

## KINETICS OF GAS EMISSION FROM ALUMINOSILICATES USED AS A RELAXING ADDITIVE FOR MOULDING AND CORE SANDS

Received – Priljeno: 2020-12-17  
Accepted – Prihvačeno: 2021-03-10  
Original Scientific Paper – Izvorni znanstveni rad

The article presents the results of gas emissions generated during heating of mineral additives – aluminosilicates (perlite ore and vermiculite). The test on a laboratory stand for a 1 g sample at 1 000 °C was carried out. It has been shown, that there is a correlation between the degree of fragmentation and the amount of gas generated. The finest fraction of perlite ore caused a similar quantitative gas emission as ground vermiculite. The presence of additives in molding sands, regardless of the size of fraction, should not affect the formation of casting defects. The addition of perlite ore and vermiculite does not effect the ecological properties of moulding sand.

*Keywords:* perlite ore, vermiculite, heating, gas, emission

### INTRODUCTION

An unquestionable advantage of moulding and core sands with inorganic binders used in the casting of metal alloys is the small amount of harmful products of thermal decomposition formed during the pouring of liquid metal [1]. Moulding sands with inorganic binders can be hardened through a chemical reaction by introducing a hardener or by using a physical agent (e.g. temperature, microwave). Regardless of the curing agent, the sands are characterised by a strength increase under the influence of a temperature of about 800 °C, which results in difficulties in knocking out and poor suitability to mechanical regeneration. These inconveniences can be considered the most important disadvantages of moulding sands with inorganic binders. For many years, research has been conducted on the elimination or reduction of poor knock-out properties of such sands. Apart from modifying the structure of inorganic binders [2, 3] or using other types of hardeners [4], one of the directions of research is the introduction of various types of additives to moulding and core sands [5, 6].

Perlite ore is a transformed extrusive rock made of volcanic glass, and its structure contains 2,0 - 5,0 % by volume of water. From a chemical point of view, it is a metastable, amorphous, hydrated potassium sodium aluminium silicate. Due to its chemical nature (pH of about 7), it is classified in the group of inert materials. The density of perlite ore is from 2,23 to 2,40 Mg/m<sup>3</sup>, whereas its apparent density is about 1,30 Mg/m<sup>3</sup>. Water in perlite ore is stored in various forms. Most of the water exists as

OH groups, single hydroxyl groups, or as hydroxyl pairs. The amount of water accumulated on the outer surface of the perlite and in its inner spaces depends on their size and shape. The polarity of the surface is also a decisive factor. If the internal spaces in the perlite ore are large enough, water molecules can join the OH groups present on the surface by means of hydrogen bonding forces. However, this connection is quite weak and the water present in this form is removed at temperatures up to 150 °C. A certain amount of water is removed from the perlite ore only during the thermal decomposition of the structure, i.e. at temperatures above 800 °C. A characteristic physicochemical feature of perlite is its ability to swell when heated quickly to temperatures above 850 - 870 °C. A violent dehydroxylation reaction of the water bound in the structure of the perlite ore then takes place. The water vapourises and the perlite structure changes irreversibly. Compared to raw perlite ore, the expanded form is characterised by a 10 - 40-fold increased volume, a density in the range 0,05 - 0,15 Mg/m<sup>3</sup>, vapour permeability, chemical and thermal inertness, and resistance to moisture, algae and fungi [7-11].

Vermiculite (Mg,Fe,Al)<sub>3</sub>(Al,Si)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O belongs to the group of clay minerals known as smectites. Smectites are the second group, after mica, of 2:1 type packet phyllosilicates, where the octahedron layer is closed between two tetrahedron layers with their peaks facing each other. Sites in the octahedral layers are occupied by Mg<sup>2+</sup> ions. Therefore, the content of magnesium in these minerals is definitely higher, and the content of aluminium lower, than in the case of montmorillonite. The individual layers are electrically neutral, the inter-layer cations occupy about a third of the volume and can be exchanged (similar to montmorillonite) [12-18]. Ver-

A. Bobrowski (e-mail: arturb@agh.edu.pl). D. Drożyński, K. Kaczmarek, B. Grabowska, S. Cukrowicz, AGH University of Science and Technology, Krakow, Poland

miculite contains both OH groups, i.e. structural water, but also H<sub>2</sub>O molecules adsorbed on the surface of the crystallites and in the inter-packet spaces, i.e. adsorbed water. The phyllosilicate hydration process does not change the basic structure of the 2:1 type packages from which they are built. In turn, the dehydroxylation reaction of 2:1 type dioctahedral phyllosilicates occurring at high temperature results in the reorganisation of the octahedral layer. As a result of heating, the inter-packet water is converted into water vapour, which results in a 15 - 30-fold increase in volume, a process called exfoliation. This consists in separating the grains into thin lamellae, which results in an increase in volume and a reduction in density [18-23].

