ISSN (Online): 2319-7064
Index Copernicus Value (2013): 6.14 | Impact Factor (2014): 5.611

The Effect of Using Commercial Red and Black Iron Oxides as a Concrete Admixtures on its Physiochemical and Mechanical Properties

Essam A. Kishar[2], Muhammad Y. Alasqalani[1], Yahya R. Sarraj[3], Doaa A. Ahmed[4]

[1]Chemistry Department, Women College, Ain Shams University, Cairo, Egypt.

[2]Scientific research department, Israa University-Gaza, Palestine.

[3] Civil Engineering Department, Islamic University-Gaza, Palestine.

[4] Chemistry Department, Women College, Ain Shams University, Cairo, Egypt.

Abstract: ***Study discuss the effect of using commercial red and black iron oxides (RIO and BIO) as a concrete admixtures in percentages do not exceeded 2.5% of each oxide from the amount of cement, this study tested the effect of every portion from each oxide at different ages on the compressive strength as well as the workability represented as a values of slump. We conclude that the optimum portion of RIO is 2.5%, but for BIO is 1%, while the proposed uses of RIO in concrete technology are retarder through slump increment reach to 50%, coloring material and mineral admixture through Compressive Strength increment (7-365 days) 5.5-12.8%. On the other hand BIO will propose as, coloring material and mineral admixture through Compressive Strength increment (7-365 days) 22.2-30.8%. SEM-images are clearly show the formation of Calcium hydroxide phase at 7-days while at 1-year the C-S-H phase is a predominate one, in both cases of RIO and BIO. XRD-pattern is supported the results outcomes through SEM-images.***

Keywords: RIO, BIO, Compressive strength, SEM, slump

1. Introduction

Admixtures are those ingredients in concrete other than Portland cement, water, and aggregates that are added to the mixture immediately before or during mixing. Admixtures can be classified by function as follows:

1) Air-entraining admixtures
2) Water-reducing admixtures
3) Plasticizers
4) Accelerating admixtures
5) Retarding admixtures 6. specialty admixtures: which include corrosion inhibitors, shrinkage control, alkali-silica reactivity inhibitors, and coloring. ***[1]***.

Iron oxides classified as coloring admixture, in addition it improve some mechanical properties as out lined in ***[2],*** which conclude that, The using of nano ZrO_2, Fe_3O_4, TiO_2 and Al_2O_3 with constant content will enhance the mechanical properties of fresh and hardened concrete as compressive strength, indirect tensile strength and durability. The same result is adopted in ***[3]***, work; it can be used, iron oxide , as pigment with percent less than 4% in concrete. The iron oxide will enhance some of the mechanical properties of hardened concrete as compressive and flexure strength.

Fe_3O_4 is used as a black pigment and is known as C.I pigment black 11 (C.I. No.77499). Iron (III) oxide is also used as a pigment, under names "Pigment Brown 6", "Pigment Brown 7", and "Pigment Red 101"; Iron (II, III) oxid (black iron oxide) is a chemical compound with formula Fe_3O_4. It contains both Fe^{2+} and Fe^{3+} ions and sometimes formulate as $FeO{\cdot}Fe_2O_3$.

In the work of ***[4]***, in soil the following behavior of iron oxides is proposed, when surface of iron oxides is covered with OH ions attached to Fe (III) atoms; these species are called surface functional groups and contribute substantially to the specific adsorption of various anions as inner sphere complexes. Common sorbates are phosphate, silicate, arsenate and humic compounds, as well as cations such as heavy metals. This adsorption makes the soil mantle act as an efficient sink for these ions and molecules thereby restricting the electrostatic interactions.

2. Experimental

2.1 Materials

- Portland cement of mark CEM I 52.5N obtained from El-Arish cement factory. Its chemical composition is given in Table (1)

Table 1: Chemical composition of the used ordinary Portland cement (OPC)

Oxide (%)	OPC
SiO_2	22.12
Al_2O_3	5.**56**
Fe_2O_3	**3**.69
CaO	62.87
Na_2O	0.29
K_2O	0.11
Cl	0.02
MgO	2.36
SO_3	0.91
Free CaO	0.92
Ignition Loss	**1.22**

- **Red and black iron oxides:**

The main physical and chemical properties is listed in Table (2) according to Fisher Scientific Company for red iron oxide, and Procter Johnson Company for black iron oxide.

