Crystallization in Pores and Voids of Cement Mortar

Pandieswari M #1, Selvaraj R *2 and Gopalakrishna GVT #3

#Department of civil engineering, PSNA College of Engineering and Technology, Dindigul, Tamil Nadu, India

1 pandieswarim1994@gmail.com

3 gvtgkrishna@gmail.com

* CSIR-CECRI, Karaikudi, Tamil Nadu, India

2 selvarajcecri@gmail.com

Abstract- **Durability of concrete plays a major role in construction industry. The main reason for such durability problems is transport properties of cement mortar after the cement mortar set. Permeation, absorption and diffusion of water through the pores and pore connectivity causes a durability problem. In this study, these pores and pores connecting pathways are blocked by the process of pores crystallization. This is achieved by admixing certain well known crystals forming chemicals such as sodium acetates, potassium acetates and other salts of sulphates at various percentages and allowing the cement mortars to for crystals. It is also studied by spraying a brush application of these chemicals and other water soluble polymers to block the pores and allow the growth of crystals in the pores. This process of arresting transport of water into the mortar is partially new concept which has worked well and reduction in penetration of water is measured by sorption, Electrical resistance, Hollow cylinder method and Water absorption. The results are discussed in detail and optimum solution percentages are explained.**

Keywords: Durability, Crystal growth, Pores, Pore connectivity, Sorption, Penetration.

I. INTRODUCTION

Concrete is the most commonly used construction material, but due to its porous nature it results in deterioration of structures. Therefore, the penetration of undesired substances can cause progressive damage [6], although water is very important to concrete during the curing stage, it is considered to be an undesirable substance that could cause several damages to the concrete [3]. Deterioration also occurs based on exposure conditions, which reduces the durability of the structure [7]. Some of the systems are currently in practice to minimize the damages due to moisture penetration in the pore connectivity, where pore block effect is introduced; this barrier system is successful in preventing the water penetration [5]. Along with pore blocking effect, waterproofing additives are also added to the concrete to increase the structural durability by blocking the pores by growth of crystals, this way the repair and maintenance cost are reduced and then the life of the concrete is increased [9]. Water proofing creates a barrier when the coating is applied, some waterproofing can also be used as admixture in mixture, with the objective to reduce the capillary porosity of concrete, making it less porous and more resistant to aggressive agents [10]. Selection of admixture for crystal growth in pores plays a major role in preventing the water penetration, by this study some of the moisture associated problems such as – Freeze and thaw damages, acid attack, chloride ion diffusion, sulphate attacks, etc can be avoided [12].

In this research work several crystal growing chemicals and acetates are used for growth of crystals in the pores of concrete for blocking the pore connectivity and then denying the access to aggressive species [3]. To evaluate the crystalline waterproofing products efficiency, the most commonly used tests are – water absorption, chloride penetration, electrical conductivity, etc. The purpose of this study is to analyse the use of crystalline waterproofing as admixture and comparing their performances with control [8]. Also the study is conducted to know what kind of crystals those are and whether it is capable to seal the pore or crack [1].

II. MATERIALS AND METHODS

Portland pozzolanic cement of 43 grade, Dalmia Vajram has been utilized**.** River sand of zone III has been used in this investigation. Later it was washed and dried before sieve analyses, where the fineness modulus of fine aggregate is 2.51. Only the sand which has been passed through 600μm has been used for casting purposes of specific gravity = 2.63. Only the tap water is used for mixing and curing process, which is clean from any contaminants including alkalis, acids, oil, salt, organic materials, etc. portable water (of pH value 7.1) was used in casting of cement mortar specimens. The following water proofing admixture were used for this investigations- Sodium acetate, magnesium acetate, potassium acetate, ethyl acetate, methyl acetate, calcium sulphate, sodium sulphate, calcium carbide,

sodium silicate, sodium bicarbonates, all these chemicals were purchased from the local chemical supplier (HiMedia, Laboratories, Pvt. Ltd., Mumbai-86).

