6th International Conference on
Materials Science and Restoration - MSR VI
Aedificatio Publishers
1-14(2003)

Long-term behaviour of cement based coatings in drinking water reservoirs

A. Gerdes[1] and F.H. Wittmann[2]
[1] Professor for Construction Chemistry, University of Applied Sciences Karlsruhe, Germany
and
Institute for Technical Chemistry (ITC-WGT), Karlsruhe Research Centre, Germany
[2]Aedificat Institute, Freiburg i. Br., Germany

Summary

The inner surfaces of drinking water reservoirs are usually coated with cement based materials. In recent years, more and more damages to these coatings were noticed, where a local, quickly proceeding decomposition of the coating is a characteristic feature. Based on the results of various research, new coatings have been developed, which are said to be much more resistant to the machinery of damage designated as hydrolytic corrosion of cement-based materials. These new coatings, applied to the inner surface of a selected drinking water reservoir, were to be tested under practical conditions. Furthermore, different combinations of materials and application techniques were to be examined with regard to their significance in terms of resistance. In this contribution, a selection of results of these tests will be introduced. It will be shown that the pore structure, characterized by total porosity and pore size distribution, is the key factor for the resistance to hydrolytic decomposition. Without a sufficient layer thickness, however, even a dense structure, which can be rather produced using a machine but a manual application method, will not do to prevent the coating from decomposing rapidly. Using the findings of various research, technical requirements for cement based coatings were phrased that could be checked using handy quality control measures, and which have proved in practice in a huge number of drinking water reservoirs.

1 Introduction

Storage of drinking water mainly takes place in earth-covered concrete reservoirs. Both in case of newly manufactured or renovated reservoirs, their inner surfaces are often provided with cement based coatings for technical and visual reasons. In recent years, more and more damages to these coatings were noticed, where a local, quickly proceeding decomposition of the coating is a characteristic feature. As these damages, generally described with hydrolytic corrosion of the cement-based material, could not be reasoned by means of the mechanisms of damage known so far, a series of research activities was initiated [1-4] in order to determine the causes and process of the damage. The findings were discussed in a controversial way, and to this day there is no generally accepted consensus on the mechanism of damage.

Based on the findings on hand, however, new coatings have been developed any way, which are said to have larger resistance to the decomposition of the cement-bsaed material.

In this contribution, a report is given on a long-term trial in practice, in which apart from new coating materials the impact of application techniques on the durability of these systems was to be characterised too. Accompanying this practical project, a quality control concept has been developed which has been successfully used for about 6 years in Switzerland. At this point, the content and implementation of this concept shall be also described and discussed.

2 Hydrolytic corrosion of cement-based materials – characteristics and mechanism of damage

2.1 Preliminary remarks

In order to make understandable the approach used during the development of new materials or during the determination of quality control measures, the typical features of the relevant damage shall be described and the mechanisms of damage discussed so far be introduced in brief in this paper. The chemical analysis is required, above all, in order to distinguish this type of damage from other mechanisms of damage (e.g. leaching through soft water). This indisputable identification is a precondition, however, in order to plan a durable repair, but it also represents the basis for the development of a handy and target-oriented quality control. As for the details regarding characterisation of the damage and the describing models it is referred to [5-7].

2.2 Typical characteristics of hydrolytic corrosion of cement-based material

2.2.1 Appearance

The appearance of this damage is marked by the fact that stains occur with a diameter from a few millimetres up to about 5 cm. In many cases – but not always - the surface is brown coloured. In a number of cases it was noticed that the stains are arranged in a vertical or horizontal line. Now and then even an orthogonal arrangement was noticed (see Figure 1a and 1b). This specific appearance resulted in the fact that the position of the reinforcement was determined on site and compared with the position of the stains. It was found that although the stains are not always arranged above the reinforcement, this is very often the case.

With these stains, no change in volume of the material, that is swelling or shrinkage, could be observed. That is why many cases of damage have not been recognised as such in the first instance, because operators of drinking water reservoirs are used to the fact that due to he water ingredients (iron, manganese) brown sediments occur

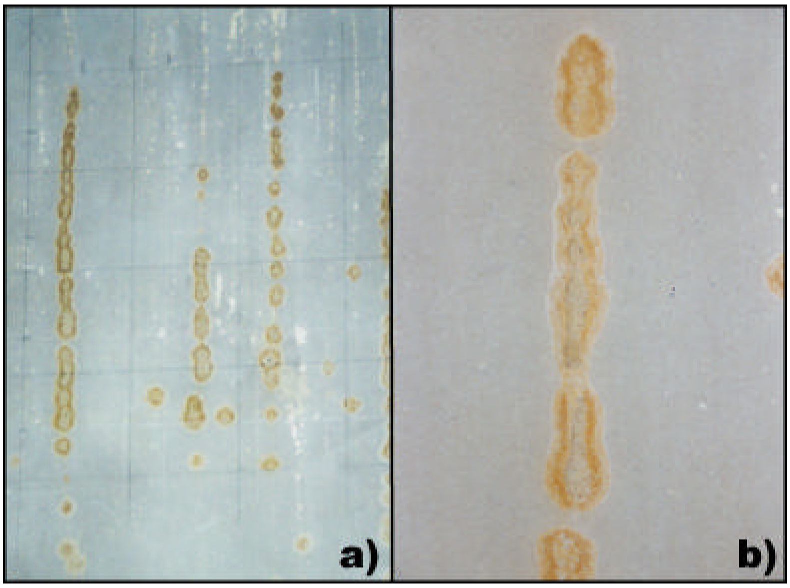

Figure 1: Typical damage pattern in a drinking water reservoir
a) Vertical arrangement of stains
b) Individual stains „grow“ together at a later date.

brown sediments occur on the white coatings.

