

Study of the Effects of Ceramic Nano-Pigments in Cement Mortar Corrosion Caused by Chlorine Ions

R. Moradpour, S.B. Ahmadi, T. Parhizkar, M. Ghodsian, E. Taheri-Nassaj

Abstract—Superfine pigments that consist of natural and artificial pigments and are made of mineral soil with special characteristics are used in cementitious materials for various purposes. These pigments can decrease the amount of cement needed without loss of performance and strength and also change the monotonous and turbid colours of concrete into various attractive and light colours. In this study, the mechanical strength and resistance against chloride and halogen attacks of cement mortars containing ceramic nano-pigments in an affected environment are studied. This research suggests utilisation of ceramic nano-pigments between 50 and 1000 nm, obtaining full-depth coloured concrete, preventing chlorine penetration in the concrete up to a certain depth, and controlling corrosion in steel rebar with the Potentiostat (EG&G) apparatus.

Keywords—Nano-structures, Corrosion, Mechanical properties, Nano-pigments.

I. INTRODUCTION

TODAY, with the rapid advances in science and technology worldwide, new materials are manufactured with low pollution to promote desirable environmental conditions. Different types of concrete have been used in the 20th century to construct structures that include bridges, dams, skyscrapers, docks, and canals. Lime and mortar compounds are some of the most ancient construction materials used by mankind [1]. The Persians, Egyptians and Greeks utilised these construction materials, which are still here today. In later centuries, pozzolan and trass were included to improve the properties of the compounds. Over time, this material was further developed through experiments. In recent decades, attempts have been made to create coloured concrete by applying chromogenic materials. These chromogenic materials are divided into two groups: organic and inorganic materials. Inorganic colour contents possess unique characteristics, such as fire resistance, heat resistance, corrosion resistance, purity, and a micro-crystalline or poly-crystalline structure.

R. Moradpour is a researcher in the Department of Civil Engineering at Tarbiat Modares University, Tehran, Iran (e-mail: moradpour@modares.ac.ir).

S. B. Ahmadi is an educational instructor in the Project Management Department at Tarbiat Modares University, Tehran, Iran (phone: 98-21-82883702; fax: 98-21-88008090; e-mail: sbahmadi@modares.ac.ir).

T. Parhizkar is an associate professor with Building and Housing Research Center, Tehran, Iran (e-mail: parhizkar@bhrc.ac.ir).

M. Ghodsian is a professor in the Department of Civil Engineering at Tarbiat Modares University, Tehran, Iran (e-mail: ghods@modares.ac.ir).

E. Taheri-Nassaj is an associate professor in the Department of Materials Science and Engineering at Tarbiat Modares University, Tehran, Iran (e-mail: taheri@modares.ac.ir).

Comparatively, they are impermeable to halogens, acids, carbon dioxide and water [2].

Additives are used to reduce manufacturing costs and improve the quality of the compound [3]. The cement production process produces a great deal of air pollution, and the huge volumes of cement and concrete that are produced account for 5–8% of manmade CO₂ emissions [4]. Thus, reducing cement consumption effectively reduces human impact on the environment. Additives can also increase concrete strength and durability and resistance to corrosion [5]. However, in many conditions, coloured concrete is a suitable substitute for costly materials, such as stones and tiles [6].

Ceramic pigments with wide variation and distribution in grain size are completely restorable in the environment and are collated in natural cycles. These pigments can decrease the amount of cement needed without loss of performance and strength and also change the monotonous and turbid colours of concrete into various attractive and light colours. One of the other advantages of the pigments is that they fill gaps and pores, which not only prevent crack growth, but also protect against rapid water evaporation of concrete [7]. Pigments can make up about 3 to 7% of the cement weight [8]. If pigments are added to the concrete during the mixture phase, further coating expenses can be avoided [9]. Some effective parameters in manufacturing coloured concrete are colour combinations, composition methodology, percentage of colour mixture, curing time and spilling in the specified place [10].

