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Case Study

Scientific studies on decorated mud mortar of Ajanta

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ABSTRACT

This study is an attempt to reveal the decorated earthen plaster of Ajanta. The mud plaster of Ajanta caves has been analyzed with the help of physical and analytical tools. The results indicate that high silt (>70%) low clay soil may have been mixed purposefully with lime (calcite) for the reason to enhance the cementing characteristics. The presence of calcium oxalate was detected from FTIR spectra may have been the resultant product of proteic materials presented in mud plaster. Ferrugineous silicate along with rarer gluconite–celendonite and white zeolites were also perceived from SEM and FTIR spectral analysis. The existence of quartz and sepiolite in mud mortar was also detected from XRD and SEM studies. The vegetal matter might have been added to tailor the construction behavior. The analytical results authenticate the similarity of earthen plaster of Ajanta and alluvion deposits of Waghura River just in front of caves, probably used as raw material in improvement of new material that suits for restoration for optimize performance and compatibility with the existing materials.

1. Introduction

Ajanta caves (World Heritage Site) have beautiful murals of 2nd BCE to 4th AD that represent highest point of artistic and technical achievement in India's greatest cultural fluorescence – the Golden Age (Walter, 2009). The present study approach to conserve the wall murals of Ajanta is based on proper understanding of materials, technology and causes of deterioration that favors minimal intervention and preventive conservation (Sharma, 2007). The conservation studies so far carried at Ajanta include monitoring of macro- and micro-environments of the caves, engineering geological surveys, rocks and minerals analysis (Sinha, 2010) along with bio-deterioration studies (Cacace et al., 2008). In addition the research investigations have also been conducted about the pigments and paintings technique at Ajanta (Artioli et al., 2008). As there is hardly any publication available on the materials and techniques used by ancient Indians to create Ajanta wall paintings, a dedicated investigation of material composition, structural support, plaster, paint layer, etc. is needed for better understanding.

Traditional mud plaster is made with soil composed of sand, silt and clay with straw sometimes added to prevent excessive cracking during drying. For earthen support to function well, an equal distribution of silt, sand and clay is desirable. Too much silt is neither a good binder nor an aggregate and produces a material that is prone to shrinkage and cracking. Clays also called phyllosilicates is a term related to grain size (<2 μm) and grain shape in most cases is that of a sheet much thinner

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than wider and attracted to one another by electrolytic forces (Basma Adnan et al., 1996). The non-clays are of grain size greater than clays and are generally divided into the grain size categories of silt (2–50 μm in diameter) and sand (50 μm–2 mm in diameter). Non-clays materials have relatively small attraction for water because of their small surface as compared to their volume and are also non-plastic. The non-clays grains are shaped in more irregular manner with grain to grain contact surface area is reduced and contact cohesion is much lower (Prost et al., 1998).

The clay minerals in general consist of equal parts of expandable clays (smeitite and mixed layer illite/smeitite) and non-expandable clays (kaolinite or chlorite) with minor quartz, calcite and feldspar (Smith and Austin, 1989). The expandable clay minerals are sticky than non-expandable clay and are effective in binding silt and sand particles together. In order to overcome the inadoptability of local resources, other materials are often added to the earth such as vegetal matter (Miller, 1934; Roberto, 1994) or calcite or perhaps lime (Jerome, 1993; Austin George, 1990). In this way the shrinkage of the clay is significantly reduced as calcite or lime may also serve as binder. However, possibility of using reactive fillers in earthen grouts has still not been fully explored. It has been observed that materials such as calcite, silica, ferric oxide, and so on. act like a cementing agent forming chemical bridges between clay micelles that may reduce swelling of clays (Forth, 1990). It has also been observed that some clay materials are generally frequented by zeolites, gluconites or iron oxide minerals indicating the existence of high silica activity in aqueous solution, affecting silicate crystallization. Iron oxides are also very strong coloring agent for clays. Besides, protein may react chemically by the process of exchange of inorganic cations in the clays with organic one – a mechanism relating to the ability of amino acids to encourage clay flocculation (Griffin, 1999).

This paper focuses on in situ examination of Ajanta painted plaster along with scientific investigation on its nature and characteristics. The analytical techniques used for characterization are optical microscopy, laser light scattering, polarized light microscope, scanning electron microscope, XRF, X-ray diffraction, FTIR, sieve analysis, etc. Some research was also carried in the field relating to earthen plaster and paint layer which has provided base for conservation in this specialized area of work.

