

VOLUME STABILITY METALLURGICAL SLAGS METHODIC ASSESSMENT

VOLKOVÁ Anežka, BURDA Jiří, KLIMSZOVÁ Andrea, VLČEK Jozef

*VSB - Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, Institute of Industrial Ceramics, Ostrava, Czech Republic, EU, anezka.volkova@vsb.cz***Abstract**

Slag from iron and steel metallurgy can be divided into the blast furnace slag and ladle slag (ladle slag are divided into furnace slag and ladle slag). Slag is a by product of the metallurgical industry and it is the subject of several research. Slag can't be considered as waste material. Slag is a valuable resource because it has a suitable raw material composition. Most of the produced slag is currently utilized material. However a significant proportion of slag is still land filled. Currently, there are several ways of utilization blast furnace slag and steel slag. Utilization of granulated blast furnace slag is satisfactory. Blast furnace slag is used in the production of cement or concrete. Use of steel slag is difficult and its applications bring a lower value. Slag from steel furnaces is usually processed in less valuable stones. For a specific application slag is besides her origin critical chemical and phase composition, method of processing but also other factors such as its time of land filling. This article focuses causes of instability slag volume. Next article will be also paid attention blast furnace slag, ladle slag and used periklas (MgO).

Keywords: Volume stability, ladle slag, blast furnace slag, sand bath, use periklas (MgO)

1. INTRODUCTION

It is currently interested in using both blast furnace and steel slag in the building. Slag introduce alternative natural stoneware and feedstock for the preparation of the binder material in the building.

Slag is a by-product of the production of iron steel. Slag from the iron and steel metallurgy divided into blast furnace and steelmaking slag (slag furnace to differentiate - eg. convector slag from the oxygen and electric arc furnace, ladle furnace slag further - produced in the ladle during steel processing in secondary metallurgy).

Chemical and mineralogical composition of the slag is very variable because of the variety of devices in which originate variability of the manufactured product and the proportion of crystalline phase and glass depends on the cooling rate of the molten slag. Blast furnace slag is currently already found its application. Granulated blast furnace slag is added after milling Portland clinker for the manufacture of portland cements, or is added to the concrete mixture [1].

Slowly cooled blast furnace slag, known as artificial compact aggregates is also used for more demanding applications. Material use of steelmaking slag is clearly more limited. The simplest is to recycle it in the melting furnaces Metallurgical Plant. The furnace steel slag also expressed interest in the construction industry. Of slags can be prepared aggregate, wherein the limiting problem is the instability of its volume [5].

The problem with steel slag is the presence of free CaO and MgO, where in the hydration of these components are formed hydroxides portlandite $\text{Ca}(\text{OH})_2$ and brucite $\text{Mg}(\text{OH})_2$, which cause the so-called swelling. Portlandite ($\text{Ca}(\text{OH})_2$) has a lower density than calcium oxide (CaO), and therefore the reaction is manifested by an increase in volume. The source of free lime are insoluble (residual) residues rocks dosed into the furnace and lime, which precipitates during the cooling process and during conversion from C_3S to C_2S [4]. How to reliably assess the dimensional stability is the key to widespread use of steel slag [2,3].

2. PRINCIPLE TEST METHOD FOR MEASURING VOLUME STABILITY OF OXIDE SYSTEMS

Principle of the test method is the monitoring of volume changes of inorganic heterogeneous waste materials based on oxidic systems caused by reaction with water. The test monitor continuous changes in volume depending on the time action of the water sample. The test assembly (see Fig. 1) is composed of the reaction vessel, the reaction vessel lid, a water reservoir, interconnecting tubing, the temperature sensor, and the distance meter data collection system.

Test is carried out under standard laboratory conditions, ie. $(20 \pm 3) \text{ }^\circ\text{C}$. A reaction vessel (see Fig. 2) and the water tank was placed in a sand bath. System is backfilled with sand. The activities of the state system of collecting data from the temperature sensor and odometer. Read and writes the distance from the bottom of the reaction vessel odometer H_1 . The sample is placed in a stainless steel 2/3 volume of the reaction vessel, the cap height H_2 is placed on the test sample. The temperature sensor is placed in a sand bath, to sense the temperature of the sand at a height level corresponding to 1/2 the height of the sample in the reaction vessel. Read and writes the distance eyelids odometer $H_{3,0}$. On the basis of the measured distances (bottom empty reaction vessel since the measurement distance from the distance meter lids and height of the cap) according to formula (6) calculates an initial sample height h_0 .