The use of concrete is limited in certain weather conditions. Many environments result in concrete corrosion and strength reduction. The durability of reinforced concrete structures is ensured by both the physical and chemical protection of the embedded steel against corrosion [11]. The most common cause of the deterioration of reinforced concrete structures is corrosion of the reinforcement caused by localised breakdown of the passive film on the steel by chloride ions. Because of the impact of this deterioration on both safety and economy, the ability to accurately and reliably measure the corrosion condition of the reinforcing bars (rebars) in the concrete is essential [12]. For example, it has been reported that corrosion in tropical environments mainly occurs because of the high chloride deposition rates (74–1120 mg/m² per day) on the concrete surface. A relative humidity (RH) that exceeds 80% for 98% of the year and an average yearly temperature of 21°C that may reach 41°C in the spring and summer contribute to an accelerated corrosion process [13].

Chlorine ions and halogens are the most destructive agents for rebars in concrete [14]. In addition, carbonation, which takes place in industrial surroundings, contains enough carbon dioxide and adequate humidity to decrease the pH of concrete from 13, which can create a protective layer on steel, to less than 8. Consequently, the protective layer is no longer stable, and corrosion begins [15]. Corrosion resulting from chlorine ions requires a critical amount of chlorine ions, known as the chloride threshold. Corrosion mainly occurs because of the high rate at which chloride is deposited on the concrete surface (74-1120 mg/m² per day). The critical amount of chloride for corrosion to begin is about 0.2 wt. % of chlorine ions [16]. The amount of chloride depends on the electrolytic paths in the system. The electrolytic path, along with the moisture and oxygen content, determines the ease of ion transport through the bulk matrix to the steel/paste interface. Consequently, the transport properties depend on the micro structural characteristics of the bulk cementitious materials, i.e., porosity, pore interconnectivity, and pore size distribution [17].

Permeability, which is the extent to which external media, such as liquids, gases, diverse aggressive ions and other pollutants, can penetrate concrete [18], [19], is considered to be one of the most important characteristics that control the durability of cement-based concrete composites [20]-[23]. With a decrease in the permeability of a concrete surface, aggressive factors can be prevented from entering the concrete. In recent research, the destruction costs in America resulting from chlorine ions and continuous corrosion processes were estimated to be more than one billion dollars [24].

In present research the influence of ceramic nanopigments on the mechanical and corrosion resistance of cement based composites are experimentally studied. The SEM, Measuring potential and mechanical tests are performed in order to verify the effect of ceramic nanopigment on the microstructure, subsequent variation of mechanical properties and corrosion resistance of these cement based composites caused by chlorine ions.

II. MATERIAL AND MIX PROPORTION

A. Materials Properties

Class 52.5 N white cement was used to produce all of the samples (Although white cement is not normally exposed to chemical attack, it has been used to investigate the effect of ceramic nano-pigment on mortars color and appearance). Table I shows the chemical and physical composition of the cement.

TABLE I
CHEMICAL AND MINERAL COMPOSITION OF THE CEMENT

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	LSF	C ₃ S	C ₂ S
%	23.71	4.4	0.45	65.8	1.48	1.62	91.6	52.78	10.90

The ceramic nano-pigments used in this study were produced by Nano Almas Nafis Omid Company (Iran, Tehran) as a commercial product. Fig. 1 shows a scanning electron

micrograph (SEM) and X-ray diffraction (XRD) spectrum of ceramic nano-pigments. The aggregate used in this study was made from granule-shaped washed siliceous sandstone with a diameter of 1-6mm. 50mm × 50mm × 50mm and 150mm × 150mm × 150mm cubical moulds were used for comprehensive strength and permeability tests, respectively. A steel bar with a diameter of 10mm was prepared from an ordinary round bolt and was placed in the centre of the samples.

