IN: SIEGESMUND, S. & MIDDENDORF, B. (ED.): MONUMENT FUTURE: DECAY AND CONSERVATION OF STONE.

- PROCEEDINGS OF THE 14TH INTERNATIONAL CONGRESS ON THE DETERIORATION AND CONSERVATION OF STONE
VOLUME I AND VOLUME II. MITTELDEUTSCHER VERLAG 2020.

PRELIMINARY STUDY ON LIME MORTARS USED FOR STONE MASONRY OF THE GREAT WALL BUILT BY MING DYNASTY IN CHINA

Tanja Dettmering^{1,3}, Zhaoyi Liu², Yuyang Tang², Yijie Wang³, Shibing Dai³

1 August-Bebel-College, Richard-Wagner-Straße 45, 63069 Offenbach, Germany, e-mail: dettmering@august-bebel-schule.de
2 Academy for Heritage Architecture Research, Beijing University of Civil Engineering and Architecture, No. 1 Zhan Lan Guan Road Xi
Cheng district, Beijing City, 100044 Beijing, China

3 Architectural Conservation Laboratory CAUP Tongji University, No. 1239 Siping Road, 200092 Shanghai, China

Abstract

The Great Wall in China was designated as UNESCO cultural world heritage in 1987. Exterior masonry made from natural stones, bricks and lime mortar is one of the most attractive features. Due to an intentional use of regional occurring stone deposits and kilned clay bricks, the great wall construction might follow a specific quality system according to knowledge in the past. One of the most remarkable characteristics is that both dolomitic and calcium limes with less aggregates were used for bedding and pointing mortars. Those mortars show very high strengths and excellent bondings to natural stones and kilned clay bricks. According to preliminary investigations besides calcite and aragonite, minerals of magnesium carbonate, mostly magnesite (MgCO₃) and others were identified in mortars collected from non-restored parts from the Wall in Beijing, Hebei & Shanxi Province. Comprehensive researches shall be carried out to understand traditional lime technique, especially slaking technique and to reveal durability of traditional lime mortars under industrial pollution. Confronted with damages because of both anthropic and natural forces specific stone conservation strategies have to be figured out based on recommended further investigations. Especially compatible lime mortars or alternatives for sustainable conservation shall be specified.

<u>Keywords</u>: great wall, natural stone masonry, lime mortars, dolomitic lime, deterioration, conservation

Introduction – Great wall built by Ming Dynasty

The Great Wall, actually a network of fortifications rather than a single structure, was continuously constructed, rebuilt and extended by Ming dynasty (1368–1644), representing the world's largest military structure (Luo et al. 1993) Fig. 1). A recent government mapping project revealed that the entire Great Wall structure spans some 5,500 miles (8,850 kilometers) from the Korean border west into the Gobi desert. According to the Chinese Cultural Heritage Office in June 2012, a total of 43,721 individual sites or locations of the Great Wall were identified as part of an extensive archaeological survey.

Despite of many restoration campaigns and reconstruction activities in the past four decades (WHC, 2018), parts of the Great Wall are still in danger to collapse (Fig. 2), even shortly after restoration.

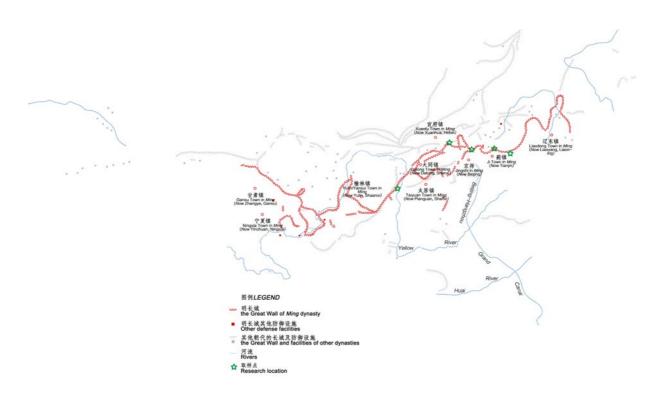


Figure 1: the Great Wall built by Ming Dynasty (red marked) and location of preliminary researches (green stars), Source: Liu Zhaoyi & Dai Shibing

A recent joint research project of the Academy for Heritage Architecture Research at Beijing University of Civil Engineering and Architecture in cooperation with the Architectural Conservation Laboratory of Tongji Uinversity, Shanghai, is brought to life to figure out a proper conservation concept and adoptable technology. In its context the preliminary studies on lime mortars dealing with brick and stone masonry come in the first place.