Only by means of cleaning works (e.g. using high-pressure cleaners) the damaged coating material was washed out. What remained were scar-shaped pits which clearly showed that not only the coating, but also the underlying concrete is destructed by this mechanism of damage (see Figure 2a and 2b).

2.2.2 Mechanical properties

As already mentioned in the previous section, the material in the stains has completely lost its stability. It is soft and talc-like so that it can already be removed from the damaged areas without the help of tools (see Figure 3).

2.2.3 Chemical composition of the damaged coating material

In comparison to the material composition of the undamaged coating, an analysis of the damaged material shows clear differences with two elements that can be easily determined by means of a chemical analysis:

- Content of calcium hydroxide
- Content of calcium carbonate.

According to these analyses, the calcium hydroxide content of the coating being intact, which depending on the relevant composition is between 5 and 10 mass percentage points, has dropped to values being close to zero. At this point it must be pointed out, however, that such findings are not sufficient to indisputably identify hydrolytic corrosion. This results from the fact that also an attack by soft water might lead to a leaching of the cement-based material and thus, to all intents and purposes, to a softening of the material. That is why on assessing the damage the results of the calcium carbonate determination have to be additionally taken into consideration. With damages resulting from hydrolytic corrosion, to be exact, there can be always noticed an increase in the calcium

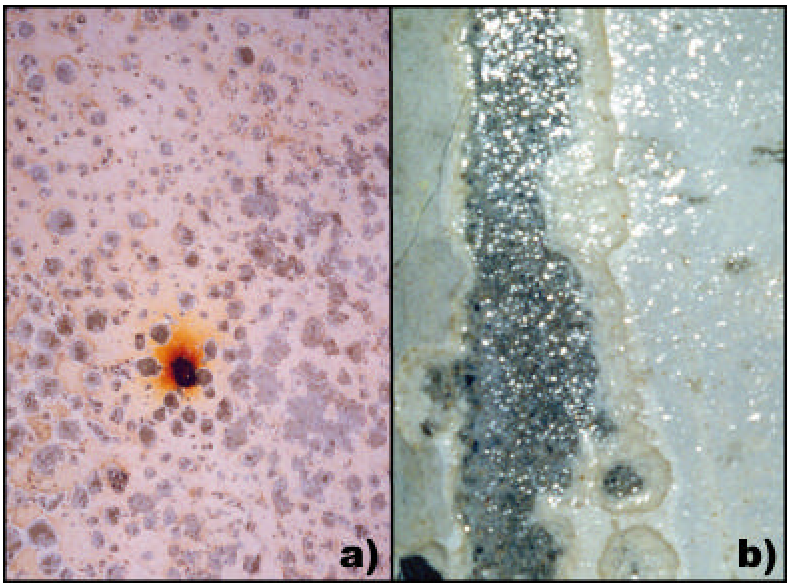

Figure 2: Damage to the supporting concrete
a) Bottom area of a damaged tank
b) Detailed picture of a stain after cleaning

carbonate content. The values of the calcium carbonate content, which may be between 10% and 50% depending on the relevant material composition, determined for the material from the damaged areas, that is the stains, are clearly higher. In some cases, an increase in calcium carbonate content up to three times the amount of the original content was measured. This clear increase is due to the chemical reactions which with hydrolytic corrosion take place between the elements of water and the cement-based materials.

In order to definitely identify the damage it thus necessary that both chemical analyses are carried out and the findings are compared to the results for materials from undamaged areas.

2.2.4 Speed of the course of damage

As cement based materials are used in a huge number of applications, they are exposed to different chemical attacks depending on the relevant use which may lead to material damage. Depending on the relevant boundary conditions, this may normally take a few years up to some centuries.

With hydrolytic corrosion, however, damages were noticed in some cases only after 6 months after completion of the coating. In other cases it took several years until these typical stains could be noticed. It was found out, above all, that the damage to the underlying concrete took place much more slowly. This also explains the observation made in practice, according to which the new coatings in very old tanks from the beginning of the 20th century already show damages, whereas the originally applied cement mortars are still completely undamaged.

2.2.5 Summary

Damages caused by hydrolytic corrosion of cement stone can be indisputably identified by means of

Figure 3: Softened material from a damaged area that can be easily removed manually.

- the appearance
- the chemical analysis of the calcium hydroxide and calcium carbonate content
- the course of damage.

