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Gas Evolution of GEOPOL® W Sand Mixture and Comparison with Organic Binders

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Abstract

The article deals with the gas development of the geopolymer binder system hardened by heat and provides the comparison with organic binder systems. The GEOPOL® W technology is completely inorganic binder system, based on water. This fact allow that the gas generated during pouring is based on water vapour only. No dangerous emissions, fumes or unpleasant odours are developed. The calculated amount of water vapour generated from GEOPOL® W sand mixture is 1.9 cm^3/g. The measured volume of gas for GEOPOL® W is 4.3 cm^3/g. The measurement of gas evolution proves that the inorganic binder system GEOPOL® W generates very low volume of gas (water vapour) in comparison with PUR cold box amine and Croning. The amount of gas is several times lower than PUR cold box amine (3.7x) and Croning (4.2x). The experiment results are consistent with the literature sources. The difference between the calculated and the measured gas volume is justified by the reverse moisture absorption from the air after dehydration during storing and preparing the sand samples. Minimal generated volumes of gas/water vapour brings, mainly as was stated no dangerous emissions, also the following advantages: minimal risk of bubble defects creation, the good castings without defects, reduced costs for exhaust air treatment, no condensates on dies, reduced costs for cleaning.

Keywords: Geopolymer binder; GEOPOL®, Gas evolution, Core, Environment

1. Introduction

The geopolymers were discovered and terminology was introduced by Davidovits in the seventies of the last century [1]. Earlier in 1957 Gluchovskij investigated the problem of alkali-activated slag binders, he called the technology "soil silicate concretes" and the binders "soil cements" [2]. These are materials that belong to alkaline aluminosilicates, so they are purely inorganic materials. The geopolymers contain silicon, aluminium and some alkaline element, such as sodium or potassium. In nature, such materials appear and are called zeolites. The geopolymers are not formed due to geological processes, they are artificially prepared and they are called so because their composition approaches natural rocks. The geopolymers consist of tetrahedron chains of SiO_4 and AlO_4 Fig. 1 [1] [3][4].

The ratio of the proportion of aluminium and silicon ranges from 1:1 to 1:35 (various ratios SiO_4 and AlO_4 tetrahedrons). According to the aluminium content varies the chemical and the physical properties of the resultant polymer, as well as its applications, vary with the content of aluminium. The usage of geopolymers is extensive. The resulting product has many advantages in comparison with the conventional materials.

Geopolymers are, for example, also used in the solidification of hazardous waste, ceramics, and the refractory materials industry. Generally speaking, the main properties of the geopolymers for which they are used, are fire resistance, high heat resistance, and low thermal expansion [1] [3][4].

The geopolymers with a high molar ratio of SiO_2/Al_2O_3, sometimes called geopolymer resins, are liquid substances with similar properties to colloidal solutions of alkali silicates – water glass. One of the possibilities of using geopolymer resins is the usage as a foundry binder. Either elevated temperatures or chemical hardening is used for hardening [3][5].

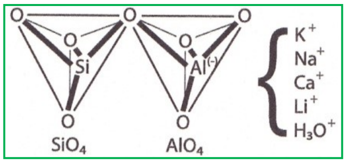

Fig. 1. The basic structural unit of geopolymers [1]

1.1. Geopolymers for foundry industry

The GEOPOL® technology is currently used in the foundries for three basic production processes/technologies: (1) for self-hardening moulding mixtures, (2) sand mixtures hardened by gaseous carbon dioxide and (3) the hot box technology with hot air hardening [3].

More and more emphasis is put on the clean and environment-friendly operations. Many foundries are exposed to a great pressure. This leads to the introduction of new technologies, most often based on inorganic chemistry, which are more acceptable in terms of the environment and sustainable development. The geopolymer binder systems and GEOPOL® technology are undoubtedly among these new technologies. A new environmentally friendly binder system GEOPOL® has been developed using a geopolymeric inorganic binder for the production of conventional moulds and cores in the Czech Republic [3].

The binder is an inorganic geopolymer precursor with a low degree of polymerization. The hardening occurs by the action of heat or hardeners. There is an increase in the degree of polymerization and formation of an inorganic polymer during the hardening reaction. Model of inorganic polymer was described by Davidovits [1] and updated by Barbosa [6] and later by Rowles [7], see Fig. 2.