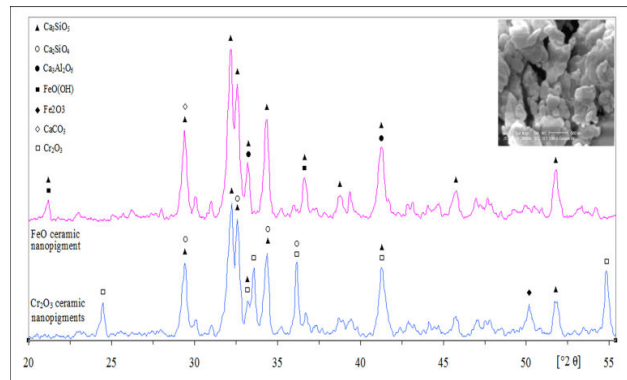


Fig. 1 XRD spectrum and a scanning electron micrograph of ceramic nano-pigments

B. Mix Proportions of the Specimens

The details of the mix proportions per cubic meter of cement mortar are given in Table II, where PC denotes plain cement mortar. CPC3 and CPC5 denote cement mortar containing 3% and 5% of Cr₂O₃ ceramic nano-pigment by the weight of the binder, respectively. Finally, FPC3 and FPC5 denote concrete mortar containing 3% and 5% FeO ceramic nano-pigment by the weight of binder, respectively. For the same water-cement ratio (w/c=0.4), the super plasticiser dosages are shown as a percentage of the weights of cementitious materials (Table II).

TABLE II
MIX PROPORTION OF SPECIMENS (kg/m³)

Mix	W ¹	C ²	F.A. ³	FeO.C ³	Cr ₂ O ₃ C. ⁵	UNF ⁶ (%)	Defoamer (%)
PC	240	590	1478	0	0	0.5	0.1
CPC3	240	590	1478	0	17.7	0.5	0.1
CPC5	240	590	1478	0	29.5	0.5	0.1
FPC3	240	590	1478	17.7	0	0.5	0.1
FPC5	240	590	1478	29.5	0	0.5	0.1

1. Cement
2. Water
3. Fine aggregate
4. FeO ceramic nano-pigment
5. Cr₂O₃ ceramic nano-pigment
6. Super plasticizer

To fabricate the concrete mortar containing ceramic nano-pigments, a water-reducing agent (a type of β-naphthalene sulfonic acid and formaldehyde condensates) is first mixed into the water in a mortar mixer, and then nanoparticles are added and stirred at high speed for 5 min. A defoamer is added while stirring. Cement and sand were mixed at low speed for 3 min in a concrete centrifugal blender. Then, the mixture of

water, the water-reducing agent, the ceramic nano-pigments and the defoamer were poured slowly and stirred 2min to achieve a homogeneous mix. Fresh concrete mortar was cast into the moulds constructed for the mechanical strength and permeability tests. During casting, an external vibrator was used to facilitate compaction and reduce the number of air bubbles. The specimens were de-moulded after 24h and cured by immersing them in a saturated lime water solution in a basin at a temperature of $20 \pm 3^\circ\text{C}$ for the prescribed period, and then the specimens were placed in the laboratory for 24h before the test.

III. EXPERIMENTAL RESULTS

A. Compressive and Permeability Tests

The mechanical test and permeability tests to determine the depth of chlorine penetration were performed, and the results for the plain samples and the samples containing ceramic nano-pigment are presented in Figs. 2 and 3. Fig. 2 shows that ceramic nano-pigments that are less than 100 nm had a better effect on mechanical strength compared with other samples, and for Cr_2O_3 , the compressive strength increased from 48 MPa (for plain concrete) to 62.3 MPa for cement mortar containing nano-pigment after 7 days. After 28 days, the compressive strength increased from 59.3 MPa for plain concrete to 77 for cement mortar containing nano-pigment.

