X-Ray Data Services

UNIVERSIDAD DE MÁLAGA

Caso práctico: X-RAY DATA SERVICES

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XDS: X-Ray Data Services

Spin-off de la Universidad de Málaga

Training

(Data collection, Analysis interpretation, ...)

Innovation & Knowledge transfer

(Research collaborations, Project assessment, ...)

X-RAY DATA SERVICES

Analysis

(Rietveld phase analysis, Amorphous determination, SAXS, ...)

Consulting

(Protocol validation, Regulations, ...)

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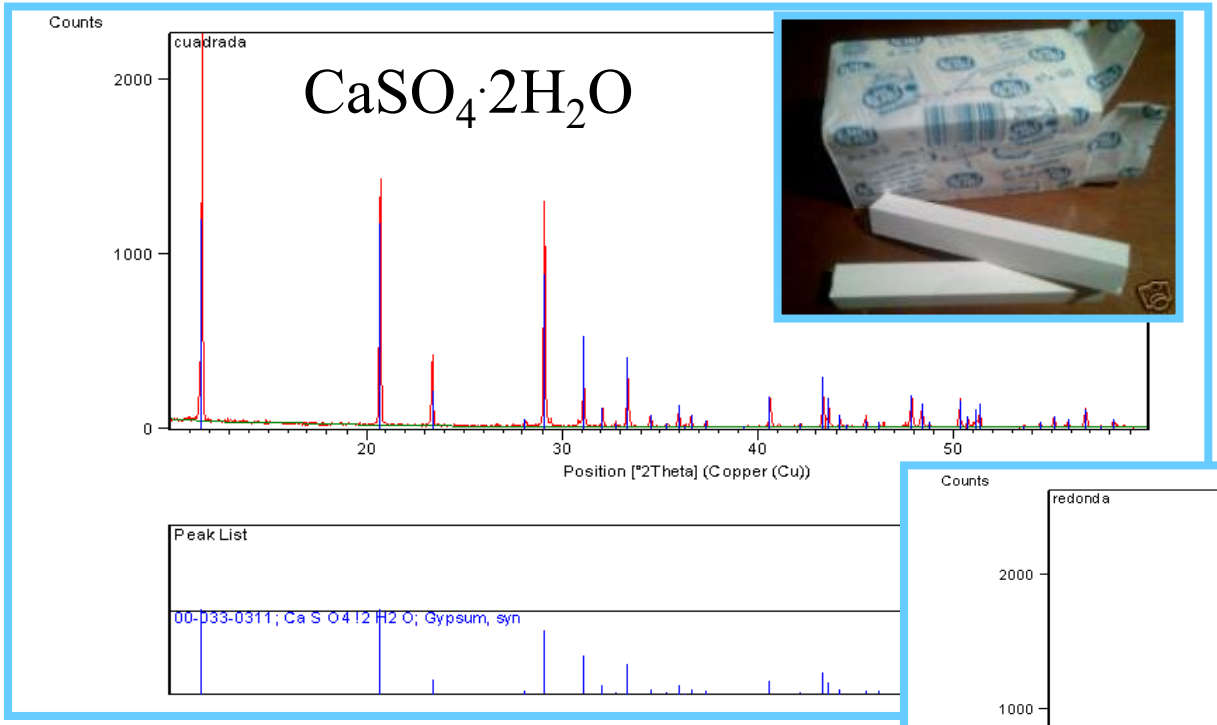
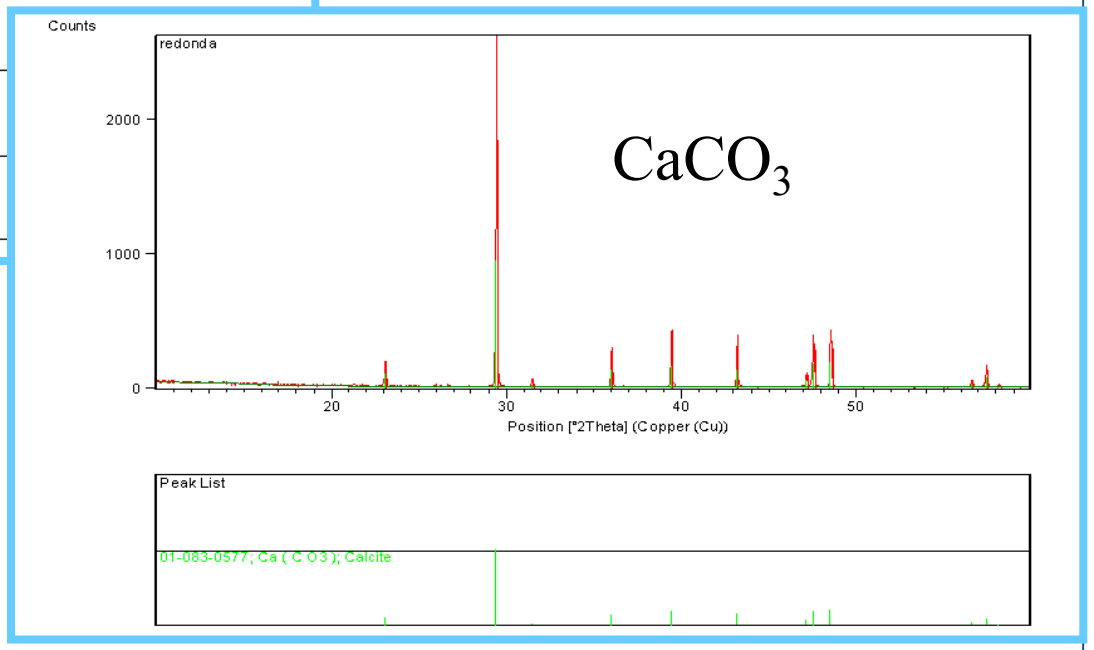
The powder diffraction pattern