Perlite ore is in the form of material with various grain sizes, while vermiculite is in the form of lamellae that must be ground into a powder. The aim of this study was to show the effect of the grain size (grain size) of the perlite ore on the amount of gases (water vapour) produced during rapid heating. The article presents the results of gas emission tests for 3 fractions of perlite ore and ground vermiculite. The amount of gases generated under the influence of high temperature of the liquid metal is important due to the possibility of casting defects, such as blisters, punctures or porosity. Apart from the binder, a factor that may cause defects on the surface of the castings is the type and quality of the protective coating used [24, 25].

## METHOD AND WORK TECHNOLOGY

The vermiculite grinding process was carried out in a laboratory ball mill. Gas generation tests were carried out on a stand designed and built at the Faculty of Foundry Engineering, AGH, which includes a furnace with a quartz reaction tube, a peristaltic pump, and a PLC recorder. The tests were carried out for 3 types of perlite ore (PO) from Slovak deposits with various grain sizes and for crushed (ground) vermiculite (V). A 1 g samples were weighed in a ceramic boat and placed in a quartz reaction tube of the furnace heated to 1 000 °C. Recordings were performed at time intervals of 2 seconds until a stabilised measurement result was achieved. Three measurements were made for each test sample. Gas generation tests were preceded by a sieve analysis.

## RESULTS AND THEIR DISCUSSION

Table 1 shows the results of the sieve analysis for the tested mineral additives.

Table 2 presents the characteristic parameters of the tested materials obtained on the basis of the sieve analysis.

The results of the sieve analysis presented in Table 2 show that the PO-3 perlite ore sample had the highest mean grain size. Moreover, this sample had the highest degree of homogeneity, the smallest specific surface area (2,93 m<sup>2</sup>/kg), and 99,34 % of the main fraction was collected on three adjacent sieves. Among the ex-

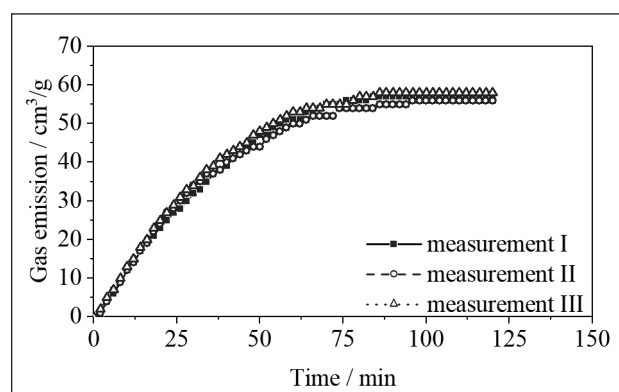


Figure 1 Gas emission from the perlite ore (PO-1)

Table 1 Sieve analysis of perlite ore and vermiculite

| Sieve number | Recalculated screenings |        |        |        |
|--------------|-------------------------|--------|--------|--------|
|              | PO-1                    | PO-2   | PO-3   | V      |
| 1,600        | 0,00                    | 0,00   | 0,00   | 0,00   |
| 0,800        | 0,03                    | 0,01   | 35,81  | 0,00   |
| 0,630        | 0,07                    | 0,09   | 56,91  | 0,00   |
| 0,400        | 0,06                    | 53,78  | 6,62   | 0,06   |
| 0,320        | 0,47                    | 27,56  | 0,14   | 0,13   |
| 0,200        | 3,76                    | 9,98   | 0,12   | 3,36   |
| 0,160        | 1,94                    | 3,56   | 0,08   | 9,83   |
| 0,100        | 38,84                   | 3,71   | 0,06   | 22,54  |
| 0,071        | 37,54                   | 0,69   | 0,08   | 13,34  |
| 0,056        | 1,06                    | 0,05   | 0,03   | 3,66   |
| Bottom       | 16,23                   | 0,57   | 0,15   | 47,08  |
| Sum          | 100,00                  | 100,00 | 100,00 | 100,00 |