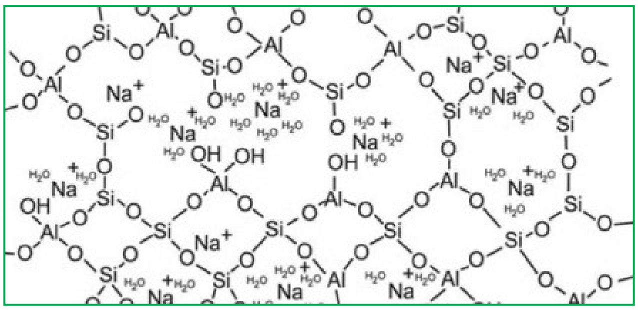
Fig. 2. Scheme and model of inorganic polymer by Davidovits [1] and updated by Barbosa [6] and later by Rowles (bottom) [7]

The GEOPOL® is odourless technology and generates no pollutants, so it has a minimal negative impact on the environment. Due to the chemical nature of the geopolymer binder, the mechanical reclaimability of used sand mixture is feasible [3][8].

The emissions are one of the fundamental environmental troubles of foundries. Foundries have to take into account an increasing cost related to solving these environmental problems. They are increasingly interested in technologies with more favourable environmental characteristics and are trying to introduce them into operation. The environmental pressure is even greater in economically developed countries. There is also increased interest in the development of new technologies and their implementation [3].

In general, it is expected that the inorganic binder systems achieve significant reductions in emissions. The comparison of the binder systems from the point of view of the BTEX and the PAH shows in graphs in Fig. 3 [9].

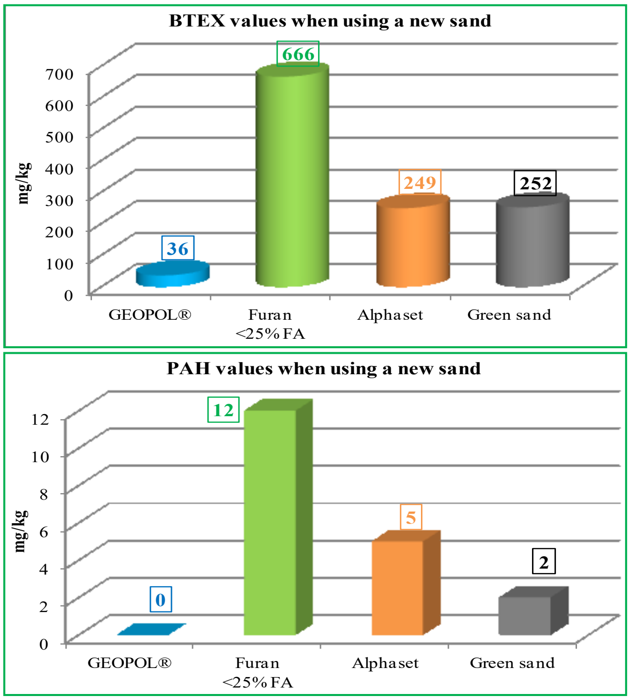

Fig. 3. Results of pollutant measurement during pouring, comparison of organic and inorganic binder systems [9]

1.2. Hot box and hot air hardening process

GEOPOL® W binders are used for the production of cores, that are hardened by heat. In this technology, the hardening is caused by dehydration, so it means by a physical process. The technology is suitable for serial and mass core production. The whole technology is purely inorganic; thus, it has a minimal impact on the environment and ensures favourable hygienic conditions [8].

The principle of this technology is as such: the sand mixture is shot into a heated core box and the hardening of the sand mixture in the hot core box is speeded up by blowing the hot air through it at the same time. Suitable temperatures of the core and the hot air range from 100 to 200 °C. The temperatures from 150 to 200 °C allow to obtain a long storage time and prevent the reverse cores hydration. Dehydration can also be achieved by microwave hardening [8].

It is recommended to use the GEOTEK powder additive, which has a beneficial effect on the reduced wettability of the cores and the increases cold and hot strength of the cores [10][11].

