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1987

Link to publication

Citation for published version (APA):
Hedenblad, G. (1987). *Effect of soluble salt on the sorption isotherm*. (Report TVBM; Vol. 3035). Division of Building Materials, LTH, Lund University.

Total number of authors:
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CODEN: LUTVDG/(TVBM-3035)/1-10/(1988)
ISSN 0348-7911

EFFECT OF SOLUBLE SALT ON THE SORPTION ISOTHERM

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RESEARCH SUPPORTED WITH GRANTS FROM THE SWEDISH COUNCIL FOR BUILDING RESEARCH
REPORT TVBM-3035, Lund, Sweden, 1988

SUMMARY

The presence of salt in an aqueous solution affects the relative humidity (RH) over the aqueous solution in a manner which has been known at least since the 1940's. However, this knowledge has not been taken into account to any greater extent in discussions or determinations of isothermal equilibria of materials, although the water in the pore systems in many cases contains dissolved salts.

The following report exemplifies calculations on the influence of salt on moisture binding in coarse porous non-hygroscopic materials (e.g. brick) and material based on cement. The contents of alkali (sodium- and potassium compounds) in cement lowers for example equilibrium RH for completely moisture-saturated concrete to a value below 100%; for normal Swedish concrete 97-98%.

EFFECT OF SOLUBLE SALTS ON THE SORPTION ISOTHERM

When a material contains different kinds of salts, e.g. NaCl or NaOH, the isothermal equilibrium is affected.

According to Claesson (1977) the relation between RH at saturation (ϕ_m) and the state of unsaturated salt solutions can be described at thermodynamical equilibrium, e.g. at constant temperature and equilibrium between vapour phase and liquid phase.

$$P_\ell - P_s = \frac{RT}{V_\ell} \ell n\ (\phi_m) + \frac{RTM_w}{V_\ell} \cdot v \cdot \phi^\alpha \cdot m^\alpha \qquad (1)$$

where

P_ℓ = pressure in liquid Pa
P_s = water vapour pressure at saturation Pa
R = molar gas constant 8.314 J mol^{-1} K^{-1}
T = temperature in Kelvin
V_ℓ = molar volume of water $= M_w/\rho_\ell = 18 \cdot 10^{-6}$ m^3 mol^{-1}
M_w = molecular weight of water = 0.018 kg mol^{-1}
v = number of ions per salt molecule
ϕ^α = osmotic coefficient, a function of T, P_ℓ and m^α
m^α = molality, number of moles of solute per kg solvent

In Robinson and Stokes (1955), where the coefficients are given as a function of m^α at +25°C, one has disregarded the influence of P_ℓ and P_s writing

$$\ell n(\phi_m) = -v \cdot m^\alpha \cdot M_w \cdot \phi^\alpha \qquad (2)$$

This gives a slight error in the case with plane liquid surfaces, normal atmospheric pressure in the liquid and a saturation pressure for water at +20°C.

In Appendix I, ϕ^α is given for some common salts.

Fig.1 and Fig.2 show the effect of concentration on saturation-RH for NaCl and KCl in aqueous solution.

From Fig.1 and Fig.2 it is clear that the relation between the concentration of the unsaturated salt solution and saturation-RH can be approximated to a straight line without making too great an error. The RH of the saturated salt solution remains constant.

