure 5: Microscopy vs Bogue for C_3S: no correlation

Conclusion

This case study compared quantitative results obtained on a series of clinker samples (industrial samples taken under real kiln operation conditions) using three methods: Bogue formulæ, microscopy and Compact Integrated XRD using an ARL 9900 Series Total Cement Analyzer.

The results from Bogue are clearly not satisfactory, as expected. The comparison between microscopy and quantitative XRD data shows that it is possible to exploit the unique Compact Integrated XRD system of ARL 9900 Series in real process conditions for clinker phases analysis.

As C_3S phase provides resistance to cement such XRD analysis can help predict the 3-day resistance to compression of the future cement obtained from these clinkers while 7-day resistance and 28-day resistance can be influenced by other factors like fineness and particle size distribution for example.

Acknowledgements

The authors would like to thank Mr. Eric Hovsepian, Mr. Didier Bonvin and Dr. Ravi Yellepeddi of Thermo Fisher Scientific, Switzerland, for their collaboration and useful discussions.

To see our full X-ray product portfolio, please visit **www.thermoscientific.com/xray**

Figure 6: ARL 9900 Total Cement Analyzer fully automated with transport belt from automatic mill and press