The International Journal of Engineering and Science (IJES)
|| Volume || 7 || Issue || 9 Ver.II || Pages || PP 15-26 || 2018 ||
ISSN (e): 2319 – 1813 ISSN (p): 23-19 – 1805

Geopol® Binder System. Environment Friendly Mould And Core Production.

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---***ABSTRACT***---

The production technologies directly or indirectly affect all living and non-living objects around us. The foundry industry is no exception in this regard. Foundries face demanding requirements of customers for quality and more favourable production processes while they also have to take into account and integrate technical and legislative requirements and ensure the protection of health and safety of workers.

Inorganic binder systems are becoming more and more interesting for foundries. The geopolymers have achieved the worldwide fame thank to Mr Davidovits. He focuses on the field of civil engineering but it is not the only area to which geopolymers can bring something new, progressive, and innovative. Geopolymers are also being successfully used in the foundry industry. And why? What is their advantage? It is a unique inorganic binder system GEOPOL®, which is needed and welcomed in terms of the environment, the work environment, and the sustainable resources.

The GEOPOL® technology is currently used in the foundry industry for three basic production processes: (1) the process for self-hardening moulding mixtures, (2) sand mixtures hardened by gaseous carbon dioxide and (3) the GEOPOL® W technology, the hot box technology with hot air hardening. The latest listed process of heat hardening is the major advancement in the casting of high-volume series, particularly in the automotive industry, despite the fact that the self-hardening sand mixtures are still the most widespread process used. While using new sand, 1.6 to 2.0% of binder is usually used, while in combination with the reclaim sand, 1.8 to 2.0% of binder is used.

The GEOPOL® technology not only solves the binder system and the modes of hardening, but also deals with the entire foundry production process. Low emissions produced during mixing of sand mixtures, moulding, handling, and pouring bring a relatively significant improvement of work conditions in foundries (no VOCs). The GEOPOL® is a odourless technology (the minimum content of soluble carbon compounds), 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. A high percentage of the reclaim sand can be used again for the preparation of the moulding mixture. This eliminates the disposal of the excess moulding sand in landfills and burdening the landscape with waste. The higher utilization of the reclaim sand and the savings on input materials improve the overall economic balance. The following basic parameters of the reclaim sand are monitored: the sodium oxide content, the conductibility, the moisture, the pH, and the dust content. Up to 85% of the reclaim sand can be used to reach optimal values of these parameters. This article also deals with the two-stage mechanical reclamation. The second stage is an atritation reclaimer (abbreviated AT), which was developed especially for the geopolymer mixtures.

The aim of this paper is to provide a theoretical and practical overview of the GEOPOL® binder system and introduce possible ways of moulds and cores production in foundries.

KEYWORDS: *geopolymer, GEOPOL®, binder, mould, core, casting, work environment, environment, foundry*

Date of Submission: 25-08-2018 Date of acceptance: 08-09-2018

I. INTRODUCTION. WHAT ARE GEOPOLYMERS

The use of inorganic binder for foundry needs has been known since the fifties of the twentieth century. In 1947, Mr. Lev Petrzela of the nowadays Czech Republic, got patented a sodium silicate sand mixture. This discovery was revolutionary for foundries, since it enabled the production of moulds and cores without drying and launched further development of the second generation of inorganic and then organic binders systems.

In the seventies of the last century, the geopolymers were discovered. 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 (Figure 1) [1], [2].

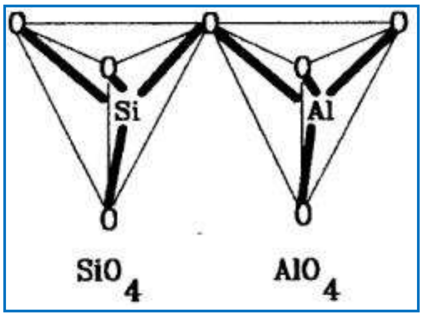

Figure 1: *The basic structural unit of geopolymers.*

The geopolymers are the focus of interest in a number of industries. 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. Especially in the construction industry, these alkali-activated aluminosilicates are given considerable attention. In these applications, a geopolymer is formed during the process. The geopolymer is created in the reaction between the silicon-containing material and aluminium-containing material (fly ash, slag) and an alkaline activator. 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 [2].

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.

According to some archaeological publications, Egyptian pyramids are not of carved blocks but casted from the geopolymers (Figure 2) [3], which is an interesting idea.

