Simulation of Industrial Furnacing with Powder X-ray Diffraction

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Abstract

By adapting a Guinier–Lenné high-temperature powder X-ray diffraction camera to include a gas rinsing system and a specially designed mini-environmental cell, the conditions of industrial furnacing can be more realistically simulated. These modifications are described together with an illustration of their successful use with ultramarine, a blue pigment produced by industrial furnacing. The method described is particularly suitable when problems of size scale and volatilization cannot otherwise be overcome.

1. Introduction

Powder X-ray diffraction (PXRD) is potentially one of the most powerful techniques for the study of both structural transformations and chemical reactions at elevated temperatures. Further, by continuously recording the X-ray diffraction pattern throughout the experiment, as is possible for example with a Guinier–Lenné high-temperature PXRD camera (see for instance Klug & Alexander, 1974), one can in principle set up a dynamic experiment to cover all stages of chemical and structural interest. As alternative or supplementary techniques, the various modes of microscopy and chemical analysis can combine usefully, though the evidence from these techniques will be indirect and invariably with structural ambiguities.

This communication describes how to adapt the Guinier–Lenné camera to experimental situations which previously had been thought to be outside the realm of PXRD.

2. The general problems of simulating industrial furnacing

The three main problems anticipated in adapting a Guinier–Lenné camera to simulating an industrial furnace are as follows.

(i) The provision must usually be made for an appropriate gaseous environment: the full implications of this are discussed later.

(ii) The need for X-ray transmission limits the specimen size to a maximum thickness dictated by X-ray absorption. Typical PXRD specimen dimensions are ~0.1 mm.

(iii) In industrial furnacing the specimen:chamber volume ratio can easily be maintained close to unity, whereas in the experimental environment the dual limitations of X-ray geometry (see Fig. 1) and X-ray transmission [(ii) above] lead to corresponding ratios at least two orders of magnitude smaller.

The critical importance of these three problems may not be immediately apparent. It can be best illustrated by reference to a model industrial problem.

3. Manufacture of ultramarine—a model problem in industrial furnacing

The synthetic blue pigment ultramarine is a product of industrial furnacing and its manufacture is energy intensive and therefore costly. The basic ingredients and recipe for production are well known and detailed in patents such as those of Beardsley & Whiting (1948), Gessler & Kumins (1955) and van Order & Hill (1957), and the chemistry and structure of the finished product have also been studied (Jaeger, 1929; Leschewski, 1935; Hofmann, Herzenstiel, Schonenmann & Schwarz, 1969) though a proper structural elucidation of the reactions involved has not so far been forthcoming.

The total industrial cycle (Cork, 1978) involves a complex set of chemical and structural transformations of a multicomponent system. Also, the furnace to sample volume ratio is necessarily close to unity in order to maintain a concentrated sulphurous environment at crucial stages of the cycle. Further, bulk sample units are essential since the outer 10 to 20 mm 'skin' of the final product is useless (and discarded) owing to surface deterioration with loss of sulphur: one might well compare this 10 to 20 mm dimension with that of the maximum sample size (<5 mm) for PXRD! All in all the simulation of the industrial ultramarine furnacing presents a formidable challenge for high-temperature PXRD.
4. PXRD mini-environmental cell

Earlier attempts such as those of Kakudo, Tagayasu & Takeo (1951), Poncelet & Fripiat (1970), Stelmaszczyk (1972) and Fentiman (1980) to simulate the formation of ultramarine were never completely successful chiefly because sulphur exsolved excessively during the cycle owing to the large furnace volume. These are the very two problems discussed earlier [(i) and (ii)], yet they are easily circumvented industrially by virtue of the large-scale effects considered above. Thus, with hindsight it is now clear that the simulation of ultramarine production could never have been achieved using conventional high-temperature PXRD.

Since the problem of the small powder sample size is insuperable we have to turn to designing somewhat artificial ways of preventing sulphur loss from the powder. The first of such devices, then, is to make provision for both inert and sulphurous gaseous environments in the Guinier–Lenné camera system. This has been installed in the Birkbeck set-up by using a gas rinsing system in which nitrogen and/or SO$_2$ can be continuously flushed through the furnace. The system is illustrated schematically in Fig. 1, while the environmental conditions are indicated in Fig. 3(a).

Secondly, the furnace to sample volume ratio is drastically reduced by the incorporation of a mini-environmental ‘Birkbeck’ cell developed to replace the standard platinum-mesh sample holder. The essential features of this cell, illustrated in Fig. 2, are the heat-resisting 0.12 mm thick stainless-steel former, the central hole of which contains the powder specimen, and which is covered by thin (~5 μm thickness) mica sheets either side, which act as cell windows to the incident and diffracted X-rays. Mica is an ideal window material in view of its availability, ease of preparation (paring/splitting down to required thickness), resistance to high temperature, its relative transparency to X-rays (at $\lambda = 1.54$ Å its linear absorption coefficient is ~100 cm$^{-1}$), and that any undesirable interference from mica diffraction can be eliminated by careful orientation of the mica window sheets and confirmation from a trial (blank specimen) run. The powder sample is in practice held in place by the stainless-steel former and mica windows, the mica windows being affixed to the steel by a stainless-steel clip or by heat-resistant adhesive. Finally, one of the mica windows is pierced to provide a pin hole which plays a key role in the whole arrangement. This vent is primarily to eliminate the gradual build up of gaseous pressure in the cell, as the reactions proceed, which would otherwise culminate in a terminal explosion as was experienced in the earlier trials. On the other hand, the hole size must be severely limited so as not to allow excessive loss of sulphur. In practice, a pin hole of 100 μm appears to offer the compromise needed between the extremes of release and restraint.

Thirdly, the industrial recipe is modified to include an extra dosage of sulphur in the laboratory ingredients and the total cycle is speeded up: both these features act as additional precautions against excess sulphur loss particularly throughout the initial heating portion of the cycle.

5. Results and conclusions

With the set-up described, one of the authors (SET) has succeeded in producing ultramarine under laboratory PXRD conditions. Thus the problems [(i) to (iii) in §2] have been overcome by a combination of the use of the Birkbeck mini-environmental cell and adjustments to the chemical mix and industrial cycle. Not surprisingly, success cannot be guaranteed on every attempt in view of the sensitive nature of the physical and chemical variables involved, though to date three
out of 12 such attempts have produced *bona fide* ultramarine as evidenced by the colour (optical absorption) properties and by the diffraction pattern of the ultimate products.

A fuller exposition of the transformations involved must await a later publication, but we are now able to itemize the main structural changes that occur as evidenced by the diffraction patterns, and to relate these to the relevant temperature-time coordinate on the furnacing cycle. Fig. 3(a) gives the laboratory environmental cycle which can be regarded as a compressed (1:4 in time) version of the industrial counterpart. A typical diffractogram is shown in Fig. 3(b) which directly relates to Fig. 3(a). From these data we can fix with some precision (+10 K, ±5 min) the following chain of structural events.

We can thus see that specially geared environmental-cell high-temperature PXRD can successfully simulate the solid-state transformations occurring in a complex industrial furnace. The data is sufficiently good to give accurate indications of the type of chemical reactions and temperature ranges involved: this information can be used to make suggestions as to more efficient usage of energy in the industrial furnace by way of choice of raw ingredients and temperature cycle.

These results on ultramarine production are part of an on-going collaboration with an industrial partner. The authors wish to thank the Science and Engineering Research Council and Reckitt's Colours Limited (Mr W. B. Cork and Mr G. Cattle) for a CASE studentship (SET) in support of this work.

**References**


