

## INFLUENCE OF HYDROTHERMAL CURING ON G-OIL WELL CEMENT PROPERTIES

MARTIN PALOU, VLADIMÍR ŽIVICA, LUBOMÍR BÁGEL AND TOMÁŠ IFKA

G-Oil Well well cement has been cured under standard and hydrothermal conditions with different steam pressures and temperatures. Compressive strength, pore structure parameters, microstructure and hydrated products were evaluated after 7 days` curing by using SEM, MIP and Simulated TGA/DSC. Obtained results showed that the 7 days aged sample cured under standard conditions has the highest compressive strength with compact pore structure and hydrated products similar to those found after hydration of Ordinary Portland cement. With increasing the temperature and pressure from standard conditions (25 °C, 10 125 Pa) to hydrothermal ones (150 °C and 0.3 MPa, 200 °C and 1.2 MPa), compressive strength has drastically decreased from  $77.5 \pm 2.0$  MPa to  $20.5 \pm 1.0$  MPa due to the transformation of original hydrated products (C-S-H) to crystallized  $\alpha$ -C<sub>2</sub>S<sub>2</sub>H and C<sub>6</sub>S<sub>2</sub>H<sub>3</sub>. The crystallization has led, under hydrothermal curing, to the increase of permeability and pore structure depletion. The final compressive strength, after curing for 7 days at 150 °C ( $51.8 \pm 2.0$ MPa) and 200 °C ( $20.5 \pm 1.0$  MPa) which significantly exceeds the recommended values of 3.45 MPa according to API to hold many casings of oil wells is questionable for application in geothermal ones.

### 1. Introduction

Ordinary Portland cement (OPC) is the main inorganic binder used in a civil and engineering construction due to its ability to react with water to form workable slurry that sets and hardens after a certain period. The reaction with water, so-called hydration is a complex of chemical and physical processes taking place after contact of the anhydrous solid with water leading to the formation of new products responsible for consolidation, strength development and durability of constructions. The hydration runs via chemical reaction between different minerals of cement (C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A, and C<sub>4</sub>AF) and water to form gelatinous or semicrystalline calcium silicate hydrate, denoted C-S-H; calcium sulfoaluminate hydrate (ettringite or monosulphate) and calcium hydroxide giving appropriate strength and durability to set cement. As the cement is used under different climatic conditions, the temperature becomes a pertinent key factor that influences the kinetics and mechanism of hydration, and the nature of hydrated products. Many studies have investigated the

temperature dependence of the rate of hydration, and most of them found that it can be described by an Arrhenius equation with an effective activation energy,  $\Delta E$  of about 35 – 40 kJ/mole (Ježo et al., 2010, Feng et al., 2009). Authors (Zhang et al., 2010, Jupe et al., 2008) have investigated hydration of OPC under different saturated steam pressure at the temperature range from 120 °C to 350 °C. Up to 110 °C tobermorite ( $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$ ) is formed and between 120 °C and 350 °C  $\alpha\text{-C}_2\text{SH}$  and xonotlite ( $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ ) associated with the volume reduction appear as major products with an increase in porosity. Consequently, concrete under a high temperature undergoes strength retrogression due to enumerated transformations and reactions, causing progressive breakdown of cement gel structure and loss in its load-bearing capacity, reduced durability, and increased tendency of drying shrinkage, structural cracking, and associated aggregate color changes (Richardson, 1999).