Table 2 The characteristic parameters of the tested materials

| Parameter                           | PO-1   | PO-2  | PO-3  | V      |
|-------------------------------------|--------|-------|-------|--------|
| Graininess number AFS               | 150,52 | 41,36 | 16,52 | 199,91 |
| Average grain size / mm             | 0,08   | 0,31  | 0,77  | 0,06   |
| Geometric mean / mm                 | 0,09   | 0,39  | 0,83  | 0,07   |
| Arithmetic mean / mm                | 0,11   | 0,41  | 0,87  | 0,09   |
| Harmonic mean / mm                  | 0,08   | 0,34  | 0,77  | 0,06   |
| Median / mm                         | 0,10   | 0,42  | 0,73  | 0,07   |
| Main fraction / %                   | 92,61  | 91,32 | 99,34 | 82,96  |
| Distribution factor                 | 1,27   | 1,20  | 1,15  | 1,93   |
| Inclination indicator               | 1,04   | 0,99  | 1,22  | 0,98   |
| Homogeneity degree / %              | 61,00  | 74,00 | 76,00 | 21,00  |
| Proper surface / m <sup>2</sup> /kg | 27,36  | 6,60  | 2,93  | 38,35  |

amined samples of perlite ore, the PO-1 sample, which is also characterised by the lowest degree of homogeneity but the highest number of granularity (L = 150,52), had the highest specific surface area resulting from the highest degree of grinding. A sample of ground vermiculite had the largest specific surface resulting from the greatest grinding, as evidenced by the highest number of grains. In turn, this sample had the lowest degree of homogeneity, with the main fraction accounting for 82,96 % of the total.

Figures 1 - 5 show the results of gas activity determination for samples of perlite (PO) ore and vermiculite (V) conducted at a temperature of 1 000 °C.

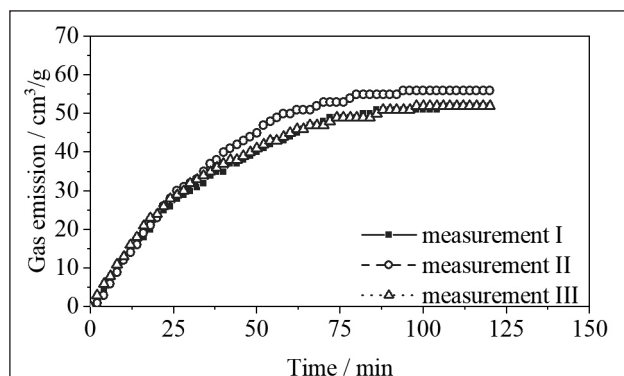


Figure 2 Gas emission from the perlite ore (PO-2)

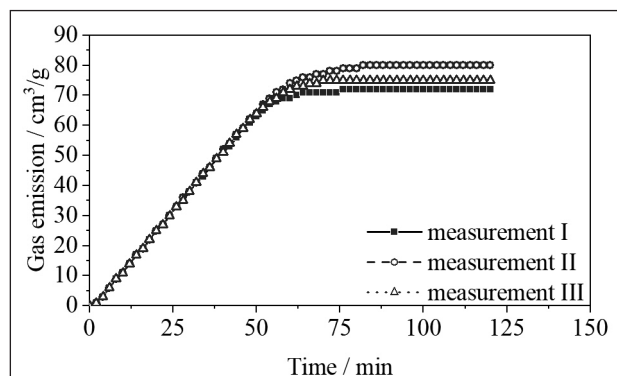


Figure 4 Gas emission from the vermiculite (V)

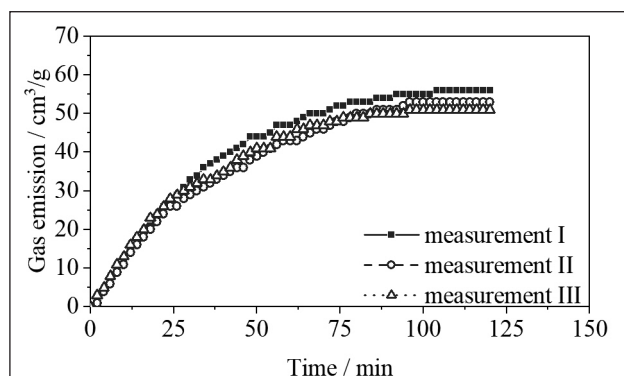


Figure 3 Gas emission from the perlite ore (PO-3)

