HISTORIC CONCRETE – LOOKING AT THE LITTLE THINGS

HISTORISCHER BETON – DER BLICK AUF DIE KLEINEN DINGE

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SUMMARY

As part of the close cooperation between the Materials Testing Institute at University Stuttgart and the Baden-Württemberg State Office for Monument Preservation (LAD), the concrete project of the LAD tested which information can be obtained from small concrete samples using current methods and interdisciplinary discussion. Two micro-samples (a piece of concrete and a white crust) were taken from a railroad bridge in Stuttgart and characterized using various analytical methods. The concrete is the original building material with travertine as aggregate and brick dust as an additive. The white crust is a lime sinter with impurities of salts. With minimal intervention in the building fabric, existing information and assumptions about the composition could be confirmed and further questions about the material combination and possible causes of damage could be formulated.

ZUSAMMENFASSUNG

Im Rahmen der engen Zusammenarbeit zwischen Materialprüfungsanstalt Universität Stuttgart und dem Landesamt für Denkmalpflege Baden-Württemberg (LAD) wurde innerhalb des Betonprojektes des LAD erprobt, welche Informationen an Kleinstproben aus Beton mit heutigen Methoden und fachübergreifender Diskussion ermittelt werden können. Von einer Bahnbrücke in Stuttgart wurden zwei Kleinstproben (ein Stück Beton und eine weiße Kruste) entnommen und mittels unterschiedlichster Analytikmethoden charakterisiert. Bei dem Beton handelt es sich um den bauzeitlichen Beton mit Travertin als Gesteinskörnung und Ziegelmehl als Zusatzstoff. Die weiße Kruste ist ein Kalksinter mit Salzverunreinigungen. Mit einem minimalsten Eingriff in die Bausubstanz, konnten bestehende Informationen und Vermutungen zur Zusammensetzung bestätigt und weiterführende Fragestellungen zur Materialkombination und möglichen Schadensursachen verfasst werden.

1. INTRODUCTION

Concrete has been used in Germany since the mid-19th century. The first cement plants appeared in northern Germany around 1850 and quickly spread from there to the west and south [1]. The relevance of concrete as a building material has developed steadily since its discovery, for example from the invisible replacement of structural natural stone masonry to the imitation of decorative natural stone façades and today's exposed concrete, which stands for itself. Due to the good connection to the north of Germany via the Rhine and abundant and easily accessible deposits of limestone and marl in the Swabian Alb region, this early development is clearly visible in the still-existing buildings in Baden-Württemberg [2].
As part of the Concrete Project of the Landesamt für Denkmalpflege Baden-Württemberg (State Office for the Preservation of Monuments), further denoted as LAD, this history of concrete development was documented on the basis of selected buildings. This ranges from engineering and high-rise buildings from the middle of the 19th century to imposing buildings made of reinforced concrete in the 20th century and the modern use of the building material for daring architecture and art objects, including for example the works of Hajek, who is a famous artist around Stuttgart. [3] In addition, the materiality of different periods was analysed intensively to make recommendations for the protection of listed contemporary testimonies to this history.
An example of this are early structures necessary for railway traffic, such as the railway bridge with adjoining railway embankment in Bad Cannstatt, Stuttgart. Small samples from this bridge were investigated through close cooperation between the Materialprüfungsanstalt Stuttgart (Materials Testing Institute) and the LAD. The main question here was whether such a small sample quantity is sufficient for a fundamental analysis using today's examination methods. If the sample quantity is enough for an analysis, the limits of the individual investigation methods should be explored. This will allow sample quantities for future projects to be better estimated and interventions in the monument to be minimised.

2. SITE AND SAMPLE DESCRIPTION

The samples analysed in this study originate from the abutment and the adjoining embankment of a railway bridge in Bad Cannstatt, Stuttgart. It was built between 1912 and 1914. The surfaces of the abutments contain ornamental reliefs belonging to the city of Stuttgart and the quartier of Bad Cannstatt. An overview of the site from two directions can be seen in Fig. 1.

Fig. 1: Overview of the railway bridge in Bad Cannstatt, Stuttgart. Top: view from Stuttgart, showing the regional abutments of Stuttgart (left) and Bad Cannstatt (right). Bottom: view from Bad Cannstatt. (Source: F. Pilz, LAD)

The surface of the structure shows typical signs of weather and vegetation induced erosion. The concrete displays small fracture nets along edges and faces, with some parts already breaking of in small chunks revealing deeper concrete layers behind. Further along some cracks show white efflorescence and crustal formations on the concrete. From two specific sites like these the samples for this study have been taken:

- Two small (ca. 1-1.5 cm in diameter) samples, further denoted as *concrete*, see Fig. 2. They show brittle fracture failure and have been collected in the base area below the right coat of arms (view from Bad Cannstatt), as seen in Fig. 2.