A. Mixture proportions

For the entire test, cement mortar of 1:3 was taken for w/c ratio of 0.43, where entire chemical was used in various dosages. Hand mixing was carried out, the measured quantity of cement, sand, water with admixture of required quantity was mixed thoroughly in a pan, until it reaches the uniformity. This operation is continued until homogeneous mortar is achieved. Mortar specimens were cast using PVC moulds and rubber moulds as shown in figure 1. After 24 hrs, the specimen were demolded and cured in a water tank as shown in figure 2, until 28 days.

Fig 1. Casting of specimens

B. Experimental investigation

1) Compressive Strength Test:

Specimens were taken out from water after 28 days of curing, cleaned and dried. Later it was placed and kept on the plate and then he loads were applied gradually. The ultimate load were observed (i.e., the load applied till the failure of specimen occurs). The test was conducted in a compression testing machine (in AIMIL brand of capacity 1000kN as shown in figure 2), for cylinder specimen of 60mm x 120mm dimension.

Fig 2. Compression testing machine

2) Split tensile test

This test was tested in AIMIL brand of 1000k N capacity of compression testing machine as shown in figure 3. To obtain splitting tensile strength, a cylinder of dimension 60mm x 120mm was split along its length. Results for specimen of various chemical dosages are as shown in table 2, after obtaining the failure load, the split tensile strength can be determined by the following equation –

$F_{ct} = [(2*P)/(\pi*D*L)]$ in N/mm^2.

Fig 3. Split tensile machine

3) Rate of absorption of water (Sorptivity)

This test was done to determine the initial rate of absorption for small cylinder with dimension 50mm x 80mm, for 1 hr duration (specimens with and without chemicals of various dosages), and the initial rate of absorption is calculated using digital balance as shown in figure, results are shown in table 1.

4) Hollow core water absorption test

This test was conducted for hollow disc of 83mm x 50mm dimension, which contains an inset cylinder at its center (with dimension 40mm x 25mm) for determination of water absorbed in axial and radial directions, by filling the core portion with water for a period of time as shown in table

III. RESULTS AND DISCUSSION

The measurement of the coefficient of water absorption was performed in various time periods for 60minutes, the results determined for all time periods are depicted in table 1 below. The time period assigned “0” represents dry weight of specimen with the age of 28 days after curing which is cast with and without chemical admixture of various dosages. It is found that the combination made with sodium bicarbonate found to be the best water resistant admixture and the next to this the combination made with ethyl acetate, and finally combination made with magnesium acetate.

The split tensile strength of cement mortar with water proofing admixture was higher than of ordinary cement mortar and the value was approximately 12% of the cylinder compressive strength. The results of this test are shown in table 2 below.

