Historic mortars with burned alum shale as an artificial pozzolan

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Abstract From the mid-18th century extensive research in Sweden and in present day Finland focused on the development of mortars with hydraulic properties, the results mainly published by the Royal Swedish Academy of Science. The aim was to replace imported Italian pozzolan and Dutch trass with a pozzolan produced in Sweden. Several products based on burned alum shale were developed. Cambrian alum shales with a high content of bitumen were fired without additional fuel to produce pozzolanic shale ash. The bituminous alum shale was used directly as a fuel in the lime burning process from the late 18th century. The alum shale mortars have a red-brown colour due to the high content of iron oxides. The mortars are hard, strong and generally have a good durability, both as masonry mortars and renders. Microscopic analysis shows that often only a skeleton remains of the shale particles and that large parts of the particles are consumed by the pozzolanic reaction. The field of application was initially restricted to structures in contact with water, such as locks in canals and harbours, but conventional building construction was also an early application.

1 Introduction

In the 17th century, waterside construction in Sweden was largely managed by Dutch engineers using Dutch techniques and pozzolanic trass mortars. One example is the city of Gothenburg, which was established on the marshy banks near the mouth of the Göta River in 1621. It was built by Dutch engineers using a Dutch city plan.

Later on, during the 18th century, mercantilist ideas grew stronger; these were accompanied by an increasing belief in the need to make knowledge and natural resources useful. According to this economic theory, the wealth of the nation was important. Wealth for the people was not considered a useful target; quite the contrary, poverty for the common people was seen as a necessary motivation for people to work. This focus on the wealth of the nation rather than its population was reflected in many leading-edge building projects at the time in Sweden as well as in other parts of Europe. A number of demanding canal building projects were completed in Sweden during the 18th century and the first half of the 19th century. These required a suitable building material of which mortars that could harden under water were an important part. The political leadership in Sweden during the mid-18th century was much in favour of research. As a result of this a number of prominent researchers in the field of chemistry and mineralogy were engaged in the development of suitable mortars that could be based on Swedish materials [1-5]. The line that was most favoured was the use of synthetic pozzolans based on shale ash sourced from burned alum shale. As a result, Sweden concentrated on the development of mortars with these properties while other European countries were more focused on the development of hydraulic binders.

2 Limestone and alum shales used for lime and pozzolan production in Sweden

The limestone used for lime production in Sweden is of two main types. One type is a sedimentary limestone from the counties of Skåne, Öland, Gotland Västergötland, Östergötland, Närke and Jämtland. Their chemical composition ranges from a pure limestone at a few sites to those with a high content of silica; the age of these limestones range from Tertiary to Cambrian. The other rock type used is a Pre-Cambrian metamorphic marble of a calcitic and dolomitic composition from southern central Sweden.

Alum shales of Cambrian age are widespread in Scandinavia and on the eastern side of the Baltic Sea. These are characterised by a high content of organic material, commonly about 10% and sometimes as high as 30%. They are also characterised by the high content of elements such as uranium, thorium, vanadium and molybdenum [6]. These shales occur in several areas in Sweden, but it is only the alum shales on the island of Öland and in the counties of Västergötland, Östergötland and Närke that have organic contents high enough for use as a fuel.

3 Development of mortars with artificial pozzolans

There are several early examples of mortars with burned alum shale. Early occurrences include 12th century lime paintings in Fornåsa [7] and medieval masonry churches in the county of Jämtland in northern central Sweden. In these cases the alum shale was probably burned with the limestone. Alum shale mortars were used in a few rare cases in the masonry of medieval castles in central Sweden [8]. These examples may sometimes reflect local practices where alum shale mortars were intentionally used as early as the medieval period.

The following description of the early development of hydraulic and pozzolanic materials in Sweden is based mainly on Johansson [9] and to some extent Strömbäck [10].

