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A petrochemical study of Mughal plasters of Quila-I-Ark, Aurangabad with respect to technology and repair

Abstract. *This paper reports the mineralogical composition of western India's 16-17th century Mughal plasters of Quila-I-Ark, Aurangabad to prepare compatible repair mortar and document ancient Indian lime technology. Analytical studies were undertaken for aggregate grain size distribution, thin section analysis, Fourier Transform Infrared Spectrometer (FTIR), X-ray diffraction (XRD), and chemical composition of the plasters by x-ray fluorescence (XRF analysis). The analysis revealed the inclusion of large size basaltic aggregate grains mostly sourced from the water channel of nearby Harsullake. Some of the plaster works show prominent inclusion of small size grains pointing different periods of construction. Creamy white zeolites were found specifically added in the mortar mix to maintain a certain level of humidity during the dry season. The zeolite is highly porous and breaks easily both in dry and wet conditions. The calcite rich limestone with traces of magnesium was sourced as raw material for the plasters. Based on mineralogical composition and binder/aggregate ratio, three phases of historical constructions were documented. FTIR and thin section analysis showed the mixing of some proteinaceous adhesive juice in the lime for improvement in rheological and waterproof properties. The high quantity of large size aggregate grains ensured better carbonation of lime and the source of aggregates remained the same for all phases of historical constructions. The cementation index (C.I.) and hydraulicity index (H.I.) vary between 0.10 to 0.96 and 0.20 to 3.43, respectively showing the plaster is aerial lime with traces of magnesium.*

The plaster is feebly hydraulic as the hydraulic component calculated varies between 0.88 to 6.10 percent in different samples. A moderate strength plaster with a lime/silica ratio close to 0.33 was prepared for most phases of construction except a few isolated locations. The analytical data will now help to prepare compatible mortar with identical additives for a major repair.

Keywords: *ancient mortar; aggregates; non-hydraulic; mineralogy; organic additives; provenance*

Introduction.

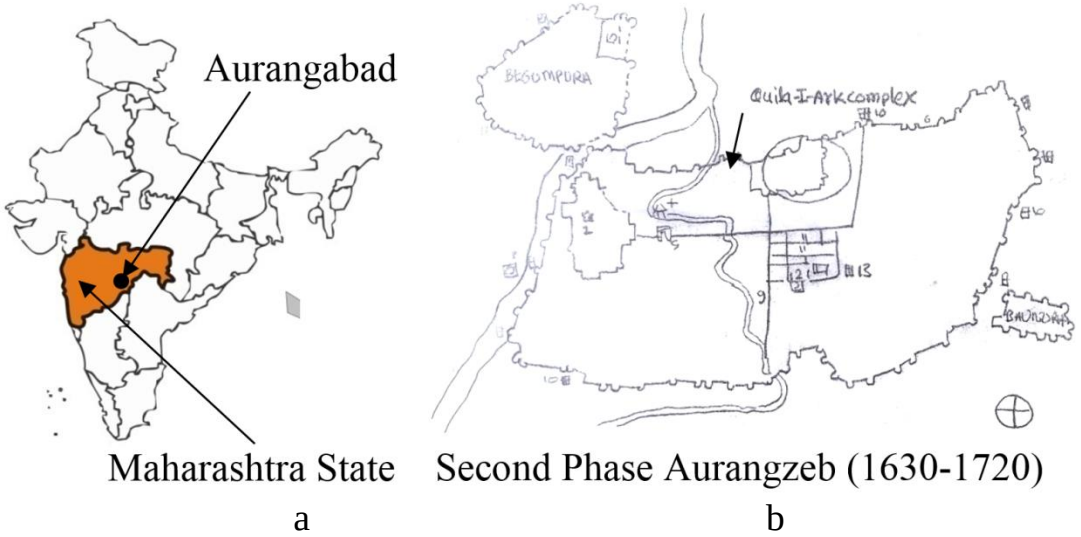
For architectural conservation of ancient lime works, a thorough knowledge of all the physicochemical properties of ancient lime is desired to prepare compatible repair mortar matching in composition & microstructural characteristics. The conservators of historic mortars try to gather information about mortar composition, possible causes of damage, and different phases of building constructions based on mortar characterization (Papayianni, 2009; Jedrzejewska, 1960; Cliver, 1974). The other important areas of investigations for the preparation of compatible repair mortars are the hydraulicity of the binder, the aggregate/binder ratio, the grading of aggregate grains, and their nature (Leslie & Gibbons, 1999). From the analytical reports on ancient mortars, the archaeologists particularly look towards the chronology and spatial distribution of raw materials and the final product to gather adequate information about the socio-economic conditions of the dynasty, the provenance of the raw materials and the process of burning and mixing of mortar ingredients (Leslie & Hughes, 2002; Viaene et al., 1997). Due to topography and uneven wall surfaces, very often the plaster is applied in thickness. This helps in the slow removal of water from the pores of stone/brick walls to save the inner building materials. Very often in historical periods, the plasters have been applied in several layers with a distinctive difference in the materials for each layer having different thermal and hygric expansion coefficients. The high percentage of open pores in mortar layers and high hygroscopicitycontribute to the removal of water from the underlying building materials. The porosity and pore structures in ancient plasters are related to grain size distribution and the binder/aggregate arrangements within the plaster. The size and distribution ofpores are also linked to the carbonation rate, dimensions of the calcite crystals, and those of aggregates. Lime mortar with large size aggregates shows better carbonation due to the easy accessibility of atmospheric carbon dioxide (Singh, Sanjeev, & Singh, 2020). In general, the porosity of ancient plasters and mortars varies between 20% to 45% in most cases. However, the high heterogeneity in composition and high porosity may also affect the durability of the plasters by making them easily attackable by external damaging agents. This further contributes to the deterioration of underlying building materials by stimulating access to damaging agents. The environmental deterioration of lime mortar is mainly caused by the chemical dissolution of micro-crystalline binding calcite when the pore dimensions are adequate. The calcium carbonate with its equilibrium pH of 9.93 is far from neutral. When in contact with water having dissolved

CO_2, the solubility of calcite will increase until reaching an equilibrium. Anydissolution of binder lime will further cause enhancement of porosity and permeability and a decrease in mechanical strength. The leaching of calcium salts from the plaster surfaces will also disturb the aesthetic look of the historical constructions. The burning of limestone and slaking conditionsin general play an important role in the reactiveness of lime and long-lasting slaking in the pits enhance durability (Davey, 1961; Boynton, 1966). From the analysis of many ancient Indian plasters & mortars of different archaeologist periods (Singh, Kumar, & Sabale, 2018; Singh, Waghmare, & Vinodh Kumar, 2014; Singh & Sharma, 1995; Singh, Ganorkar, Rama Rao, & Role of chemistry in archaeology, 1992), it appears that the technicians were well aware of the grading of aggregates (Malinowski, 1981; Baronio, Binda, & Lombardini, 1997; Malinowski, & Garfinkel, 1991), the proportion of lime to sand and selection of aggregates of suitable size and quantity as filler for plasterworks. To further improve the rheological, mechanical and waterproofing characteristics of the plasters, organic additives, vegetal fibers, animal hairs, etc. were also added as reinforcement in Indian plasters. The nature and type of inorganic aggregates found in Indian plasterworks are very diverse because they were selectively sourced from different geological formations including several types of sand resources and crushed rock formations etc. Any study on the mineralogy of the aggregates will reflect their geological origin and give valuable information about their provenance. The aggregates may or may not react with the binding calcite thus modifying the setting, aging, and hardening properties of the mortar. The historic mortars may be hydraulic or aerial binding lime depending on the amount, size, and characteristics of aggregate grains used as fillers. A great improvement in the mechanical property of the mortars was noticed on the addition of pozzolanic admixture in mortar mix (Singh, Sanjeev, & Singh, 2020) that may also considerably reduce the porosity of the plasters.