Next to temperature, humidity is a determinant factor for the hydration of cement paste. It can prevent the shrinkage of concrete during the early period of applications. The coupled effect of elevated temperatures and steam pressure in environments denoted as hydrothermal ones, are a common characteristic of geothermal, oil and gas wells (Le Saout et al., 2006, Gaurina-Medimurec et al., 1994, Jupe et al., 2008, Kalousek, 1979). In these environments, temperatures and pressures are so high (up to 200 °C and 1.5 MPa in deep wells) that they challenge the capabilities of construction materials used in the wells. For this purpose, special class of cements, denoted G-Oil Well cements (**GOWC**), is used for cementing work in the drilling of oil wells where cement hydration runs under high temperatures and pressures of water vapor. Cement slurry placed in the annular space between the well steel casing and the geological formations surrounding the well bore has to provide zonal isolation. In addition to the high pressure and temperature, oil well cements must be able to resist the attack of corrosive fluids. Therefore, a successful oil well cementing seal must have low permeability and adequate durability to ensure the long-term protection of the casing steel. Incomplete zonal isolation and/or a weak hydraulic seal between the casing and the cement, and between the cement and the formations may cause oil spills and the well may never run at its full producing potential (Smith et al., 1975). Thus, oil and gas well cementing operations face additional challenges in contrast to common cementing work above the ground. The type of cement depends on the temperature, pressure, depth and chemical composition of environments. For cementing these wells as a protective layer of dwell during the exploitation of natural gas and petroleum (William et al., 2005), the API (American Petroleum Institute) Specifications for Materials and Testing for Well Cements (API Specification 10A, 2002) has established 9 special classes of cements. They are arranged according to the depths, to which they are placed, and the pressures and temperatures to which they are exposed (Nelson, 1999). Oil well cements are usually made from Portland cement clinker or from blended hydraulic cements.

The investigation of hydrothermal curing conditions on the behavior of oil wells cement is an important task required not only for the oil industries but also for those researchers involved in the development of new cementing materials for more severe hydrothermal conditions of application. Furthermore, there has been comparatively less work done on the coupled effect of pressure and temperature on hydration.

The literature contains many references pertaining to the performance of calcium silicate hydrates at temperatures up to 150 °C, but little has been published concerning higher temperatures associated with steam pressure. The present study attempts to develop a better understanding of the coupled effects of temperature and pressure on early hydration of G-Oil Well cement. The G-Oil cement paste was cured under standard and hydrothermal conditions of 0.3 MPa (150 °C) and 1.2 MPa (200 °C).

## 2. Experimental

The hydration products formed under hydrothermal conditions and their stability were investigated by Simultaneous Thermal Analysis (DTA and TG) Mettler Toledo TGA/DSC STRA system (Mettler-Toledo, Switzerland), where the sample was placed in an open vessel under air atmosphere, and measured at a heating rate of 10 °C/minute up to 1 000 °C.

### Autoclave and hydrothermal conditions used

The pressures of 0.3 MPa (150 °C) and 1.2 MPa (200 °C) were applied during autoclaving of 7 days. At the end of autoclaving period, the hot prisms were taken off and inserted in hot water. Cooling of water was accelerated gradually by adding the cold water until the handling temperature of approximately 40 °C was achieved.

**Mercury intrusion porosimeter** Quantachrome Poremaster 60GT (Quantachrome UK Limited) was used for the determination of pore structure characteristics (total porosity, distribution of pore sizes and permeability). Two or three pieces of dried samples with the diameter less than 10 mm and total mass max. 2 g were used for the tests. The maximum applied pressure of mercury was 414 MPa, equivalent to a Washburn pore radius of 1.8 nm.

Scanning Electron Microscope, JEOL JSM-7600F equipped with EDX was used for microstructure observations.

Oil well Portland cement of Class G HSR was from Holcim OJSC “Volskement”, Saratov region, Russia. The chemical composition of cement (%) and mineralogical composition of clinker (%) given by the producer are reported in Table 1.

