Use of Rhenish trass in marine concrete: A microscopic and durability perspective

T.G. Nijland, J.A. Larbi, M.R. de Rooij, R.B. Polder

TNO Built Environment and Geosciences, Delft, The Netherlands

Use of Rhenish trass in (historic) lime mortars is well known. However, its application to concrete has not been investigated elaborately. In the past, trass was used as a pozzolanic addition to concrete for marine structures in the Netherlands. Recent investigations of several structures have shown that identification of trass in aged concretes by polarization-and-fluorescence microscopy is difficult. In order to facilitate PFM studies, historic mixtures were recast. Two mixtures have been recast, viz. a mixture of 300 kg m^{-3} ordinary Portland cement (CEM I) and another mixture of 310 kg m^{-3} ground granulated blastfurnace slag cement (CEM III/B), both with an addition of 10 % trass by cement mass. Concrete mixes were originally designed for a major lock, built in the 1920's, and a quay constructed in Rotterdam harbour in the 1970's, respectively. Difficulties of recognizing trass in aged concretes by PFM and apparent effects of trass on both microstructure of the concrete and durability are discussed. Durability in a maritime environment has extensively been studied in the case of Rotterdam harbour. It is shown that addition of 10 % of trass to CEM III/B has no effect on the durability of concrete.

Key words: Marine concrete, trass, microscopy, resistivity, durability, field experience, ASR

1 Introduction

Partial replacement of Portland cement clinker by either natural (e.g. trass, diatomaceous earth, etc.) or industrial pozzolana (e.g. pulverized coal fly ash) or latent hydraulic materials (e.g. ground granulated blast furnace slag) generally has a beneficial influence on the durability of concrete (e.g. Biczök 1972, Massazza 1993, 2002). Though some of these are a relatively recent 'invention', binders based on natural pozzolana such as trass combined with lime were already in use by the Romans (e.g. Lamprecht 1996). In the Netherlands and northwestern Europe in general, trass, i.e. ground Rhenish tuff, has been used in binders since medieval times. In the past, tuff from the German Eifel area was imported, and ground locally, in order to guarantee the quality of the produced trass.

From the Netherlands, use of trass as pozzolana spread to Germany, France and England. Since the invention of modern concrete, trass has also been used as replacement of, or in addition to, Portland clinker. In the Netherlands, this was done for marine structures in particular, as early as the 1920's, but also still in the 1970's.

As stated already, Rhenish trass is finely ground trachytic tuff, a series of volcanic rocks from the Eifel area, Germany. Other types of trass include Bavarian trass, which is a ground suevite rock, also from Germany, and rhyolitic trasses from Hungary and Romania (e.g. Dreyfus 1950, Wesely 1961). The pozzolanicity of trass is generally attributed to the presence of volcanic glass, providing the reactive silica (e.g. Biczök 1972, Hewlett 1998). However, several studies show that this glass has been replaced by zeolites to a considerable extent (Sersale & Aiello 1964, Nijland et al. 2003), which also have a capacity to react with lime, though less than the trass as a whole (Liebig & Althaus 1998). Trass cements have been used in several European countries, including Germany, Hungary and Turkey. Nowadays, the European cement standard NEN-EN 197-1 (2000) covers two classes of cement containing natural pozzolana, viz. Portland-pozzolana cement (CEM II/A-P and CEM II/B-P), in which the pozzolana is, by definition, a natural one, and pozzolanic cement (CEM IV/A and CEM IV/B), in which the pozzolana can be either natural or industrial.

Hydration products of trass (or volcanic ash) cements are similar to those of ordinary Portland cement and blast furnace slag cement, viz. C-S-H, ettringite, monosulfate, tetracalciumaluminate hydrate and portlandite, with C-S-H having lower Ca/Si and higher Ca/Al ratios due to the pozzolanic reaction (Ludwig & Schwiete 1963, Massazza 2002, Escalante-Garcia & Sharp 2004). The main difference in microstructure between trass cement and ordinary Portland cement is the absence of large portlandite crystals and the presence of hydration shells around non-reacted trass particles; otherwise the microstructure does not essentially differ from that of ordinary Portland cement (Massazza 2002). Total porosity is slightly higher, but the mesopores are smaller (Takemoto & Uchikawa 1980, Massazza 2002). Both porosity and permeability decrease with progress of the pozzolanic reaction. Massazza (1993, 2002) concludes that permeability of trass cement concrete is lower, because of the relatively high fraction of large pores that are only connected by smaller ones. Janotka and Mojumdar (2003) showed that in hardened trass cement mortar the amount of fine pores was higher and that of large pores smaller relative to Portland cement.

In order to obtain a better understanding of the effect of trass on long term durability of concrete, two marine structures have been assessed of which design & contract documents show that trass was added to the concrete mixture. Both case studies will be discussed below, with special emphasis on microscopic aspects. One structure dates back to 1973, whereas the other was constructed in the 1920's. In order to facilitate microscopic interpretation, two mixtures have been remade and studied at 28 days.