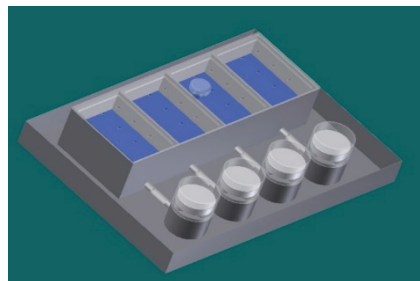
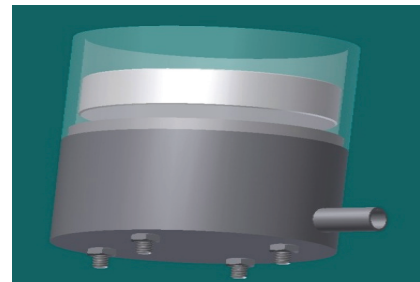
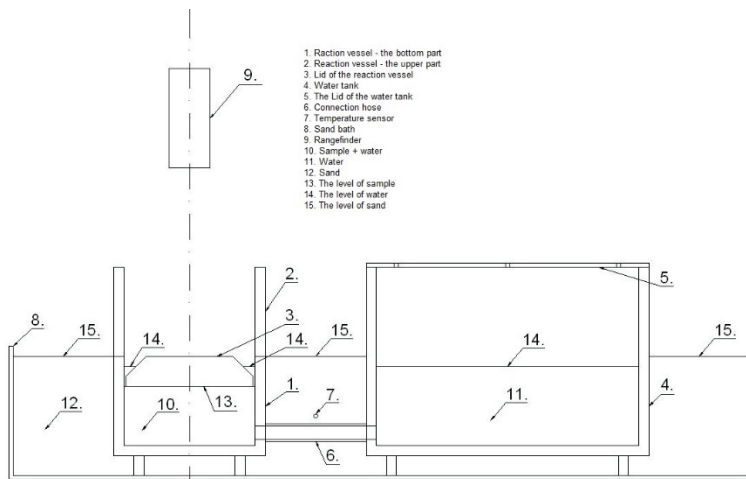


Fig. 1 Schematic test equipment (above)
Fig. 2 Model reaction vessel (top right)
Fig. 3 Model test equipment (bottom right)

Demineralized water is poured in the water tank. After pouring water creates conditions for the reactions, which may cause the volume chase of the sample and this moment is consireded the beginning of the test. Power turns immediately after pouring the water into the sand bath. The current relative volume change is calculated by equation 1 to 5. After 24 hours from the start of the test, the recorded value of the relative volume changes will continually compared with the value value recorded before before 24 pm and expressed the difference between these values.

Multiple test samples (**Fig. 3**) can simultaneously measure in a sand bath in different reaction vessels. Observed changes in volume δV for each assai is calculated according to the above relationships and the reset shall be accurate to 1 decimal point.

$$\delta V = \frac{\Delta V}{V_0} \cdot 100 \text{ (%)}$$
(1)

$$V_0 = h_0 \cdot S \text{ (mm}^3\text{)}$$
(2)

$$\Delta V = \Delta h \cdot S \text{ (mm}^3\text{)}$$
(3)

$$\Delta h = h - h_0 \quad (\text{mm}) \quad (4)$$

$$h = H_1 - H_2 - H_3 \quad (\text{mm}) \quad (5)$$

$$h_0 = H_1 - H_2 - H_{3,0} \quad (\text{mm}) \quad (6)$$

where δV is the relative change in the volume (%),
 ΔV - change volume (mm³),
 V_0 - volume sample at start of the test (mm³),
 Δh - height different (mm),
 S - inner surface of the base of the reaction vessel (mm²),
 h - current height sample (mm),
 h_0 - height of the sample at the beginning of the test (mm),
 H_1 - distance to the bottom of the empty flask of contactless distance measuring equipment (mm),
 H_2 - the height of the lid of the reaction vessel (mm),
 H_3 - current distance from the lid of the reaction vessel contactless meter distance (mm),
 $H_{3,0}$ - the distance from the lid of the reaction vessel contactless distance meter at the beginning of the test (mm).

The test reset is the average value of the final volume chase δV , which is determined from the individual determinations. Final volume chase is determined according to the formulas (1) to (5), hen introduced into equation (5) by substituting the current distance of the lid of the reaction vessel by a distance meter, which was measured at the moment of fulfillment of the condition for terminative the test. Together with the final volume change value shall be set temperature sand bath. The test also allows to evaluace changes in the volume of the sample depending on time [6].