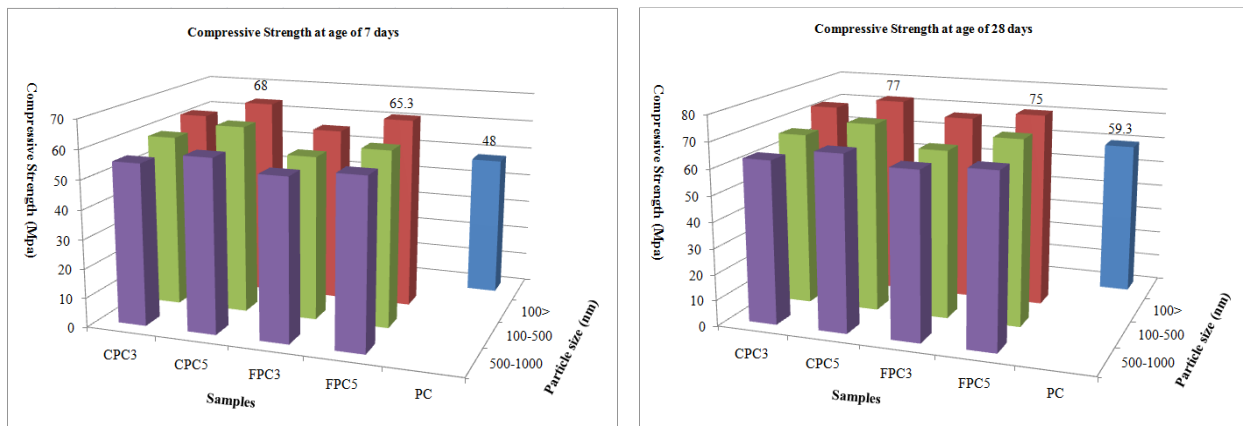


Fig. 2 Compressive strength of the samples at the age of 7 days (left) and 28 days (right)

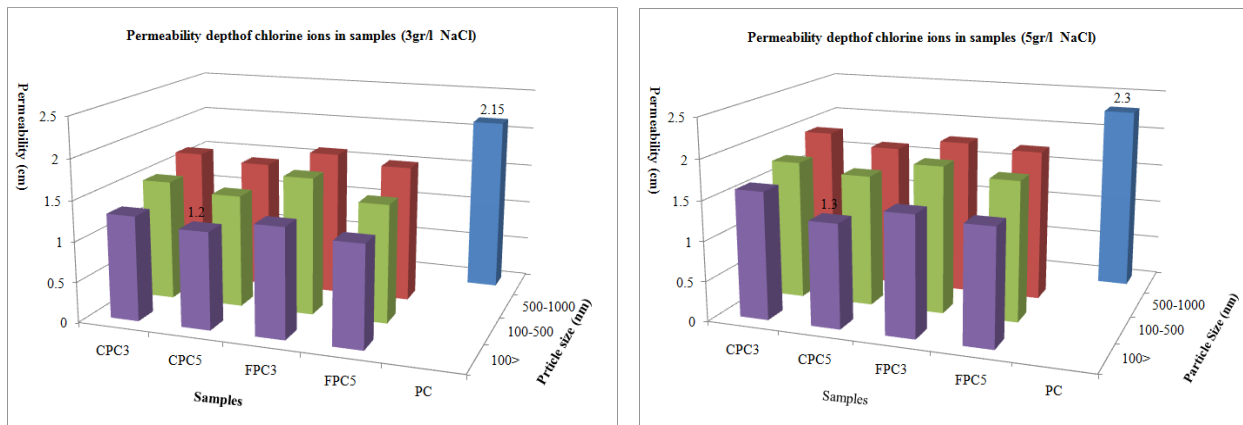


Fig. 3 Penetration depth of chlorine ions into the samples in a molar solution of 3gr/lit NaCl (left) and 5 gr/lit (right)