Table Error! No text of specified style in document.**:** Physical and chemical properties of Red and Black iron oxide

Property	Red Iron oxide	Black Iron oxide
Molecular formula	Fe_2O_3	Fe_3O_4
Appearance	Red Powder	Black Powder
Toxicity	Not toxic	Not toxic
Solubility in water	Insoluble	Insoluble
Normal Size (nm)	~ 100	~ 100
pH in 5%w/w concentration	Not available	4-8
Bulk Density kg/m^3	1550	1500

- **Aggregate:**

Aggregates used in this study achieved specification of ASTM.

- **Water:**

Tape water is used for all mixing and curing of concrete.

2.2. Techniques and Instrumentation

2.2.1. Mix Design

After finishing of all tests for concrete constituent and ensure that all material like water, aggregate, sand and cement are according to ASTM specification, the concrete will design with strength 30 MPa at 28 days age. The job mix will be designed according to Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete [5]. The design criteria that used in the current study is as:

1) **Compressive strength:** The most strength of normal concrete for general use is 30 MPa for cubic strength and ***25 MPa*** for cylinder strength so the mix will be design for that strength.
2) **Slump:** The most slump of normal concrete for general use is between 25 to 100 mm and the mix is designed for slump around 75 to 100 mm.
3) **Nominal maximum aggregate size:** The nominal maximum aggregate size in the job mix is 25 mm.
4) **Water cement ratio:** The water cement ratio in the job mix is 0.569.
5) **The final average weight for job mix:** The final average weight for the job mix is list in Table (3).

Table 31: The final average weight for the job mix

Material	Weight (kg)	Volume (m^3)
Entrapped air	0	0.0150
Water	182	0.1650
Cement	320	0. 1016
Coarse aggregate	1161	0.4519
Fine aggregate	687	0.2665
Total	2350	1.000

2.2.2. Preparation of Concrete Specimen

2.2.2.1. Mixing Procedure

The concrete will mix according to Standard Method of Making and Curing Test Specimens in the Laboratory [6].

2.2.2.2. Curing of hardened concrete:

After 20-40 hour, the hardened concrete will be removed from the molds very carefully to prevent any defect in the samples. After that, the samples will be placed in curing water tank at temperature 21-25°C until the period of testing.

2.2.2.3. Testing program

The main aim of this research is to study the effect of red and black iron oxides on the mechanical properties of fresh and hardened concrete and find the ability to obtain high strength concrete using components as limestone aggregate, sand, cement and, red and black iron oxides which valuable in local market. To study the effects of red and black iron oxides on the mechanical property of fresh and hardened concrete should be flow many testes on fresh and hardened concrete, these tests are explained as following.

Fresh concrete test and sampling:

1) Slump Test according to [7]:
2) Sampling of fresh concrete in several molds according to [6]:

Testing of Hardened Concrete

After completing the curing process for hardened concrete, many tests should be made to study physiochemical and mechanical properties of hardened concrete as below.

1) Compressive strength According to [8] and [9].
2) Stopping of hydration: This is performed after doing the compressive strength test by taking about 10 g of the crushed hardened pastes and putting into a beaker containing 100 ml of acetone/ethyl alcohol (1:1 by volume) to stop the hydration process. The mixture is stirred for 0.5 hr. The residue is filtered off, ished with ethanol and dried at 50 ° C for about 24 hrs. The dried samples are then stored in a desiccator for the following physico-chemical analysis.
3) X-Ray Diffraction analysis (XRD): XRD patterns of the samples are recorded by using a Philips X Pert MPD diffractometer using copper target with nickel filter under working conditions of 40 kilovolts and 20 milliampers.
4) Scanning Electron Microscopic (SEM) measurements: The morphology and microstructure of the dried hydrated samples are studied using JEOL JEM -1200 EXII electron microscope. The specimens are coated with a thin film of gold under a vacuum evaporator with cathode rays then analyzed.

3. Results and Discussion

3.1 Black iron oxide

The following table will outline the results of slump as well as compressive strength of concrete using black iron oxides (BIO):

Table 4: Slump and compressive strength of concrete using BIO

Portion (M/C*%)	Slump (cm)	Compressive strength (kg/cm^2)				
		7-days	28-days	96-days	6-mon.	1-year
0	8	360	375	385	395	390
0.5	7	440	450	450	470	500
1	8.5	440	460	470	480	510
1.5	9.5	410	420	400	450	455
2	12	390	405	430	470	480
2.5	13	380	400	420	420	430

*M/C = amount of iron oxide in grams (M) / amount of cement in grams (C)

BIO produce approximately linear behavior of slump increasing, this fashion illustrated in Fig. 1, the maximum increasing of concrete slump, which is 13cm, produced by 2.5% portion. Detectable increasing in the concrete compressive strength using BIO as admixture, this increasing comes to be in maximum value at 1% portion at one year age, Fig. 2, outline the pattern of concrete compressive strength using BIO.