Figure 2: *Egyptian pyramid.*

II. THE GEOPOLYMERS FOR FOUNDRY INDUSTRY.

In the foundry industry, we can see the tendency to use inorganic systems at the expense of organic binder systems for a long time. It is a response to the environmental requirements of the legislation, castings customer requirements, health and safety of workers.

The organic binder systems, which currently dominate in foundries and are the major competitive barrier, undoubtedly have a number of disadvantages due to their chemical nature. The main disadvantages include the release of volatile organic compounds during the preparation of the moulding and core mixture and during the handling of moulds and cores. Furthermore, the emissions generated during the pouring, cooling, and shakeout of castings are very annoying and hazardous. Wastes are classified as hazardous and have a significant environmental impact. It is necessary to observe a number of safety regulations during the handling and the storing of incoming raw materials – chemicals substances.

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.

In the Czech Republic, a new environmentally friendly binder system GEOPOL® has been developed using a geopolymeric inorganic binder for the production of conventional moulds and cores. These polymers are also referred to as polysialates and are composed of chains of tetrahedrons of SiO_4 and AlO_4 (Figure 1). The resulting properties of the binder depend on the ratio of these components and on the preparation of the geopolymer. The distribution of the basic structural units of the geopolymer binder is shown in table 1.

Table. 1: *The distribution of the basic structural units of the geopolymer binder (weight %).*

Type of geopolymer binder	Monomers	Dimers	Higher polymers
GEOPOL® 618	86.9	4.5	8.6
GEOPOL® 510	91.4	6.6	2.1
GEOPOL® W10	81.4	11.6	7.1

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 (Figure 3).

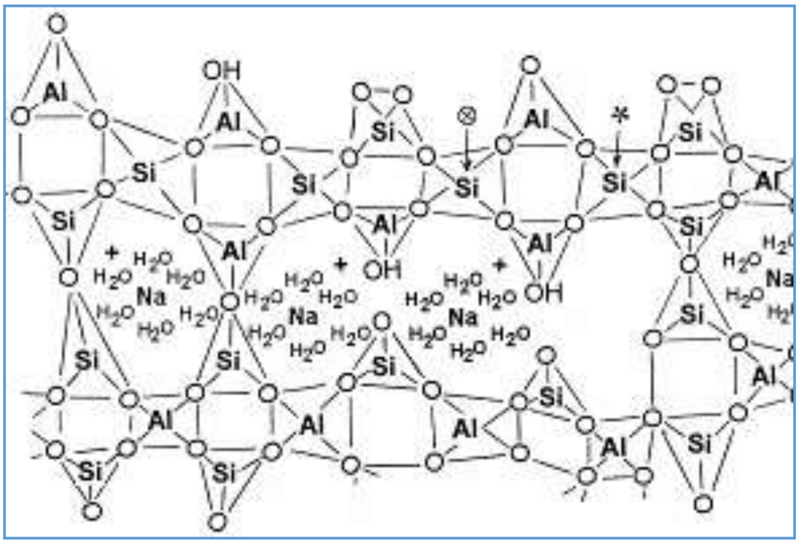

Figure 3: *Scheme and model of inorganic polymer [4].*

III. GEOPOL® ST TECHNOLOGY, self-hardening moulding mixtures

The technology of self-hardening mixtures is for moulds and cores production. The geopolymer binder for this technology is a clear viscous liquid with a low degree of polymerization. By the action of the hardener, the degree of polymerization is increased and a polymer with high binding ability is formed. The polymerization process of this binder is quite different, for example, from the gelation of sodium silicate. Sodium silicate by the treatment with an ester hardener forms the gel practically at the same time after the incubation period. All the liquid phase is closed in the gel. During gel standing, a phenomenon known as syneresis occurs, whereby the liquid phase is separated from the gel. The amount of extracted liquid is about 10 to 15% and corresponds to the free water content of the colloidal solution.

In the geopolymer binder, polymerization takes place by the action of the hardener so that gradually the liquid increases the viscosity and changes to the solid polymer. There is no syneresis. The polymerization process results in a solid inorganic polymer with a characteristic structure [1]. The water is enclosed within the solid inorganic polymer. The geopolymer binder has a high bonding strength. The possibility of low addition levels of geopolymer binder in the self-hardening mixtures is confirmed also by the long-term experience of foundries, where the geopolymer binder system is used. The sufficient addition level of the binder to achieve the required operational strengths and properties of the moulds and cores ranges from 1.4 to 1.8% in the sand mixtures with a new sand and from 1.8 to 2.0% in the sand mixtures with 75 to 100% of reclaimed sand.

