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Technical Report

Reinforcement of the terracotta sculpture by geopolymer composite

Tomas Hanzlíček [a,*], Michaela Steinerová [a], Pavel Straka [a], Ivana Perná [a], Petr Siegl [b], Tereza Švarcová [b]

[a] Institute of Rock Structure and Mechanics of the Academy of Sciences of the Czech Republic, v.v.i., V Holešovičkách 41, 182 09 Prague 8, Czech Republic
[b] The Academy of Fine Arts in Prague, The School of Restoration, U Akademie 4, 170 22 Prague 7, Czech Republic

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ABSTRACT

Presented paper opens the possibility to use the geopolymer binder as fixing and joining material in restoration of the valuable historical objects. Special geopolymer composite was prepared to match the structure and color for reinforcement of the terracotta Baroque statue. The application in the cavity of the sculpture creates system of consolidating rims and ribs. The geopolymer technique was applied only on the unseen part of the statue, which ensured the stability and durability of the object without disrupting the aesthetics for the viewer. The exterior modulation and final restoration was carried out using classic technologies, specifically calcite-bonding agents, and is not the subject of this paper.

1. Introduction

Contemporary civilization considers the conservation of our cultural heritage for future generations as an essential duty. Monuments and art works of past centuries can be now preserved and safeguarded through new technologies. One such case would be the interdisciplinary cooperation between the School of Restoration of the Academy of Fine Arts in Prague, which has long continued its tradition as "The Czech Restoration School", with its main aim being the preservation of cultural heritage, and the Academy of Sciences on the one hand and laboratories of the Institute of Chemical Technology, Prague on the other. In this particular case, modern analytical methods were exploited to determine which materials were originally used and their composition. Additionally, this cooperation has brought new materials and techniques to cases where it is difficult or impossible to use standard restoration practices.

The terracotta sculpture of The Virgin and Child with the Infant St. John from the collection of the National Gallery in Prague is just such a specific nonstandard restoration task. The Baroque terracotta sculpture by Giuseppe Maria Mazza (1653–1741), which was acquired to the collection in the first half of the 19th century, was severely damaged. The restoration of the sculpture with a height of 1.42 m and the only work by the Bologna sculptor in Prague presented a unique challenge for the Restoration School of the Academy of Fine Arts in Prague.

Due to the large extent of the damage both on the original modulation and to the instability of the whole sculpture construction, it was necessary to begin with extensive research of the condition of the sculpture and then designs a carefully planned technique for the reconstruction and preservation of G.M. Mazza's masterpiece. Once the surface was perfectly cleaned, it was possible to see the original coloring of the terracotta body and also the extensive damages and fragmentation were uncovered. As the cleaning work proceeded, it became more and more evident that the main task would be to find a way of making the whole object compact. The main aim was to prepare a stable and durable inner skeleton which would hold the fragmented parts together and affix them to the front modulation, thus ensuring stability. This possibility offers the geopolymer composite.

2. Geopolymer background

In past 40 years, the "alkali activated" or "geopolymer composites" [1–3] were studied very profoundly in many laboratories and institutions all over the world. It was found [4] that thermal activated kalolinitic clay on temperature above 600 °C and less than 900 °C present very important change in Al^{3+} coordination. Raw material with its typical octa-coordination of [6] Al^{3+}, changes its position according to the temperature and dwell to tetra coordinated [4] Al^{3+}. The studies of MAS-NMR of $^{27}Al^{3+}$ and $^{29}Si^{4+}$ and understanding of the shifts presented by this analysis opened new possibilities – formulation of non cement binding materials.

The hydration of the "activated" kaolinitic clays (temperature and dwell differs according to the type of kaolinite and granular size of it proceeds in alkali aqueous solutions when primary formed hydrolytic precursors react as follow [5]:

$$\underset{\text{solid particles}}{\text{Al—Si}} + OH^- = \underset{\text{monomer}}{Al(OH)_4^-} + \underset{\text{monomer}}{{}^-OSi(OH)_3} \quad (1)$$

$$^-OSi(OH)_3 + OH^- = {}^-OSi(OH)_2O^- + H_2O \quad (2)$$

$$^-OSi(OH)_2O^- + OH^- = {}^-O\overset{\overset{O^-}{|}}{Si}(OH)O^- + H_2O \quad (3)$$

* Corresponding author. Tel.: +420 266009268; fax: +420 284680105.
E-mail address: hanzlicek@irsm.cas.cz (T. Hanzlíček).