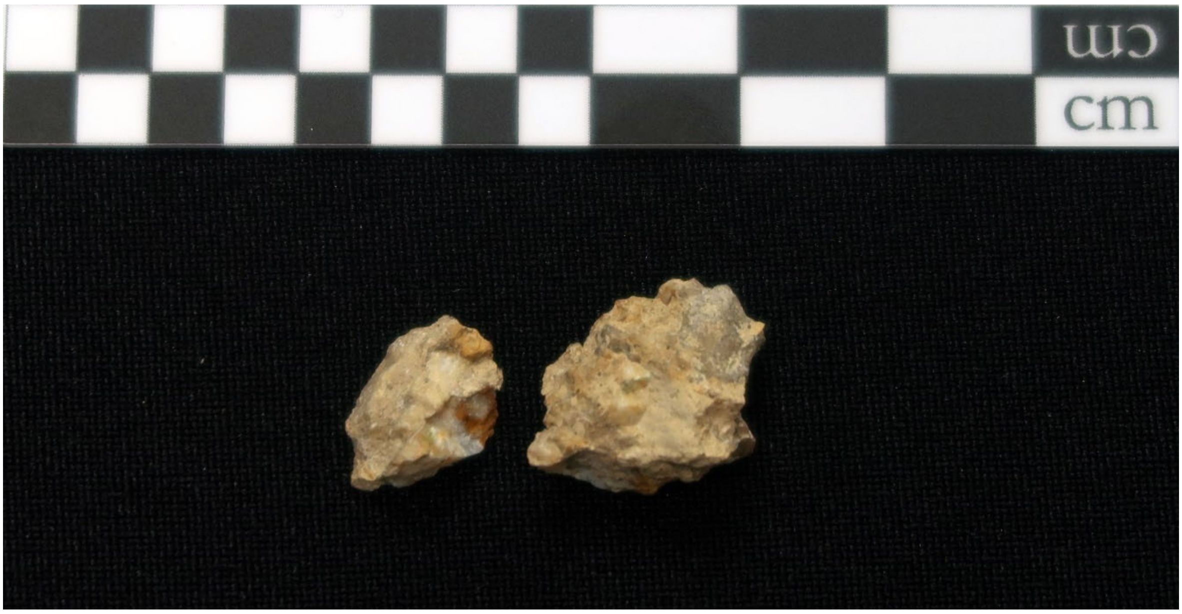

Fig. 2: Overview of the sample „concrete" showing two beige-brown pebbles

- A sample of white crust, further denoted as sample crust, see Fig. 3. This was taken from the extension of the railroad embankment near the abutment of Stuttgart (viewed from Stuttgart).

Fig. 3: Backside overview of the sample "crust". At the top a few white areas are visible, but on the back, green overgrowth of biological colonisation on top of a beige-brown material can be seen

3. METHODS

In this study multiple analytic techniques have been applied, though both samples have been studied differently. The techniques used here were optical microscopy (OM) of thick sections and polarized light microscopy (PLM) for thin sections, X-ray diffraction (XRD) for mineralogical analysis and thermogravimetry (TG-DSC) for phase transition analysis.

For the *concrete*, the samples were embedded into Araldite 2020 epoxy resin with a fluorescent pigment. The hardened probe was then cut and one half was ground and polished to allow for optical study of the thick section. For this a ZEISS Stemi SV 11 stereomicroscope with a LEICA MEB 115 confocal light source and a LEICA DFC 295 camera were used. Image analysis was carried out using the LEICA Application Suite software, version 4.13.0. With this an overview of the internal structure could be generated and further techniques such as etching and colouring could be applied to this sample in future studies.

The other half was further prepared into a covered 30 µm thin section. This was then analysed under a LEITZ ORTHOPLAN-POL microscope with a LEICA DFC 290 HD camera to identify the concrete constituents and aggregates. Pictures were analysed again using the Leica Application Suite software, version 4.13.0. By using the fluorescent pigment in the resin, a value of the water-cement-ratio (or w/c-value) can be estimated given a large enough section of binding material.

For the *crust,* a different approach was used. First, a part of the sample was broken off and embedded into SCANDIPLEX epoxy resin. This was then ground and polished using water as a lubricant and SiC grinding and polishing papers. With the so-prepared surface, the internal structure was studied.

Such a preparation leads to the loss of easily soluble components, such as certain salts. To detect these, X-ray diffraction of an aliquot of the *crust* was carried out. For this, the white residue was carefully removed from the remaining piece using a scalpel, ground, and sieved to a fineness of < 63 µm. This powder was then subdivided into two aliquots. One of these was analysed for its mineralogical composition using XRD in a Bruker AXS D8 with Cu radiation and a Sol-X-semiconducting detector. Evaluation of the resulting data was carried out using the EVA 2 software package from Bruker.

The other subsample was analysed using TG-DSC to study phase transitions, and mass losses as well as to infer possible non-crystalline components within the material. For this, a Netzsch STA 409 Simultan TG-DSC with a temperature interval from 25-950°C, a constant heating rate of 10 K/min, and N_2 as a flushing gas was applied. Data evaluation was carried out using the Netzsch Proteus Thermal Analysis software package, version 6.1.0.

4. RESULTS

4.1 Concrete analysis

4.1.1 Optical microscopy

Fig. 4: Overview of the thick section from the "concrete" sample, embedded in fluorescent epoxy resin. The binding material appears bright, with only small particles inside. There is one large aggregate in the center and more remnants of other aggregates along the sides.

The thick section of the *concrete* sample can be seen in Fig. 4. The sample size is 15 x 11 mm. It is composed of a large, 6 x 8 mm wide, greyish aggregate in the centre and a beige-coloured binding material and other remnants of aggregates on the sides. Within the binding material, the largest particles appear reddish, with a diameter between 500 to 1000 µm. Most grains, however, are small, less than 200 µm in diameter, mostly with a clear or dark grey appearance.

4.1.2 Polarized light microscopy (PLM)

An overview image of the thin section in linear polarized light (LPL) and cross-polarised light can be seen in Fig. 5 top.