When compared with PUR cold box amine technology, the comparable (higher) strengths are achieved at the same or shorter hardening time and the collapsibility of the cores after pouring is significantly better. Core strengths and other properties depend on the addition level of the sand mixture and on the parameters of the production processes. Flexural strength after hardening and cooling reaches up to 5.5 MPa [10][11].

The composition of the sand mixture for core production made by the GEOPOL® W technology [10]:

- Sand. Generally quartz sand.
- GEOPOL® W binder, addition level ranging from 1.4 to 1.8%, based on sand quantity (quartz sand).
- Accelerator GEOTEK W, addition level ranging from 0.3 to 0.9%, based on sand weight, generally 50% of binder weight.

The addition of 1.8% of binder and 0.9% of accelerator ensures optimum strengths, which was verified/confirmed by the production process [10].

Very good results are achieved in the production of aluminium and non-ferrous alloy castings. We are currently working on the development of binder system for castings made of steel and cast iron [10].

The GEOPOL® W binder system is suitable for most quartz and non-quarts sands such as CERABEADS, olivine sand, chromite sand, aluminosilicate sands. The addition levels are in Table 1.

Table 1.
Addition level of binder GEOPOL® for technology GEOPOL® W hardened by heat on different foundry sands [10].

GEOPOL® W technology hardened by heat	
Foundry sand	**Addition levels** [wt. % on sand weight]
Quartz sand	1.4 – 1.8
CERABEADS	1.8 – 2.5
Addition levels of additive GEOTEK are from 0.3 to 0.9% based on sand.	

1.3. Gas evolution

The literary sources [12][13][14][15][16][17] state that inorganic binder systems hardened by heat significantly reduces gas evolution during pouring.

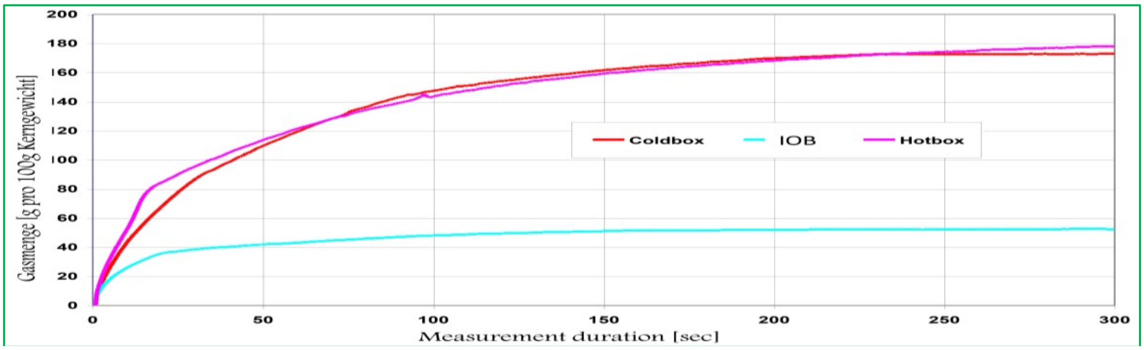

Fig. 4. The gas evolution of inorganic binder (IOB, AWB) in comparison with PUR cold box amin and Hot box processes [13][14]

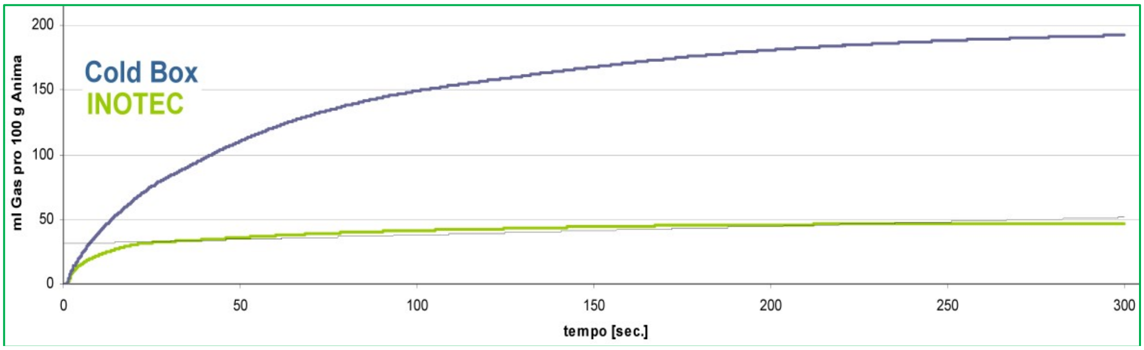

Fig. 5. The gas evolution of inorganic binder INOTEC in comparison with PUR cold box amine process [12]