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$$M^{+} + \underset{\text{monomer}}{{}^{-}OSi(OH)_3} = \underset{\text{monomer}}{M^{+-}OSi(OH)_3} \quad (4)$$

$$2M^{+} + \underset{\text{monomer}}{{}^{-}OSi(OH)_2O^{-}} = \underset{\text{monomer}}{M^{+-}OSi(OH)_2O^{-+}M} \quad (5)$$

$$3M^{+} + \overset{\overset{O^{-}}{|}}{{}^{-}OSi(OH)O^{-}} = \overset{\overset{M^{+}O}{|}}{M^{+}OSi(OH)O^{+}M} \quad (6)$$

$$M^{+} + Al(OH)_4 + OH^{-} = \underset{\text{monomer}}{M^{+-}OAl(OH)_3} + H_2O \quad (7)$$

$$\underset{\text{monomer}}{{}^{-}OSi(OH)_3} + \underset{\text{monomer}}{M^{+-}OSi(OH)_3} + M^{+} = \underset{\text{dimmer}}{M^{+-}OSi(OH)_2{-}O{-}Si{-}(OH)_3} + MOH \quad (8)$$

$$\underset{\text{monomer}}{{}^{-}OSi(OH)_2O^{-}} + \underset{\text{monomer}}{M^{+-}OSi(OH)_3} + M^{+} = \underset{\text{dimmer}}{M^{+-}OSi(OH)_2{-}O{-}Si(OH)_2O^{-}} + MOH \quad (9)$$

$$M^{+} = K^{+} \text{or } Na^{+}$$

The dimmers, trimmers and longer and longer chains end in hardening of mainly amorphous 3D net during 10–12 h. Basic property of the finally formed 3D net is its setting and hardening in ambient temperature and pressure. For the calculation of different type of composites is important that formed 3D net could accepts many different kind of materials (sand, mica, etc.) and encapsulated them into the formed net. Some other materials (ash, slag) are further chemically bonded into the siloxo-sial net.

This property opens possibility to appropriate the quality of geopolymer composite to the material which to be fixed or substituted. Wide variety of the additives to the basic binding clayed agent change the porosity, strength and appearance – from the porous, like sandstone material to the compact material.

In presented case the main question to answer was a formulation of composite which would be firm and stabile enough to hold the weight of the statue and would perfect joint ceramic–terracotta body.

3. Experimental

3.1. Materials

The demand of restores was to associate the geopolymer material to the original ceramic in porosity, color and chemical composition as close as possible. The chemical analysis of statue material is presented in Table 1.

Also important was XRD analysis (not presented) of mentioned material and former decision: use of the components to be combined with geopolymer matrix. The XRD analysis of the original terracotta identified 32 wt.% of silica (SiO_2), 13 wt.% of calcite ($CaCO_3$), 19 wt.% of albit ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$ – sodium feldspar), 11 wt.% of micas, 24 wt.% of montmorillonite and 1 wt.% of gypsum ($CaSO_4 \cdot 2H_2O$). To follow the demands of restorers was necessary to find clayed material with appropriate color (light red) for matrix and different additives: fine granulated sand, calcite combined by naturally fired shale and montmorillonitic raw clay.

The geopolymer matrix was made from two kaolinitic clays. One with higher content of Fe^{3+} ions, calculated by chemical analyses as hematite (α-Fe_2O_3) exceeding 2.57 wt.%. The original form of Fe^{3+} ions is lepidocrocite (FeO(OH)). The clay activation (thermally treatment) causes dark red coloring. This clay is a waste material of washed white sand used in glass industry. This material contents more than 48 wt.% of fine grained (predominantly particles of 0.2 mm) silica sand. The second clay, light in color, is richer in kaolinite (85 wt.%) and contains very fine particles of silica sand (15 wt.%). The demanded color was obtained by mixing the light and red clay (weight ratio 2:1). The thermal treatment (750 °C with the dwell of 6 h) of the mixture offers the matrix material for final composite.

