Mineralogical Analysis of Historical Lime Mortar Using XRD and SEM Analysis

Shraddha Singh[1], Rashmi Sakalle[2]
Truba Institute of Engineering & Information Technology, Bhopal (M.P.), India[1,2]

Abstract- *India is a large country with a diverse population." India's cultural heritage and ancient ruins, which include buildings and other archaeological sites and remains, are unique, vast, and diverse. It's incredible how many heritage places there are. The reality that these monuments are the recollections of over a thousand living witnesses to history's golden age. Lime mortar was mainly used to make ancient building buildings until the introduction of cement and other construction materials. It is more important than ever to rebuild landmark buildings that have started to deteriorate and are on the brink of being abandoned. For historic building renovations, a lime mortar study was performed. Using SEM, EDX and XRD methods, this thesis analyses historical and contemporary lime mortars. SEM, EDX and XRD were used to study historic and recent lime mortars, and the mineralogical properties of lime mortars were determined.*

Keywords:- Mineralogical analysis, historical mortars, new lime mortar, XRD analysis, SEM analysis, EDX analysis.

Introduction

Cultural treasures such as heritage monuments should be preserved. When renovating historical buildings, monument preservation should be taken into account. When renovating heritage buildings, the most important consideration is that the methodological techniques used are consistent with the original substance. Because lime mortar was used to create heritage buildings and monuments, and because monuments deteriorate over time, it is advantageous to use new lime mortar construction materials to assist in their renovation. When the wrong materials are used in the renovation of historical structures, the entire structure and its constituent parts deteriorate quickly. They should also lose their geographical, documentary, and aesthetic value. The materials used in restoration are often chosen without conducting extensive research or deciding what problems they may cause, resulting in short- and long-term negative effects on the structure. It is critical to use appropriate criteria when selecting repair mortars, taking into account the requirements for environmental resistance as well as compatibility with existing materials. To determine the mineralogical characteristics of both lime mortars, a scanning electron microscope with energy dispersive spectroscopy (SEM–EDS) and X-ray diffraction (XRD) were used to determine the chemical and mineralogical composition of both historical and new lime mortars.

SEM analysis is an effective investigative technique that produces detailed, high magnification images of a sample's surface topography using a directed beam of electrons. If an area of concern on the sample has been detected and analysed using SEM, experts will use energy-dispersive x-ray spectroscopy, or EDX analysis, to delve further into the material's information.

The x-ray technology Energy Dispersive X-Ray Analysis (EDX), often recognized as EDS or EDAX, is used to explain the characteristics of material properties. Components in competitive analysis, data management, obtain better, and other requirements are all possible. X-Ray Diffraction (XRD) is a method for obtaining more detailed knowledge about crystalline molecules, such as the detection and quantification of crystalline phase morphology. This is a valuable method for positively identifying a contaminant or corrosion substance, as well as for identifying foreign phases in crystalline powder purity analyses. Both historical and new lime mortar samples were obtained for the test analysis of lime mortars. In the case of historical lime mortar, only a small amount of sample could be extracted from a historical site because it was a preserved monument and large sample collection was not possible, and for the new lime mortar blend, the sample was prepared with lime, surkhi, sand, in a 1:3 ratio and some amount of jute lintel and jiggery. The samples from both lime mortars were pounded in a grinding tool to achieve a fine powdered shape of the material. All powdered lime mortar samples were analyzed using a scanning electron microscope, EDX and X-ray diffraction.

II. Analysis of Lime Mortar

SEM analysis –
SEM (Scanning Electron Microscopy) is a test technique that uses an electric field to analyze a material and create a magnification for examination. SEM analysis, also known as SEM microscopy, is a technique for microanalysis and failure treatment of environmental inorganic materials that is very accurate. High magnification electron microscopy generates large images and accurately tests very useful details and materials.

EDX analysis-
The x-ray technique Energy Dispersive X-Ray Analysis (EDX), is used to determine the elemental composition of materials. Materials and product analysis, data recovery, providing quality, and other applications are all feasible.

