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Aragonite–vaterite–calcite: Polymorphs of $CaCO_3$ in 7th century CE lime plasters of Alampur group of temples, India

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HIGHLIGHTS

- Presence of aragonite–vaterite–calcite: Polymorphs of $CaCO_3$ in the ancient lime works of Alampur.
- Occurrence of polymorphs may be either due to the biotic mineralization process or by self healing of lime in wet and dry cycle in presence of Mg.
- Sub-angular to sub-rounded, medium to low maturity sand and coarse silt aggregates were detected in the plaster.
- This study is crucial in evaluating the compatible materials in the conservation of built heritage.

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ABSTRACT

This paper study the occurrence of aragonite–vaterite–calcite: Polymorphs of $CaCO_3$ in the ancient lime plaster works of south India's Alampur group of temples that was under submerged condition due to past construction of Srisailam hydroelectric dam on Tungabhadra river just nearby the temples. For the proper examination of the Alampur plaster, we used analytical methods such as onsite observation, petrological thin section, XRF, XRD, FTIR, SEM – EDX and Raman Spectroscopy. The presence of polymorphs of $CaCO_3$ was confirmed through XRD, FTIR, SEM – EDX and Raman Spectra of the plaster. The occurrence of $CaCO_3$ polymorphs may be due to the action of invertebrates on initial submergence, self healing of the lime due to wet and dry cycle in the presence of Mg that promoted the formation of polymorphs. Microscopic mineralogical analysis showed mixing of sub-angular to sub-rounded, medium to low maturity sand and coarse silt character aggregates of silica rich lithology. The identification of phthalocyanine blue dye in the plaster by Raman spectroscopy may be part of present day rituals. This work is a holistic approach to find out the composition of ancient lime towards protecting the sand stone masonry of the temple by applying compatible lime plasters to arrest the deterioration.

1. Introduction

The lime plaster restoration works to our ancient architectural heritage demand advanced knowledge and better understanding about the building materials. The composition of historic mortars may often vary depending on the geological location and period of construction. The survival of ancient plaster works strongly depends on levels of alteration/ deterioration due to their high solubility in comparison to brick or stone. The plasters are mainly composed of binder; aggregate mixed with some additive, however, pure lime has been detected in some ancient plaster works [1]. The binder provides consistency to the plaster. Until the discovery of Portland cement in 19th century, lime was the main binder utilized for the preparation of mortar. Aggregates in the mortar/plasters are normally local sand or rock fragments of variable size and shapes generally found added. Considering the characteristics of both the components, the lime mortar is morphologically quite identical to sedimentary rock with carbonate cement. Hence, geological and morphological investigations are most appropriate device for the characterization of lime works.

A most reliable approach for the restoration and conservation of ancient mortars requires an advanced knowledge about its composition. Several reviews on the methodology used for the characterization of mortars have already been published [2,3]. However, the development of suitable repair mortar for historic monuments requires specific knowledge about chemical and mineralogical composition of ancient mortar besides information about mechanical and physical properties [4]. It has recently been suggested that mortars may be characterized either by their mineralogical

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composition or by micro structural appearance [5]. In contrast, an understanding of all physico-chemical property is found to be fundamental in better understanding of the mortar [6] especially, with regard to its composition. The mineralogical and chemical analysis of the mortars yield information about the characteristics of binders, the type and grading of aggregates and about quantitative composition of mortars.

Mortars with different binder types (like lime, gypsum or mud) have extensively been used in our historical buildings, but mortar with lime as binder is commonly encountered all over the country. Although sand has frequently been used as an aggregate in mortars, other materials (calcareous and other natural or artificial aggregate, like brick, stone fragments, pozzolana etc.) have also been widely employed [7,8]. The contemporary industrial and historic binders can be divided into two groups: - hydraulic and non-hydraulic. When water is added to hydraulic binder such as hydraulic lime or cement, C_2S (belite) and C_3S (alite) react with water and hydrated calcium silicate is formed, respectively. The carbon, sulphur and hydrogen are responsible for the binding properties of hydraulic composites as well as for their cohesiveness and strength. Mortars made with non hydraulic binders may also contains hydrated materials as hydraulicity can reside not only in the binder, but also in other mortar components such as aggregates, kiln fuel contamination or pozzolanic additions [9].

The superficial architectural modifications and restorations mainly introduced in the field of conservation in distant past, make difficult to distinguish the various construction steps taken for the structure stability besides hindering the identification of original mortars especially when identical binders and aggregates have been used. Estimation of proportions of binder/aggregate within mortars is commonly used to characterize them during conservation of monuments. This proportion depends not only on the historical period but also on the mortar type and its function [10]. Now different approaches are being considered by the researchers to characterize mortars from various point of view. However, the degradation of mortars and its composition, texture and physico-chemical characteristics have received much attention in recent conservation research, since it provides information about the proper synthesis of new compatible mortars for conservation purposes [11,12].

