



Rietveld quantification of γ -C₂S conversion rate supported by synchrotron X-ray diffraction images*

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Abstract: The pure γ -Ca₂SiO₄ (γ -C₂S) phase was prepared at 1623 K of calcining temperature, 10 h of holding time and furnace cooling. The β -C₂S phase was obtained through γ -C₂S conversion with the following calcination system which was adopted at 1473 K of calcining temperature, 1 h of holding time and then water-cooling. The conversion rate of γ -C₂S was studied by the Rietveld quantitative laboratory X-ray powder diffraction supported by synchrotron X-ray diffraction images. The refinement results show that the final conversion rate of γ -C₂S is higher than 92%. The absolute error of the γ -C₂S conversion rate between two Rietveld refinements (sample with or without α -Al₂O₃) is 3.6%, which shows that the Rietveld quantitative X-ray diffraction analysis is an appropriate and accurate method to quantify the γ -C₂S conversion rate.

Key words: γ -C₂S, β -C₂S, Rietveld quantification, Synchrotron X-ray diffraction image

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1 Introduction

With the rapid development of the cement industry, how to reduce the energy consumption and CO₂ emission is still an important issue to be addressed (Popescu *et al.*, 2003; Liu *et al.*, 2011; Wang and Liu, 2011). Belite cement (BC), which contains more than 50% (in weight) of Ca₂SiO₄ (C₂S), has such advantages as lower calcination temperature, less calcium content, and lower heat of hydration. Therefore, it draws wide attention of many researchers (Chatterjee, 1996; Fukuda and Ito., 1999; Morsli *et al.*, 2007; García-Díaz *et al.*, 2011). However, BC has a chief disadvantage of low mechanical strength at its

early age. This is mainly due to the low activity of β -C₂S which is the key phase in BC. In order to improve the activity of β -C₂S, many researchers focused on monomineral preparation and modification of β -C₂S (Chen and Wang, 2000; Fukuda *et al.*, 2001; Li *et al.*, 2006). One of the monomineral preparation methods for pure β -C₂S is calcining the sample repeatedly to obtain pure γ -C₂S and then the β -C₂S is prepared through phase conversion. Yet γ -C₂S at the most stable phase at room temperature cannot be converted into β form completely during the heating and cooling period. Hence, it is significant to quantify the γ -C₂S conversion rate, which has aroused great concern (Zhang, 1995). In the past, traditional quantitative X-ray diffraction analysis (QXDA) (such as internal standard, external standard, and *K* value method) as a direct measurement was used to quantify the γ -C₂S phase conversion rate. However, it only can be applied to a single peak analysis, and polymorphs of β -C₂S and γ -C₂S have a strong peak overlap. Thus,

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errors will appear if the traditional QXDA method is used. Besides, it is difficult to prepare completely pure β -C₂S to establish a correct phase-analysis calibration curve. Therefore, both of the above factors may lead to serious errors. The recent development of the Rietveld QXDA technique can eliminate or minimize the errors by minimizing the differences between the experimental pattern and calculated pattern (Rietveld, 1969; De la Torre *et al.*, 2003; 2008; Scrivener *et al.*, 2004; Le Saoût *et al.*, 2011). With the primary purpose of assuring that the laboratory X-ray powder diffraction (LXRD) pattern is effective for the Rietveld QXDA technique in quantifying the conversion rate of γ -C₂S into β -C₂S, synchrotron X-ray diffraction images and integrated diffraction patterns are analyzed in this study.

2 Experimental

2.1 Synthesis of β -C₂S and α -Al₂O₃

A mixture of stoichiometric proportion of CaCO₃ and SiO₂ (99.99%, Sinopharm Chemical Reagent Co., Ltd. (SCRC)) was prepared to get C₂S. The mixture was ground in an agate ball mill at 200 r/min for 30 min, pelletized, heated at 1623 K for 10 h and cooled by turning off the furnace. The resulting solid sample underwent a change, through the above process to decrease the free lime (f-CaO) content to less than 1%, which could ensure pure γ -C₂S would be obtained. After that, the sample was ground and heated twice in a Pt crucible at 1473 K for 1 h. The cooling system for this phase conversion was first adopted as air-cooling and then water-cooling was applied (when the calcining process is finished, a sample in the platinum crucible was rapidly taken out and immersed into water, the height of which was lower than the platinum crucible to avoid contacting with C₂S) as the second approach.