2. Materials and methods

Particle size analysis by laser scanning was carried out for only a few representative sample of mud plaster of Ajanta. Understanding the characteristics and properties of earth as building material requires to go through range of analysis and test. In the present study particle size analysis, XRD, microscopy and thin section analysis were used to assess the mineral composition of earthen support and local materials at Ajanta. Aggregates in the earthen plasters were identified by dissolving the sample in 15% dilute hydrochloric acid and sieving it after complete dry. The aggregate components were subjected to petrological analysis to confirm their composition and grain size. The chemical composition of the plaster was analyzed through XRF for the range of samples extracted from different caves under geotechnical investigation of Ajanta caves. The components of the earthen plasters were also identified through XRD, SEM and FTIR techniques. CHN analyzer and microscopy were adopted to identify organic additives and performance characteristics were assessed through plastic and liquid limit testing.

3. Results and discussion

The chemical composition of mud plasters in the form of major oxides was determined using X-ray fluorescence spectroscopy. From the chemical analysis it is observed that lime has invariably been added to influence shrinkage of the local material that also acts as binder for the Ajanta's earthen plaster. The addition of lime into the mud plaster of Ajanta has also been confirmed by the reaction with dilute hydrochloric acid which gave effervescence. Calcite was probably added to overcome inadaptability of local resource material as it acts as cementing agent in the earth mixture forming chemical bridges (Rodríguez-Navarro, 1800). The remarkable color of the earthen plaster is due to the presence of iron oxide. It is also observed that in some of the earthen plaster more of the organic additives have been added since proteins can chemically react with clays (Theng, 1982, 2012). However, with time the proteineous material might has now been transformed into calcium oxalate which is also observed under the FTIR spectrum of Ajanta plaster. Besides, in most of the plasters organic fibers and seeds were admixed to improve tensile strength and reduce cracking.

The organic percentage of samples was determined by using carbon, hydrogen, nitrogen (CHN) analyzer. The combustion products (NO_2, CO_2, SO_2, H_2O) were separated by chromatographic column which was detected by thermal conductivity detector (TCD) that gave output signal proportional to the concentration of the individual components. From the result (Table 1) it is observed that proteic materials mixed with vegetal fibers and seeds have been added to the earthen plaster of cave No. 21 along with calcite. The calcite and proteic materials might have enhanced the binding properties of the earthen plaster of Ajanta.

The earthen plasters of Ajanta were observed under petrological microscope and the principal mineralogical components expressed were of Plagioclase, pyroxene, mica (tr), quartz (tr), and iron oxide. The earthen plaster by virtue of the exclusive prevalence of plagioclase associated with pyroxene indicates a composition of an 'eutectoid' nature, attributable to the original basaltic formation form which majority of the starting materials have been derived. With regard to traces of plaster of Paris in some samples, it may be due to its use in modern time for consolidation of decorated surfaces. Further, with regard to the presence of phyllosilicates, iron oxides and iron hydroxides in various samples, it is due to preparatory materials in clay which is made up of crystalline and amorphous phases rich in ferrous substances.

Table 1
Organic percentage of mud plaster sample.

Sample no.	7	8	9
Nitrogen	0.560	0.400	0.624
Hydrogen	1.38	1.561	0.958
Carbon	8.95	8.239	5.613
Total organic content	12.75	10.2	9.19

Four samples bearing No. 2, 5, 8 and 9 were subjected to particle size distribution characteristics by using laser diffraction analysis. Three trials for the measurement of the particle size distribution of each sample were conducted and average of the result was taken. The particle size distribution graph is shown in Fig. 1. From the graph it is observed that soil for earthen plaster of Ajanta is coarser than what was expected and contains far less clay size particles. Grain size analysis shows that majority of the materials are silt sized (>75%) followed by clay sized (about 15%) and then sand sized particles (9–15%). As more coarse grains are present in Ajanta earthen plaster, it shows a slight rigid behavior with tendency to deform by grain breakage. When clays are compacted in most dense manner, the porosity is near about 5–10% in most cases. With addition of high percentage of silt and low quantity of sand, the porosity of the earthen plaster has increased to about 20–25% with specific gravity about 2.70–2.90. As percentage of elements of <2 mm and that of elements <80 μm allow the assessment of overall texture of the mud plaster (Griffin, 1991), it can be assumed that earthen plaster is of medium texture. The particle size distribution or soil structure also precisely influences the humidity transfer (Kathleen, 1997). From the ternary diagram (not shown here) it is observed that silt loam soil probably from river bed of Waghura River was exploited for making mud mortar of Ajanta.

This finding clearly supports the idea that materials for mud plaster were chosen with great care and their properties modified. As the earthen plaster of Ajanta is characterized by high silt, relatively low swelling clay and low quantity of sand, to ensure maximum adoptability with the original material particle size analysis test was performed on the dry bed soil of seasonal Waghura River in front of Ajanta caves.

