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## Examination of microstructure of solidification product containing hazardous sludge

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### Abstract

The tests involved with the microstructure evaluation must be also added to the processes which significantly support the evaluation of long-term durability of solidification product (SP). Monitoring the microstructure by analyses such as scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and differential thermal analysis (DTA) it can be assumed according to the new compounds being formed during the hydration whether the hydration products are modified. Moreover, it could also be determined how the pollutants contained in input hazardous waste (HW) are incorporated in solidification product (SP) matrix. Within this work four different types of sludges (S) containing dangerous substances, mainly heavy metals were selected as input hazardous waste (HW) for laboratory preparation of samples of the solidification products (SP) for the microstructure analyses. On the basis of the findings from microstructure analyses it can be assumed whether contaminants contained in input HW, sludges, is immobilized into the matrices of solidification products (SP) by incorporating into the hydration products of SP matrix.

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**Keywords:** Solidification product; contaminants; scanning electron microscop; differential thermal analysis; X-ray diffraction

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### 1. Introduction

To still larger extent there is an effort to use the solidification/stabilization (S/S) process for transformation of hazardous waste (HW) in new secondary raw materials suitable for preparation of building materials. It has been

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demonstrated [1] that S/S technology is currently applied in the treatment of HW prior to landfilling. S/S technology is particularly effective when dealing with heavy-metal bearing sludge, even if chemical and microstructural changes induced in the solidification product (SP) with cement matrix are incompletely understood [2,3].

In the Czech Republic the solidification product (SP) has been used in the form of granulate as technological material at landfills and also as reclamation material. In this way not only the disposal of hazardous waste (HW) or safe storage of produced solidification products (SP) at landfill for strongly lower fees are provided but also directly its application as useful material replacing natural resources of raw materials. Monitoring the microstructure of SP interior structure can be clarified together with physical and chemical mechanisms occurring during the S/S processes. The study of solidification product (SP) microstructure may also help to elucidate the way of contaminant incorporating in SP matrix structure. However, majority of minerals contained in SP can be defined only informatively, because the microstructure of SP has not been sufficiently examined, especially due to different chemical composition of various input hazardous waste (HW). Since the amount of contaminants are not reduced by S/S process and other physical and chemical barriers preventing these pollutants to proceed further to the environment are created it is necessary to pay attention also to SP long-term durability and verify stability of its properties. Applied solidification agents, homogenization grade of solidification mixture and ambient conditions mostly decide on the success of hazardous waste (HW) solidification.

Cement, fly ash and lime are the most frequently used solidification agents. Conner [4] pointed out that cement is widely used solidification agent of low-level radioactive, hazardous wastes, mixed wastes, and remediation of contaminated sites because it has many advantages. Shi et al. [5,6] stated that solidification/stabilization (S/S) process of contaminants by cements includes the following three aspects: chemical fixation of contaminants – chemical interactions between the main hydration products of the cement and the contaminants; physical adsorption of the contaminants on the surface of hydration products of the cements and finally physical encapsulation of HW (low permeability of the hardened solidification mixtures).

## 2. Materials

### 2.1. Input hazardous waste

Not only the suitable properties for solidification/stabilization (S/S) using inorganic binders were among the main parameters of the selection of input hazardous wastes (HW) but there was also the requirement that S/S was desirable also in economic point of view. The cost-effective criterion is represented by minimal annual production of HW set to 10 tons, because S/S of lower waste volume will not be effective. Therefore, four different sludge (S) types were selected as input HW for laboratory preparation of solidification products (SP). They were inorganic wastes containing dangerous substances. As the most suitable the following HW were selected: sludge from metal machining, neutralisation sludge (S1); sludge from wire drawing processes (S2) and two types of sludge from the chemical and physical processes containing hazardous substances (S3 and S4). Sludge types marked as S3 and S4 are formed by neutralising of galvanic baths intended for surface treatment of metal elements using  $\text{Ca}(\text{OH})_2$  and their subsequent drying. Sludges S3 and S4 can be classified according to Environmental Protection Agency (EPA's) F-code Resource Conservation and Recovery Act (RCRA) HW listings to the code F019 that is one of the wastes generated from common industrial and manufacturing processes. The wastewater treatment sludges F019 are generated from the treatment of the rinse and overflow wastewaters from the chemical conversion coating process. The highest production – 500 tons annually is registered with sludge S1 and S4 and on that ground it is necessary to resolve further processing of these HW types, because currently they are only stored at landfills for HW, which is not cost effective and it is unacceptable from the ecological point of view.