The imaging capability of the microscope defines the material of significance in EDX applications, which are connections to Electron Microscopy equipment (Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM)). EDX analysis creates spectra with characteristic peaks to the elements that make up the true characteristics of the material in investigation. Image analysis and element representation of a sample was also possibilities.

XRD analysis –
X-Ray Diffraction, or XRD for short, is a non-destructive analysis method for examining the formation of crystal structures.

X - ray diffraction has been used to classify the crystalline phases contained in a substance but also disclose elemental analysis information by analyzing the crystalline structure. The phases are identified by comparing the acquired data to that in reference databases.

Minerals, composites, alkaline earth, and unidentified components may all benefit from X-ray diffraction. Almost all of the samples analyzed at Element are formulated as finely powdered and analysed by powder x - ray.

III. Result & Discussions

SEM \EDX analysis:
When SEM \EDX analysis was performed on both lime mortars (historical and new lime mortar), certain elements peaks were determined, and their weight and atomic percentage were also determined. From these elements peaks, mineral compositions were also determined in both lime mortar.

Lime mortars Elements peaks were determined in EDX figure 1,3 and it is possible to determine which type of minerals are present in lime mortar based on these peaks elements. minerals' were determined from lime mortars SEM images in figure 2,4 and from SEM \ EDX analysis, it was determined the type minerals' were present in historical and new lime mortar.

The presence of Si and O elements in the EDX peaks suggests the presence of Quartz. Quartz was a crystalline mineral made up of silicon and oxygen atoms that was rigid and brittle. The atoms are linked by a SiO_4 silicon-oxygen tetrahedra arrangement. Since two tetrahedra exchange each oxygen atom, the overall chemical formula is SiO_2, suggesting that Quartz was present in both lime mortars.

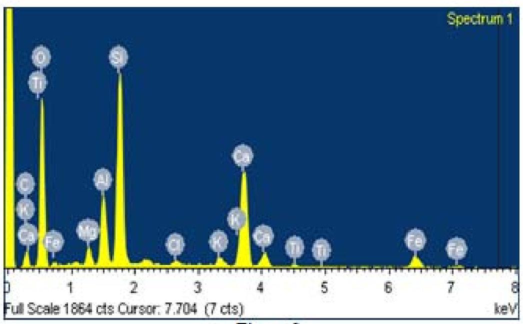

Figure 3

new lime mortar EDX images

Figure 4

New lime mortar SEM images (mag 5000x3.7mm)

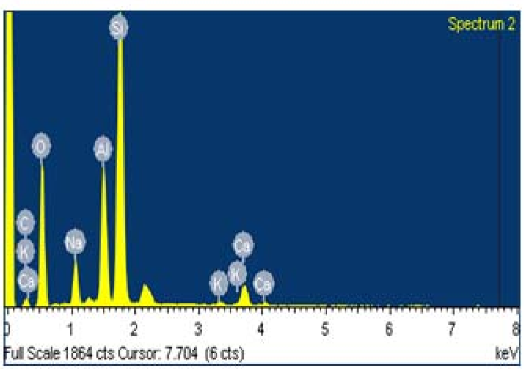

Figure 1

historical lime mortar EDX image

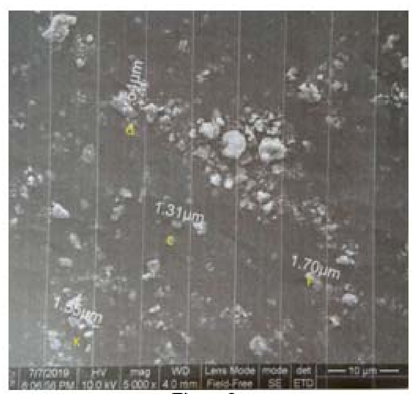

Figure 2

historical lime mortar SEM image (mag 5000x4.0 mm)

Since the Si element weight percent in historical lime mortar was 26.53 and the atomic percent was 17.77, and the Si element weight percent in new lime mortar was 14.10 and the atomic percent was 9.59, it could be concluded that the Si element weight percent and atomic percent in Quartz minerals were higher in historical lime mortars than in new lime mortars.

