Study of hydration process of ternesite clinker

M Fridrichova, D Gazdic, K Dvorak, J Mokra and K Kulisek
Faculty of Civil Engineering, Brno University of Technology, Veveri 331/95, 602 00 Brno, Czech Republic

Abstract. Currently ternesite, \( \text{Ca}_5(\text{SiO}_4)_2\text{SO}_4 \), is used in the cement production, is one of two key phases of calcium sulfoaluminate cement. Some investigators claim that this phase is nearly inert or very low reactive and it hydrates only after later age of hydration. In order to improve knowledge in this field, process of hydration of neat ternesite clinker under specific conditions of exposure was observed in this study. Ternesite was prepared by firing of raw meal consisting of high calcium limestone, microsilica and calcium sulfate hydrate. The resulting ternesite clinker was subsequently hydrated in four storage environments. Kinetics of hydration process was monitored in water and in environment of saturated carbonic acid, at two different temperatures of 5 and 40 °C. Mineralogical composition of hydrated samples was analyzed by X-Ray diffraction analysis (XRD) and by differential thermal analysis (DTA) in particular ages of hydration. Based on the results, it can be claimed that rate of decomposition of ternesite was related to conditions of storage. The rate of decomposition was significantly accelerated by the environment of carbonic acid and also by the elevated temperature. Presence of calcium carbonates in mineralogical forms of calcite, vaterite and aragonite, coupled with gypsum and thaumasite was identified.

1. Introduction
Ternesite, also known as the sulfo-spurrite [1], is a colorless to light blue mineral with a composition of \( \text{Ca}_5(\text{SiO}_4)_2\text{SO}_4 \), shorthand \( \text{C}_5\text{S}_2\text{S} \). It can be found in xonotlits rich in calcium [2]. This mineral is orthorhombic and without cleavage, creates long prismatic crystals in radial structure [3].

Ternesite occurs in cement kiln coating in small quantities where is green due to addition of iron ions [3,4]. Shen et al. [5] claims that ternesite is formed as an intermediate phase approximately at temperature of 900 °C, authors [3, 6] state temperature 1100 °C. To create ternesite, respectively stabilize it at temperature higher than 1200 °C (up to 1250 °C), a mineralizing agent has to be taken into consideration during the firing – phosphates or fluorides, or ternesite has to be produced in two steps terminated by slow cooling to 800 °C [6]. That is for the reason ternesite is formed mainly at temperature range between 1200 °C and 950 °C [4]. Ternesite is released into decomposition products belite and anhydrite [1] at temperatures higher than 1200°C, Ukrainczyk et al. [7] state the temperature range 1200-1280 °C. Irran et al. [3] claims decomposition occurs at temperature higher 1150 °C or higher than 1300 °C in open system (platinum crucibles) respectively.

In general, ternesite is considered to be almost inert or to react only at later stages of hydration – is not hydraulically active [1,2,4,8-10]. But it immediately reacts with water in the presence of alumina ions (e. g. coming from blast furnace slag, metakaolin, anhydrite) and forms solid framework [9,11].

In recent years, ternesite is mainly utilized in cement industry due to reduction of CO\(_2\) emissions. Ternesite is a main phase in ternesite calcium-sulphoaluminate clinker/cement and an additive in calcium-sulphoaluminate (ferrite) (belite) clinker/cement, CSA(F)(B) [5,6,12]. Researchers from Heidelberg Technology Centre in Germany registered patents for the Belite-Calciumsulfoaluminate-
Ternesite (BCT) clinker [2,6,8,10]. Not only belite, but also ternesite is the main reactive phase in this clinker [1, 4]. BCT clinker reacts with water to give hydration products, such as strätlingite, monosulfoaluminate, silicon hydrogarnets and C-S-H phases [6]. Calcium-sulfoaluminate (CSA) cements are fired at lower temperatures, around 1250 °C, and generate up to 30 % less emissions of CO₂ than ordinary Portland cements, which are fired at temperatures of approximately 1450 °C. By-products such as fly ash or blast furnace slag can be used as source of aluminum instead of expensive natural bauxite. Moreover, these cements are easily to grind, therefore the energy demand for grinding and milling processes is reduced [12].

The aim of this work was synthesis of ternesite and subsequent monitoring of the hydration process to improve knowledge in this field. In order to follow the progress of hydration ability, hydration of ternesite in four storage environments, namely in storage in water and in the presence of carbonic acid and at low and higher temperature in both cases was observed.