For Cr_2O_3 , the ceramic nano-pigment, and particles that were 500-1000nm, the compressive strength increased from 48 MPa for plain concrete to 59 MPa for cement mortar containing nano-pigment after 7 days and from 59.3 MPa to 67.6MPa after 28 days, which is the lowest effect on the mechanical properties between all samples. As observed, the compressive strengths increased in mortars containing ceramic nano-pigments and, in all cases, were higher than those of control cement mortars; this trend is less pronounced when

nanoparticles are added in high amounts. For FeO , a ceramic nano-pigment less than 100nm, the compressive strength increased after 7 days from 48 MPa for plain concrete to 65.3 MPa for cement mortar containing nano-pigment and from 59.3 MPa for plain concrete to 75 MPa for cement mortar containing nano-pigment after 28 days. For FeO , ceramic nano-pigments and particles that were 500-1000 nm, the compressive strength increased after 7 days from 48 MPa for plain concrete to 57.3 MPa for cement mortar containing

nano-pigment and from 59.3 MPa for plain concrete to 66 MPa after 28 days, which is the smallest change in mechanical properties among all the FPCs samples.

Similar to the compressive strength, the permeability depths of samples containing ceramic nano-pigments were lower than those of sample PC. As shown in Fig. 3, the permeability depth of FPC5 and CPC5 were 1.25 and 1.2cm after 28 days, respectively. Thus, the permeability depth of FPC5 and CPC5 were 42 and 44% lower than that of PC. For these samples, the effect of ceramic nano-pigments on the mechanical strength at early stages was greater due to the porous structure of the cement mortar. The compressive strength increased as the concentration of ceramic nano-pigments increased, and the following trend was observed: PC < FPC3 < FPC5 and PC < CPC3 < CPC5.

B. Corrosion Tests (Measuring Potential)

To prepare samples for the corrosion test, one standing bar, which is 6cm in length and 1cm in diameter, was placed in the middle of the 5cm × 5cm × 5cm samples. Initially, iron bolts were fixed in the middle of the samples using two clamps, and the mortars were cast into the moulds and were compacted using a ramrod. To easily access the armature, a circular groove was created on its body 1cm from the top, and a fine wire was fixed inside the groove according to the standard (ASTM C876-91) for later tests. Then, it was covered by soldering. To limit the armature corrosion just to the portion in the concrete mortar where the armature was placed, 2cm of the shaft was covered by tar to prevent corrosion. Steel bars were placed 1cm from the bottom of the mould in the concrete mortar. The steel rebar primary corrosion was cleaned using sandpaper; their grease was cleaned using caustic soda, and then superficial thin layers on the steel rebar surface were washed using acids. After curing for seven days, the samples were settled in a molar solution of NaCl made of lab salt and distilled water for 3 months. They were checked during the week for potential tests with the potentiostat apparatus (EG&G). It is shown in Figs. 4 (a)-(e) that no corrosion occurred in cement mortars containing ceramic nano-pigments.