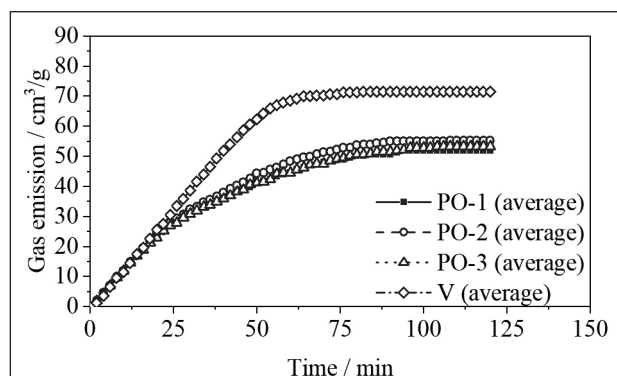


Figure 5 Summary of gas emission test results for all tested samples (average of three measurements)

From the results of gas production studies presented in Figures 1 - 5, it can be concluded that the degree of grinding of the perlite ore does not significantly affect the amount of gases (water vapour) generated during its heating. It should be noted that the largest portion of gas (though only slightly) was released from the PO-2 sample. The highest gas formation was observed for the ground vermiculite sample. A sample of the same mass (1 g) produced an average of about 20 cm<sup>3</sup> more gas than perlite ore, which equates to 33 % higher gas emissions.

The higher gas formation of vermiculite indicates a greater amount of water accumulated in the material structure. Thus, when pouring the moulds with the liquid casting alloy at a temperature above 1 000 °C, more energy is released due to the rapidly occurring dehydroxylation reaction combined with a significant increase in volume. Thus, vermiculite has a more favourable effect on the reduction of the final strength of moulding sands with inorganic binders and on improving their knock-out properties. This makes it possible to use a smaller amount of the additive in order to obtain the desired effects. Vermiculite is introduced into moulding and core sands in the form of a powder, and therefore may have a negative effect on the ability of the mould to evacuate gases (permeability) and grindability. Therefore, it should be dosed to the moulding and core sands in an appropriate amount. It should be particularly emphasized that the introduction of mineral (inorganic) additives does not result in a deterioration of the ecological properties of the sand.

## CONCLUSIONS

The degree of grinding of the perlite ore does not significantly affect the amount of gases (water vapour) generated during its heating.

The vermiculite sample of the same mass (1 g) produced an average of about 20 cm<sup>3</sup> more gas than perlite ore, which equates to 33 % higher gas emissions.

The vermiculite has a more favourable effect on the reduction of the final strength of moulding sands with inorganic binders and on improving their knock-out properties.

The vermiculite should be dosed to the moulding and core sands in an appropriate amount - possible reduction of permeability and grindability.

It should be particularly emphasized that the introduction of mineral (inorganic) additives does not result in a deterioration of the ecological properties of the moulding and core sands.

## Acknowledgements

The study was performed within the EU Project PROM NAWA, POWR.03.03.00-IP.08-00-P13/18.

## REFERENCES

- [1] A. Bobrowski, M. Holtzer, S. Żymankowska – Kumon, R. Dańko, Harmfulness assessment of moulding sands with a geopolymer binder and a new hardener, in an aspect of the