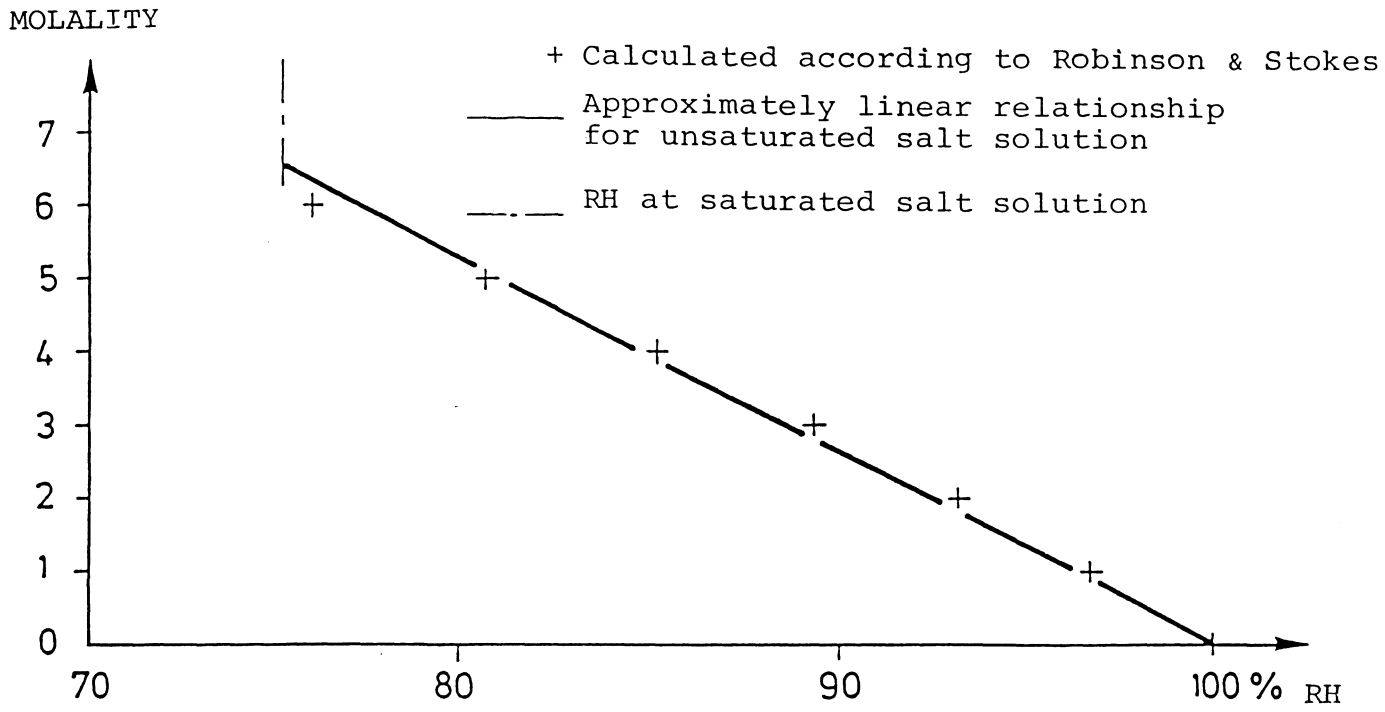

Fig 1. Effect of concentration on saturation-RH for NaCl in aqueous solution (1 mole = 58.5 g).