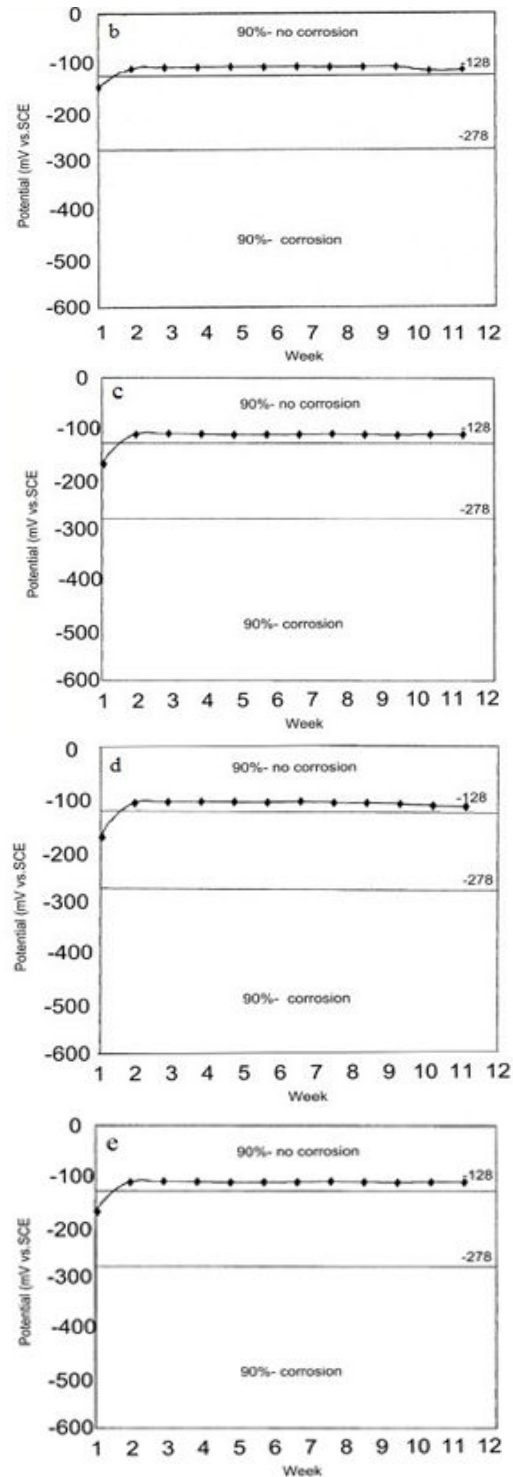
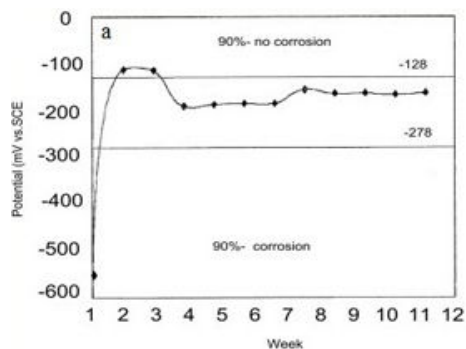


Fig. 4 Potential chart for a) plain mortar, b) samples containing 3% Cr₂O₃ ceramic nano-pigments, c) samples containing 5% Cr₂O₃ ceramic nano-pigments, d) samples containing 3% FeO ceramic nano-pigments, e) samples containing 5% FeO ceramic nano-pigments

In these figures, the zones with potentials greater than -128 mV and less than -278 mV are non-corroded zones and corroded zones, respectively. The zone between -278 mV and -128 mV is the corrosion threshold zone. In Fig. 4 (a), which shows the plain concrete mortar sample, the chlorine ion has penetrated the corrosion threshold zone, while for concrete mortar samples containing ceramic nano-pigments, penetration occurs in the non-corroded zone. These results show that utilising ceramic nano-pigments is useful for decreasing the corrosion of concrete steel rebar.

C. Investigation of Cement Mortar Microstructure (Scanning Electronic Microscope Analysis)

To verify the mechanism predicted by the compressive strength test, an SEM test was conducted. The test results revealed that additional ceramic nano-pigments affected the nanostructure behaviour and led to differences in the microstructure of the hardened pastes.

In order to perform a SEM test, the specimens were cut directly from the concrete cubes. The specimens had diameters of approximately 5 mm. The specimens were regular, and the surface was completely flat. Fig. 5 shows the electronic scanning photographs of PC (a & b) and cement mortar containing nano-pigment (c & d) after 28 days. Fig. 5 shows a denser matrix for cement mortar containing ceramic nano-pigments compared to that of plain concrete.

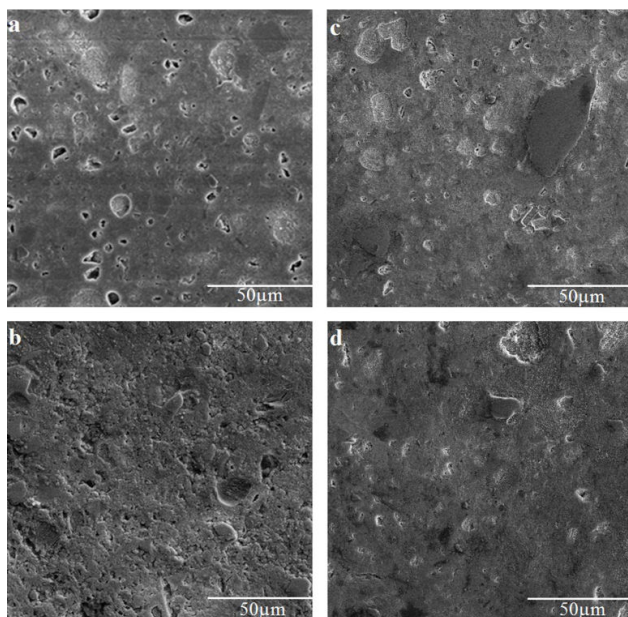


Fig. 5 Microstructure of plain (a & b) and cement mortar containing ceramic nano-pigments (c & d) at a curing age of 28 days

