

# High-Temperature X-Ray Powder Diffraction of Secondary Gypsum

D. Gazdič, I. Hájková, M. Fridrichová

**Abstract**—This paper involved the performance of a high-temperature X-Ray powder diffraction analysis (XRD) of a sample of chemical gypsum generated in the production of titanium white; this gypsum originates by neutralizing highly acidic water with limestone suspension. Specifically, it was gypsum formed in the first stage of neutralization when the resulting material contains, apart from gypsum, a number of waste products resulting from the decomposition of ilmenite by sulphuric acid. So it can be described as *red titanogypsum*. By conducting the experiment using XRD apparatus Bruker D8 Advance with a Cu anode ( $\lambda\alpha=1.54184 \text{ \AA}$ ) equipped with high-temperature chamber Anton Paar HTK 16, it was possible to identify clearly in the sample each phase transition in the system of  $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ .

**Keywords**—Anhydrite, Gypsum, Bassanite, Hematite, XRD, Powder, High-Temperature.

## I. INTRODUCTION

TO produce high-quality sulphate such as anhydrite-based binder natural anhydrite is used, or gypsum burned at a certain temperature. However, anhydrite itself is a substance which has a very slow hydration capability caused by low water solubility. Therefore, it is necessary to add to anhydrite initiating additives known as exciters, which can accelerate anhydrite reactivity purposefully. Generally, anhydrite mortar compound is well-known, but its use in our territory has been limited by a missing natural resource. Currently, this material has seen expansion caused by the growing production of synthetic gypsum. In the past, sulphate binders were produced on an anhydrite basis with internal excitation – these were Scott gypsum compound, De Wylde, Borax gypsum compound and Keane cement. Anhydrite was also imported from abroad. Currently, anhydrite mortar compound is used in the production of self-levelling anhydrite screeds or structures made of liquid screeds [8]-[10].

The only usable gypsum deposit in the Czech Republic is bound to primarily formed the Miocene sediments of the Opava Basin (a marginal part of the Carpathian foredeep) but a greater part of the productive Baden lies in Poland. Gypsum was formed by precipitation from a supersaturated solution

during silting of clays that form the bottom layer of grey colour and contain about 50% of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The upper layers are formed by macro crystalline gypsum with cavities filled with clay containing 84% to 90 % of gypsum and overlying rock containing about 60% of dihydrate. Mining in 2012 produced around 14 kt of gypsum of 70-80% purity [6], [13].

Our country has small reserves of natural gypsum to meet the demand. Moreover, due to its lower quality as well as in terms of sustainable development and economic aspects, it is currently replaced to a large extent by waste gypsums, which are, in terms of legislation, identified as secondary energy products (flue-gas desulphurization gypsum from Coal Power Plant, waste sulphates from glass factories, from the production of titanium white, fertilizers, citric acid etc.). They are mostly chemically very pure raw materials containing over 90% of gypsums that are considered safe in terms of health and the environment (including their ascertained natural radioactivity). However, they differ from the natural raw material in small grain size, bulk density, crystal type and higher moisture content, which is a drawback stemming from the technological process of production [7], [13].

Chemically, gypsum is calcium sulphate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The dihydrate crystal lattice has a layered structure composed of the layers of  $\text{CaSO}_4$  connected with the layers of  $\text{H}_2\text{O}$ . The  $\text{CaSO}_4$  layer consists of strings Ca-stoms and  $\text{SO}_4$  groups, see Fig. 1.

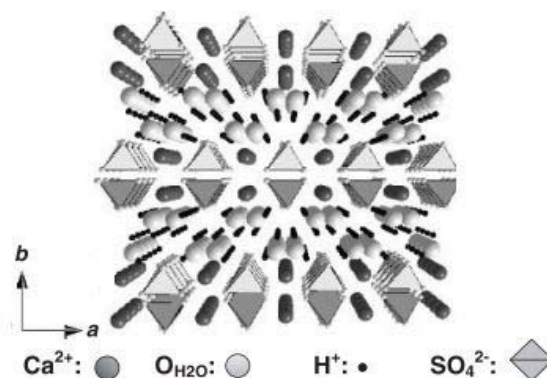


Fig. 1 The structure of gypsum (view from the c-axis) [3]

Gypsum loses crystalline bound water applying heat. By gradual heating of the gypsum we can obtain its various modifications:

- calcium sulfate hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ), also known as mineral bassanite, exists in different morphologic

Dominik Gazdič is with Brno University of Technology, Faculty of Civil Engineering, Institute of Technology of Building Materials and Components, Veverí 95, 602 00 Brno, Czech Republic (phone: 420-541-147501; fax: 420-541-147502; e-mail: gazdic.d@fce.vutbr.cz).