Table 1. Oxide and mineralogical composition of G-Oil Well cement

Cement oxide		Clinker minerals		
Oxide	Composition/%	Designation	Formula	Composition/%
CaO	64.0	Alite	3CaO.SiO <sub>2</sub>	65.0
SiO <sub>2</sub>	21.0	Belite	2CaO.SiO <sub>2</sub>	12.0
Al <sub>2</sub> O <sub>3</sub>	4.5	Aluminates	3CaO.Al <sub>2</sub> O <sub>3</sub>	2.5
Fe <sub>2</sub> O <sub>3</sub>	5.5	Aluminate-ferrites	4CaO.Al <sub>2</sub> O <sub>3</sub> .Fe <sub>2</sub> O <sub>3</sub>	17.5
MgO	1.5			
SO <sub>3</sub>	2.5			

### Mixing procedure and test specimens

Appropriate pastes were prepared by mixing oil well cement with adequate quantity of water as determined by a workability procedure (water to cement ratio of 0.35). Six prisms with the dimensions of 160 × 40 × 40 mm were prepared from paste to be cured under various conditions during 7 days. **GOWC0** denotes samples cured under the standard condition of 20 °C and 100 % rel. humidity- **GOWC0.3** represents those cured under the hydrothermal condition of 0.3 MPa (150 °C) and **GOWC1.2** those cured under the thermal condition of 1.2 MPa (200 °C). The specimens were exposed to the steam curing condition at 100 °C for 30 min and after this pre-curing procedure still hot hardened specimens were quickly demolded and inserted into the autoclave. In each curing time, three samples were implemented and average values of the compressive strength of samples were calculated and recorded as the total compressive strength in the corresponding time.

## Results and discussion

The DTG and TG characteristics of samples **GOWC0**, **GOWC0.3** and **GOWC1.2** are depicted in Figures 1 – 3.

Sample **GOWC0** was cured under the standard condition of 20 °C in environment with 100 % relative humidity. TG and DTG curves (Fig. 1) of standardly cured oil well cement slurry show that its hydration process is similar to that of Portland cement. The presence C-S-H gel and ettringite in the hardened paste is indicated by the dehydration effects under 200 °C with peaks at 100 °C and 150 °C respectively. This result is also corroborated by weight loss curves obtained from TG curves showing substantial water losses in the range of 100 – 200 °C. The main endothermic peak is observed on DTG curve in the range of 400 – 500 °C with maximum at 450 °C. This peak results from the thermal degradation of  $\text{Ca}(\text{OH})_2$  present in the cured sample. Furthermore, it is evident that a part of hydrated product was carbonated, as it is demonstrated by two peaks between 600 – 700 °C and 800 – 900 °C. The total mass loss is 11.28 %, of which 82 % represent the part of water chemically bond (C-S-H, ettringite, CH, gypsum) and the rest results from the thermal decomposition of carbonated products.