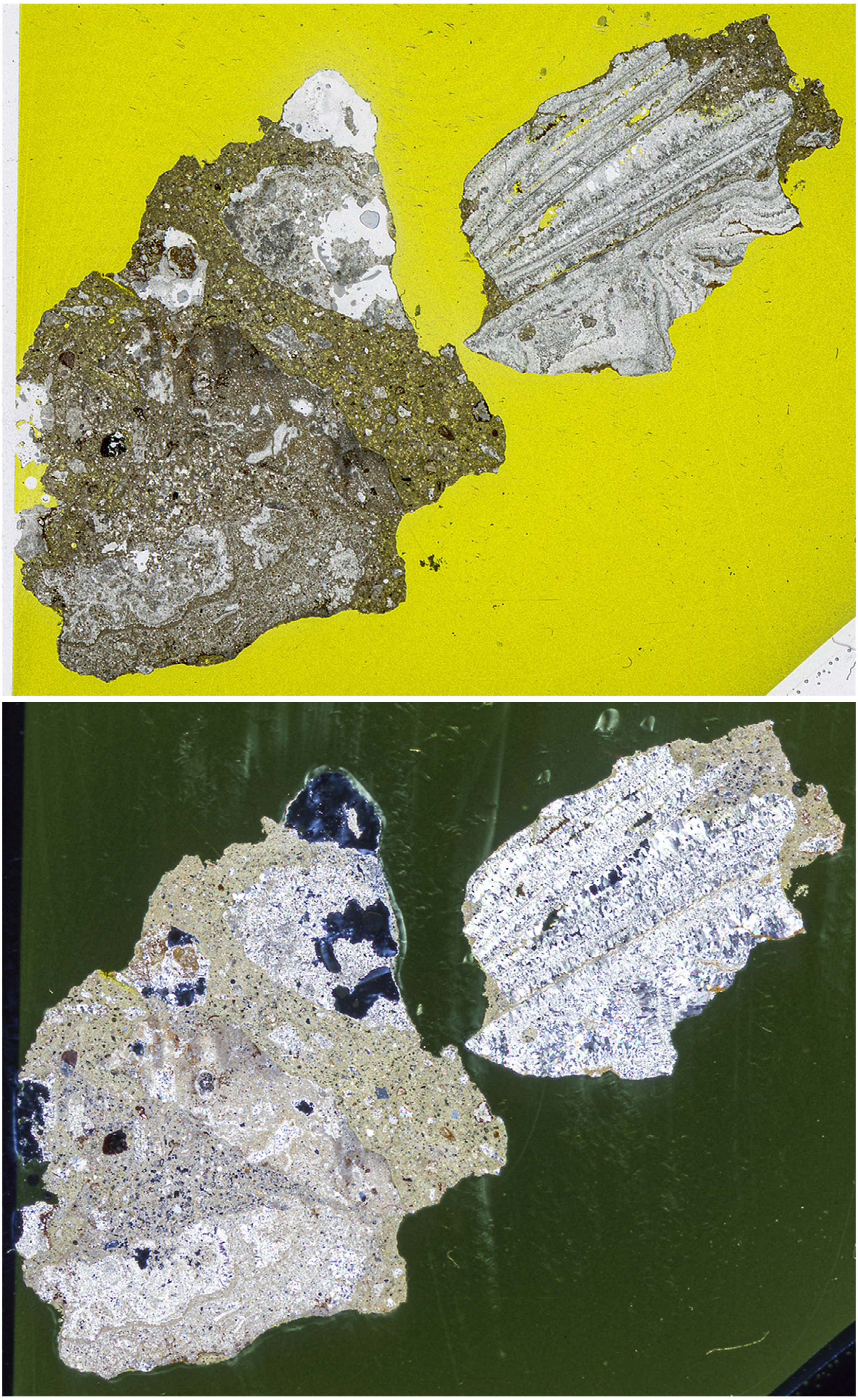

Fig. 5: Thin section overview of sample "concrete". LPL is visible at the top, XPL at the bottom

The thin section contains two parts: on the left is a larger particle, the corresponding sample to the thick section from the previous chapter; The second (in the upper right corner) is the smaller sample from Fig. 2. It is mostly made up of a layered material and very little binder. The layers in the corner particle consist of calcite, identifiable by higher-order white interference colours. The individual layers appear straight in one part and wavelike in another, indicating it being a piece of lime sinter. As more binding material was available in the other particle, most analyses were carried out on this.

In concordance with the thick section, most of the corresponding particle is comprised of rock fragments, well visible in Fig. 5. The aggregates consist of mostly micritic and sparitic calcite, seldomly veins or pore fillings of calcite are visible. Within the micritic portions lie angular quartz grains with a diameter of < 100 µm. Further sampling is necessary to accurately determine the used aggregate, but the characteristics fit well with the regional material "Cannstatter Travertin", a travertine limestone which is abundant in the region of Stuttgart.

The binding material only appears as a roughly 3 mm wide zone between these grains. In this instance, none of the previously visible reddish particles are visible. Optically it appears very similar to the travertine, though a bit more yellow, probably due to the used resin. The interference colours of the binding material appear similar to those of the micritic areas of the aggregates, possibly indicating complete carbonation of the matrix.

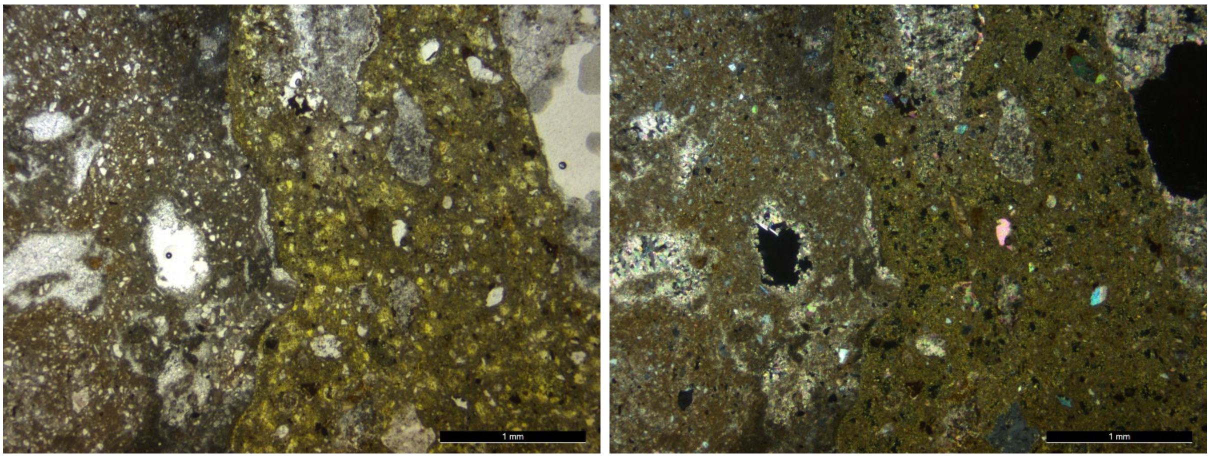

Fig. 6: Comparison of aggregate (left half) and binding material (right half). The higher porosity of the binder can be traced by the yellow resin in LPL (left). In XPL (right) the interference colours of binder and aggregate appear very similar indicating a high degree of carbonation