Figure 1: General view of the quay wall in Hartel Harbour

2 Case studies

*2.1 **Case 1, Hartel Harbour, Rotterdam: Blast furnace slag cement with 10 % trass***

The structure is situated in the Port of Rotterdam (Figure 1). It was investigated as part of a study into durability of marine structures (Polder & De Rooij 2005, De Rooij & Polder 2005). It is a quay wall, located on the eastern side of the Hartel Harbour, close to the beginning of the harbour. The quay wall was built in 1973 and has a length of 730 m and a stemming water height of 9.5 m. The structure was closed off from tidal movements and seawater until November 1997, when the Beerdam was opened. The quay wall has been constructed by casting concrete in-situ in wooden formwork. The concrete mixture for reinforced concrete contained at least 310 kg blast furnace slag cement, class A (comparable to modern CEM III/B 42.5 N) and 30 kg trass per cubic meter of concrete. In general, the concrete mixture was designed to have a slump of 60 mm. The quality of the concrete was supposed to be K 300 (nowadays comparable to C20/25). According to the construction drawings, the concrete cover should be 40 mm.

At about 30 years age, testing and sampling was performed (De Rooij & Polder 2005, Polder & De Rooij 2005), including collecting cores for microscopic analysis. Eight core samples have been investigated. In all cases, the binder was blast furnace slag cement, with high slag content (> 65 %m/m), most likely equivalent to CEM III/B. According to the original files, about 10 %m/m trass (related to the amount of ground granulated blast furnace cement) was added to the binder. At first, this component could not be identified in thin sections. Therefore, original concrete mixtures have been recast (see below). After studying samples from the latter, it was possible to identify non-reacted trass particles in the cement paste (Figure 2).

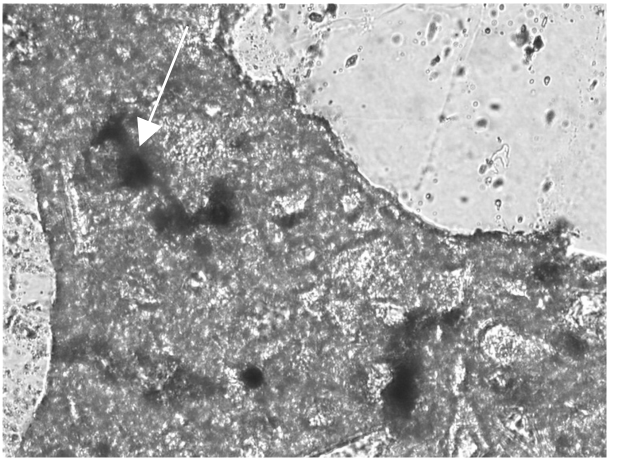

Figure 2: Non-reacted trass particle in the cement paste of concrete based on blastfurnace slag cement with 10 %m/m of trass at the age of 30 years. View 0.35 x 0.22 mm

The degree of hydration was found to be high, indicating that most of the clinker particles and a considerable fraction of both the slag and trass particles had hydrated. The cement paste in all samples examined was homogeneous, indicating that the dispersion of the cement particles in the mixing water of the concrete has optimally been achieved. The capillary porosity of the carbonated areas of the cement paste was distinctly higher than that of the non-carbonated parts. The original water-cement ratio of the concrete, estimated from the capillary porosity of the cement paste by means of fluorescent microscopy was about 0.45. The estimation of the capillary porosity is based on comparison to reference samples of known composition and water/cement ratio. For this purpose, original mixtures have been recast (see below). However, the reference samples are much younger than the samples from the structure. Therefore, it is possible due to a much higher degree of hydration, that the original water/cement ratio has been higher than is estimated from comparison with the reference samples. Portlandite contents are low, as might be expected in a concrete mix containing a high amount of pozzolana (slag and trass).

The bond between the cement paste and the aggregate particles was found to be excellent. Most of the microcracks found in the cement paste are very fine (width ≤ 5 μm) and do not run across the aggregate-cement paste interfaces. The low level and size of microcracking present suggests that transport of aggressive substances will be very difficult. No evidence was found for deterioration of the concrete due to alkali-silica reaction, sulfate attack, leaching or frost.

The results of the PFM studies show that the quality of the concrete in the samples examined is in general good. Homogeneity of the mix and the cement paste is good, the capillary porosity is quite low, the bonding of the cement paste to the aggregate particles is excellent and the extent of (micro)cracking is quite normal. In addition, the depth of carbonation in the concrete is moderate: A maximum depth of 5 mm over a period of 25 - 30 years since construction of the structure. Given the fact that the cement paste below the carbonation front is quite dense, homogeneous and not intensely cracked, it is not expected that this value shall increase considerably. No evidence has been found for deterioration of the concrete due to either chemical (such as alkali-silica reaction, sulfate attack and leaching), or physical attack (such as frost). Also no presence of brucite, $Mg(OH)_2$, was found in the samples investigated.