Iveta Hájková is with Brno University of Technology, Faculty of Civil Engineering, Institute of Technology of Building Materials and Components, Veverí 95, 602 00 Brno, Czech Republic (phone: 420-541-148215; fax: 420-541-147502; e-mail: hajkova.i@fce.vutbr.cz).

Marcela Fridrichová is with Brno University of Technology, Faculty of Civil Engineering, Veverí 95, 602 00 Brno, Czech Republic (phone: 420-541-147501; fax: 420-541-147502; e-mail: fridrichova.m@fce.vutbr.cz).

forms  $\alpha$ ,  $\beta$  and  $\beta'$ ,  $\alpha$ -form crystallizes in the monoclinic form and  $\beta$ -form in the trigonal form

- anhydrite III ( $\text{CaSO}_4$  III) – temperature between 110-220°C, metastable modification, exists analog with bassanite in three different forms  $\alpha$ ,  $\beta$  and  $\beta'$ ,
- anhydrite II ( $\text{CaSO}_4$  II) – temperature above 300°C, less soluble anhydrite, stable modification,
- anhydrite I ( $\text{CaSO}_4$  I) – temperature above 1180°C.

The structures of bassanite and anhydrite III are considered to be very similar and using XRD analysis very heavily recognizable [1], [2], [5], [11].

X-ray diffraction analysis (XRD) - diffraction methods of structural analysis are based on X-ray radiation interference on crystal lattice of solid substance. In a crystalline substance there are mutually parallel levels distant from one another in so called inter-lattice distance. Each crystalline matter contains many various levels in inter-lattice levels. These values are characteristic for the given crystalline substance. Under specific conditions an interference (fade-in) of X-ray radiation occurs. The radiation interference with crystal lattice shows with its intensity growth. Identification of present crystalline phases is carried out by comparison of values  $d$  and  $I$ , deducted from diffraction pattern with values stated in libraries (databases) of particular minerals [14].

Using the high-temperature XRD analysis (HT-XRD) it is possible to monitor the specimen qualitative composition at simultaneous increase of temperature [14].

## II. METHODOLOGY

The experiment was conducted using gypsum that is obtained in the first stage of neutralization of selected acidic waste water aside from the production of titanium white. This acidic water is generated by the decomposition of ilmenite by sulphuric acid. The neutralization takes place using an aqueous suspension of finely ground limestone, followed by separation in centrifuges and washing the accompanying water-soluble salts. In the first stage of neutralization, the resulting gypsum is contaminated by a number of impurities such as  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ .

In the second stage, very pure gypsum is generated that is non-flammable, non-aggressive, non-toxic and, following two-stage purification, of white colour due to residual amounts of  $\text{TiO}_2$ . The 'impurified gypsum' from the first stage of neutralization is of black-green colour due to the content of iron oxides. The colour changes to reddish brown due to oxidation. Currently, it is used in our country for purposes of surface reclamation of strip mine, landfills or as a sub-base material for road construction [16].

For the purpose of the experiment, a sample of gypsum was dried to constant weight because the moisture content in the supplied sample was, according to [12], determined at the value of 45.4%.

A HT-XRD analysis was performed using apparatus Bruker D8 Advance with a Cu anode ( $\lambda_{\text{Cu}}=1.54184 \text{ \AA}$ ) equipped with High-Temperature Chamber Anton Paar HTK 16, see Fig. 2. Overall view of the chamber is shown in Fig. 3. This chamber is a heating stage of XRD studies. It is a strip-heater type of

chamber with direct sample heating from room temperature to 1600°C. Depending on the experimental requirements, various types of heating strips (Pt, W, Ta, others on request) can be mounted inside the chamber, and XRD investigations can be done with the sample in vacuum, air or inert gas [4].

Strip of Pt was used for measurement. XRD investigation was done with the sample in air.