Until 1970–1980, wet chemical analysis was mostly used in the characterization of ancient mortars (Jedrzejewska, 1960; Cliver, 1974; Papayianni, Pachta, & Stefanidou, 2013). With the advancement of many investigative techniques, the mortar is now characterized by chemical and microscopical techniques that have refined our present understanding about its composition, original material, and possible provenance (Cuezva et al., 2016; Miriello et al., 2013; Schiavon & Mazzocchin, 2009). In the present work an attempt has been made to characterize the 16^{th}–17^{th}century lime plasters of the Mughal monument of Quila-I-Ark of Aurangabad, Maharashtra using petrological, chemical and instrumentation techniques of FTIR, XRF, XRD. The main purpose of this investigation is to prepare compatible plasters with identical aggregates and additives for major repair of the fort plaster.

Quila-I-Ark.

Aurangabad, the cultural capital of western India Maharashtra state is located in the Sahyadri hill range of the Deccan plateau (Fig. 1a). The world-famous rock-cut caves of Ajanta-Ellora is situated close to Aurangabad.



a b

Figure 1. Aurangabad, the cultural capital of western India Maharashtra: a – location of Aurangabad; b – fortification wall around Quila-I-Ark.

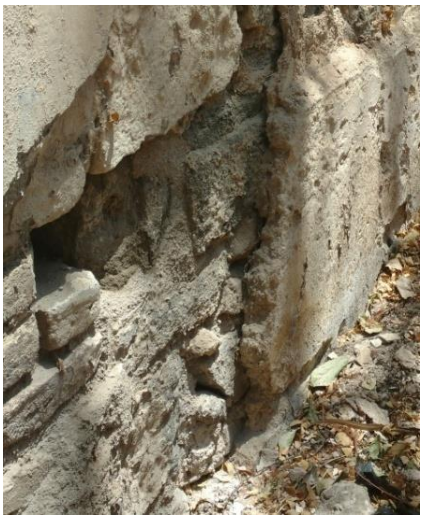
On appointment as viceroy of the Dakhan in 1653 for the second time, the Mughal king Aurangzeb made Fatehpur his capital and called it Aurangabad (Jayavanta, Patel, & Kamathe, 2015). On arrival ofShivajiMahraj in 1666 and Maratha warriors in 1682, a fortification wall around the city was constructed to protect from the sudden attack of Marathas (Fig. 1b). The Aurangzeb himself arrived in 1692 and ordered the construction of a magnificent palace to the north of the city near the great water reservoir, the ruins are now seen in the Quila-I-Ark. Shortly after the death of Aurangzeb, the Nizam-ul-Mulk arrived at Aurangabad in 1720 to establish his dynasty in Dakhanbut in around 1724 he transferred his capital from Aurangabad to Hyderabad (Beed district, 1969). During the political reign of Aurangzeb (1618–1707) various monuments and fortified Quila-I-Ark were constructed with three-layered moat walls for the city. The Quila-I-Ark was the court of Aurangzeb with several princes and noblemen in attendance and comprises of several structures like Diwan-e-Khas, MardanaMahal, Shahi Masjid, fortification walls, and five gates. The unplanned and hazardous developments around the fort complex and encroachment have now ruined the whole distinctive characters of the area. Many ancients structures have fallen or ruined due to the growth of trees and shrubs (Fig. 2). The ancient plasters are falling and building fabric is slowly collapsing for want of restoration.

Materials & Methods.

On visual inspection and observations under a magnifying lens, it is seen that lime plaster is applied in two layers. The inner thick rough plaster layer and outer smooth layer (Fig. 3).

a

b

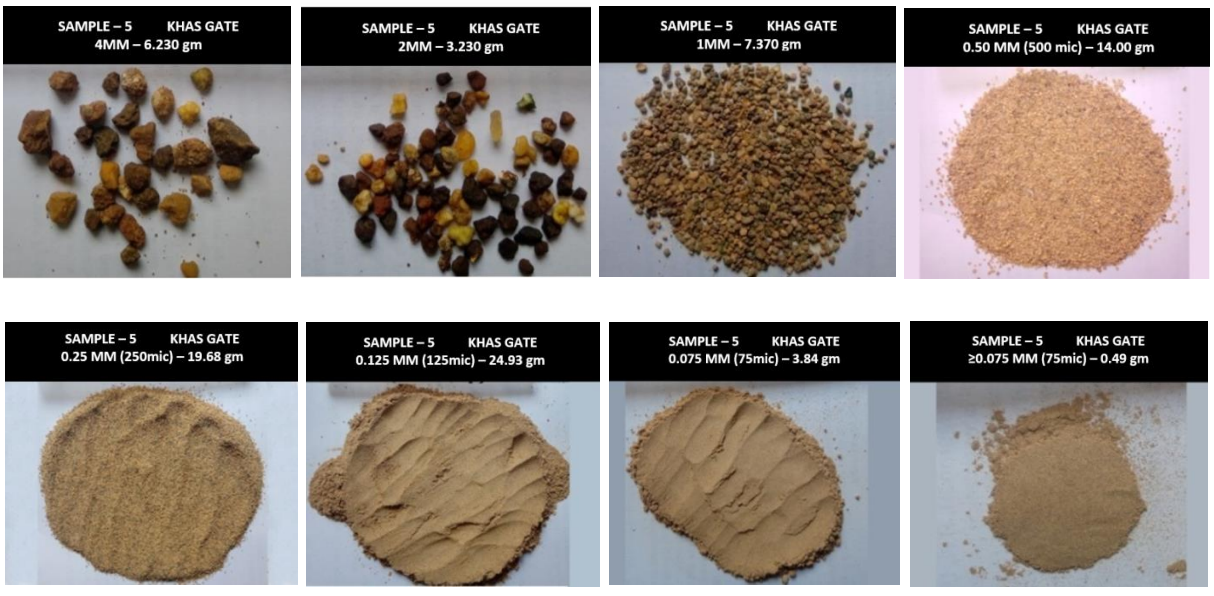


c

Figure 2. Quila-I-Ark: a – general view of Quila-I-Ark; b – growth of trees and shrubs on the monument; c – view showing layers of damaged plasters.


