Amorphous/crystalline quantification methods in semicrystalline materials: Mg-carbonate minerals

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INTRODUCTION

Procedures based on X-ray diffraction (XRD) provide detailed information about crystallographic properties of materials as phase identification, lattice parameters, texture, crystallite size or stress of single crystals and polycrystalline materials (Ameh, 2019).

In an XRD experiment, a set of lattice planes, referred as *(hkl)*, is selected by the incident conditions allowing the crystal lattice spacing d_{hkl} determination through the well-known Bragg's law: $2d \sin\theta = n\lambda$; where λ = wavelength of the X-ray source, θ = geometrical known Bragg 2-theta angle, and d = spacing between adjacent parallel crystallographic planes (Gilmore, 2004). This simple equation describes the interaction between X-rays and lattice planes of a crystalline solid. However, in a XRD pattern it may represent phases of different crystalline and amorphous nature. At present, novel instrumentation based on X-ray diffraction is available to analyse the characteristics of materials at different scales and degrees of resolution. In addition, advanced calculation procedures and software tools allow the determination of crystallinity parameters of a wide range of crystalline/amorphous hetero-phases.

The separation of amorphous and crystalline contributions in XRD data is a necessary step in the study of the structure of the less-ordered regions and the calculation of the crystallinity parameters of semicrystalline materials. Within the aforementioned context, the development of different procedures based on XRD techniques can be useful and informative in the characterization of minerals, including amorphous content as well as other crystalline phases. In this communication, different methods for the calculation of the crystalline/amorphous ratio from several samples of Mg-carbonate precipitates were analysed and compared.

METHODOLOGY

Precipitation of magnesium carbonate phases (crystalline/amorphous) was performed using a Titrino 905 (Metrohm) at controlled temperature (25ºC±0.2ºC) and under continuous stirring. The experiments were carried out by adding 100 mM $MgCl_2$ solution to a 50 mM K_2CO_3 at a rate of 0.2mL/min. Several experimental runs were separated, and the solids were filtered for further XRD analyses.

The synchrotron XRD experiments were obtained at the high-resolution MSPD beamline (ALBA, Barcelona, Spain). The S-XRD patterns were acquired using a MYTHEN position-sensitive detector. The wavelength λ = 0.952729Å, was selected with a double-crystal Si (111) monochromator. The powder materials were filled in Ø = 0.7 mm borosilicate capillaries (Hilgenberg GmbH, Germany) using an empty capillary for background corrections. The capillaries were rotated during data collection to improve diffracting particle statistics. The data acquisition time was ~ 30 min per pattern over the angular range 1–35° (2θ). Instrumental parameters were calculated by refining XRD data collected from a LaB_6 660b NIST standard. The XRD patterns were analyzed using HighScore Plus 2.2.4 (PANalytical, Almelo, The Netherlands) software. Phase identification was performed by matching the experimental XRD patterns with the PDF-2 database.

The calculation of the percentages of the amorphous/crystalline phases was obtained by the Full method, the Integration method and the K-factor approach (Hammond, 2001; O'Connor, B., & Raven, M., 1988). The Full

method calculates the crystallinity by directly subtracting the amorphous background from the XRD pattern. Then, the intensities of the amorphous pattern and the whole original pattern, including both the crystalline and the amorphous contributions, are then calculated. The following equations are used to obtained amorphous and crystalline percentages (%):

$$Amorphous\ (\%) = 100\ x\ \frac{Itotal - Icrystalline}{Itotal} \qquad Crystalline\ \ (\%) = 100\ x\ \frac{Icrystalline}{Itotal}$$

The Integration method uses a straight-line background (with the highest 2theta values as a reference, approximately continuous – background signal) and compares the area under the full pattern with the area under the crystalline peaks using the following equation:

$$Crystallinity\ (\%) = 100\ x\ \frac{Area\ crystalline\ XRD\ peaks}{Area\ under\ all\ \ XRD\ peaks}$$

The K-factor method used an external intensity standard (100% crystalline material) to set all Rietveld adjustments onto an absolute scan, acting as an instrument internal constant during refinement calculations. The calculation of the percentage crystalline phase is obtained using the formula:

$$Crystallinity\ (\%) = \frac{Scale\ factor * ZMV *\ \mu\ sample}{K - factor}$$

where Z is the number of formula units for unit cell, M is the molecular weight of the formula, V is the unit cell per volume and μ sample indicates the mass absorption of the sample.

RESULTS AND DISCUSSION

The results obtained by K-factor method indicate a high amorphous magnesium carbonate content (around 90%) and the simultaneous precipitation of magnesium carbonate hydrated (i.e., nesquehonite: 8.4%; hydromagnesite: 0.8%) and anhydrous (magnesite: 0.2%) crystalline phases. The other methods for calculating these crystalline/amorphous ratios (i.e., Full method and Integration method) underestimate the relative amount of amorphous in the range of 50-70%. For measurements of crystalline/amorphous ratios, the K-factor method produces better results due to the improved adjustment of the background "effect" in the XRD pattern. However, the challenge of this method is to determine a precise experimental background and the need to measure and refine a crystalline standard in each experimental condition.

A thorough knowledge of the amorphous and crystalline phases within materials, as well as their relative contributions and effect on resulting structurally based properties, will enable optimization of crystallization processes for use in many industrial and technological applications. This study constitutes a comparative approach to different methods for obtaining these crystalline/amorphous ratios in carbonate minerals.

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