2. Methodology

The experiment was based on the study of hydration of ternesite clinker in four different storage environments. Raw meal for ternesite was synthesized from three components: high calcium limestone – calcium carbonate, CaCO₃ (purity 99.00 %), gypsum – industry by-product from flue gas desulfurization, CaSO₄·2H₂O (purity 95.51 %) and microsilica, SiO₂ (purity 98.00 %). Raw materials were dried to a constant weight (limestone and microsilica at temperature of 105°C, gypsum at 40 °C) using circulating oven BINDER ED APT line II with forced circulation. The dosage of respective oxides was based on stoichiometric proportions of particular components in ternesite, 5CaO·2SiO₂·SO₃, namely 5 mol of CaO, 2 mol of microsilica and 1 mol of calcium sulfate hydrate, specifically (taking purities into consideration). The dosage was performed with accuracy of ± 0.01g. Subsequently, the raw materials were blended with isopropylalcohol into consistency of suspension which was crushed and homogenized in a planetary mill for 20 minutes by 300 rpm using FRITSCH Pulverisette 6 with stainless steel grinding bodies. The resulting slurry was completely dried at temperature of 40 °C to a constant weight. Approximately 25 g of dry powder mix was poured into 5 platinum crucibles and manually compacted. The firing process was performed in a laboratory furnace CLASIC 2018S CLARE 4.0 at temperature of 1150 °C at heating rate of 10 °C/min, soak 1 hour and next quenched by air flow. Ternesite clinker was ground in the planetary mill for 10 minutes by 500 rpm before the hydration. The storage environments of exposure were chosen with respect to possible processes, as follows. One half of samples was placed into the environment of saturated carbonic acid with the aim to support supposed formation of thaumasite, into whose structure is built the carbonate unit. One half of these samples was put into CO₂ saturated water and the second half of these samples into pure water.

Hydration in water was executed that ground ternesite was poured into a bottle of volume of 11 which was filled by water of temperature of around 7°C. Hydration in the presence of saturated carbonic acid was executed in a pressure bottle and water was saturated by carbon dioxide. All the samples were placed into the storage environments up to 90 days:

- Saturated carbonic acid, temperature 5 °C – CO₂/5°C.
- Saturated carbonic acid, temperature 40 °C – CO₂/40°C.
- Water, temperature 5 °C – w/5°C.
- Water, temperature 40 °C – w/40°C.

Mineralogical composition was regularly characterized by XRD using diffractometer Empyrean PANAnalytical with Cu K-alpha cathode (λ = 1.54184 Å) and PIXcel3D detector. The testing was supplemented by quantitative TG/DTA analysis using TGA/DTA851 Mettler Toledo (the heating rate 10 °C/min, open air conditions). Samples of hydrated ternesite clinker were ground in a XRD-Mill McCrone (Micronising mill) before testing. The measurement of XRD analysis was carried out under conditions, as follows: generator settings were 45 kV and 40 mA; scan range 5–80°, step size of 0.0131°, 255 active channels. The XRD patterns were analyzed by software HighScore Plus with PDF-2 powder diffraction files database.
3. Results
Figure 1 to 4 show the XRD patterns of the hydrated ternesite clinker exposed to the individual storage environments.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of hydrated ternesite clinker, CO$_2$/5°C.

![Figure 2](image2.png)

**Figure 2.** XRD patterns of hydrated ternesite clinker, CO$_2$/40°C.

![Figure 3](image3.png)

**Figure 3.** XRD patterns of hydrated ternesite clinker, w/5°C.
Figure 4. XRD patterns of hydrated ternesite clinker, w/40°C.

Table 1 presents the minerals identified in the XRD patterns of hydrated ternesite clinker.

Table 1. List of identified minerals in samples.

| Mineral                        | Marking | ICDD-PDF-card |
|--------------------------------|---------|---------------|
| Aragonite, CaCO₃               | A       | 00-041-1475   |
| Calcite, CaCO₃                 | C       | 00-005-0586   |
| Gypsum, CaSO₄·2H₂O            | G       | 00-033-0311   |
| Ternesite, 5CaO·2SiO₂·SO₃     | T       | 00-049-1807   |
| Thaumasite, CaSiO₃·CaCO₃·CaSO₄·15H₂O | Th     | 00-046-1360   |
| Vaterite, CaCO₃                | V       | 01-072-0506   |

TG and DTA curves for individual samples of clinker in specific ages of hydration were obtained by differential thermal analysis. From the course of curves, presence of calcium carbonate in the form of calcite and mildly crystalline phases of vaterite and aragonite was identified, gypsum and thaumasite were also found. Content of gypsum and also the sum of CaO coming from calcium hydroxide and carbonate (marked as ∑CaO) were calculated. From the quantification, the figure 5 and 6 graphically provide the results depending on the age of hydration and the storage environment.
4. Discussion

It is quoted in the literature [1,2,4,8-10] that ternesite is nearly inert when mixed with water, or reacts only at later stages of hydration. According to the experiment performed on the clear ternesite clinker using XRD, decomposition of ternesite already at an age of 1 day of hydration was observed. In the environment of carbonic acid, the rate of decomposition of ternesite was very high. Gypsum, calcite or vaterite and aragonite were identified as the products of decomposition. No new products of hydration of ternesite with water were observed in this environment. Assumed formation of thaumasite was not recorded. Regarding the temperature of storage, the rate of decomposition at the temperature of 40 °C was greater than at 5 °C. No more lines of ternesite were found at an age of 90 days of hydration, complete decomposition occurred.