SAMPLE - 2 JANANA MAHAL
4 MM - 5.460 gm
SAMPLE - 2 JANANA MAHAL
2 MM - 5. 240 gm
SAMPLE - 2 JANANA MAHAL
1 MM - 8. 680 gm
SAMPLE - 2 JANANA MAHAL
0.50 MM (500 mic) - 17. 660 gm
SAMPLE - 2 JANANA MAHAL
0.250 MM (250 mic) - 16. 440 gm
SAMPLE - 2 JANANA MAHAL
0.125 MM (125 mic) - 12. 380 gm
SAMPLE - 2 JANANA MAHAL
0.075 MM (75 mic) - 4. 50 gm
SAMPLE - 2 JANANA MAHAL
⩾0.075 MM (75 mic) - 0. 310 gm

a


SAMPLE – 5 KHAS GATE
4MM – 6.230 gm
SAMPLE – 5 KHAS GATE
2MM – 3.230 gm
SAMPLE – 5 KHAS GATE
1MM – 7.370 gm
SAMPLE – 5 KHAS GATE
0.50 MM (500 mic) – 14.00 gm
SAMPLE – 5 KHAS GATE
0.25 MM (250mic) – 19.68 gm
SAMPLE – 5 KHAS GATE
0.125 MM (125mic) – 24.93 gm
SAMPLE – 5 KHAS GATE
0.075 MM (75mic) – 3.84 gm
SAMPLE – 5 KHAS GATE
≥0.075 MM (75mic) – 0.49 gm

b

c

d

Figure 3. Acid insoluble aggregates in the plaster samples: a – No. 2; b – No. 5; c – No. 6; d – No. 7.

The samples for analysis were collected from different locations of the monument as shown in table 1. These plaster samples represent different phases of the historic construction of the monument. The samples were collected from the edges of damaged plasters with the help of small chisel by rejecting any external contamination. The samples were immediately packed in a sterilized container for further laboratory investigations.

As no inclusion of calcareous grains as filler was noticed in the plaster, the aggregate analysis was performed by dissolving the known weight of the plaster in 25% dilute hydrochloric acid. The plaster sample was first gently broken using mortar and pestle taking due precaution not to break any aggregate grains. The sample was subsequently dissolved in 25% dilute hydrochloric acid and left overnight and filtered using a vacuum. The wet residue was again dissolved in hydrogen peroxide solution overnight followed by slow evaporation on a hotplate. The aggregate was washed with distilled water, centrifuged, dried at 105^0C, and subsequently weighed that gave actual sand content of the plaster. The insoluble residue was subsequently mechanically sieved with ISO565 series sieve. The sieved aggregates were used to estimate grain size distribution and grain shape analysis for the plaster.

Table 1. Showing the location of collected lime plaster samples.

Sample No.	The lime plasters samples for analysis were collected from the following points of Quila-I-Arch
1	Outer wall Shahi Masjid
2	Arched room at the wall near Jananamahal
3	Wall near Moti Masjid
4	Zebunnissa palace wall
5	Khas gate, Quila-I-Ark
6	Wall of Mardana Masjid
7	Wall of Moti Masjid

Due to the complexity and heterogeneity of historic mortars, the thin section is the first step for the mineralogical characterization of the plaster. The study of the polished section under the reflected light microscope is very useful in identifying many minerals & hydraulic phases. The preparation of fault free thin section of uniform thickness requires great precision. For thin section preparation, the sample was first dried at 80^0C to remove any entrapped moisture and to avoid the formation of microcracks during sample preparation. The sample was impregnated in low viscous resin under vacuum and a thin section was prepared for grinding & polishing to get a uniform thickness of 30mμ (Table 2). The thin section was observed under Carl Zeiss Jenpol polarising microscope. The thin section images were used for the petrological–mineralogical characterization of the mortar constituents as well as microscopic observation of different mineral phases in the matrix.

Table 2. Grain size analysis of lime plaster Quila-I-Ark (wt%)

Size	Sample 2	Sample 5	Sample 6	Sample 7
4 mm	22.26	22.88	6.230	5.46
2 mm	8.54	4.61	3.23	5.24
1 mm	7.36	4.38	7.37	8.68
500 μm	5.31	5.14	14.00	17.66
250 μm	3.41	8.04	19.68	16.44
125 μm	9.908	19.36	24.93	12.38
75 μm	6.320	8.25	3.84	4.50
≤75 μm	1.240	1.04	0.49	0.310

All the lime plaster samples were analyzed under Micro XRF (Artax 200 Bruker, Germany) at National Research Laboratory for Conservation of cultural property (NRLC), Lucknow. The instrument was operated at 50kV, 700mA current, and data collection time was 300 live seconds. At least four measurements were taken and the data averaged. The results are reported in table 3 in the form of major oxides. The hydraulicity index (H.I.) and cementation index (C.I.) of soluble silica of the plasters were determined as per equation suggested by Elsen et.al. (Elsen, Van Balen, & Mertens, 2012) and Boynton (Boynton, 1966), respectively. As reporting chemical analysis data in standard oxide form does not reflect the true nature of any plaster, it is essential to estimate the mineralogical composition of the plaster based on its chemical composition. In the present work mineralogical composition of plaster has also been evaluated from its chemical composition and data listed in table 4–6.

Table 3. Chemical composition of lime plasters Quila-I-Ark – Aurangabad (wt%)

Sample No	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	MnO	LOI	Total
1	41.59	6.08	3.96	24.22	2.78	0.23	0.19	0.09	0.69	0.06	19.34	99.23
2	45.41	7.77	6.62	18.24	3.01	1.45	1.04	0.99	0.42	0.13	15.33	100.41
3	08.03	2.38	1.81	45.86	1.88	1.05	0.84	0.04	0.28	0.04	37.75	99.96
4	07.09	1.56	1.32	48.20	1.38	0.03	0.79	0.03	0.56	0.04	38.82	99.82
5	59.54	3.71	1.03	17.21	1.66	0.30	0.45	0.08	0.12	0.03	17.21	101.34
6	60.15	4.91	0.52	18.43	0.71	1.18	1.24	0.12	0.07	0.02	13.57	100.92
7	56.91	4.63	0.53	18.83	1.72	0.12	1.05	0.06	0.07	0.02	15.78	99.72

The lime plaster samples were analyzed under fouriertransform infrared spectrometer (FTIR) (Model agilent 600) at the Archaeological Survey of India (ASI) laboratory at Aurangabad. The KBr pellet technique was used in the FTIR recording of spectra in the spectral range of 400–4000 cm^{-1}. The resolution of the instrument was 4 cm^{-1} and the number of scans was 32 within the standard wave number. The precision of the instrument was ±5 cm^{-1}.

The mineralogical composition was obtained by analyzing the plaster samples by X-ray diffractogram (Model PAN analytical X per PRO). The single-crystal X-ray diffractogram was operated at 40 keV, 40mA current using Ni fitter with an optimized diffraction angle at 50–90^0 (2θ). The XRD analysis was performed at the advance instrumentation center, IIT, New Delhi.

