INVESTIGATIONS ON THE TIGHTNESS OF IMPREGNATED CONCRETE AGAINST HAZARDOUS ORGANIC FLUIDS

UNTERSUCHUNGEN ZUM EINDRINGEN VON UMWELTGEFÄHRDENDEN FLÜSSIGKEITEN IN IMPRÄGNIERTEN BETON

RECHERCHE DE COMPORTEMENT DE BETON IMPREGNE CONTRE DES LIQUIDES ORGANIQUES

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SUMMARY

The research of the effectiveness of surface protection systems with different specifications applied to selected concrete surfaces with different porosities are subject matter of this research. The results are compared with the behaviour of untreated concrete (reference material) concerning tightness.
The penetration tests were executed with three testing fluids and nine different surface protection systems. The result was a up to 30 % lower penetration rate of organic fluids an almost complete tightness against water.

ZUSAMMENFASSUNG

Es wird über Untersuchungen zur Wirkungsweise von Oberflächenschutzsystemen unterschiedlicher Spezifikation auf ausgewählten Betonoberflächen mit verschiedener Porosität berichtet. Die Oberflächenschutzsysteme werden hinsichtlich der Dichtigkeitswirkung mit dem Verhalten von unbehandeltem Beton (Nullversuch) verglichen.
Die Eindringversuche wurden mit drei Prüfflüssigkeiten und neun verschiedenen Oberflächenschtzsystemen durchgeführt. Dabei ergab sich eine bis zu 30 % geringere Eindringmenge bei organischen Flüssigeiten und eine nahezu vollständige Abdichtung bei Wasser.

RESUME

On réfère des recherches sur la mode de fonctionment et l'efficacité des systèmes pour la protection superficielle avec la specification differente sur

des surfaces de béton choisis avec une porosité differente. Les systèmes pour la protection superficielle sont comparés en regard de l'effet de imperméabilité avec le comportement de béton non traité (l'experiment nul).
Les expériments de pénétration sont réalisés avec trois fluides d'essai et neuf systèmes pour la protection superficielle differentes. Le résultat était jusqu'à 30 % dose de penetration reduit pour les liquides organiques et à peu près l'étanchéificational complet pur l'eau.

KEYWORDS: Surface protection systems, concrete, porosity, hazardous fluids, penetration, tightness, reference experiment

1 INTRODUCTION

The successful use of concrete structures as a secondary barrier against hazardous organic fluids with a limited duration of contact requires often a sealing of the surface consistent of plastic, metal or glas.
These measures ensure impermeability of the structure while concrete acts as structural material. The weathering resistance and ageing stability especially of plastic-layers are critical. The application of different reaction resins on the surface of a concrete structure as an impregnation has the main goal to increase fluid-tightness within the pores. Vapour diffusion is not impeded. The impregnated structure is used like a structure without a surface layer.
The function and effectiveness of standart or little modified surface protection systems on concrete surfaces with different porosities are tested.

The testing parameters are:

- specification of the surface protection system,
- properties of concrete,
- comparison of the fluid uptake and penetration depth of non sealed concrete specimens (reference experiment) and specimens impregnated with reaction resins of different specifications.

2 CONCRETE

The concrete specimens were casted in a cylindrical mould and had the following dimensions:

height:	150 mm
diameter:	100 mm

<u>concrete composition:</u>	320 kg cement per m^3 0/16 mm aggregates w/c = 0.58
<u>storage conditions:</u>	7 days at 100 % relative humidity and afterwards at 20°C and 40 % - 60 % relative humidity

The total porosity was measured with a helium pycnometer and showed the following results over the height of the samples:

top of casted cylinder:	18,2 %
middle of casted cylinder:	11,8 %
bottom of casted cylinder:	12,8 %

The significant difference in the porosity close to the surface of the top of the cylinder is a result of the production-process of the cylinders. Therefore two different testing series became necessary:
For the first testing series the reaction resins were applied to the upper side of the concrete cylinder; the bottom of the cylinder was used for the second testing series.

The humidity of concrete cylinders were determined according to DIN 1048 Part 5 by drying till constance of mass. The average value was 2.9 mass-%. The cube compressive strength was 43.0 N/mm² at the age of 28 days and 57.7 N/mm² at the time of testing.

3 SURFACE PROTECTION SYSTEMS

3.1 Reaction Resins

Besides the distinction of surface protection systems in impregnation materials, sealings and coatings, the kind of hardening is also used for classification:

3.1.1 One-Component Systems

The resin particles are dispersed in form of free drops in a watery emulsion. In systems containing oganic solvents the plastic molecules are fine-dissolved in the solvent. A coat of emulsifiers around every drop of the emulsion protects the particles from sticking together. The emulsion or the solvent evaporate and the plastic particles polymerize.
Together with pigments, filler and additives a coating almost free of pores is built up.