α -Al₂O₃ was synthesized by γ -Al₂O₃ according to the following procedure (De la Torre *et al.*, 2003). The powder of γ -Al₂O₃ was ground in an agate ball mill at 200 r/min for 30 min, heated at 1373 K for 4 h and cooled by turning off the furnace. Then the product was ground and heated at 1423 K for 6 h through a second-round thermal treatment.

2.2 Experimental test

The content of f-CaO in samples was determined by the glycerol-ethanol method. LXRD patterns were recorded by Rigaku X-ray diffractometer (D/max2550VB3+/PC, Rigaku International Corporation, Japan). The instrument settings for LXRD are described in Table 1. All Rietveld refinements were carried out through the GSAS software (Larson and Von Dreele, 2004). 2D synchrotron X-ray diffraction (SXR-2D) experiments were performed at the beamline BL14B1 of Shanghai Synchrotron Radiation Facility in China. SXR-2D images were recorded using a 3072×3072 charge-coupled device (CCD) detector and processed by the FIT2D software (Hammersley, 1998). Experimental parameters for SXR-2D are listed in Table 2.

Table 1 LXRD instrument settings

Scanning type	Continuous scanning	Step scanning
X-ray radiation (CuK _α ($\lambda=1.54$))	40 kV/100 mA	40 kV/250 mA
DivSlit (°)	1	1/2
DivH.L.Slit (mm)	10	10
SctSlit (°)	1	1/2
RecSlit (mm)	0.3	0.15
Angular range, 2θ (°)	5–70	5–70
Step width (°)	0.02	0.018
Scan speed (°/min)	2	–
Count time (s)	–	5.2
Diffractometer	Rigaku D/max2550	
Monochromator	Fixed Monochromator	
Goniometer	RINT2000 vertical	

Table 2 Experimental parameters for SXR-2D

Description	Value
Size of horizontal pixels (μm)	73.242
Size of vertical pixels (μm)	73.242
Distance of sample to detector (mm)	113.6133
Wavelength (nm)	0.12398
Beam size (mm)	0.4×0.4
Exposure time (s)	30
Polarisation factor	0.93

3 Results and discussion

The LXRD patterns of γ -C₂S are shown in Fig. 1. A1 and A2 were the mixture of CaCO₃ and SiO₂ heated once and twice, respectively. The content of f-CaO in A2 was determined as 0.2%, which was

decreased significantly from A1 that was about 2.4%. Also, as seen from the LXR D pattern, the general trend of f-CaO was as expected. The characteristic peaks of f-CaO ($2\theta=32.2^\circ$, $d=0.27774$ nm and $2\theta=37.3^\circ$, $d=0.24059$ nm) disappeared in A2. The indexing result showed that the LXR D pattern of A2 matched well with the standard powder diffraction file card (No. 49-1672).

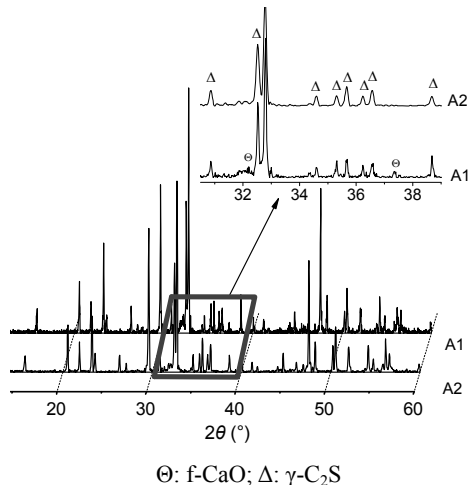


Fig. 1 LXR D patterns of β -C₂S

The calcination system of phase conversion was adopted as previously described. The LXR D patterns of β -C₂S cooled at the first and second times are shown in Fig. 2 (continuous scanning) and Fig. 3 (step scanning), respectively. After the sample was calcinated for the second time and cooled in water, the intensity of γ -C₂S unique distinguishing peaks at $2\theta=29.6^\circ$ and 47.5° decreased significantly, which indicated that only a small quantity of γ -C₂S existed in the sample (Fig. 3).