Table 4. Aggregate and a soluble component of the plaster (in percentage)

Sample No.	Acid soluble component	Insoluble HCl	Total	Cementation Index (C.I.)	Hydraulicity Index (H.I.)
1	46.60	52.63	99.23	0.69	1.91
2	39.40	60.89	100.29	0.96	2.81
3	86.89	13.50	100.39	0.11	0.26
4	85.90	12.25	98.15	0.10	0.20
5	33.56	64.86	98.42	0.45	3.41
6	32.45	67.23	99.68	0.61	3.43
7	36.85	63.15	100.00	0.41	3.02

Table 5. Hydraulic and other components of the plaster (in percentage)

Sample No.	MgCO3	Hydraulic	$CaCO_3$	Quartz	Non-hydraulic	Total
1	5.83	6.10	35.91	23.45	29.18	100.47
2	6.35	5.94	27.27	23.99	36.90	100.45
3	3.94	0.88	81.09	2.68	11.82	100.41
4	2.90	1.46	83.76	0.47	11.78	100.37
5	3.48	2.82	28.28	51.40	13.16	99.14
6	1.49	4.32	29.06	47.78	18.45	101.10
7	3.60	2.30	31.57	48.37	14.78	100.62

Table 6.% mineralogical composition of the plaster

No.	R_2O_3	N-H R_2O_3	SiO_2 Ins_{HCl}	$CaCO_{3+}$ $MgCO_3$	CaO/ SiO_2	MgO/ CaO	CaO_{Silic}	CO_3^{2-}
1	51.63	0.56	0.79	41.74	0.58	0.11	3.55	25.71
2	59.8	0.62	0.75	33.62	0.40	0.16	2.97	13.09
3	12.22	0.97	0.59	85.03	5.71	0.04	0.44	28.82
4	9.97	1.18	0.58	86.66	6.79	0.03	0.73	29.90
5	64.28	0.20	0.92	31.76	0.29	0.10	1.41	11.51
6	65.58	0.28	0.89	30.55	0.31	0.04	2.16	11.56
7	62.07	0.24	0.90	35.17	0.33	0.09	1.15	12.53

Results and Discussion.

1. Aggregate Analysis.

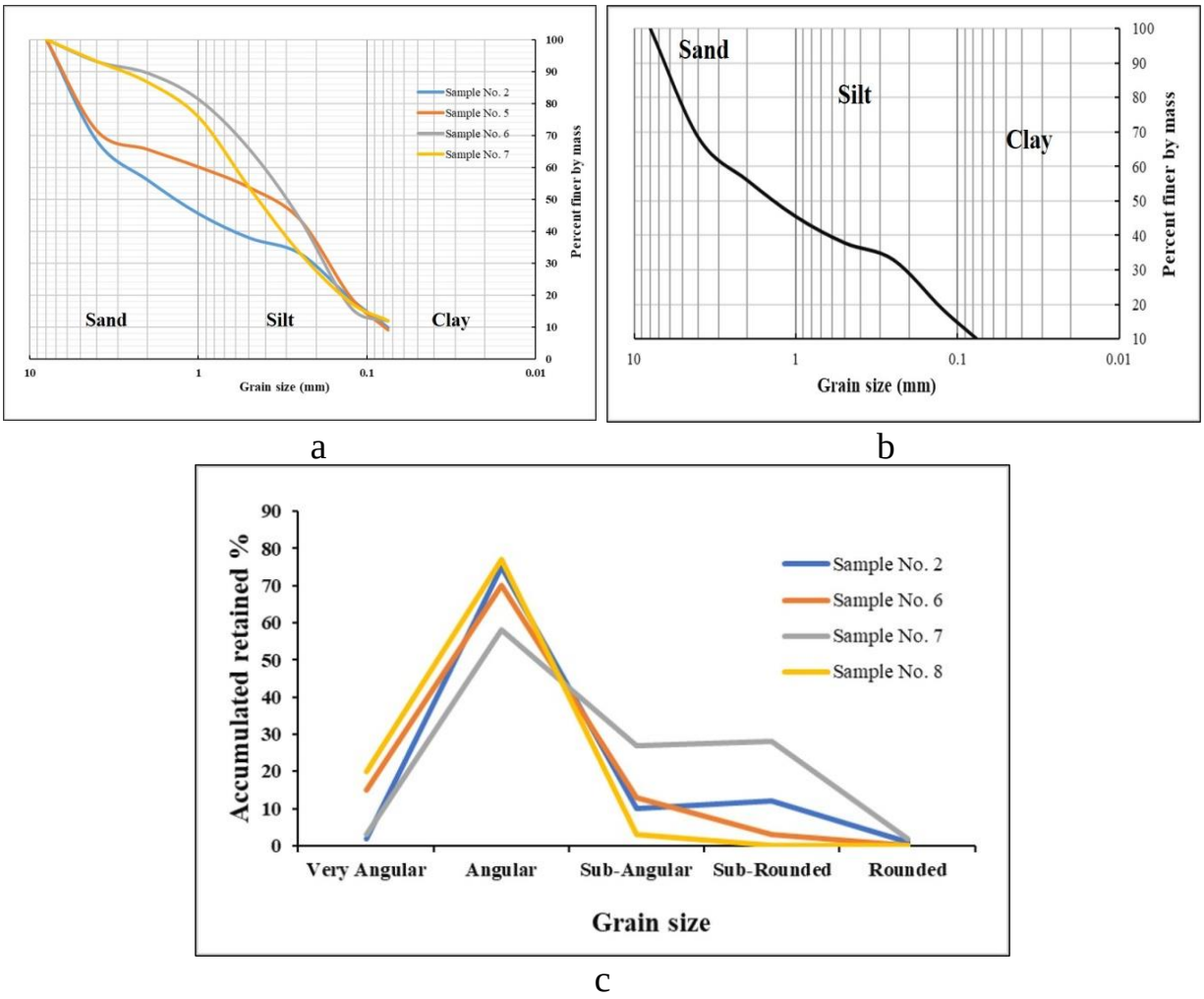
The acid-insoluble part of the plaster was mechanically sieved to examine the size of the aggregate grains.The plaster samples 2, 5, 6, and 7 were subjected to aggregate analysis, and insoluble fractions separated through sieve analysis are shown in figure 3. All the samples showed coarse to medium grained inclusion of aggregate grains as filler. The coarse grain aggregates vary in size from 4 mm to 1 mm and mostly derived from weathering of basaltic rocks of local origin. From figure 3 it is observed that all the fort plasters were preferably mixed with greyish brown, light brown to creamy white colored unsorted aggregate grains of local origin. The creamy white aggregates soak water and changes to reddish-brown color. The creamy white aggregate also crushes very easily both in dry & wet conditions and shows porous nature. Aurangabad and its surrounding are the dry regions of Maharashtra having acute drinking water deficiency. The climate is mostly dry with day temperature reaching up to 38–40^{0}C in the summer season. The hot climatic condition may desiccate the lime works of the region and cause loss to the plasters. It appears that the technicians deliberately added the hygroscopic creamy white porous aggregates to retain moisture for the long survival of plasterworks. The increased moisture in the plaster has also facilitated a better carbonation reaction. The creamy white aggregates have been identified as zeolites of local origin (Singh & Arbad, 2015). All the aggregate grains mixed in the plaster are the decay product of amygdaloidal basalt of light brown to reddish-brown color. The other finer fragments of aggregate grains are in the size range of 500 to 75 micron with particles < 75-micron size is very less in the quantity (Fig. 3).