The additives, silica sand combined with chalk, montmorillonitic raw clay and naturally fired shale, corresponded chemically to the original terracotta. The naturally fired shale is taken from the deposit of the upper layers clayed materials extracted from the coal mines close to Pilsen (Czech Republic). The deposit (more than 10 million tons) contained the rests of coal which with pressure of the stacked material slowly burn, converting the clayed material to the fired shale. The chalk in form of finely milled powder is practically pure $CaCO_3$ used in restoration ateliers as ordinary filler. Common trade name is the "China chalk" (floated whiting). The chemical composition of the used materials is presented in Table 2.

The combination of fired shale and silica sand lowered the shrinkage of the composite geopolymer and addition of raw clay provided certain plasticity necessary for the application. One of the important advantages of the geopolymer composite is a fact that material could reach similarity with ceramics [6].

Table 1
Chemical composition of historical terracotta.

Terracotta	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	Fe_2O_3	TiO_2	L.O.I.
Wt.%	51.96	16.00	12.95	<0.11	4.063	10.32	1.17	0.15

Table 2
Chemical composition of the fillers (all figures in wt.%).

Material	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	Fe_2O_3	TiO_2	L.O.I.
Fired shale	54.69	28.63	0.59	<0.11	3.72	7.1	1.42	1.6
Montmorillonitic raw clay	57.04	17.60	1.03	<0.11	3.146	9.938	1.47	8.00
Chalk	3.25	0.45	55.68	<0.11	<0.11	0.15	0.05	40.32

4. Methodology

The chemical analyses were obtained by the XRF analyses (Spectro IQ, Kleve, Germany, where a target material is a palladium, target angle 90° from the central ray and focal spot is 1 mm × 1 mm square, maximum Anode Dissipation 50 Watts with 10 cfm forced air cooling). The method for XRF-analysis uses pressed pellets and the proportion between analyzed material and binding additive is 4:0.9 (weight of powdered material to the weight of wax). In all analyses the HWC Hoechst wax (Germany) was used.

The terracotta material was analyzed by XRD analysis (Phillips Source Data, path 0.050, 2Th. angle range 3.0–65.0, Cu-lamp) to identify the type of the mineralogical composition.

4.1. Preparation of the reinforcement mass

The choice and quantity of the fillers were defined according to the composition of the original body detected by XRD analyses. The final composition of the reinforcement mass respects the generally dominant contents of silica and calcite. The combination of two clays gives color and rate of bonding agent (geopolymer) to fillers respect the porosity of the ceramic body.

The final geopolymer composite was formulated as:

28 wt.% of prepared matrix
72 wt.% of fillers mixture.

We found that for the perfect joint between the ceramic terracotta body and geopolymer composite presented combination, as result of experiment sets, of fillers is appropriate (color, porosity, appearance and chemical composition):

Silica sand (grade 0–0.4 mm) 72 wt.%
Chalk (powdered) 9 wt.%
Fired shale (powdered) 12 wt.%
Montmorillonitic raw clay 7 wt.%.

The geopolymer matrix composition in case of used clay mixture with chemicals and water was as follow:

Ratios in molar rates: SiO_2/Al_2O_3 2.65; Na_2O/Al_2O_3 0.67; H_2O/Na_2O 16.00.

In all geopolymer matrices and composites the content of water, generally calculated as H_2O/Na_2O ratio, is very important. If the support of the application of geopolymer mixture is porous (case of low temperature fired ceramic body – terracotta) the best way is to leave prepared composite for certain time (from 20 to 60 min according to the porosity) and let to start the poly-condensation. The water content is in that process captured (see Eqs. (1)–(9)) and could not be drained by porous support of application.