A large part of the technology used for waterside construction in Sweden during the 17th and the first half of the 18th century was imported from the Netherlands where the techniques were partly developed during the expansion of Amsterdam in the early 17th century. This prompted Sven Rinman to make a visit to the Netherlands in 1746-47. He was later involved in research on the topic of shale ash production at Garphyttan in 1770-71. The purpose of this shale ash production plant was the development of a cement that could be used for waterside construction. Rinman studied 23 different mortar mixes based on burned alum shale, brick dust, slag and trass; he showed that the mortars based on hard burned, partly melted, alum shale and lime did harden in water and that these mortars had properties comparable to the trass mortars. The mortars produced had no added aggregate and therefore the burned alum shale served also as an aggregate in these mortars. Production of Garphytte Cement continued from 1779 to 1828 with an annual production of 50 tons. The cement was delivered to mines and used in the construction of locks, houses and bridges such as the Norrbro Bridge in Stockholm (1788).

Johan Ulfström was responsible for the repair of canal locks in the Hjälmare Canal in 1772. He developed a mortar called "Ulfström Cement" based on a burned alum shale or trass which was mixed to a stiff paste with hydraulic lime and water for two hours. The mortar had to be used within a few hours after mixing.

Another researcher, Bengt Qwist Andersson, was responsible for cement and clinker production at Brinkebergskulle from 1770. He performed tests on different imported natural pozzolans as well as burned alum shale. Assessment of the burned alum shale used here demonstrated that it had properties similar to volcanic pozzolans.

The alum shale mortars were further developed in connection with the building of several canals and locks in Sweden during the late 18th and early 19th centuries. There was at this time an active programme of research and development in this field. The most important work was probably conducted by Gustaf Erik Pasch, who in 1817 began researching mortars for the construction of the Göta Canal. In his research he investigated the importance of the burning temperature and particle size distribution in alum shale ash. The alum shales could be burned at low temperatures but the important factor was that the particles were finely milled. He also investigated the mix proportions of the mortars. He suggested a number of mortar mixes where the mix proportions of lime, sand and alum shale ash varied with the lime used.

4 Production and utilisation

Alum shale lime mortar was called “cement”, while “Swedish Cement” was a name used by Sven Rinman. The manufacture of mixed and burned alum shale lime mortar required an industrial process that was initiated just after the first successful attempts at production had been completed. Manufacturing was concentrated at two major cement factories. One of them was at Garphyttan which was commissioned in 1771 as a direct result of Sven Rinman’s trials in 1770-71. Alum shale lime mortar was made here until about 1828, for use in hydraulic engineering projects etc, in Mälardalen and Stockholm, and possibly also for the 1800 Locks at Trollhättan. Another factory was established at Brinkebergskulle. Planning for a “cement and clinker works” was started as early as 1761, but the manufacture of clinker only began in 1770 and the manufacture of cement probably did not start until 1772 when the work on Gustaf’s Locks commenced (Fig. 1). Qwist Andersson was responsible for production in both cases.

The mortar was not solely used for infrastructure projects, although its main application was initially the locks in the Hjälmare Canal and Brinkebergskulle (1772 and 1772-78 respectively), it was also used in housing projects. The Old Town Hall in Skövde (1775-76) is a very early example and is probably the first of its kind in Sweden.

Alum shale lime mortar from Brinkebergskulle was used for the locks in the Hjälmare Canal and Brinkebergskulle, and also as a cement mortar for joints in the construction of various buildings at the neighbouring Onsjö Manor (1774-93), as well as joints in the locks that were constructed in the Göta River at the end of the 1700s and possibly also in the 1800 Locks at Trollhättan. All these projects were in the west of Sweden.

Consequently, with the development of two alum shale lime factories, at Garphyttan and Brinkebergskulle, this type of mortar gained a strong position. The mortar was utilised in demanding construction and building projects during the 1800s until the introduction of Portland cement at the beginning of the 1860s, and above all from the start of the 1880s when domestic production of Portland cement was in force in Sweden.