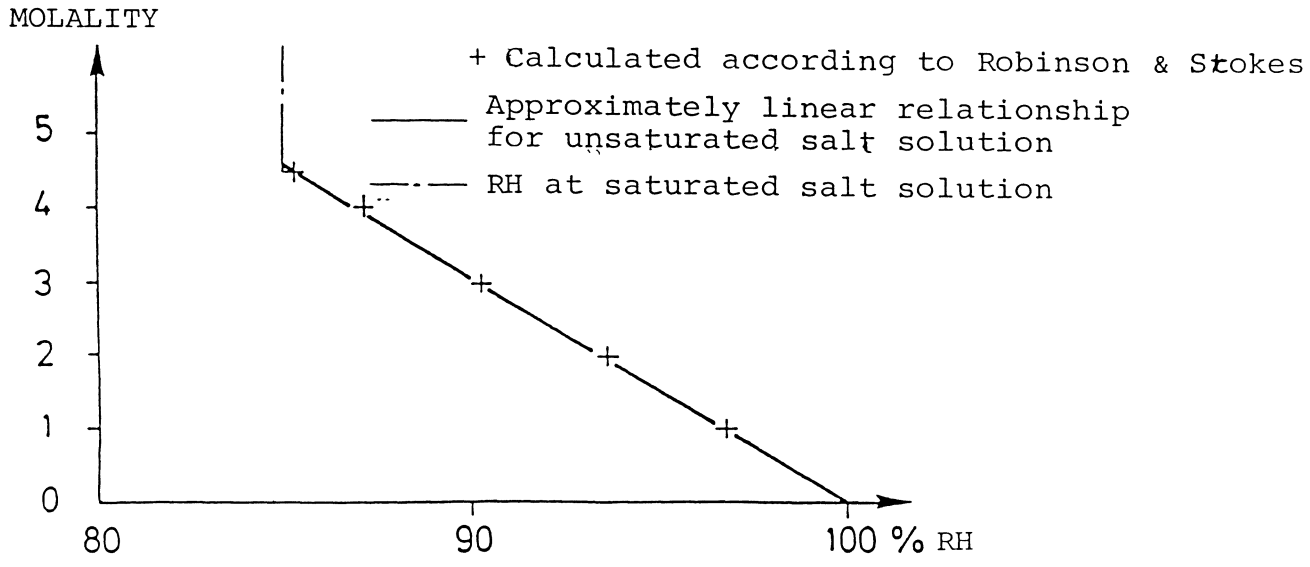

Fig 2. Effect of concentration on saturation-RH for KCl in aqueous solution (1 mole = 73.6 g)

Non-hygroscopic material

According to Hillerborg (1987), it is possible to calculate the humidity equilibrium curve for a coarse porous material which is not hygroscopic, but which contains salt e.g. NaCl. For RH values below saturation-RH for the saturated solution, all moisture is released from the salt. When RH is exactly equal to the saturation-RH of the saturated solution,the isotherm changes with a jump. The salt is brought to equilibrium when it is just saturated. For higher RH than for the saturated salt solution, the moisture content increases substantially at increased RH.

Example:

A non-hygroscopic brick contains 11 kg NaCl per m^3. The porosity is 35%. Exactly saturated NaCl-solution is in equilibrium with 75% RH and contains about 380 g salt per liter of water, see Fig.1.

W denotes the moisture content.

ϕ = 75%: 0.38kg NaCl binds 1 kg of water, 11 kg binds 11/0.38 =28.9 kg of water per m^3 brick

$75<\phi\leq100$: Linear interpolation between 380 g NaCl per kg of water gives 75%RH and no NaCl gives 100% RH. The salt concentration per kg of water is 11/W.

$$\phi=100-(100-75)\cdot 11/W/0.38$$ which gives

$$W=25\cdot 11/0.38/(100-\phi)$$

At a moisture content of 350 kg/m^3 the pore system is filled up, and for this reason the plateau is obtained at about 98% RH.

The isotherm is shown in Fig. 3.

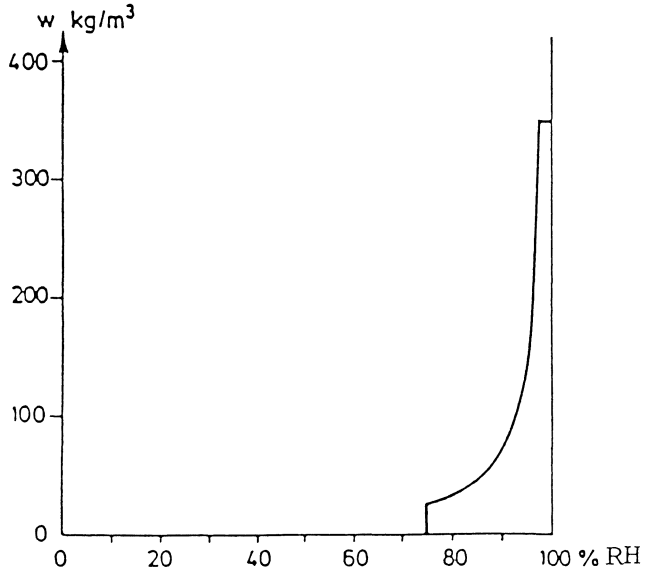

Fig. 3. The influence of NaCl on the isotherm for non-hygroscopic brick. Theoretical curve.

Concrete, cement mortar, and concrete paste

In the case of concrete it is above all the contents of alkali metal compounds, chiefly as potassium hydroxide (KOH) and sodium hydroxide (NaOH), that can affect the humidity equilibrium curve. Peterson (1987) has calculated, for Slite Standardcement (Slite Std), that the contents of alkali metal hydroxides is about 0.34 moles per kg cement, mainly as KOH.