Table 1. Determination of coefficient of water absorption

Specimen	at 0min (in gm)	at 5min (in gm)	at 10min (in gm)	at 15min (in gm)	at 20min (in gm)	at 30min (in gm)	at 45min (in gm)	at 60min (in gm)	Absorption coeff. ($k_{a)}$ x10^{-9} (mm^2/s)
Control	295.89	297.67	298.21	298.61	299.18	299.66	300.72	301.42	3.36
$Ca_2.SO_4$ 2%	314.48	315.08	315.30	315.48	315.65	315.84	316.38	316.79	0.6
$Ca_2.SO_4$ 4%	295.4	296.30	296.60	296.93	297.25	297.65	298.1	298.5	1.0
$Ca_2.SO_4$ 6%	300.80	302.25	302.52	302.78	303.14	303.44	303.88	304.37	1.4
$Ca_2.SO_4$ 8%	126.48	127.03	127.08	127.36	127.56	127.58	127.93	128.15	0.8
$Ca.C_2$ 2%	303.03	303.85	304.18	304.22	304.35	304.74	305.05	305.52	0.7
$Ca.C_2$4%	309.05	310.25	310.52	310.65	310.90	311.35	311.85	312.40	1.23
$Ca.C_2$6%	320.15	321.1	321.55	321.72	322.08	322.44	322.84	323.32	1.10
$Ca.C_2$8%	123.95	124.38	124.60	124.70	124.80	124.93	125.08	125.31	0.6
$Na_2.Si.O_3$ 2%	317.05	318.20	318.75	318.90	319.02	31.65	320.24	320.85	1.58
$Na_2.Si.O_3$ 4%	300.35	301.80	302.22	302.50	302.75	303.30	304.07	304.54	1.9
$Na_2.Si.O_3$ 6%	309.40	310.31	310.62	310.71	310.91	311.16	311.58	312.10	0.8
$Na_2.Si.O_3$ 8%	306.73	311.22	312.10	312.5	312.95	313.62	314.35	314.98	7.5
$CH_3COOC_2H_5$ 2%	296.58	297.43	297.76	298.18	298.52	299.08	299.65	300.31	1.53
$CH_3COOC_2H_5$ 4%	278.6	283.28	284.78	285.3	285.75	286.75	287.70	288.30	10.3
$CH_3COOC_2H_5$ 6%	298.43	300.15	301.09	301.5	301.70	302.35	303.01	303.60	2.94
$CH_3COOC_2H_5$ 8%	276.19	280.98	282.52	283.69	285.27	287.20	289.31	291.12	24.5
$Na.H.CO_3$ 2%	301.6	305.97	307.03	308.08	308.65	309.7	310.88	311.62	11.2
$Na.H.CO_3$ 4%	288.95	297.56	299.35	300.72	301.35	302.97	305.06	306.53	34.1
$Na.H.CO_3$ 6%	266.75	276.91	279.73	281.73	282.75	285.02	288.15	290.24	60.7
$Na.H.CO_3$ 8%	296.92	299.5	300.5	301.17	301.96	303.01	304.35	305.42	7.9
$Na_2.SO_4$ 2%	301.10	301.74	301.83	302.12	302.31	302.48	302.78	303.11	0.4
$Na_2.SO_4$ 4%	301.49	302.30	302.25	302.68	303.05	303.15	303.64	304.02	0.7
$Na_2.SO_4$ 6%	301.11	301.68	301.75	302.13	302.3	302.49	302.98	303.32	0.58
$Na_2.SO_4$ 8%	316.71	317.44	317.72	318.06	318.23	318.47	318.88	319.18	0.7
$CH_3.COOCH_3$ 2%	306.76	308.03	308.49	308.75	309.01	309.45	309.80	310.15	1.27
$CH_3.COOCH_3$ 4%	309.42	310.22	310.37	310.75	310.76	311.31	311.82	312.38	0.1
$CH_3.COOCH_3$ 6%	324.08	325.45	325.79	326.1	326.3	326.70	327.2	327.55	1.32
$CH_3.COOCH_3$ 8%	306.30	307.72	307.93	308.34	308.78	308.96	309.44	309.95	1.5
CH_3COOK 2%	293.23	295.33	294.75	295.02	295.17	295.70	296.35	296.78	1.4
CH_3COOK 4%	287.85	288.6	288.91	289.12	289.45	289.76	290.15	290.5	0.8
CH_3COOK 6%	308.40	309.41	309.46	309.99	310.25	310.89	311.33	311.81	1.27
CH_3COOK 8%	309.29	310.26	310.58	310.98	311.34	311.62	312.20	312.53	1.2
CH_3COOK 10%	295.05	296.1	296.54	296.77	296.89	297.3	297.9	298.20	1.09
$CH_3.COONa$ 2%	296.11	297.08	297.28	297.41	297.64	297.83	298.31	298.48	0.6
$CH_3.COONa$ 4%	302.33	303.20	303.50	303.67	303.99	304.41	304.91	305.35	1
$CH_3.COONa$ 6%	303.11	303.72	304.19	304.32	304.58	304.83	305.35	305.61	0.7
$CH_3.COONa$ 8%	300.69	300.78	301.04	301.25	301.42	301.71	302.09	302.30	2.15
$Mg(CH_3.COO)_2$ 2%	266.28	270.65	270.94	271.71	271.75	272.32	273.15	273.64	6.0
$Mg(CH_3.COO)_2$ 4%	269.1	273.95	274.65	275	275.40	276.03	276.63	277.15	7.1
$Mg(CH_3.COO)_2$ 6%	271.03	273.62	274.25	274.72	275.71	276.21	277.22	278.04	5.4
$Mg(CH_3.COO)_2$ 8%	288.13	290.03	290.40	290.75	291.27	291.57	292.23	296.7	2.26

Table 2. Results of compressive strength and split tensile strength.