But the precondition for this is that all these issues are captured and assessed, because interpretation of individual results bears the risk of misinterpretations.

2.3 Models of the mechanism of damage

2.3.1 Preliminary remarks

In this contribution, the individual models shall be introduced only in brief. In a further contribution to be released soon, however, the individual models shall be described and discussed in detail [8].

2.3.2 Attack through drinking water

An analysis of the waters from the reservoirs affected showed that they are to be classified as hard to very hard in terms of their carbonate hardness, but that according to usual evaluation criteria they have to be rated as being not concrete-aggressive.

2.3.3 Attack through acidic cleaners

Drinking water reservoirs are regularly cleaned. During the process, acidic cleaners are also used. That is why the assumption has been put forward that acidic cleaners cause these damages or are at least jointly responsible for them. This thesis could not be confirmed to be absolutely certain. This can, among other things, be reasoned by means of the following findings.

The damages also occurred in reservoirs which were demonstrably not treated with these cleaners. Moreover – due to the composition of the cleaner – it should have been possible to notice a different damage pattern. Instead of stain formation, the coating should dissolve extensively.

2.3.4 Microbiological attack to the coating

The destruction of cement based materials through micro organisms in the area of sewage works or cooling towers has been known for a long time.

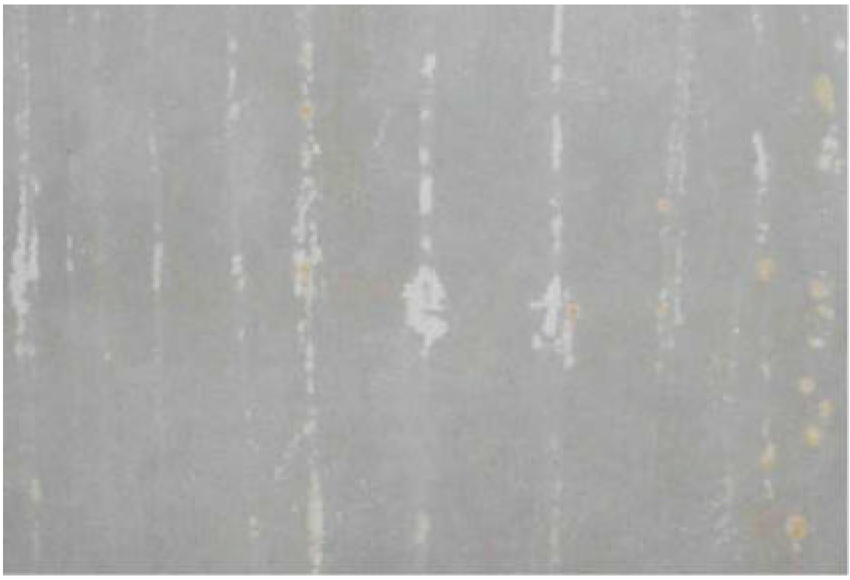

Figure 4: Stains with a white surface

With the mechanism of damage discussed here, however, some aspects point against the thesis that a microbiological attack sets off this damage. At this point, the issue cannot be addressed in detail, but these arguments shall be listed in note form anyway.

- The pH value of the coating is too high in order to allow for a high colonisation density of the micro organisms which are held responsible for the decomposition.
- The existing carbon sources (water, coating material) which can be used microbiologically are insufficient for the amount of carbonate formed.
- Bacteria could only be proved on the surface, but not in deeper, damaged areas of the coating.
- The speed with which the coating is decomposed is not in accordance with the colonisation density observed. So in reservoirs which were destructed only after 6 months of their completion, there could not be observed any brown discolouring which according to Flemming and Herb is caused by micro organisms (see Figure 4) [9].

2.3.5 Hydrolytic corrosion of cement based materials

This model describes a coupled process consisting of transport and chemical reaction of ingredients of water with components of the coating. In Figure 5, these processes are schematically illustrated.

1. Reaction step 1: Transport of ionic hydrogen carbonate (HCO_3^-) to the coating.
2. Reaction step 2: Chemical conversion of ionic hydrogen carbonate (HCO_3^-) into ionic carbonate (CO_3^{2-}).

Under this model, the water contained in the hydrogen carbonate (HCO_3^-) is transported into the coating in reaction step 1. During the process, the transport resistance of the coating, characterised by total porosity and porosity size distribution, plays a central role for the speed of damage. The electrical potentials measured in a huge number of reservoirs between reinforcement and stainless steel fixtures are a possible explanation for the acceleration of transport processes and the local

