SEM and XRD Analyses and Testing of Milled Natural Oxides Used for Colored Concrete

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ABSTRACT

This study aims at using some of the available rocks in Jordan after grinding and processing as pigments to produce colored concrete. It also aims at studying the properties of colored concrete that could be used in the production of concrete products, such as curb stones, wall panels, claddings and many other precast elements in comparison *in lieu* of imported pigments. Realizing the objectives of this research and within the scope of this study, the physical and mechanical properties of such materials have been recorded and documented. The experimental investigation has dealt with the mechanical properties of hardened concrete by testing specimens in compression, direct tension, splitting and flexure. The obtained results have been compared with the well-known empirical code formulae. The color of the produced concrete can only be judged by inspection. The microstructure of the produced concrete was studied by using XRD and SEM analyses to investigate the bond between the aggregates and the colored paste. Beam analysis was used to determine the elements in the resulting matrix. It should be noted that no additives, admixtures or any other workability agents, such as accelerators or retarders, were used. Of prime concern was to produce colored concrete and achieve a realistic concrete strength. Recommendations for further research were also outlined.

KEYWORDS: Colored concrete, SEM, XRD, White cement, Zeolite tuff, Zircon sand.

INTRODUCTION

Jordan is a rich country in minerals that are regarded resources of energy along with other industrial raw materials which may increase the country income if investigated and utilized in a good way. In this research, the possibility of producing colored concrete using available raw materials as pigments was studied. In developed countries, colored concrete can be considered one of the most successful ways to improve the outward show of a project. There are numerous ways to enhance concrete projects with beautiful colors, such as using colored aggregates, varying the surface finish and coloring the concrete paste with pigments. Pigments can be defined as materials that can change the color of light reflected according to selective color absorption. Pigments have been used to color concrete for about a century. Pigments actually tint the color of the paste portion of concrete and are used with white cement to reflect the real color. In a recent study, Ribeiro et al. (2013) have studied the rheological properties and hydration behavior of Portland cement mortars containing calcined red mud. The most common pigments are made of iron oxide pigments. Hyun-Soo Lee et al.

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(1989) showed the influence of iron oxide pigments on the properties of concrete interlocking blocks. In general, pigments are inert and may not react with cement. Therefore, they are not considered as part of the cementitious material content. Instead, pigments bond with the cement *via* the hydration process, masking the color of cement grains. The color generated is sensitive to many things. Some of the critical ones include water-cement (w/c) ratio, curing procedure, cement type and form. It is crucial to minimize fluctuations in these variables from batch to batch in order to minimize color variations. Nawasreh et al. (2006) documented several technical reports about mineral oxides that are available in Jordan. Recently, Alnawafleh et al. (2013) discussed the status of geologic and economic potentials of minerals and industrial rocks in Jordan. The materials used in this research are found in Jordan with the amounts shown in Table 1.

Table 1. Amounts of minerals

	
Red Zeolite Tuff	Dark Zeolite Tuff
$2038x10^6$ tons	
	
Zircon Sand	Bentonite
$9600x10^6$ tons	$105x10^6$ tons

EXPERIMENTAL PROGRAM

In this research, the studied minerals were brought from the Natural Resources Authority in Amman and milled to very small sizes reaching 45 µm. The milled materials are: red zeolite tuff, dark grey zeolite tuff, zircon sand, bentonite and lime. One of the machines used in milling is the ball mill shown in Figure 1. The powders of minerals are shown in Figure 2.

MATERIAL DESCRIPTION

Cement

Concrete mixes were prepared using white cement produced by Jordan Cement Factory according to Jordan standard specification (JSS 115/2005) for white cement industry. The physical and chemical properties of white cement are shown in Table 2. The specific surface area = 4000 cm^2/g.

Figure (1): Ball mill machine

Figure (2): Milled minerals

Table 2. White cement composition

Item	Constituent%,
SiO_2	20-25
Al_2O_3	3-6
Fe_2O_3	0.5
CaO	63-68
MgO	1-3
Mn_2O_3	0.25
SO_3	2-4

Aggregates

Crushed limestone coarse aggregates and silica sand are used in the current research. The properties of aggregates are presented in Table 3. Gradation curves according to ASTM C 136 are shown in Figure 3.