- emission of substances from the btex group, *Archives of Metallurgy and Materials*, 40 (2015) 1, 341-344. DOI: 10.1515/amm-2015-0056.
- [2] A. Bobrowski, B. Stypuła, B. Hutera, A. Kmita, D. Drożyński, M. Starowicz, FTIR spectroscopy of water glass - the binder moulding modified by ZnO nanoparticles, *Metalurgija* 51 (2012) 4, 477-480.
- [3] A. Bobrowski, A. Kmita, M. Starowicz, B. Stypuła, B. Hutera, Effect of magnesium oxide nanoparticles on water glass structure, *Archives of Foundry Engineering*, 12 (2012) 3, 9-12. DOI: 10.2478/v10266-012-0073-2.
- [4] St. M. Dobosz, K. Major-Gabryś, Self-hardening moulding sands with water glass and new ester hardener. *Material Engineering*, 27 (2006) 3, 576-579 (in Polish).
- [5] Z. Chun-Xi, Recent advances in waterglass sand technologies, *China Foundry* 4 (2007) 1, 013-017.
- [6] J. Wang, Z. Fan, H. Wang, X. Dong, N. Huang, An improved sodium silicate binder modified by ultra-fine powder materials, *China Foundry* 4 (2007) 1, 026-030.
- [7] M. Samar, S. Saxena, Study of chemical and physical properties of perlite and its application in India, *International Journal of Science Technology and Management* 5 (2016) 4, 70-80.
- [8] M. Földvári, Handbook of thermogravimetric system of minerals and its use in geological practice, Geological Institute of Hungary, Budapest, 2011, pp. 37-38.
- [9] A. Bolewski, M. Budkiewicz, P. Wyszomirski, Ceramic raw materials, Geological Publishers, Warszawa, 1991, pp. 18-20 (in Polish).
- [10] W. Pichór, A. Janiec, Thermal stability of expanded perlite modified by mullite, *Ceramics International* 35 (2009), 527-530, DOI:10.1016/j.ceramint.2007.10.008.
- [11] A. Burkowicz, Expanded perlite - a little known thermal insulation material in Poland, *Scientific Journals of the Institute of Mineral and Energy Economy of the Polish Academy of Sciences*, 96 (2016), 7-22.
- [12] A. Campos, S. Moreno, R. Molina, Characterization of vermiculite by XRD and spectroscopic techniques, *Earth Science Research Journal* 13 (2009) 2, 108-118.
- [13] L. Chmielarz, Adsorbents and catalysts: selected technologies and the environment, Rzeszów, 2012, pp. 7-29 (in Polish).
- [14] M. Handke, Crystallochemistry of silicates, University Scientific and Technical Publishers AGH UST, Kraków, 2008, pp. 186-190 (in Polish).
- [15] S. Hillier, E.M.M. Marwa, C.M. Rice, On the mechanism of exfoliation of vermiculite, *Clay Minerals*, 48 (2013), 563-582. DOI: 10.1180/claymin.2013.048.4.01.
- [16] S. Rebilasová, P. Peikertová, K. Gröplová, L. Neuwirthová, Proceedings, NanoCon 2011, Brno, Czech Republic, 2011.
- [17] M. Holtzer, A. Bobrowski, B. Grabowska, Montmorillonite: a comparison of methods for its determination in foundry bentonites, *Metalurgija*, 50 (2011) 2, 119-122.
- [18] A. Derkowski, V.A. Drits, D.K. McCarty, Nature of rehydroxylation in dioctahedral 2:1 layer clay minerals, *American Mineralogist* 97 (2012), 610-629. DOI: <https://doi.org/10.2138/am.2012.3871>.
- [19] A. Derkowski, V.A. Drits, D.K. McCarty, Rehydration in a dehydrated-dehydroxylated smectite in environment of low water vapor content, *American Mineralogist* 97 (2012), 110-127. DOI: 10.2138/am.2012.3872.
- [20] V.A. Drits, A. Derkowski, D.K. McCarty, Kinetics of partial dehydroxylation in dioctahedral 2:1 layer clay minerals, *American Mineralogist* 97 (2012), 930-950. DOI: <https://doi.org/10.2138/am.2012.3971>.
- [21] S.A. Suvorov, V.V. Skurikhin, Vermiculite - a promising material for high - temperature heat insulators, *Refractories and Industrial Ceramics* 44 (2003) 3, 186-187. DOI: <https://doi.org/10.1023/A:1026312619843>.
- [22] X. Huo, L. Wu, L. Liao, Z. Xia, L. Wang, The effect of interlayer cations on the expansion of vermiculite, *Powder Technology* 224 (2012), 241-246. DOI: 10.1016/j.powtec.2012.02.059.
- [23] C. Marcos, I. Rodríguez, Expansibility of vermiculites irradiated with microwaves, *Applied Clay Science* 51 (2011), 33-37. <https://doi.org/10.1016/j.clay.2010.10.019>.
- [24] M. Holtzer, A. Bobrowski, D. Drożyński, J. Mocek, Investigations of protective coatings for castings of high-manganese cast steels, *Archives of Foundry Engineering*, 13 (2013) 1, 39-44, DOI: 10.2478/AFE-2013-0008.
- [25] J. Zych, Analysis of castings defects, AGH University Scientific and Didactic Publishing House, Kraków, 2001 (in Polish).

**Note:** The responsible translator for English language: "ANGOS" Translation Office, Krakow, Poland.