

## **Metal Soaps for the Production of Integral Water Repellent Concrete**

**W. Li<sup>1, 2</sup>, F. H. Wittmann<sup>2, 3</sup>, R. Jiang<sup>2</sup>, T. Zhao<sup>2</sup> and R. Wolfseher<sup>4</sup>**

<sup>1</sup>Institute of Oceanology, Chinese Academy of Sciences, Qingdao, China

<sup>2</sup>Qingdao Technological University, Qingdao, China

<sup>3</sup>Aedificat Institute Freiburg, Germany

<sup>4</sup>Wolfseher und Partner, Zurich, Switzerland

### **Abstract**

It has been shown and verified in practice that surface impregnation of cement-based materials with silane prevents capillary uptake of water and aqueous salt solutions such as seawater. Integral water repellent concrete can also be manufactured by adding silane-based compounds to the fresh mix of concrete or mortar. Service life of concrete structures in aggressive environment can be significantly extended by water repellent treatment. In this contribution the influence of metal soaps to fresh concrete on water repellency of the hardened material has been investigated. The chloride penetration of integral water repellent concrete has been determined after exposure to seawater. The distribution of the metal salts in the treated concrete has also been studied. It has been found that chloride penetration into integral water repellent concrete after adding metal salts to the fresh mix has been slowed down considerably. Although a complete chloride barrier could not be achieved by the addition of metal soaps the service life of reinforced concrete structures can certainly be extended considerable by means of this technology.

**Keywords:** metal soaps, integral water repellent concrete, chloride penetration

## **1 Introduction**

Water absorption into and water migration in concrete is at the origin of major degradation mechanisms of reinforced concrete structures. The structure of concrete can be weakened by hydrolysis [1, 2], high water content increases the risk of frost damage, and aggressive compounds dissolved in water can be transported deep into the pore space of concrete by capillary action [3, 4]. Capillary absorption of concrete can be practically suppressed by water repellent treatment of the surface. In this way durability and service life of reinforced concrete structures can be significantly increased.

Thousands of years ago natural products such as oils, fats or waxes have been applied to avoid excessive water uptake by capillary action of natural stones and cement-based materials. More recently silane-based compounds are used in practice. In most cases the surface of hardened concrete is impregnated with liquid silane [3]. Silane reacts in the pore space of concrete and forms finally a thin network of silicon resin on the surface of hydration products of cement. Bridges tunnels and other important elements of the infrastructure have been and are protected successfully by water repellent surface treatment for many years by now. In some cases it would be more convenient if the entire volume of concrete would be water repellent. This aim cannot be achieved, however, by surface impregnation of structural elements with conventional dimensions, as the penetration depth is seldom more than 10 mm. Structural concrete elements can be made integral water repellent, however, by adding silane emulsion to the fresh mix for instance [4]. Recent test series have shown that deep surface impregnation is more efficient than integral water repellent treatment. But service life of reinforced concrete structures can still be significantly increased by integral water repellent concrete.

In this contribution the efficiency of metal soaps for the production of integral water repellent concrete shall be investigated. Although metal soaps are used in practice for many years already in different cement-based products very few publications on capillary absorption of concrete with metal soaps added exist in the literature [5-7]. One major aim of this contribution is to find out if addition of metal soaps to fresh concrete is a promising technology to increase service life of reinforced concrete structures in aggressive environment.

## **2 Experimental**

For all tests described in this contribution a standard concrete with a water-cement ratio of 0.5 has been prepared as a basis for reference. The composition of this concrete is given in Table 1. Ordinary Portland cement, river sand with a maximum diameter of 5 mm and broken coarse aggregate with a maximum diameter of 25 mm, both from Qingdao region, have been used.

**Table 1:** Composition of plain concrete given as kg/m<sup>3</sup>

Components	Cement	Gravel	Sand	Water	W/C
Mass/volume	320	1267	653	160	0.5

0.5 % and 1 %, related to the mass of cement, of four types of metal soaps have been added to all four different types of concrete. The metal soaps have been obtained from Peter Greven Fett-Chemie Company, Germany. The four types of metal soaps have the following designation: LIGAPHOB ZN 502, LIGA Zinkstearat 101, LIGA Calciumstearat 860, and LIGAPHOB ZN 101 PLUS.