Alum shale lime mortar was used extensively during the 1800s for projects such as the Göta Canal (1810-32) etc. This mortar was further developed by Gustaf Erik Pasch, who experimented with the choice of lime and mixing ratios. Natural hydraulic lime, both from orthoceratite limestone and strong bituminous antraconite, was preferred following comprehensive trials. Knowledge concerning production and utilisation of alum shale lime mortar was subsequently spread in Sweden through publication in the building handbooks of the 1800s and the early 1900s.

Fig. 1 Gustaf´s Locks at Brinkebergskulle in the Göta River, constructed 1772-78 with an alum shale mortar from the cement factory at Brinkebergskulle. Photo: Sölve Johansson 1989.

Alum shale lime mortar was also manufactured at Vargön under the name of "Vargö cement" during the period 1840-88, for projects such as the Locks in Trollhättan (1838-44), Stockholm Lock (1843-50), Saima Canal in Finland (1847-56) and the Dalsland Canal (1864-68). The initiative for this cement manufacture was taken by colonel engineer Nils Ericson.

In addition, local manufacturing of alum shale lime mortar probably occurred in Västergötland, where a very large number of buildings have been reported as using this type of mortar. This applies not only to the prominent buildings commissioned by the state, such as law courts and church buildings, but also to modest private buildings and housing.

Alum shale lime mortar was utilised above all for bricklaying and jointing, but it has also been used for rendering and broom finishing. The latter was used especially on exposed façades facing south and west. It was also utilised as a set mortar in the mounting of façade ornamentation, for example on Karlstad Town Hall. This type of façade ornamentation consisted of gypsum and natural cement.

Knowledge about the production and use of alum shale lime mortar obviously did not disappear with the rising popularity of Portland cement in construction and hydraulic engineering projects in the 1880s. Its use did however become limited. Alum shale lime mortar - or rather alum shale lime cement mortar – was used in the making of red Örebro render during the 1910s and 1920s (Fig. 2). The burnt alum shale for this production was brought from Lanna and Latorp, from sites such as Garphyttan. This mortar is still produced as a restoration mortar for buildings originally built using the Örebro render.

The usage of alum shale mortar for house building increased during the 19th century. In the 1920s the process was adapted for the production of autoclave-aerated concrete. Production continued until the 1970s, when it was abandoned due to the high radon emissions deriving from the uranium content in the shale ash present in these blocks.

Fig. 2 Örebro render at domestic house in central Örebro. The house was built 1912-13 with a red render based on burnt alum shale from Latorp near Garphyttan. Photo: Sölve Johansson 2002.

5 Microstructural characteristics

5.1 Methods

The quantitative microscopic analysis was performed according to the methods described by Lindqvist & Sandström [11] and the COM-C1 method [12]. Size distribution was assessed using NT BUILD 486. The chemical analysis of acid-soluble components was performed according to the methods described in Lindqvist et al [13]. The scanning microscopy was performed using Jeol 5100LV equipped with a Link Inca EDS equipment for micro chemical analysis. The instrument was used in low vacuum mode. XRD was used to identify mineral phases and amorphous hydration products. The instrument used was a Siemens D5000 powder diffractometer, operating with Cu K_α radiation for 2θ range between 10° and 70° at 0.5°/min. About thirty samples have been analysed and those presented in the tables have been selected in order to illustrate the variation of properties in a representative way.

5.2 *Microstructural characteristics*

The colour of the paste in the shale ash mortars is a relatively dark red, which is mainly due to the presence of iron oxides and hydroxides from the burned shale. In several cases the paste is uncarbonated or not fully carbonated; an uncarbonated paste implies the presence of CSH gel. The cement index, assessed through analysis of acid-soluble components, gives a hydraulicity that ranges from that of a pure lime mortar to a strongly hydraulic mortar (Table 1). There are small remnants of unhydrated cement clinker grains in some of the mortars which probably come from the burning of a lime shale mix, mainly in samples from the 18^{th} and 19^{th} century mortars – a technique favoured by Sven Rinman in the 1770s. An example is sample SP6 from the masonry of a private house built in 1788. This sample also contains the calcium silica mineral gismondite. There is also cement clinker in samples from locks built 1788 and 1844. The latter samples are not included in the tables. The main part of the CSH-gel is formed through a pozzolanic reaction which is probably based on the formation of reactive glass during the burning process.