In an initial calculus it is assumed that no alkali metals are bound in the hydration products. Concerning concrete paste or concrete with different w_o/C of Slite Std, concentrations of alkali metal hydroxides are obtained according to Table 1, at complete hydration and water saturation.

Example:

$w_o/C=1.0$ $w_e^{100} = (w_o/C - 0.19\alpha)C$ Degree of hydration $\alpha=1$ $C=1$ kg

$w_e^{100} = (1.0-0.19*1)*1 = 0.81$ kg of water per kg cement.

The concentration (c) of KOH+NaOH=0.34/0.81=0.42 mol/kg of water.

According to Appendix I, $\phi^{\alpha}=0.944+0.02 / 0.10 * (0.953-0.944)=0.946$

for KOH $v=2$ ($KOH=K^+ + OH^-$)

$\ln\phi_m=-2*0.42*0.018*0.946$ $\phi_m=0.986=98.6$ %

Table 1. Influence of NaOH-KOH in pore solution at different w_o/C and total hydration when no alkali metals are assumed to be bound in hydration products.

w_o/C	(NaOH+KOH)/kg of water mol/kg	RH %
1.0	0.42	98.6
0.8	0.56	98.1
0.7	0.67	97.7
0.6	0.83	97.1
0.5	1.10	96.1
0.4	1.62	93.9

On the basis of mass balance calculations and experimental data, Taylor (1987) has worked out an equation for determining alkali ion concentration in pore solution, where consideration has been taken to the binding of alkali cations in hydration products.

$$c = m_r/(100\cdot w_o/C - V_b + (b\cdot P)) \quad (3)$$

c = concentration of the ion in question in pore solution(mol/lite

m_r = quantity of alkali cation (Na^+ or K^+) released by the cement (mmol) per 100 g cement

w_o/C = water-cement ratio

V_b = volume or weight of bound water (cm^3 or g) = 31.6 g/100 g cement at total hydration and drying in 11 % RH and ambient temperature.

b = binding factor, 31.0 for Na^+ and 20.0 for K^+ (cm^3)

P = 1 at total hydration of the products which bind alkali cations.

For cement paste or concrete of Slite Std cement, Table 2 is obtained from the contents of Na^+ and K^+ in the pore solution. Slite Std is assumed to contain 0.28 mol K^+ per kg and 0.06 mol Na^+ per kg.

Example:

w_o/C = 1.0

K^+ = 0.28 mol/kg = 28 mmol/100g

c = 28/(100* 1-31.6 + 20 * 1) = 0.32 mol/liter

Table 2. Contents of Na^+ and K^+ in the pore solution at different w_o/C and total hydration when some of the alkali metals are bound in the hydration products according to eq. (3).

w_o/C	K^+ mol/l	Na^+ mol/l	$K^+ + Na^+$ mol/l
1	0.32	0.06	0.38
0.8	0.41	0.08	0.49
0.7	0.48	0.09	0.57
0.6	0.58	0.10	0.68
0.5	0.73	0.12	0.85
0.4	0.99	0.15	1.14

With the ϕ^{α} given in Appendix I for KOH, the RH maximum can be calculated according to eq. (2). As a tentative guess, values have been chosen according to Table 2 instead of Table 1. The relation between water-cement ratio and the RH maximum in cement products is shown in Table 3. In the case where hydration is not total, the RH values obtained are even lower than in Table 3.

Table 3. The relation between w_o/C and maximum RH in cement products at total hydration and membrane hardening. Contents of Na^+ and K^+ according to Table 2.

w_o/C	estimated RH
1.0	98.8
0.8	98.4
0.7	98.0
0.6	97.6
0.5	97.0
0.4	95.9

Nilsson (1977) has presented desorption isotherms for essentially Slite Std with different w_o/C and different degrees of hydration (α).

When RH maximum in the material according to the above is added to these humidity equilibrium curves, the isotherms are obtained according to Fig. 4. Maximum RH is calculated and the part connecting the curve to the original curve is drawn by free-hand.

