



A3 - Phase Analysis

A3 - O1

CAN THE RIETVELD METHOD BE SUCCESSFULLY APPLIED TO THE SEVERELY SUPERIMPOSED DIFFRACTION PATTERNS OF TECHNICAL PRODUCTS CONTAINING SEVEN SOLID SOLUTIONS AND A STOICHIOMETRIC PHASE?

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Many countries require the removal of phosphorus from wastewater before discharge to the ambient environment and the development of technologies for the reuse of the recovered phosphorus [1]. By doing this, local rivers and lakes are protected from eutrophication (phosphorus pollution), and the world's limited resources of mineral phosphorus, which are estimated to be exhausted in about 250 years, can be used more economically. Although phosphorus recovery from sewage sludge is already practised on a larger scale, the economical and ecologically *sensible* reuse of millions of tons p.a. of recovered phosphates is still being debated. The principal obstacle for the reuse of ashes from sewage sludge incineration as phosphate fertilizer in agriculture is their high content of ecologically harmful heavy metals, such as Zn, Cu, Cd, Hg, which exceeds the

legal limits considerably. A new technology [2] is being developed at the BAM that reduces the content of ecologically harmful heavy metals in ashes from sewage sludge incineration to a value, orders of magnitude below today's legal limits. Ashes from sewage sludge incineration treated with *this* technology *can* be used as ecologically desirable, high-quality fertilizers. In addition, this treatment increases the bioavailability of the phosphorus content from a low original value of 50 to 100%, thus resulting in cost effectiveness, an essential advantage of the technology. The new technology has been developed on chemical intuition and decades of experience. A detailed explanation of the phase transformation processes accompanying this thermochemical treatment of ashes from sewage sludge incineration is the aim of this paper.

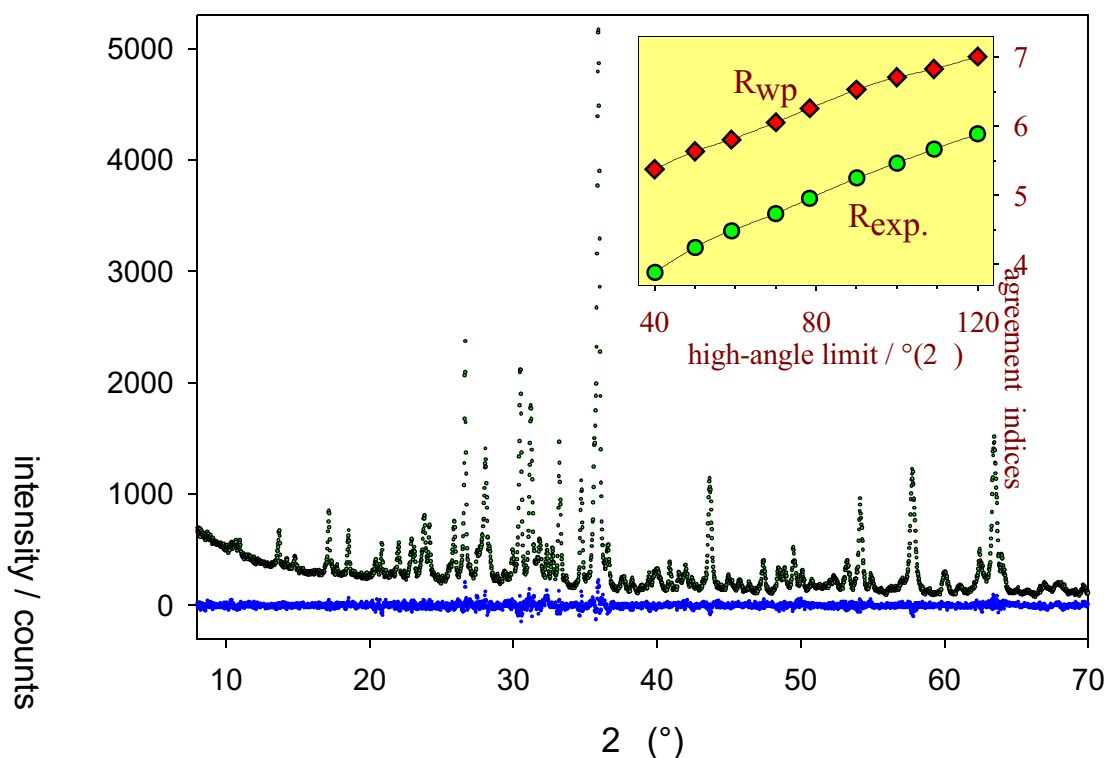


Fig. 1. Observed (dotted line) and calculated (solid line) diffraction pattern, difference curve and agreement indices (small box) for one type of ashes from sewage sludge incineration after being processed by the thermochemical treatment developed at the BAM (phase composition: seven solid solutions and a stoichiometric phase)