is the fingerprint of a crystalline material / compound



Chalk identification



PDF

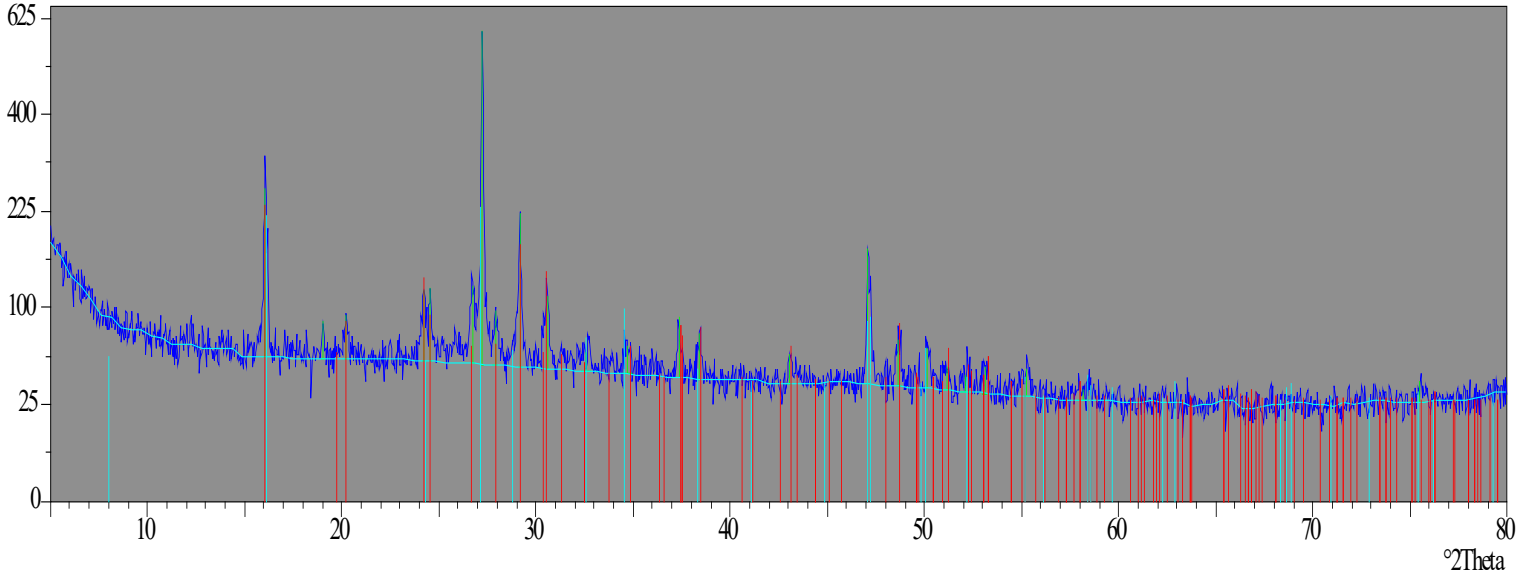
- identification

Why powder diffraction is so important and useful

Example from ‘Policía científica de Madrid’

- Drug analysis:
  Black cocaine is one which does not give a positive colorimetric test.
  It is chemically ‘masked’ !!

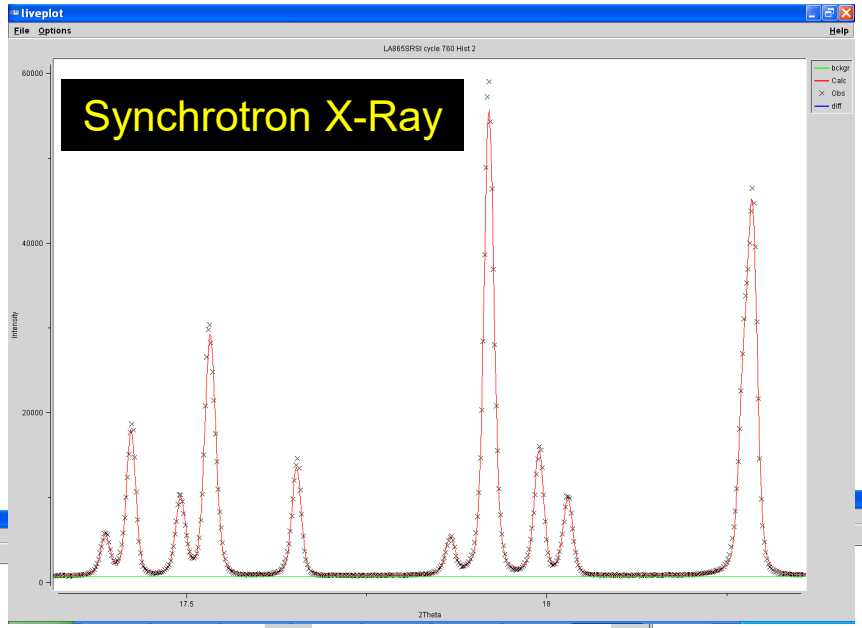
Powder diffraction easily identifies the ‘active principle’ **cocaine** plus the added substance **copper tiocianate** for interfering the test.