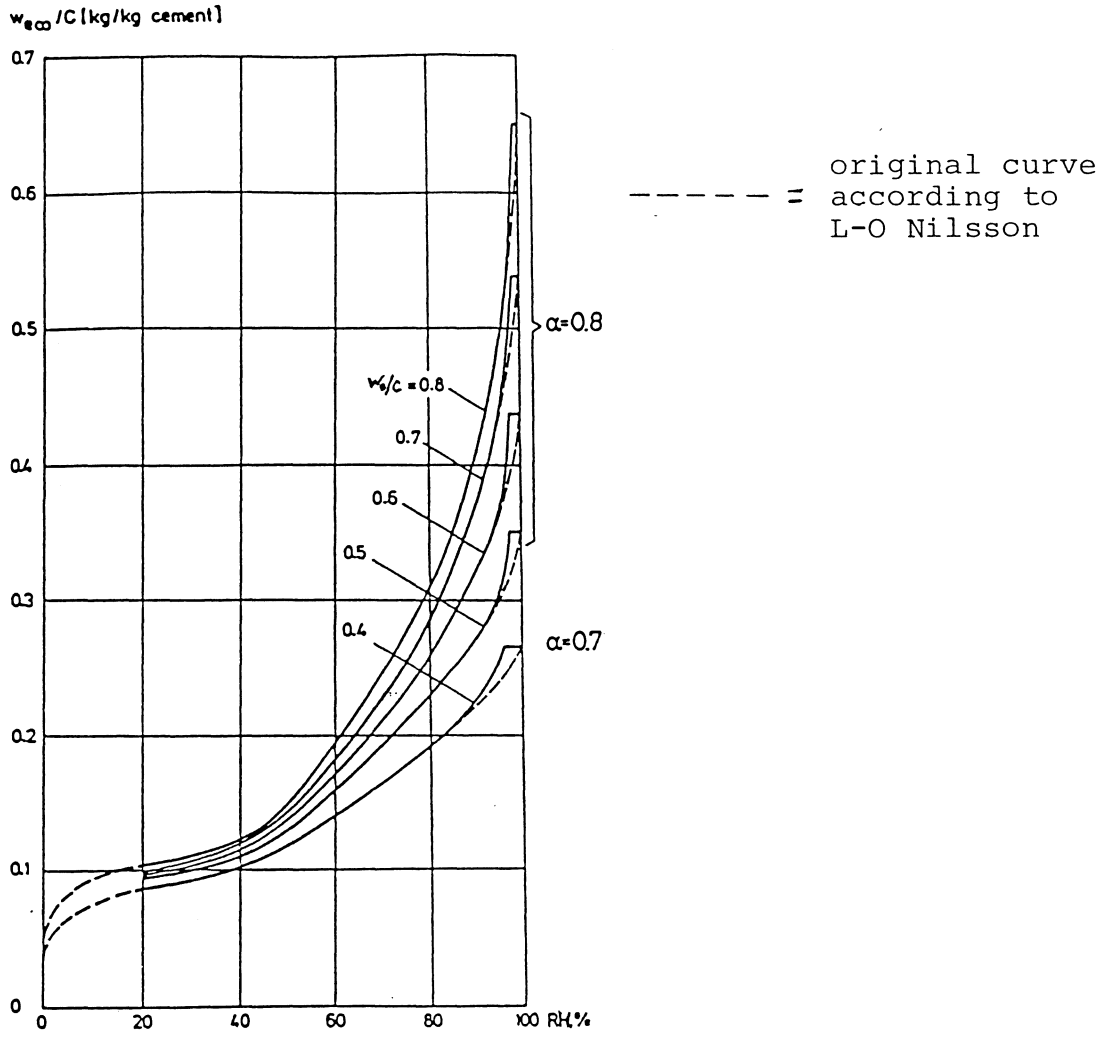

Fig.4. Desorption isotherms for different w_o/C and degrees of hydration. Based on isotherms according to Nilsson (1980).

In principle, the corresponding plateau is obtained for absorption isotherms of cement materials with high alkali contents. Ahlgren (1972) has shown absorption isotherms for concrete which have probably been produced by Limhamn Cement. This type of cement was manufactured according to the "wet method", and had a low content of NaOH and KOH.