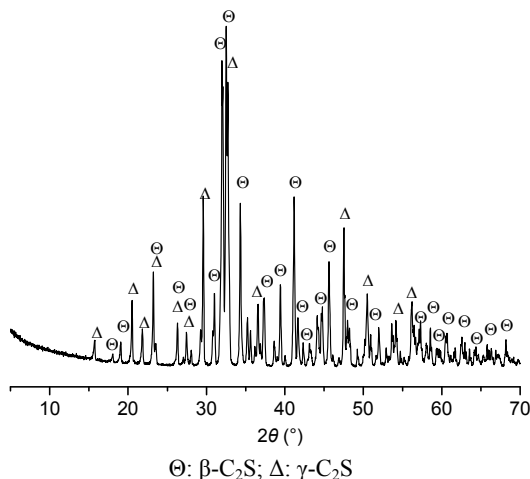


Fig. 2 LXR D pattern of β -C₂S air-cooled at the first time

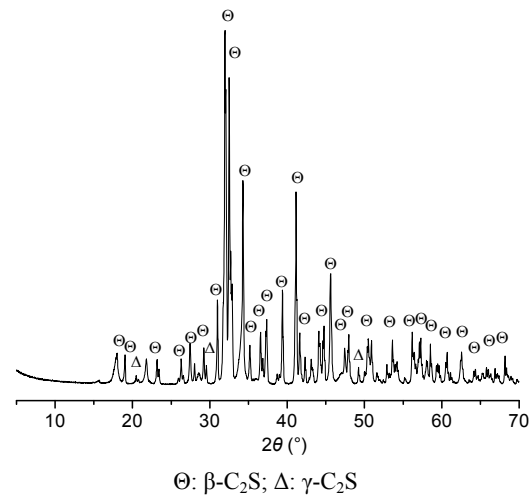


Fig. 3 LXR D pattern of β -C₂S water-cooled at the second time

Before calculating the quantity of γ -C₂S and β -C₂S by the Rietveld method, it is essential to ensure the high quality and reproducibility of the X-ray diffraction data. The key issue for the point detector data is that the diffracting particles in all directions are sufficient and randomly distributed. Thus, after being fine-ground, the sample whose LXR D pattern would be refined by the GSAS software was taken for SXRD-2D analysis at room temperature. SXRD-2D patterns were recorded using a flat CCD detector, mounted perpendicular to the incident beam behind the sample. The sample was adhered between two pieces of polyimide tape (Fig. 4). To obtain factual diffraction data of the sample, the same polyimide tape without powder was also immediately exposed at the incident beam for 30 s after finishing the test of the former sample. Synchrotron X-ray diffraction data were processed with the FIT2D software and transmission X-ray diffraction images of the

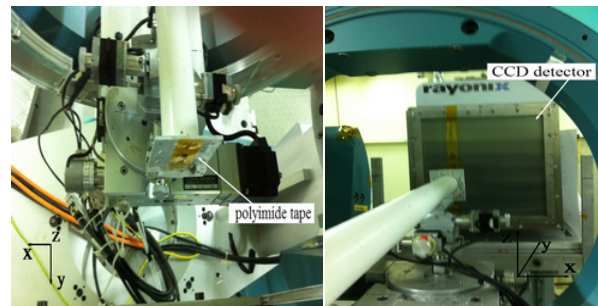


Fig. 4 Experimental station at BL14B1 (y -axis: ray direction, Shanghai Synchrotron Radiation Facility (SSRF), China)

sample with and without polyimide tape are depicted in Fig. 5. Debye-Scherrer cones of C_2S powder diffraction (Fig. 5b) were continuous and individual grains were rarely visible. This indicated that the particles of C_2S were ideal in size and were fulfilled by random distribution, which would reduce the irreproducibility error against poor analysis during the Rietveld refinement.

In the SXRD-2D experiment, lanthanum hexaboride as a standard was used to calibrate the sample-to-detector distance and refine the instrumental parameters. An integrated 1D diffraction pattern of C_2S (Fig. 6) was obtained from a 2D synchrotron diffraction image. As it was integrated from the whole 2D image data, the integrated diffraction pattern revealed more accurately the relative diffraction peak intensities at different values of d-spacing. To some extent, it can be a preliminary criterion to analyze the reliability of the laboratory Bragg-Brentano geometry X-ray diffraction data. The comparison between Fig. 6 and Fig. 3 shows a good corresponding relationship which indicates the fine-ground powder of C_2S heated for a second time and cooled in water had a good reproducibility to be refined by the Rietveld method.