The air content in the mortars shows a large variation. The shape of the air voids varies from irregular and elongated to well-rounded. Fluorescent microscopy shows that there are generally very few cracks; these are mainly in the form of shrinkage cracks and cracks between different layers of renders, and occasionally as open cracks between the different layers in the same layer of render. In some cases the shrinkage cracks can occur around and within shale ash particles.

Table 1 Results from analysis of acid soluble components given in weight-%. The cementation index CI according to Eckel [14] is also given in the table. SP6 masonry mortar private house 1788, SP4 military fortress 1779-1782, SP47 and SP48 town hall 1775-1776.

Sample	Mg	Al	Fe	CaO	SiO_2	CI
SP6	0.34	0.94	0.34	8.6	1.22	0.52
SP4	0.77	1.17	0.23	17	1.66	0.34
SP47	0.084	0.551	0.35	11.19	2.929	0.85
SP48	0.06	0.128	0.111	11.53	0.386	0.12

The aggregate is mostly fine grained with a maximum grain size of 2 or 4 mm with a well graded size distribution (Table 2). Other properties, such as the shape of the aggregate, show no difference when compared to other mortar types from the same region and time.

Table 2 Examples of grain size distributions given in volume-% based on microscopic assessment

mm	SP47 Vol-%	SP48 Vol-%	S1Out Vol-%	S1 In Vol-%	SP41 Vol-%	SP40 Vol-%
4	100					
2	87			100		
1	78	100	100	90	100	100
0.5	46	95	96	59	74	74
0.25	20	75	75	32	33	33
0.125	5	19	26	9	8	8
0.063	0.5	1.8	3	1.6	0.9	0.9

Preserved shale particles, which are elongated often with an ellipsoid shape, display internal shrinkage cracks and adhesion cracks due to the shrinkage of the shale ash particles. The finer particles have largely reacted, leaving just the larger shale ash particles which have to a large extent also reacted to different degrees. These range from intact or almost intact particles, to mainly fine-grained particles, where only a skeleton of the iron oxides and hydroxides remain (Figs. 3 and 4).

The mix proportions, based on point counting, vary from very binder-rich to those that compare with modern pozzolanic mortars (Table 3).

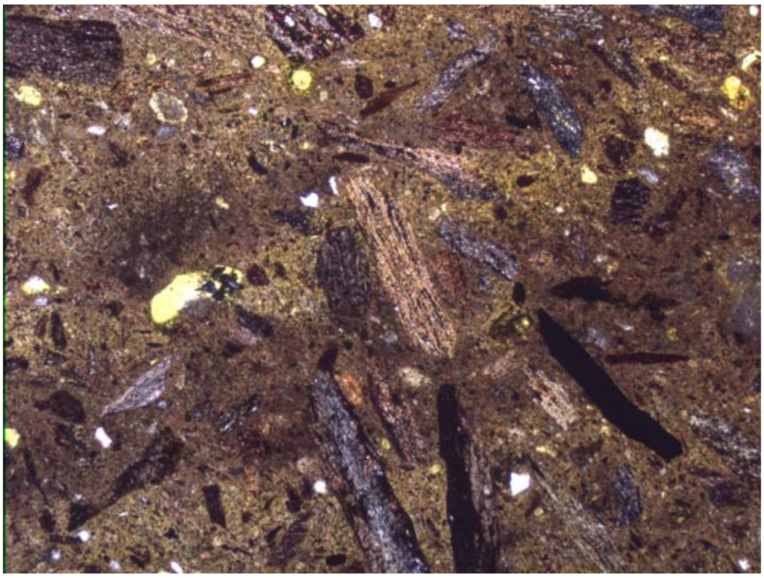

Fig. 3. A sample with a high amount of shale ash particles that is partly or almost fully reacted. Sample SP9 from a private building built in 1788. The image was taken by optical microscope using plain light, the surface measures 2.7 x 2.0 mm^2.