For this fact, the mixed mass was left for approximately one hour in rest after mixing, thus achieving an increase of viscosity through the poly-condensation mentioned above. After one hour the composite mixture was applied and molded. The subsequent setting and hardening started at the place of application. If the application had been done before the viscosity increased, the formed ribs or rims could have collapsed under their own weight, but if the application had been too delayed, the joining between the ceramic body and the geopolymer would not have been completed. The workable time is quite long – it could be several hours, and there is time to work it even in the case of complex application, the complete hardening occurs after 12 h.

5. Results and discussion

The prepared mass very well and easily penetrated the cracks and fissures of the ceramic body and joined them. Fig. 1 (below) depicts an example of a layer of the geopolymer composite binder joining two fragments of the original terracotta material. On this picture is possible to notice a marked difference in the shade of the cross-section as against the surface. The surface of the geopolymer mixture almost exactly corresponds with the color of the ceramic body which it joins, but the cross-section is considerably lighter. This can be explained by the movement of Fe^{3+} hydrated forms which are slowly carried by evaporating water and color the surface [7].

Fig. 1. The cross-section of the geopolymer joint between two ceramic–terracotta bodies.

5.1. The application of geopolymer composite

The sculpture was placed into a plaster bed and fixed in a metal frame, in which the whole object was laid face down. All fragments and damaged pieces of the rear part as well as all the fillers from the inner space were then carefully removed. Cleaning of the inner space from various kinds of fillers revealed that the main body of the sitting Virgin (Figs. 2 and 3) had probably been molded from one piece of compact clay. The inner clay material had been removed before the sculpture wad dried and fired. Due to the weight and size of the sculpture, this work had not been done properly, which had resulted in differences in the thickness of the ceramic body. This variation in the thickness was most likely the reason why the sculpture was damaged by cracking immediately after first firing at an estimated temperature lower than 800 °C. This estimation is based on experience of corresponding author – more than 30 years in ceramic industry and UN expertises all over the world and on supporting indirect data: black core, detection of albit by XRD analysis, porosity, and touch on surface. The fissures and cracks were identified in the whole structure inside the sculpture. The forms and types were typical for drying cracks which widen during the firing. Therefore, the inner filler (plaster–lime composition) was applied to promote the stabilization. The analysis of the fillers also identified lime-hardened rosin (a natural

Fig. 2. The sculpture before the restoration – front view.

Fig. 3. The sculpture before the restoration – rear view.

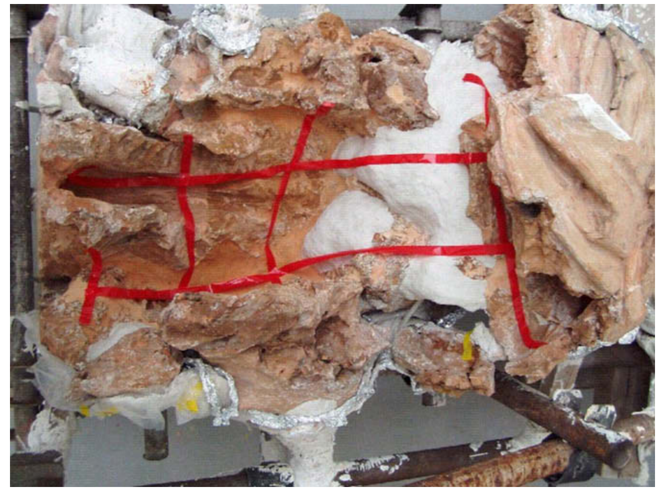

Fig. 4. The plan of the distribution of the ribs and rims.