Why SXRPD?

$La_{8.65}Sr_{1.35}Si_6O_{26.325}$

Three patterns:

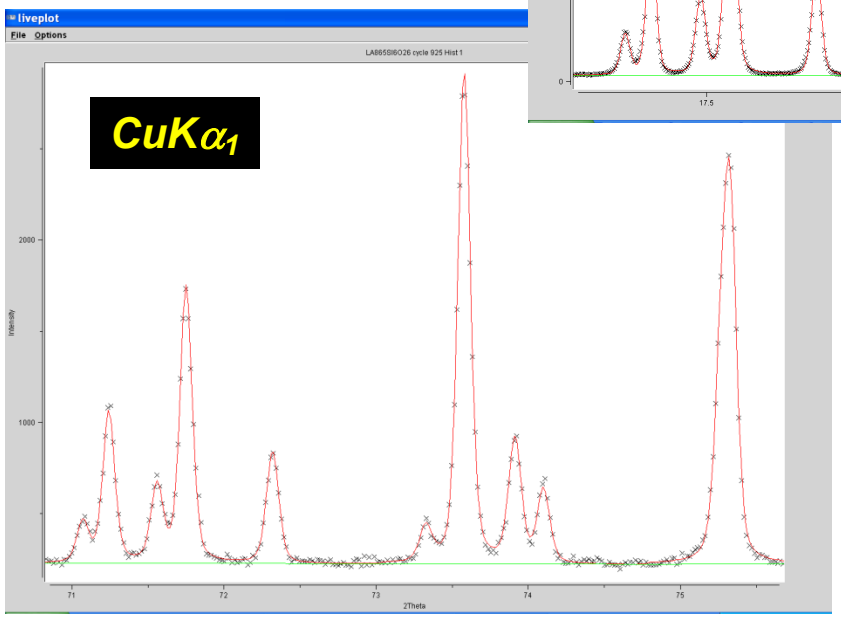


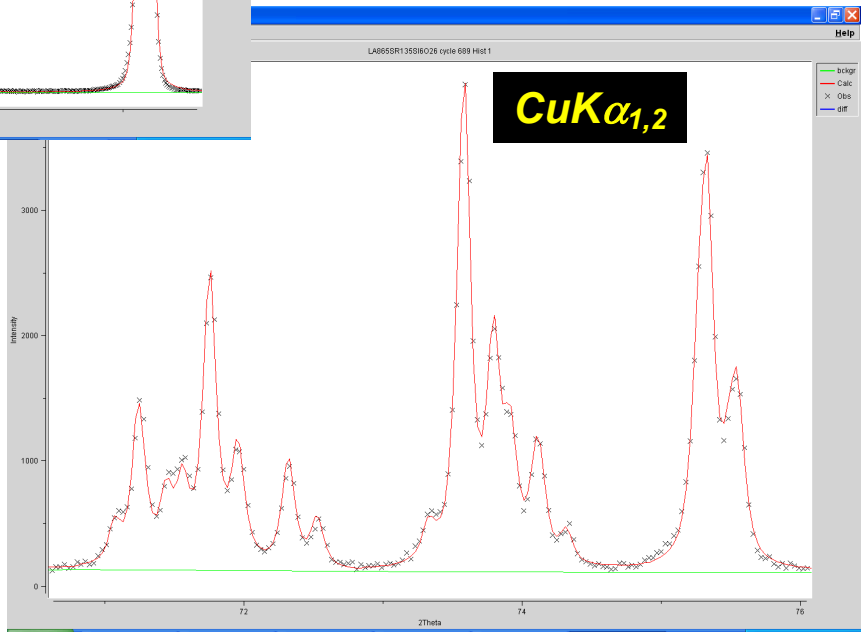
Better data

→ **Better analyses**

→ **Lower LoQ, LoD**

→ **Experimental conf.**





Unique collaboration between Henkel and the University of Malaga towards eco-cement characterization at the ALBA Synchrotron

Working together, scientists from Henkel, ALBA and University of Malaga, using synchrotron-based high-resolution powder X-ray diffraction, have conducted a series of novel experiments to study in real time the setting behavior of new cement formulations.

● The work is an excellent example of a successful collaboration between industry (Henkel), academia (University of Malaga) and a research institution (ALBA), each making their own, unique contribution to the development of new, sustainable technology.

high-energy X-ray beam (8 to 50 keV) and state-of-the-art X-ray detectors. This allowed acquisition of powder X-ray patterns both at high speed to monitor the changes in cement formulations, as well as with high resolution, producing high-quality data, suitable for quantitative analysis (Fig. 20). Thanks to good planning of ALBA staff, and especially the

Industry News

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➢ Cement

Objectives: To perform an accurate full mineralogical analysis of anhydrous and hydrated materials, including the quantification of Amorphous and Crystalline non-quantified (ACn) contents by SXRPD, Rietveld method and the Internal Standard methodology.