In order to examine the input HW, sludges, and to evaluate their negative impact on the environment the leachability test was carried out according to the European standard EN 12457-4. It has been demonstrated [7] that due to the complexity of the leaching process and the number of factors influencing release, no single leaching test or single set of leaching conditions (e.g. extraction medium) is appropriate for the entire range of leach testing objectives and applications. On the basis of water leachate pH it can be assumed that S1 sludge has neutral character, S2 is slightly acid and S3 and S4 are of alkali nature. With regard to the leachability test results, the evaluation with limits stated in the Regulation no. 294/2005 on conditions of waste storage at landfills and their

utilization on terrain surfaces we can assume that the leachability class IIa was exceeded by S2 sludge where the required values of dissolved organic carbon (DOC) and Molybdenum (Mo) were exceeded. Metals occurring in the sludges cannot be destroyed and so must be converted to their least soluble or reactive form to prevent re-release into the environment. Conner and Hoeffner [8] stated that the main mechanisms for metal stabilization consist of pH control and buffering, speciation/precipitation, oxidation/reduction, and sorption/ion exchange.

## 2.2. Solidification formulas

The samples of solidification products (SP) with which the microstructure was monitored were selected upon the detailed laboratory examination of large number of solidification formulas. Within this verification physical and mechanical properties of SP were defined together with ecological requirements like the leachability and ecotoxicity testing. Solidification formulas used for preparing the samples for microstructure analysis are shown in Table 1. The formulas differ in type and amount of input HW (sludge) and amount of solidification agents. The formulas SP-1 and SP-2 contain 30% of sludge, SP-3 40% and SP-4 50% of sludge amount. As suitable solidification agents Portland mixed cement with granulated blast furnace slag and limestone (CEM II/B-M (S-LL) 32,5R), fly ash from pulverized coal combustion (PCC fly ash) and fly ash from circulating fluidized bed combustion (CFBC fly ash) were selected. The selection of specific resources took place with regard to the economic and environmental points of view and accessibility. Debroy and Dara [9] demonstrated the immobilization of zinc and lead present in waste sludges by chemical fixation and encapsulation methods using lime-pozzolan and fiber-reinforced lime-pozzolan admixtures.

Table 1. Composition of the solidification products (SP) – solidification formulas.

Component	SP-1	SP-2	SP-3	SP-4
HW – Sludge (wt.%)	30	30	40	50
CEM II/B-M (S-LL) 32,5R (wt.%)	10	10	20	5
PCC fly ash (wt.%)	30	30	25	20
CFBC fly ash (wt.%)	30	30	15	25

## 2.3. Sample preparation

SP-1 and SP-2 samples for determination of microstructure were prepared in the form of pellets on the special granulation plate made for this purpose. Vacenovska et al. [10] discovered that granules prepared on the granulation plate are more compact and also the results of strength and leaching tests shows better results of such created granules. From SP-3 and SP-4 formulas cubical samples of SP with dimensions 100 × 100 × 100 mm were prepared. Same samples were also used for the determination of bulk density and compressive strength during the basic laboratory examination of large number of initial solidification formulas. During the pellets production lower amount of water was used than with the preparation of other samples. With pellets the water weight and weight of all other components except HW ratio expressed in percentage was approximately 20 wt.% and with cube samples it was approximately 40 wt.%.