The important parameters for all self-hardening sand mixtures are the bench life (working time) of the sand mixture and the stripping time. A mould strength tester has been proven to be a very practical measurement method in both laboratory and operational measurements of the bench life and the stripping time. In the initial stages of hardening, it allows to measure quickly and easily the increase of strengths in dependence on time on the test pieces and specific moulds or cores. The ratio of the bench life and stripping time is comparable to existing organic and inorganic binder systems (alkaline phenolic systems, furans, water glass ester processes).

The bench life of the self-hardening mixtures with geopolymer binder system can be set by a suitable liquid hardener. The mostly used are the SA series hardener and GEOFIX, a new series of hardeners. The bench life of the sand mixture can be set in the range from 2 to 90 minutes. Thus, it can be said that by the selection or combination of hardeners, the desired parameters can be set for a particular production.

The composition of the self-hardening sand mixture:

- Sand.
- GEOPOL® 618 binder, addition level ranging from 1.4 to 2.0%, based on the sand quantity.
- Hardener, addition level ranging from 14 to 18%, based on the binder quantity.

The schematic mould and core production of the self-hardening sand mixture is shown in Figure 4, Figures 5 through 9 show real moulds, cores and castings. In Figure 9, it can be seen that during the pouring process only minimal emissions to the atmosphere (environment) are generated, essentially it is just a water vapour.

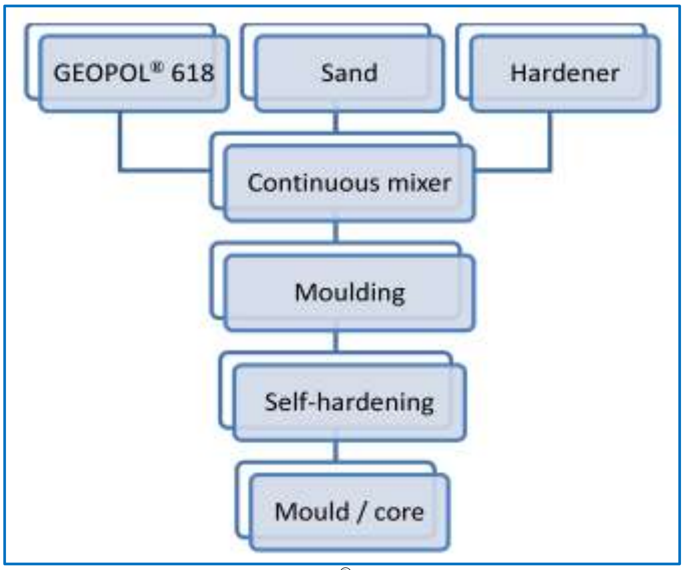

Figure 4: *Scheme of GEOPOL® moulds and cores production.*

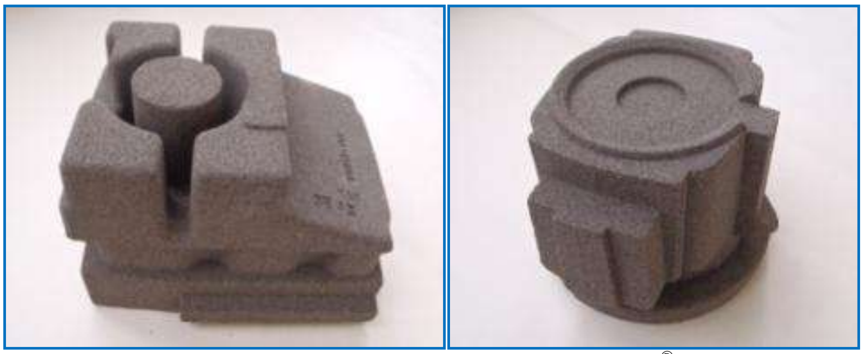

Figure 5: *Smaller cores made from 100% reclaimed sand by the GEOPOL® technology, the self-hardening sand mixture.*