The Fig. 4 states the IOB (AWB) inorganic binder system and PUR cold box amin and Hotbox in comparison (COGAS® test). The differences between IOB and organic binders are significant, IOB has more than three times lower gas developed. Almost the same course of gas evolution has the INOTEC process, almost four times lower volume of gas in comparison with PUR cold box amine. Both IOB and Inotec measurements were measured for 300 seconds and are presented in different units, but that does not alter the actual comparison. The articles [16][17] state that cores made of CORDIS process show different behaviour of gas shock than cores made in organic binders, see Fig.6.

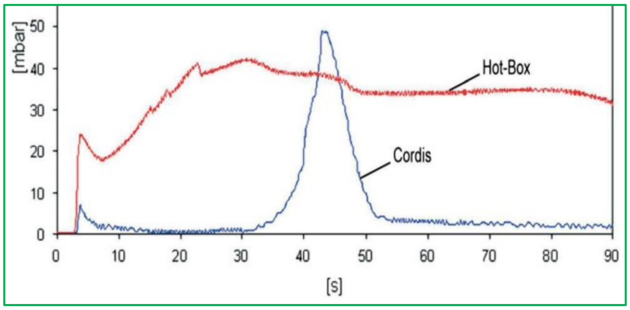

Fig. 6. Gas shock with hotbox and CORDIS cores [16][17]

2. Experiment procedure

The main goal of the experiment is compare the gas evolution of GEOPOL® W sand mixture with PUR cold box amine and Croning. In addition, to prove the amount of gas evolved by calculation.

2.1. Materials and samples

Standard materials were used for samples for measuring of gas evolution. The sand mixture composition of all three processes show Table 2, Table 3 and Table 4.

Table 2.
GEOPOL® W sand mixture composition.

Material	Addition level [wt %]
BK 31, quartz sand	100
GEOPOL W20, binder	1.8
GEOTEK W303, powder additive	0.5

Table 3.
PUR cold box amine sand mixture composition.

Material	Addition level [wt %]
BK 31, quartz sand	100
Permacure 744, part 1, binder	1.8
Permacure 744, part 1, binder	0.5
DMIPA, catalysator	0.5 cm^3

Table 4.
Composition of standard commercial shell core sand mixture.

Material	Addition level [wt %]
Quartz sand	100
Binder	2.0

2.2. Methods of measuring

The measurement was made at the Technical University of Liberec, Faculty of Mechanical Engineering.

The principle of the measuring is scanning of the pressure developed by combustion of the sand sample inside the electrical resistance furnace. The sample is heated by the radiant heat inside the closed furnace space. The sand sample in the weight of 1.00±0.01 g is heated inside the open molybdenum combustion boat. Each of three sand mixtures was tested on minimally five samples. All samples were rapidly heated by radiant heat at 1200 °C in the closed furnace chamber, which is connected with measuring system only. The measuring system monitoring the pressure of developed gas in time.

The apparatus consists of resistance tube furnace, Mars type with heated chamber, ceramic tube, quartz tube, temperature regulator and temperature sensor. The furnace is equipped by cooling and by gas outlet. The pressure sensor is connected with computer through Analog/Digital converter. The computer is equipped with graphic interpretation of measured values, it means (1) volume of developed gases in dependence on time, (2) volume of developed gases in dependence on temperature and (3) temperature inside the furnace in dependence on time. The complete measuring apparatus is shown on Fig. 7.