Construction technique

The Great Wall is constructed with local materials. At least four types of wall constructions can be distinguished. The first type of wall is built with natural stones and bricks mostly filled with natural stones (Fig. 3). For long stretches it only consisted of accumulated stone remnants with well dressed (mostly local) natural stone as a foundation and less well worked natural stones as a whole body. The second type of the wall is based on a stone foundation about 6 meters wide; both wall sides were usually built from bricks whose interstices have been filled with various materials, in partic-

ular soil, stones, wood and pieces of bricks, also in most cases rammed earth. The masonry crown, as the outer walls, too, was made of bricks, occupied on two sides with bronzed breastworks, so that the total paragraph?

hight was on average 6 to 8 meters. Between rammed earth and stone/brick envelope there was lime improved soil grouts. Lime mortar with soilstone gravel was normally used as a supporting layer of the wall top pavements. It has been proven that the bricks were burned in furnaces near the wall (brickyard), while the natural stones came from nearby quarries.

The third type of wall is similar to the second one, but interior surface is made of rammed earth without brick masonry. The forth type of the wall is only composed by rammed earth, especially in western regions.

Lime mortars were extensively used for bedding and pointing (Fig. 4), but also for grouting of voids within stone/brick masonries and stabilisation of soils. Lime plasters were also found in few watch tower ruins. But only the bedding and pointing lime mortars will be further discussed in this paper.



Figure 2: Wall surface from granite and bricks with white dolomitic lime mortar showing cracks and delamination, Source: Dai Shibing



Figure 3: Wall constructed with natural stones in Beijing, Source: Wang Yijie



Figure 4: Pointing and bedding mortars (above calcium lime with hydraulic components, below dolomitic lime). Source: Dai Shibing

Lime Mortars from Stone Masonry

Visual investigations showed that both bedding and pointing lime mortars are made of pure lime with very few agrregates (Fig. 4). In most cases bedding mortars are the same in colour and texture

as pointing mortars. However there are also new pointing mortars slightly different from bedding mortars. The forms of pointing vary from flush, tuck and double struck.

To characterize selected mortars, their chemical and mineralogical compositions (Tab. 1) were examined paragraph?

as well as their technological properties (not illustrated in this paper). Firstly samples were analysed wet-chemically to separate aggregate and binder according to Wisser and Knöfel (1987). Qualitative X-ray diffractometry (XRD) to determine mineral phases, binder type and aggregate followed (Middendorf et al., 2005). Individual samples were verified microscopically after semiquantitative X-ray diffractometric analyses by Rietveld.

Noticeable at first sight is the low level of aggregate common to all mortars. The lime content (original binders) ranges from 67 wt% to 97 wt%. The content of calcium and magnesium also varies. According to european standards, those limes can be classified into at least four categories, calcium lime, CL90, CL80 and CL70 respectively NHL to dolomite lime DL90-30, DL90-5 or DL80-30 (Dettmering and Kollmann, 2019).

Exemplarily samples with relatively high contents of Magnesium (Jiangmaoyu-JMY, Beijing) and lower amounts of Calcite (CaO approx. 30 wt%) and such of high calcite contents (Xinguanwu - XGW, Shanxi Province) with CaO 40-50 wt% and changing proportions of SiO, or hydraulic components at very low MgO contents (1-1,5 wt%) were additionally examined by microscopic analyses and Rietveld to specify their characteristic proportions (Fig. 5 & 6). JMY represents a bedding and jointing mortar in a composite of brick and natural stone masonry (granite). It originates of a wall section belonging to a garrison in Beijing. The dense structure of a homogeneous binder matrix of a lime mortar with a high binder content of about 95-wt% is containing lumps of lime (Fig. 6). Those lumps are one of the characteristic features of many historical mortars resulting naturally during the slaking process reducing the mortar's water requirements.

In JMY bedding and jointing mortar lump particles are distributed differing between predominantly

Table 1: Chemical compositions and formulations (main carbonates and other components) of selected bedding and pointing mortars built in Ming Dynasty. Source: CAUP, Tongji University (-: not tested).