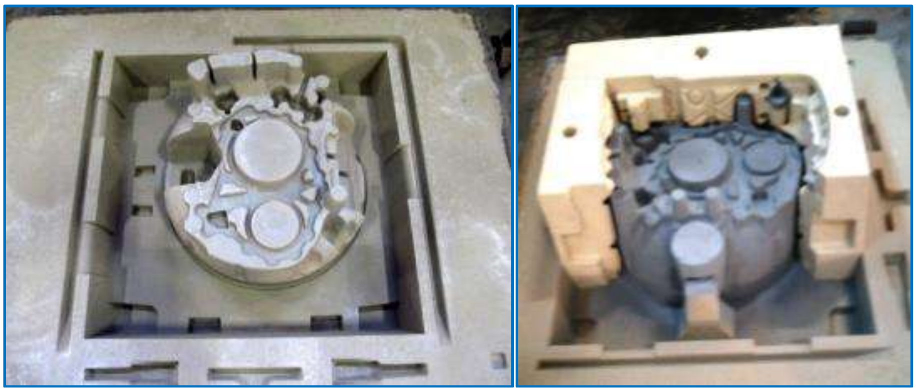

Figure 6: *Example of the produced smaller moulds, gearbox.*

Figure 7: *Example of the produced casting, gearbox.*

Figure 8: *Production of the large moulds using polystyrene patterns.*

Figure 9: *There are almost no emissions, exhalations during pouring.*

IV. GEOPOL® CO_2 TECHNOLOGY, sand mixtures hardened by gaseous carbon dioxide

The inorganic geopolymer system is also applicable in the production of cores, or even moulds, hardened by gas from the outside by the gaseous carbon dioxide (CO_2). During the curing process with gaseous CO_2, the polymerization and the formation of an inorganic polymer occur.

In order to achieve higher immediate strengths, as well as core storage strength, GEOTEK accelerators, both liquid and powdery, can be added to the sand mixture. The additive is used to achieve higher immediate strengths, to improve storability and collapsibility. The collapsibility of the cores after pouring is similar to the alkaline-condensed phenolic resin binder sand mixtures hardened by gaseous CO_2. The type of this additive is selected according to the requirements of the properties of the sand mixtures and the produced cores and the sand used. The sand mixture can be stored for up to 24 hours without changing the quality while the air is prevented from coming [5]. Accelerators speed up the hardening of cores and reduce the consumption of CO_2. In comparison to the sodium silicate, the hardening time is shorter; however, in comparison to the alkaline-condensed phenolic resin hardened by CO_2, the hardening time is longer.

For more efficient hardening, it is possible to use the cycling of CO_2 gas flow through the core or CO_2 dilution by air. The heated CO_2 could be also used in the hardening process.

The water is tightly bound in the binder and reduces the risk of bubbles and cavities due to the formation of water vapours. The cores show low gas generation.

The composition of the sand mixture hardened by gaseous carbon dioxide, GEOPOL® CO_2:

- Sand.
- GEOPOL® 510 binder, addition level ranging from 2.3 to 3.0%, based on sand quantity.
- Accelerator GEOTEK, addition level ranging from 0.5 to 0.8%, based on sand quantity.

The production scheme of cores made from GEOPOL® sand mixture hardened by CO_2 is shown in Figure 10. Figures 11 through 13 are examples of cores and castings.

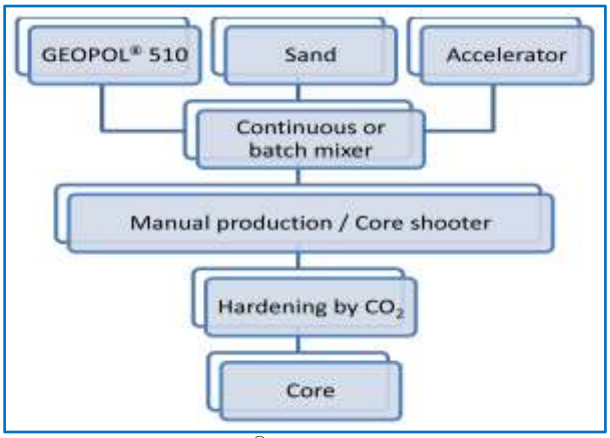

Figure 10: *GEOPOL® CO_2 core production scheme.*

Figure 11: *Large core made on the core shooting machine.*

Figure 12: *Small cores made on the core shooting machine, addition level: 100 weight parts of sand ST55, 3.0 weight parts of GEOPOL® binder, 0.7 weight parts of GEOTEK accelerator.*

Figure 13: *Grey cast iron casting, the core is made from GEOPOL® CO_2 sand mixture.*

V. GEOPOL® W TECHNOLOGY

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 [6].