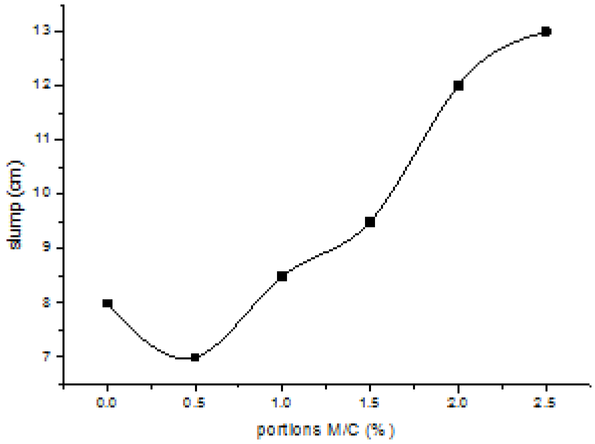


Figure 1: Effect of BIO on the concrete slump

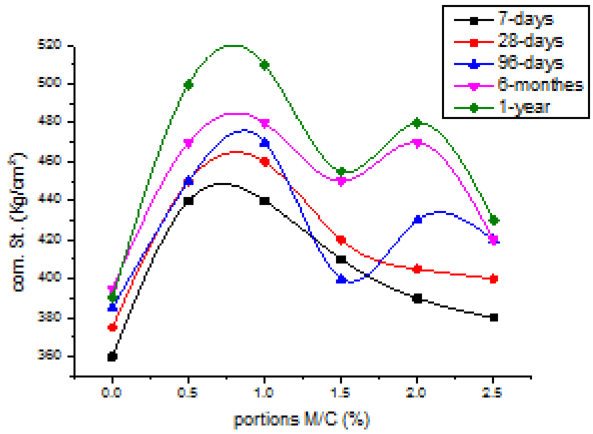


Figure 2: Compressive strength of concrete using BIO with different ages

3.2. Red iron oxide

In case of red iron oxides (RIO), the following table will outline the results of slump as well as compressive strength of concrete using (RIO):

Table 5: Slump and compressive strength of concrete using RIO

Portion (M/C*%)	Slump (cm)	Compressive strength (kg/cm^2)				
		7-days	28-days	96-days	6-mon.	1-year
8	360	375	385	395	390	8
6	340	350	355	355	360	6
11	320	335	340	350	350	11
9	360	380	390	400	400	9
12	370	385	390	410	420	12
12.	380	395	400	420	440	12.

RIO make a unique curve which alternating between increasing and decreasing of concrete slump using different portions, this fashion is outline in Fig. 3.

RIO shows relatively small increment in the concrete compressive strength at different ages according to Fig. 4, and this increment in maximum at 2.5% portion for 1-year age.

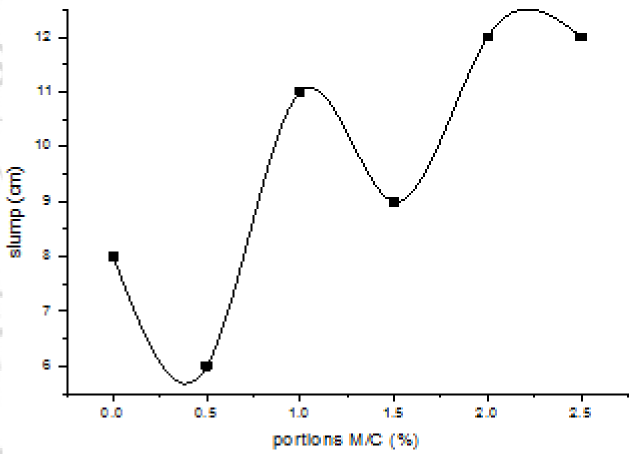


Figure 3: Effect of RIO on the concrete slump

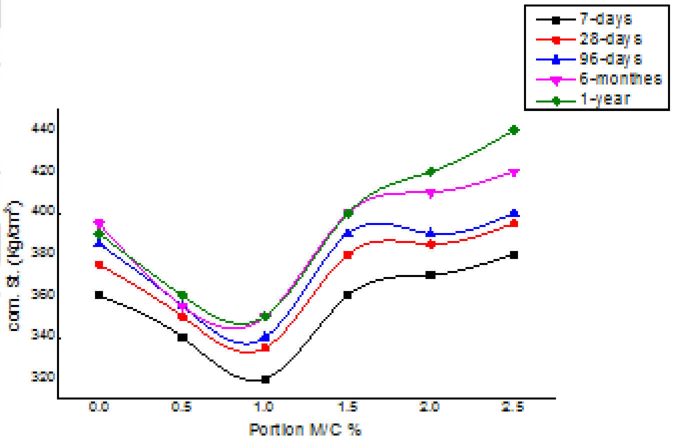


Figure 4: Compressive strength of concrete using RIO with different portions at different ages

In general there are increase in workability as well as increase in compressive strength, but the optimum portion addition shifted from 1% in case of BIO to be 2.5% for RIO.