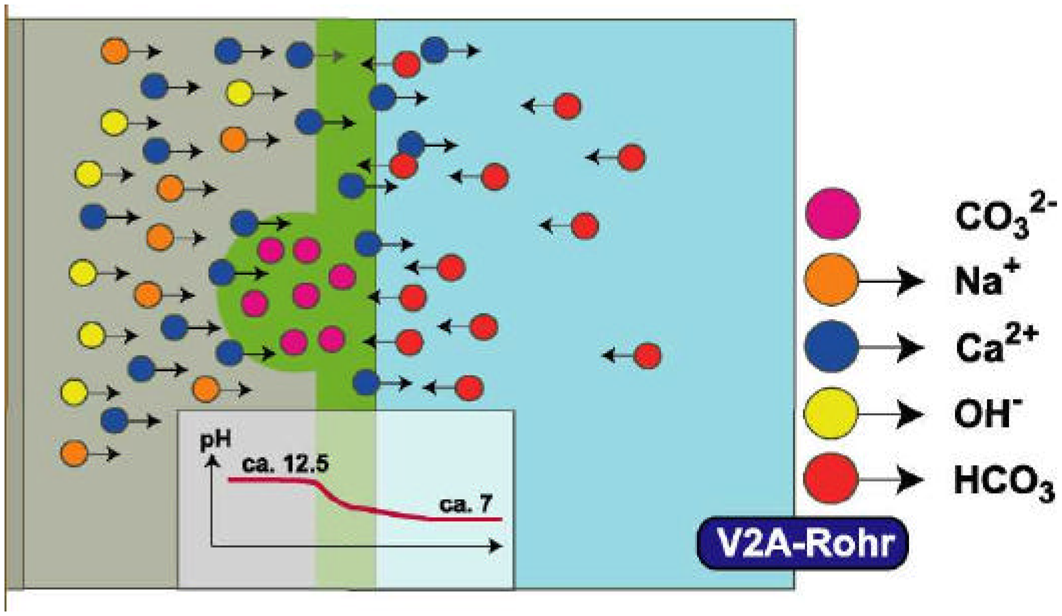

Figure 5: Schematic diagram of hydrolytic corrosion of cement based materials

occurrence of the damage, but they are not a precondition for the process of a diffusive ionic transport.

In reaction step 2, a ph-dependent conversion of ionic hydrogen carbonate (HCO_3^-) into ionic carbonate (CO_3^{2-}) initially takes place within the coating. With 14 mg/l, the solubility of the calcium carbonate, however, is clearly lower than the hydrogen carbonate concentration in hard water (> 1000 mg/l). That is why the result is a precipitation of calcium carbonate by using up calcium hydroxide which is created as a reaction product during the hydration of the cement. When the calcium hydroxide is used up completely, then the dropping pH value in the pore solution can only be stabilised through a release of additional calcium hydroxide. As the released calcium hydroxide immediately reacts with the hydrogen carbonate that permeated, complete leaching of the cement-based material takes place with a decomposition of hydration products in the end [6].

2.3.6 Transport by means of hydraulic gradients

With this mechanism that has been proposed only recently the hydrogen carbonate dissolved in the water shall be caused by means of a hydraulic gradient that shall adjust itself through changes in the water level in relation to the relevant utilisation. The data published so far on this issue is currently not yet sufficient to be able to discuss this mechanism in detail[10].

2.4 Summary

The findings of various studies carried out in the laboratory and on objects in practice show that the resistance of coatings used is decisively determined by the following factors:

- Total porosity
- Pore size distribution
- Layer thickness

These findings were used as a starting point for the development of new coatings, with which the structure is considerably denser and which are also applied using a larger layer thickness.

In a reservoir, various coatings were applied in different ways and the long-term behaviour characterised by means of chemical analyses over a period of 5 (five) years. Essential results of these examinations will be introduced in the following.

3 Long-term behaviour of drinking water reservoir coatings in a practical test

3.1 Introduction

To the drinking water reservoir Rosenberg, St. Gallen, coatings customary in trade were applied which can be characterised by the following factors:

- Total porosity determined by means of mercury intrusion porosimetry: approximately 30 to 35% volume percentage
- Capillary pore share of the total porosity: > 60%
- Average layer thickness: approx. 3 mm.

On these coatings, the damages described were observed only after 6 months of completion. This tank was selected due to the high speed with which the damages developed in order to examine newly developed coatings, various material combinations and application techniques with regard to their resistance to this mechanism of damage.

3.2 Description of test areas

In February 1997, the damaged coating on the western wall of a water chamber in the Rosenberg reservoir in Gossau was removed by means of high-pressure water jets. On this wall, a total of 6 test areas (A to F) were established with an area of approximately 20 square metres each. An additional area of about 8 square metres (G) was established on the southern side of the tank. As for this area it was waived to remove the damaged coating as described above.

Three different products were used to establish the test areas. Product I and product II are cement based coatings in a maximum grain size of about 1 or 2 millimetres. Product III, a polymer-modified mortar, was used for levelling the rough concrete surface. The products were applied to the individual areas in different layer thickness. Furthermore, the application technique’s impact on the material properties should be characterised. That is why the coating was applied to one area manually and to another area by machine (see Table 1).

After completion of the test areas, the tank was used again under usual operating conditions. In the course of the following years core samples were taken from the test areas and analysed at various times. In the following section, the studies carried out and findings gained will be introduced and discussed.