Detailed analysis using electron microscopy demonstrates that shale ash particles that may seem inert at low magnification show a reaction at higher magnification. Shale ash particles may display sharp grain boundaries in the low magnification BSE images as well as in the chemical distribution. At higher magnification it can be seen that there is a zone of paste that is enriched in Si surrounding the shale ash particle (Figs. 5 and 6).

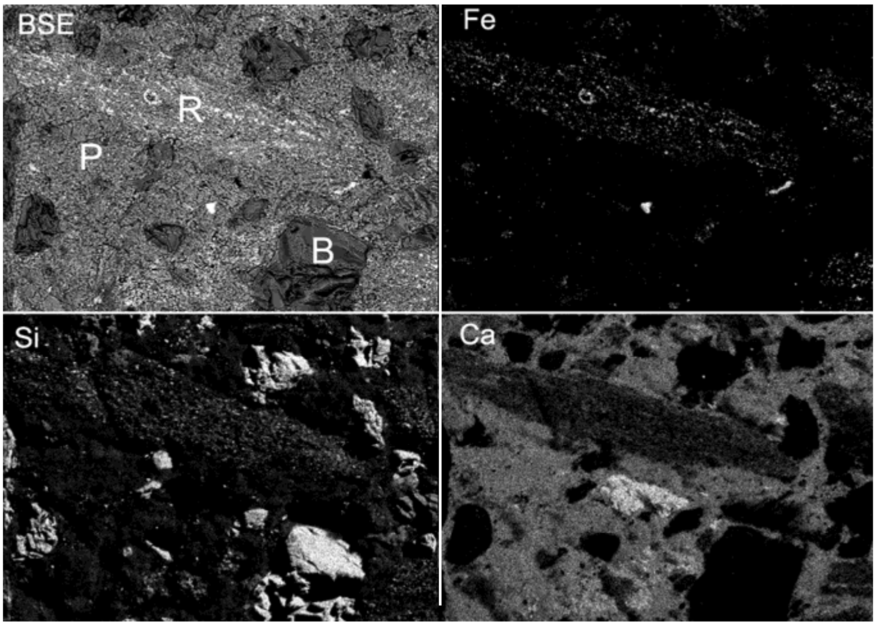

Fig. 4 Shows the back scatter electron image (BSE) combined with EDS maps of the distribution of iron (Fe), silica (Si) and calcium of an almost totally reacted shale ash particle. R: burned shale, P: lime paste, B: aggregate. Repair mortar from a royal castle in south eastern Sweden. Probably 19th century. The instrumental magnification is 200x.

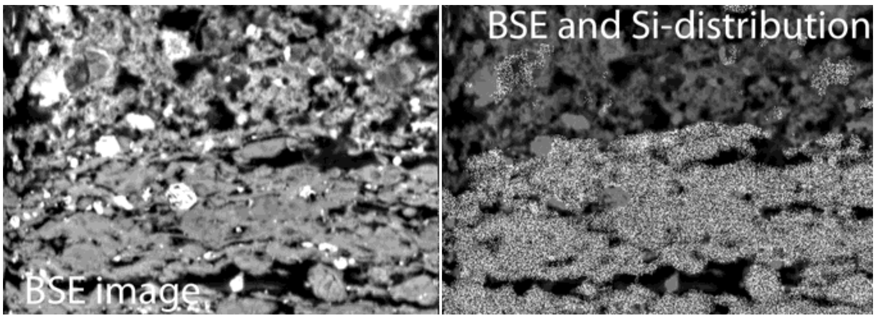

Fig. 5 The right hand image shows as white dots the distribution of Si^{4+} close to the shale ash particle seen in the lower part of the image. The Si-element map were transformed to binary image using adaptive grey value segmentation and then combined with the BSE image. Sample SP51 render on the old town hall in Skövde, 1775-1776. Instrumental magnification 1500x.