The amount of various size aggregate grains is shown in table 2. As the Quila-I-Ark was constructed in different historical periods, we find non-uniformity in the number of aggregate grains mixed in plaster works. Wherein samples 2 & 5 showed large addition of big size aggregate grains (1 mm – 4 mm) mostly in the range of 31.87– 38.16 wt%,the plaster samples 6 & 7 show high addition of aggregate grains in the size range of 125 to 500 micron (58.61 to 46.48 wt%). The addition of a varied quantity of aggregates grains of different grain sizes indicates different phases of construction though the source of aggregates remained almost the same. It is also observed that in the majority of the cases aggregate grains mixed during the plaster preparation vary from 64.33 to 79.77 weight percentage per 100 gm of plaster sample.

2. Granulometric Analysis.

The grain size distribution is a powerful tool to describe site geomorphic settings, interpretation of fluid dynamics in the natural environment and to distinguish local sediment transport mechanisms (Huggett, 2007). Grain size analysis also helps to understand the size and shape of aggregate grains, the source of aggregate grains, depositional environment, and provenance. The grain size distribution of plaster samples 2, 5, 6 & 7 is shown in figure 4(a-b). The majority of the grains are of coarse sand to medium silt size and the percentage of clay size grains is very negligible. This

indicates that the inner plaster layer is mostly rough with coarse size aggregate grains of local origin. The coarse grains have helped in better carbonation of lime besides increasing mechanical property. From the grain shape analysis of the plaster (Fig. 4c), it is observed that the majority of the grains are angular to sub-angular with very angular to sub-rounded grains quite less in the plaster.



a b

c

Figure 4. Characteristics of the composition of plaster: a – grain size distribution of the plasters; b – average of grain size distribution; c – grain shape analysis of the plasters.

From the microscopic view of the fort plasters, it is observed that aggregate grains were derived from weathered basaltic rock of Sahayadri range of hills. The source of sediments is in-situ deposits of local origin probably sourced from the water channel of nearbyHarsullake situated at the foot of the hills near the fort. The aggregates were probably surface in-situ deposits of water channel originating from the surrounding basaltic hillock. The aggregate grains show angular to sub-angular shapes denoting that the sediments have traveled less distance from their source of origin. The sediments belong to fluvial in origin and traveled to short distance as no round-shaped grains identified. Microscopic observation of sediments shows the major presence of

plagioclase, orthoclase, and silicate minerals. This indicates the basalt as the pre-existing rock.

3. Thin Section Analysis.

The thin section analysis of plaster samples 2 & 3 is shown in figure 5(a-f).

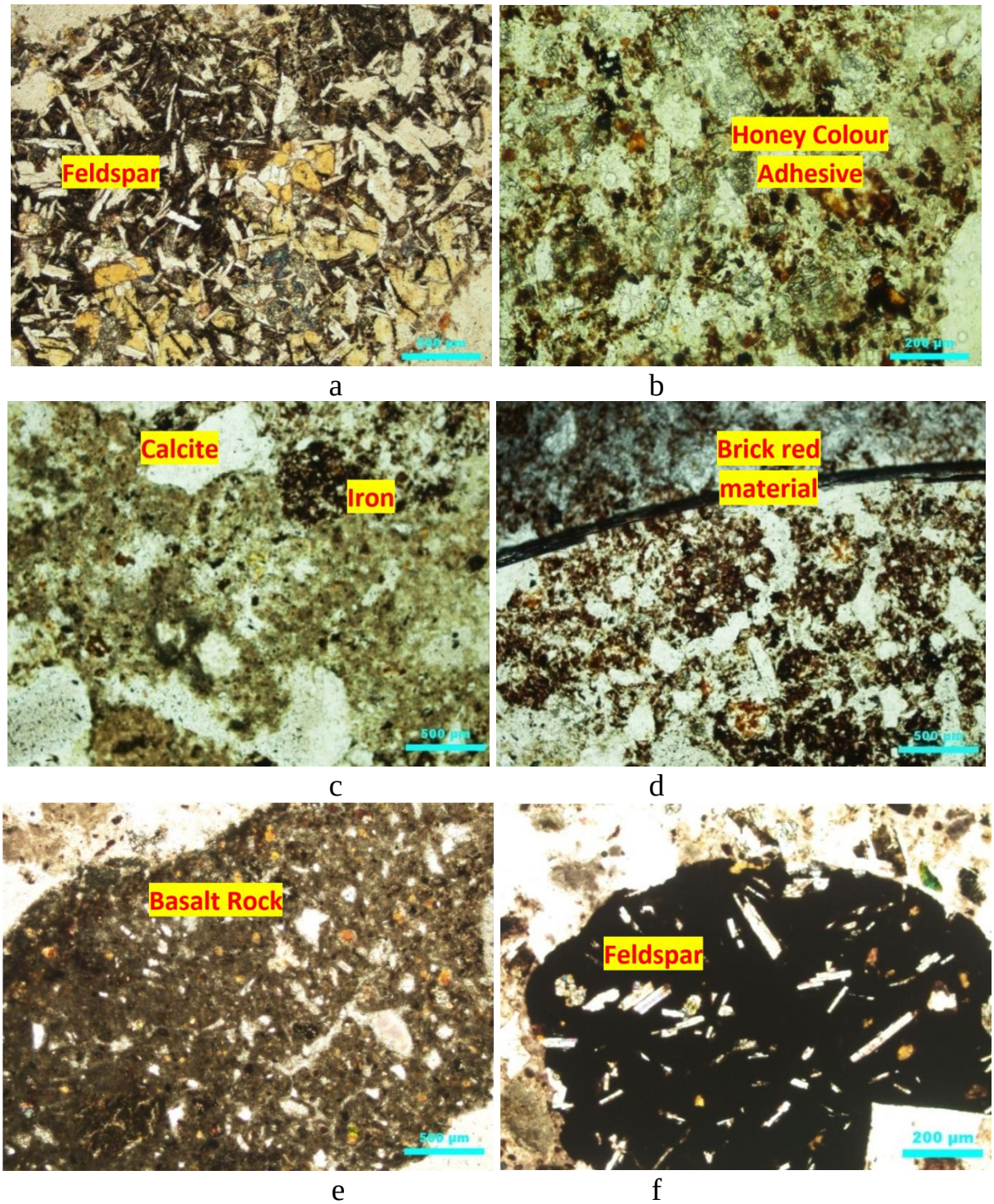


Figure 5. Thin section analysis of plaster:a-d – sample No. 2; e-f – sample No. 3.