In-situ early age hydration of cement-based materials by synchrotron X-ray powder diffraction

Cement (anhydrous and paste) characterisation

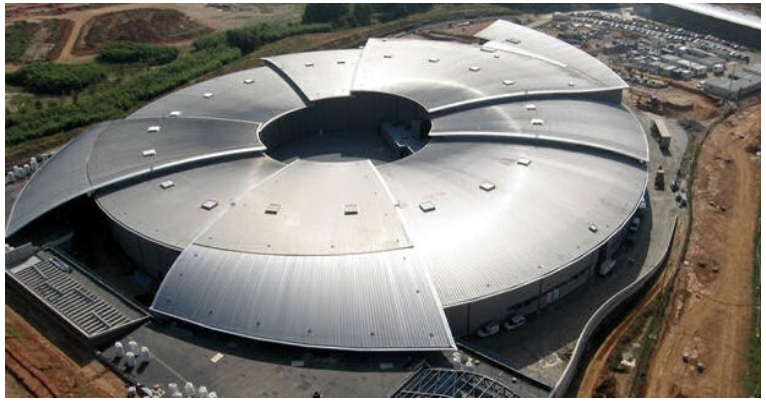
RAW MATERIALS

Henkel binder_H1:

Bassanite 75 wt%, Alite 15 wt%, Metakaolin 10 wt%

The studied sample was an environmentally-friendly cement sample from Henkel, composed of bassanite mixed with 15wt% Portland cement and 10wt% Metakaolin, labelled H1.

SXRPD (BL04-MSPD, ALBA)



Data collection

λ= 0.620085(3) Å

Debye Scherrer configuration

Capillaries were spun

Angular range 1-35º (in 2θ)

15 minutes per pattern

MYTHEN Detector

In-situ early age hydration of cement-based materials by synchrotron X-ray powder diffraction

Cement (anhydrous and paste) characterisation

SAMPLE PREPARATION

Henkel binder_H1

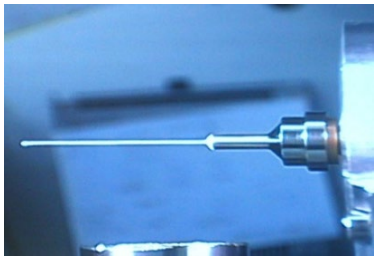
Bassanite 75 wt%, Alite 15 wt%, Metakaolin 10 wt%

+

15 wt% of Quartz (internal standard)

20 minutes →

HYDRATION PROCEDURE

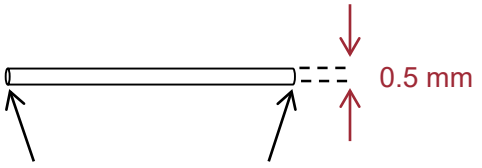


Cement

+

Water

→



Sealed with wax

w/c = 0.375

In-situ early age hydration of cement-based materials by synchrotron X-ray powder diffraction

- The very fast dissolution of bassanite has been quantified showing the accuracy of the methodology.

- The principal hydration product is gypsum. This phase appears after 15 minutes from the dissolution of bassanite.

- After about 5 hours of hydration, gypsum starts to hydrate to form ettringite.

- These results are crucial in the understanding and development of improved cement materials.

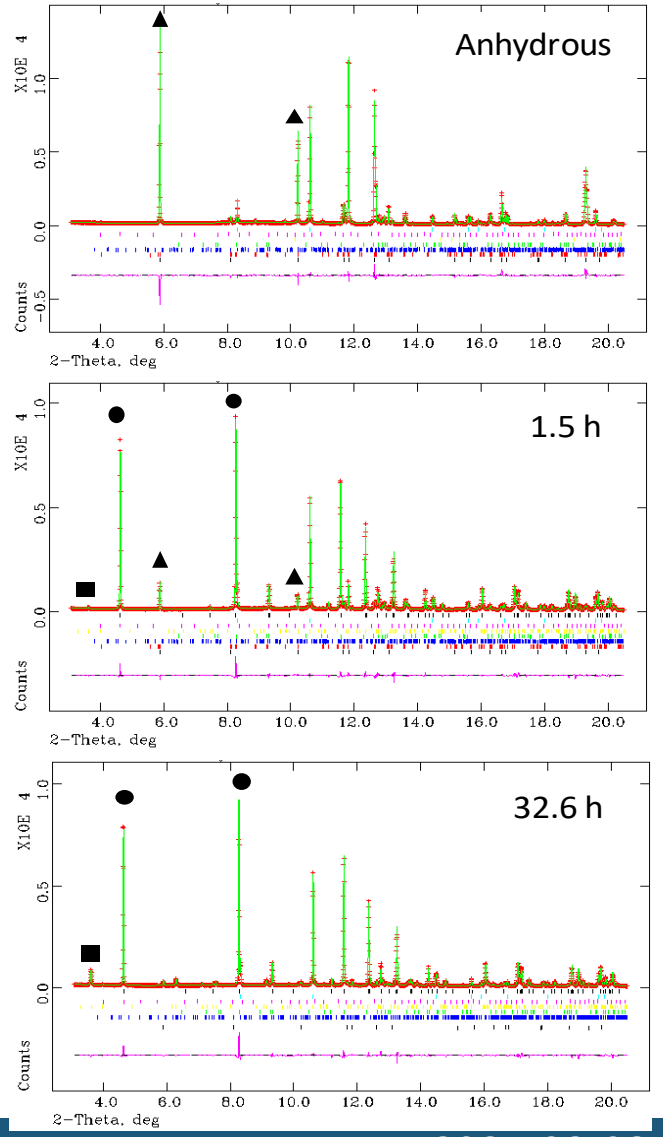


Figure. Rietveld plots for anhydrous (top), hydrated after 1.5 hours (middle) and 32.6 hours (bottom) H1 cement.