3.1.2 Two-Component Systems

A defined amount of the component resin and hardener are intensively mixed together and harden by polyaddition.

3.2 Epoxy Resins

Epoxy resins are highly polymeric, duroplastic compounds, produced by cross - linking of polymeric chains [1]. The very reactive epoxy-group is significant:

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  H   H
  |   |
- C - C -
   \ /
    H
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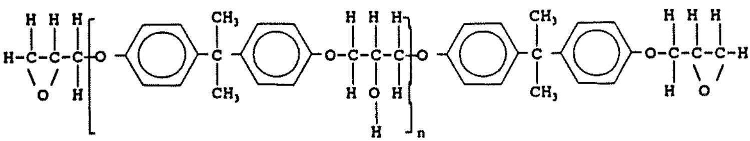
3.2.1 The Resin as Component

The production of epoxy resins is based on epichlorhydrin and bisphenol A and F which are responsible for the consistence of the reaction resins. The viscosity of these reaction resins ranges between 15000 and 50000 mPa·s [2].

The following formula shows that the resins differ in the number n of repeated formula units with one hydroxy-group:



3.2.2 The Hardener as Component

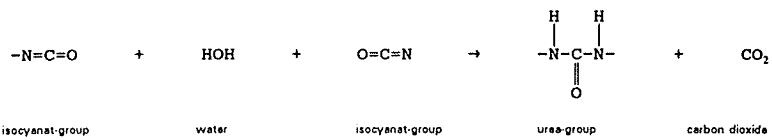
Amines are exclusively used as hardeners in cold-setting epoxy systems. The number n of functional amino-groups - $[CH_2]_2$-NH - is responsible for the con-

stitution of either a linear chain polymer ($n \leq 2$) or a cross linked duroplastic polymer ($n > 2$) [3].
Reactive additives are responsible for the successful use of epoxy resins in civil engineering. They participate directly in the cross-linking reaction and influence viscosity, workability and final properties of the hardened resin. Organic solvents or water may be used as additives.

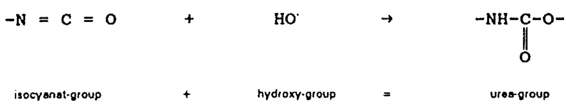
3.3 Polyurethane

3.3.1 One-Component Polyurethane Resins

Polyurethane plastics are a product of the reaction of isocyanat-groups and water under synthesis of urea-groups [3], [4]:



3.3.2 Two-Component Polyurethane Resins



Isocyanat- and hydroxy-compounds can be polyfunctional, i.e. they have more than one functional group.
In a reaction of polyfunctional isocyanat- and hydroxy-molecules in exactly defined mixing quantities polymeric chains can be built up linear or cross-linked.

These polymers can be classified as duroplastics, they are unmeltable and unsolvable.

3.4 Silicon Organic Compounds [1], [3] ,[5]

3.4.1 Silicon Resins

The end product silicon resin is dissolved in an organic solvent with a concentration of 5 to 8 %. The organic solvent serves as transport media for the silicon resin into the construction material. After the evaporation of the solvent (physical drying) is finished, the hydrophobic effect is immediately built up because of the chemical reaction between Si-OH - compounds of the silicon resin and the concrete surface.
The high sensitivity against humidity, the low content of active substance in connection with a high evaporation rate of the solvent on concrete surfaces with low porosity cause problems concerning the efficiency of this impregnation method.

3.4.2 Silanes

These very low molecular compounds are dissolved in water or organic solvents with a solid content from 20 to 100 %. Hydroxyfunctional compounds (i.e. H_2O) and an alkaline media are necessary as catalysts to build up the silicon resin.
The high vapour pressure of the silanes may be a problem during the application under high temperature or in windy weather. A high amount of reactive content is possibly lost through evaporation, this means a diminuation of substance.

3.4.3 Oligomeric Alkylalkoxisiloxanes / Siloxanes

Concerning the material properties, siloxanes have an intermediate position between silicon resins and silanes. By adding water during the production process oligomeric siloxanes are being built up. The smaller molecular size enables them to penetrate quicker and deeper into concrete than silicon resins and they are also distinguished by a lower vaporisation rate.