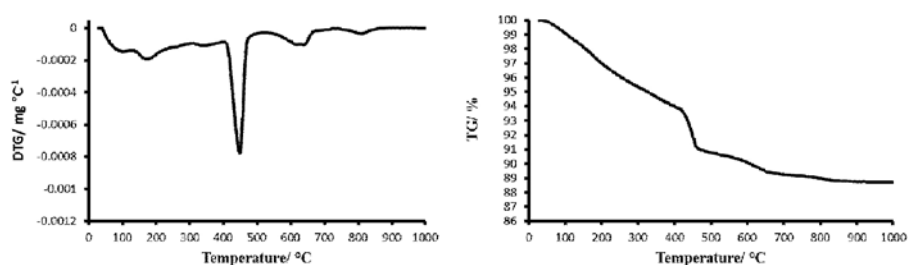


Figure 1. DTG and TG curves of the cured sample under standard condition

Sample **GOWC0.3** is oil well cement cured in the hydrothermal condition with 0.3 MPa (150 °C) during 7 days. If the main product of hydration remains calcium hydroxide, it is clear that the effect of hydrothermal curing has led to a decrease of calcium silicate hydrates and ettringite, but it has supported the formation of a new product with endothermic peak located at 520 °C. Carbonation is less pronounced due to the isolated conduction in autoclave. The nature of these products is a subject of many controversial studies. It was documented by (Ramachandran et al.) that  $\alpha\text{-C}_2\text{SH}$  crystalline with high permeability is a product of thermal transformation of C-S-H under higher temperature and pressure conditions. In a modelled study of reaction between  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$  under hydrothermal curing conditions, Šauman (1964) has found that at steam pressure of 0.8 MPa the products obtained are  $\alpha\text{-C}_2\text{SH}$ ,  $\text{C}_6\text{S}_2\text{H}_3$  and  $\text{Ca}(\text{OH})_2$  after 2 hours, but only  $\alpha\text{-C}_2\text{SH}$  and  $\text{Ca}(\text{OH})_2$  after 7 days. But at 0.8-1.6 MPa the hydration products are  $\alpha\text{-C}_2\text{SH}$  after 8 hours and  $\text{C}_6\text{S}_2\text{H}_3$  (Jaffeite, similar properties as  $\alpha\text{-C}_2\text{SH}$ ) with trace of  $\alpha\text{-C}_2\text{SH}$  after about 4 days. Midgley and Chopra (1960) have found that a paste of  $\text{C}_3\text{S}$  hydrated for 7 days at 180 °C contained only  $\text{C}_3\text{S}_2\text{H}_3$ . From these findings, it is clear that the nature of hydrated products depends not only on hydrothermal curing conditions, but also on the curing period. Differently from what has been reported by one or another authors, one can postulate that in G-Oil Well cement paste cured for 7 days at 150 and 200 °C, the formation of  $\text{C}_6\text{S}_2\text{H}_3$  has been occurred. It was reported by Collepari (1972) that  $\text{C}_6\text{S}_2\text{H}_3$  decomposes between 500 and 550 °C with the peak at 530 °C. It cannot be excluded, however, that  $\alpha\text{-C}_2\text{SH}$  has been prior formed and then transformed into  $\text{C}_6\text{S}_2\text{H}_3$  under the effect of temperatures. The total mass loss (Fig. 2) is 11.19 %, of

which 41.46 % represents the part of water chemically bond in C-S-H and ettringite, 40.93 % in CH and  $\alpha$ -C<sub>2</sub>SH, and 4 % in C<sub>6</sub>S<sub>2</sub>H<sub>3</sub>, and the rest results from the thermal decomposition of carbonated products, about 13.42 %. Carbonation is less pronounced under isolated autoclave curing conditions.

Sample **GOWCI.2** is cured under the hydrothermal condition with 1.2 MPa (200 °C). The conditions are more severe than the previous ones. Figure 3 shows that the main change in the constitution of G-Oil cement paste occurs during autoclaving at 200 °C for 7 days. As a result of hydrothermal curing effect, calcium silicate hydrate (C-S-H) fully disappeared, as it can be seen by the absence of endothermic peak in interval between 100 °C and 130 °C. The hydration is much more advanced, as it can be demonstrated by the intensity of endothermic peak characterizing the thermal decomposition of CH at 450 °C.

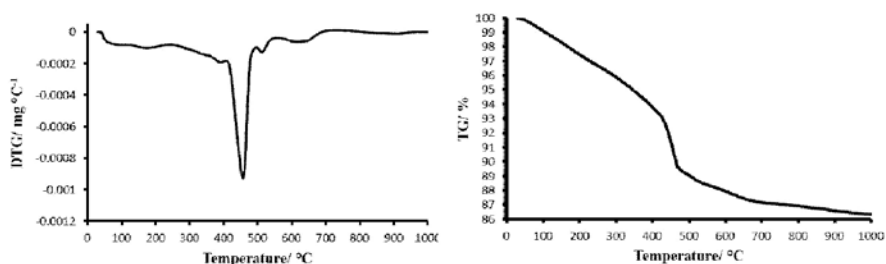


Figure 2. DTG and TG curves of the cured sample under hydrothermal condition 0.3 MPa, 150 °C