Since the O element weight percent in historical lime mortar was 45.00 and the atomic percent was 52.93, and the O element weight percent in new lime mortar was 53.97 and the atomic percent was 64.43, it was determined that the O element weight percent and atomic percent in Quartz minerals were higher in new lime mortars than in historical lime mortars.

When C and Ca elements are present in EDX peaks, it can be determined that Calcite is a carbonate mineral. calcium carbonate in its most robust form (CaCO3). Calcite is a hard mineral that is used to test the permeability of scrapes. Aragonite and vaterite, both calcium carbonate minerals, are polymeric calcium carbonate compounds .and it's present in both lime mortars.
Since the C element weight percent and atomic percent in historical lime mortars were 11.02 and 17.27, respectively, and the C element weight percent and atomic percent in new lime mortars were 8.77 and 13.94, it was concluded that the C element weight percent and atomic percent in Calcite minerals were higher in historical lime mortars than in new lime mortars.
Since the Ca element weight percent in historical lime mortar was 2.72 and the atomic percent was 1.28, and the Ca element weight percent in new lime mortar was 11.80 and the atomic percent was 5.62, it was determined that the Ca element weight percent and atomic percent in calcite minerals in modern lime mortars were higher than in traditional lime mortars.
Feldspars (KAlSi3O8 – NaAlSi3O8 – CaAl2Si2O8) are tectosilicate minerals where K and Na elements are present in EDX peaks. Feldspar is a mineral that is found in a variety of sedimentary rocks. It's a kind of calcium feldspar known as K-feldspar. Feldspar's structure is monoclinic. potassium feldspar endmember (K-spar) The chemical compound KAlSi3O8 has the formula KAlSi3O. albite endmember The chemical compound NaAlSi3O8 has the formula NaAlSi3O. anorthite's endmember The mineral CaAl2Si2O8 has the chemical formula CaAl2Si2O8. It can be concluded that feldspar was present in both lime mortars.
Since the K element weight percent and atomic percent in historical lime mortars were 0.41 and 0.72, respectively, and 0.80 and 0.39 in new lime mortars, it was concluded that the K element weight percent in feldspar minerals in new lime mortars was higher than in historical lime mortars. Historical lime mortars had a higher atomic percent of feldspar minerals than new lime mortars.
Since the Na element weight percent in historical lime mortar was 4.70 and the atomic percent was 3.85, and the Na element weight percent in new lime mortar was 4.70 and the atomic percent was 3.85, the Na element weight percent and atomic percent in feldsher minerals in modern lime mortar and traditional lime mortar were estimated to be equal.
When Al elements are present in EDX peaks, Kaolinite (Al2Si2O5(OH)4) is identified as a clay mineral with the chemical formula Al2Si2O5(OH)4. It's a highly desirable industrial mineral. It's a layered silicate mineral made up of two octahedral sheets of silica (SiO 4) and alumina (AlO6) octahedra joined by oxygen atoms. Rocks that are kaolinite-rich have a lot of kaolinite in them. Kaolinite has a triclinic crystal system. The presence of kaolinite in both lime mortars can thus be observed.
Since the Al element weight percent and atomic percent in historical lime mortars were 9.62 and 6.71, respectively, compared to 4.60 and 3.26 in new lime mortars, it was concluded that the Al element weight and atomic percent in kaolinite minerals were higher in historical lime mortars.
While Mg elements are detected in EDX peaks, Dolomite is identified as an anhydrous carbonate mineral composed mainly of calcium magnesium carbonate (CaMg(CO3)2). Dolomite is a sedimentary carbonate rock that is predominantly composed of the mineral dolomite. The word "dolostone" is often used to refer to the dolomitic rock type. Dolomite crystallises using the trigonal-rhombohedral system The existence of Dolomite can indeed be seen in new lime mortar.
Mg element weight percent and atomic percent in new lime mortars were 1.42 and 1.11, respectively, and this element was present in Dolomite mineral.
Since some Fe, Ti, and Cl elements were contained in small quantities in the EDX peaks of new lime mortar, some additional materials were present.
Cl weight percent 0.35 and atomic percent 0.19, Ti weight percent 0.38 and atomic percent 0.15, and Fe weight percent 3.80 and atomic percent 1.30 were all determined in a new lime mortar.
Historical lime mortar EDX analysis table:

Element	Si	C	K	Na	O	Al	Ca
Weight %	26.53	11.02	0.41	4.70	45.00	9.62	2.72
Atomic %	17.77	17.27	0.72	3.85	52.93	6.71	1.28
Old lime mortar sample	Sio2 Quartz (Q)	CaCo3 Calcite (C)	KAlSi3O8 Feldspear (F)	NaAlSi3O8 Feldspear (F)	Sio2 Quartz (Q)	(Al2Si2O5(OH)4) Kaolinite (K)	CaCo3 Calcite (C)

Table 1

New lime mortar EDX analysis table :

Element	Si	C	K	Mg	Na	Al	O	Ca	Fe	Ti	Cl
Weight %	14.10	8.77	0.80	1.42	4.70	4.60	53.97	11.80	3.80	0.38	0.35
Atomic %	9.59	13.94	0.39	1.11	3.85	3.26	64.43	5.62	1.30	0.15	0.19
New lime mortar sample	Sio2 Quartz (Q)	CaCo3 Calcite (C)	KAlSi3O8 Feldspear(F)	(CaMg(CO3)2) Dolomite (D)	NaAlSi3O8 Feldspear (F)	Al Kaolinite (K)	Sio2 Quartz (Q)	CaCo3 Calcite (C)	Fe	Ti	Cl

Table 2

Images and peaks of calcite (Ca), quartz (Q), Kaolinite (K), and feldspar were determined in historical lime mortar using SEM and EDX . Using the figure and peaks, it was possible to determine which minerals are present in historical lime mortar.

The images and peaks of calcite (C), quartz (Q), dolomite (D), feldspar (F), Kaolinite (K), Ti, Fe, and Cl were determined using SEM and EDX analysis.The minerals in modern lime mortars were identified.

After SEM EDX analysis in both lime mortars, mineral images and peaks were obtained.Since receiving images of the materials, researchers have discovered that all lime mortars are mineralogical identical and that some materials, such as Q, C, K, and F, are present in both lime mortars with different mineralogical percentages, while others, such as D, A, Fe, Ti, and Cl, are only found in contemporary lime mortars