Data analysis

Table. Derived RQPA results (wt%) for H1_Q sample including the overall amorphous content (amorphous, not-quantified crystalline phase(s) and free water).

Phases	0h	15min	60min	1.5h	2h	6h	11h	20h	32.6h
Bassanite ($C\underline{S}H_{0.5}$)	53.4(2)	54.9(2)	23.0(2)	7.8(2)	3.8(2)	1.0(1)	1.8(2)	1.4(2)	1.4(2)
Alite (C_3S)	6.3 (2)	5.7(2)	6.2(2)	5.9(2)	6.0(2)	5.7(2)	5.1(2)	3.5(2)	2.7(2)
Belite (C_2S)	0.4(1)	0.5(1)	0.3(1)	0.6(1)	0.7(1)	0.5(1)	0.8(1)	0.5(1)	0.4(1)
Tricalcium aluminate (C_3A)	0.4(1)	0.5(1)	0.4(1)	0.4(1)	0.4(1)	0.3(1)	0.3(1)	0.3(1)	0.2(1)
Gypsum ($C\underline{S}H_2$)	0.0	5.0(2)	43.2(2)	61.0(2)	64.8(2)	66.6(2)	68.6(2)	61.2(2)	61.6(2)
Ettringite ($C_6A\underline{S}_3H_{32}$)	0.0	0.3(1)	0.4(1)	0.4(1)	0.5(1)	1.2(1)	2.2(1)	3.4(2)	6.5(2)
A (Amorphous+free water)	38.7(3)	32.3(4)	25.6(4)	22.8(4)	22.8(4)	23.7(3)	20.2(4)	28.5(4)	26.0(4)

CERAMICS MATERIALS

Information obtained by X-Ray Diffraction and Rietveld method

- Mineralogical characterization.

- Quantification of crystalline phases and amorphous / non-diffracting material.

- Mineralogical phase evolution with temperature.

- Influence of elements/dopants in the crystallochemistry (solid solutions).

- Microstructural studies.

- Crystal structure determination (new phases).

Mineralogical phase evolution with temperature

- Kaolinite decreases after 500ºC.

- Quartz is present at all firing temperatures.

- Mullite phase is formed from 1100ºC to 1230ºC.

- The transformation of β-quartz to β-cristobalite does not take place.

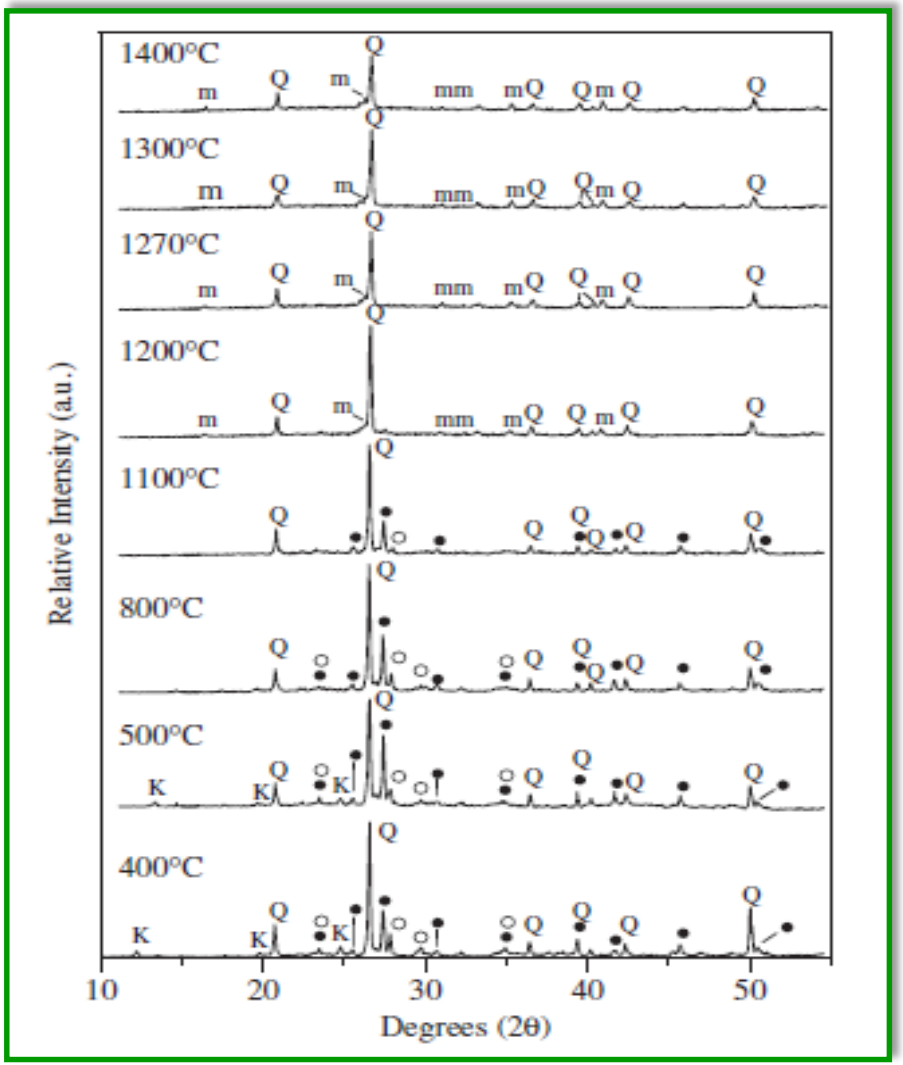


Fig. 1. X-ray diffractograms of a standard stoneware body fired in the 400º - 1400ºC interval. Q, quartz; K, kaolinite; ●, microcline; ○, albite; m, mullite