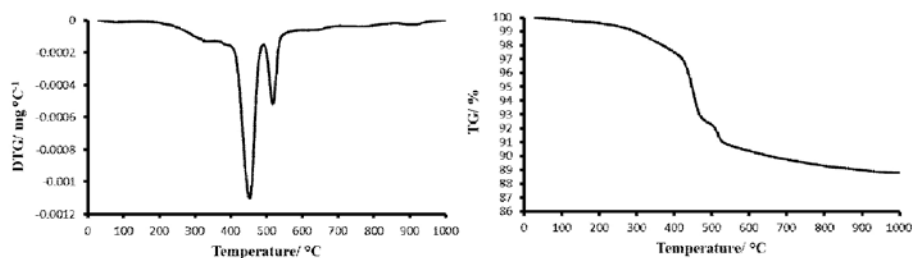


Figure 3. DTG and TG curves of the cured samples under hydrothermal condition 1.2 MPa, 200 °C

As it was reported (Le Saout et al., 2006), when the well temperature exceeds 110 °C, the new abundant phase formed in the sample hydration of an oil well cement is  $\alpha$ -dicalcium silicate hydrate  $\alpha$ -C<sub>2</sub>SH (Ca<sub>2</sub>SiO<sub>3</sub>(OH)<sub>2</sub>), which forms bulk materials that are too weak and permeable to seal the well. According to authors (Le Saout et al., 2006),  $\alpha$ -CSH<sub>2</sub> decomposes at 480 °C, but due to the overlapping of the thermal decomposition effect of CH at maximum 450 °C, the direct identification cannot be possible. The endothermic peak found at 530 °C is attributed to the decomposition of C<sub>6</sub>S<sub>2</sub>H<sub>3</sub> (Jaffeite) with a negative effect on the performance of G-Oil Well cement. The total mass loss (Fig. 3) is 11.19 %, of which 4.55 % can be attributed to the part of water chemically bond in C-S-H and ettringite, 64.52 % in CH and  $\alpha$ -C<sub>2</sub>SH, 16.90 % in C<sub>6</sub>S<sub>2</sub>H<sub>3</sub>, and the rest 14 % results from the thermal decomposition of carbonated products.

The microstructures of samples cured under different conditions are shown in Figure 4. Under standard conditions, SEM investigation shows a dense paste structure of C-S-H gels and with micro pores.

Microstructure of sample cured in autoclave at hydrothermal pressure of 0.3 MPa shows a matrix with still crystallized mineral phases, but at a lower extent. The hydration products appear as relatively dense in a heterogeneous matrix.

The sample cured under hydrothermal pressure of 1.2 MPa presents a porous structure with well-developed crystals. SEM shows a less dense and open microstructure with large pores due to coupled effect of temperature and pressure. The development of crystals resulting from the transformation of C-S-H to  $C_6S_2H_3$  (Jaffeite) via  $\alpha-C_2SH$  is the main cause of pore structure degradation and compressive strength depletion, as it is presented in Table 2.

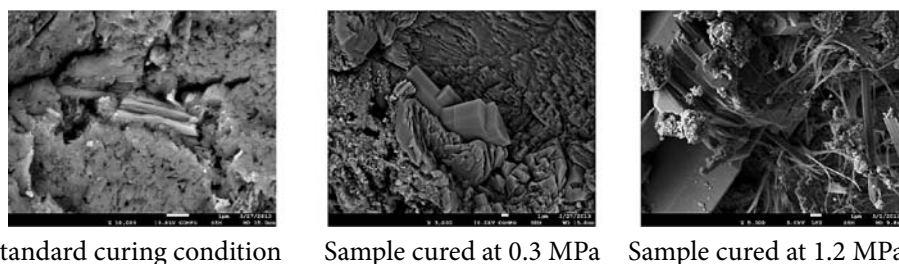


Figure 4. SEM micrographs of G-Oil Well cement cured under different conditions

Table 2. Mechanical properties

	Curing conditions		
	standard	hydrothermal	hydrothermal
	20 °C, 100 % rel. humidity	0.3 MPa 150 °C	1.2 MPa 200 °C
Compressive strength/ MPa	77.5 ± 2.0	51.8 ± 2.0	20.5 ± 1.0
Hydraulic permeability/ m s <sup>-1</sup>	<b>2 x 10<sup>-15</sup></b>	<b>7 x 10<sup>-15</sup></b>	<b>199 x 10<sup>-15</sup></b>