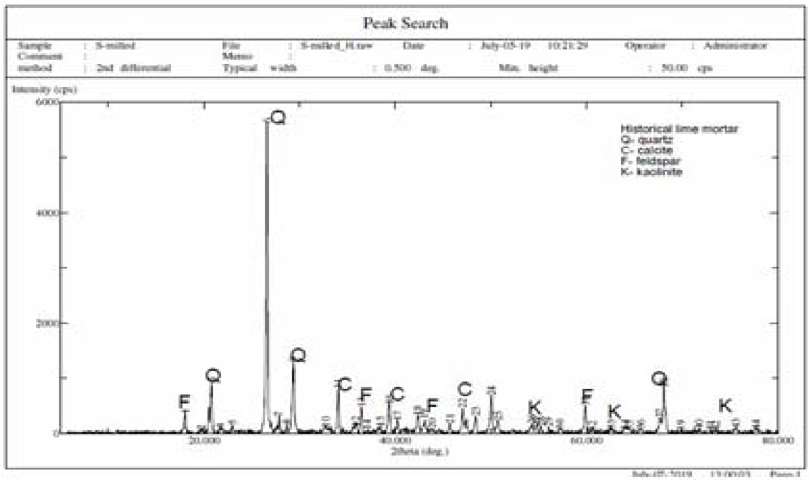

Figure 5: Historical lime mortar XRD result

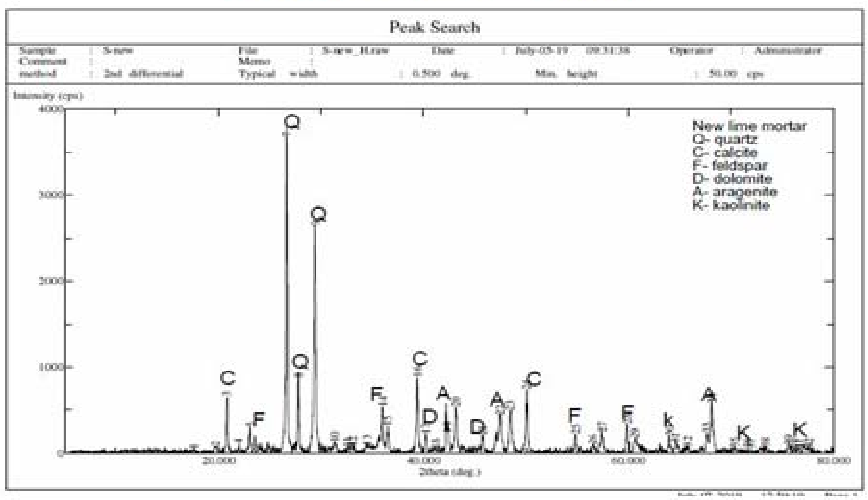

Figure 6: New lime mortar XRD result

X-Ray Diffraction (XRD):

X-Ray Diffraction (XRD) is a method for obtaining more detailed knowledge about crystalline molecules, such as the detection and quantification of crystalline phase morphology. This is a valuable method for positively identifying a contaminant or corrosion substance, as well as for identifying foreign phases in crystalline powder purity analyses.

XRD analysis was carried out on a powdered sample of historical lime mortar, and some peaks were obtained; these peaks reflect mineral stage, and minerals characterization was carried out using these peaks. During peaks In traditional lime mortars, the minerals Q, C, K, and F were identified. XRD analysis was performed on a new lime mortar driven sample, and the materials peaks were recorded during the process. These peaks should provide us with more data on mineral properties The minerals found at these peaks were Q,C,D,F,K and A. Based on these peaks, it was possible to predict which mineral groups were present in new lime mortar and historical lime mortar. More information could be found in JCPDS books .

The results were identical, showing that old and new mortars are similar mineralogical properties. The texture of the current mortar is identical to that of the previous samples. As a result, used blends were remarkably similar to traditional or antique blends, which is a considerable accomplishment. The following images and data indicate how close the current mix is to the previous one. Its worth remembering that the percentages vary because all of the samples contain the same fundamental elements, such as F, Q, C, and K. Some rocks, such as D, A, Fe, Ti, and Cl, can be found in the current lime mortar.

SEM, EDX, and XRD analysis were used to obtain images of these samples as well as peak measurements. A mineralogical study using SEM and XRD methods revealed that quartz, feldspar, calcite, and kaolinite minerals were present in both historical and new lime mortars, but their contents differed. In the new lime mortar, other minerals such as dolomite and aragenite were also present, and some Ti, Fe, and Cl elements were present in small amounts that did not affect the new lime mortar. The materials used during restoration projects should be consistent with others and equivalent to the original materials used in historic buildings. Then it will be possible to decide whether or not fresh lime mortar will be used in historical building renovations.

IV. Conclusion

Using SEM, EDX, and XRD experiments, the aim of this study was to determine the suitability of a modern lime mortar mix for historical building renovation. Images of these materials , as well as their peak measurements, were calculated using SEM, EDX, and XRD analysis. The findings are comparable, meaning that the mineralogical characteristics of both old and new mortars are the same. The texture of the new mortar is similar to that of the previous samples. As a result, modern blends are similar to old or traditional blends. implying that modern lime mortar should be used in historic building reconstruction and that doing so will prevent historic structures from degrading K, Q, C, and F minerals are the same in historical and modern lime mortars, while D, A, Ti, Fe, and Cl minerals are present in new lime mortar.