Under higher resolution, the differences between aggregate and binder are highlighted, see Fig. 6. In LPL, the binding material is well distinguishable from the aggregate, due to the yellow hue of the resin. The large aggregate appears brownish and there are smaller aggregate fragments present within the binding material. Further, small calcite and quartz crystals (< 100 µm) are visible within the binder as well. The non-binder particles show a continuous grain size distribution and are generally angular. The binding material shows a high porosity of yellow, resin filled pores and is completely carbonated, no restitic portlandite was identified anywhere in the section. The irregular shape of the pores and general distribution of the resin indicate beginning dissolution of the fully carbonated binder.

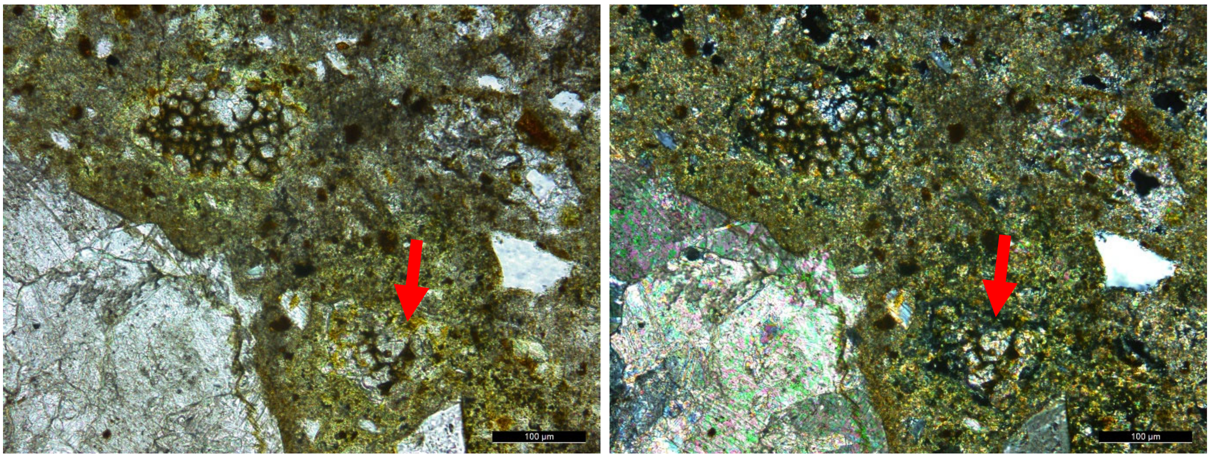

Fig. 7: Clinker aggregates within the binding material, mostly comprised of round belite grains and few alite crystals (see red arrow). Around the crystals brownish rims are visible. High interference colours in XPL (right) indicate pseudomorphic substitution of the clinker minerals with calcite

Within the binder many relict clinker aggregates were identified, see Fig. 7. The majority show only belite (C_2S) crystals, with a round, “grape-like” appearance and rimmed with brownish aluminate and/or ferrite. In some instances, small amounts of alite (C_3S) were identified by its more angular shape and internal clarity, see red arrow in Fig. 7. Most aggregates show a clear border to the binding material and sometimes even remainders of the previous reaction rim are conserved, see Fig. 8. The clinker grain size normally lies between 100 to 200 µm, though multiple clinkers with sizes exceeding 200 µm have been recorded as well.

Apart from the clinkers, the binder contains the aforementioned rock fragments and even smaller mineral grains, see Fig. 8. As visible there, small reddish to black particles were identified throughout the matrix, mostly below 50 µm in diameter, though larger conglomerates have also been found. This could indicate the use of ground brick dust as a pigment for the concrete.

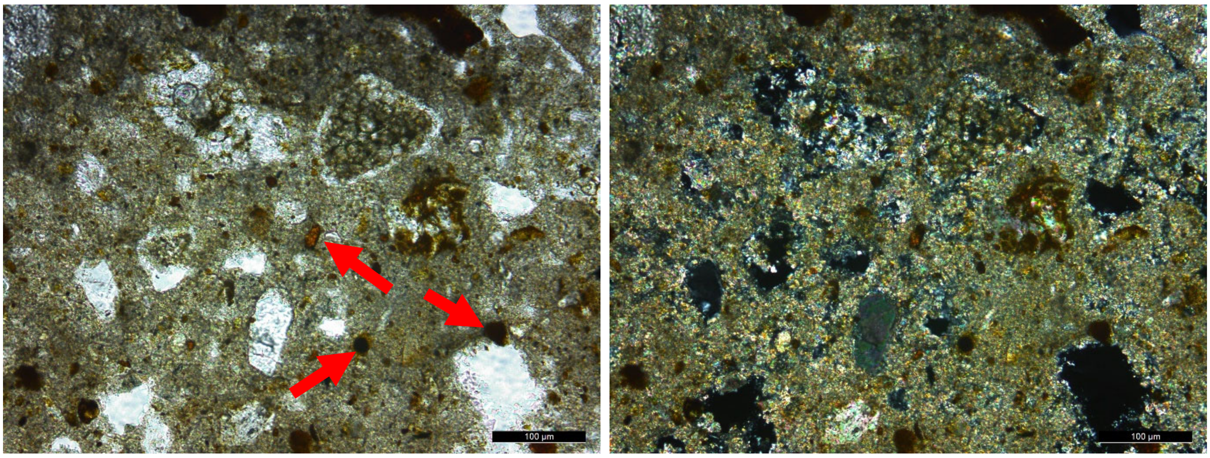

Fig. 8: Binding material containing a clinker aggregate with a reaction rim, multiple pores and quartz grains and small reddish particles, see arrow.