Hydrothermal curing of the hardened G-Oil Well cement for 7 days, provided a decrease in compressive strength compared to the cement paste cured under standard condition. The main cause of this strength depletion is the change in a pore structure due to the transformation of initial C-S-H to  $C_6S_2H_3$  through  $\alpha-C_2SH$  crystals.

Engineering properties of cement composites for oil well application such as strength, permeability and diffusivity (and thus durability) and shrinkage are intimately associated with porosity and pore size distribution (Day and Marsh, 1988). The volume and size distribution of pores affects not only the mechanical strength of cement based materials, but also its durability.

The pore size distribution (PSD) of cement pastes cured under different hydrothermal regimes is depicted in Figure 5. The effect of hydrothermal effect is evidenced by the intensity and position of the peak, by the length and bimodal characteristic of PSD.

Permeability is a measure of the ability of a fluid to flow through porous samples when subjected to a differential pressure. Therefore, permeability coefficient  $K$  is one of the essential properties used in the evaluation of cement paste durability. It was calculated by the software Poremaster during a porosimetric analysis according the following model:

$$K = \frac{\phi d_p^2}{32} \quad (1)$$

where  $\phi$  is the powder bed porosity and  $d_p$  the average pore diameter.

This parameter is characteristic for cementitious materials for application in oil well. As it can be seen in Table 2, the permeability coefficient has markedly increased with increasing the temperature/pressure. The primary function of well cement is to isolate/seal the casing from the well bore. This seal prevents the migration of fluids into the annulus and upwards to the surface. Therefore, it is imperative that the well cement exhibits very low permeability.

The PSD of samples cured under different conditions is recorded in Figure 5. With increasing the temperature/pressure, the maximum concentration of pores is displaced towards higher size. This is the demonstration of hydrothermal curing on the pore structure of G-Oil Well cement paste. In other words, due to pore size distribution change with curing conditions, the permeability of the specimen becomes higher at higher temperatures. This makes the specimen easier to the water to flow through it and to attack the steel casing.

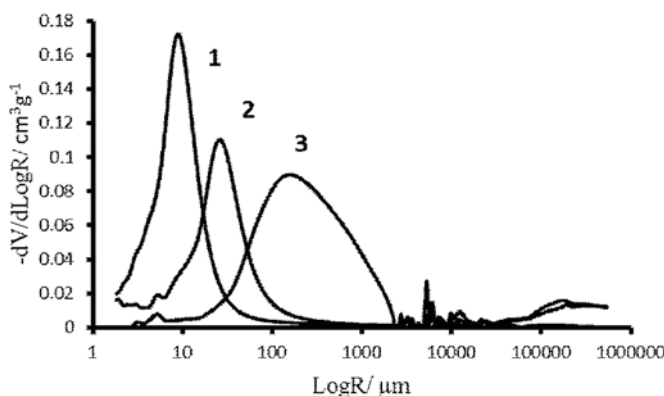


Figure 5. Influence of curing conditions on the PSD of G-Oil Well cement paste: 1-GOWC0, 2-GOWC0.3, 3-GOWC1.2

*NB. The cement chemical nomenclature used means C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, F = F<sub>2</sub>O<sub>3</sub> and H = H<sub>2</sub>O in cement chemistry.*

### 3. Conclusion

The cement paste from oil well cement subjected to hydrothermal curing has presented different mechanical and physical characteristics. TGA has identified different hydrated products according to curing conditions. The main hydration products of cured class G-Oil Well cement under the standard condition are C-S-H gel, Ca(OH)<sub>2</sub> and calcite resulting from carbonation. As the temperature or pressure of hydrothermal curing increases, the peak characterizing the presence of C-S-H decreases as a result of its crystallization in to C<sub>6</sub>S<sub>2</sub>H<sub>3</sub> via C<sub>2</sub>SH. This crystallization causes a reduction in solid volume and is accompanied by an increase in permeability and the reduction in com-

pressive strength known as strength retrogression. The transformation of C-S-H to  $\alpha$ -C<sub>2</sub>SH causes the depletion of microstructure and it enhances the total porosity.