IV. DISCUSSION

The aforementioned results suggest that the effects of ceramic nano-pigments on the mechanical properties and corrosion of cement mortar were greater in proximity to chlorine ions. Potential graphs of potential versus time indicate the changes in the samples. These graphs display

noticeable changes for the plain concrete sample. Corroded zones on the samples surfaces are not initially distinct, but the EG&G device results can show corrosion existence if there is an electric current. Ceramic nano-pigments are extremely small, and a uniform dispersion of particles leads to a high-quality microstructure. According to Wu's 'centroplasm' hypothesis, aggregates, sand and other particles act as a centroplasm, or skeleton, and nano-particles behave as a gel or transmitter substance. The binding force between the centroplasm and transmitter substance has a significant effect on the strength of concrete [25], [26]. Nano-particles are distributed throughout the cement paste, forming a 'sub-centroplasm.' Moreover, nano-particles can bind to hydrated products that are located near the transition zone between nano-particles and hydrated products [26]. Ceramic nano-pigment particles which are small and capable of reacting with other cement ingredients due to their chemical composition significantly reduce cement mortar corrosion. Among them, Cr_2O_3 ceramic nano-pigments had a greater effect on the mechanical strength of cement mortar than FeO ceramic nano-pigments due to its chemical and physical characteristics.

The results in these tests show that the appropriate structure of nano-pigments and settling of the nanoparticles among the permeable spaces of the ions increases the concrete quality and delays steel rebar corrosion. Figs 2 and 3 show that, under the same conditions, Cr_2O_3 ceramic nano-pigments have a better effect on mechanical properties and permeability and in addition to better mechanical properties, the permeability was lower than that of the FeO ceramic nano-pigments because of their physical and chemical properties based on the XRD patterns for ceramic pigments and colored cements; overall, for the samples containing ceramic nano-pigments, the compressive mechanical properties and permeability were improved after 7 days and 28 days, which is very important and proves the superior mechanical performance of colourful cement mortars with ceramic nano-pigments.

V. CONCLUSION

Based on the results of the mechanical tests, the following conclusions may be drawn:

The compressive strengths of the cement mortars mixed with ceramic nano-pigment were higher than that of plain concrete.

Ceramic nano-pigments increase the impermeability of the samples in comparison with plain concrete samples, and corrosion problems can be controlled and highly reduced in humid conditions near corrosive gases and fluids through the use of ceramic nano-pigments.

Due to the reduction of vacancies, permeability of chlorine ions in concrete is reduced and thus prevents corrosion in concrete and steel rebar; thus, the mechanical performance of cement mortars with ceramic nano-pigment is superior to previous compounds in addition to the changing monotonous and turbid colours of concrete into various attractive and light colours.

ACKNOWLEDGMENT

The authors would like to thank Professor Luis Alfonso Maldonado López from Cinvesta Merida University, Professor A. Poursaei of Purdue University and Professor B. Bavarian from California State University, Northridge, whose advice and suggestions are gratefully acknowledged.