## 3. Methods

### 3.1. Scanning electron microscopy (SEM)

In order to elucidate the microstructure of SP-1 and SP-2 samples Magellan scanning electron microscope (SEM) was used. It is a modern type of SEM with resolution under 1 nanometer within the whole scale of electrons. In order to determine the microstructure of SP-3 and SP-4 TESCAN MIRA3 LM scanning electron microscope (SEM) with definition in high-vacuum mode up to 1.2 nm at 30 kV was used. SP-1 and SP-2 samples were one year old while SP-3 and SP-4 samples were 2 years old. SEM is mainly used as additional analysis to differential thermal

analysis (DTA) and X-ray powder diffraction (XRD) analysis. Before the microstructure determination of SP all the samples had to be cleaned from surface impurities and dust and they also had to be coated with gold.

### 3.2. X-ray powder diffraction analysis (XRD)

Using X-ray powder diffraction (XRD) analysis the interior crystalline structure of solidification products (SP) can be defined. Also some types of crystalline phases that are produced and modified during the hydration process of SP can be monitored. The manner how particular contaminants, mainly heavy metals, are incorporated into SP matrix is important piece of knowledge. Samples for XRD analysis were prepared by grinding and subsequent sieving through 0.063 mm screen. The sample prepared in this way was placed in circular metal bracket, then it was levelled with bracket surface and finally it was put into XRD analyzer.

### 3.3. Differential thermal analysis (DTA)

Differential thermal analysis (DTA) is another analysis helping to clarify the microstructure of SP. It verifies the difference of temperature between the studied sample and inert material or virtual sample within the same temperature programme depending on the temperature. Thermogravimetric (TG), differential thermogravimetric (DTG) and DTA curves are the outputs. TG curve serves mainly to the determination of partial and total weight defect of thermal disintegration, for instance the loss of water crystalline bound molecules can be monitored. Chaipanich and Nochaiya [11] stated that TG curve, for example, is routinely applied to quantify the amount of calcium hydroxide and carbonates in hydrated cement paste. DTG curve provides for more precise determination of starts and ends of particular event within the thermal disintegration. Using the DTA curve endothermic (thermal disintegration, change of modifications) and exothermic (crystallization) can be verified. The DTA analysis was carried out using the following instrument – Mettler Toledo TGA/SDTA 851, the thermal gravimetric analyzer with maximal heating temperature 1,100 °C. DTA analysis was carried out with one year aged SP samples SP-3 and SP-4. SP samples for DTA analysis were ground and sieved by sieving over the 0.063 mm screen while weight of the samples moved within 20 to 40 mg. The weighed samples were put in the corundum pot which was put on the scale arm in the furnace. The samples were heated up to approximately 1,000 °C.

## 4. Results and discussion

### 4.1. Scanning electron microscopy (SEM)

In the following figures (Fig. 1 (a) – (d)) there are photomicrographs of all four verified SP taken using the scanning electron microscope (SEM). From the photomicrographs taken by SEM a compact, homogeneous structure with low amount of voids can be seen in the microstructure of SP sample, in particular, Fig. 1 (a) captures portlandite ( $\text{Ca}(\text{OH})_2$ ) grain in SP-1 microstructure, its task is to keep sufficiently high pH value so that the contaminants could not be released from SP matrix. Zampori et al. [12] indicate that attention needs to be driven on the mobility of  $\text{Ca}^{2+}$  ion inside the cement matrix: leached  $\text{Ca}^{2+}$  can derive mainly from the dissolution of portlandite and from desorption from the amorphous calcium silicate hydrate (CSH) gel. Fig. 1 (b) shows the microstructure of SP-2 when similar microstructures like ettringite were seen. Buttler et al. [13] stated that in the SEM ettringite is sometimes seen, but not as commonly as XRD suggested. In the microstructure of SP-4 more unreacted grains of PCC fly ash were registered with function as aggregates, also higher amount of pervasive ettringite able to immobilise majority of contaminants containing heavy metals was registered. From Fig. 1 it was further found that the main binder component of SP were the cement and fly ash hydration products – CSH gels, portlandite and ettringite. Fig. 1 (c) shows gypsum grains surrounded CSH gels and in Fig. 1 (d) the fly ash grain captured in CSH gel amorphous phase can be seen. The sample SP-4 was too flimsy, it was difficult to handle and prepare it for microscopic analysis. On that ground particular phases of this sample are hardly distinguishable, nevertheless CSH phase and the fly ash grain can be clearly seen in the photomicrograph.