Mineralogical phase evolution with temperature

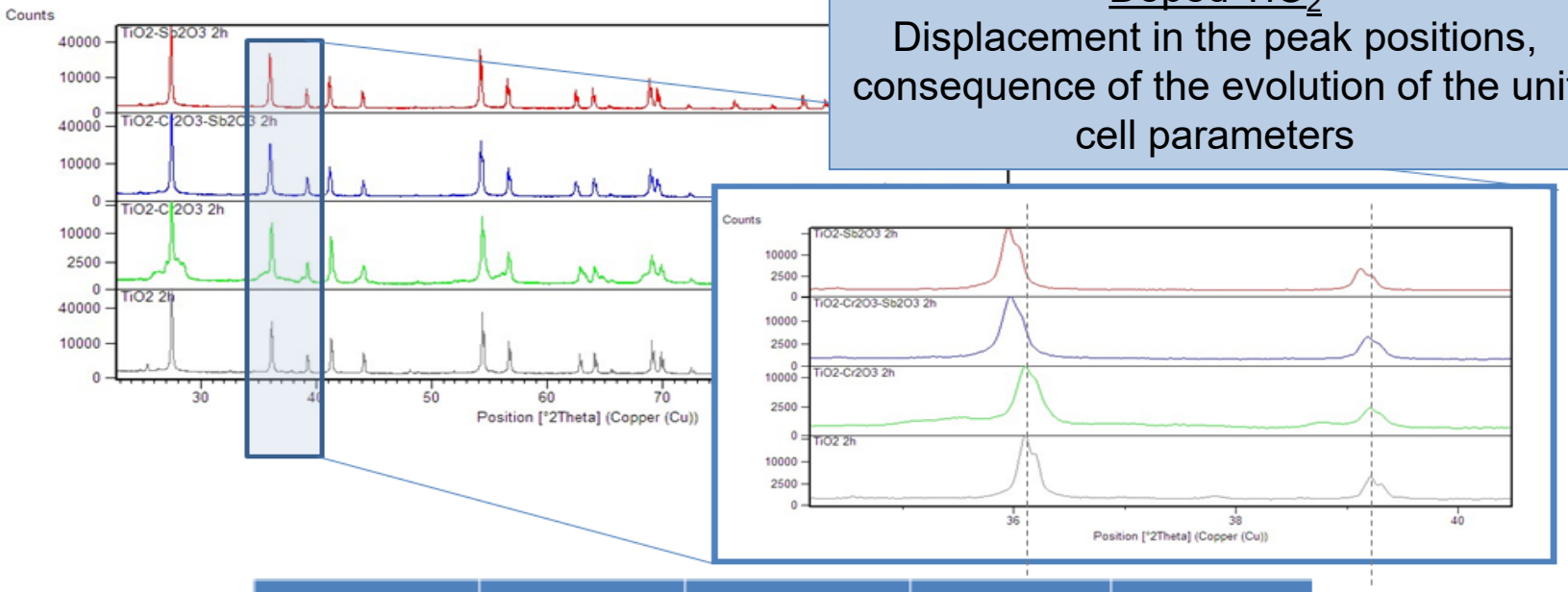
	Temperature (ºC)						
	1000	**1100**	**1200**	**1230**	**1260**	**1300**	**1400**
Amorphous phase	45 (1)	53 (1)	57 (1)	62 (1)	61 (1)	61 (1)	67 (1)
Quartz	29.3 (2)	28.1 (2)	27.6 (2)	24.1 (1)	24.5 (1)	24.7 (1)	19.3 (3)
Microcline	17.4 (3)	15.4 (4)	3.2 (3)	-	-	-	-
Albite	3.2 (3)	-	-	-	-	-	-
Muscovite	5.1 (4)	-	-	-	-	-	-
Mullite	-	3.5 (3)	12.2 (3)	14.0 (2)	14.5 (2)	14.3 (2)	13.7 (2)