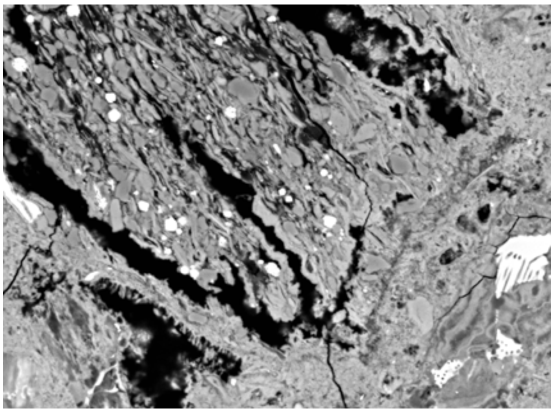

Fig. 6 SEM/BSE image of a shale ash particle rim which is partly decomposed by a pozzolanic reaction. As a result of the reaction there is no sharp contact between the particle and the surrounding paste. The ash particle shows internal shrinkage cracks. Sample SP51 render on the old town hall in Skövde, 1775-1776. Instrumental magnification 750x.

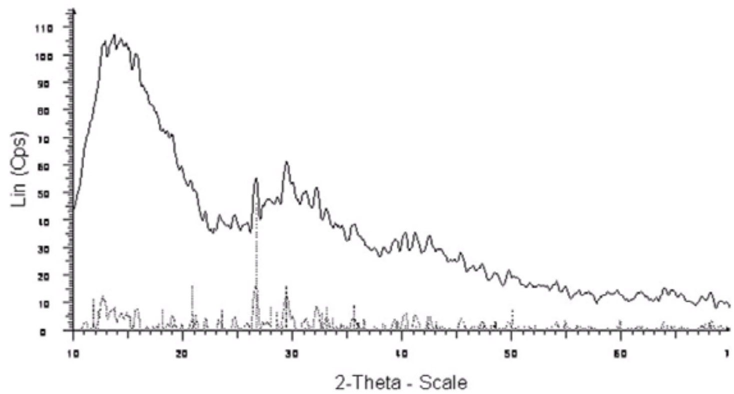

Fig. 7 X-ray diffractograms of the sample SP6. The broad band shows the presence of an amorphous CSH-phase. The diffractogram is shown after smoothing.

X-ray diffraction shows a broad hump in the range 10° to 20° 2θ and around 30° 2θ implying that the sample contains amorphous CSH gel (Fig. 7). XRD analysis also shows the presence of the minerals calcite, hematite and the zeolite gismondite [9].

6 State of preservation

The old canals and locks that are mentioned in the text are protected as fixed ancient monuments in accordance with Swedish legislation concerning the preservation of historic monuments and the buildings that have been examined in most cases are architectural monuments. This signifies that these constructions and buildings are well protected. It is necessary however, in connection with measures taken on these objects, to ensure that all forms of mortar are protected in practice, e.g. jointing mortar, grout and finishing mortar.

Table 3 Examples of mortar compositions based on microscopic analysis. Results are given in volume percentages. The samples come from masonry and renders of houses in Sweden. The samples are ordered by age, with the oldest which are from 1750 to the left and the youngest from 1905 to the right.

	SP42 Vol %	SP4 Vol %	Näs 2 Vol %	SP13 Vol %	S1out Vol %	B thin Vol %
Air	5	5	8	3	4	4
Aggregate	43	7	37	37	36	51
Paste	49	69	40	55	59	37
Lime lump	0	0	10	0	1	7
Cement	2.2	0	0	0	1	1
Shale ash	2	18	4	5	2	1
Period	1750	1779	1820	1865-68	1890	1905
Mortar	Masonry	Masonry	Masonry	Masonry	Rend	Rend
Type	House	Fortress	Church	Lock	House	House
Location	Skåne	West Sweden	Northern central Sweden)	West Sweden	West Sweden	West Sweden