The river bed soil is mineralogically identical to the original mud plaster and shows similar particle size distribution. The revealing difference is that the earthen plaster contains about more than 70% silt. It is possible that Waghura river bed soil was most likely adopted for making earthen plaster of Ajanta or some other local soil was used that already contained sandy aggregates. Considering the external compositional similarity of raw material, it is recommended to use river bed soil for conservation by appropriately modifying its characteristics by adding other aggregates and organic binders to match the original. The finding clearly points to the fact that materials for mud plaster were chosen with great care and its properties modified and that the same care needs to be taken during conservation interventions. The finding also dispels the general concept that composition of these materials is random and the earth was dug as per convenient and made useable with little water and straw. Experiment conducted to determine the plastic limit of Ajanta earthen plaster show that due to low clay and high silt, the plaster is non-plastic.

The earthen plaster of Ajanta was subjected to aggregate analysis with dual purpose of its separation as well as characterization. For this, the mud plaster was dissolved in 15% hydrochloric acid and effervescence of reaction of calcite

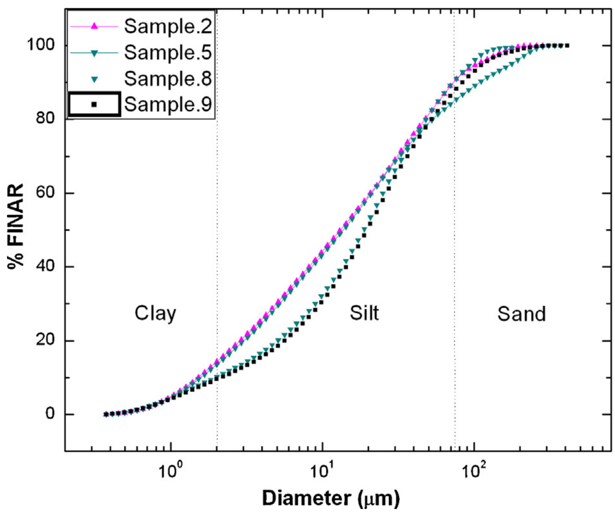

Fig. 1. Particle size distribution of mud plaster of Ajanta.

was observed. After filtration and drying the remaining samples was subjected to sieve analysis. Each of the components was further studied through petrological microscope and few components through FTIR spectrum. From the analysis it is observed that gluconites and zeolites were used as aggregates for making earthen plaster of Ajanta. However, addition of this material, as aggregate in mud plaster has seldom been reported.

Few fragments of earthen plaster were treated with 15% hydrochloric acid and effervescence was observed. The sample was washed with deionized water and dried at 70 °C. This sample was subjected to analysis by FTIR using KBr pellet. From the FTIR spectrum of the sample (not shown) the intense band of silicate around 1000 cm^{-1} indicates the gray preparatory layer mainly consists of silicate material. The characteristic band of calcium carbonate is absent in the spectrum. In another experiment, FTIR of fragment of earthen plaster was carried out without dissolution in dilute HCL. Fig. 2 shows the spectrum under FTIR for this sample. In this case also along with intense band of silicate, kaolin and band of calcium oxalate at 2900 cm^{-1} is observed. The weak absorption bands at 1400 cm^{-1} indicate the presence of small quantity of calcium carbonate. The calcium oxalate tends to indicate the presence of proteic material which functioned as binder for earthen plaster. Calcium oxalate is in fact the product of oxidative decomposition of organic materials. The bright green color inclusion separated through sieve analysis was also seen under FTIR. Fig. 3 shows the spectrum for the green inclusion. From the spectrum it is observed that green inclusion is made up of celandonite or gluconite abundantly found around Ajanta basaltic hills. Besides, in this spectrum peaks for proteic material (2900 cm^{-1}) and three amide bands at 1650, 1550 and 1450 cm^{-1} are present which confirms use of proteic binding material in the earthen mortar. The white transparent acute angled crystals of aggregate were also observed under FTIR which was recognized as zeolites as silica peak in the FTIR spectrum. This material was also found hygroscopic room temperature. Further, the vegetal fiber from the earthen plaster was separated and observed under FTIR. Small quantities of calcium carbonate are also seen to be present in the spectrum of vegetal fiber. The abundant presence of calcium oxalate in the earthen mortar is without doubt attributable to the organic binding material used in the preparation of plaster.