References

[1] Angelica M. Palomino,S. E. Burns ,Georgia Institute of Technology,J. Carlos Santamarina Mixtures of fine-grained minerals – kaolinite and carbonate grains December 2008 Clays and Clay Minerals 56(6):599-611 DOI: 10.1346/CCMN.2008.0560601.

[2] Balksten, K., & Steenari, B.-M. (2008).A method to recreate historic mortars applied at Norr-landa church on the island of Gotland, Sweden. Presented at the Proceedings of Historical Mortars Conference HMC-2008, Lisbon, Portugal 2008.

[3] Brady, John B., and Boardman, Shelby J., 1995, Introducing Mineralogy Students to X-ray Diffraction Through Optical Diffraction Experiments Using Lasers. Jour. Geol. Education, v. 43 #5, 471-476.

[4] Daniele Pereira da Silva Dalto , Roberto Carlos da Conceição Ribeiro , Luanna Cavalcanti Rebecchi de Moura (2018)Characterization of the Lime Mortars of the Rui Barbosa House Museum in Rio De Janeiro, Brazil Minerals 2018, 8(2), 50; https://doi.org/10.3390/min8020050.

[5] Dutrow, Barb, 1997, Better Living Through Minerals X-ray Diffraction of Household Products, in: Brady, J., Mogk, D., and Perkins D. (eds.) Teaching Mineralogy, Mineralogical Society of America, p. 349-359.

[6] Goffredo S, Vergni P, Reggi M, Caroselli E, Sparla F, Levy O, Dubinsky Z, Falini G. The skeletal organic matrix from Mediterranean coral Balanophyllia europaea influences calcium carbonate precipitation. PLoS

One. 2011;6(7):e22338. doi: 10.1371/journal.pone.0022338. Epub 2011 Jul 22. PMID: 21799830; PMCID: PMC3142144.

[7] Hollecher, Kurt, A Long-Term Mineralogy Practical Exam, in: Brady, J., Mogk, D., and Perkins D. (eds.) Teaching Mineralogy, Mineralogical Society of America, p. 43-46.

[8] João Pires 2015 Simple Analysis of Historical Lime Mortars Journal of Chemical Education 2015 92 (3), 521-523 DOI: 10.1021/ed500336.

[9] Kadİr, S., Külah, T., Erkoyun, H. et al. Geology,Mineralogy,Geochemistry, and Genesis of Bentonite Deposits in Miocene Volcano–Sedimentary Units of the Balikesir Region, Western Anatolia, Turkey. Clays Clay Miner. 67, 371–398 (2019). https://doi.org/10.1007/s42860-019-00029.

[10] Kristin Balksten(2010)Understanding historic mortar and their variations – a condition for performing restorations with traditional materials.

[11] Kristin Balkstan , Britt-Marie Steenari (2010) The Influence of Particle Size and Structure in Hydrated Lime on the Properties of the Lime Putty and Lime Mortar International Journal of Architectural Heritage 4(2):86-101 DOI: 10.1080/15583050902822681.

[12] Kong Y, Wang P, Liu S, Zhao G, Peng Y. SEM Analysis of the Interfacial Transition Zone between Cement-Glass Powder Paste and Aggregate of Mortar under Microwave Curing. Materials (Basel). 2016 Aug 27;9(9):733. doi: 10.3390/ma9090733. PMID: 28773854; PMCID: PMC5457086.

[13] Shi qiang Fang , Bing Jian Zhang ,Ye Zheng The identification of organic additives in traditional lime mortar March 2014 Journal of Cultural Heritage 15(2):144–150 DOI: 10.1016/j.culher.2013.04.00.

[14] Shanke Liu ,Cheng Han ,Jianming Liu Study of K-Feldspar and Lime Hydrothermal Reaction: Phase and Mechanism with Reaction Temperature and Increasing Ca/Si Ratio.

[15] Venugopal B, Manivannan M, Vigneshwaran K V,Surya S,Thilagar T(2018) Study on the Performance Enhancement of Lime Mortar.