4.1.3 Summary

The *concrete* sample mostly consists of a travertine aggregate, possibly originating from regional deposits near Bad Cannstatt, Stuttgart. Analysis of the binding material indicate a historic cement of mostly belite and small amounts of alite contained in clinkers ground to a medium size between 100 to 200 µm. Clinker aggregates above 200 µm in diameter are common. All clinkers have been completely pseudomorphically substituted by calcite and the binding material shows signs of weather induced dissolution. Multiple fragments of crushed up travertine and brick dust have been identified and were possibly used to adjust the colour of the concrete to achieve closer resemblance to the natural stone.

4.2 Crust analysis

4.2.1 Optical microscopy

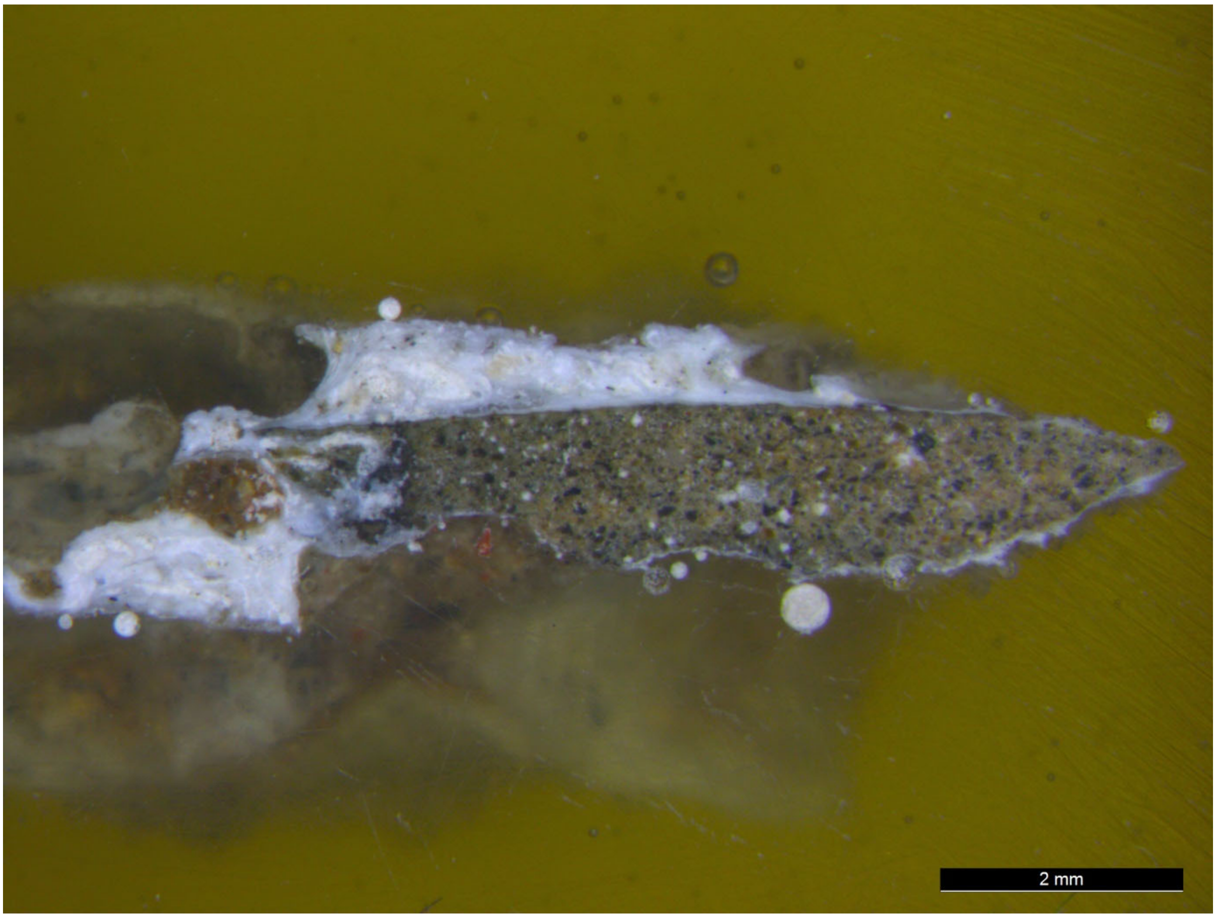

Fig. 9: Overview of the thick section from the sample "crust". Two distinct areas are visible, a bright white surficial deposit that is also present at the bottom side of the sample. The other material is beige and contains small grains (< 250 µm)

The thick section overview of the sample crust can be seen in Fig. 9. Generally, two areas can be distinguished: a beige, grain-containing material – most probably a small piece of the bridge concrete, from here on denoted as mortar – and the bright white deposit on its surface and bottom. The white deposit shows thicknesses between only a few µm and up to nearly 1 mm in its widest parts.

There is a sharp border between the two materials, though small pores within the mortar are filled with white residue. It is unclear whether this is primary or an effect of the sample preparation, though the latter is more likely as air pores within the resin are similarly filled in.