Table 3. Properties of aggregates

Property	Aggregates	
	Coarse	Fine
Dry Specific Gravity	2.44	2.19
Wet Specific Gravity	2.50	2.38
Absorption, %	2.28	8.93
Fineness Modulus	-	5.854

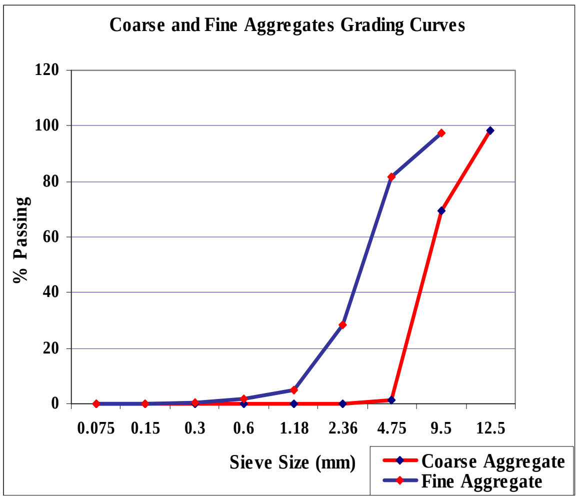


Figure (3): Gradation curves

Table 4. Composition of zircon sand

Mineral	Grade
Zircon	0.67-3.75%
Cerium	499-2168 ppm
Lanthanum	224-1065 ppm
Titanium	1.61-4.91%

Zircon Sand

As a raw of heavy mineral available in Jordan, its mineralogical composition is shown in Table 4.

Pigments Mineral Oxides

Pigments used to produce colored concrete were some raw materials available in Jordan and provided by the Natural Resources Authority, Amman.

Zeolite Tuffs

They are regarded as hydrated framework aluminum silicates of alkali and alkaline earth elements. This material was used as cheap reddish brown, grey and red pigments. The milled minerals were mixed with the other concrete constituents.

Lime

This material is a byproduct of the manufacturing process of white cement. It is produced in large amounts by the White Cement Factory, has no significant use and causes an environmental problem. It has been considered as a waste material for many years and several attempts have been made to find a suitable use for this material, but none of them was successful. It is used as a white pigment.

Bentonite

It is an absorbent aluminum phyllosilicate, impure clay consisting mostly of montmorillonite. There are different types of bentonite, each named after the respective dominant element, such as potassium (K), sodium (Na), calcium (Ca) and aluminum (Al). Experts debate a number of nomenclatorial problems with the classification of bentonite clays. Bentonite usually forms from weathering of volcanic ash, most often in the presence of water. However, the term bentonite has been used to describe clay beds of uncertain origin.

Mix Proportions

For all mix proportions (excluding mineral oxides) course aggregates: fine aggregates: sand: cement = 1100: 809: 373: 550 kg. The water used amounted to

308 liters. The amounts of mineral oxides added to the concrete mixes are shown in Table 5.

Table 5. Pigment weights, kg

Mix No.	Type of Pigment	Weight
1	Red Zeolite	74
2	Red Zeolite	111
3	Zircon Sand	185
4	Zeolite Tuff	74
5	Dark Grey Zeolite	74
6	Lime	148
7	Bentonite	74

From each mix, 12 cubes of 100×100×100 mm, 12 cylinders of 6"×12" and 12 prisms of 160×40×40 mm were cast. Specimens as shown in Figure 4 were tested to determine compressive, splitting and flexural strengths.