Ashes from sewage sludge incineration are non-equilibrium mixtures of a large number of interdispersed crystallographic phases. This complicates the applicability and the significance of results of many microscopical, spectroscopic, thermoanalytical and theoretical methods. Therefore, X-ray powder diffraction (XRPD) is the method of choice for studying i) the phase composition of ashes from sewage sludge incineration and ii) the solid-state reactions occurring during thermochemical treatment. Of course, the presence of a large number of solid solution phases in these materials also presents an exceptional challenge to the XRPD method, and qualitative (and semi-quantitative) phase analyses are not straight-forward. Instead, any solution found with the help of crystallographic databanks and search/match routines has to be regarded as a *proposal* only and must be validated. As there is no *independent* analytical method for the confirmation of the phase analysis of ashes from sewage sludge incineration and for the structure refinement of some of their constituents, procedures that can test the *internal consistency* of the XRPD results gain special significance here. The procedure serving this purpose best is the Rietveld method, especially if the profiles of the diffraction lines are described by the fundamental parameter approach. This method enables the fitting of the diffraction pattern calculated from the approximately determined phase composition of the sample to the experimentally observed diffraction pattern within a large 2 θ range. Thus, the reliability of the phase analysis results can be checked for internal consistency and the best alternative proposal selected. In doing so, the Rietveld method should by no means be used as a black-box method. Instead it is mandatory to consider the often ignored methodical problems of the Rietveld method, see for instance [3] and references therein, as well as the chemical and mineralogical specifics of the samples under investigation. Making use of mineralogically well-founded restraints for the lattice parameters and the site occupancy factors of the multi-dimensional

solid-solution series is often helpful, and sometimes even necessary. Besides this, in the present work, wherever possible, partial results of the Rietveld analyses were checked by the additional analyses of tailor-made model samples with simplified chemical and phase compositions. A close collaboration between the specialist for the Rietveld method and the chemist synthesising the model samples was one of the key-factors for the successful completion of this challenging analytical task.

The subject of this investigation was ashes from sewage sludge incineration from several municipal wastewater treatment plants, each of which used a different precipitation process. These ashes were characterized both in their original state and after thermochemical treatment according to the technology developed at the BAM [2]. The diffraction patterns of these ashes were collected and analysed by the Rietveld method. Excellent agreement between the calculated and the observed diffraction patterns was achieved for all investigated samples, see Fig. 1. The results produced in this phase-analytical investigation provide an explanation for the repeatedly reported observation [4] that the bioavailability of phosphorus deteriorates with the presence of iron ions. At the same time, the solution to this relevant problem became obvious.

In summary, the title question of this paper can be answered with 'Yes'.

1. <http://www.nhm.ac.uk/mineralogy/phos/> (Natural History Museum, London).
2. Köcher, P., Kley, G., Brenneis, R. 'Method for the separation of ecologically harmful heavy metals from ashes from sewage sludge incineration', German patent 102 43 840.4; accepted 30.01.2004.
3. Peplinski, B., Kleeberg, R., Bergmann, J. (2004) Materials Science Forum **443-444**, 45-50.
4. Römer, W., Samir I.S. (2002) J. Plant Nutr. Soil Sci. **165**, 83-91.

A3 - O2**HIGH THROUGHPUT POWDER DIFFRACTION – NEW METHODS TO CHARACTERISE LARGE DATASETS**

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With modern robotic systems and data collection methods, it is quite possible to measure 1000 powder diffraction patterns in a few days, and such volumes of data are becoming commonplace in pharmaceutical laboratories where the search for polymorphs and salts is of great importance. The problem arises as to what to do with such volumes of data; in particular how it can be meaningfully analysed, and how it can be grouped into classes when there is no reference database of pure phases? We have developed two computer programs to address these issues [1, 2] that use statistical

techniques of multivariate analysis and classification to solve these problems. The formalism works as follows:

1. Full profile data are optionally pre-processed with background removal, smoothing *via* wavelets, and peak searching.

2. Each of the n patterns is correlated with every other pattern using the Pearson and Spearman coefficients to generate an $(n \times n)$ correlation matrix.

3. This is used to generate a distance matrix which acts as a source of classification to generate dendrograms, mul-



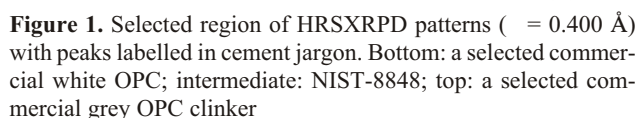
Several other visualisation tools can also be utilised. Additionally, in the presence of a database of pure phases



[2] Barr, G. Dong, W. & Gilmore, C.J., (2004). *J. Appl. Cryst.* **37**, 243-252.