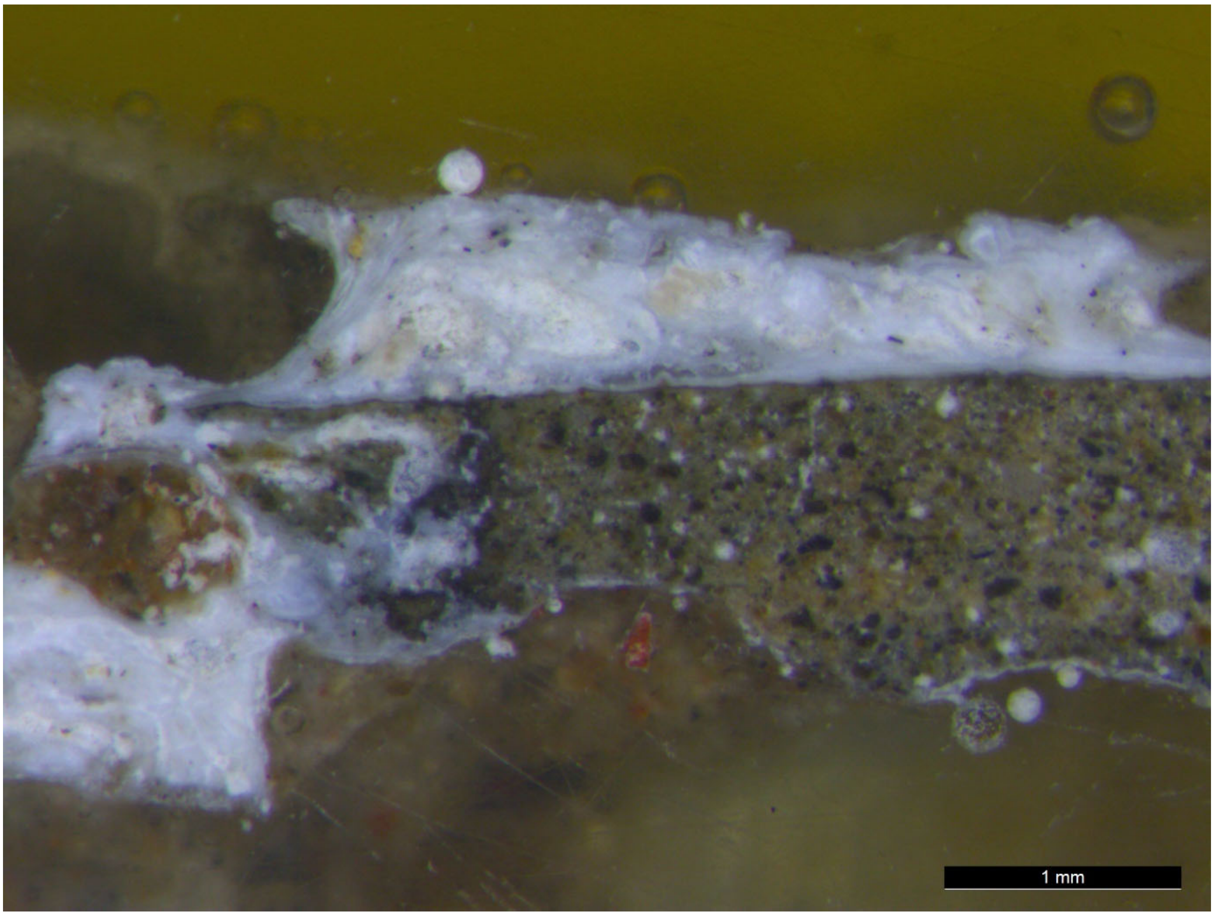

Fig. 10: A closer view of the contact between the "crust" and the "mortar". Within the crust, laminated structures are apparent and the border shows a sharp contact. Black particles around 100 are visible in a beige-coloured matrix within the mortar. Smaller particles were not resolvable under the stereomicroscope

Under higher resolution, see Fig. 10, laminated structures within the *crust* become visible, with flowing, fluid-like features. The layers appear very thin, at most 100 µm thick each. Further, a few discoloured areas are visible, not apparent using smaller resolutions. This could indicate material impurities or intrusion of the resin into voids of the sample.

4.2.2 X-ray diffraction (XRD)

The XRD results are shown in Fig. 11. The white residue separated from sample *crust* is majorly constituted by calcite, $CaCO_3$. Further, small amounts of quartz, SiO_2, were identified, probably representing the sand within the mortar below the white deposit. Trace amounts of salts, Pentahydrite and Niter, KNO_3, are also present, indicating salt contamination of the structure.