Together with the Hartel Harbour quay wall, two other marine structures in the Port of Rotterdam have been investigated, viz. the Caland Canal and Europa Harbour quay walls; the latter have been constructed in 1968 and 1984, respectively. In all three cases, structures have been inspected and a test area of about 1 m^2 of concrete surface was investigated in depth to collect the following data: Visual examination and description of test area, measurement of rebar positions and depths; determination of carbonation depth;

measurement of concrete resistivity; measurement of rebar potential. In addition, core samples were collected for laboratory research, in order to determine chloride profiles, microsctrucutre (PFM), rapid chloride migration, resistivity measurements, splitting tensile and compressive strength (De Rooij & Polder 2005, Polder & De Rooij 2005). Transport characteristics of the concretes, essential in evaluating durability, have been assessed by:

- Electrical resistivity as measured on site using a surface probe (Wenner method, WEN);
- Electrical resistivity of cores between two steel plates after storage in a fog room (TEM);
- Electrical resistivity of cores after water saturation under vacuum (VAC);
- Surface chloride content from fitting diffusion curves to measured chloride profiles;
- Apparent chloride diffusion coefficient from fitting measured choride profiles;
- Rapid chloride migration coefficient of cores after water saturation under vacuum (RCM).

Results are given in Table 1.

Table 1. Transport characteristics of three harbour structures (De Rooij & Polder 2005, Polder & De Rooij 2005). See text for explanation of resistivity methods.

Structure (quay wall)		Hartel	Caland	Europa
Cement		CEM III/B + trass	CEM III/B	CEM III/B
Year of construction		1973	1968	1984
Length	m	730	725	1300
Resistivity				
- WEN	Ωm	6350	1260	1460
- TEM	Ωm	910	840	620
- VAC	Ωm	165	410	150
Surface chloride content	%	2.9	3.9	3.9
Apparent chloride diffusion coefficient	10^{-12} m^2 s^{-1}	0.12	0.19	0.12
Rapid chloride migration coefficient	10^{-12} m^2 s^{-1}	2.07	1.31	3.88

Without going into detail, the results in Table 1 show that:

- Hartel Harbour resistivity as measured on site (WEN) is higher than for both other structures; this can be explained by a lower humidity of the concrete due to differences in precipitation prior to measuring and/or a different orientation.
- Caland Canal resistivity as measured in the laboratory is higher than for both other structures, both just 'wet' (TEM) or completely saturated (VAC).
- Correspondingly, the rapid chloride migration coefficient (RCM) for Caland Canal is lower than for both other structures, as resistivity and transport coefficients are inversely proportional.
- The surface chloride content for Hartel Harbour is lower, possibly related to its later exposure to chloride.

In general, out of three structures investigated in the Port of Rotterdam, samples removed from Caland harbour show best concrete quality as assessed from microscopic analysis; this structure was built in 1968 using ground granulated blast furnace slag cement, equivalent to a current CEM III/B, but without trass. In all three structures, the concrete has an apparent water-to-cement ratio of about 0.45 as estimated by PFM.

All three structures do not show any sign of corrosion due to chloride ingress or carbonation yet. This is in line with the relatively large concrete cover depth and the relatively low chloride content at the position of the reinforcement. None of the three structures has reached critical values with regard to durability yet, evaluated using concrete durability models such as DURACRETE (2000) (De Rooij & Polder 2005). In case of Hartel Harbour, the concrete has been exposed to chloride for only 6 years, starting when the concrete was about 24 years old. Nevertheless, chloride penetration attained similar levels as in the concretes of Caland Canal, exposed to chloride for 35 years, and Europa Harbour, exposed to chloride for 19 years. Though current transport models are not able to account for two different exposure regimes (De Rooij & Polder 2005), this seems to indicate that chloride ingress is progressing more rapidly in the Hartel Harbour concrete made with ground granulated blastfurnace slag cement (CEM III/B) with 10 % of trass than in Caland Canal and Europa Harbour concretes made with only ground granulated blastfurnace slag cement (CEM III/B). Addition of 10 % of trass did apparently not result in higher resistance to ionic transport and related concrete durability. Neither is any effect on compressive and splitting tensile strength and density discernable.

2.2 ***Case 2, Noordersluis, IJmuiden: Ordinary Portland cement with 25 % trass***

The Noordersluis (Northern Lock) at IJmuiden is the main lock in the North Sea Channel, which connects the Port of Amsterdam to the North Sea. It was built in the 1920's. The construction formed a major new part of Dutch infrastructure. It was also a trial project, in which different binders and concrete mixtures were investigated. In several mixtures, Rhenish trass was used. Trass was used in an amount of 25 % relative to Portland cement, with cement contents ranging from 140 tot 260 l. Mixtures with lower cement (140 – 200 l) and hence lower trass contents were used for the piles and sheet piling, whereas mixtures with higher cement (225 – 260 l) contents were used for the walls of the actual lock. Designed water/cement ratio for the latter mixtures was 0.40. In addition, mixtures with ground granulated blastfurnace slag cement, but without trass, have been used for these walls. These contained 240 l cement. Finally, concrete mixtures for the non-reinforced upper part of the structure were made with 260 l Portland cement, without trass (Van Rooijen 1994).

In the thin section specimens of Portland cement concrete removed from this lock, which supposedly contains about 25 %m/m of trass, no evidence of trass was found. The mix was found to be highly non-homogenous, with considerable amounts of voids, and low in cement paste. Moreover, the cement paste was low in C-S-H but rich in crystalline phases, apparently due to the high degree of hydration of the clinker particles and the prolonged exposure to relatively high moisture. In all thin sections examined, the amount of calcium hydroxide and ettringite was found to be relatively high both in voids and in cracks (Figure 3). The characteristics of the mixes examined here were very similar to those of plain Portland cement concrete mixes of comparable age and exposed to similar conditions. These observations are contrary to the expected characteristics of concrete prepared with trass as described previously.