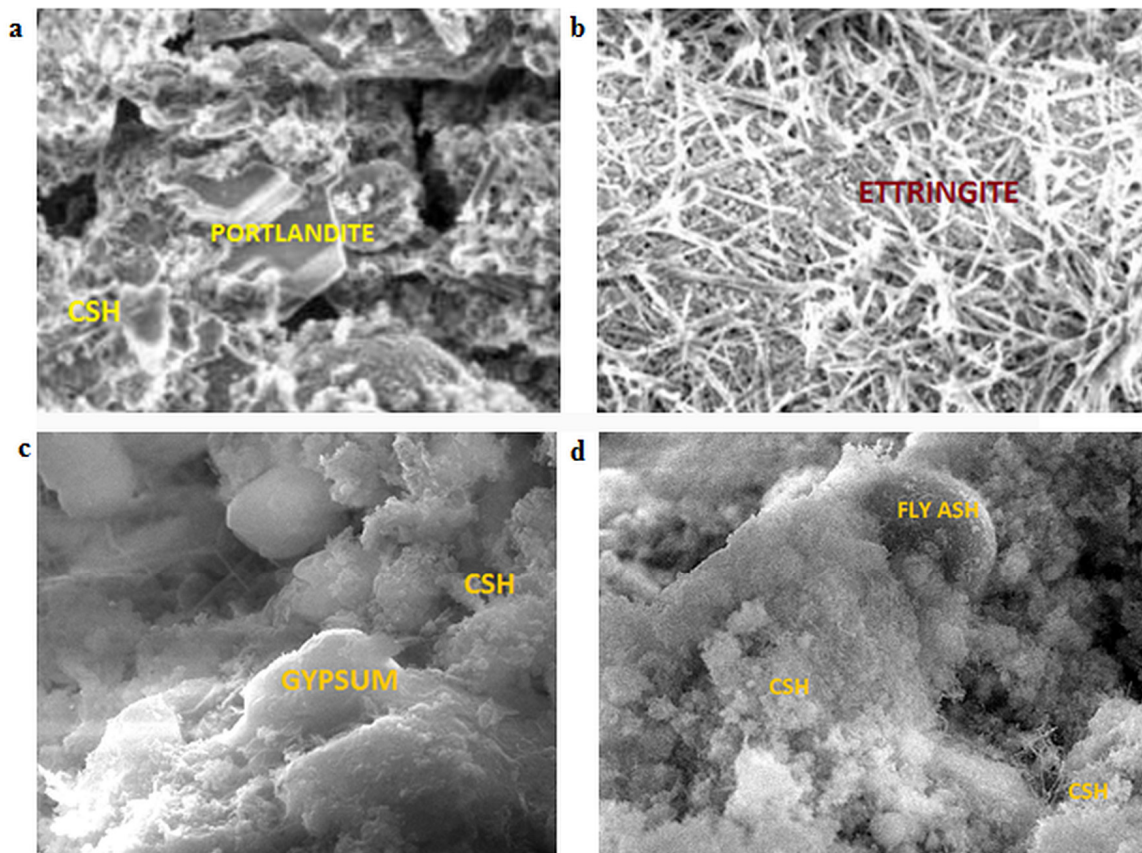


Fig. 1. (a) SEM photomicrograph of SP-1 (15,000×); (b) SEM photomicrograph of SP-2 (15,000×); (c) SEM photomicrograph of SP-3 (10,000×); (d) SEM photomicrograph of SP-4 (5,000×).