First cubes with an edge length of 100 mm have been cast in steel forms. After one day curing under wet burlap, the steel form has been removed and the cubes were allowed to harden in a humid chamber (T=20 °C, RH>95 %). At an age of 28 days the cubes were cut into two halves parallel to the direction of casting. These half cubes were then exposed to the laboratory atmosphere (T=20 °C and RH=65 %) for four weeks for drying. Then the four small surfaces (50 x 100 mm) were sealed with wax. The specimens were then ready for capillary absorption. The surface originally in contact with the steel form of each half cube was then put in contact with water or with 5 % aqueous NaCl solution. The weight gain has been measured by weighing after regular intervals of absorption.

### **3 Results and discussion**

#### **3.1 Compressive strength**

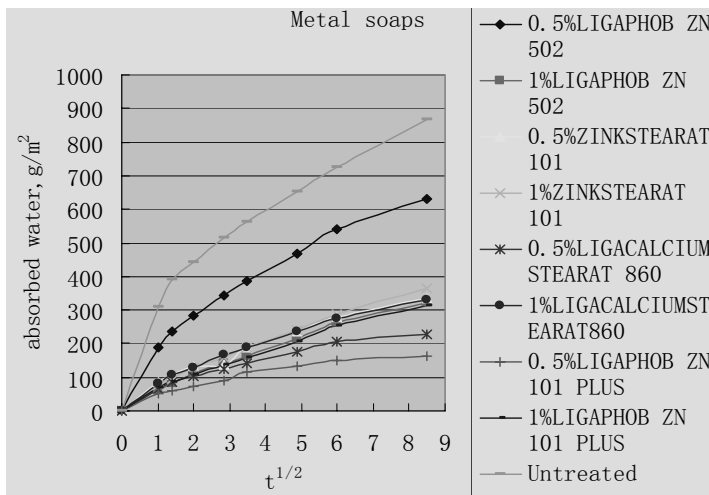
Compressive strength of the different types of concrete has been determined at an age of 28 days in order to characterize mechanical properties. Results are compiled in Table 2. Each value given in Table 2 is the average of at least 3 test results. Addition of metal soap to the fresh concrete reduces compressive strength significantly. The compressive strength may be reduced by up to 50 % of the strength of neat reference concrete by addition of 1 % of metal soap. This observation is an indication that the presence of metal soaps in the pore liquid has a strong influence on hydration of Portland cement. For practical applications this strength decrease has to be compensated by a reduction of the water-cement ratio.

**Table 2:** Compressive strength of neat concrete (reference) and concrete with different metal soaps added

	Dosage %	Compressive strength	
		MPa	%
Neat concrete	0	54.2	100
LIGAPHOB ZN 502	0.5	35.0	64.6
	1.0	30.4	56.1
Zinkstearat 101	0.5	37.2	68.6
	1.0	29.8	55.0
LIGA Calciumstearat 860	0.5	34.6	63.8
	1.0	31.0	57.2
LIGAPHOB ZN101 Plus	0.5	32.7	60.3
	1.0	27.0	49.8

### 3.2 Capillary absorption

The absorption of water by capillary action has been measured as function of time. Results have been plotted on a square root of time scale and they are shown in Figure 1.