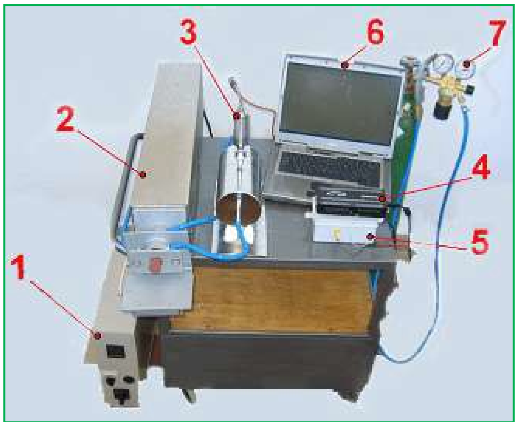

Fig. 7. The detail of the measuring apparatus of gas evolution of moulding and core sand mixtures. 1-furnace controller, 2-Mars furnace, 3-prussure sensor, 4-data bus, 5-voltage source for the bus, 6-PC, 7-pressure vessel with nitrogen gas (N_2).

The calibration of measuring apparatus is made before every series of individual experiments. The calibration is made by load pump or by thermal decomposition of $CaCO_3$ or by thermal decomposition of $KHCO_3$. On the Fig. 8 is the front part of the gas evolution measuring apparatus (left), it means position where the sample is inserted to the oven and shows also the buffer tank with integrated pressure sensor (right).

The image group (Fig. 9) shows the removal of solid residues of the monitored mixture from the measuring device after gas evolution measurement.

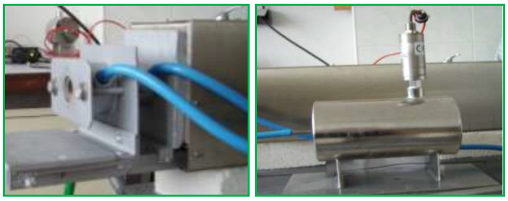

Fig. 8. View of the front part of gas evolution measuring device (left) and the buffer tank with integrated pressure sensor (right)

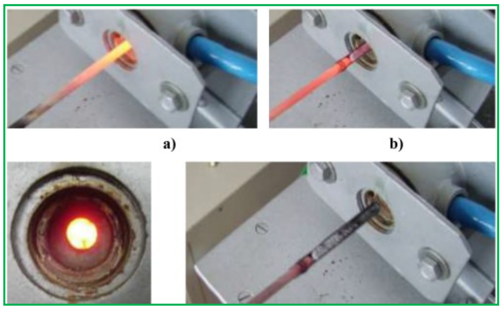

Fig. 9. Inlet opening of the gas evolution measuring device

2.3. Calculation of gases generated

GEOPOL(R) W binder consists of about 57.0% of water (loose and tightly bound water). Hardening by heat remove from the binder about 48.5% of free water. It means, 8.5 % of tightly bound water is still in the geopolymer structure.

Next the sand mixture consists generally of quartz sand and powder additive, too. The quartz sand usually has max 0.2% of water and powder additive max 0.3%. Both waters from sand and additive are removed from the sand mixture during the hardening process.

The sand mixture GEOPOL® W does not include any other chemical compound which could be thermally decomposed.

Calculation of gases evolved during pouring (thermal load) from one gram of GEOPOL® W sand mixture: The volume of 1 mol of ideal gas in standard condition (at temperature 273 °K and pressure 101 325 Pa) is constant and equals to 22.41 $dm^3.mol^{-1}$. Molar weight of water (H_2O) is M_{H2O}=18.01528 $g.mol^{-1}$. As was calculated above, one gram of GEOPOL® W binder contain 8.5% of tightly bound water = 0.085 g after hardening. The GEOPOL® W sand mixture contains 1.8% of binder. Volume of gases (water vapour) is possible to calculate according to the formula (1). Based on these assumptions, and calculation (2)(3), one gram of GEOPOL® W sand mixture after thermal hardening generates 1.9 ml of gas.

$$V_{gas} = 22.41 \frac{m_{H2O}.1.8\%\ \text{of binder}}{M_{H2O}}, \quad (1)$$

V_{gas}...volume of gases evoluted during pouring [dm^3],
m_{H2O}...weight of water in the sand mixture [g],
M_{H2O}...molar weight of water [$g.mol^{-1}$],
1.8% of binder...addition level of binder in the sand mixture [%].

$$V_{gas} = 2241 \frac{0.085\ .0.018}{18.01528}, \quad (2)$$

$$V_{gas} = 0.0019\ dm^3 = 1.9\ cm^3 = 1.9\ ml. \quad (3)$$

3. Results and discussion

3.1. Measured figures of gas evolution

The measured values of gas evolution for those processes are on Fig. 10 as follows:

- GEOPOL® W.................4.31678281 $cm^3.g^{-1}$,
- PUR coldbox amine........ 15.94359852 $cm^3.g^{-1}$ → **3.7x**,
- Croning.......................... 18.16566039 $cm^3.g^{-1}$ → **4.2x**.