#### 4.2. Differential thermal analysis (DTA)

In Fig. 2 (a)(b) the output of Differential thermal analysis (DTA) analysis of SP-3 and SP-4 can be seen. On the basis of the evaluation of endo-delays on DTG curve some minerals most probably occurring in SP microstructures were determined. Fig. 2 (a) shows DTG curve where 5 visible endo-delays are visible while in respect of their evaluation the situation is very complex with the two first cases because at temperatures 80 – 90 °C several effects partially covering one another may appear. In this case the physically bound water is released, ettringite  $((\text{CaO})_3(\text{Al}_2\text{O}_3)(\text{CaSO}_4)_3 \cdot 32\text{H}_2\text{O})$  and gypsum  $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$  dehydrated and also calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) gels start to disintegrate. Compared to the XRD analysis results it can be claimed that first endo-delay corresponds to CSH phase and ettringite disintegration and the second one means the disintegration of gypsum. The same affirmations can be stated with both, SP-3 and SP-4 solidification products. The third endo-delay could not be defined on the basis of present knowledge in the field of SP with the cement and fly ash matrix. The fourth endo-delay with SP-4 could represent portlandite, however, this affirmation was not supported with other analytical methods. With SP-3 the fourth endo-delay on DTG curve corresponds to fine-grained calcium carbonates ( $\text{CaCO}_3$ ) and the fifth one to coarse-grained calcium carbonates ( $\text{CaCO}_3$ ) whose main representative is calcite. Bish and Duffy [14] discovered that  $\text{CaCO}_3$  decarbonation can be easily identified by DTG – it occurs at slightly higher temperature than smectite. With SP-4 only one endo-delay was found within 700 to 800 °C which can generally be considered as disintegration of  $\text{CaCO}_3$ . Further upon the determination of percentage loss of the sample on the TG curve within the temperature intervals matching particular endo-delays considering



chemical reaction products molecular weight the gypsum and carbonate amounts by percentage in SP samples were determined as it is shown in Table 2. SP-3 sample contained slightly larger quantities of calcium carbonates, most likely due to the higher content of cement in the SP matrix. The loss on ignition (LOI) was determined from the TG curve while this value is with SP-4 almost double compared to SP-3.