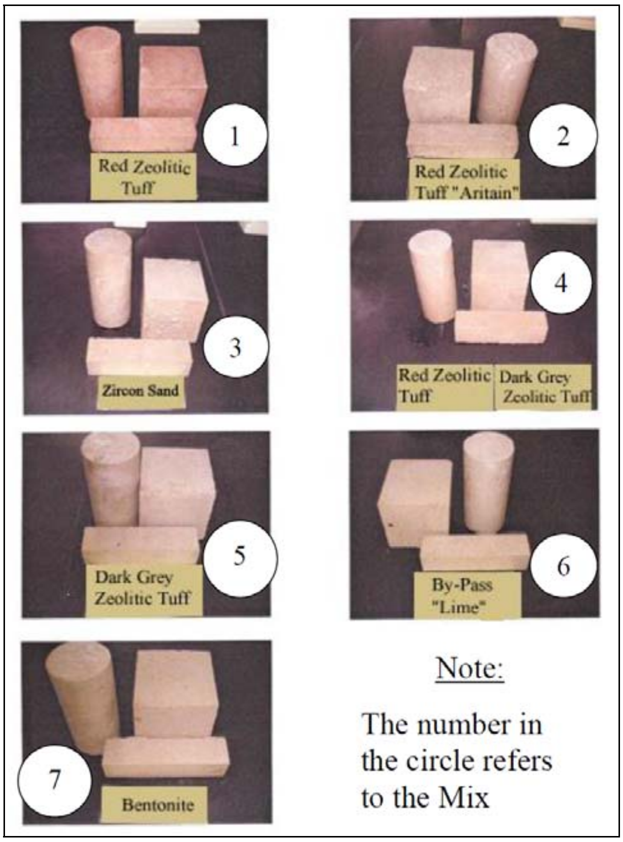


Figure (4): Produced specimens

Equipment and Test Setups

This study involved two major machines; namely: XRD and SEM machines, to determine the physical and chemical properties of the pigments used and to look into the matrix formation of the produced specimens. The principal author has designed special grips for direct tension. Direct shear was tested by an apparatus that is usually used for testing rock specimens. All equipment and test setups are shown in Figure 5. It is necessary to document the mechanical properties of the produced colored concrete aiming at laying out the basis for future development in terms of workability by using super-plasticizers, strength and perhaps self-compacting colored concrete. The experimental investigation was focused on twofold objectives; namely: the color of concrete and its strength.

RESULTS AND DISCUSSION

The resulting concrete is colored. The color of every pigment after mixing with the white concrete is illustrated in Table 6. The concrete is a structural concrete, since the compressive strength is achieved. The results of the colored concrete strength are recorded at failure, and the compressive strength values of the colored concrete mixes are comparable to those of conventional concrete made with similar mix proportions. Accordingly, the properties of the produced colored concrete were described through the classical testing procedures for compression, flexure, direct tension, splitting and direct shear. The recorded deformations *versus* applied load on the cylindrical concrete specimens were documented to estimate compressive stresses and the corresponding vertical strains. Since colors are preferable in vertical structural elements, it was important to measure the diametric compressive force by applying the splitting tensile strength. The results of the splitting test for the specimens are shown in Table 7.

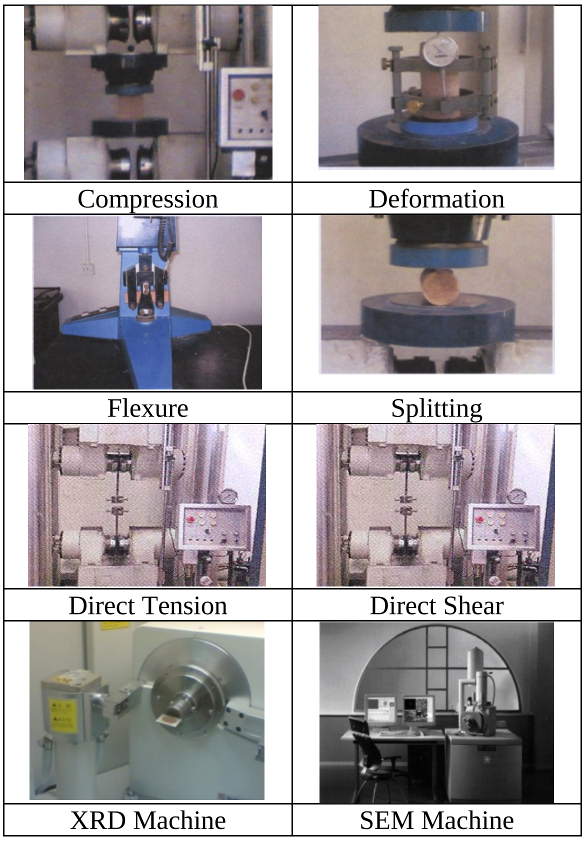


Figure (5): Equipment and test setups

The minerals which play the role of pigments in this research were tested using X-Ray Diffraction (XRD) technique to verify the existence of damaging elements. The values are coping with the predicted values according to ACI provisions.