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 moistening. Dehydration can also be achieved by microwave hardening.

It is recommended to use the GEOTEK W301 or GEOTEK W302 powder additive, which has a beneficial effect on the reduced wettability of the cores and the increases the cold and hot strength of the cores.

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 4.5 MPa.
The composition of the sand mixture for core production made by the GEOPOL® W technology:

- Sand.
- GEOPOL® W10, or W11 binder, addition level ranging from 1.4 to 2.0%, based on sand quantity.
- Accelerator GEOTEK W301, or W301, addition level ranging from 0.3 to 0.9%, based on sand quantity.

The addition of 1.8% of binder and 0.5% of accelerator ensures optimum strength, which was verified/confirmed by the production process.

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. The GEOPOL® W binder system is suitable for most quartz and non-quartz sands. The scheme of the core production hardened by heat is shown in Figure 14.

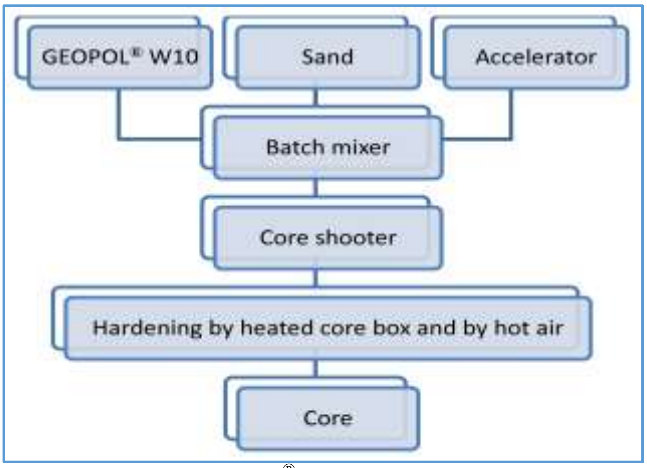

Figure 14: *GEOPOL® W core production scheme.*

The temperature field of the heated core box and the temperature distribution on the core surface itself is shown in Figure 15. Coated cores cored to the die and castings just after pouring are shown in Figure 16. More favourable effect of the geopolymer binder system on the work environment and the environment can be seen in Figure 17. The differences between inorganic and organic binder systems are, at first glance, significant. The cores made by GEOPOL® W technology does not generate smoke, fume, odour, and smell during the process of pouring. Only hardly noticeable aroma is formed when the die is opened [6].

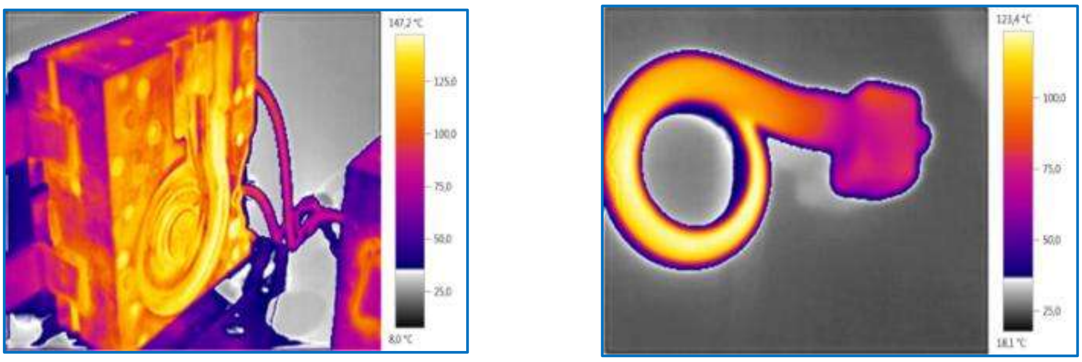

Figure 15: *Temperatures distribution on the core box and on the core surface just after the removal from the core box.*

Figure 16: *Coated cores cored to the metal mould (left). Castings after pouring (right).*

Figure 17: *Comparison of gas evolution after pouring. Castings immediately after pouring, the PUR cold box amine technology (organic binder)(left). Opening of the die immediately after pouring, cores made by GEOPOL® W technology (inorganic binder)(right).*

The cores made by the GEOPOL® W technology can be manufactured in the same production cycle as the cores made by the PUR cold box amine technology. The manufactured cores do not need any extra care, it means that conventional coatings can be applied. The cores can be stored in standard foundry conditions without having affected the final casting quality. There is no deformation of the cores. The very good collapsibility of the cores from the castings after pouring and the substantial reduction of the decoring process time (aluminium alloy castings) has been confirmed [6].