3.3 Studies carried out

As already explained, the resistance against hydrolytic decomposition is determined by the characteristics of pore structure and layer thickness. After applying the coatings, several drill cores were thus taken from the individual areas. The thickness of single layers were checked on these drill cores. The corresponding values are listed in Table 1. Moreover, total porosity and pore size distribution were determined with the help of the mercury intrusion porosimetry. In order to be able in the further course of examinations to recognise decomposition of the coating even before staining occurred, the calcium hydroxide and calcium carbonate contents of the samples were determined. Determination of the calcium hydroxide

Table 1: Test areas established in the Rosenberg drinking water reservoir

Field	Structure of Coating	Layer Thickness [mm]
A	Coating I, applied by machine	3
B	Coating I, applied manually	3
C	Coating I, applied by machine in 3 layers	5
D	Coating II, applied by machine , surface smoothened	10
E	Coating II, applied by machine Coating I, applied by machine	10 3
F	Coating III, applied by machine Coating I, applied by machine	10-12 3
G	Coating I applied by machine to an already damaged coating after roughening	3

content took place using the Franke method [11], determination of the calcium carbonate content took place by means of wet chemical pressure measurement with a mini carbonate bomb [11].

3.4 Results of the practical tests

3.4.1 Influence of total porosity and pore size distribution

As the examinations have shown, the transport of ionic hydrogen carbonate into the coating is the speed-determining step for the hydrolytic decomposition of the cement stone. When developing new coatings, it was thus attached great importance to a low porosity and a low share of capillary pores.

As for the test area E, the material II with a maximum grain size of 2 mm was applied first of all. Due to the low cement content, which is dependent on the formulation, low values have to be reckoned with regarding the total porosity with this coating. As a top coat, another layer of material I was applied onto this coating II. The typical pore size distributions for the coating I or II are displayed in Figure 6. In the same Figure, the pore size distribution and total porosity of the coatings used by then are listed on the right side for comparison. It is clearly shown here that the total porosity of the newly developed coatings only makes up about 40% in comparison with the values of conventional coatings. It must be particularly mentioned that the capillary pores which are relevant for the transport processes are virtually not existing any more with coatings I or II, whereas with the old coatings a clear maximum value in the range between 0.3 and 3 µm can be determined.

The significance of these factors for the durability of these coatings becomes clear directly through the photographs of the various types of coating shown in Figure 6. While even after 5 years of test duration no stains could be observed with the coating of area E, the conventional coating after 6 months already was strewn with stains, that is completely destructed. These findings are also confirmed by the chemical analyses of the coating carried out after 5 years. Also after 5 years, the calcium hydroxide content of the samples taken from area E is still greater than 5 mass percentage points.

3.4.2 Influence of coating thickness

By varying the coating thickness, the influence on the resistance to hydrolytic corrosion was to be characterised. For this purpose, the test area C was established in which coating A was applied in a layer thickness of 5 mm. With a value of 12.34 volume percentage points, the measurement of total porosity was comparable to the value of 11.72 volume percentage points measured for the coating of test area A.