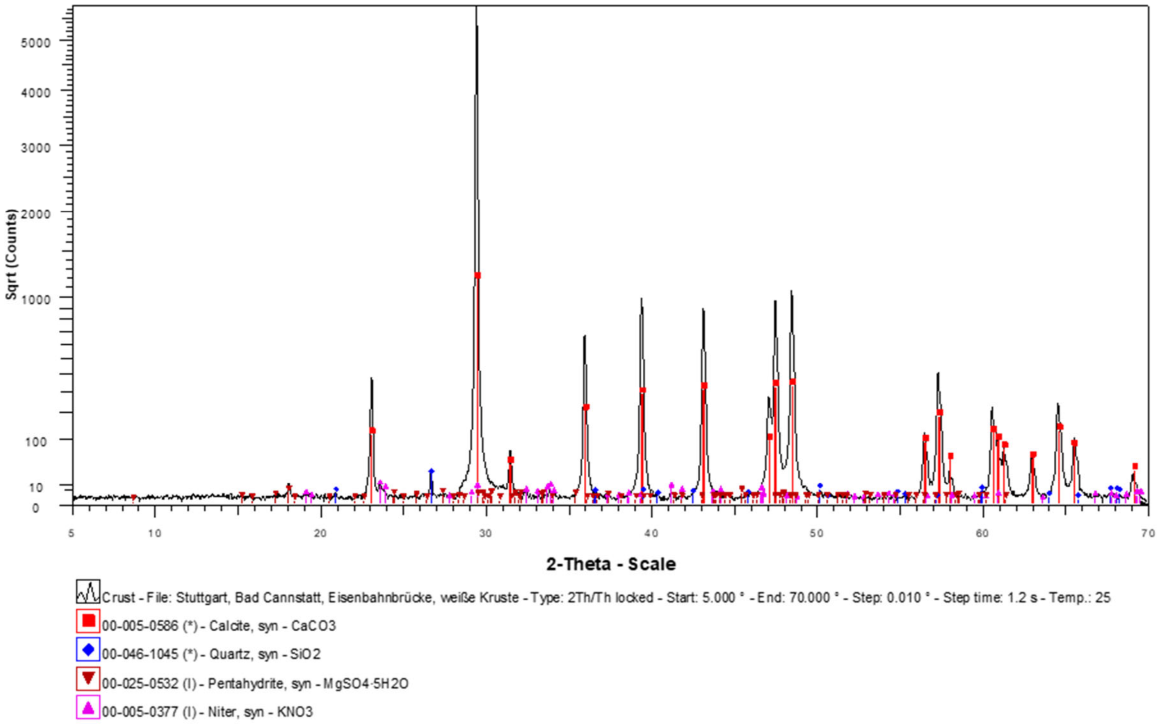

Fig. 11: X-ray diffractogram of the white deposit from sample "crust"

4.2.3 Thermal analysis (TG-DSC)

The results from the TG-DSC analysis are found in Fig. 12. The total mass loss of the run was nearly 42 wt.-%. This can be split into two different steps: a minor mass loss of around 2.5 wt.-% between 25 and 600°C, probably related to the release of adhered water and the decomposition of miniscule contents of organic matter; And a second, major mass loss of nearly 39.5 wt.-% between 600 and 780°C due to the decarbonation reaction of calcite. No other phase transitions or further mass loss above 780°C have been observed.

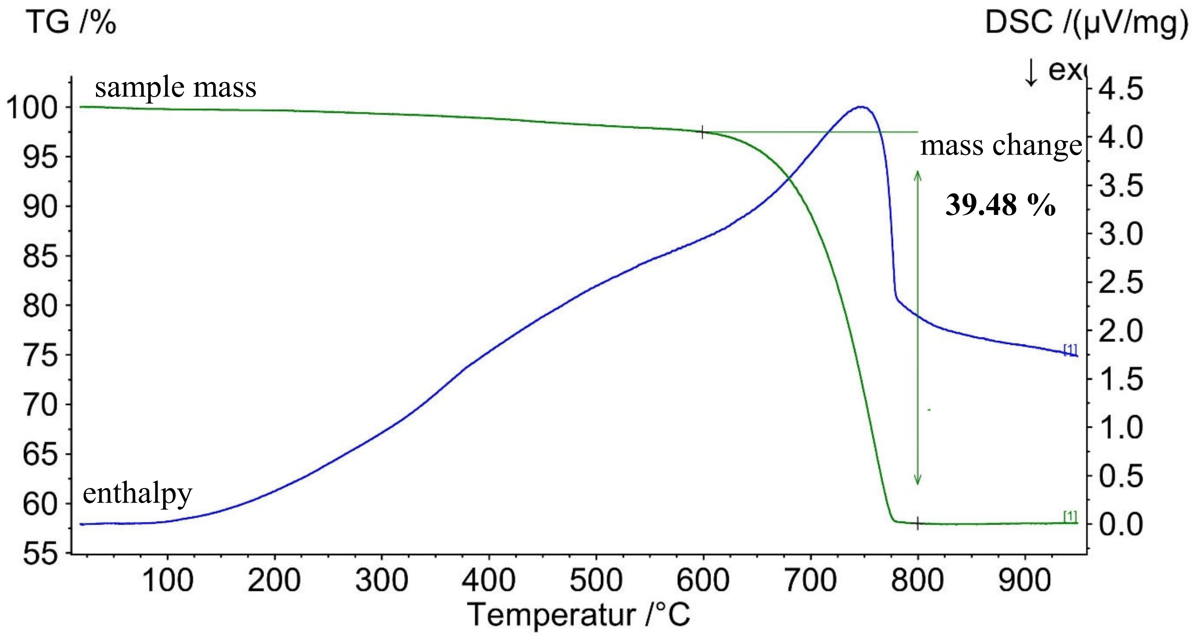

Fig. 12: Results from the TG-DSC run. The green curve represents the mass change of the sample, the blue one represents the changes in enthalpy, recording phase transitions like melting, evaporating, decomposition, and recrystallization

4.2.4 Summary

The *crust* is constituted of two materials: a thin piece of mortar, most likely a part of the concrete binder as no larger aggregates were found, and the white deposit that is layered on top but also surrounds the sample as a whole. This white deposit shows a laminar internal structure with flowing textures and it is nearly completely made up of calcite, with trace impurities of salts. It can therefore be assumed that this sample is a lime sinter, probably formed due to the leaching processes affecting the concrete structure, much like sinter formation in natural settings.

5. DISCUSSION

5.1 Concrete status and crustal formation

The results of this study have shown that the *concrete* sample is fully carbonated. Such a feature is not unexpected as it was taken from the surface of the sampling site and the integrity of the material at this location was already compromised. As no drilling core was taken, the carbonation depth can only be assumed. However, the present damages in the form of large-scale fracture networks and the formation of lime sinters indicate that the main damage process here is freeze-thaw attack with ample amounts of water inside the structure. The concrete of this bridge shows a high degree of porosity, which is primarily caused by the then typical production practices and then enhanced through leaching of the binder [4,5]. The bridge is not protected from rainfall and no constructive elements to inhibit water intake are visible. This allows for saturation of the porous network of the concrete, which is critical for freeze-thaw attack, forming the large fractures now visible.