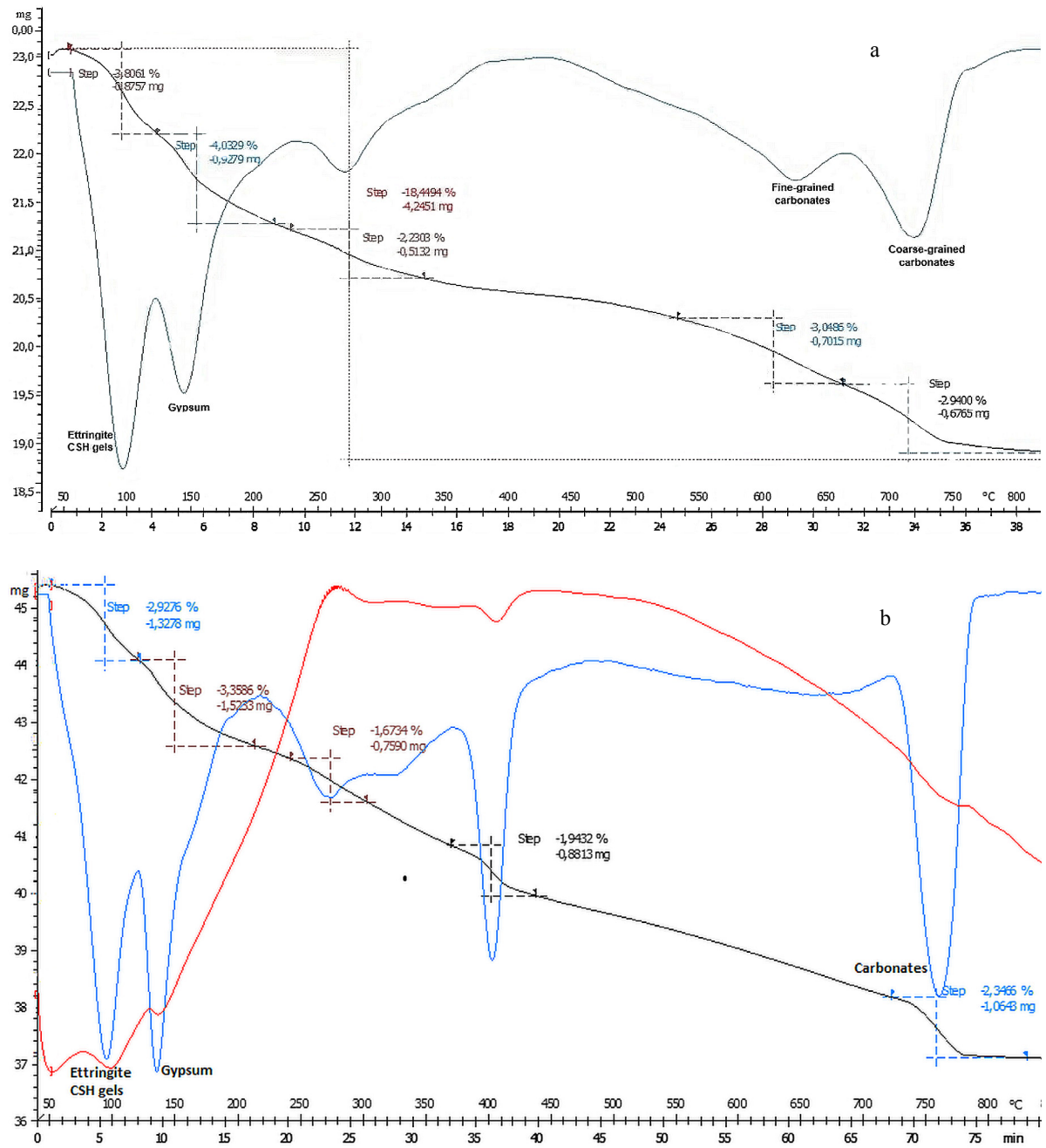


Fig. 2. (a) Results of DTA analysis –SP-3;  
(b) Results of DTA analysis –SP-4.

Table 2. Calculated amount (%) of gypsum, carbonates and LOI resulting from DTA analysis.

Sample	Gypsum ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ )	Carbonates ( $\text{CaCO}_3$ )	LOI
SP-3	38.6	6.9	18.5
SP-4	32.1	5.3	36.0

#### 4.3. X-ray powder diffraction analysis (XRD)

Minerals contained in SP can be defined by X-ray powder diffraction (XRD) only informatively because the microstructure of this material has not been examined very well so far especially due to different chemical composition of input HW. On the basis of chemical composition of input raw materials and SP and evaluation of XRD patterns (Fig. 3) it can be assumed that the microstructure of SP-3 and SP-4 consists mainly from minerals ettringite, quartz, gypsum and calcite. Portlandite occurring during the hydration initial phases most probably converted to carbonates because the samples were already aged one year, stored in laboratory conditions, where carbon dioxide ( $\text{CO}_2$ ) could penetrate. In the XRD patterns of SP-3 and SP-4 same minerals can be determined and therefore we can assumed that their microstructures are similar despite they differ by the input HW itself. Calcite, ettringite and gypsum were found in SP also with DTA analysis and so these minerals most probably occur in the monitored SP. Yousuf et al. [15] stated that SP is very likely to be a multi-phase material and when cementitious materials are present, poorly crystalline phases, impure phases, and solid solutions between can make phase identification difficult. Recent results from Roy et al. [16] showed that none of portlandite ( $\text{Ca}(\text{OH})_2$ ) could be presently detected in the XRD pattern of SP containing sludge (Ni, Cr, Cd, Hg) in a Class C fly ash- $\text{Ca}(\text{OH})_2$  matrix with 0, 2, 5, and 8 wt.% zinc nitrate, whereas several calcium carbonate peaks could be found.