**Figure 1:** Capillary water absorption by neat concrete and by integral water repellent concrete with metal soaps

**Table 3:** Initial coefficient of capillary absorption  $A_i$  for neat concrete and concrete containing metal soaps

	Dosage %	Coefficient $A_i$ $\text{g/m}^2 \text{ h}^{0.5}$	Coefficient $A_i$ %
Neat concrete	0	312	100
LIGAPHOB ZN 502	0.5	195	62.5
	1.0	76	24.4
Zinkstearat 101	0.5	79	25.3
	1.0	82	26.6
LIGA Calciumstearat 860	0.5	91	29.2
	1.0	93	29.8
LIGAPHOB ZN101 Plus	0.5	52	16.7
	1.5	74	23.7

In a simple capillary porous system the water uptake as function of time can be described approximately by means of a square root of time function:

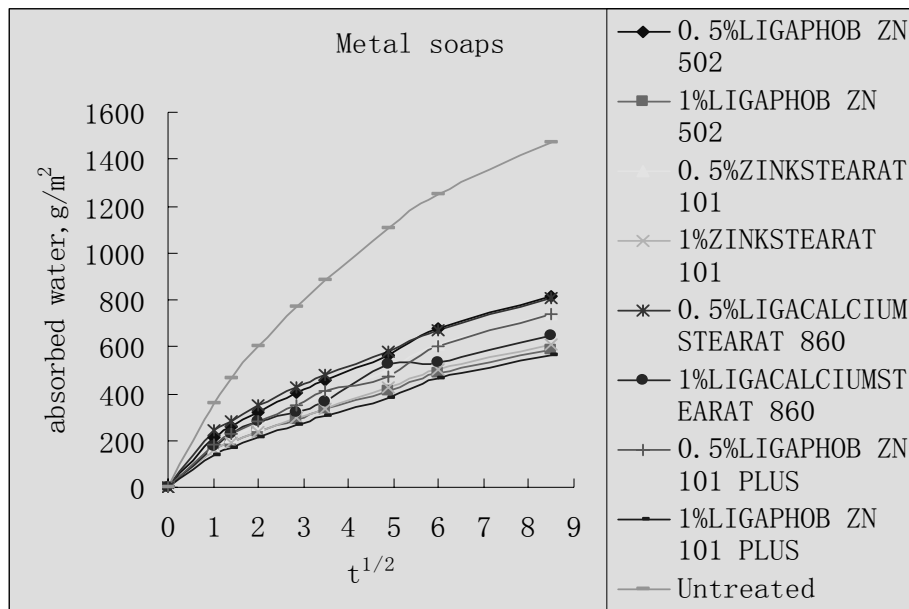
$$\Delta W(t) = A\sqrt{t} \quad (1)$$

This function describes capillary absorption of concrete within certain time intervals only in a realistic way. Because of several influences the coefficient of capillary absorption  $A$  depends on the penetration depth. One major reason is the fact that the skin of concrete has a higher porosity than the bulk material. But we can use the initial value of  $A_i$  to characterize capillary absorption of concrete and the influence of added metal soaps on capillary absorption. Values determined for the first hour of contact between the concrete surface and water are compiled in Table 3.

Capillary absorption is significantly reduced by addition of metal soaps. It can be observed, however, that addition of 1 % of a metal soap does not reduce further capillary absorption as compared with concrete containing 0.5 %, with the exception of LIGAPHOB ZN 502. With the three other metal soaps a slight increase of capillary absorption is observed even when dosage is increased from 0.5 % to 1 %. Further studies are needed to find out an optimum dosage of metal soaps. It may well be below 0.5 %.

On concrete, which has been made integral water repellent by addition of silane emulsion it has been observed that the siloxane concentration was at maximum close to the surface [8]. It may be assumed that silane

emulsion is transported during the drying process with the water into the surface near zone, where it can react. In order to check if in concrete made integral water repellent with metal soaps a similar effect can be observed a layer with a thickness of 5 mm has been cut of the surface with a diamond saw. Then capillary absorption through the fresh surface has been determined again. Results of this second series of tests are shown in Figure 2.