Once inside, such water will enhance leaching processes, which have already been studied previously [6]. The most important process here is the exchange of fluids within the pore network: the normal solution, enriched in dissolved Ca^{2+} and OH, is replaced through introduction of meteoric water. This new pore solution has a lower pH, causing more dissolution of crystalline portlandite. The leached surplus of calcium ions is brought to the outside of the material, where, upon contact with CO_2 from the atmosphere, it can react to form calcite – the material which mostly constitutes the *crust* sample studied here. Other factors – such as dissolved calcite from the aggregates – probably only play a minor role in this, as the solubility of portlandite is orders of magnitude higher than that of calcite under ambient conditions. Via this process the formation of the lime sinter or *crust* samples over the long lifespan of the construct can be explained.

The incorporation of nitrates at a bridge like this is most likely due to biogenic sources, e.g. anthropogenic or animal waste products. The identified Mg-sulfate salts, however, require a Mg^{2+} source, normally stemming from dolomite or magnesite. In the studied sample no such phases were identified, which could be a sampling effect. As these salts have a very high damage potential in porous building materials [7], further study of used aggregates and other additives should be carried out to estimate the Mg-reservoir in the concrete.

5.2 Clinker aggregates and historic comparison

The remaining clinker aggregates in the binding material consist mainly of belite crystals and only contain minor amounts of alite. This fits nicely with previous studies on historic concretes, which found that there has been a change in the major phase mineralogy of clinker aggregates [8]. Corish and Jackson describe a change from belite-rich clinker aggregates towards more alite-rich clinkers over the years, with the tipping point roughly around the time of the World Wars. They mostly relate this with innovations in the technology of rotary kilns and also with increased demand for concretes with a better early strength development. Given the construction date of this studied railway bridge from 1912 to 1914, our findings underline the study of Corish and Jackson. Though further research on objects from other time periods and especially the transitional period is necessary.

Furthermore, the measured sizes of the clinker aggregates with a median width of 100-200 µm and sometimes even exceeding 300 µm fit well with other historic concrete constructions of a similar age, e.g. the artificial stones of the Sanatorium Garden in St. Blasien. A reason for this, in modern terms speaking, very coarse cement were most probably the then valid norms and regulations regarding ground cement sieving. This is most likely the reason so many clinker aggregates can be seen, as these larger aggregates show reaction rims, but are still preserved. This indicates an incomplete cement reaction. One possible theory could be that without todays concrete additives, the historic concrete was mixed without sufficient water, essentially allowing first hydration processes to occur. With the first reaction rims formed and not enough water being present, large clinker grains could not react fully. Over decades the clinker minerals were then either slowly replaced by calcite, preserving their original shape or even fully preserved if the hydration hull stayed intact. Further analysis of these aggregates via microscopy on more material and possible electron microscopy and elemental measurements might provide useful information on this.

5.3 Study limitations and future points of interests

The here analysed sample of an historic concrete was not an ideal sample. Its contact with the main structure was already compromised upon sampling, its size was too small to be considered representative and a full characterisation of the used aggregate, any additives and of the binding material itself was not possible.

Nonetheless, a great deal of information about the then produced concrete was retrieved from this small sample. The binder can be described as a time-appropriate cement, mostly belite crystals in clinker aggregates way too big to allow for full hydration, even if sufficient water was present at the time of mixing. It was modified by an addition of brick dust and stone meal from the used aggregate, a possibly locally sourced travertine from the region of Stuttgart. Though it is unclear if the addition of brick dust was only for colouring, its hydraulic properties or to allow for better water retention. The concrete sample was fully carbonated and shows increased porosity as well as leaching of calcium resulting in the formation of lime sinters on the outside. The main damage process here is most probably freeze-thaw attack in conjunction with minor salt contents.

Still, all of these findings can be improved upon. A full characterisation of the used aggregate was not possible, as the studied sample only contained two separate grains. Neither was it possible to infer upon the grain size distribution of the concrete. The source for magnesium, now forming trace amounts of Mg-sulfate salts in the lime sinters, is unclear as well. In general, salt concentrations within the structure could not be studied here and should certainly be analysed, as they are one of the main drivers of building deterioration.

So, while a good amount of information could be achieved in this study, the limiting factor here most certainly was the amount of sampling material. For future studies we would recommend, as long as it is following conservatory practices, to consider sampling concrete structures via core-drilling, at least in questions regarding material composition. With such samples a much more representative amount of material can be retrieved, allowing for a better study of changes along the depth of the material, more precise analytics and, most importantly, more robust conclusions. By sampling in this manner, a material backlog can be created, future studies can be carried out easier and proper conservatory measures for the monument can be established faster and with more certainty.

Other possible analyses for assessment of historic concrete structures like the railway bridge in Bad Cannstatt should include the assessment of the carbonation depth, physical parameters of the concrete, like the E-modulus or the compression strength, and depth profiles of salt contents. Additionally, the study of the relict clinker grains – their mineralogy, chemistry and reaction textures – could provide useful insight into the changes of cement production and reactivity. Lastly, further study of the lime sinter and the adjacent piece of *mortar* is advisable, to determine differences in comparison with the *concrete* sample and possible the core concrete of the bridge. For this, additional funds for other microscopic or spectroscopic methods should be made available.

6. CONCLUSION

This case study served to assess the limits of the analytical techniques used here on the basis of a non-representative sample. In addition, a goal-orientated collaboration between research and heritage conservation took place in the form of knowledge transfer and discussion.

The here-applied methods show that even in cases where only minimal material can be sampled, surprising amounts of information can be extracted. However, it has become clear that for some investigations, such as a representative material investigation and the determination of basic material parameters, larger sample quantities and additional sampling methods are required. The efficacy and limits of non-invasive methods regarding material parameters or contaminations with salts have not been tested here, but should be evaluated in future studies.

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