	Epoxy Resin	Polyureth.	OSilicone Resin
Kind of Polyreaction	Polyaddition	Polyaddition	Polycondensation
Kind of Plastic	Duroplastic	Duroplastic, Elastomeric	Elastomeric
Polarity of the Compound	polar	very polar	nearly not polar
Kind of Solvent or Dispersion	org. Solvent Disp. with Water	org. Solvent Disp. with Water	org. Solvent Disp. with Water
Application	Impregnation Sealing Coating	Sealing	Impregnation
Resist. to Infl. of Temp.	good	-80 - 120°C	-50 - 180°C
Chemical Shrinkage	0,2 - 0,4 %	0,2 - 0,3 %	
Resist. to Chemicals			
Ketone	partly resistant	resistant	resistant
Alkane	partly resistant	partly resistant	
Water	resistant	resistant	resistant
Alcohol	resistant	partly resistant	resistant

Table 1. Properties of reaction resins [13]

Surface Protection System	Chemical Characteristics	Kind of Solvent or Dispersion	Characteristic of the Surface Protection System	Active Ingredient non-voltile Matter (N.V.M.)	Visco-sity (mPas)	Load Character-istics
OS 1	liquid epoxy-resin with amine-hardener two-comp. system	solvent-free	coating	97 M-% (N.V.M.)	10000	mechan. 1d hardend 7d
OS 2	liquid epoxy-resin with amine-hardener two-comp. system	solvent containing	impregnation/ sealing	30 M-% (N.V.M.)	ca. 3	mechan. 1d hardend 7d
OS 3	Epoxysystem two-comp. system	solvent-free	sealing	97 M-% (N.V.M.)	250	mechan. 1d chem. 7d
OS 4	polyalcoholemul. a. aromatic polyisocyanat two-comp. system	solvent containing	sealing/ coating	no specifi-cation (n.s.)	1200	no specification (n.s.)
OS 5	aromatic polyisocyanat-prepolymer one-comp. system	solvent containing	impregnation/ sealing	(n.s.)	200	(n.s.)
OS 6	low molecular alcylalcoxysilan with additives one-comp. system	solvent containing	impregnation	10 M-% (N.V.M.)	1-2	(n.s.)
OS 7	oligomer siloxan	solvent containing	impregnation	(n.s.)	ca. 2	(n.s.)
OS 8	Isobutyl-tri-ethoxysilan one-comp. system	solvent-free	impregnation	99 M-%	0,95	(n.s.)
OS 9	silan-siloxan-basis two-comp. system	solvent containing	water and oil repellent	16 M-%	(n.s.)	mechan. 1d

Table 2. Technical data according to the specifications of the producers (n.s.: no specification given)

4 TESTING FLUIDS

The kind of testing fluid affects the mode of action of the applied surface protection system very much. There are physical changes in transport phenomena (capillary fluid transport and gas diffusion) and there are chemical reactions between the testing fluid, humidity of the specimen, reaction resin and concrete [6].
All these phenomena are caused by the testing fluid and can be summed up:

The **decomposition** results in a spreading of the reaction resin with an irreversible damage.

A **swelling** is caused by the absorption of gases or liquids. The adhesion and strength of the reaction resin are reduced and the permeability for the substances, that are responsible for the swelling, is increased. The process of swelling is reversible by drying.

The **dissolving** of a reaction resin results in the destruction of the barrier-effect. The fluid can penetrate unimpededly.

It is a scientific finding, that the testing fluids aceton and n-heptane penetrate very quickly and deep into uncoated concrete [7], [11], [12]. Viscosity, surface tension and the number of C-atomes (the length of the chain) are the responsible parameters for the penetration process. A differentiation into polar and not polar fluids leads to the chosen representatives: aceton and n-heptane.

Water was used as a comparing fluid at every testing series.

Fluid	Chemical formula	Dyn. viscosity mPa·s	Surface tension mNm^{-1}	Specific gravity kgm^{-3}	Water solubility at 20°C
Aceton	C_3H_6O	0.316	23.70	790	infinitely soluble
n-Heptane	C_7H_{16}	0.405	20.3	680	non-soluble
Water	H_2O	1	72.75	998.2	infinitely soluble

Table 3. Relevant properties of the testing fluids

5 TESTING SERIES

5.1 Systematic of the Testing Programme

Table 4 shows the systematic of the parameters

Surface Protection System	Testing Side o: Top Side u: Bottom Side	Testing Fluids		
		Aceton	Heptane	Water
OS 1	o			
	u			
OS 2	o			
	u			
....				
OS 9	o			
	u			
Reference Experiment	o			
	u			

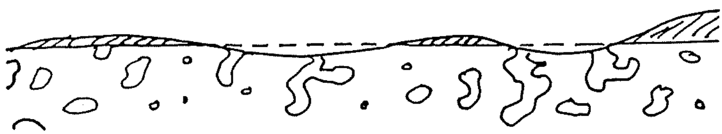
Table 4. Classification of the testing parameters

5.2 Pre Experimental Arrangements

Different viscosities of the surface protection systems are responsible for different results of the application at the surface characterized as impregnations, sealings or thin coatings (intermediate stages and modifications included). Therefore the surfaces for testing with the applied surface protection systems (epoxy, polyurethane) needed to be abraded, thus only the surface protection system penetrating the structure remains for testing.