Modulus of Rupture

This test was carried out according to ASTM C 293. 40x40x160mm prisms were tested. It is a measure of tensile strength of plain concrete to resist failure under bending. Flexural strength is expressed as the modulus of rupture, f_r. The modulus of rupture was then calculated by the formula $f_r = 3PL/2bd^2$, where: $b = 40\ mm$, $d = 40\ mm$, $L = 160\ mm$ and P is the applied load. The calculated results are presented in Table 8.

Table 6. Observed colors

Mineral	Color
Bentonite	Greenish
Red Zeolite	Dark Pink
Black Zeolite	Gray
Zircon Sand	Brown
Red Zeolite Tuff	Brown
Lime	White

Table 7. Compressive and splitting strengths, MPa

Mix No.	f_{cu}	f_c'	f_{sp}
1	37.73	27.00	2.246
2	35.86	25.10	3.218
3	34.03	23.14	2.708
4	38.30	27.56	2.850
5	37.87	28.40	2.804
6	32.33	23.30	2.466
7	28.98	20.74	2.656

Compressive Strength

It is regarded as one of the most important properties of hardened concrete. Further, it is the main property that the concrete mix design is based on. It is also used for the classification of concrete in national and international codes. The recorded results for the seven mixes of colored concrete specimens, whether cylinders or cubes, are presented in Table 8. It should be noted that the compressive strength of concrete was highly influenced by the type of pigment used and the *w/c* ratio of the mix. As is clear from the lime and bentonite mixes, these two mixes have higher *w/c* ratios, because lime and bentonite absorb water in their nature. For all colored concrete mixes, $f_c' = (0.70 – 0.72) f_{cu}$.

Splitting Tensile Strength

The results of tested cylindrical specimens under line load have been recorded. It can be seen from the results of the seven mixes that all parameters which influence the characteristics of the microstructure of the cement matrix and of the interfacial transition zone are of decisive importance with respect to the tensile load bearing behavior. Table 8 shows the calculated splitting tensile stresses for the seven mixes.

Table 8. Colored concrete strength indices

Mix No.		1	2	3	4	5	6	7
Measured	f_c'	27.00	25.10	23.14	27.56	28.40	23.30	20.74
	w	22.99	22.66	23.90	24.45	23.73	22.80	22.29
	f_{sp}	2.246	3.218	2.708	2.850	2.804	2.466	2.656
	f_t'	1.730	1.668	1.602	1.748	1.775	1.607	1.517
	f_r	6.850	7.260	6.710	8.210	7.210	6.760	5.800
Calculated	f_t'	1.123	1.609	1.354	1.425	1.402	1.233	1.328
	f_{sp}	2.700	2.505	2.313	2.756	2.841	2.331	2.074
	f_r	3.222	3.103	2.982	3.255	3.305	2.993	2.824
	$^{*}E_c$	24630	23238	24168	27291	24489	22300	20608
	$^{**}E_c$	24422	23547	22609	24673	25047	22687	21404
$f_t' = (0.5 - 0.7)\, f_{sp}'$; $f_{sp}' \cong 0.10\, f_c'$; $f_r = 0.62\sqrt{f_c'}$; $^{*}E_c = 0.043\mathrm{w}^{1.5}\sqrt{f_c'}$; $^{**}E_c = 4700\sqrt{f_c'}$								