The mineralogical composition of earthen plaster was determined by using X-ray diffraction (XRD) spectrometer. The sample was scanned from 2θ ranging from 5° to 120°. The presence of minerals was confirmed with the help of data files presented by JCPDS 1994. The quantitative analysis of mineral phases in clay rich samples has always been subject to discussion. The X-ray diffraction studies of earthen plaster show the major component to be feldspar, quartz, calcite and sepiolite, a clay mineral in minor quantity. The quartz, feldspar and most of the clay minerals and some of the calcite are derived from mechanical/chemical breakdown of older basaltic rock. Sepiolite has fibrous or lath-like morphologies.

SEM images show inclusion of coarse black ferruginous silicate material (pyroxene and mica) along with green celandonite and white silica inclusion probably bound together with the proteic material of which the only evidence remains today is in the form of calcium oxalate. The small nuclei with abundant iron and magnesium associated with silicon and aluminum may be indicative of the dispersion of celandonite within the material. Fig. 4a–c attributed to quartz in the magnification of 100×, 400×, 1000× whereas in the magnification of 3000×, sepiolite (Fig. 4d) was also seen with fibrous structure in addition with quartz. The result correlates with the XRD studies. It is an interesting feature to notice the presence of sepiolite in the ancient mud plaster. In recent years, as for instance, sepiolite (Maritinez-Ramirez et al., 1995;

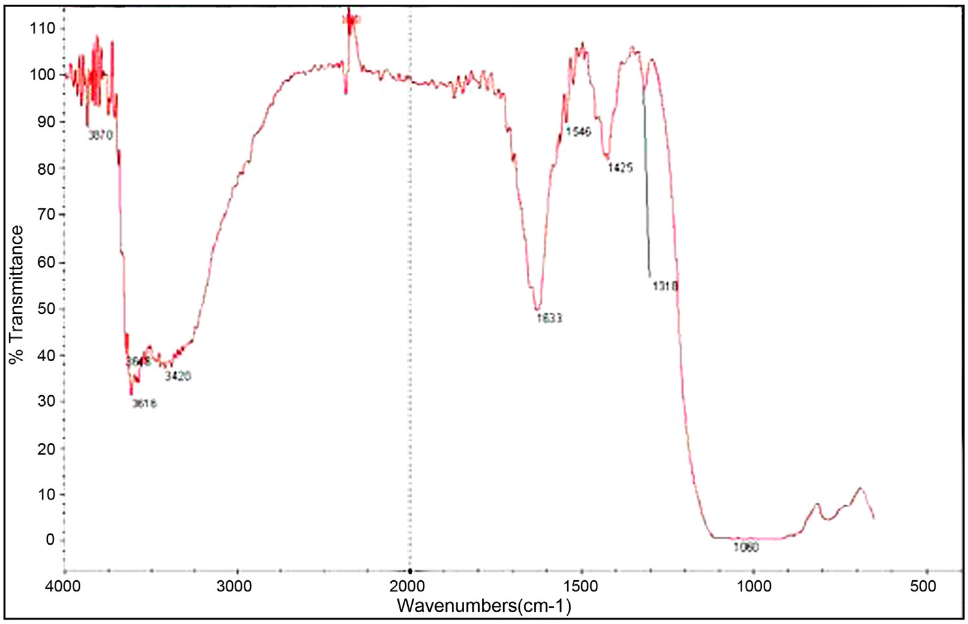

Fig. 2. FTIR spectrum of preparatory earthen plaster at Ajanta.

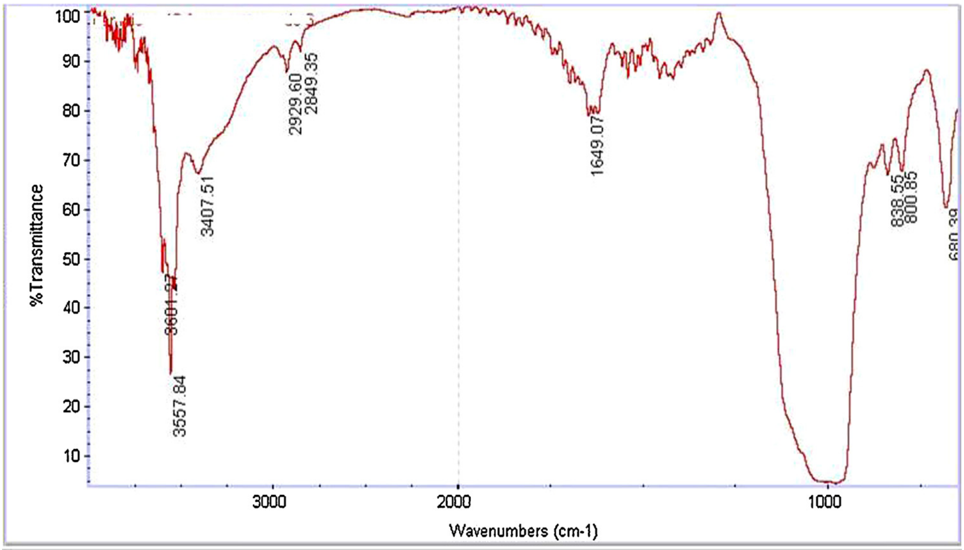

Fig. 3. FTIR spectrum of green color grain.