The gas evolution GEOPOL® W is several times lower than PUR cold box amine (3.7x) and Croning (4.2x). The curves of gas evolution and differences correspond to results in [12][13][14].

The measured value 4.3 $cm^3.g^{-1}$ of gas evolution of GEOPOL® W sand mixture in comparison with calculated volume of gases 1.9 $cm^3.g^{-1}$ is 2.3 times higher. The reason could be, the sand mixture had to absorb moisture from the air after dehydration during storing and preparing the samples or the dehydration was not complete and the core after hardening still includes small amount of free water.

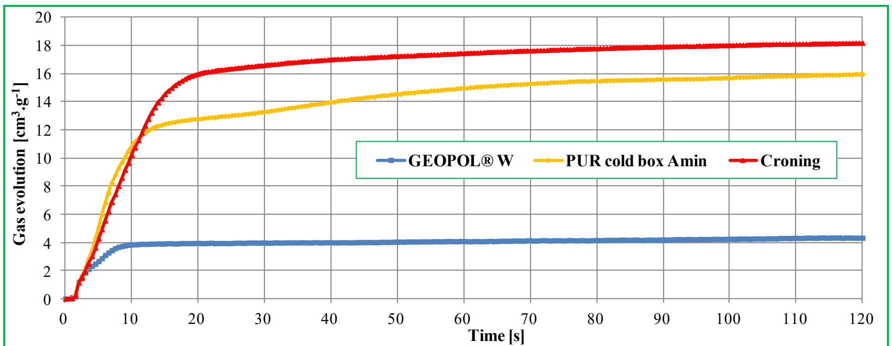

Fig. 10. Gas evolution of inorganic binder system GEOPOL® W and organic binder systems PUR cold box amin and Croning.

The measured results also show the speed of gas evolution within 20 seconds. The gas evolution is almost the same, the Croning has the highest value of 15.96 $cm^3.g^{-1}$, PUR cold box amine 12.78 $cm^3.g^{-1}$ and GEOPOL® W 3.95 $cm^3.g^{-1}$. In a more detailed view, it is clear that the gas volume generated after 20 seconds for GEOPOL® W is 91.4% of the final value, for the PUR cold box it is 80.2% and Croning 87.8%. It confirms that that gas evolution is the fastest with GEOPOL® W cores. It can be argued that the generated gas from GEOPOL® W cores is formed very quickly and prevents penetration of the molten metal to the core and at the same time the volume and pressure of gas are small enough to avoid gas casting defects.

4. Conclusions

The presented research paper proves lower gas evolution of GEOPOL® W core in comparison with PUR cold box amine and Croning. Total gas evolution value is 3.7 times lower, respectively 4.2 times lower than organic cores. Measured value 4.3 $cm^3.g^{-1}$ is 2.3 times higher than calculated 1.9 $cm^3.g^{-1}$ one. The reason could be moisture absorption from the air or dehydration was not complete.

Against the organic binders GEOPOL® W brings significant benefits at the casting production:

- The generated gas is water vapour only due to the chemical nature of the geopolymer binder system.
- The cores do not produce other emissions. No dangerous emissions, fumes or unpleasant odours are developed. Reduced costs for exhaust air treatment.
- It allows the production of defect free castings. Low gas evolution drastically minimises the risk of gas casting defects. Less gas from core = less casting defects.
- Eliminate emissions means increase productivity and quality.
- There are no condensate deposits on the die surface. Improved productivity due to absence of cleaning of the die.
- Castings surfaces are comparable with organic cores or better.

Finally, the GEOPOL® W binder system is suitable for serial castings production made of aluminium alloys, iron and steel.

Acknowledgements

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