Rietveld QXRD pattern of β - C_2S air-cooled at the first time and water-cooled at the second time are respectively shown in Fig. 7 and Fig. 8. As seen

from the above two figures, the refinements were stable and the fits were satisfactory as indicated by the smoothness of the Yobs–Ycalc (Yobs–Ycalc means the differences between observed (Yobs) and calculated (Ycalc) pattern) curve and the R -factors, which illustrated that the quantification of the γ - C_2S conversion rate was reliable. The quantity of γ - C_2S and β - C_2S obtained at the end of the refinement process and the least square R -factors like R_F , R_{WP} , and R_P are displayed in Table 3. The Rietveld weight fractions of β - C_2S and γ - C_2S in the air-cooled sample were 69.0% and 31.0%, respectively. After the sample was calcined and water-cooled for the second time, the Rietveld weight fraction of β - C_2S in the sample

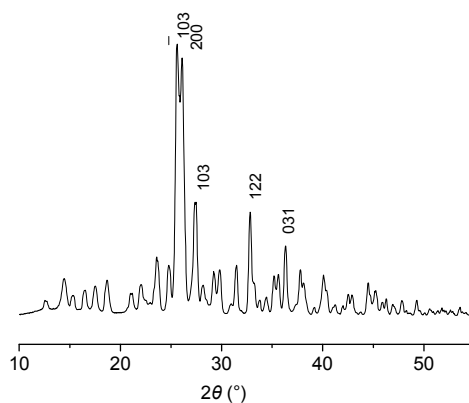


Fig. 6 Integrated diffraction pattern of C_2S converted from synchrotron diffraction image (Fig. 5b)

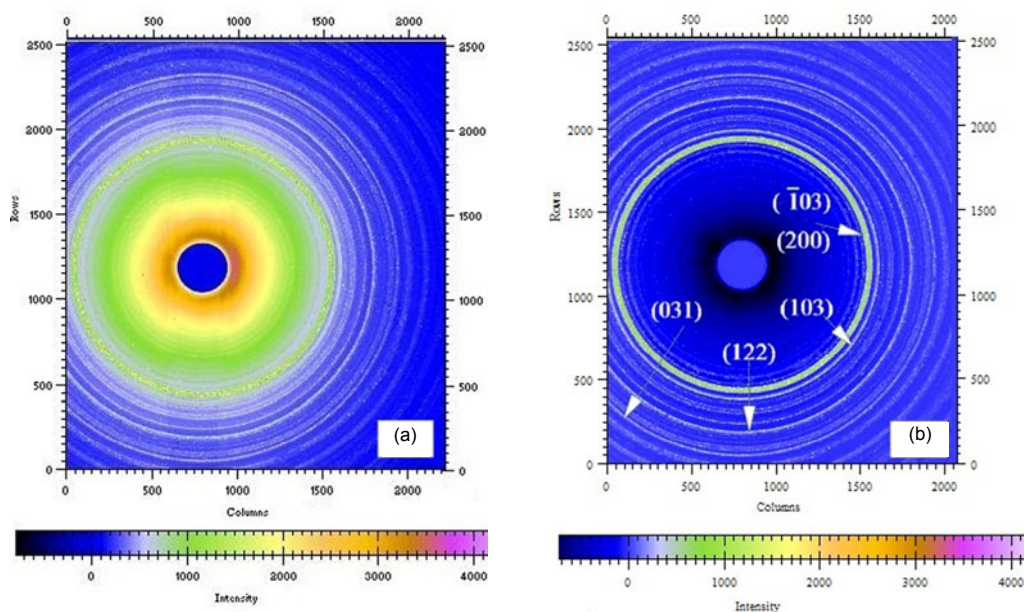


Fig. 5 Synchrotron X-ray diffraction images of C_2S sample with (a) and without (b) polyimide tape (Fig. 5b is obtained through subtracting the transmission X-ray diffraction images of polyimide tape from Fig. 5a)

reached 92.7%, which indicated that most of the β -C₂S had been prepared through the γ -C₂S conversion.