Optimum temperature ~ 1230ºC

Martín-Márquez et al., J. Am. Ceram. Soc., (2009), 92, 229-234

Pigments Industry

Study of a series of inorganic pigments



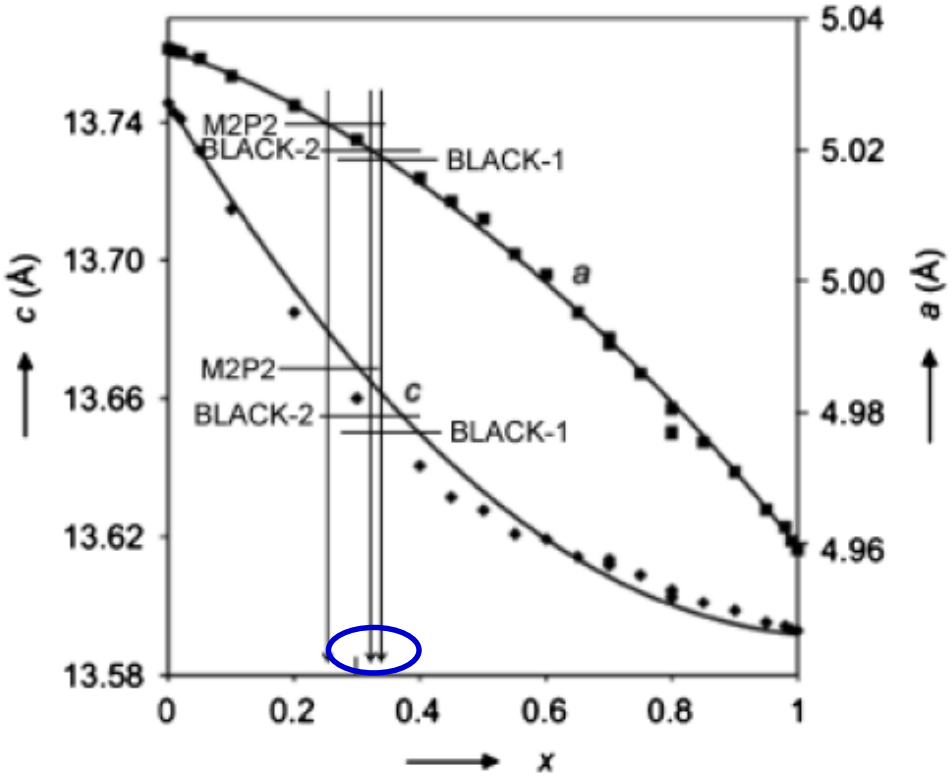
Doped TiO_2

Displacement in the peak positions, consequence of the evolution of the unit cell parameters

Lattice parameters	TiO_2	TiO_2-Cr_2O_3	TiO_2-Sb_2O_3-Cr_2O_3	TiO_2-Sb_2O_3
a,b/ Å	4.59470(3)	4.5958(2)	4.59812(5)	4.60537(3)
c/ Å	2.95955(2)	2.9591(2)	2.97424(4)	2.97434(2)
V/ 10^6 pm^3	62.48	62.50	62.88	63.08

Solid solutions formation

Ceramic Pigment: $(Cr_xFe_{1-x})_2O_3$ solid solution

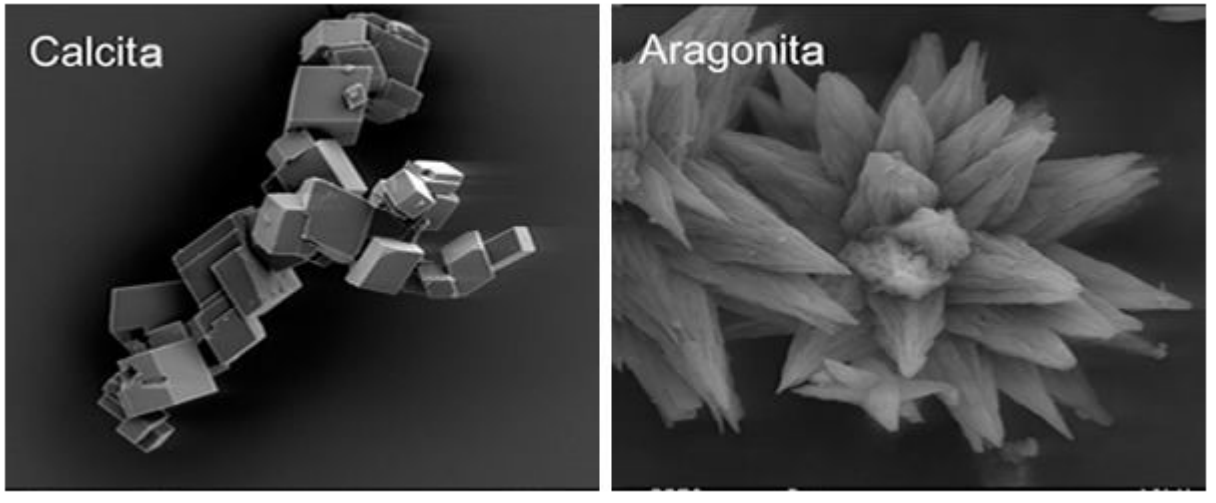


wt% of chromium is within the corundum structure

Indirectly determined from the analysis of unit cell parameters.

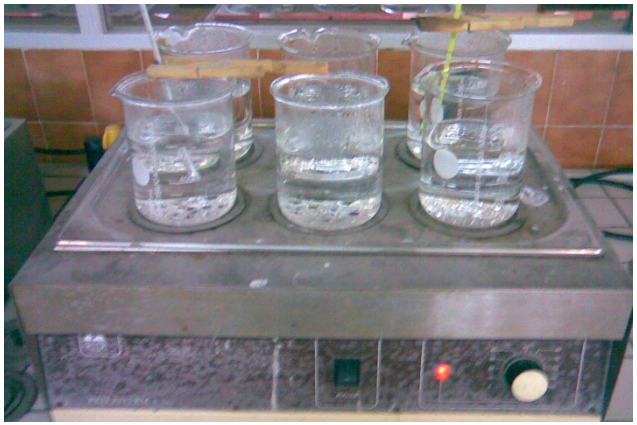
Differences of ~1 wt% in Cr content can be measured by high-resolution XRD