Specimen	Compressive strength (N/mm^2)	Tensile strength (N/mm^2)
Control	28.12	3.34
$Ca_2.SO_4$ 2%	34.18	4.10
$Ca_2.SO_4$ 4%	33.73	4.04
$Ca_2.SO_4$ 6%	28.67	3.94
$Ca_2.SO_4$ 8%	22.14	2.85
$Ca.C_2$ 2%	37.11	4.45
$Ca.C_2$4%	38.14	4.67
$Ca.C_2$6%	39.16	4.7
$Ca.C_2$8%	44.64	5.86
$Na_2.Si.O_3$ 2%	32.23	3.34
$Na_2.Si.O_3$ 4%	30.17	3.92
$Na_2.Si.O_3$ 6%	28.07	3.67
$Na_2.Si.O_3$ 8%	24.02	2.88
$CH_3COOC_2H_5$ 2%	31.02	3.41
$CH_3COOC_2H_5$ 4%	18.11	2.17
$CH_3COOC_2H_5$ 6%	9.06	1.08
$CH_3COOC_2H_5$ 8%	7.34	0.81
$Na.H.CO_3$ 2%	32.84	4.92
$Na.H.CO_3$ 4%	26.14	3.14
$Na.H.CO_3$ 6%	20.07	2.61
$Na.H.CO_3$ 8%	14.83	1.63
$Na_2.SO_4$ 2%	22.04	2.65
$Na_2.SO_4$ 4%	24.11	2.84
$Na_2.SO_4$ 6%	30.16	3.32
$Na_2.SO_4$ 8%	34.84	3.45
$CH_3.COOCH_3$ 2%	19.78	2.37
$CH_3.COOCH_3$ 4%	26.81	3.49
$CH_3.COOCH_3$ 6%	32	3.52
$CH_3.COOCH_3$ 8%	34.45	4.1
CH_3COOK 2%	30.14	3.62
CH_3COOK 4%	29.77	4.2
CH_3COOK 6%	28.14	3.1
CH_3COOK 8%	27.67	3.6
CH_3COOK 10%	24.11	2.9
$CH_3.COONa$ 2%	15.26	1.7
$CH_3.COONa$ 4%	16.87	1.84
$CH_3.COONa$ 6%	21.41	2.67
$CH_3.COONa$ 8%	25.61	2.82
$Mg(CH_3.COO)_2$ 2%	16.17	2.01
$Mg(CH_3.COO)_2$ 4%	18.87	2.35
$Mg(CH_3.COO)_2$ 6%	19.96	2.41
$Mg(CH_3.COO)_2$ 8%	24.11	2.90

Fig 4. Specimen under sorptivity test

To determine the water absorbed in axial and radial direction, hollow specimens was filled with water and analysed for certain time duration as shown in table 3. The combinations comprising calcium carbide, sodium silicate, methyl acetate, calcium sulpate and sodium sulphate found to give good results, as these specimens has lower absorption. Poor values was obtained for ethyl acetate and sodium bicarbonates.

Fig 5. Water absorption test for hollow core specimen

The compressive strength of cement mortar with and without admixtures are shown in table 2. The compressive strength of mortar with water proofing admixture was higher than that of reference concrete. The compressive strength of methyl acetate with 8%, 6% magnesium acetate with 6%, calcium carbide with 6%, 8%, calcium sulphate with 4%, sodium sulphate with 6% of water weight gives more than that of reference concrete. The results of these test indicate that the addition of these water proofing admixture increases the compressive strength.

IV. CONCLUSIONS

1. This study is based on crystallization by various dosages of chemicals solutions (i.e., 10 different chemicals with 41 different combinations of specimens, excluding the control). From the 10 combinations, the calcium carbide with cement mortar found to give the highest compressive strength. In this combination as the ratio of dosage is increased, the strength is also increasing. Next to this combination the calcium sulphate admixed mortars found to give higher compressive strength. In this case as the percentage of dosages increases, strength gradually reduced. Next to this the combination comprising sodium sulphate found to give good compressive strength values. As the percentage is increased the strength is also increasing.
2. The combinations comprising ethyl acetate, sodium acetate, magnesium acetate found to give lower values compared to the control strength.
3. The split tensile strength of all the mixes is approximately 12% of the cylinder compressive strength, the trend of strength variations is similar to cylinder compressive strength.