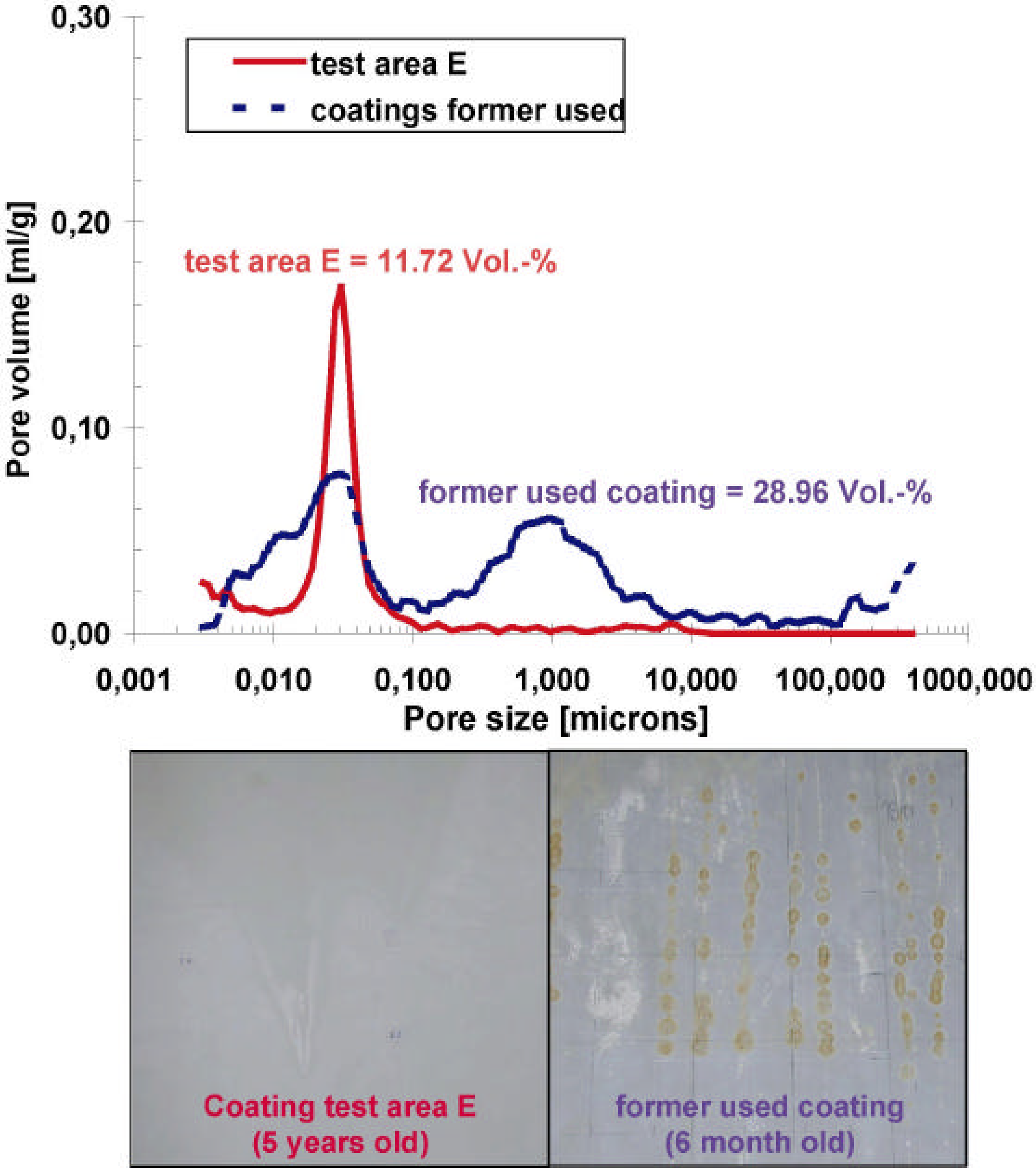

Figure 6: Comparison of pore properties between samples from test area A and those from an old coating

Also with regard to pore size distribution, there could not be determined any significant differences between both areas. However, the influence of the layer thickness on the resistance of the coating can be read off Figure 7. In contrast to the coating on test area A, significant amounts of calcium hydroxide are detectable with test area C even after 5 years. This indicates that the transport of hydrogen carbonate into the coating of area C and the conversion of calcium hydroxide into calcium carbonate takes place. In contrast to the thinner coating, however, calcium hydroxide can be transported from greater depths via diffusion to the border area with coating C. In this way, the decomposition of cement stone is prolonged. On this area, only isolated stains could be observed after 5 years of application.

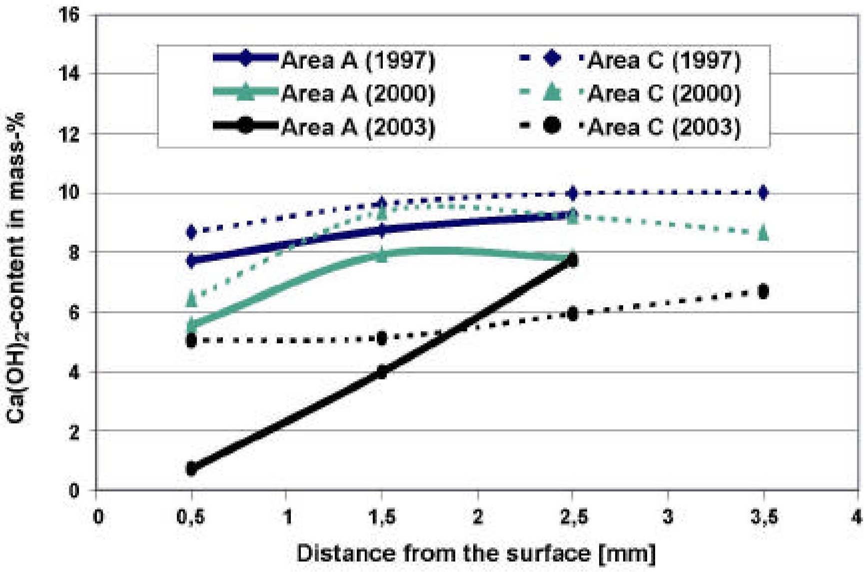

Figure 7: Average calcium hydroxide content as a function of test duration for areas A and C

3.4.3 Influence of application technology

Coating I was manually applied to test area A, whereas the same coating was applied to test area B in a comparable layer thickness by machine. In Figure 8a, the results regarding total porosity and pore size distribution are graphically displayed.

Following that it can be noticed that the coating applied manually shows a clearly higher total porosity with 15.68 volume percentage than the coating processed by machine (11.72 volume %). This is mainly due to the higher pore share of between 100 and 1,000 µm.

These process-related differences also become apparent in the resistance of the coatings to the hydrolytic decomposition. In Figure 8b, the depth profile of the calcium hydroxide content is shown as a function of the test duration. The curve progression clearly shows that the calcium hydroxide content after a test duration of 5 years is distinctly lower with a coating applied manually than with a coating applied by machine. This is consistent with the observation that after 5 years the test area B was again strewn with stains, whereas a clearly lower amount of stains could be detected with area A.

4 Discussion

Both the examinations in the laboratory and the practical test in the drinking water reservoir initially show that the pore structure is essential for the resistance of the coatings used to the hydrolytic decomposition. And so the service life of the coatings could be increased tenfold in the present case. This dense pore structure can be rather achieved by means of machine processing than by means of manual application.