The absence of clear evidence or characteristics of trass applied in the specimens examined may either be due to 1) complete reaction or hydration of the trass used, leaving hardly any residue in the cement paste to be identified, 2) insufficient (non-optimum) application of trass, 3) use of trass with different mineralogical characteristics from the one used in the reference mixes examined in this study, thus making it difficult for residues to be identified, or 4) combinations of the above causes.

In case of the Noordersluis, the question whether trass was part of the concrete mixes, as indicated by archive data summarized by Van Rooijen (1994), is of importance with respect to alkali-silica reaction (ASR). Both natural zeolites (Naiqian et al. 1998) and ground zeolite-rich tuff (Sersale & Frigione 1987) have been demonstrated to be effective additions to prevent or suppress ASR. Sersale & Frigione (1987) used a chabazite- and phillipsite-rich tuff. Rhenish trass used in case of the Noordersluis has the same zeolite assemblage (e.g. Sersale & Aiello 1964, Nijland et al. 2003). In the Noordersluis, deleterious ASR has been diagnosed in several parts of the lock made with Portland cement (Siemes 1995, Siemes & Larbi 1996). According to archive data, trass was part of all concrete mixtures based on Portland cement in the actual lock (i.e. excluding the non-reinforced upper part).

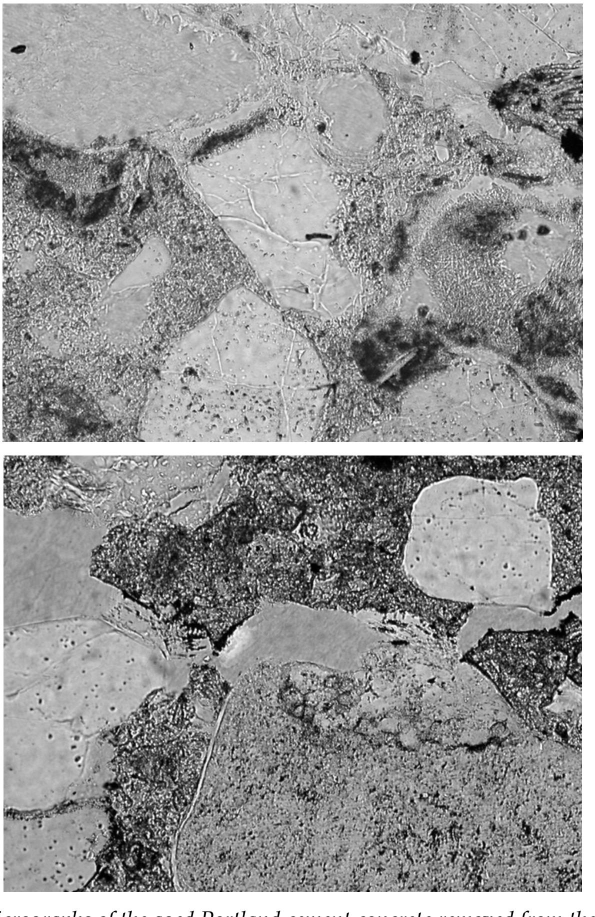

Figure 3: PFM micrographs of the aged Portland cement concrete removed from the Noordersluis lock showing calcium hydroxide and ettringite in voids in the cement paste. View 0.7 x 0.45 mm

Nevertheless, deleterious ASR occurred in concrete that, according to original documents, should contain trass in addition to Portland cement. Several explanations may be put forward: 1) All trass has reacted and could not be identified anymore. At the time when the cores have been collected, the concrete had an age of about 75 years, and the binder matrix still contained a large amount of well developed portlandite crystals. This may imply that either a surplus of free portlandite was present, no or a smaller amount of trass was used, or the pozzolanic reaction was hampered. 2) Trass was not used at all, and archive data are not correct. 3) The amount of trass used at the Noordersluis is simply too low to suppress ASR. Sersale and Frigione (1987) show the trass to be effective by 30 % replacement or higher, whereas at the Noordersluis a slightly lower amount was prescribed (25 %). If trass was added to the mix and the pozzolanic reaction was somehow hampered, considerable amounts of remnants of the trass should still be present in the concrete and be identifiable in thin section. This is not the case. Alternatively, all trass may have been reacted. Arguments may be put forward in favour and against the latter hypothesis.

In favour of the hypothesis is the fact that one gram of currently commercially available Rhenish trass consumes about 0,1 g of portlandite from a calcium-saturated solution (at 15 days), i.e. about 10 % of its own weight (T.G. Nijland & R.P.J. van Hees, unpubl. data). According to documents, 25 % of trass was added relative to cement (instead of as cement replacement). One part of Portland cement produces about 25 % of its own weight of portlandite. Hence, a surplus of free portlandite should have been available (even if all components in the trass were pozzolanic), which agrees with the observation that abundant portlandite is still present in the binder matrix. Against the hypothesis argues the fact that, in case of historic trass – lime mortars common in historic masonry in the Netherlands, coarser, non-reactive trass particles are nearly always present and easily identified in thin sections by microscopy, even after centuries, though in this case a surplus of lime is available for reaction. Historic trass may have been coarser ground or of less pozzolanic nature (cf. Van der Kloes 1924) than trass used at the Noordersluis, but still, it seems unlikely that all components were pozzolanic (and could have dissappeared by pozzolanic reaction). In addition to these considerations, it should be realized that mixing, placing and compaction methods of the 1930's were not as efficient as current ones. This may have incluenced distribution of trass, the way it reacted, and, by consequence, the possibility to identify its presence by microscopy after 75 years. Considering all possibilities, it seems likely that no trass was used in the investigated concrete.