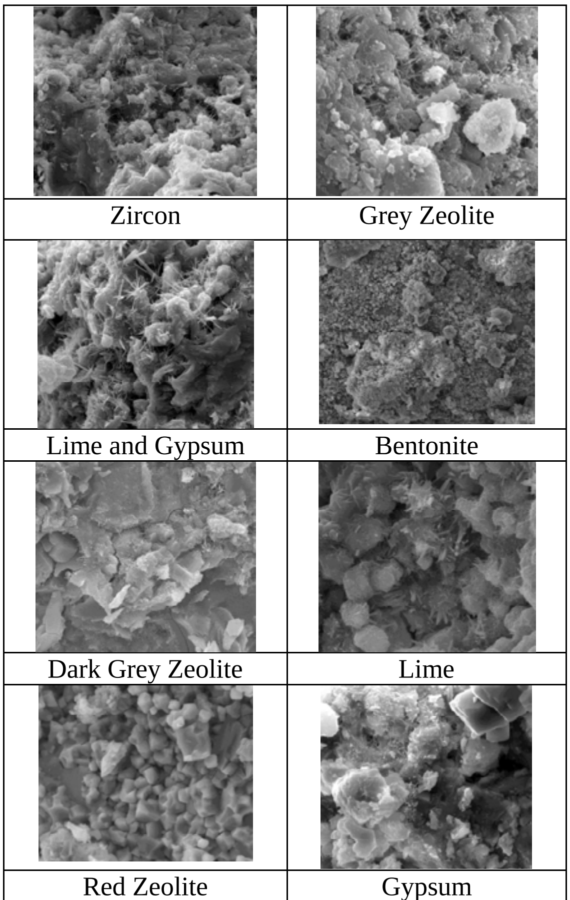


Figure (6): SEM micrographs of hardened colored concrete

Deformation Curves of Colored Concrete

The stress-strain curves for the seven mixes were plotted as shown in Figure 7. The resulting curves showed good trends that are complying with the concrete behavior, which started linear then completed with non-linear manner.

Direct Tensile Strength

Using the specially designed grips prepared to test prisms under direct tension load, tensile stresses, f_t', were calculated for specimens from the seven mixes. The results are shown in Table 8.

Modulus of Elasticity

Based on the ACI equations for estimating the modulus of elasticity of colored concrete, E_c, the computed values are nearly acceptable for all concrete mixes except for mix no. 4, where the concrete density, *w*, is noticeably higher than in other mixes.

Concluding Remarks

From Table 8, it is clear that the experimental values of splitting tensile strength and direct tension are conforming with the ACI equation values. The differences are in the flexural strength values due to two reasons. The first is that the specimen behaves like a deep beam, while the second is that the failure was due to a combination of shear and flexure. In other words, it was not due to flexure only. As can be seen in Table 9, the coefficients between the flexural strength and the square root of compressive strength are higher in comparison with the ACI code value (0.62).

Table 9. Regression models for colored concrete strengths

Mix No.	f_c\` and f_{cu}	f_{sp} and f_c\`	f_r and $(f_c`)^{0.5}$
1	$f_c` = 0.706265 f_{cu}$	$f_{sp} = 0.080843 f_c`$	$f_r = 1.323901 (f_c`)^{0.5}$
2	$f_c` = 0.696745 f_{cu}$	$f_{sp} = 0.128765 f_c`$	$f_r = 1.498657 (f_c`)^{0.5}$
3	$f_c` = 0.676885 f_{cu}$	$f_{sp} = 0.121506\ f_c`$	$f_r = 1.411866 (f_c`)^{0.5}$
4	$f_c` = 0.716236 f_{cu}$	$f_{sp} = 0.103613 f_c`$	$f_r =1.5944280 (f_c`)^{0.5}$
5	$f_c`= 0.713679 f_{uc}$	$f_{sp} = 0.085772 f_c`$	$f_r = 1.377373 (f_c`)^{0.5}$
5	$f_c` = 0.721365 f_{cu}$	$f_{sp} = 0.103343 f_c`$	$f_r = 1.430783 (f_c`)^{0.5}$
7	$f_c` = 0.715286 f_{cu}$	$f_{sp} = 0.128409 f_c`$	$f_r = 1.236677 (f_c`)^{0.5}$