To evaluate the accuracy of the Rietveld quantity phase analysis of C₂S, an artificial mixture of β -C₂S and α -Al₂O₃ were prepared in appropriate proportions ($m_{\text{C}_2\text{S}}=0.4964$ g and $m_{\text{Al}_2\text{O}_3}=0.5036$ g) and the LXR D pattern of the mixture would be refined by GSAS software again. Before that, the mixture was ground in an agate mortar about 15 min for the first time and another 30 min for the second time. They were separately exposed at the synchrotron X-ray incident beam and the original PGM format images of SXRD-2D are shown in Fig. 9. By comparing the two images, Debye-Scherrer cones in Fig. 9b were much smoother and had a better continuation, telling of a very fine and randomly oriented microstructure of the sample. This is mainly because with the grinding time increasing, the particles size in the mixture became smaller, forming a better random distributed sample. Figs. 10 and 11 are respectively a 1D diffraction pattern (converted from SXRD-2D images) and a Rietveld QXRD plot of the mixture. Their perfect

consistency made this LXR D step scanning pattern available for the Rietveld refinement.

The Rietveld quantification phase analysis results for a mixture of C₂S and α -Al₂O₃ after refinement are shown in Table 4. The relatively smoothness of the Yobs–Ycalc curve and small value of the *R*-factors indicates that the fits are in good agreement. From Table 4, several conclusions can be drawn: (1) The relative error between the weighted fraction and Rietveld weight fraction of phases (C₂S and α -Al₂O₃) is only 2.6%, which sufficiently shows an accurate

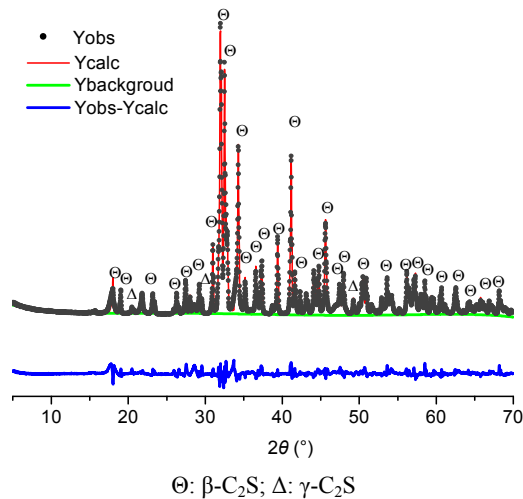


Fig. 8 Rietveld QXRD pattern of β -C₂S water-cooled at the second time
Θ: β -C₂S; Δ: γ -C₂S

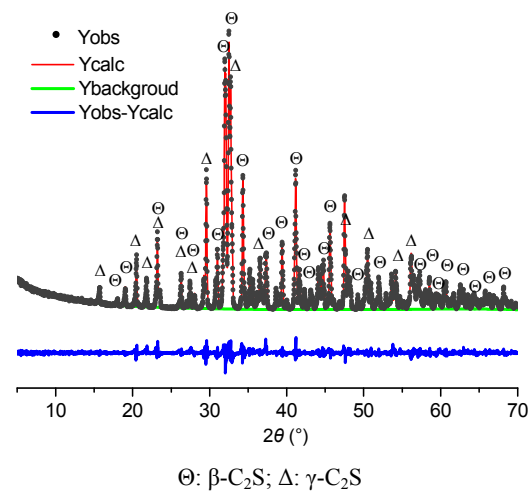


Fig. 7 Rietveld QXRD pattern of β -C₂S air-cooled at the first time
Θ: β -C₂S; Δ: γ -C₂S

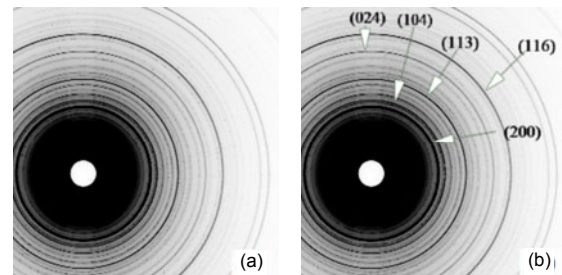


Fig. 9 SXRD-2D images of β -C₂S and α -Al₂O₃ mixture ground for 15 min (a) and another 30 min (b) (partial crystal plane indexes have been pointed out)

Table 3 Rietveld QXRD results of C₂S

Sample	Polymorph	Rietveld weight fraction (%)	<i>R_F</i> (%)	<i>R_{WP}</i> (%)	<i>R_P</i> (%)
Air-cooling (first time)	β -C ₂ S	69.0(1)	4.15	9.63	7.02
	γ -C ₂ S	31.0(2)			
	Σ (C ₂ S)	100			
Water-cooling (second time)	β -C ₂ S	92.7(4)	6.05	11.04	7.76
	γ -C ₂ S	7.3(3)			
	Σ (C ₂ S)	100			