3 Recast mixtures

3.1 Microstructure of trass cement concrete at 28 days

Finely ground trass used in combination with Portland cement or ground granulated blast furnace slag cement to prepare concrete behaves as a pozzolan, similar to pulverised fuel ash, silica fume or metakaolin. It has relatively high contents of silica (SiO_2) and alumina (Al_2O_3), which under suitable conditions of high alkalinity (pH ≥ 13) and high moisture content can undergo the pozzolanic reaction to produce cementitious material. In general, trass reacts relatively slow, compared to other pozzolana such as pulverised fuel ash, silica fume or metakaolin. At early ages of hydration of the cement, it acts as a filler in the concrete mix with most of the individual particles serving as nucleation sites for precipitation of the cement hydration products, such as calcium hydroxide, $Ca(OH)_2$, monosulfate aluminate hydrate (AFm) and ettringite (Aft). As the alkalinity of the system increases, the trass gradually dissolves and undergoes pozzolanic reaction with $Ca(OH)_2$ and the alkali in the pore solution to form cementitious products. As this process progresses, the $Ca(OH)_2$ concentration of the cement paste decreases while the compactness and density of the cement paste increases. In general, the use of trass, in combination with Portland cement or ground granulated blast furnace slag cement to prepare concrete tends, in the long-term, to improve the concrete's mechanical properties and durability.

For this study, four series of laboratory-made reference concrete specimens have been cast, each with a water-binder ratio of 0.45:

- Portland cement, CEM I 32.5 R;
- Blast furnace slag cement, CEM III/B 42.5 N;
- Portland cement, CEM I 32.5 R containing 10 % Rhenish trass (by cement mass);
- Blast furnace slag cement, CEM III/B 42.5 N containing 10 % of Rhenish trass (by cement mass).

Specifications of cements and trass used are given in Table 2. All four concretes were prepared with river-dredged sand and gravel (Dmax 32 mm). The cement content ranged between 300 kg m^{-3} and 310 kg m^{-3}. Concretes were cured under water and have been studied at 28 days.

Table 2. Specification of cements and trass used for recast concrete. All data from producer's specifications, except the Blaine of trass, which has been determined by TNO's laboratory.

		CEM I 32.5 R	CEM III/B 42.5 N	Trass
SiO_2	%m/m	21	30	59.0
Al_2O_3	%m/m	5	10	18.7
Fe_2O_3	%m/m	3	1.5	5.6
MnO	%m/m	-	-	0.3
MgO	%m/m	2	8	1.9
CaO	%m/m	64	46	3.8
Na_2O	%m/m	-	-	3.9
K2O	%m/m	-	-	5.0
Na_2O_e	%m/m	0.6	0.5	-
SO_3	%m/m	3.0	3.0	0.3
Cl	%m/m	c 0.02	c 0.03	-
Insoluble rest	%m/m	c 2	c 1	-
LOI	%m/m	c 3	nil	6.4
C_3S	%m/m	63		
C_2S	%m/m	13		
C_3A	%m/m	8		
C_4AF	%m/m	9		
Blast furnace slag slag			c 70	
Blaine	$m^2\ kg^{-1}$	270	490	560

In general, the main differences between the microstructure of the trass-based concretes and the control concretes without trass, with regard to the mix itself, can be summarized as follows:

- The homogeneity of the trass-bearing mixes was better than that of the plain mixes: In thin sections of both trass-bearing concrete specimens (CEM I 32.5 + 10 wt.% of trass and CEM III/B + 10 wt.% of trass), the aggregate particles were found to be homogenously distributed in the cement paste.
- The bonding of cement paste to the aggregate particles was found to be considerably better in the trass-bearing mixes than in the corresponding mixes without trass. Also, the interfacial zone between the aggregate particles and the bulk cement paste was denser and contained smaller amount of micro-pores compared to corresponding mixes without trass. In the former case, the enhanced compactness of the interfacial

zone seemed to have subsequently improved the adhesion of the cement paste to the individual aggregate particles, causing the paste to form a nearly continuous phase from the aggregate surface into the bulk cement matrix (Fig. 4).

- In the trass-bearing mixes, evidence of micro-bleeding was absent, suggesting that optimum distribution of the mix water in the concrete during formulation was achieved. In the corresponding plain mixes, evidence of micro-bleeding was locally present, especially in the CEM I 32.5 mix.
- The amount of microcracks was slightly higher in the trass-bearing mixes than in the corresponding control mixes without trass.