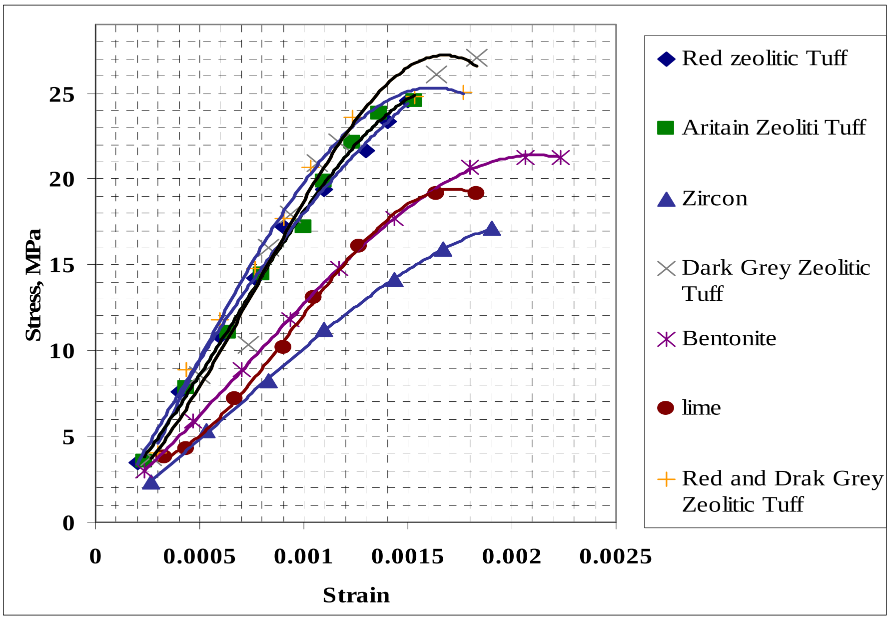


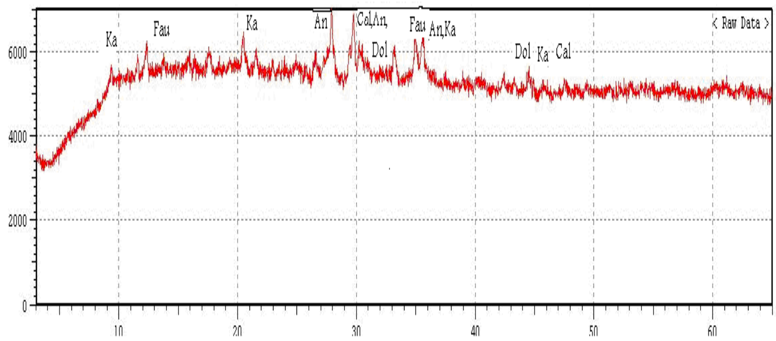
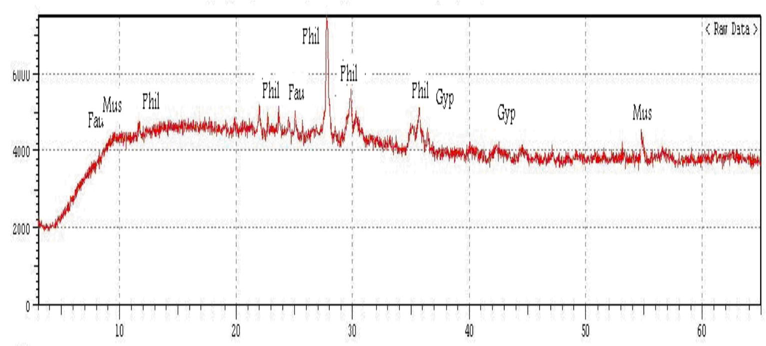
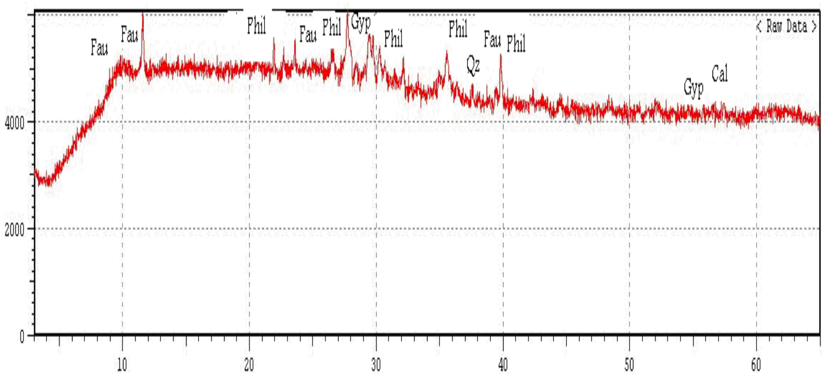
Figure (7): Stress-strain relationships for the seven colored concrete specimens