Province	Location	Mortar Cate- gory, visual Characterris- tics	Chemical Composition (wt%)				Chemical Formulation (XRD)		Estimated Lime Cate-
			Original Binder	Hydraulic Compo- nent in Binder	Ca0	Mg0	Main Car- bonates	Other For- mulations	gories
Liaoning	Suizhong	Bedding mor- tar, pure	87–97	0,9-3,5	51-55	1.4-2.2	CaCO ₃	SiO2	CL-80/90
Hebei	Zunhua	Bedding, pure	81–97	1,7-4,7	32–37	21-22	CaCO ₃ MgCO ₃ , CaMg(CO ₃) ₂ , Mg ₅ (CO ₃) ₄ (OH) ₂ · 4H ₂ O	-	DL80-30/ DL90-30
	QinHuang-	-	82-95	4,2-8,8	45-49	1,8-3,5	CaCO ₃	_	CL80-90
	dao	Bedding mortar, with sand	93	3,7	46	2,5	_	-	CL90
		Bedding, very soft	97	4,8	51	4,1	-	-	CL90-5
		Bedding, pure	95-96	3,2-5,2	52-62	1-2	CaCO ₃	SiO ₂	CL90
			91	2,5	29	16,0	CaCO ₃	SiO ₂ , Ca(FeMg) (CO ₃) ₂	DL90-30
	Zhang- jia-kou		93	1,2	-	8,9	$Mg_{5}(CO_{3})_{4}$ $(OH)_{2} \cdot$ $4H_{2}O$	CaCO ₃ SiO ₂ , MgCO ₃	DL90-5
		Bedding, high strength	99	0,6	-	6,8	CaCO ₃ , MgCO ₃	-	DL90-5
		Bedding, very porous, weathered	86	1,4	-	5,05	-	-	DL80-5
Beijing	Shuiguang	Bedding	99,2	0,3	29	15,7	Mg ₅ (CO ₃) ₄ (OH) ₂ · 4H ₂ O	CaCO ₃ MgCO ₃	DL90-30
	Jiangmao-yu (JMY)		95–97	1,4	30-31	15,5-16,2	Mg ₅ (CO ₃) ₄ (OH) ₂ · 4H ₂ O CaCO ₃	CaCO ₃ SiO ₂ ,MgCO ₃	DL90-30
Shanxi	Xinguang- wu (XGW)		82	3,5	50	1,1	CaCO ₃	SiO ₂	CL80
			67	7,1	39	1,5	CaCO ₃	SiO ₂ /CSH?	NHL or CL70
		Pointing	82	5,9	49	1,2	CaCO ₃	SiO ₂ /CSH?	NHL/or CL80
		Bedding/ Fangsi	69-79	1,2-3,9	52-61	1,3-2,2	CaCO ₃	SiO ₂	CL70/80

 $50-150\,\mu m$ in sizes with some larger pieces up to $2\,mm$.

Few aggregates were identified as quartz, bricks with smaller fragments, calcium silicates, mica, feldspar particles as well as smaller charcoal traces.

X-ray diffractometry from comparative samples provided evidence for a magnesium-rich carbonate, huntit as well as its conversion form hydromagnesite (Fig. 7). Magnesite, carbonating next to calcite during the hardening process after firing and the subsequently slaking process, shows a higher

solubility behavior, forming hydromagnesite in the presence of moisture. The distribution of hydromagnesite has led to a partial dissolution phenomena and a recrystallization to less soluble gypsum (Fig. 6). Semiquantitative X-ray diffractometric analyse of JMY (Fig. 7) determined by Rietveld provided predominantly calcite (> 57%, 5% aragonite), hydromagnesite (27%) and magnesite (9%) as phase components, categorized as dolomitic lime known today as DL90-30. The lime mortars from Zunhua in Hebei Province have almost the same properties as XGW.

In contrast to the occurrence of dolomitic lime mortars containing more or less pure calcite lime are dominating in western Shanxi province, Xinguanwu (XGW). It can be assigned to the third type

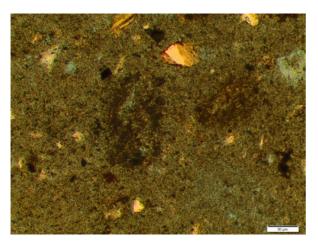


Figure 5: Shows a representative thin section to characterize the microstructures of Xinguanwu bedding mortar with lumps of lime. Source: Dettmering/Middendorf.

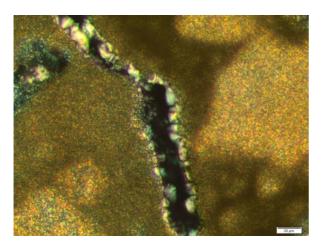


Figure 6: Shows a representative thin section to characterize dolomitic bedding mortar with gypsum in cracks from Jiangmaoyu/Beijing. Source: Dettmering/Middendorf.