Iron (II, III) oxide (black iron oxide) is a chemical compound with formula Fe_3O_4. It contains both Fe^{2+} and Fe^{3+} ions and sometimes formulate as $FeO{\cdot}Fe_2O_3$. This composition give black iron oxide opportunity to be more reactive than Fe_2O_3 (red iron oxide) spatially at media like concrete media.

As ***[4],*** postulate in their work, which pointed in brief in the binging of this article, when surface of iron oxides is covered with OH^- ions attached to Fe III ions, these species are called surface functional groups and contribute substantially to the specific adsorption of various anions as inner sphere complexes. Common sorbates are phosphate, silicate, arsenate and sulfate, as well as cations such as heavy metals, or calcium in concrete environment. This adsorption makes the Fe environment act as an efficient sink for these ions thereby restricting the electrostatic interactions.

Surface adsorption operates through Fe–OH groups at the surface of Fe-oxides and results from the completion of the ligand shell of surface Fe atoms. These groups attain negative or positive charge by dissociation or association of protons, depending on the pH of the surrounding.

$$=FeOH \longrightarrow =FeO^- + H^+ \text{ (Dissociation).}$$
$$=FeOH + H^+ \longrightarrow =FeOH_2^+ \text{ (Association).}$$

Furthermore, these complex processes are affected by the presence of other ions, such as Ca^{2+}, both of which serve as an electrolyte, which combine with the hydroxides and oxides of iron to precipitate a variety of Ca-Fe-O-OH species.[10]

From the above discussion, BIO and RIO act as retarder through inhibiting the ionic reactions occur in the concrete environment at early age, which inflect as increasing in the workability of concrete.

On the other hand, the presence of different oxidation states of iron in BIO may promote the formation of different phases in the Ca-Fe-O-OH moiety, which explaine the compressive strength increases. There are some evidences support the above approach as

- By increasing, the percent of BIO, at percentage above 3% the concrete start to segregate, that mean the binding action of cement started to inhibit.
- The maximum increasing of compressive strength for BIO achieved at 1% for different ages, but the slump increases by portions of BIO increase, which enhances the assumption of surface adsorption at the surface of Fe-oxides.
- We tend to make simple experiment to explain the action of Ca-ion in the mixture, by testing the concrete included 5% of calcium carbonate, and then test this concrete by adding 1% BIO.

The result of this experiment is out lined in the Fig.5, which indicate that BIO modify the compressive strength of that concrete using calcium carbonate, which may indicate the formation of phases that enhanced the compressive strength. As well as the slump increases from 10cm to 13cm, which may support the surface adsorption assumption.

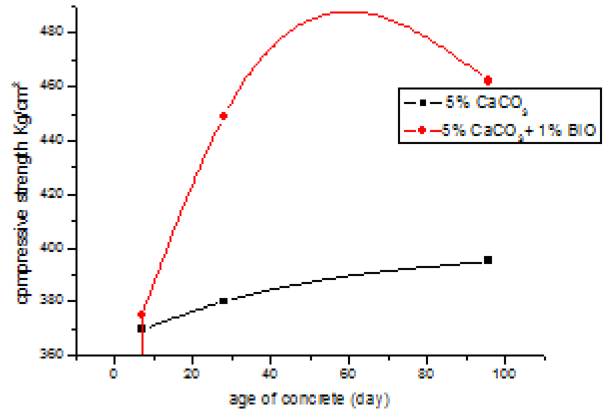
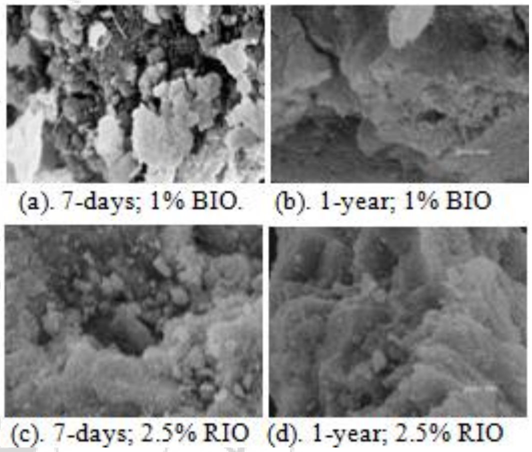


Figure 5: Effect of combination between BIO and calcium carbonate on concrete

SEM images may give additional clarification of the situation that achieved using iron oxides on concrete as admixtures as follow:



The above SEM-images are clearly show the formation of CH phase at 7-days while at 1-year the C-S-H phase is a predominate one, in both cases of RIO and BIO.