Starting from Ahlgren's absorption isotherms and assuming that the moisture qualities of the cement are in other respects similar to cement produced according to the "dry method" , e.g. Slite Std, it is possible to calculate the effect of NaOH and KOH. The modified absorption theory according to Hillerborg (1985) has been used. The thickness t for the absorbed layers are made equal, and a model with slit shaped pores is assumed, that is, the liquid surfaces are assumed to

to be plane.

$$t = \frac{5.25\phi_1}{(1-\phi_1/\phi_{m1})(1-\phi_1/\phi_{m1}+15\phi_1)} = \frac{5.25\phi_2}{(1-\phi_2/\phi_{m2})(1-\phi_2/\phi_{m2}+15\phi_2)}$$

ϕ_1 = RH according to Ahlgren's absorption isotherm
ϕ_{m1} = saturated RH for cement in Ahlgren's experiment
ϕ_2 = searched RH for concrete with high contents of NaOH and KOH
ϕ_{m2} = saturated RH for cement with high contents of NaOH and KOH

Example:

Concrete K 25; C =284 kg/m^3, std; w_o/C =0.65; W_n/C =0.24; l_o =3.0%; maximum size of stones = 32 mm.

Starting from Table 2, we obtain $Na^+ + K^+$ which is $\simeq$ 0.63 mol/liter pore solution, which gives an RH saturation = 97.8%. The absolute quantity of $Na^+ + K^+$ is maintained even at lower RH, while the quantity of water evaporable at 105°C is reduced in principle according to Ahlgren's original isotherm in Fig.5.

For ex. at ϕ_1 = 50 % we obtain in the original isotherm
W = 35 kg/m^3 W_n/C=0.24 according to figure legend
$W_e^{100} = (w_o/C - 0.19\alpha)C = (0.65-0.19*4*0.24)*284 \approx 130$ kg/m^3 concrete
Concentration (c) at 50 % RH of KOH=0.63*130/35=2.34 mol KOH/l
Eq.(2) gives $\ln\phi_{m2} = -2*2.34*0.018*1.164$ ϕ_{m2} =90.7 %
ϕ_{m1} = 100 %

Eq. 4 gives

$$\frac{0.50}{(1-0.50/1.00)*(1-0.50/1.00+15*0.5)} = \frac{\phi_2}{(1-\phi_2/0.907)*(1-\phi_2/0.907+15\phi_2)}$$