REFERENCES

- [1] A.M. Neville, "Properties of Concrete," New Jersey: Prentice Hall, 1996.
- [2] G. Batis, "Kouloumbi N, Pantazopoulou P. Protection of reinforced concrete by coatings and corrosion inhibitors," *Pigm Resin Technol* 2000; 29(3): 159-163.
- [3] A. Ramazaniyanpour, T. Parhizkar, "Additives and their application in concrete," Tehran: Building and Housing Research Center Press, 1997.
- [4] K.L. Scrivener, R. James Kirkpatrick, "Innovation in use and research on cementitious material," *Cem Concr Res* 2008; (38): 128-136.
- [5] www.concretenetwork.com.
- [6] N. Paris, M. Chusid, "Color in Concrete: Beauty and Durability," *Conc Inter* 1994; 21 (1): 60-63.
- [7] A. Ramazaniyanpour, "Collection of articles on increasing material in the concrete development technology," Tehran: Amirkabir University of Technological Press, 1989.
- [8] J. Ellis, R. Warren, D. Dryhurst, "Bringing Color to concrete," *Concrete* 1996; 30(1): 38-40.
- [9] C.J. Lysdale, "A state of the art review," *Concrete* 1989; 23(7): 29-34.
- [10] K. Jung, "Color synthesizer for making colored concrete," *Concrete Plant* 1993; 11(3): 71-73.
- [11] G. Fajardo, P. Valdez, J. Pacheco, "Corrosion of steel rebar embedded in natural pozzolan based mortars exposed to chlorides," *Constr Build Mater* 2009; 23: 768-774.
- [12] A. Poursaei, C.M. Hansson, "Potential pitfalls in assessing chloride-induced corrosion of steel in concrete," *Cem Concr Res* 2009; 39: 391-400.
- [13] L. Maldonado, "Chloride threshold for corrosion of galvanized Reinforcement in concrete exposed in the Mexican Caribbean," *Mater Corros* 2009; 60: 536-539.
- [14] G.K. Glass, B. Reddy, N.R. Buenfeld, "The participation of bound chloride in passive film breakdown on steel in concrete," *Corros Sci* 2000; 42(11): 2013-2021.
- [15] M. Forshyth, "Corrosion and protection of steel Concrete," *Mater Corros* 1997; 22(4): 13-16.
- [16] A. Benture, S. Diamond, N.S. Berkr, "Steel Corrosion in Concrete," London: E&FN SPON, 1997.
- [17] D.A. Koleva, J. Hu, A.L.A. Fraaij, K.V. Breugel, J.H.W. De-Wit, "Microstructural analysis of plain and reinforced mortars under chloride-induced deterioration," *Cem Concr Res* 2007; 37: 604-617.
- [18] P. Mohr, W. Hansen, E. Jensen, I. Pane, "Transport properties of concrete pavements with excellent long-term inservice performance," *Cem Concr Res* 2000; 30: 1903-1910.
- [19] L. Basheer, J. Kropp, D.J. Cleland, "Assessment of the durability of concrete from its permeation properties: a review," *Constr Build Mater* 2001; 15: 93-103.
- [20] M.G. Alexander, B.J. Magee, "Durability performance of concrete containing condensed silica fume," *Cem Concr Res* 1999; 29: 917-922.
- [21] B.H. Oh, S.W. Cha, B.S. Jang, S.Y. Jang, "Development of high-performance concrete having high resistance to chloride penetration," *Nucl Eng Des* 2002; 212: 221-231.
- [22] M-hua. Zhang, H. Li, "The resistance chloride penetration of concrete containing nano-particles for pavement," In: *Proceedings of ECCM-7 Conference*, San Diego, March, 2006. p. 61750E.1-61750E.8.
- [23] W. Chalee, C. Jaturapitakul, P. Chindaprasirt, "Predicting the chloride penetration of fly ash concrete in seawater," *Mar Struct* 2009; 22(3): 1-13.
- [24] Y. Auyeung, P. Balagura, L. Chung, "Bond behavior of Corroded reinforcement bars," *ACI Mater J* 2000; 97(2): 214-221.
- [25] W. Zhongwei, L. Huizhen, "High Performance Concrete," Beijing: China Railway Publishing Company, 1999.
- [26] H. Li, H.G. Xiao, J. Yuan, J. Ou, "Microstructure of cement mortar with nano-particles," *Composites: Part B* 2004; 35: 185-189.