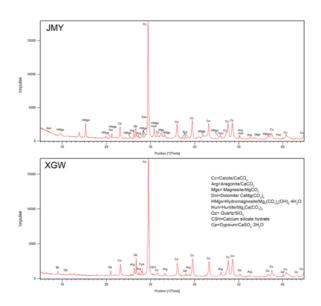


Figure 7: XRD of two typical lime mortars (JMY: dolomitic lime; XGW: calcium lime with hydraulic components. Source: Dettmering/Middendorf.

of wall with an interior surface made of rammed earth and an outer cladding of brickstone masonry. Due to the geology and the appearance of the limes, it is obvious that also silicious and argiliceous limestones were used to build the wall "Xin-GuanWu", which runs over three mountain passes. Raw materials of the lime mortars had different marl contents. This is partly confirmed in X-ray and wet-chemical analyzes of collected mortars. The average CaO contents of comparative samples are about 39–49 wt.%. The binder proportions vary between 67 and 82 wt.%. The calcium carbonate content determined by Rietveld analysis ammounts to a calcite content of 78% and an aragonite content of 10% (Fig. 7).

In addition small amounts of gypsum (< 1%) could be identified as a minor phase. X-ray diffractometry reflexes around 32–33° 2Theta indicate CSH-phases. Microscopically the larger lime lumps in the order of 150–200 µm appear to be covered by cloud-like structures (Fig. 5 left) typical of CSH phases (Válek et al. 2012); finely crystalline phases were also identified in the homogeneous matrix. Wet-chemical analyzes according to Wisser and Knöfel of comparable samples suggest an NHL or CL80.

Conclusion, discussion and further researches

First investigations show that the bedding and pointing lime from the Great Wall are characterized by high lime content without or with low proportion aggregates although lime used ranged from pure dolomitic lime to pure calcium lime. It is not yet firmly clearified wheather the limes with hydraulic components were also used.

Lime lumps are caused by the use of coarse-grained lime, which might be produced in the dry slaking process. They can act as a lime reservoir in the binder or as an aggregate. The detection of dolomite in the XRD could be an indication for the simultaneous use as a binder and as an aggregate. Based on the first studies, further XRD analyses in combination with transmitted and reflected light microscopic investigations as well as scanning electron microscopy are necessary. Further investigations are needed to determine reliable and precise data of the historic mortars with regard to grain size distribution, binder/aggregate-ratio and air void porosity, pore contents and pore radius distributions. With the help of further analyzes regarding their lime binders, their high proportion of lime-containing matrix a basis for the investigation of suitable mortar formulations can be worked out. Comprehensive researches shall be carried out to reveal durability of traditional lime mortars under industrial pollution. First examinations of the dolomitic calcareous masonry of the Great Wall show that severe changes occur due to the effects of air pollutants. Mortars used for the re-construction and restoration in the past four decades shall also be evaluated. Experimental burning and slaking tests to replicate historic technique have been started. More compatible pointing mortars based on natural hydraulic lime have been tested. Various grouts for structural purposes are in development under a new reseach framework.

Acknowledgement

This research was initiated by the China National Cultural Heritage Administration and supported by National Natural Science Foundation of China

(No 51978472 & 51738008) and the Open Projects Fund (No 2019010109) of Tongji University, China. Thanks go to Professor Bernhard Middendorf, providing the opportunity for cooperating referring microscopic and XRD Rietveld analyses.

References

Auras, M., Meinhardt, J., Snethlage, R. 2010. Leitfaden Naturstein-Monitoring – Nachkontrolle und Wartung als zukunftsweisende Erhaltungsstrategien, Fraunhofer IRB Verlag.

Dai, S. 2018. Preliminary study on wind slaked lime used before Qing Dynasty in China. Journal of Architectural Conservation, Vol. 24, 2, 91–104.

Dettmering, T. 2019. Modernized traditional lime plasters for modern historic living of built heritage, Case Studies from Germany with Reflection for China, Built Heritage Studies Vol. 3, No.1, Tongji-University Press, Shanghai.

Dettmering, T., Kollmann, H. 2019. Putze in Bausanierung und Denkmalpflege, 3. Überarbeitete Auflage, Beuth-Verlag, Berlin.

Middendorf, B., Hughes, JJ., Callebaut, K, Baronio, G., Papayianni, I. 2005. Investigative methods for the characterization of historic mortars. Part 2: chemical characterization. Mater Struct. 38: 771–80.

Válek, J., Hughes, J.J., Groot, C.J., W.P. 2012. Historic Mortars Characterisation, Assessment and Repair, Springer, Springer Dordrecht Heidelberg New York London, RILEM Bookseries Vol 7.

Wisser, S., Knöfel, D. 1987. Untersuchungen an historischen Putz- u. Mauermörteln. T.1Analysengang. Bautenschutz und Bausanierung. 10. S. 124–6.

WHC World Heritage Committee. 2018. The Great Wall.

State of Conservation Report. https://whc.unes
co.org/en/sessions/43com/documents/#state_
of_conservation_reports