Calcite is the main binding material for the plaster and figure 4c shows the calcite grains in the plaster. The calcite is white buffy to crypto-crystalline under a thin section. An opaque brown iron oxide mineral in the thin section is seen forming part of cementing material. Figure 5(a, e, f) shows the abundantly present feldspar grains of basaltic origin as aggregate in the plaster. Most of the grains are plagioclase feldspar distributed in the calcite matrix. Fig. 4b shows a honey color organic additive mixed in the plaster.

The presence of organic adhesive in the plaster was also confirmed through FTIR analysis. Figure 5d shows the presence of a brick red color material in the plasterworks which could not be identified. The plaster is mainly composed of calcite, feldspar, and local origin basalt rock aggregates. Calcite is the ground matrix in the plaster.

4. Chemical composition of the plasters.

The chemical composition of plaster samples 1 to 7 is shown in table 3 in the form of major oxides (wt%). From the wt% of silica three phases of historical construction for the fort are estimated. Samples 1 & 2 show silica in the range of 41.59–45.41wt%, in sample 3 & 4 silica wt% is 7.09–8.03, and in the rest of the samples, the SiO_2percentage is in the range of 56.91 to 69.15 wt%. The samples showing low content of sand is also marked by high wt% of CaO. The CaOwt% in samples 1 & 2 is between 18.24–24.22, sample 3 & 4 is 45.86–48.20 wt% and in samples 5–7 between 17.21 to 18.83 wt%. There is considerable wt% of alumina denoting the addition of aggregates rich in plagioclase feldspar. The iron content found in the plaster is between 0.52 to 6.62 wt% due to the addition of ferruginous sand as filler for the plasters.

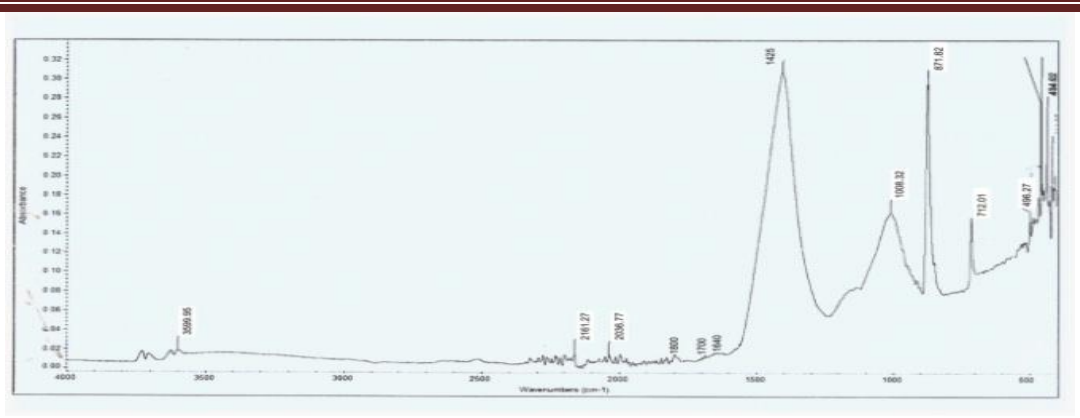
Since chemical composition does not give desired information about the nature and characteristics of binder & fillers in the plasters, a detailed mineralogical composition was sought. To derive the mineralogical composition of the plasters based on chemical composition data, the modified three equation system suggested in the literature was used (Singh, 1993; Charola et al., 1984).

The plaster samples were sprayed with phenolphthalein indicator and no color change was noticed indicating the absence of any uncarbonated lime. The hydraulic silicate present in the plaster was differentiated from the non-hydraulic by dissolution in 1:4 HCl solution and the value is shown as $Ins._{HCl}$. The loss on ignition (LOI) of the plasters was used in the calculation of calcium and magnesium carbonate. It was assumed that traces of magnesium present in the plaster has completely carbonated. The cementation index (C.I.) and Hydraulicity index (H.I.) of the plaster are shown in table 4. The various components of the plasters obtained through the three equation systems are shown in Table 5–6. SiO_{2flux} corresponds to all hydraulic (H) and non-hydraulic (N.H.) components. CaO_{silic} is the calcium bound to hydraulic silicate. The non-hydraulic components are the main source of iron and alumina in the plaster and the ratio of $N\text{-}H/R_2O_3$almost gives a constant value for most of the samples. This indicates that the source of non-hydraulic components for the Quila-I-Ark plasters remained almost the same in different phases of construction. The ratio of SiO_2/Ins_{HCl}

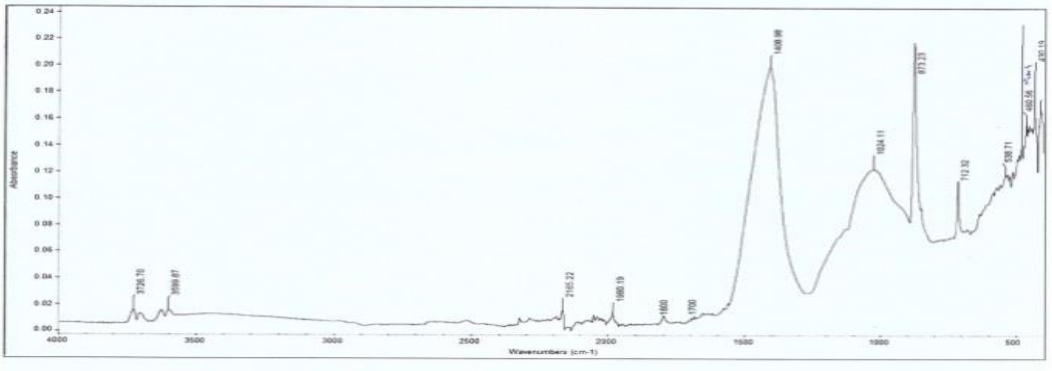
varies between 0.58–0.92 further confirming the source of aggregates for the plasters remained the same. The R_2O_3 content of the plaster (Table 6) samples 3 & 4 is the minimum (9.97–12.22 wt%) indicating preparation of low mechanical strength plaster vulnerable to damage. These samples also show high content of $CaCO_3$ + $MgCO_3$ as the values lie between 85.03–86.66%. The CaO/SiO_2 ratio of the plaster samples 1, 2, 5, 6 & 7 varies between 0.29 to 0.58and in most cases close to 0.33 for a moderate strength plaster. Sample 3 and 4 show the low addition of filler in the lime mix. The MgO content in the plaster varies between 0.71 to 3.01 wt% (Table 3) showing the use of carboniferous limestone with traces of magnesium as raw material for the plaster works. The hydraulic component in the plaster (Table 4) varies between 1.46 to 6.10% indicating the plaster as mostly non-hydraulic. The cementation index (C.I.) for soluble silica (Table 5) varies between 0.10 to 0.96 and the low value indicates formulation of non-hydraulic aerial lime for fort plasterworks. The hydraulicity index (H.I.) value of the plaster is quite low indicating the use of aerial lime. The quartz content of samples 3 & 4 is very low (0.47 to 2.68%) indicating preparation of low mechanical strength plaster in some phases of historical construction (Table 5). The plaster with less amount of silica also shows low content of non-hydraulic aggregate and a high amount of lime that leads to the preparation of plaster of low mechanical strength. The value obtained for CO_3^{2-} showed a large variation for sample 3 & 4 compared to other samples (Table 6). The MgO/CaO ratio lies between 0.03 to 0.11(Table 6) indicating the use of carboniferous limestone with traces of magnesium as raw material for the plaster.