Fig. 2 Apparatus Bruker D8 Advance [15]

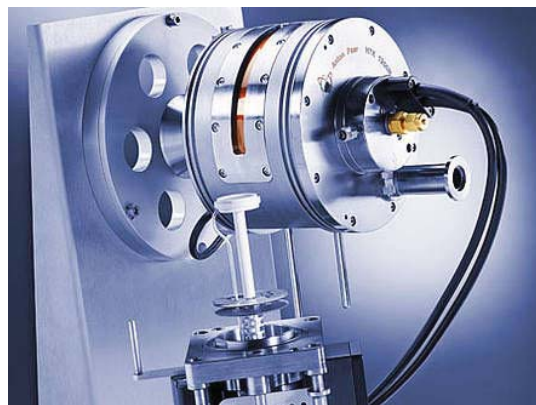


Fig. 3 High-temperature chamber Anton Paar HTK - overall view [4]

The description of the main components of this chamber is shown in Fig. 4. Measurements were taken during isothermal holding times within the temperature range of 30-1000°C at the temperatures of 30, 100 and then at intervals of 100°C, see Fig. 5. The increase in temperature was 1°C/1 sec., followed by an isothermal holding time, when XRD measurements were performed on the sample at a given temperature. The measurement were performed within the angular range of 10-

$40^\circ 2\theta$  with an increment of  $0.05^\circ 2\theta$  and real time to increment 150,4 sec. Measurement time of 1 step was 0,8s, PSD detector records signals by means of 188 channels. The total measurement time until the temperature reached  $1000^\circ\text{C}$  was 1 hour and 45 min.

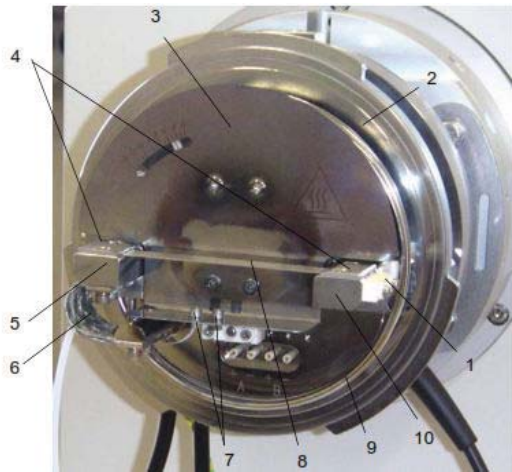


Fig. 4 High-temperature chamber Anton Paar HTK - front view of the base plate [4] 1 – Clamping joint for W3Re/W25Re-thermocouple, 2 – Base plate, water cooled, 3 – Radiation shielding with heating-filament pre-stress gauge, 4 – Clamps with integrated alignment slits, 5 – Moveable block for fixing the heating strip, water cooled, 6 – High current cable, 7 – Thermocouple ceramic guide, 8 – Heating strip, 9 – Cooling water pipe, 10 – Fixed support block for heating strip, water-cooled

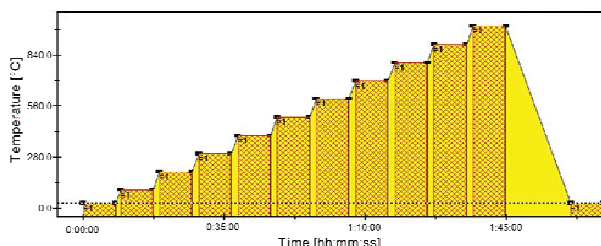


Fig. 5 The temperature regime of the experiment

To identify the peaks and the individual phases software EVA (Bruker Analytical X-Ray Systems) was used. ICDD-PDF and ICSD data were used for qualitative analysis of the diffraction patterns.

### III. MEASUREMENTS

For the sample of chemical gypsum, the experiment output was a diffractogram shown in Fig. 6 and 2D record of the experiment, see Fig. 7.

According to the y-axis are sorted in ascending XRD individual records for each temperature, 30-1000°C.