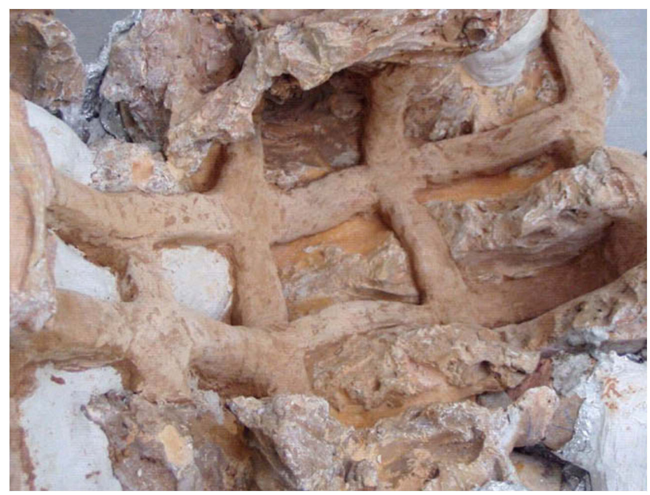

Fig. 5. The ribs of the geopolymer reinforcing the inner part of the front of the sculpture.

product commonly used as binding material in restoration works), which was very often used as a bonding agent in the past. A basic question after perfect cleaning of all types of fillers and armatures was to find a material which could stabilize the whole object and fix the outer modulation of the fractured lower and rear parts.

Apart from having a composition with similar porosity and silica sand/calcite proportion, the prepared geopolymer composite was also to match the color shade of the original ceramic mass part, which was predominantly ochre with different shades in different parts of the sculpture, which had been caused by differing temperatures during firing; it was unlikely for the temperature to be uniformly distributed throughout the kiln with the height of the sculpture being 1.42 m. As a result of the varying content of hematite corresponding to the varying firing temperature, the color varied from ochre brown to light red. The shade selected for the geopolymer composite was light ochre (the prevailing color of the inside) so as to approximate the shade of the inner part of the sculpture as much as possible. The Fig. 4 shows the plan of the distribution of the ribs and rims, originally marked by red plastic tape strips, later replaced by plasticine straps of 40×40 mm (long $\times$ high), which were subsequently filled with the geopolymer composite. Missing parts of the outer modulation and large cracks were, before the application of the geopolymer composite, replaced with plasticine (white spots on the left side in Fig. 5) to avoid the penetration of the geopolymer to the visible modulation of the sculpture.

The ribs were covered during the hardening at night (for approximately 12 h) by a plastic sheet to keep the necessary amount of water in the geopolymer composite, i.e. prevent the fast evaporation of water from the surface of the geopolymer. Fig. 5 below shows the hardened composite securely attached to the original terracotta material. The most important part of the stabilization, enabled by the behavior of the geopolymer, is connecting the already hardened part of the ribs with the freshly applied ones. The geopolymer then finally yields a construction of circular horizontal rims vertically supported by ribs, with the fragmented parts of terracotta firmly affixed to all of them.

Fig. 6 shows the upright sculpture while the affixation of the two bottom eagles is being prepared – two-thirds of the rims of the upper part, done before, are visible inside. The small white strip between the eagles' wings is the plasticine serving as a support for the geopolymer joining. The geopolymer composite does not react with the plasticine, which can thus be removed easily.

Fig. 7 shows the next step of restoration – the upright sculpture standing in a metal frame with the rear fragmented parts now attached and held in place by the geopolymer rims inside. This figure also depicts the heavy damage on the rear side and almost complete fragmentation, discovered after cleaning. It is also visible that several parts are missing, for instance the head of the right eagle. Also the broken bottom parts of the terracotta material, namely the "black core" inside the ceramic body, support the assumption that the firing temperature was low and unevenly distributed.

Fig. 6. View on the rear of the opened upright sculpture and preparation for the affixing of the bottom eagles.

Fig. 7. View of the rear of the upright sculpture – the affixation of the fragments.

A final look at the inner geopolymer stabilizing construction is shown in Fig. 8. The picture was taken before the restoration of the outer modulation began, which was carried out using traditional techniques. The opening on the side of the sculpture, under the sitting Virgin's shoulder shows the final stage of the horizontal, circular rims and vertical ribs perfectly joining the ceramic body and thus ensuring the stability of the object. The upper part of the picture shows the joining of the geopolymer bands going up to the neck of the sculpture.