This form of pre experimental arrangement may be fatal for certain surface protection systems: surface protection systems with high viscosity and little penetration depth can be destroyed locally or as a whole.

Following sketch illustrates this influence:



The capillary suction test to evaluate the coefficient of water absorption described in DIN 52617 is used as experimental set-up. The marginal climatic conditions during the test ranged concerning temperature from 18 to 20°C and relative humidity from 50 to 60 %.

5.3 Testing Parameters

5.3.1 Fluid Uptake

The penetrating quantity is determined gravimetrically according to the procedures described in DIN 52617.

5.3.2 Penetration Depth

5.3.2.1 Observation on Lateral Area

Because of the use of casted conrete samples and of clear epoxy resin to seal the lateral area, it is possible to observe the penetration depths on the surface of the cylinder. Due to the interfacial effects between the epoxy resin of the lateral area and the surface of the concrete the determined data is not exact.

5.3.2.2 Observation of the Penetration Depth on the Surface of Fracture of the Cracked Concrete Cylinder

The applied testing liquids aceton and n-heptan are because of their high vapour pressure very volatile. Therefore a definite boundary of the penetration front cannot be detected.

5.3.2.3 Detection of the Penetration Depth with H_2SO_4

The samples are split at the end of the test after 72 hours. Immediately afterwards the surfaces of the fracture are thinly dampened with concentrated sulphuric acid, partly dried with the help of a Bunsen burner and subsequently intensively scorched [9]. The applied sulphuric acid decomposes respectively affects the surface of concrete and sulphonation products (C-SO_3-H) remain.

The quantity and quality of these products cannot be exactly specified in a chemical way. Unlike at a burning process, where besides carbon dioxide and water mineral ashes stay behind, not exactly defined C-O-H compounds are produced, i.e. aldehydes, ketones and acids. These products dye the concrete surface black and allow to determine the penetration front of the saturated area. This method is till now the only detection-method for fluids with high vapour pressure. Besides the regulations concerning health and safety at work other disadvantages can be mentioned:

- The amount of lost fluid between splitting of the sample and application of the sulphoric acid is not possible.

- According to the testing fluid, the microstructure of the concrete and the saturation of the pores, the penetration front is marked in different gray steps and not exactly as a front.

5.4 Testing Results: Fluid Uptake

The fluid uptake of all specimens of this testing series follows closely the capillary fluid transport. This effect is independent from testing site, testing fluid and kind of surface protection system. If the abscissa is scaled in the square-root-relation of time, the penetration process is linear.

Fig. 1 shows as an example results from the most interesting surface protection systems.

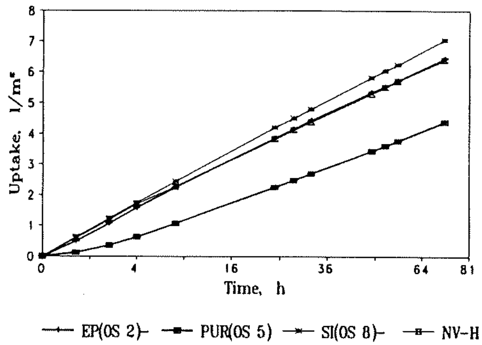


Fig. 1. Capillary fluid absorption of n-heptane over 72 h (NV: reference concrete).

Starting on the assumption, that the reduction of the free porosity in the areas near the concrete surface by applicating a surface protection system results in a strong barrier-effect at least at the beginning of the fluid uptake. The results of the testing series with aceton and n-heptane do not confirm this theory. Independent from the specification of the surface protection system a continious reduction of the fluid uptake over the whole testing period according to the standart test could be detected. Although some of the pores are completely filled with reaction resin (i.e. sealings), no barrier effect was noticed. The explanations for this effects are described in chapter 4.

Water as a testing fluid and the classic silicon-organic impregnations show an excellent durable and effective barrier against fluid uptake in contradiction to the results of organic fluids.