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High-Resolution Synchrotron X-ray Powder Diffraction (HRSXRPD) overcomes these drawbacks. Rotating capillary geometry (transmission) avoids preferred orientation. High energy X-rays minimise microabsorption and a large amount of sample is tested leading to good particle statistic. High resolution data minimize the overlapping and parallel synchrotron X-rays geometry, with an analyser crystal, do not show optical aberrations. Hence, we have used HRSXRPD to get good QPA of commercial OPC [1] and to show that accurate Rietveld QPA for cements can be obtained [2].



Here, we will report several QPA of OPC by using HRSXRPD. We will report data for white Portland clinkers, grey Portland clinkers and reference NIST 8488 clinker. The direct evidence of the co-existence of two alite phases in some patterns is highlighted. The alite phase(s) crystallise in the monoclinic MIII superstructure. The Figure shows a selected white OPC with a single alite (bottom) and a selected grey OPC clinker with two alites (top). The reference NIST 8488 clinker (intermediate) has also been analysed and it has two different alites. Furthermore, $-Al_2O_3$ has been added to determine the non-diffracting contents of the studied samples. Full QPA of several OPC and the relevance of these results for the LXRPD analyses will be discussed. We will show the differences in the QPA

of some cements with two alites by using medium resolution $CuK_{1,2}$ laboratory data and high-resolution strictly monochromatic CuK_1 laboratory X-ray powder diffraction data.

- [1] A.G. de la Torre, A. Cabeza, A. Calvente, S. Bruque, M.A.G. Aranda "Full Phase Analysis of Portland Clinker by Penetrating Synchrotron X-rays" *Analytical Chemistry* **73**, 151 (2001).
- [2] A.G. de la Torre and M.A.G. Aranda "Accuracy in Rietveld Quantitative Phase Analysis of Portland Cements" *Journal of Applied Crystallography* **36**, 1169 (2003).

A3 - O4

X-RAY POWDER MICRODIFFRACTION IN THE ANALYSIS OF ART WORKS

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Analysis of samples smaller than 1 mm has always been a problem for powder diffractometry. X-ray powder microdiffraction is a new laboratory technique, extremely quickly developing in last three years, and becoming available mainly due to hardware development of conventional powder diffractometers. Common X-ray tube and monocapillary producing a quasiparallel beam combined with a sensitive/fast solid-state detector enable direct phase analysis from 0.1 mm spots using a traditional diffractometer in less than 1 day. It is possible to analyse a selected place on a solid sample with irregular shape.

The microdiffraction was applied to analyses of colour layers of art works, e.g. canvas and wall painting and polychromy on wood. Materials research of colour layers helps to date artworks and identify repaints, to study painting techniques of different authors and historical periods. Powder diffraction is extremely well suited to distinguish inorganic pigments of different natural provenance and to reveal secondary mineralization deteriorating artworks.

The fragments with characteristic dimensions 1x1x0.2 mm were examined by a combination of SEM/EDX and optical microscopy (fig. 1). Microdiffraction was used to confirm the presence of mineral pigments assumed indirectly on the base of their elemental composition, to identify the minerals in earthy pigments and, in the case of wall paintings, to describe the phase composition of secondary salt efflorescences.

In the case of polychrome funeral insignias from the Prague castle tombs, the microdiffraction was able to directly identify the structural forms and a method of mediaeval preparation of two different lead-tin yellows used to paint the royal crown of Charles IV. (Fig. 2). In the first fragment, the lead-tin yellow of type I (Pb_2SnO_4) was identified. In the second fragment, SEM/EDX indicated an

excess of tin and the presence of silicon, which is typical for the lead-tin yellow of type II, *i.e.* type I recrystallized in the flux with SiO_2 . However, type II was not confirmed by powder X-ray microdiffraction, the excess Sn was found as cassiterite and Si as quartz.

In the case of Renaissance wall paintings from Malta, the microdiffraction was able to distinguish among different crystalline salts built by common elements (Ca, Mg, K, S, O, N, H) and to indicate those formed as a result of previous restoration of the painting. (Fig. 3).

Based on microdiffraction measurements, bole grounds of Baroque paintings were distinguished according to their mineralogy: kaolinite, illite, smectites, hematite ($-Fe_2O_3$), goethite ($-FeOOH$), and jarosite (basic ferric sulphate) were found as a result of different natural genesis and further treatment of earthy pigments used.



Figure 1: Optical microphotograph of fragment of Funeral Crown of Charles IV.