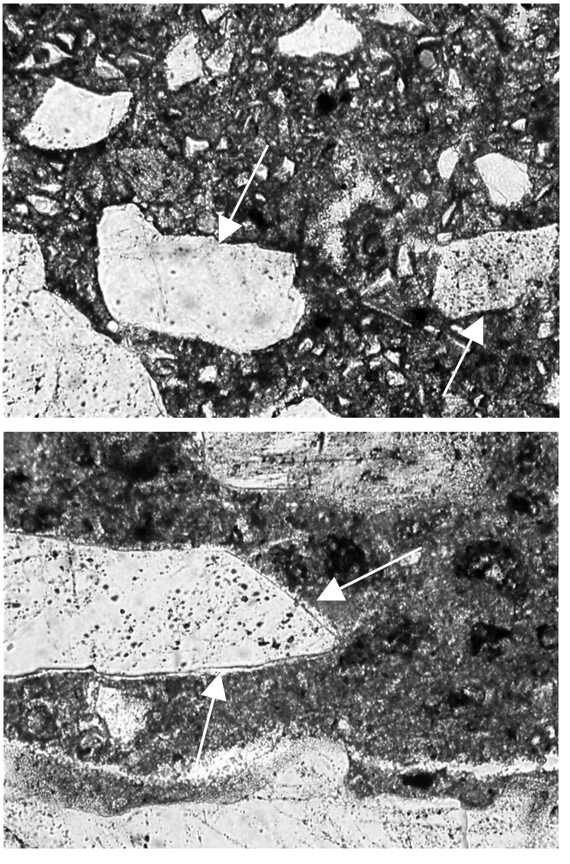

Figure 4: PFM micrographs of the trass-based concrete mixes showing bonding of the cement paste to the aggregate particles. Left: CEM III/B, right: CEM I. View is 0.7 mm x 0.45 mm

The main differences between the microstructure of the trass-bearing concretes and the plain concretes, in relation to the cement paste or matrix, can be summarized as follows:

- In the presence of trass, the matrix or cement paste was found to be denser (more compact) than that of the corresponding plain mixes.
- In the presence of trass, the concentration of $Ca(OH)_2$, in both trass-bearing mixes, especially the concentration in the CEM III/B mix, was much lower than the concentration in the corresponding mixes without trass. In the mixes with trass, $Ca(OH)_2$ occurs as finely divided crystals intermixed with the cement paste, especially in the direct vicinity of the aggregate particles (Fig. 5). In most cases,

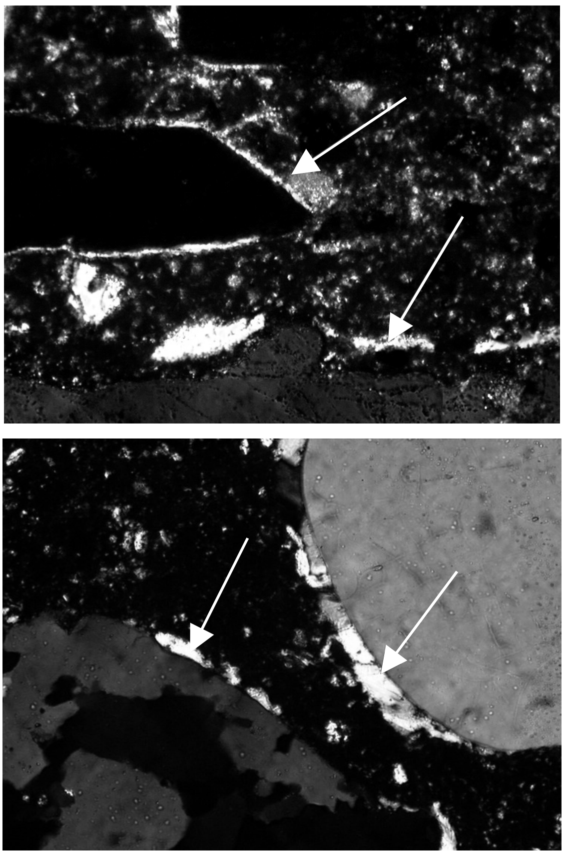

Figure 5: PFM micrographs illustrating the difference in the concentration of $Ca(OH)_2$ in the cement paste between CEMI + 10 % trass (left) and CEM III/B + 10 % trass (right). Note the lower abundance of portlandite, visible as bright spots, in the matrix of the cement paste between the aggregate particles in the latter. View 0.7 x 0.45 mm

however, $Ca(OH)_2$ is hardly visible at the paste-aggregate interfacial zone. Especially in the CEM III/B mix, it is rarely identified.

- Nearly all the voids in the trass-bearing mixes were empty, without any crystalline phases, such as portlandite, monosulfate aluminate or ettringite. In the mixes without trass, crystalline phases, mainly portlandite, fine needle-shaped crystals of ettringite and mixtures of these two phases were found in a number of voids (Fig. 6).
- In general, the cement paste in the trass-bearing mixes is more homogenous and dense under the microscope in plane polarised light than the corresponding cement pastes without trass.