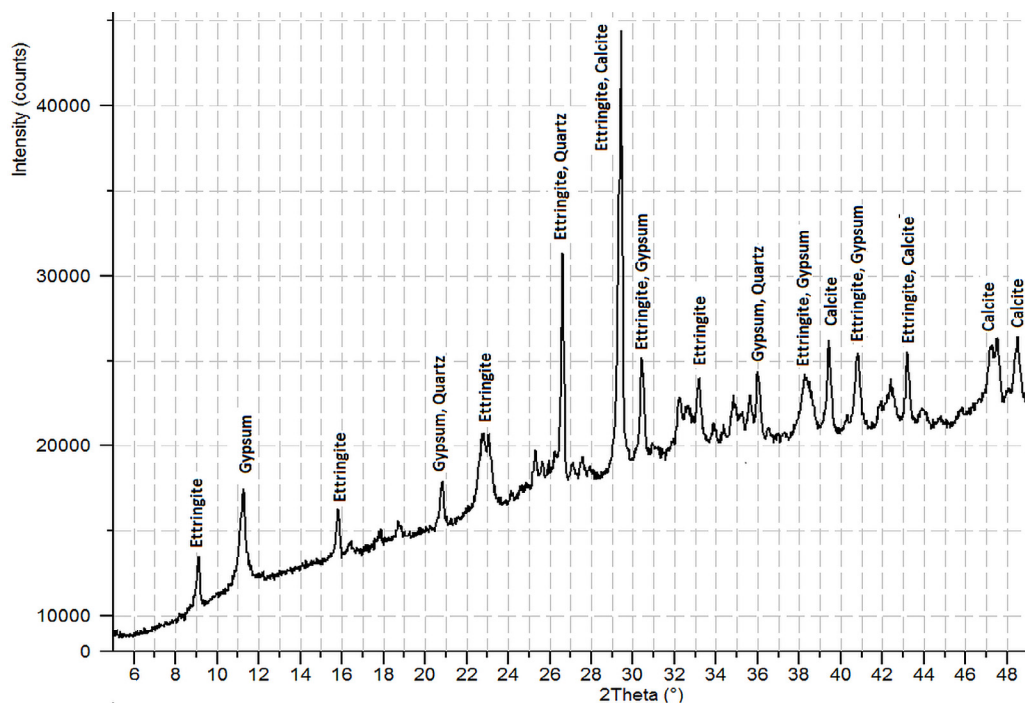


Fig. 3. XRD pattern of SP-3 (1 year).

## 5. Conclusion

Within the monitoring of solidification products (SP) microstructure the SP-3 and SP-4 solidification products were examined in detail. SP contain hazardous waste (HW) in the form of wastewater treatment sludge F019 (S3, S4) incorporated in cement-fly ash matrix. On the basis of evaluation of the performed analyses – SEM, DTA, XRD we can assume that the microstructure of these SP types is formed mostly by amorphous CSH phases, acicular ettringite which is able to incorporate in its structure heavy metals contained in sludge, calcium carbonates occurring mostly due to the application of cement as solidification agent and gypsum whose formation strongly relates to high content of sulphates in the input HW. The presence of quartz was confirmed just on the basis of XRD analysis, with SEM the quartz crystals were not found. On the basis of the findings from carried out analyses it can be assumed that major part of contaminants contained in input HW, sludges, is immobilized into the matrices of SP mostly by incorporating into the hydration products of matrix. Therefore it can be assumed that selected input hazardous sludges did not influence negatively the hydration of SP with cement and fly ash matrix which fact points out to ecological suitability of SP and after further verification of its properties it would be reasonable to focus on its possible application as the material in building industries and land reclamation.

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