Table 3. Determination of water absorbed in hollow core specimens

Specimen	Dry wt (g)	Saturated wt (g)	Quantity of water poured every one hour								
			initial	1 hr	2 hrs	3 hrs	4 hrs	5 hrs	6 hrs	7 hrs	24 hrs
$Ca_2.SO_4$ 2%	524.34	549.95	26	3	1	1	-	-	-	-	3
$Ca_2.SO_4$ 4%	582.49	628.92	33	3	1	-	-	-	-	-	7
$Ca_2.SO_4$ 6%	553.48	589.04	36	3	1	1	-	1	-	-	4
$Ca_2.SO_4$ 8%	522.33	553	39	2	1	1	-	1	1	-	6
$Ca.C_2$ 2%	536.39	567.97	33	3	1	-	1	2	2	2	14
$Ca.C_2$4%	572.06	599.67	22	2	-	-	-	1	1	1	6
$Ca.C_2$6%	491.66	529.02	41	3	-	-	1	1	1	1	4
$Ca.C_2$8%	524.85	549.90	25	3	1	1	-	1	1	1	4
$Na_2.Si.O_3$ 2%	577.42	615.46	34	2	1	-	-	1	1	-	1
$Na_2.Si.O_3$ 4%	532.15	562.42	30	3	-	1	-	1	-	1	3
$Na_2.Si.O_3$ 6%	543.58	576.62	38	2	1	1	1	1	-	1	2
$Na_2.Si.O_3$ 8%	553.05	58.76	36	2	1	1	1	-	-	-	6
$CH_3COOC_2H_5$ 2%	509.75	549.75	41	24	5	6	4	6	5	5	36
$CH_3COOC_2H_5$ 4%	599.65	632.56	31	4	-	-	1	-	-	1	1
$CH_3COOC_2H_5$ 6%	546.55	586.26	41	15	5	3	2	4	2	2	13
$CH_3COOC_2H_5$ 8%	516.75	552.60	36	19	8	5	1	4	1	2	12
$Na.H.CO_3$ 2%	53.70	603.67	41	29	6	4	3	5	4	5	37
$Na.H.CO_3$ 4%	472.40	517.56	46	36	17	17	13	20	16	17	34
$Na.H.CO_3$ 6%	509.0	550.42	42	34	7	8	6	9	8	9	38
$Na.H.CO_3$ 8%	500.88	541.43	41	28	5	6	3	7	5	4	35
$Na_2.SO_4$ 2%	552.50	582.55	30	2	-	-	1	1	-	1	2
$Na_2.SO_4$ 4%	549.68	578.90	30	2	-	-	1	1	-	1	3
$Na_2.SO_4$ 6%	590.20	634.25	30	1	-	-	-	-	-	1	1
$Na_2.SO_4$ 8%	563.00	585.47	23	3	1	1	1	1	-	1	5
$CH_3.COOCH_3$ 2%	558.23	583.92	25	2	3	-	2	-	1	2	9
$CH_3.COOCH_3$ 4%	570.95	595.26	25	1	-	-	2	1	-	1	3
$CH_3.COOCH_3$ 6%	555.90	584.48	30	2	1	-	2	-	-	1	1
$CH_3.COOCH_3$ 8%	577.30	602.27	25	4	-	-	2	1	-	2	4
CH_3COOK 2%	541.61	573.73	33	2	-	-	1	1	-	-	2
CH_3COOK 4%	525.04	560.12	36	2	2	1	1	1	1	2	9
CH_3COOK 6%	517.40	552.62	36	4	2	2	1	1	1	-	10
CH_3COOK 8%	513.13	549.31	36	3	-	-	1	1	-	2	6
CH_3COOK 10%	564.13	592.60	30	5	1	1	-	-	-	2	6
$CH_3.COONa$ 2%	549.80	584.68	36	3	1	-	-	1	-	1	2
$CH_3.COONa$ 4%	561.50	592.88	32	2	-	-	1	-	-	1	2
$CH_3.COONa$ 6%	578.50	625.34	43	1	-	-	2	1	2	2	11
$CH_3.COONa$ 8%	556.97	583.36	28	2	-	1	1	-	-	2	5
$Mg(CH_3.COO)_2$ 2%	535.89	563.73	28	4	1	2	2	-	-	2	9
$Mg(CH_3.COO)_2$ 4%	576.03	607.65	32	3	1	1	1	-	2	-	10
$Mg(CH_3.COO)_2$ 6%	513.50	552.05	39	11	2	2	1	1	1	2	10
$Mg(CH_3.COO)_2$ 8%	513.25	551.36	39	5	1	1	-	1	-	2	12
Control	556.18	595.47	40	4	1	1	1	1	-	1	7