3. DETERMINATION OF CHANGES IN VOLUME OF WASTE SYSTEMS BASED OXIDE EXPOSURE TO WATER

To determine volume changes of selected two of ladle slag (designated as sample 1 - **Fig. 4**, the second ladle slag is designated as sample 4 - **Fig. 5**), steel slag gradually cooling designated as sample 3 and the last sample, which exhibited a large volumetric changes was used dolomite building material designated as sample 2 - **Fig. 7** (see **Table 1**).



Fig. 4 Sample 1

Fig. 5 Sample

Fig. 6 Experimental equipment

Fig. 7 Sample 2

Fig. 6 shows an experimental apparatus for measuring volume changes. The sand bath ST 82 is positioned for a demineralized water reservoir along with the associated sample beakers with lids and nylon. Reservoirs are separated by partitions, it is possible in each beaker to maintain water level separately according to the current volume of the sample. The water level in the reservoirs is gradually refills due to evaporation. The height is measured lids total of 4 laser sensors distance. For measuring sample temperature, water and sand baths are used sheathed thermocouple type K outputs from all the sensors are measured and recorded using data loggers into a laptop computer.

Fig. 6 Experimental equipment **Fig. 7** Sample 4.

In addition to the measured volume changes observed samples, was performed X-ray diffraction analysis on the powder X-ray diffractometer Bruker D8 Advance in the laboratory of the Centre for Nanotechnology Technical University of Ostrava. Dentistry was measured before and after the measurement of volume stability. The dentistry was measured with the Pycnomatic & Pycnomatic, workplace IET Technical University of Ostrava. Further, the weight changes were calculated always before and after measuring the volume stability.

Table 1 Description of the samples used

Component/Sample	1	2	3	4
	hm. %			
Fe _{celk}	12.3	0.7	3.69	12.4
S	0.22	-	0.19	0.24
SiO ₂	18.9	0.8	11.67	19.6
CaO	45.1	59	49.3	45.3
MgO	4.1	39	9.79	4.0
Al ₂ O ₃	7.2	-	18.37	7.4
FeO	-	-	2.7	-
Fe ₂ O ₃	-	-	2.27	-
MnO	1.7	-	5.47	1.8
K ₂ O	0.03	-	0.02	0.03
TiO ₂	0.42	-	0.33	0.46
Cr ₂ O ₃	0.45	-	0.06	0.48
P ₂ O ₅	0.44	-	0.09	0.43
V ₂ O ₅	-	-	0.51	-

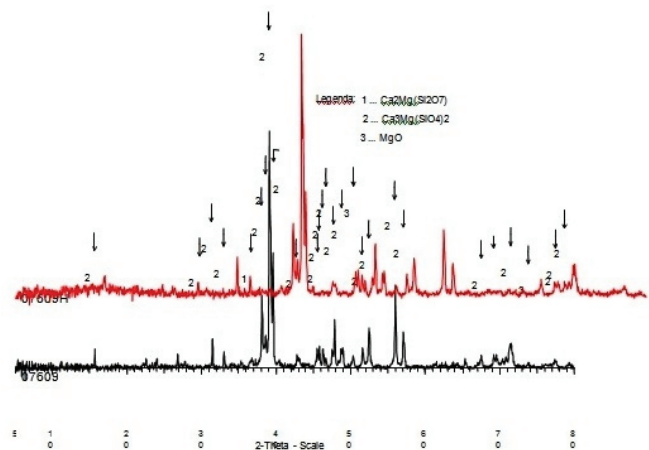


Fig. 8 The diffraction pattern of sample 1

4. RESULTS AND FORUMS

For the processed samples were measured X-ray diffraction. Sample 1 contained akermanite phase, merwinite and periklase. After the test volume stability phase composition did not change significantly. In sample 2, the main phases of CaO and MgO. After hydration can observe the presence of portlandite (Ca(OH)₂), brucite (Mg(OH)₂). Given the present components is following the course of the experiment visible surge portlandite causing the displacement of instability. In sample 3, the main phases of β-C₂S, periklase (MgO), CaO, SiO₂, portlandite (Ca(OH)₂) and brucite (Mg(OH)₂). Sample 3 contained a proportion of CaO and MgO