7 Discussion/conclusion

Alum shale lime mortar, which was called “cement”, emerged in 1770 as a direct result of Swedish research into mortars during the 1700s which had the main objective to find domestic supplies for hydraulic engineering projects. This constituted a breakthrough for the Swedish pozzolana mortars. The brickdust lime mortar that had been introduced a century earlier was only partially pozzolanic. The production and utilisation of both natural cement and alum shale lime mortar required an industrial process that started after the first successful attempts. The utilisation was not only for infrastructure projects, for which the mortar primarily was intended, initially the locks in the Hjälmare Canal and Brinkebergskulle (1772 and 1772-78 respectively), but also in housing projects. The Old Town Hall at Skövde (1775-76) is a very early example, probably the first of its kind in Sweden. Its utilisation as mortar, grout and render was extensive until the 1880s when these types of mortar were replaced by Portland cement. Alum shale lime mortar was used from the 1770s until the 1920s for a variety of purposes, e.g. jointing and render. One type of alum shale lime mortar is the Örebro render from the 1910s and 1920s, which came into use again in the 1990s for restoration objects. The micro structural analysis confirms the pozzolanic properties of the burned alum shale. The analysis furthermore illustrates the variation and development of this type of mortars.

8 Acknowledgement

The XRD analyses were performed by Dr Britt-Marie Stenari, Chalmers, and the analysis of acid soluble components by Peter Nyman, SP, which is kindly acknowledged.

9 References

1. Gadd PA (1770) Rön och försök med murbruk och ciment-arter. Kungliga Svenska Vetenskapsakademiens handlingar XXXI 189-206
2. Pash GE (1824) Berättelse om de vid Motala ström anställde Murbruksförsök, inlämnade till Götha Canals Direction år 1818 och 1822 års Berättelse om de vid Göta Kanal anställda Murbruksförsök. Jernkontorets annaler Stockholm 1824, p 192-296
3. Qwist Andersson B (1770) Försök anstäldte på Trass. Kungliga Svenska Vetenskapsakademiens handlingar XXXI, 49-66
4. Qwist Andersson B (1772a) Försök med Terra Puzzolana och cement. Senare stycket. Kungliga Svenska Vetenskapsakademiens handlingar XXXIII, 120-132
5. Qwist Andersson B (1772b) Försök med Terra Puzzolana och cement. Kungliga Svenska Vetenskapsakademiens handlingar XXXIII, 28-42
6. Andersson A, Dahlman B, Gee DG, Snäll S (1985) The Scandinavian Alum Shales, Sveriges Geologiska Undersökning Ca 56, 50 pp
7. Henningsson A (2003) The Romanesque wall painting above the vaults in Fornåsa Church. Examination and developing of a conservation proposal. Documented in GIS. Dipl thesis on CD. University of Applied Science, Cologne
8. Feldt AC, Modén E (2001) Murbruk som källmaterial. Östergötlands museum. Rapport 19:2001. Linköping
9. Johansson S (2007) Hydraulic lime mortar Its Production and Utilisation in Sweden in Buildings from the Middle Ages until present Time. Göteborg Studies in Conservation 20, 327 p (In Swedish with summary in English)
10. Strömbäck L (1993) Gustaf Erik Pasch, Göta kanal och bruket av hydrauliskt cement. In: Polhem. - Göteborg: Svenska nationalkommittén för teknikhistoria (SNT), 1983-. - ISSN 0281-2142. ; 1993 (11), s. 135-143
11. Lindqvist JE, Sandström M (2000) Quantitative analysis of historical mortars using optical microscopy. Materials and Structures vol 33, 612-617
12. COM-C1 (2001) Assessment of mix proportions in historical mortars using quantitative optical microscopy. RILEM TC-COM: Characterization of old mortars. Materials and Structures vol 34, 387-388
13. Lindqvist JE, Nijland T, von Konow T, Wester Plesser TS, Nyman P, Larbi J, van Hees R (2006) Analysis of mortars with additives. Nordtest Technical Report 594

Eckel EC (1922) Cement Limes and Plasters. New