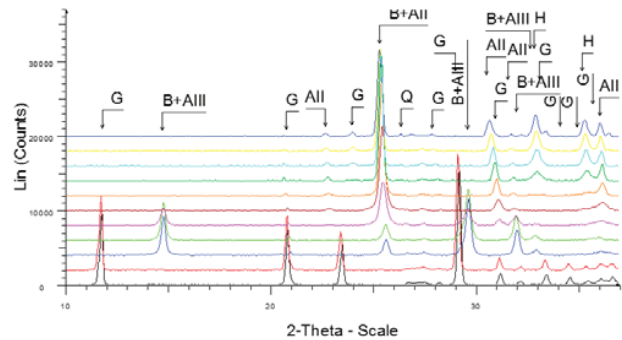


Fig. 6 Diffraction pattern of gypsum sample

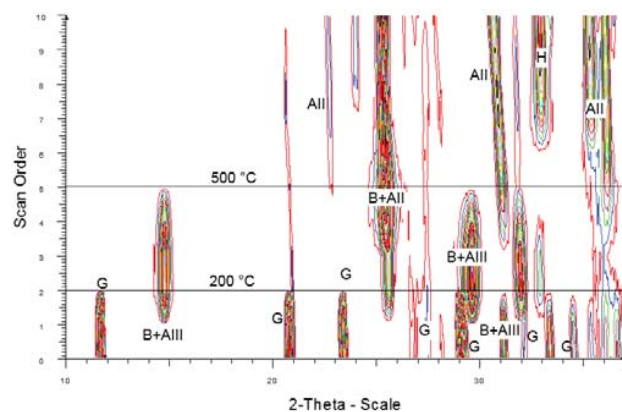


Fig. 7 2D record of the experiment

While evaluating these records, diffraction lines of the following minerals were found:

- gypsum (G) – ICDD-No. 00-033-0311, main peaks  $d_{hkl}[\text{\AA}]$ (intensity): 7.630(100), 4.283(100), 3.799(17), 3.065(75), 2.873(45)
- bassanite<sup>1</sup> (B) – ICSD-No. 98-007-9528, main peaks  $d_{hkl}[\text{\AA}]$ (intensity): 6.003(100), 3.470(53.2), 3.001(91.3)
- anhydrite II (AII) – ICSD-No. 98-001-6382, main peaks  $d_{hkl}[\text{\AA}]$ (intensity): 3.503(100), 3.499(99.1), 2.852(60.2)
- anhydrite III (AIII) – ICDD-No. 01-083-0437, main peaks  $d_{hkl}[\text{\AA}]$ (intensity): 6.038(100), 3.486(15.1), 3.019(44.2), 2.794(40.3)
- hematite (H) – ICSD-No. 98-002-4004, main peaks  $d_{hkl}[\text{\AA}]$ (intensity): 2.700(100), 2.519(79.7)

A list of phase transformations in a sample of chemical gypsum:

- $30^\circ\text{C}$  – only gypsum identified in the sample
- $100^\circ\text{C}$  – a slight decrease in the intensity of gypsum diffraction lines
- $200\text{--}300^\circ\text{C}$  – within the measured angular range, only bassanite (+ anhydrite III)\* was identified
- $400^\circ\text{C}$  – a slight decrease in the intensity of anhydrite III diffraction lines, anhydrite II appears
- $500^\circ\text{C}$  – within the measured angular range, only anhydrite II was identified

<sup>1</sup> Bassanite ( $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$  and anhydrite III cannot be distinguished clearly on the basis of an X-ray diffraction record)



- 600°C – within the measured angular range, hematite appears in addition to anhydrite II; the hematite content increases until the temperature of 800°C
- 600-800°C – increasing crystallinity can be deduced from the change of the anhydrite II diffraction line profile

#### IV. CONCLUSION

In the paper was briefly summarizes the theory of sulfate binders and gypsum industry current situation in the Czech Republic. Czech Republic has only a very small source of gypsum and anhydrite source even completely missing, has a large pool of industrial gypsum, whose potential is not fully exploited.

The experiment was carried out a high temperature XRD powder analysis of gypsum, which is produced as secondary energy products in the first stage of neutralization of selected acidic waste water from the production of titanium white.

Using this method can be at a rough guess determined the existence of the phases produced during heating, in the case of gypsum phase processes of transformation in  $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$  system. In the case of the sample it was found that the presence of gypsum was completed at about 200°C and bassanite at about 500°C. Minimum recorded temperature firing process for obtaining pure anhydrite II (without the presence of anhydrite III - undesirable by its properties) was 500°C.