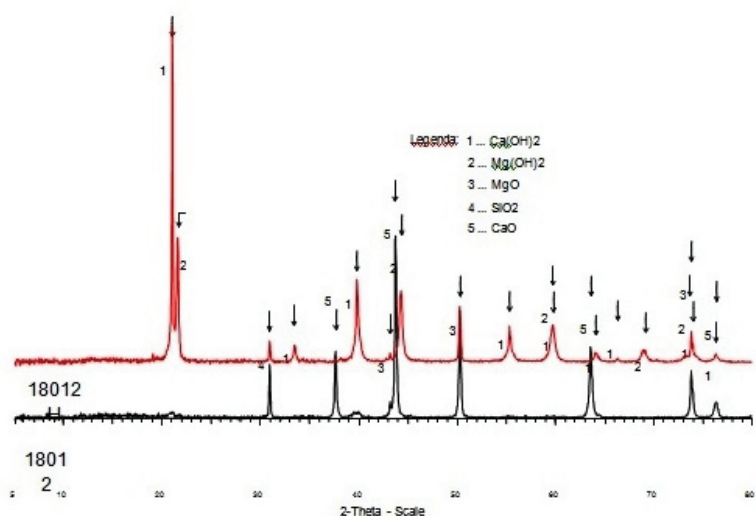


Fig. 9 The diffraction pattern of sample 2

and β -C₂S phases, of SiO₂. After hydration the recorded phase formation portlandite and brucite. Sample 4 contained C₂S phases, phase content mixed oxides of CaO, SiO₂ and FeO, Al₂O₃ to MgO. Hydration of the phase composition of the sample significantly not changed. In **Figs. 8 and 9**, the diffraction pattern of Sample 1 and 2.

By comparing the densities of the samples before and after the measurement of volume stability are shown in **Table 2**. The sample 1 and sample 4 has a density before and after the measurement volume stability is very similar. Samples 2 and 3 show a higher density change. The intensity changes in density correlates with a change volume **Table 3**.

Table 2 Comparison of density of the samples before and after the measurement of volume stability ing.cm^{-3}

Sample	Dentisty (g.cm^{-3})		$\Delta\rho$ (%)
	before	after	
1	3.31	3.29	-0.6
2	2.87	2.38	-17.1
3	3.22	3.04	-5.59
4	3.42	3.38	-1.16

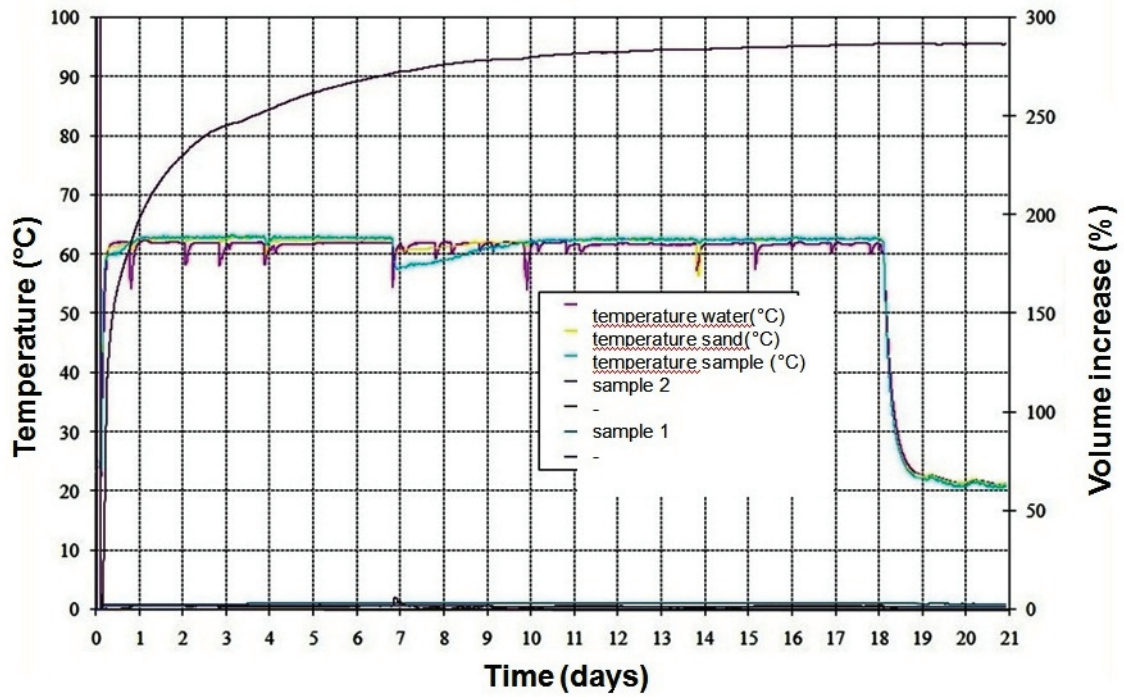
Weight and volume changes are calculated in **Table 3**. The mass change (samples are weighed after drying) is highest for Sample 2, and 29 % (29.1 grams - which is due to the effect of hydration of CaO and MgO, from which arose Portlandit and brucite which caused the. swelling). Volume change of the sample reached 300%. Another significant change in volume - 41 % was observed in the sample 3. Samples 1 and 4 show a lackluster volume increases - 3 respectively. 6 %. Volume changes observed samples are caused mainly by hydration of CaO and MgO present. The contents of these components was observed mainly in sample 2 and 3. The volume changes correspond to changes in density.