India has numerous monuments designed and carved with beautiful lime plaster works. These plasters, mostly made from locally available materials have stood destructive action of the nature to a large extent with a few exceptions on account of its unique characteristics. The conservation of these plasters for posterity and scientific methodology to understand methods and techniques of preparation of these simple materials are now attracting archaeologist and archaeological conservators in the Indian sub-continent. Although the plasters/mortars of many important cultures of the world have been investigated, very little work have been done on ancient Indian lime works as few published data is available [13–15]. Studies indicate that mortars have been prepared using any local available material at the construction site. The limestone (carboniferous, dolomite or perhaps even chalk) is said to have been burnt, slacked with water and stored for at least a month or perhaps as much as a year [16]. For building industry, lime was mixed with sand and organic additives in the preparation of plaster although at few instances pure lime has also been detected [1]. The preparation of sand used as filler to the lime used as binder differs in plaster of different periods and this has a direct impact on strength and durability of the plaster. It is interesting to study these wonderful building materials which were prepared with very simple technology but having many characteristic features far superior to that of cement. Another important constituent of plaster is the addition of organic additives, a feature still in use [17]. The various organic additives which were found mixed in ancient time in Indian sub-continent are rice husk, jute fibers, hemp, gum, glue, joggery and adhesive extract of many plants. These organic additives not only diminish chances of cracking of the plaster but also enhance their overall binding capacity. It is difficult to determine exact nature of these organic additives since it has altered much during course of time. Moreover, the overall concentration of organic additives varies not only in different archaeological period but also in different locations of the same monument.

Until 1980, the characterization of historic mortars was mostly based on traditional wet chemical analysis and interpretation of results was difficult. Later instrumented methods like optical microscope, X-ray diffraction (XRD), scanning electron microscope (SEM) coupled with energy dispersive X-ray spectroscopy (EDX), simultaneous differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) were extensively introduced for better characterization and examination of mortars [18].

Chemical and mineralogical characterization of plasters may also be used to understand chronological aspects of the evolution of historical mortars/plasters [19]. Several methods have been applied to answer questions related to formulation of repair strategies and replacement of mortars in built monuments as well as to gain knowledge about its provenance and technological interference [20–22]. This compositional approach has widely been used to characterize cultural heritage artifacts and also mortars for restoration and treatment work besides studying manufacturing technology and dating [23–26] specifically by using trace elements.

The temple town of Alampur (Fig. 1a) is situated in Mahabubnagar district of Telangana state, about 200 km from the famous city of Hyderabad. Alampur is the meeting point of sacred rivers Tungbhadra and Krishna at the western gateway of Srisailam, the famous shaivite pilgrim center. The uniqueness of the group of temples of Alampur lies in their plan and design which is north Indian architectural style (Fig. 2) introduced by the chalukyas of Bedami between 650 and 750 CE. As Alampur came under submergence due to construction of Srisailam hydroelectric project, many temples were transplanted at higher places.

On observation of causes of extensive losses of lime plaster from both exterior and interior of the group of temples at Alampur, it is observed that the area show high humidity in all the seasons due to construction of Srisailam hydroelectric project dam adjacent to the temple. Humid winds are lashing the temple causing physical and material deterioration of soft lime plaster. Even the inner part of the temple was found quite humid due to lack of proper ventilation. The unfavorable environmental conditions have also caused weathering and flaking of sandstone of the temple at some place and need conservation. To save the temple from further deterioration, it is proposed to re-plaster the temple with identical lime plaster compatible to the ancient plaster as superficial layer. Hence, a detailed investigation was necessitated to understand nature and composition of lime plaster so as to synthesize plaster using compatible materials and techniques.

Calcium carbonate is a major binder used in ancient Indian lime plasters. It has three anhydrous crystalline forms; calcite, aragonite and vaterite and, three hydrated forms, viz. amorphous calcium carbonate (ACC), monohydro calcite ($CaCO_3{\cdot}H_2O$) and ikaite ($CaCO_3{\cdot}6H_2O$) [27]. Calcite is the most stable polymorphic form whereas the least stable is vaterite [28]. Aragonite which typically appears as prisms of needle like crystals and vaterite, which tend to form polycrystalline spherulites, are metastable phases. The actual crystallization of $CaCO_3$ starts from thermodynamically unstable ACC, which crystallizes spontaneously when present in aqueous solution at ambient temperatures. ACC transforms to calcite via vaterite at low temperature (<30 °C) and to aragonite via vaterite at higher temperature ($\geqslant$40 °C) [29]. Aragonite is a carbonate mineral, one of the two common, naturally occurring,