Using the findings of laboratory tests and the measurement results from the test reservoir, requirements to cement based coatings produced with thin layer mortars were defined.

- Total porosity: Less than 15 volume %
- Position of the maximum value within the pore size distribution: Less than 0.1 µm
- Layer thickness: greater than 10 mm

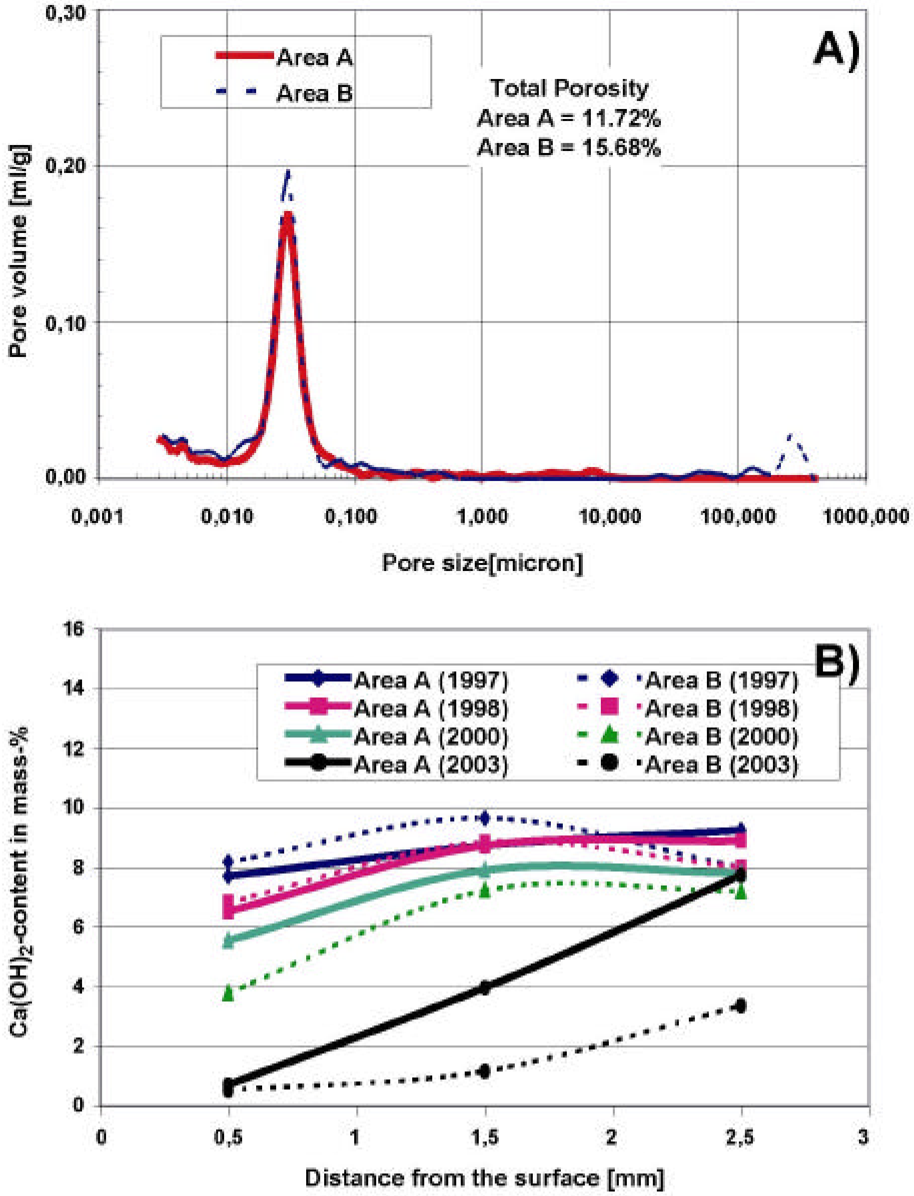

Figure 8: a) Average total porosity and pore size distribution for samples from areas A and B
b) Average calcium hydroxide content as a function of test duration for areas A and B

Within the bounds of quality control, these requirements were also checked in practice on a huge number of reservoirs [7]. In addition to the values mentioned above, the calcium hydroxide content and the calcium carbonate contents are also determined after completion of the coating in order to characterise and assess the decomposition of the coating via the service life, if necessary. This allows for early intervention if on expiration of the warranty period after 5 years, for instance, it is determined by means of a newly conducted analysis that a considerable part of the calcium hydroxide has already converted into calcium carbonate. Past experiences made in a number of drinking water reservoirs show that these requirements are sufficient in order to prevent renewed occurrence of damages in the vast majority of cases. With values of P_{28} < 12% after 28 days und P_{90} < 10% after 90 days, the requirements to the total porosity, which according to [12] will be established in the DVGW data sheet W 300 E[13] and W 312 [14] in future, are considerably lower and can also virtually not be reached by means of the described modified coatings made of thin layer mortars. Due to the findings and experience introduced here, however, it is a moot question, whether these values really have to be specified that low.

