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Report:

The experiment was a success and we have already submitted a publication to ***Journal of Applied Crystallography*** with the results of this experiment.

Abstract. The appropriated polymorphs that constituted most Portland cements have been synthesised: tricalcium silicate, dicalcium silicate, aluminate, ferrite, gypsum, bassanite and calcite. They have been used to prepare artificial mixtures, i. e., white Portland clinker, grey Portland clinker and two types of grey Portland cements. Quantitative mineralogical analyses of these mixtures have been obtained by widely available laboratory X-ray powder diffraction (λ=1.54Å) and the Rietveld method. To assess the accuracy of these analyses, high-energy synchrotron X-ray powder data (λ=0.40Å) for the same mixtures have also been studied. Furthermore, synchrotron X-ray powder data were also collected for binary mixtures of the appropriated polymorphs and corundum standard. This was done to determine the presence of impurity crystalline phases in the synthesised samples and to check the presence of non-negligible amorphous phase contents. The errors in the synchrotron X-ray analyses are quite low (usually smaller than 1 % w/w). The relative errors in the laboratory X-ray analyses are of the order of 2 % for the main phases and increase to approximately 5-10 % for the low content components. These errors are acceptable in the factories and the routine application of this methodology for industrial materials is expected soon.

Initially, we prepared seven binary mixtures of the appropriated polymorphs which are given in Table 1 with the results of the Rietveld analysis, the R_F factors for each phase and the correction factors, $\mathbf{f_c}$. $\mathbf{f_c}$ values are quite close to 1.00 which indicated that the phases have very small non-crystalline contents.

Then, we collected pattern for "simulated" Portland clinkers and cements. We prepared four mixtures: **(1) white Portland clinker** [80 % C3S, 15 % C2S, and 5 % C3A]; **(2) grey Portland clinker** [60 % C3S, 20 % C2S, 10 % C4AF and 10 % C3A]; **(3) grey Portland cement-1** [62 % C3S, 15 % C2S, 10 % C4AF, 5 % C3A, 4 % $CaSO_4 \cdot 2H_2O$ and 4 % $CaSO_4 \cdot 1/2H_2O$]; **(4) grey Portland cement-2** [65 % C3S, 10 % C2S, 5 % C4AF, 5 % C3A, 5 % $CaSO_4 \cdot 2H_2O$, 5 % $CaSO_4 \cdot 1/2H_2O$ and 5 % $CaCO_3$]. This last mixture was collected

twice to assess both precision and accuracy of the Rietveld quantitative phase analyses. As an example, the results are given in Table 2 together with similar analyses using laboratory X-ray powder diffraction.

Table 1. Weight fractions for binary mixtures and synchrotron X-ray powder diffraction results. R_F values for each phase are also given.

Binary mixture	Weighed (W_i) / %	SXRPD (R_i) / wt. %	R_F / %	f_c
C_3S	49.85	47.75(6)	5.41	0.9194
α-Al_2O_3	50.15	52.25(7)	2.20	
C_2S	49.55	50.29(4)	2.57	1.0300
α-Al_2O_3	50.45	49.71(5)	2.22	
C_3A[a]	50.14	49.68(4)	4.72	0.9818
α-Al_2O_3	49.86	50.32(5)	2.89	
C_3A[b]	50.14	49.30(3)	3.87	0.9670
α-Al_2O_3	49.86	50.70(3)	2.05	
C_4AF	50.02	47.91(4)	3.59	0.9190
α-Al_2O_3	49.98	52.09(4)	2.95	
Gypsum	50.00	50.26(4)	2.67	1.0105
α-Al_2O_3	50.00	49.74(4)	1.64	
Bassanite	49.87	49.24(6)	3.72	0.9751
α-Al_2O_3	50.13	50.76 (6)	1.53	
$CaCO_3$	51.03	52.58(4)	3.21	1.0641
α-Al_2O_3	48.97	47.42(4)	1.98	

[a] Measured in a capillary of 2 mm. [b] Measured in a capillary of 1 mm.

Table 2. Comparison of the weight fractions for artificial grey Portland cement-2. Weighed and corrected weighed mass fractions are compared with the QPA from SXRPD and LXRPD analyses by the Rietveld method.

	Weighed / %	$Weighed_c$ / %	$SXRPD_1$ / wt. %	$SXRPD_2$ / wt. %	$LXRPD_1$ / wt. %	$LXRPD_2$ / wt. %
C_3S	65.00	63.05	64.06(6)	63.78(6)	62.7(2)	63.0(2)
C_2S	10.00	10.87	9.66(11)	9.69(11)	11.5(3)	9.6(3)
C_3A	5.00	5.14	5.36(5)	5.50(4)	5.1(2)	5.1(1)
C_4AF	5.00	4.85	4.76(5)	4.94(5)	4.4(2)	4.7(2)
Gypsum	5.00	5.33	5.49(7)	5.54(7)	4.9(1)	5.8(2)
Bassanite	5.00	5.14	4.96(6)	4.85(6)	5.5(2)	5.6(2)
$CaCO_3$	5.00	5.61	5.71(6)	5.70(6)	5.9(1)	6.2(2)

The QPA of SXRPD data of Portland cements are both precise and accurate. The precision in the SXRPD data analyses is very high as shown in Table 2 where two analyses with data recorded from two different capillaries are presented. This is a very complex case with seven phases and five of them at ≈5 % w/w level. The relative errors between the two analyses (precision) in the two main phases are smaller than 0.5 % and in the low content phases are smaller than 3% (absolute errors always lower than 0.3 %). Furthermore, the SXRPD data analyses are also accurate because the determined weight fractions agree fairly well with those weighed and $weighed_c$, (the results for the other three simulated cements are given in the publication). The relative errors compared with the weighed and $weighed_c$ values (accuracy) are of the order of 1 % for the main phases and of the order of 3-4 % for the low content phases. However, SXRPD is an expensive technique useful to characterise/certify standard mixtures but the routine QPA using powder diffraction has to be carried out in house with the laboratory X-ray devices. The results from laboratory X-ray studies have acceptable low errors as shown in Table 2.

Hence, the methodology for the analysis of Portalnd cements with powder diffraction data and the Rietveld method has been assessed.