**Acknowledgements:**

V. Šimová was supported by a Grant Agency of AS CR (project number B1032401), J. Hradilová, D. Hradil and P. Bezdička acknowledge a support by Grant Agency of CR (project number 203/04/2091). Financial support by the

Ministry of Education of CR (project number LN00A028) is also gratefully acknowledged

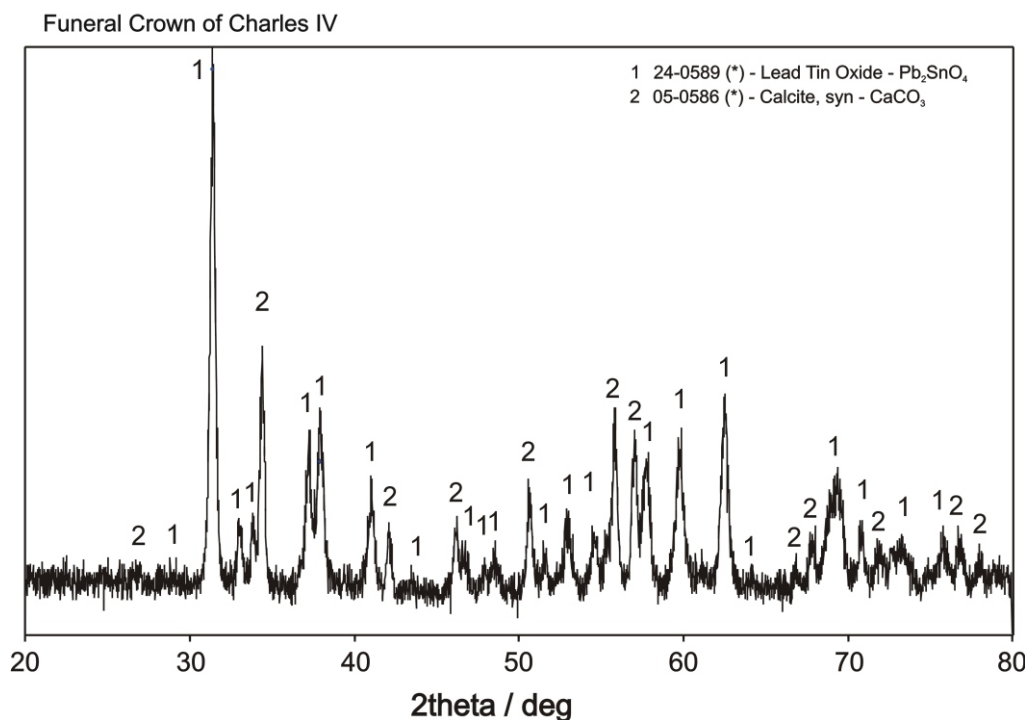


Figure 2: Diffractogram of fragment of Funeral Crown of Charles IV.

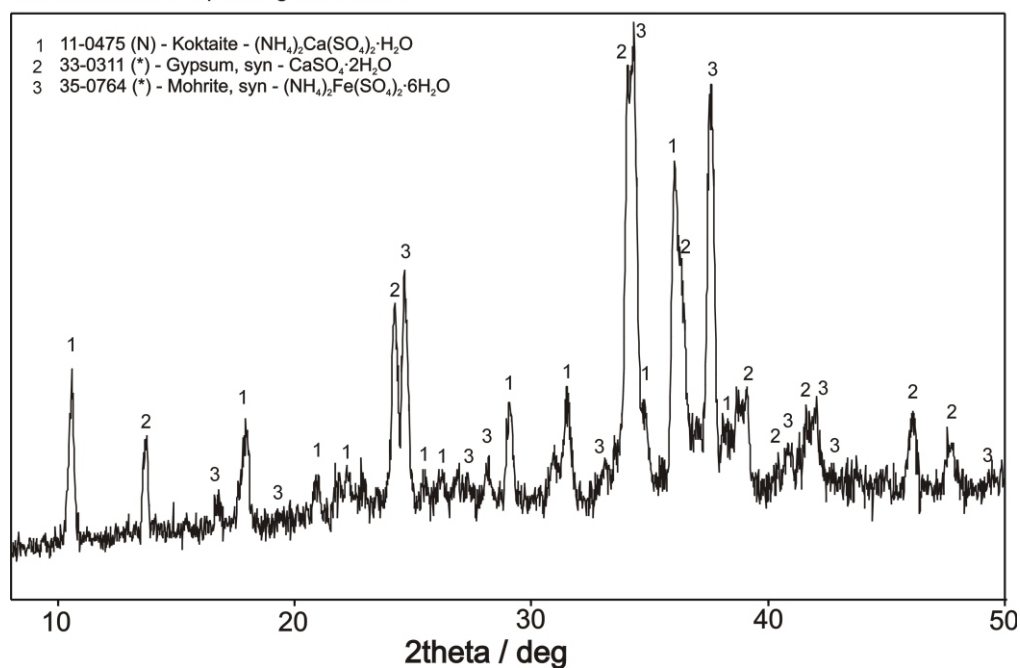
Renaissance wall painting from Malta

Figure 3: Diffractogram of fragment of Renaissance wall painting from Malta.