So it can be said that the high temperature XRD analysis is a very simple test by which are relatively easy to track individual phase changes occurring in the structure of the material during its heating, not only gypsum.

#### ACKNOWLEDGMENT

This paper was elaborated with the financial support of the project Czech Grant Agency Project No. P104/12/P619 "Study of the Kinetics of Hydration Process of Anhydrite Binder".

#### REFERENCES

- [1] S. Seufert, C. Hesse, F. Goetz-Neunhoeffer, J. Neubauer, "Quantitative determination of anhydrite III from dehydrated gypsum by XRD", *Cement and Concrete Research* 39 (2009) 936–941, ISSN: 0008-8846.
- [2] N.B. Singh, B. Middendorf, "Calcium sulphate hemihydrate hydration leading to gypsum crystallization Progress" in *Crystal Growth and Characterization of Materials*, Volume 53, Issue 1, March 2007, Pages 57–77.
- [3] Freyer, D., Voigt, W., Crystallization and Phase Stability of  $\text{CaSO}_4$  and  $\text{CaSO}_4$  – Based Salts, *Monatshefte für Chemie* 134, 693-719, 2003.
- [4] Company documents, Anton Paar GmbH, 2013.
- [5] K. Dvořák, "Study of Gypsum Dehydration Time in  $\text{CaCl}_2$  Solution". *Advanced Materials Research*. 2013. 2013(818). p. 64 - 67. ISSN 1022-6680.
- [6] Gypstrend Ltd., (online). (cit. 2014-02-10). Available from: <http://www.gypstrend.cz/?clanek=1> (in Czech)
- [7] L. Tomancová, "Utilization of waste and secondary materials as alternative fuels and raw materials in cement production". 2012. Available from: [http://www.vustah.cz/wp-content/uploads/vysledky\\_vezpom/2008\\_Tomancova.pdf](http://www.vustah.cz/wp-content/uploads/vysledky_vezpom/2008_Tomancova.pdf) (in Czech).
- [8] F. Vavřín, Binders, VUT Brno, Brno, 1987 (in Czech)
- [9] W. Schulze, W. Tischer, V. Lach, P. Ettel, Non-Cement mortars and concretes, SNTL, Praha, 1990 (in Czech)
- [10] F. Škvára, Technology of inorganic binders I, VSCHT, Praha, 1995 (in Czech)
- [11] H.J. Kuzel, M. Hauner, Zement-Kalk-Gips, 40 (1987), p. 628
- [12] Czech Technical Standard 72 1206 - Gypsum and anhydrite, as an additive to cement, 1972, CEN.
- [13] M. Fridrichova, K. Dvořák, I. Hájková "Alternative preparation of sulphated binders from secondary raw-material resources". *Advanced Materials Research*. 2014. 2014 (838-841). p. 2338-2341. ISSN 1022-6680.
- [14] D. Gazdič, I. Hájková, R. Magrla "Monitoring of Calcium Sulphate Phase Transformations Using Hightemperature X-ray Diffraction". *Advanced Materials Research*. 2014. 2014(864-867). p. 621 - 624. ISSN\~1022-6680.
- [15] Company documents, Bruker Ltd., 2014, (online). Available from: <http://www.bruker.com>
- [16] D. Gazdič "Industrial resources for the production of sulphate binders". *Advanced Materials Research* Vol. 897 (2014) pp 53-56. ISSN\~1022-6680.

**Dominik Gazdič** – Date and place of birth: 24<sup>th</sup> May 1983 in Ostrava, Czech Republic. Education: Master science degree (2001-2006) Faculty of Civil Engineering at Brno University of Technology, Institute of Technology of Building Materials and Components. PhD degree (2006-2010) at the same university. Employment: 2006 – up to now: Rosomac Ltd, grade - quality manager, assistant technologist, 2010 – up to now: Brno University of Technology, Faculty of Civil Engineering - Assistant professor. Appreciation medal Signum Prosperitatis 2010 within the scope of doctoral studies at Brno University of Technology. Expert knowledge: Technology of Binders, Technology and Utilization of Building Materials, Technology of Concrete and Elements, Recycling and Utilization of Waste Materials in Building Industry, Economy of Building Materials, Insulating Materials, Ceramics. Further significant activities: Member of organizing committee on the Scientific International Conference Silichem and International Conference Binders and Materials.