5. FTIR Analysis of the plaster.

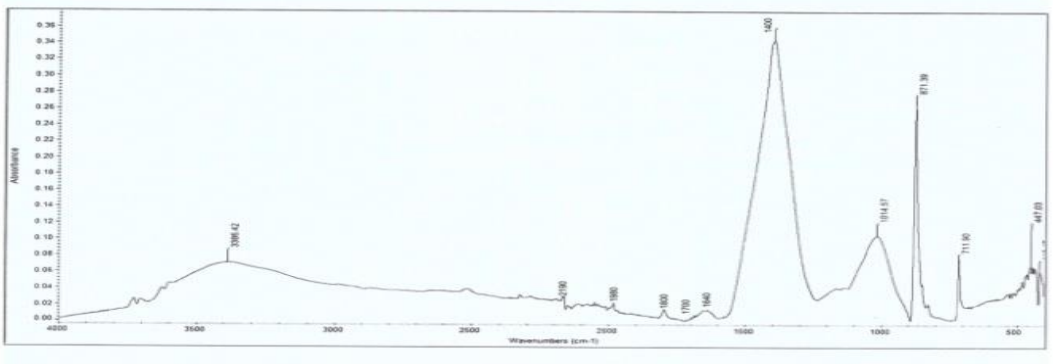
The lime plaster samples 2, 3, 5, 6 were observed under Fourier Transform Infrared Spectrophotometer for qualitative information about the functional groups in the plaster, and the spectra are shown in figure 6. The peaks around 3400–3600 cm^{-1} is mostly due to OH stretching and bending vibrations of hygroscopic water. The most characteristic peaks of calcite are observed at around 712, 872, and 1400 cm^{-1} in the spectra. The characteristic band of silicates is observed between 1008–1024 cm^{-1} in the plaster. A small peak at around 1640 cm^{-1} is observed in the spectra representing the amide group. The peaks around 1640 cm^{-1} point towards the addition of proteinaceous organic adhesive mixed during the plaster preparation. The FTIR analysis correlates to the thin section analysis of the plaster wherein honey color adhesive material was observed. The peak around 1800 cm^{-1} is that of calcite. Two very small peaks centered around 1980 cm^{-1} and 2165 cm^{-1} are observed in all the samples representing the presence of =C-C bending and C=C stretching respectively. These may be due to the presence of aromatic groups in the plaster as part of the addition of some adhesive materials as we also find a very small peak at around 1700 cm^{-1} in the samples. The peaks around 496 cm^{-1} and 432 cm^{-1} represent iron mineral derived from the addition of ferrugineous aggregate as filler in the plaster.



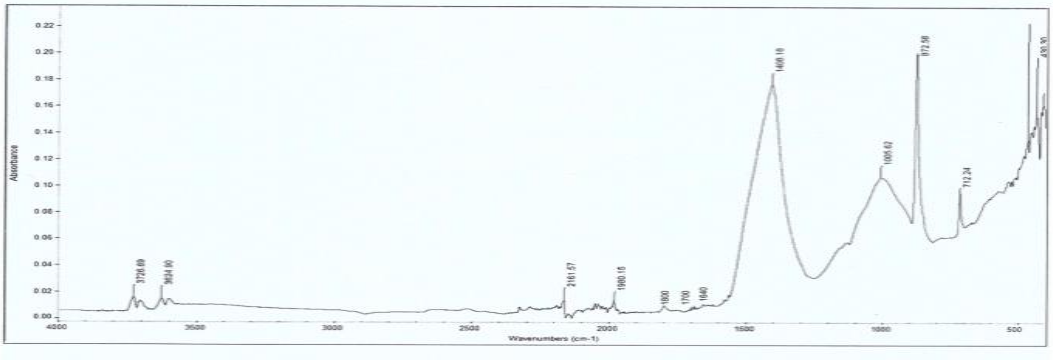
a



b



c

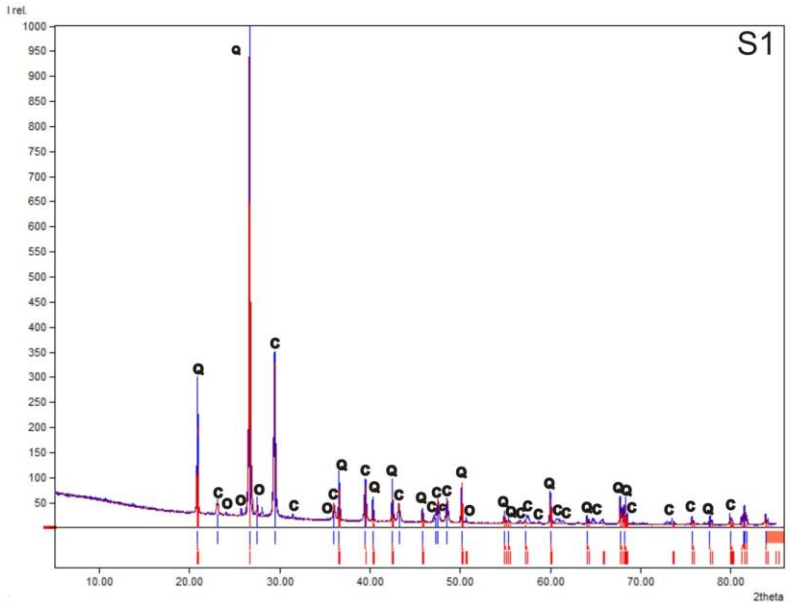


d

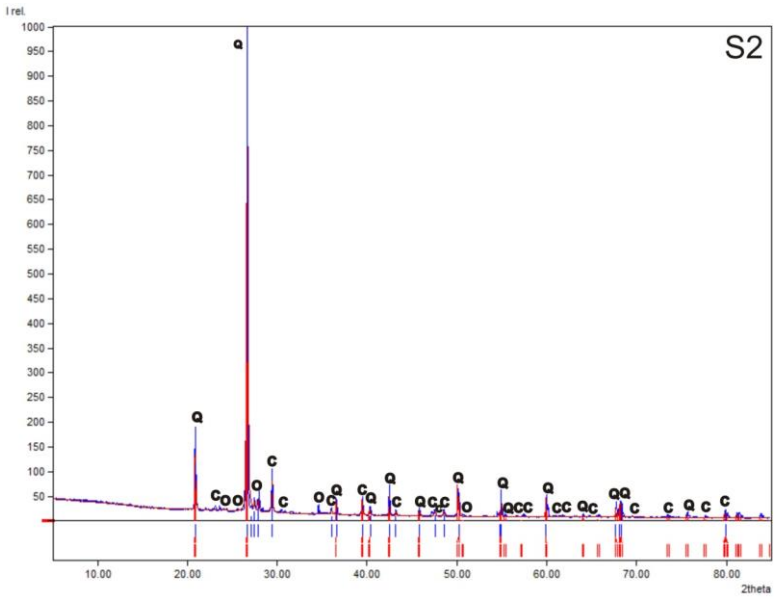
Figure 6. FTIR spectra of lime plaster sample: a –No. 2;b – No. 3;c– No. 5;d– No. 6.