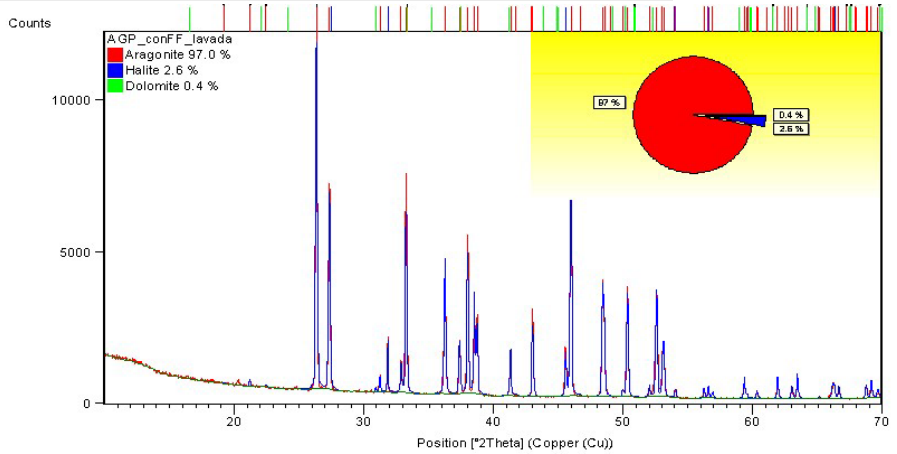
Magnetic-water-treatment for avoiding scales

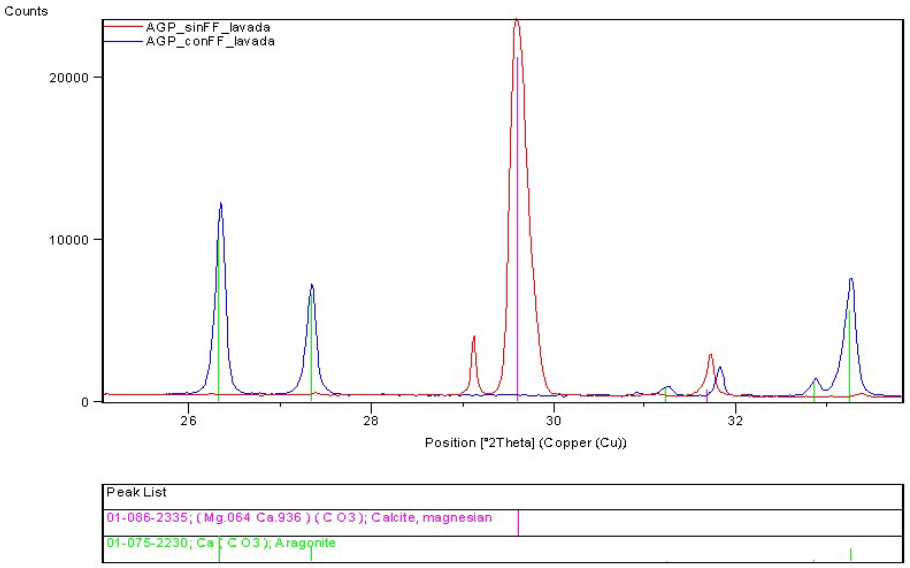


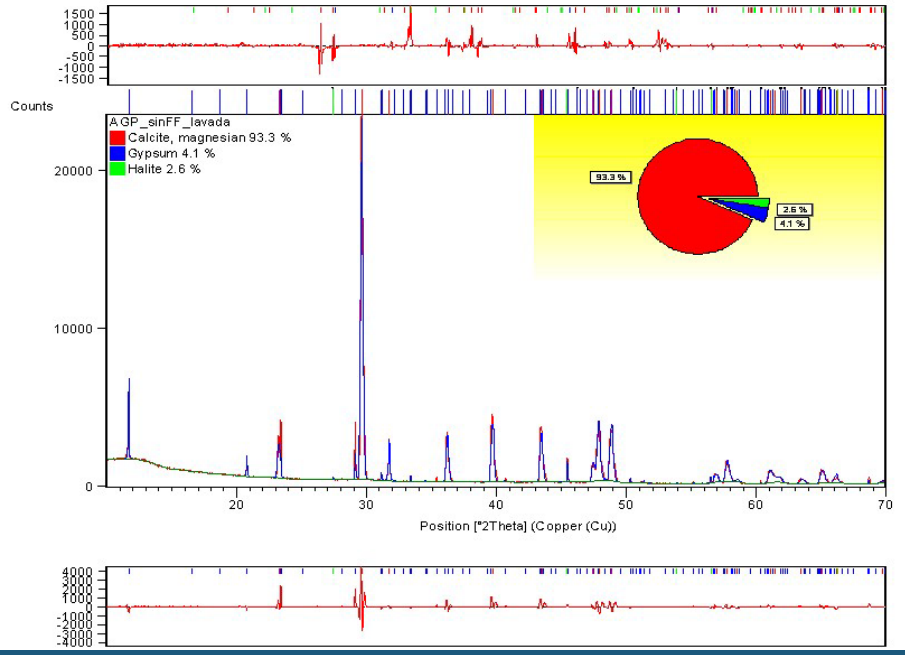
Quantitative mineralogical phase analysis

here for validating magnetic-water-treatment processes









2024-02-02

Analysis

(Phase analysis, Amorphous determination)

Innovation & Knowledge transfer

(Research collaborations, Project assessment, ...)

Training

(Data collection, Analysis interpretation, ...)

Consulting

(Protocol validation, Regulations, ...)