In order to be able to formulate these requirements beyond doubt, further examinations are necessary so that the kinetics of the course of damage can be described and predicted subject to the coating properties and the operation conditions in the reservoirs. These works are currently carried out in the ITC-WGT at the research centre in Karlsruhe.

As could be shown, the coating thickness plays a key role for the durability apart from the pore specific values. Following the findings introduced, a layer thickness of at least 10 mm is proposed, namely independent on the maximum grain size. The requirement set out in [12 to 14] that the layer thickness with mortars with a maximum grain size of less than 1 mm should be at least 5 mm appears to be too low in this context. At this point it must also be particularly pointed out, however, that the occurrence of damages cannot be avoided by increasing the layer thickness alone if the coating shows a highly porous structure (total porosity larger than 20%). In summary, it can be established that the service life of cement based coatings can be clearly prolonged if the values for total porosity, pore size distribution and layer thickness meet with the specifications introduced here. By means of a handy quality control, this can be verified also in practice at a reasonable financial effort (approx. 1 to 1.5% of the total cost of the measure).

5 Conclusions

From the examinations and findings of the practical tests, the following conclusions can be drawn:

- The service life of cement based coatings is mainly determined by total porosity, pore size distribution and layer thickness.
- Under aggressive operating conditions, the improvement of individual quality parameters (total porosity, layer thickness) does not lead to a clearly increased service life.
- By means of a handy quality control, this quality can also be achieved in practice at a reasonable effort.

6 References

[1] A. Gerdes and F.H. Wittmann, *Electrochemical Degradation of Cementitious Materials,* Proceedings of 9th International Cement Chemistry Congress, New Dehli, Volume V, 409-415 (1992)

[2] A. Gerdes und F.H. Wittmann, *Beständigkeit zementgebundener Beschichtungen unter dem Einfluss elektrischer Felder,* Int. Z. Bauinstandsetzen, 1, 73-86 (1995)

[3] D. Schoenen, *Fleckige Farbveränderungen und Zerstörung von weisser Zementmörtelauskleidung in Trinkwasserbehältern,* gwf Wasser-Abwasser, 155, 669-676 (1994)

[4] St. Herb, *Beobachtungen an zementgebundenen Beschichtungen - Typische Schäden,* in F.H. Wittmann und A. Gerdes (Hrsg.), Zementgebundene Beschichtungen in Trinkwasserbehältern, WTA-Schriftenreihe Heft 12, Aedificatio Verlag, Freiburg, 77-92 (1996)

[5] F.H. Wittmann, *Zur hydrolithischen Korrosion zementgebundener Werkstoffe,* in F.H. Wittmann und A. Gerdes (Hrsg.), Zementgebundene Beschichtungen in Trinkwasserbehältern, WTA-Schriftenreihe Heft 12, Aedificatio Verlag, Freiburg, 27-52 (1996)

Langzeitverhalten von zementgebundenen Beschichtungen in Trinkwasserbehältern

[6] A. Gerdes, *Hydrolyse einer zementgebundenen Beschichtung in ständigem Kontakt mit Wasser* in F.H. Wittmann und A.Gerdes (Hrsg.), Werkstoffwissenschaften und Bauinstandsetzen - MSR V, Aedificatio Verlag, Freiburg i. Br., 695 -706 (1999)

[7] A. Gerdes und F.H. Wittmann, *Dauerhafte zementgebundene Beschichtungen in Trinkwasserbehältern - Anforderungen für die Praxis* in F.H. Wittmann und A.Gerdes (Hrsg.), Werkstoffwissenschaften und Bauinstandsetzen - MSR V, Aedificatio Verlag, Freiburg i. Br., 707-718(1999)

[8] A. Gerdes, *Zementgebundene Beschichtungen in Trinkwasserbehältern - Teil I: Grundlagen,* erscheint demnächst in Internationale Zeitschrift für Bauinstandsetzen, 9, (2003)

[9] St. Herb, Biofilmbildung auf mineralischen Oberflächen in Trinkwasserbehältern, Beriche aus Wassergüte- und Abfallwirtschaft, Nr. 149 (1999)

[10] P. Boos, G. Thielen und C. Schmitt-Riegraf, *Technische Grundsätze bei der Instandsetzung von Trinkwasserbehältern aus Beton (Teil 1),* Beton, Heft 7+8, 399-404 (2003)

[11] H.F.W. Taylor, *Cement Chemistry,* Academic Press, London (1990)

[12] J.-J. Mönter (Techn. Komitee „Wasserspeicherung" des DVGW), Herstellung dauerhafter Oberflächen in Trinkwasserbehältern aus zementgebundenen Mörteln, Energie -Wasser-Praxis, Heft 3 (2002)

[13] DVGW-Arbeitsblatt W 312: Technische Regel Wasserspeicherung: Planung, Bau, Betriebund Instandshaltung von Wasserbehältern in der Trinkwasserversorgung (Entwurf erscheint 2002)

[14] DVGW-Merkblatt W 312: Wasserbehälter - Massnahmen zur Instandhaltung (Neufassung wird erarbeitet)