VI. EMISSIONS DURING MOULDING, POURING AND COOLING.

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. For this reason, the GEOPOL® technology is included in the environmental programme. For example, in the USA, the official goal is the change of the environmental footprint of the foundry industry. In general, it is expected that the inorganic binder systems achieve significant reductions in emissions [5]. The comparison of the binder systems from the point of view of the BTEX and the PAH shows in graphs in Figure 18.

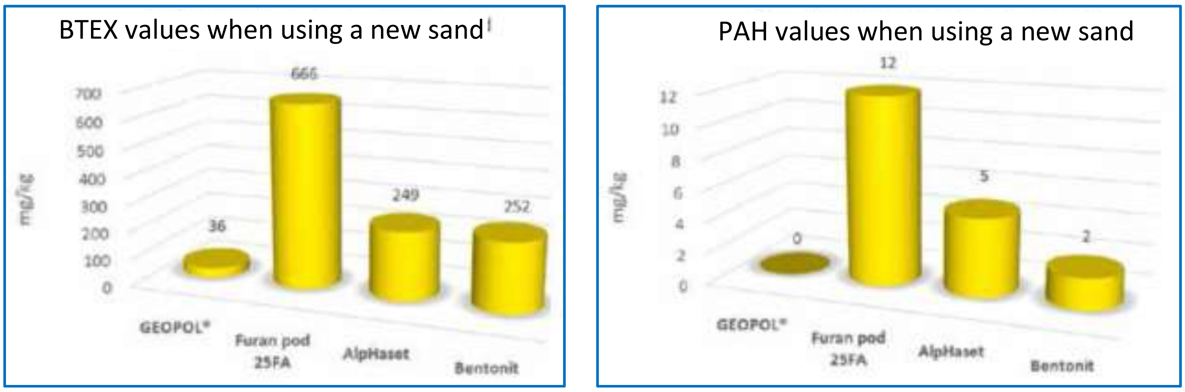

Figure 18: *Results of pollutant measurement during pouring, comparison of organic and inorganic binder systems [7].*

VII. RECLAMATION OF THE GEOPOLYMER SAND MIXTURES

The used sand mixtures with the geopolymer binder have significantly easier reclaimability, which is comparable with the organic binder systems. The better collapsibility of the used sand mixtures with geopolymer binder after pouring has been confirmed by the foundries manufacturing aluminium and non-ferrous castings. Thus, it means that with lower temperatures, the collapsibility is better than the collapsibility of the conventional organic binder systems.

It has been proven operationally that the used sand mixtures with the geopolymer binder can be successfully reclaimed through a simple vibration reclamation plant functioning on the principle of attrition. The utilization of the reclaimed sand is then 75% for the facing sand mixture and 100% for the backing sand mixture.

SAND TEAM, spol. s r.o. company has developed the secondary reclaimer (attrition unit) to increase the utilization of the reclaimed sand. When this reclaimer (secondary attrition unit) is integrated to the whole reclamation plant and is included after the primary reclamation stage, the 85 to 95% of the reclaimed sand can be used for the unit sand mixture. The secondary attrition unit works on the principle of intensive activation attrition. The principle of intensive activation attrition consists of the abrasion of the grains by rotation of metal parts of the device and the mutual rubbing of the sand grains with simultaneous dust extraction. This process also leads to the activation of the sand grain surface.

The geopolymer binder has a high cohesive strength. When the binding bridges are mechanically loaded, the binder envelopes (residues) separate from the surface of the sand grains. There is no breakage of the binder in the area of the binding bridges. The nature of destruction is adhesive, see Figure 19, similar to that of the organic self-hardening sand mixtures.