**Figure 2:** Capillary water absorption by neat concrete and by integral water repellent concrete with metal soaps after removal of a 5 mm thick surface layer

Comparing results shown in figures 1 and 2 it is obvious that capillary suction increases considerably after removing the surface near zone. This is a clear indication that also in this case the surface near zone is more water repellent than the bulk material. This observation has been confirmed by direct determination of the content of stearates as function of the distance from the surface. As the untreated specimens also absorb less water per unit of time traces of oil from the steel form have probably also contributed to a reduction of capillary absorption. The initial coefficient of capillary absorption  $A_i$  has been determined and is shown in Table 4. While the coefficient of capillary absorption  $A_i$  as measured directly on the formed surface is reduced to values between 16 and 30 % of the reference concrete, the coefficient as measured after removal of a 5 mm thick surface layer is reduced to values between 41 and 62 %.

Capillary absorption has also been determined after removal of two additional layers with a thickness of 10 and 40 mm. No significant further reduction of the efficiency of metal soaps could be observed.

**Table 4:** Initial coefficient of capillary absorption  $A_i$  for neat concrete and concrete containing metal soaps after removal of a 5 mm thick surface layer

	Dosage %	Coefficient $A_i$ $\text{g/m}^2 \text{ h}^{0.5}$	Coefficient $A_i$ %
Neat concrete	0	358	100
LIGAPHOB ZN 502	0.5	189	52.8
	1.0	171	47.8
Zinkstearat 101	0.5	192	53.6
	1.0	179	50.0
LIGA Calciumstearat 860	0.5	212	59.2
	1.0	222	62.0
LIGAPHOB ZN101 Plus	0.5	189	52.8
	1.5	148	41.3

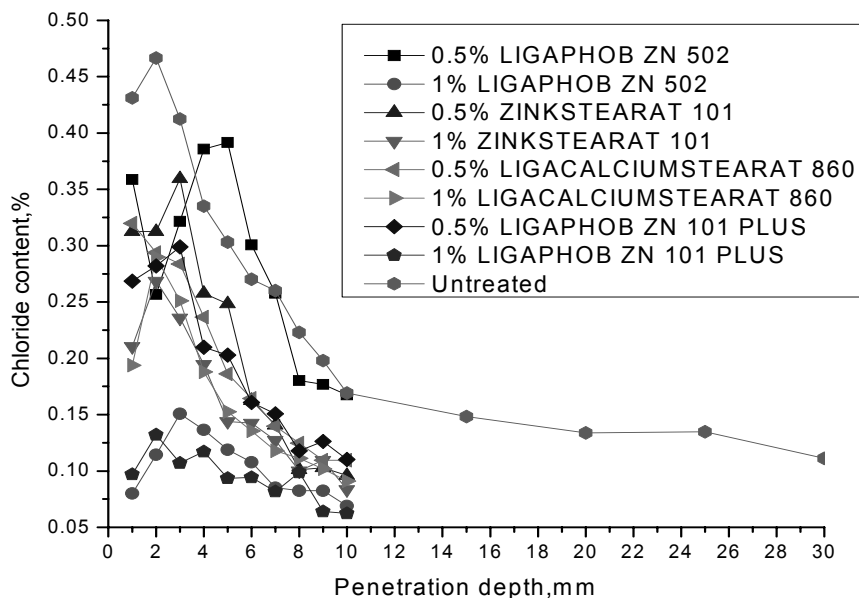
### 3.3 Chloride penetration

Water penetration by capillary action is of course an indication of the risk of penetration of chloride or any other aggressive compound dissolved in water into the pore space. The rate of chloride penetration is a dominant parameter for the estimation of service life of reinforced concrete structures in marine environment or in frequent contact with de-icing salt. After 28 days of contact with a 5 % aqueous NaCl solution the chloride profile as established in the concrete specimens has been determined.

From the surface of the chloride contaminated specimens thin layers have been milled successively. The chloride content of the powder, which has been collected, has been determined by means of ion chromatography. Chloride profiles obtained in this way are shown in Figure 3.