6. XRD Analysis of the plasters.

The XRD analysis of plaster samples 1 & 2 is shown in figure 7(a&b). From the XRD pattern of the sample, it is observed that binding material for the plaster is represented by calcite. The small quantity of dolomite analyzed by chemical analysis of the plasters could not be recognized in the XRD pattern due to its poor crystallinity (Boggs, 2011). As the plaster of Quila-I-Ark is feebly hydraulic no peaks for calcium silicate hydrate and calcium aluminate hydrate could be observed. The other important peaks observed in the diffraction pattern are quartz and orthoclase. The plagioclase feldspar is due to the addition of basaltic aggregate in the mortar mix. The XRD pattern of the plasters supports the thin section analysis.



a



b

Figure 7. XRD pattern of lime plaster samples:a – No. 1;b – No. 2.

Conclusion.

The lime plasters of Quila-I-Ark were analyzed with the purpose to prepare compatible repair mortar. Analytical data revealed at least three phases of historical construction with contrast variations in a binder to aggregate ratio. The fort plasters with high calcite content and less of aggregate were weak and found extensively damaged. The mineralogical composition indicated that the source of aggregate for the plaster works remained the same, however, the quantity of filler varied in various phases of construction. The plaster is aerial lime of very low hydraulicity and inclusion of coarse size aggregates ensured better carbonation. Creamy white color zeolites were particularly added in the plaster mix to maintain humidity in the dry season. The aggregates are weathered basaltic stone grains mostly sourced from the water channel of surrounding Sahyadri hills. The analytical data will help to prepare compatible plaster for major restoration.

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Declaration of interest.

The authors declare no conflict of interest.

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Нафтохімічне дослідження Могольських штукатурок Кіла-Е-Арк, Аурангабад, з точки зору технології та ремонту

Анотація. *У цій статті повідомляється про мінералогічний склад штукатурок Великих Моголів в Західній Індії 16–17 століть з Кіла-Е-Арк, Аурангабад для приготування сумісного ремонтного розчину і документування давньоіндійської технології виробництва вапна. Були виконані аналітичні дослідження для вивчення розподілу зерен за розмірами, аналізу тонкого*

перетину, інфрачервоної спектрометрії з перетворенням Фур'є (ІЧСПФ), дифракції рентгенівських променів і хімічного складу пластів за допомогою рентгенівської флуоресценції. Аналіз виявив включення великогабаритних зерен базальтових частинок, що надходять в основному з водного каналу озера Харсул, який знаходиться поблизу. На деяких штукатурках видно включення дрібних зерен, що вказують на різні періоди будівництва. Кремово-білі цеоліти були спеціально додані в будівельну суміш для підтримки певного рівня вологості протягом сухого сезону. Цеоліт дуже пористий і легко ламається як в сухих, так і у вологих умовах. Вапняк з високим вмістом кальциту зі слідами магнію використовувався в якості сировини для штукатурки. Ґрунтуючись на мінералогічному складі і співвідношенні поєднувач/заповнювач, були задокументовані три фази історичних будівель. ІЧСПФ і аналіз тонких зрізів показали змішування певної кількості білкового розчину, що клеїть, з вапном для поліпшення реологічних і водонепроникних властивостей. Велика кількість великих зерен заповнювача забезпечувала кращу карбонізацію вапна, і джерело наповнювачів залишалось незмінним на всіх етапах історичних будівель. Індекс цементації і індекс гідротрансформації варіюються від 0,10 до 0,96 і від 0,20 до 3,43, відповідно, показуючи, що штукатурка являє собою повітряне вапно зі слідами магнію. Штукатурка слабо гідравлічна, так як розрахунковий гідравлічний компонент коливається від 0,88 до 6,10 відсотка в різних зразках. Для більшості етапів будівництва, за винятком декількох ізольованих місць, була підготовлена штукатурка середньої міцності з співвідношенням вапна/кремнезему, близьким до 0,33. Аналітичні дані тепер допоможуть приготувати сумісний розчин з ідентичними добавками для капітального ремонту.

Ключові слова: *древній розчин; наповнювачі; негідравлічні; мінералогія; органічні добавки; походження*

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Нефтехимическое исследование Могольских штукатурок Кила-Э-Арк, Аурангабад, с точки зрения технологии и ремонта

Аннотация. *В этой статье сообщается о минералогическом составе штукатурок Великих Моголов в Западной Индии 16–17 веков из Кила-Э-Арк, Аурангабад для приготовления совместимого ремонтного раствора и документирования древнеиндийской технологии производства извести. Были*

выполнены аналитические исследования для изучения распределения зерен по размерам, анализа тонкого сечения, инфракрасной спектрометрии с преобразованием Фурье (ИКСПФ), дифракции рентгеновских лучей и химического состава пластов с помощью рентгеновской флуоресценции. Анализ выявил включение крупногабаритных зерен базальтовых частиц, поступающих в основном из водного канала близлежащего озера Харсул. На некоторых штукатурках видны включения мелких зерен, указывающих на разные периоды строительства. Кремово-белые цеолиты были специально добавлены в строительную смесь для поддержания определенного уровня влажности в течение сухого сезона. Цеолит очень пористый и легко ломается как в сухих, так и во влажных условиях. Известняк с высоким содержанием кальцита со следами магния использовался в качестве сырья для штукатурки. Основываясь на минералогическом составе и соотношении связующее/заполнитель, были задокументированы три фазы исторических построек. ИКСПФ и анализ тонких срезов показали смешивание некоторого количества белкового клеящего раствора с известью для улучшения реологических и водонепроницаемых свойств. Большое количество крупных зерен заполнителя обеспечивало лучшую карбонизацию извести, и источник заполнителей оставался неизменным на всех этапах исторических построек. Индекс цементации и индекс гидротрансформации варьируются от 0,10 до 0,96 и от 0,20 до 3,43, соответственно, показывая, что штукатурка представляет собой воздушную известь со следами магния. Штукатурка слабо гидравлическая, так как расчетный гидравлический компонент колеблется от 0,88 до 6,10 процента в разных образцах. Штукатурка средней прочности с соотношением извести/кремнезема, близким к 0,33, была подготовлена для большинства этапов строительства, за исключением нескольких изолированных мест. Аналитические данные теперь помогут приготовить совместимый раствор с идентичными добавками для капитального ремонта.

Ключевые слова: *древний раствор; заполнители; негидравлические; минералогия; органические добавки; происхождение*

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