Table 3 Weight and volume change (in %) of all samples

Sample	m sample before measurement (g)	m sample after measurement (g)	weight change (g)	weight change (%)	volume stability (%)
1	149.3	149.5	0.2	0.1	3.0
2	100.2	129.3	29.1	29.0	286.0
3	140.0	147.8	7.8	5.6	40.8
4	150.4	154.4	4.0	2.6	6.0

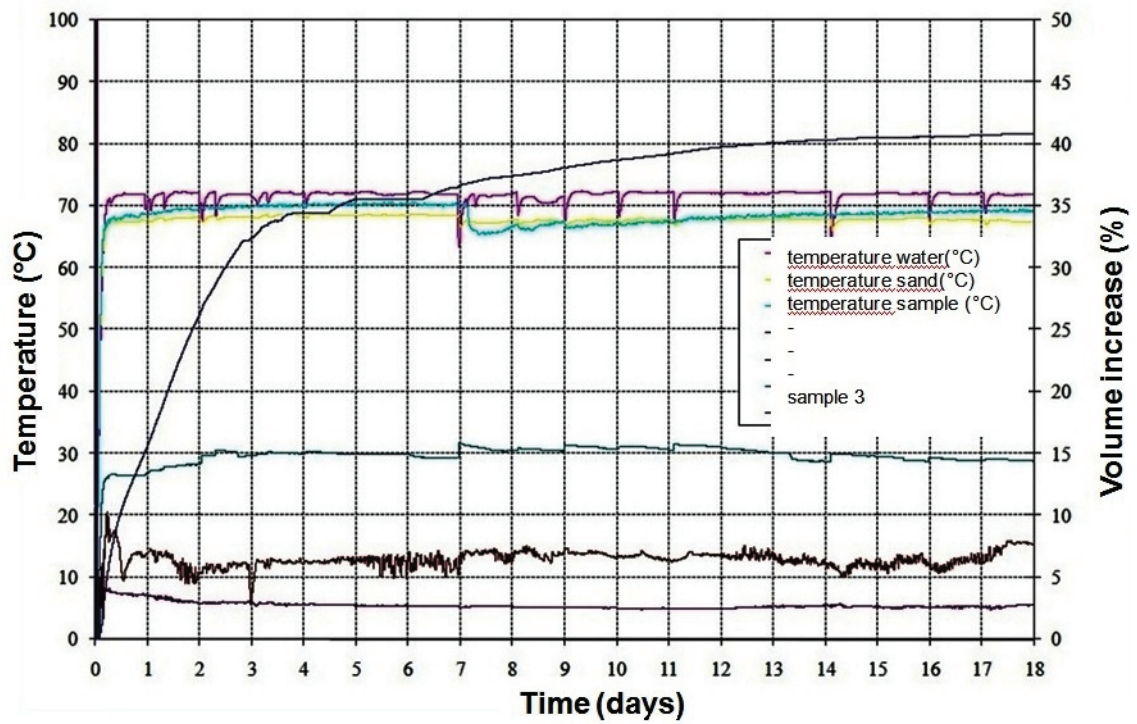
Graph (**Fig. 10**) excluding changes volume records the temperature stability of water, sand and sample. These values excluding the volume stability of the samples are almost constant over time. The peaks indicating decrease in temperature, owing to the addition of demineralized water into the reservoir. Regarding the measurement time, all series of experiments lasted about three weeks.