SEM and XRD Analyses

Scanning Electron Microscopy (SEM) is a good technique by which the microstructure of the resulting mixes becomes clear and the bond between the colored cement paste and the aggregates can be recognized. The SEM technique was applied to the seven resulting mixes. Figure 6 shows SEM micrographs of hardened colored concrete specimens.

Table 10 presents XRD traces of zeolite tuff and chemical composition for three tuffs used in this study and brought from three locations; namely: *Tal Remah*, *Mkawer* and *Al-Aritain*. The mix numbers for these tuffs are: 1, 4 and 5 as given in Table 5. From Table 8, one can observe that these pigments exhibited higher strength values relative to the rest of mixes.

Table 10. XRD traces of zeolite tuffs and their chemical composition

<table>
<tr><th>Area</th><th colspan="8">XRD Trace</th></tr>
<tr><td rowspan="3">Tal Remah</td><td colspan="8">
</td></tr>
<tr><td>Composition</td><td>SiO_2</td><td>Al_2O_3</td><td>Fe_2O_3</td><td>MgO</td><td>CaO</td><td>K_2O</td><td>Na_2O</td></tr>
<tr><td>%</td><td>42.0</td><td>12.8</td><td>12.1</td><td>10.1</td><td>8.5</td><td>0.8</td><td>4.0</td></tr>
<tr><td rowspan="3">Mkawer</td><td colspan="8">
</td></tr>
<tr><td>Composition</td><td>SiO_2</td><td>Al_2O_3</td><td>Fe_2O_3</td><td>MgO</td><td>CaO</td><td>K_2O</td><td>Na_2O</td></tr>
<tr><td>%</td><td>42.7</td><td>13.9</td><td>12.7</td><td>9.2</td><td>9.8</td><td>1.9</td><td>2.1</td></tr>
<tr><td rowspan="3">Al Aritain</td><td colspan="8">
</td></tr>
<tr><td>Composition</td><td>SiO_2</td><td>Al_2O_3</td><td>Fe_2O_3</td><td>MgO</td><td>CaO</td><td>K_2O</td><td>Na_2O</td></tr>
<tr><td>%</td><td>38.6</td><td>12.8</td><td>12.1</td><td>9.6</td><td>9.3</td><td>1.5</td><td>2.1</td></tr>
</table>

CONCLUSIONS

The following conclusions may be drawn from this study:

1. Natural resources of mineral oxides are available in Jordan in large quantities.
2. The study proved the feasibility of using these mineral oxides for colored products of concrete.
3. The use of produced pigments could be a substitute of imported chemical pigments. They are very cheap if produced on a large scale.
4. The produced concrete can be used as a structural concrete. The mechanical properties of colored concrete were recorded considering basic values without using workability agents.

RECOMMENDATIONS

Highly absorbent coloring filler materials could be further processed to alter the properties by heating, especially the "by-product" lime and similar materials. Colored aggregates that are available in Jordan can be used in the concrete mix or "seeded" into the mix. The polishing process will reveal these aggregates. Other pigments should be studied to produce other colors and to study the effect of other factors on the concrete final color. Further tests, such as abrasion resistance as related to performance and durability, may be investigated. The effect of pigment grain size on the color and strength of colored concrete may be a point to be considered. As structural concrete, the interaction with reinforcing bars and chemical effects of using oxides should be studied. The colored concrete technology by using workability agents and self-compacting colored concrete is a vital point for further research, so that this concrete can easily be cast in vertically coated walls and columns. Apart from the classical research on concrete, the extension of SEM and XRD techniques deserves significant attention. Further research should focus on nano-concrete materials in general and on colored concrete in particular.

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