The composition of the cementitious material in concrete can have a significant influence on the behavior of all chemical admixtures. Inasmuch as these admixtures affect the early stages of hydration, and are at least partly removed from solution by the early reactions, the cement phases that react most rapidly have a large influence on their action. The early reacting compounds include C3A and the alkali and calcium sulfates.[11]

This is clearly appear through the following Fig.6, of XRD-pattern of BIO as well as RIO, in the comparison with M0 (blank or control), and sand that used throughout this study.

The hydration of the cement components results are the conversion of C_3S and β-C_2S into the hydration products, calcium silicate hydrate (CSH) and calcium hydroxide (CH) as shown in above Fig.6. Accordingly, the intensity of the characteristic peaks of the reactants such as alite and belite phases decreases with increasing the hydration age.

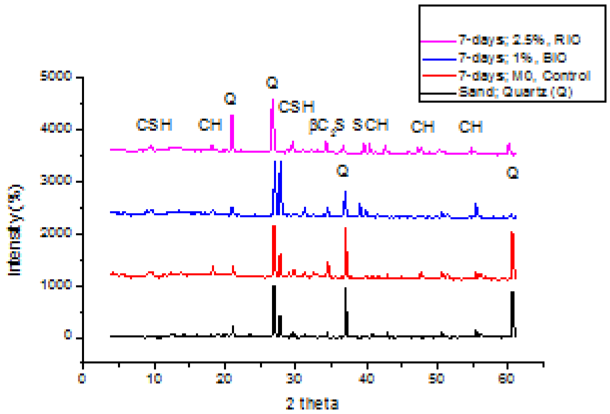


Figure 6: XRD-patterns of BIO and RIO, in the comparison with M0 (blank or control), and sand

4. Conclusion

From the obtained results it can be concluded that:

1) For BIO 1% is the optimum percent, it increase the slump 6.25% and the compressive strength by 22-30%. So it can be used as mineral admixture.
2) For RIO 2.5% is the optimum percent, it increase the slump 50% and the compressive strength by 5-3012%. So it can be used as retarder.

References

[1] PCA, Kosmatka, Steven H.; Kerkhoff, Beatrix; and Panarese, William C.; Design and Control of Concrete Mixtures, EB001, 14th edition, Portland Cement Association, Skokie, Illinois, USA, 2012.
[2] Shekari, A. H., & Razzaghi, M. S.; Influence of Nano Particles on Durability and Mechanical Properties of High Performance Concrete. Procedia Engineering, pp. 3036–3041, 2011.
[3] Lee , H. S.; Lee , J. Y.; & Yu ; M. Y. Influence of iron oxide pigments on the properties of concrete interlocking blocks. Cement and Concrete Research, pp. 1889–1896, 2003.
[4] Cornell, R.M., and Schwertmann, U., "The Iron Oxides", 2nd edn.Weinheim: Wiley-VCH, pp. 664, 2003.
[5] ACI Committee 211, "Standard Practice for Selecting Proportions for Normal", Heavyweight and Mass Concrete, ACI 211.1-91, American Concrete Institute, Farmington Hills, Michigan, 1991.
[6] ASTM C 192, 'Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory", 2000.
[7] ASTM C 143, "Standard Test Method for Slump of Hydraulic Cement Concrete", 2000.
[8] ASTM C 39, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens", 2001.
[9] BS 1881: Part 127, "Testing concrete. Method of verifying the performance of concrete using the comparative cube test", 1990.
[10] Gräfen, H.; Horn, E. M.; Schlecker, H.; Schindler, H. "Corrosion". Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, 2000.
[11] ACI Committee 225, "Guide to the selection and use of hydraulic cements", ACI 225R-99, American Concrete Institute, Farmington Hills, Michigan, 1999.

Author Profile

Muhammad Alasqalani received the B.S. and M.S. degrees in industrial and pure chemistry respectively from Al-Azhar university in 2001 and 2007. During 2008-2014, he stayed in University Collage for Applied Sciences (UCAS), as lecturer for different topics of applied and pure chemistry since September 2014 he conducted with Israa University-Gaza as head of scientific research department.