Volume increase

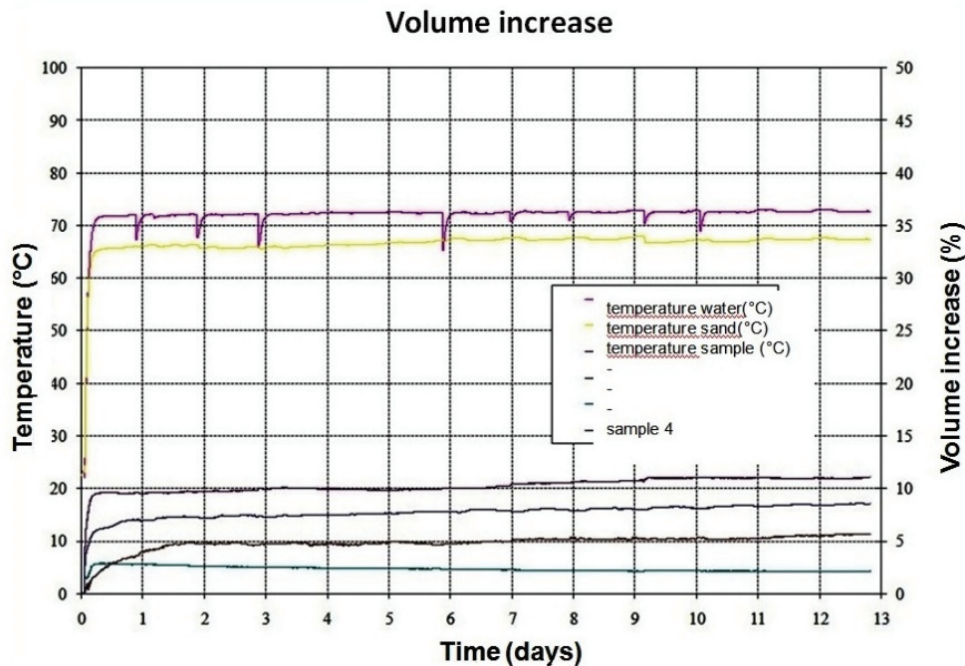


a)

Volume increase



b)



c)

Fig. 10 The graph of volume changes of the a) sample 1 (07609), 2 (18012), b) 3 (18412) and c) 4 (19812)

5. CONCLUSION

The aim of this article was to determine the dimensional stability of metallurgical slags water effect. We compared various types of ladle slag and dolomite refractory construction materials. To monitor the stability of the volume used a newly designed methodology, which is in the Czech Republic for this purpose certified. Most of the increase in volume occurred in periklase of construction materials up to about 300 %. Furthermore, it was slag volume increases 41 %. In both cases, the cause volumetric changes phase hydration of CaO and MgO to be in these materials occurred. The slags which these phases did not include volume change is reflected in the amount of 3 resp. 6 %.

ACKNOWLEDGEMENTS

This paper was created in the Project No. SP2015/86 "Reduction of the energy demands of the material production processes and project No. SP 2015/70 Specific research in the metallurgical, materials and process engineering.

REFERENCES

- [1] VLČEK, J., TOMKOVÁ, V., OVČAČÍKOVÁ, H., VOLKOVÁ, A., et al.: *Slags from production pig iron and steel making and possibilities of their processing*. In 21st International Conference on Metallurgy and Materials, METAL 2012, 23.-25.5.2012, Brno, pp. 37-42. ISBN 978-80-87294-29-1.
- [2] MONTGOMERY, D. G., WANG, G.: *Cement and Concrete Research*. 1992, 22 (5), pp. 755.
- [3] HAN, Y. M., JUNG, H. Y., SEONG, S. K.: *Geosystem Engineering*. 2002, 5 (2), pp. 38.
- [4] KRESTA, F.: *Druhotné suroviny v dopravním stavitelství*. Vysoká škola báňská - Technická univerzita Ostrava, Ostrava, 2012, 144 s. ISBN 978-80-248-2890-9.
- [5] VLČEK, J., TOMKOVÁ, V., OVČAČÍKOVÁ, H., OVČAČÍK, F., et al.: *Slags from iron and steel production: properties and their utilization*. *Metalurgija* 52 (2013) 3, pp. 329-333, ISBN 0543-5846.
- [6] VLČEK, J., BURDA, J.: *Stanovení objemových změn odpadních látek na bázi oxidických systémů působením vody*. Certifikát ověřené metodiky. Ostrava: VSB-TU Ostrava. Vydal: VÝZKUMNÝ ÚSTAV POZEMNÍCH STAVEB - CERTIFIKAČNÍ SPOLEČNOST. 2014.