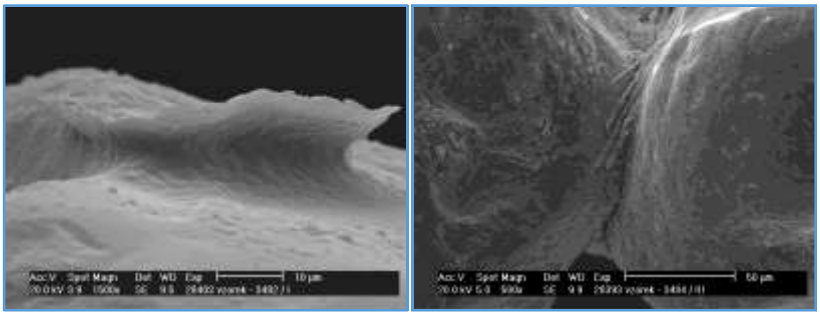

Figure 19: *The adhesive nature of destruction of the geopolymer binding bridge (left). The cohesive nature of destruction of the sodium silicate binding bridge (right).*

The schemes of the utilization of the reclaimed sand, using both primary (single stage) and secondary (two stage) reclamation, are shown in Figures 20 and 21.

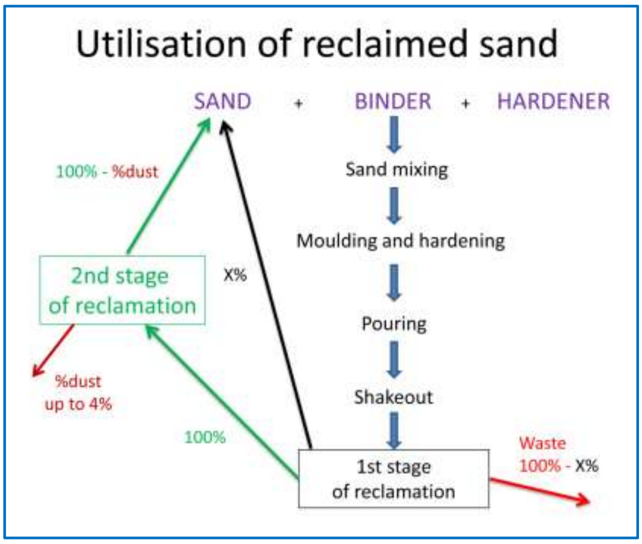

Figure 20: *Reclamation scheme of utilisation of reclaimed sand for using of primary reclamation (single-stage) and secondary reclamation (two-stage).*

Figure 21: *Reclamation plant assembly scheme with primary and secondary reclamation (left), only secondary reclamation stage (right).*

Parameters of the reclaimed sand, which allow the high utilization, i.e. up to 95% of the reclaimed sand back for mould and core production, are as follows:

- conductivity………………..... below 400 μS/cm,
- Na_2O content………............. below 0.150%,
- washout substances............... below 1.2%,
- average sand grain size…...... ±0.2 mm (deviation from the original average sand grain size).

The operating parameters in the foundry, which is manufacturing aluminium castings, having the two-stage reclamation plant installed and using the GEOPOL® ST self-hardening moulding mixtures, are as follows:

- reclaimed sand / new sand ratio……………. 85/15%,
- addition level of GEOPOL® binder……...... 1.8%,
- dust quantity... 3.5%.

VIII. CONCLUSION

The inorganic binders clearly offer a solution for the future of the foundry production. Therefore, it is already clear that the development of foundry processes will continue leading in this direction [8].

GEOPOL® technology offers applications in three foundry processes for moulds and cores production: (1) the technology of self-hardening moulding mixtures, (2) the technology of sand mixtures hardened by gaseous carbon dioxide, and (3) the technology of sand mixtures hardened by heat.

These GEOPOL® binder systems can be used in the production of castings from steel, cast iron, non-ferrous metals and their alloys, and are suitable for all types of sands. This binder system can be used as a replacement of the existing binder systems, both organic and inorganic, for the production of moulds and cores. The GEOPOL® technology delivers substantial improvements in the working conditions and environmental performance of production, compared to the current practice. It helps to solve the hygienic and environmental problems of foundries and their impacts on health, safety of workers, and overall environmental impacts.

ACKNOWLEDGEMENTS

This work was developed as part of solution of the project TA04011039, Foundry cores with the geopolymer binder. We thank the Technology Agency of the Czech Republic for their support.

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Michal Vykoukal" Geopol® Binder System. Environment Friendly Mould And Core Production."The International Journal of Engineering and Science (IJES) 7.9 (2018): 15-26