The decomposition of ternesite in the water took place substantially slowly in comparison to the former conditions. As a consequence of low rate of decomposition of ternesite clinker, gypsum and calcite were formed very gently, the diffraction lines of vaterite and aragonite were not observed. Except that, basal diffraction line of silicate mineral thaumasite, \( \text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O} \), was observed in samples at an age of 14 days. This process was well apparent for samples exposed to the temperature of 5 °C, this line was marginal for samples from the temperature of 40 °C. Authors [14, 15] describe the formation of thaumasite and the influence of the temperature on its formation. They claim the formation of thaumasite requires temperatures to 15 °C, ideally from 0 to 5 °C.

In accordance with XRD evaluation, the second biggest rate of decomposition of ternesite stored in the environment \( \text{CO}_2/40^\circ\text{C} \) of all samples was observed. On the contrary, the amount of \( \Sigma \text{CaO} \) was very low in the water storage, namely the smallest value - in accordance with the formation of thaumasite - was calculated for the samples from the environment w/5°C.

In course of time, amount of gypsum in hydrated clinker was increasing in all the observed storage environments. However, gypsum as the product of decomposition of clinker stored in the presence of carbonic acid was formed very rapidly and in a raised amount, conversely, when stored in a pure water, gypsum was formed slowly and to a markedly lesser extent.

Based on the results from DTA and TG curves of ternesite clinker after an age of 90 days of hydration, it was possible to observe which also mean quantify the mineral thaumasite. Its content was calculated as a value of around 3.2%.

5. Conclusion

This paper investigated hydration process of ternesite. For the purpose of studying it, the raw meal was prepared firstly, optimized burning regime was employed for the firing of the raw meal subsequently. The resulting ternesite clinker was hydrated and exposed in four specific environments, namely in water and in the presence of saturated carbonic acid, at the low and elevated temperature for both cases mentioned. The progress of hydration process was monitored using XRD and DTA analysis. Slow to complete decomposition of ternesite was observed within the time period studied. The rate of
decomposition depended on the conditions of storage. The highest rate of decomposition was determined for the ternesite clinker from the storage environment of saturated carbonic acid at elevated temperature, conversely, the lowest rate of decomposition of the clinker was observed in the storage in water at low temperature. When the ternesite was exposed to water environment, the formation of thaumasite was discovered, which was firstly assumed for the environment of the carbonic \( \text{CO}_2 \). It can be stated that minerals having great rate of consolidation (i.e. rate of creation and crystallization) are preferentially formed by very high rate of decomposition of the ternesite clinker. By contrast, the slow decomposition of ternesite enables consolidation of slowly formed thaumasite.

Acknowledgment
This work was financially supported by project number: GA17-24954S “The Conditions of Thermodynamic Stability and Transformation of AFt Phases” and project No. LO1408 "AdMaS UP - Advanced Materials, Structures and Technologies", supported by Ministry of Education, Youth and Sports under the „National Sustainability Programme I”.

References
[1] Ludwig H M and Zhang W 2015 Cement Concrete Res. 78 24–37
[2] Dienemann W 2013 Int. Cong. 7th VDZ (Düsseldorf) (Leimen:Heldelberg Cement AG technology Center) pp 24-27
[3] Irran E, Tillmanns E, Hentschel G 1997 Mineralogy and Petrology 6 121-132
[4] Dominguez R, Gomez-Millan J, Alvarez M, de Aza S, Contreras L and de Aza A H 2010 J. Am. Ceram. Soc. 30 1879–1885
[5] Shen Y, Qian J, Chai J and Fan Y 2014 Cem. Concr. Comp. 48 67–74
[6] HeidelbergCement New type of clinker significantly reduces \( \text{CO}_2 \) emissions Ternesite clinker (Germany)
[7] Ukrainczyk N, Mihelj N F and Sipusic J 2013 Chem. Biochem. Eng. Q. 27 83–93
[8] HeidelbergCement 2013 ZKG Int. 5
[9] Beretka J, de Vito B, Santoro L, Sherman N and Valenti G L 1993 Cement Concrete Res. 23 1205-1214
[10] Bullerjahn F and Ben Haha M 2013 Cement International 11
[11] Gartner E and Hirao H 2015 Cement Concrete Res. 78 126–142
[12] Schneider M 2015 Cement Concrete Res. 78 14–23