5.4.1 Epoxy Resins

Concluding from experiences in application and testing, the surface protection systems OS 1 and OS 3 have to be described as thin coatings or sealings because of their high viscosity. The preparation of the specimens with a film at the surface by mechanical abrading is responsible for variations in the testing results. The low viscosity of OS 2 (3 mPa•s) allows the classification of OS 2 as an impregnation.

The testing results of the fluid uptake of OS 2 according to the standart test are as follows:

The testing of the top side of the cylinders showed for aceton and n-heptane a reduction of the penetrated volume of about 10 %, for water 42 %; the reduction of aceton and n-heptane on the bottom side of the cylinders was about 25 %, the reduction of water was about 55 %.

5.4.2 Polyurethane Resins

The thin layer of surface protection system OS 4 at the surface after hardening is very tough and has a very bad bond with the concrete surface and scratches deep after abrading. Negative testing results confirm the uneffectiveness of OS 4.

OS 5 hardens with a hard film, has a low viscosity and can be classified as impregnation or sealing.

	Application of OS 5 on the Top Side	Application of OS 5 on the Bottom Side
Aceton	38 %	29 %
n-Heptane	15 %	30 %
Water	76 %	41 %

Table 5. Reduction in relative fluid uptake of OS 5 according to the reference experiment.

The relatively low effectiveness of OS 5 applied on the top side can only be explained by large variations during the production of the samples.

5.4.3 Silicon-Organic Reaction Resins

All tested reaction resins are classified as typical impregnation agents with outstanding hydrophobic properties and partly with additional oleophobic properties. These systems penetrate very deep into concrete and harden without a film at the surface. The reduction in fluid uptake of organic fluids according to the fluid uptake of the reference experiment varies widely: the testing results of n-heptane are on both testing sides within the scatter of the reference experiment. The application of OS 8 and OS 9 on the bottom side and the use of aceton as testing fluid showed a significant reduction of fluid uptake of about 25 %.

6 CONCLUSIONS

In these testing series standart reaction resins of different compositions have been applied to concrete surfaces with different porosities. The testing results have shown that the preparation of the concrete specimens and the testing procedure in accordance with DIN 52617 are suitable.

Surface protection systems containing solvents, are based most often on aliphatic hydrocarbons. In view of the chemical properties and the penetration process of the testing fluids it can be concluded, that aceton and n-heptane are critic liquids for the applied reaction resins. The testing results from the penetration tests with water prove this.

As a next step it will be necessary to study the mechanisms, that arise from the reactions

> concrete as construction material - humidity of concrete - specification of the surface protection systems - testing fluid.

The interim results according to fluid uptake are as follows:

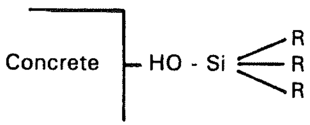
Polyurethane and Epoxy Resins

Reaction resins with a surface film have long molecule-chains and therefore a high viscosity. This limits the penetration of the reaction resins only into big pores at the concrete surface. After hardening the pores are closed completely and there is no fluid or gas transport possible. Since the surface had been ground off before the penetration started, a destruction of the filling of the pores near the surface was more or less produced. Systems with low

viscosity have good penetration dephts, interlink and active substance are reduced.
These are the reasons why the use of epoxy resins and polyurethane as impregnation materials are strictly limited. The classification as impregnations by the producers is inadmissible by definition [6].

Silicon Organic Compounds

Silicon resins are used in civil engineering as impregantion materials, as waterproofing agents, oilproofing agents, consolidation material and for antimicrobacterial treatment of porous media. This kind of reaction resin has a very high permeablity for gas, high penetration dephts and hardens without a visible surface film.
The results of this penetration tests show, that silicon resins reduce only the amount of penetrated fluid of water and aceton. This effect can be explained by the mode of action of this material:



Silicon resins consist of polar silanol compounds and not polar rest com pounds "R" (Alkyl- or Alkoxylcompounds), that reach into the pores of the concrete. The silicon molecule is connected with the concrete by a oxygen compound [10]. All not polar rest compounds R cause a shield impededing fluid transport of polar media. With an increasing difference in surface ten-

sion and polarity between R-compounds and penetrating fluid there is also a incresing effectiveness of this shield against capillary fluid transport.
These are the reasons why there is an excellent barrier-effect for water (surface tension 72.75 N/mm², very polar); the penetrated volume of aceton (surface tension 23.70 N/mm², polar) shows a significant reduction of about 25 % according to the reference experiment. N-heptan (surface tension 20.30 N/mm², not polar) has about the same penetrated fluid quantity as the standart test. This result proves the mode of action of silicon resins as impregnation materials.

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