4. From sorptivity test the coefficient of water absorption (k_a) has been calculated for all the combination of mixes as shown in figure 4, it is found that the combination made with sodium sulphate found to be best water resistant admixture, and next to this the combination made with Calcium carbide. And finally the combination made with Sodium acetate found to resist water sorption. Poor values have obtained for sodium bicarbonates.
5. In hollow core water absorption test to determination of water absorption in axial and radial direction as shown in figure 5, it was analyzed the combinations comprising calcium carbide, sodium silicate, methyl acetate, calcium sulpate and sodium sulphate found to give good results, as these specimens has lower absorption. Poor values were obtained for ethyl acetate and sodium bicarbonates.

REFERENCES

[1]. Awni Al-Otoom, Abdelaziz Al Khlaifa, Ahmed Shawaqfeh , "*Crystallization Technology for Reducing Water*

Permeability into Concrete," – ACS, vol 46, pp 5463-5467(2007).

[2]. Vinh T. N. Dao, Peter F. Dux, "*Performance of Permeability-Reducing Admixtures in Marine Concrete Structures*," ACI material journal, vol. 107-M34, pp 291-296(2010).

[3]. Navrit Bhandari, Col. Harry Sidhu, Dr Sanjay K Sharma, "*To Determine the Efficacy of Crystalline Waterproofing System in Concrete,*"vol. 03 Issue:08, pp 2129-2134(2016).

[4]. Geetha, P. Perumal, "*Experimental study on the role of waterproofing admixtures on the strength and durability of concrete*,"Journal of Engineering and Applied Sciences 4(1), pp 41-45(2009).

[5]. Mohammadreza Hassani, Kirk Vessalas, Daksh Baweja, "*Effect of chemical admixtures on water penetration of concrete*,"pp 209-216(2014).

[6]. Nasiru zakari Muhammad, Ali Keyvanfar, Muhd Zaimi Abd. Majid, "*Waterproof performance of concrete: A critical review on implementation approaches*," Elsevier vol 101, Pp 80-90(2015).

[7]. Abdurrahman A. Elgalhub, "*Limestone addition effects on concrete porosity*," cement and concrete composite 72, Pp 222-234(2016).

[8]. Yuanming Lai, "*Crystallization deformation of a saline soil during freezing and thawing process*," Applied thermal engineering 120, Pp 463-473(2017).

[9]. Vanessa Giaretton Cappellesso, Nata ´lia dos Santos Petry, Denise Carpena Coitinho Dal Molin, Angela Borges Masuero, "*Use of crystalline waterproofing to reduce capillary porosity in concrete*,"Springer- 1:9(2016).

[10]. Kyoung-MinKim ,"*Experimental Evaluation of Sodium Silicate-Based Nanosilica against Chloride Effects in Offshore Concrete,*"Volume 2014, Article ID 541035(2014).

[11]. Li-Wei Teng, Ran Huang, Jie Chen, AnCheng, "*A Study of Crystalline Mechanism of Penetration Sealer Materials*,", pp 399-412(2014).

[12]. Pavel Reiterman , Jiri pazderka, "*Crystalline coating and its influence on the water transport in concrete*," Research article ID 2513514, Pp 1-8(2016).