ϕ_2 = 0.456 = 45.6 %

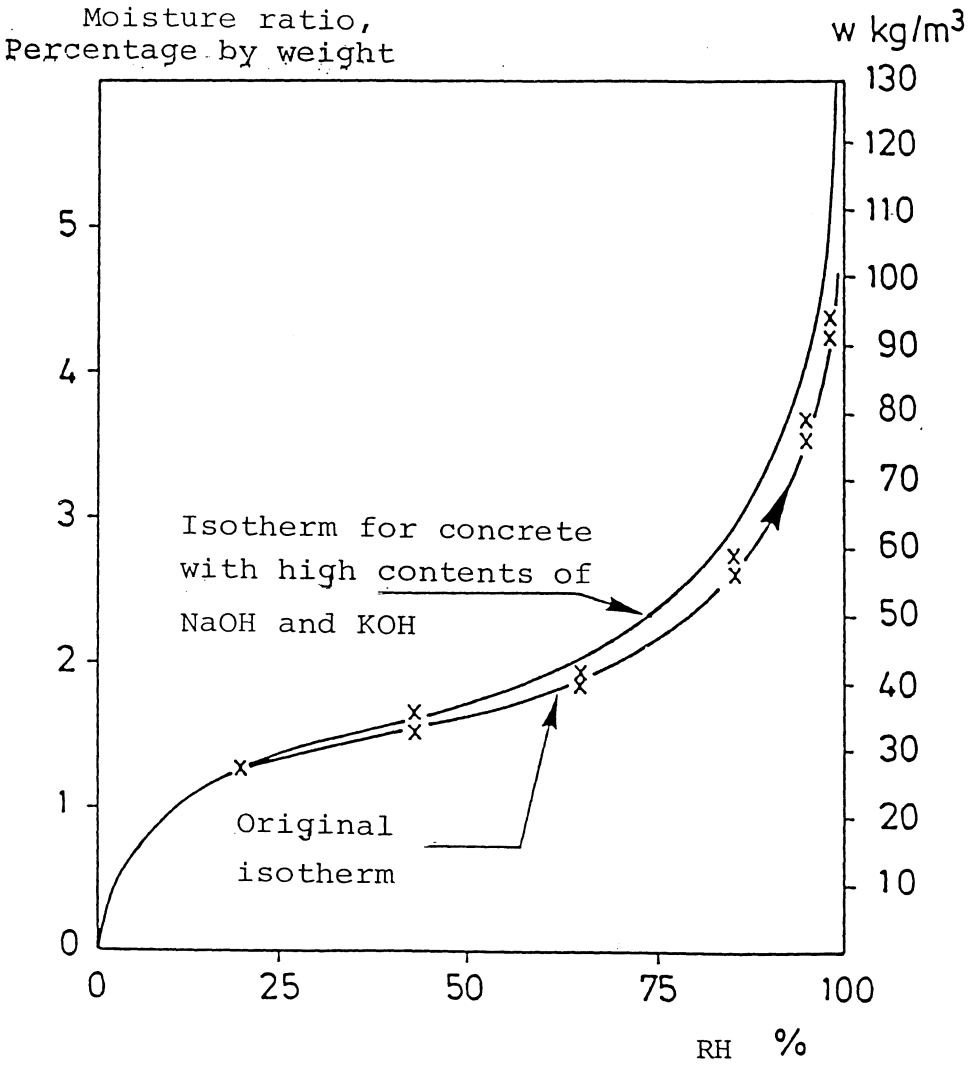

Fig 5. Effect of NaOH and KOH on absorption isotherms. Concrete K 250 P; C = 284 kg/m^3, std; w_o/C = 0.65; w_n/C = 0.24; l_o = 3.0%; maximum size of stones = 32 mm.

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Appendix I. Osmotic coefficients ϕ^{α} for unsaturated solutions at +25°C.

Molality m	NaOH	KOH	KCl	NaCl	$MgCl_2$	$CaCl_2$	Na_2SO_2	K_2SO_4
0.1	0.925	0.944	0.927	0.932	0.861	0.854	0.793	0.779
0.2	0.925	0.936	0.913	0.925	0.877	0.862	0.753	0.742
0.3	0.929	0.938	0.906	0.922	0.895	0.876	0.725	0.721
0.4	0.933	0.944	0.902	0.920	0.919	0.894	0.705	0.703
0.5	0.937	0.953	0.899	0.921	0.947	0.917	0.690	0.691
0.6	0.941	0.962	0.898	0.923	0.976	0.940	0.678	0.679
0.7	0.945	0.972	0.897	0.926	1.004	0.963	0.667	0.670
0.8	0.949	0.983	0.897	0.929	1.036	0.988	0.658	-
0.9	0.953	0.993	0.897	0.932	1.071	1.017	0.650	-
1.0	0.958	1.003	0.897	0.936	1.108	1.046	0.642	-
1.2	0.969	1.026	0.899	0.943	1.184	1.107	0.631	-
1.4	0.980	1.051	0.901	0.951	1.264	1.171	0.625	-
1.6	0.991	1.076	0.904	0.962	1.347	1.237	0.621	-
1.8	1.002	1.100	0.908	0.972	1.434	1.305	0.620	-
2.0	1.015	1.125	0.912	0.983	1.523	1.376	0.621	-
2.5	1.054	1.183	0.924	1.013	1.762	1.568	0.635	-
3.0	1.094	1.248	0.937	1.045	2.010	1.779	0.661	-
3.5	1.139	1.317	0.950	1.080	2.264	1.981	0.696	-
4.0	1.195	1.387	0.965	1.116	2.521	2.182	0.740	-
4.5	1.255	1.459	0.980	1.153	2.783	2.383	-	-
5.0	1.314	1.524	-	1.192	3.048	2.574	-	-
5.5	1.374	1.594	-	1.231	-	2.743	-	-
6.0	1.434	1.661	-	1.271	-	2.891	-	-

The osmotic coefficients are taken from Robinson and Stokes, 1955, Electrolyte Solutions (Butterworth, London). Appendix 8.10, which contains many more electrolytes.