### Acknowledgements

This article has been produced with the financial assistance of the European Regional Development Fund (ERDF) under the Operational Programme Research and Development/Measure 4.2 and with financial support from VEGA No. 1/0064/12.

### References

- [1] API (1990), Specification for material and testing for well cements. 5th ed. Washington, DC: American Petroleum Institute Spec. 10, 47 pp.
- [2] Collepari, M. and Marches, B. (1972), "Morphology and surface properties of hydrated tricalcium silicate pastes", *Cement and Concrete Research* 2, 57-65.
- [3] Day, R. L. and Marsh, B. K. (1988), "Measurement of porosity in blended cement Pastes", *Cement and Concrete Research*, 63-73.
- [4] Lin, F. and Meyer, Ch. (2009), "Hydration kinetics modeling of Portland cement considering the effects of curing temperature and applied pressure", *Cement and Concrete Research* 39, 255-265.
- [5] Gaurina-Medimurec, N., Matanovic, D. and Krklec, D. (1994). "Cement slurries for geothermal wells cementing", *Rudarsko-geološko-naftni zbornik* 6, 127-134.
- [6] Ježo, L., Palou, M., Kozánková, J. and Ifka, T. (2010), "Determination of activation effect of Ca(OH)<sub>2</sub> upon the hydration of BFS and related heat by isothermal calorimeter", *Journal of Thermal Analysis and Calorimetry* 101, 585-593.
- [7] Jupe, A. C., Wilkinson, A. P., Luke, K. and Funkhouser, G. P. (2008), "Class H cement hydration at 180 °C and high pressure in the presence of added silica", *Cement and Concrete Research* 38, 660-666.
- [8] Kalousek, G. L. (1979), Development of cement for geothermal wells, Final report BNL51024 UC 66-D.
- [9] Le Saout, G., Lécolier, E., Rivereau, A. and Zanni, H. (2006), "Chemical structure of cement aged at normal and elevated temperatures and pressures: Part I. Class G-Oil Well cement", *Cement and Concrete Research* 36, 71-78.
- [10] Ramachandran, V. S., Paroli, R. M., Beaudoin, J. J. and Delgado, A. H., "Thermal Analysis of Construction Materials", *Handbook of thermal analysis of construction materials*. Ed. VS Ramachandra et al., page 118. New York, U.S.A. 2002.
- [11] Migley, H. G. and Chopra, S. K. (1960), "Hydrothermal reactions between lime and aggregate fines", *Magazine of Concrete Research* 34, 73-82.
- [12] Richardson, I. G. (1999), "The nature of C-S-H in hardened cements", *Cement and Concrete Research* 29, 1131-1147.
- [13] Smith, R. C. and Calvert, D. G. (1975), "The Use of Sea Water in Well Cementing", *Journal of Petroleum Technology* 27, 759-764.
- [14] Šauman Z. (1964), *Silikáty*, 3, 185 (chemical abstract, vol.63, 1469a).
- [15] William, C. L. and Gary J. P. (2005), *Standard handbook of Petroleum and Gas natural engineering*, Second Edition, Linacre House, Jordan Hill, Oxford OX2 8DP, UK.
- [16] Zhang, J., Weissinger, E. A., Peethamparan, S. and Scherer, G. W. (2010), "Early hydration and setting of oil well cement", *Cement and Concrete Research* 40, 1023-1033.