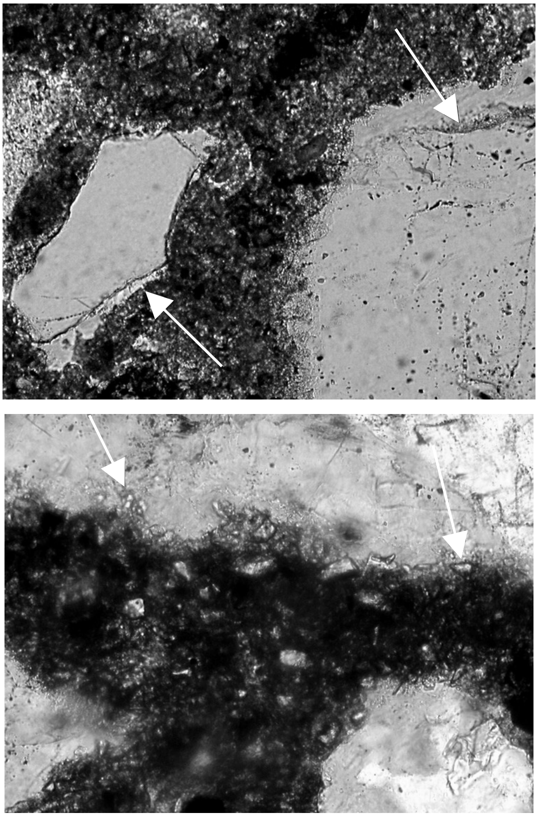

Figure 6: PFM micrographs of the reference concrete mixes without trass, illustrating the occcurrence of crystalline phases in voids in the cement paste. Left: CEM I, right: CEM III/B. View 0.7 x 0.45 mm

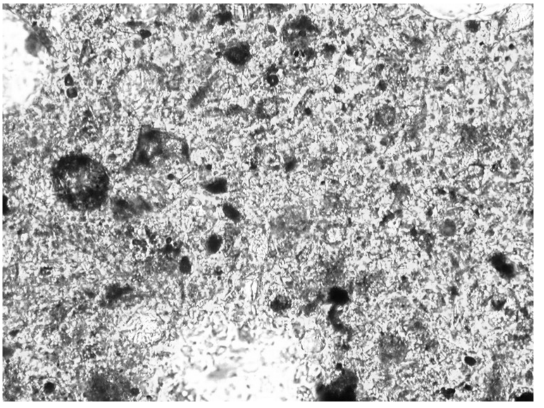

Figure 7: PFM micrograph of a thin section of unreacted trass, used in the reference concrete mixes showing the characteristics of the trass particles. View 0.7 x 0.45 mm

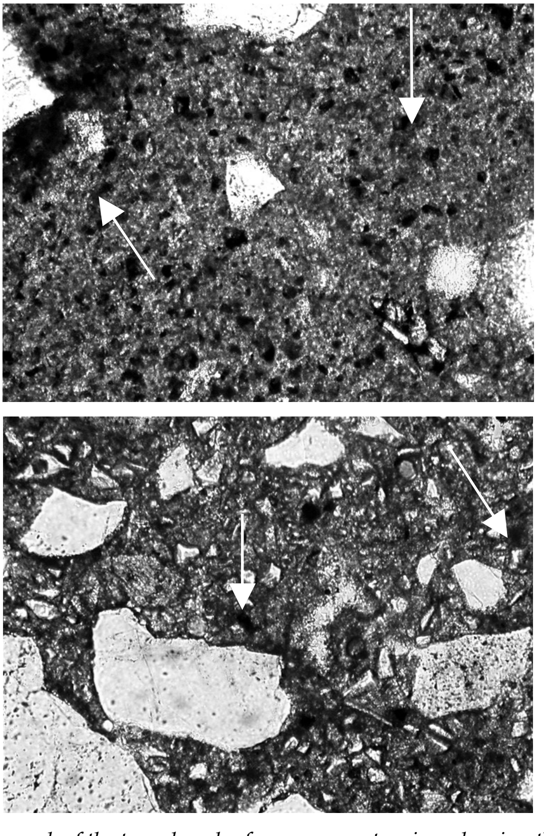

Figure 8: PFM micrograph of the trass-based reference concrete mixes showing the characteristics of the trass particles. Left: CEM I with 10 % trass, right CEM III/B with 10 % trass.
View 0.7 x 0.45 mm

3.2 *Microstructural characteristics of trass in the reference mixes*

The individual grains or particles of trass in the trass-based mixes were relatively difficult to identify, most likely because part of the trass, -especially the very fine particles-, may have reacted. Another reason may be the close resemblance of trass to the clinker particles in thin section. To ease identification of the trass particles in the mixes, a reference thin section specimen prepared from the trass used in the mixes, was used for the analysis. An overview of the reference powder trass in plane polarised light is shown in Figure 7. Identification and characterisation of the trass was easier where local agglomeration of the binder and the trass had occurred. In such cases, the non-reacted or partially reacted trass could be identified as yellow or yellowish-brown particles, usually with dark, diffused outer haloes (in plane polarised light), closely resembling to belite (C2S) clinker particles (Figure 8). In crossed polarised light, they appear completely dark or isotropic. In the present study, the trass particles could more easily be identified in the thin section specimen of the CEM I mix than in the corresponding CEM III/B mix. The apparent difficulty may be attributed to the darker colour of the CEM III/B paste, compared to that of the CEM I mix, which makes it difficult to distinguish between the clinker and the trass grains.