Andrejkovičová et al., 2011, 2012) has been added to mortars and cements to improve their characteristics. A recent study reported that the addition of sepiolite in the preparation of mortars for earth based walls restoration (Andrejkovičová et al., 2013). Addition of fine sepiolite, due to its adsorption properties for strong water for later supply to the mortar system and its micofibrous morphology, led to an improvement and flexural strength of blended air lime/air lime – metakaolin mortars,

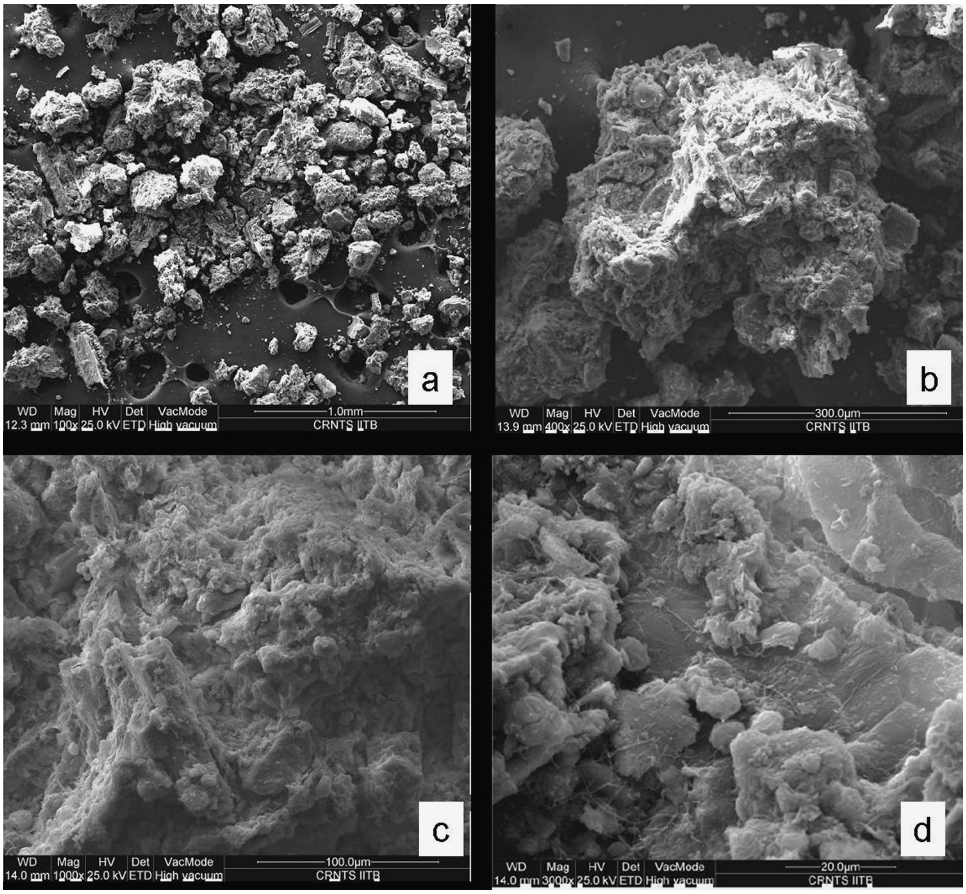

Fig. 4. (a–d) SEM image showing the structure of quartz and sepiolites.

especially at later ages of curing (Andrejkovičová et al., 2012). We may conclude that the addition sepiolite may be intentional to increase the performances of the mud plaster.

4. Conclusion

The earthen plaster of Ajanta is characterized to be having the ingredients of high silt and low clay content, the raw material for which was most probably taken from river bed of Waghura River. The performance of the plaster might had been enhanced by addition of organic additives and vegetal matter. A unique feature of presence of gluconites and zeolites in the earthen plaster has also been found. The earthen plaster is also characterized by addition of organic additives and vegetal matter. The earthen plaster is also characterized by deliberate addition of calcite to modify the properties of raw material and enhance its binding properties. It may be concluded that the addition of sepiolite may be intentional to enhance the performances of the mud plaster. This characterization has helped in the preparation of new earthen materials for conservation efforts at Ajanta for better compatibility and optimum performance.

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