R_F, *R_{WP}*, and *R_P* stand for the structure *R*-factor, the weighted profile *R*-factor, and the profile *R*-factor, respectively

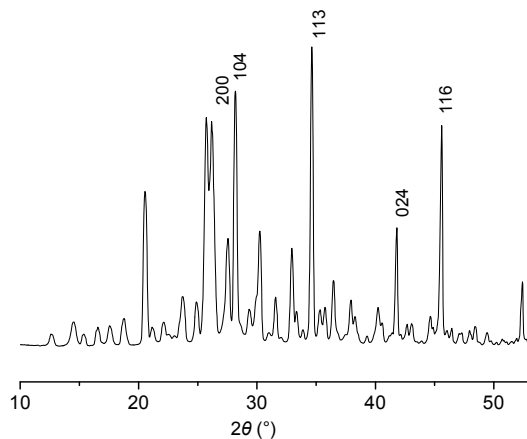


Fig. 10 Integrated diffraction pattern of C_2S and $\alpha-Al_2O_3$ mixture converted from synchrotron X-ray diffraction images (Fig. 9b)

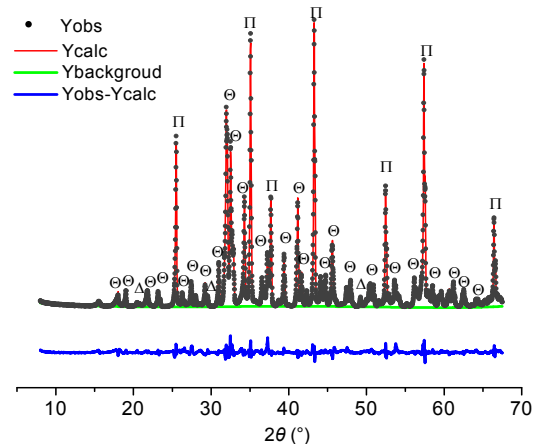


Fig. 11 Rietveld QXRD pattern for C_2S and $\alpha-Al_2O_3$ mixture
Θ: $\beta-C_2S$; Δ: $\gamma-C_2S$; Π: $\alpha-Al_2O_3$

Table 4 Rietveld QXRD results of mixture of C_2S and $\alpha-Al_2O_3$

Polymorph	Weighted fraction (%)	Rietveld weight fraction (%)	Normalization of C_2S	R_F (%)	R_{WP} (%)	R_P (%)
$\beta-C_2S$	—	46.5(4)	96.3	5.11	9.32	6.44
$\gamma-C_2S$	—	1.8(4)	3.7			
$\Sigma(C_2S)$	49.6	48.3	100			
$\alpha-Al_2O_3$	50.4	51.7(3)	—			
Total	100	100	—			

R_F , R_{WP} , and R_P stand for the structure R -factor, the weighted profile R -factor, and the profile R -factor, respectively

result based on the Rietveld refinement method; (2) The Rietveld weight fraction of $\beta-C_2S$ is 96.3%, 3.6% more than that in the C_2S without $\alpha-Al_2O_3$. The reason for the absolute error is that the low content of $\gamma-C_2S$ in the mixture has an extremely weak X-ray diffraction intensity compared with other phases in the sample, especially the $\alpha-Al_2O_3$. So the $\gamma-C_2S$ in this system might be slightly underestimated. However, these errors are acceptable and these results show that the Rietveld QXRD is an appropriate method to quantify the $\gamma-C_2S$ phase conversion.

4 Conclusions

1. The Rietveld quantification shows that the conversion rate of $\gamma-C_2S$ is higher than 92% after it was calcined at 1473 K of calcining temperature, 1 h of holding time and followed by water cooling.

2. The analysis of the 2D synchrotron diffraction image and the 1D integrated diffraction pattern can be used as an intuitive and effective method to check the randomly oriented distribution of sample and to

evaluate reproducibility of the laboratory X-ray diffraction pattern which would be refined by the Rietveld method.

3. The relative error between the weighted fraction and the Rietveld weight fraction of the phases (sample of C_2S and $\alpha-Al_2O_3$) is 2.6%. The absolute error of the $\gamma-C_2S$ conversion rate between the two LXRDRietveld refinements is 3.6%. The Rietveld QXDA analysis is an appropriate and accurate method to quantify the $\gamma-C_2S$ phase conversion.

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