4 Conclusions

From a preliminary study of both the long-term effect of trass addition to concrete and a microscopic study of trass-containing concretes, it may be concluded that:

- Addition of 10 % of trass relative to ordinary Portland cement (CEM I) and blast furnace slag cement (CEM III/B) affects the microstructure of concrete at 28 days by increased homogeneity of the mix, improvement of the interfacial zone between aggregate and cement paste, preventing local micro-bleeding.
- Addition of 10 % of trass relative to ordinary Portland cement (CEM I) and blast furnace slag cement (CEM III/B) affects the cement paste in concrete at 28 days by enhancing its visual density, lowering the amount of portlandite, and preventing the forming of crystallites of portlandite and/or ettringite in voids.
- Addition of 10 %m/m trass to ground granulated blast furnace slag cement (CEM III/B) does not have any effect on concrete durability over a period of about 30 years.
- The recognition of trass in amounts up to 25 %m/m in old, well-hydrated hardened concrete by polarization-and-fluorescence microscopy is problematic; alternatively, archive data do not correspond to the actual concrete mixes used in this case.

Acknowledgements
One of the case studies was performed within the framework of the DUMACON (Durability of Marine Structures) project, sponsored by CUR committee B82 and EZ-co grant no. 855. Recasting of original mixtures and investigation was sponsered by TNO basisfinanciering and by doelfinanciering provided by the Ministry of Transport, Public Works and Water Management. The manuscript benefitted from the comments by R.P.J. van Hees on an earlier version of the paper.

References

Biczök, I. (1972): Concrete corrosion, concrete protection. Budapest, Akadémai Kiadó.

Dreyfus, J. (1950): La chimie des ciments. Tome II. Valeurs numériques, figures et annexes. Paris, Eyrolles.

DuraCrete (2000): Final technical report. European Union Brite EuRam III, document BE95-1347/R17. Gouda, CUR.

Escalante-Garcia, J.I. and Sharp, J.H. (2004): The chemical composition and microstructure of hydration products in blended cements. Cement & Concrete Composites 26:967-976.

Hewlett, P.C. (ed.) (1998): Lea's chemistry of cement and concrete. 4th Edition, London, Arnold.

Janotka, I. and Mojumbar, S.C. (2003): Hydration of Portland cement, natural zeolite mortar in water and sulphate solution. Materiales de Construcción (53):17-27.

Lamprecht, H.O. (1996): Opus caementitium. Bautechniek der Römer, 5th Edition, Düsseldorf, Verlag Bau + Technik.

Liebig, E. and Althaus, E. (1998): Pozzolanic activity of volcanic tuff and suevite: Effects of calcination. Cement & Concrete Research (28):567-575.

Ludwig, U. and Schwiete, H.E. (1963): Kalkbindung und Neubildungen bei den Traβ-Kalk-Reaktionen. Zement, Kalk, Gips (10):421-431.

Massazza, F. (1993): Pozzolanic cements. Cement & Concrete Composites (15):185-214.

Massazza, F. (2002): Properties and applications of natural pozzolanas. In: Bensted, J. and Barnes, P. (eds.), Structure and performance of cements. London, Spon Press: 326-352.

Naiqian, F., Hongwei, J. and Enyi, C. (1998): Study on the suppression effect of natural zeolite on expansion of concrete due to alkali-aggregate reaction. Magazine of Concrete Research (50):17-24.

NEN-EN 197-1:2000. Cement – Deel 1: Samenstelling, specificatie en conformiteitscriteria voor gewone cementsoorten. Delft, NEN.

Nijland, T.G, Brendle, S.,.Hees, R.P.J. van and Haas, G.J.L.M. de (2003): Decay of Rhenish tuff in Dutch monuments. Part 1: Use, composition and weathering. Heron (48):149-166.

Polder, R.B. & Rooij, M.R. de (2005): Durability of marine concrete structures – field investigations and modelling. Heron (50):133-153.

Rooij, M.A. de and Polder, R.B. (2005): Duurzaamheid mariene betonconstructies. CUR, Gouda, CUR-report 215.

Rooijen, W. van (1994): Stand van zaken. Kolkwanden, binnenhoofd en remmingwerk. Bouwdienst Rijkswaterstaat report RN-NS-94-007.

Sersale, R. and Aiello, R. (1964): Costituzione e reattivà del 'trass' renano. L'Industria Italiana del Cemento (34):747-760.

Sersale, R. and Frigione, G. (1987): Portland – zeolite cement for minimizing alkali-aggregate reaction. Cement & Concrete Research (17):404-410.

Siemes, A.J.M. (1995). PFM-onderzoek aan betoncilinders uit de Noordersluis te IJmuiden. TNO report 95-BT-R0663-002.

Siemes, A.J.M. and Larbi, J.A. (1996): Onderzoek naar de treksterkte van het beton van de Noordersluis in IJmuiden, fase A. TNO report 96-BT-R0420-01.

Takemoto, K. and Uchikawa, H. (1980): Hydratation des ciments pouzzolaniques. Proceedings of the 7th International Congress on the Chemistry of Cement, Paris, I(IV):2-1 – 2-21.

Wessely, I. (1961): Der Traβ als hydraulischer Zusatzstoff. Zement, Kalk, Gips (7):284-293.