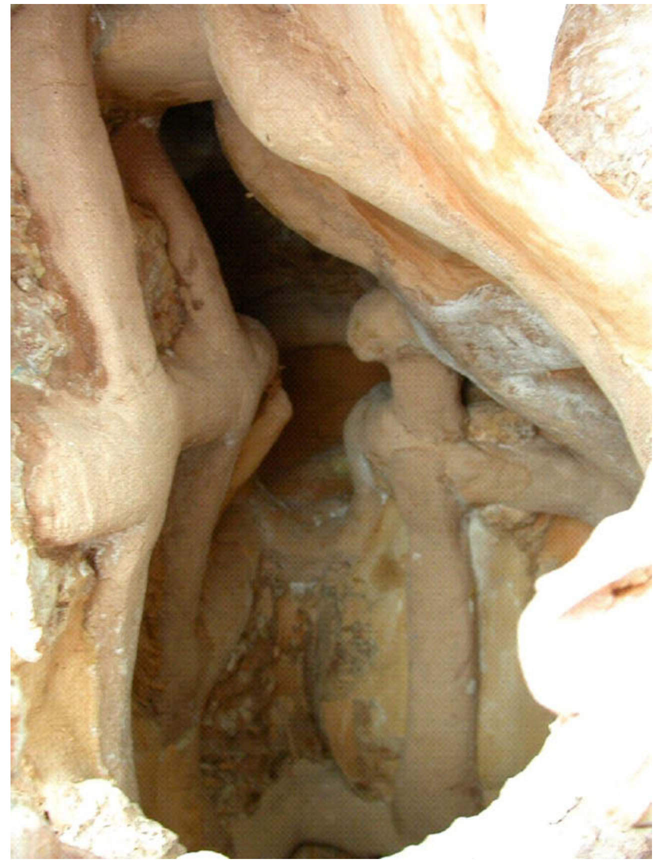

Fig. 8. Detailed view on the final stage of the geopolymer construction.

6. Conclusion

Presented paper declares and practically shows the application of geopolymer composite in a specific occasion – restoration of historical statue. The used geopolymer composite appropriate by the color and composition to the original ceramic body joints firmly even highly damaged parts of the statue. We confirm that quality and quantity of the fillers change the mechanical properties of the composite. The combination of additives could model materials with close similarity in color, porosity, mechanical properties, long term stability etc., to many different materials (e.g. sandstone, limestone, aranceous marl, ceramic bodies, etc.).

The hundreds theoretical studies on geopolymers report and present these materials as a new binding, cementious agent. These articles about the so-called material of 3rd millennium have essential deficiency – practically total absence of the industrial and restore applications.

The 3rd International Conference on alkali activated materials, held in Prague in June 2007 [8], presented only few semi-industrial applications even the main task of the conference was orientated on practical use and experience with geopolymer applications.

We could state that, according to our knowledge, there is no other application of the geopolymer composite in reinforcement of statues or restorer works as such. The wide and specific possibilities of geopolymer binder in combination with silica sand as a filler (depends on granule sizes, color and quantity) could save many sandstone statues and objects. We found that up to 92 wt.% of the sand is easily accepted and encapsulated in geopolymer matrix creating sandstone like material with its porosity, water and gas permeability but much more resistant to the acid rains and sulfur attack.

Even there is a hundreds articles (scientific and popular) about the advantages of geopolymer matrix and composites (price, environment protection, possibility in inhibition of heavy metals, resistance to the high temperatures up to 1200 °C and resistance to fire, etc.) – there is no answer about long term durability. The maximum experience is not longer than 50 years in case of experience of Gluchovskís Institute from Kiev (Ukraine) and the only long, long time experience could be found in similarities and specifications declared by Vitruvius Polio (more then 2000 years old) in its "Ten Books of Architecture" with material explanation done by Davidovits [9].

Reinforcement of the terracotta historical statue by the system of inner ribs and rims firmly joint with porous ceramic material is an extraordinary case of variability of the geopolymer composites. The collaboration of the scientific laboratory with The Academy of Fine Art on conservation and stabilization of the part of cultural heritage is not a common event. The case, where practically unknown technology for the restorers was applied on historical statue, is rare, but the result of the application is excellent.

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