It can be seen that after 28 days of contact of the concrete surface with the salt solution chloride has penetrated deeper than 20 mm into the neat concrete specimens. There is a wide scatter of the obtained chloride profiles of concrete containing metal soaps and more experiments will be necessary to obtain more reliable and quantitative results. Results obtained on specimens containing 0.5 % LIGAPHOB ZN 502 are doubtful and must be repeated, but the chloride profile of all other specimens

containing metal soap are shifted to lower penetration depth. This shift is a direct measure for the extension of service life of reinforced concrete structures in aggressive environment by adding metal soaps to the fresh concrete. Addition of 1 % of LIGAPHOB ZN 502 and of 1 % of LIGAPHOB ZN 101 Plus leads practically to an effective Chloride barrier. By optimising the concrete composition the resistance with respect to chloride penetration can certainly be further improved.



**Figure 3:** Chloride profiles as observed in neat concrete and concrete exposed to 5 % aqueous NaCl solution for 28 days

## 4 Conclusions

It has been shown that it is possible to produce integral water repellent concrete by addition of metal soaps to fresh concrete. By adding 1 % of LIGAPHOB ZN 502 or 1 % of LIGAPHOB ZN 101 Plus chloride penetration is reduced to such an extent that the integral water repellent concrete can be considered to be equipped with an effective chloride barrier. Surface life of reinforced concrete structures in aggressive environment built with this type of concrete will be extended significantly.



After optimization this type of concrete will be a substantial contribution to more durable and more sustainable construction.

Strain-hardening cement-based composites (SHCC) [9] and textile cement composites [10] are comparatively new and advanced building materials. High ductility is reached in both cases by controlled multi-crack formation. It is recommended to add metal soaps to the fresh mix of these two types of materials in order to avoid capillary absorption by micro-cracks [11]. This will improve durability and extend service life in aggressive environment significantly.

### **Acknowledgement**

Authors gratefully acknowledge financial support by National Natural Science Foundation of China, Contract No. 50739001 and Natural Science Foundation of Shandong Province, Contract No. 2009ZRA02087.

### **References**

- [1] Wittmann, F. H., Sadouki, H., and Gerdes, A., Ionentransport und Beständigkeit Zement gebundener Werkstoffe im Kontakt mit Wasser, *Int. J. Restoration of Buildings and Monuments* 6, 385-400 (2000)
- [2] Gerard, B., Hydrolysis of cement-based materials: a review, in Setzer M. J., editor, *Pore Solution in Hardened Cement Paste*, Aedificatio Publishers, pp. 271-304 (2000)
- [3] Zhan, H., Wittmann, F. H., and Zhao, T., Relation between the silicon resin profiles in Water repellent treated concrete and the effectiveness as a chloride barrier, *Int. J. Restoration of Buildings and Monuments* 11, 35-46 (2005)
- [4] Xian, Y., Wittmann, F. H., Zhao, T., and Giessler S., Chloride penetration into integral water repellent concrete. *Int. J. Restoration of Buildings and Monuments*, 13, 17-24 (2007)
- [5] Riethmayer, S., Die Metallseifen als Hydrophobierungsmittel, *Die Chem.-techn. Industrie* 57, 65-70 (196)
- [6] Riethmayer, S., Der Einfluss von Netz- und Hydrophobierungsmitteln auf die Eigenschaften von Zementmörtel, *Fette Seifen Anstrichmittel* 72, 269-274 (1970)

- [7] Stolz, H. J., Oleochemicals – important additives for building protection, ZKG International 61, 78-86 (2008)
- [8] Wittmann, F. H., Xian, Y., Zhao, T., Giessler-Plank, S., Moisture diffusion and siloxane distribution in integral water repellent concrete, Int. J. Restoration of Buildings and Monuments 14, 15-26 (2008)
- [9] van Zijl, G. and Wittmann, F. H., editors, Durability of Strain-hardening Fibre-reinforced Cement-based Composites (SHCC), Springer (2011)
- [10] Mechtcherine, V. and Kaliske, M., editors, Fracture and Damage of Advanced Fibre-reinforced Cement-based Materials, Aedificatio Publishers, Freiburg (2010)
- [11] Wittmann, F. H., Zhang, P., and Zhao, T., Significance of water repellent treatment for the durability of SHCC, another contribution to this volume