Effect of nanoparticles of $\alpha$TiO$_2$ in artificial stone of produced from sludge of stone cutting factory (SSCF)

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Abstract: In recent decades, industrial growth and increased production and consumption of natural resources, raw materials are rapidly decreased and energy. On the other hand, high-volume of production produce large amounts of waste and waste has strong negative effects on the environment. The aim of this article, waste reduction and reuse them is stone cutting factory. The present invention is production a self-cleaning artificial stone by sludge stone cutting factory (SSCF) of Lorestan in Iran, which can be used in building materials, facade, paving, stones antique and composites. Basic formulation of artificial stone is the sludge stone, 50% weight of sludge stone is cement, 1-15% weight of cement is unsaturated polyester resin (UPR), 20-30% is water, 7% weight is the filler consists of micro-silica, nanoparticles of anatase titanium dioxide ($\alpha$TiO$_2$-NP) in absence of water pool. Nanoparticles of $\alpha$TiO$_2$ cause the hydrophobicity, analysis of oil stains, eliminate of bad odor, sterilize and self-cleaning artificial stone, can by adding pigments to them be produced diversity in artificial stone. Using micro-silica decreases specific weight and the density of product the greatly reduced.

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Keywords: Artificial stone; Sludge stone cutting factory (SSCF); $\alpha$TiO$_2$ nanoparticles ($\alpha$TiO$_2$-NP); Micro-silica; Unsaturated polyester resin (UPR); Cement.

INTRODUCTION

Mineral waste can be as residual materials or worthless substances after the extraction and processing of materials considered, they are arising the valuable productions. In recent years developed the use of waste stone mines and stone cutting factory$^{1-3}$. Some of these applications can be used to the manufacture of artificial stone, stone powder, types of cement, ceramic flooring and so on. Most crushed of Lorestan in Iran are travertine stones that travertine stone is very porous$^4$. Because of the travertine stone is porous while cutting and production of decorative stone for facade of building, losses is very high$^5$. Thus, more than 40% of the ore mined is wasted which are be released in around town (Figure 1), which is considered to be a major problem for the environment.
The sludge in this factory, as seen in Figure 1, are such as stones of broken which is unusable (with the dimensions of less than 10cm×10cm), sludge of cutting of mining stone, sludge has been created from cutting and polishing the stone.

Aim of this paper is reuse sludge of stone cutting factory and productsof artificial stone with high resistance, self-cleaning, water and dust is escaping. For this purpose, is used the addition of inorganic nanoparticles and some other organic materials\cite{6-8}. The Nanoparticles of titanium dioxide (TiO$_2$-NP) has three different crystalline structures of anatase, rutile and brokit. Anatase makes a beautiful view for stone surface. For those self-cleaning behavior of TiO$_2$ is used in building materials and structures\cite{9-12}, such as: As cement mortars, exterior tiles, paving block, glasses, paints, finishing coating, road block and concrete pavement.

**MATERIALS AND DEVICES**

The $a$TiO$_2$–NP is the product of MERK, Portlandcement type II: this kind of cement has average properties is means that setting time is low and is resistant in sulphate compounds, in this type of cement decreases amounts of tri-calcium silicate and di-calcium aluminates and increases di-calcium silicate\cite{13}. Another materials: unsaturated polyester resins (UPR), micro-silica powder, Si is the product of MERK and sludgeof stone cutting factory (SSCF) (produced in factory of around doroud city).

Devices required in this study are: press or kicker, mixer, water meter or meter setting (JOINT STARS GROUP LIMITED). Templates with sizes: 5×5×5 and 16×4×4 cm$^3$.

**EXPERIMENTAL METHODS**

For test of samples are used templates with sizes: 5×5×5 and 16×4×4 cm$^3$. According of formulation of TABLE 1, the composition of artificial stone base was determined. The percent composition of weight (%Wt.) of cement was determined ratio to %Wt. of SSCF and other materials were determined to the %Wt. of cement. It should be noted that mixes or formulations of the samples are selected in accordance
Methods of preparation of artificial stone

Initially cement is weighed that is equivalent of 50% SSCF weight and water is 20-30% Wt. of cement. Water and cement mixed into blender that is stirred for one minute by low rpm. To mixture of water and cement are added SSCF, unsaturated polyester resins (UPR) and filler (7% Wt. micro Si or calcium carbonate for minimize pores) then are stirred for 1.5 minute by high rpm. The mixture is ready for molding.

The molding method of artificial stone

After cleaning the templates, templates is been fat and seams is sealing by grease, then be installed on kicker device. A layer of the mixture is poured into a templates and turn on the kicker machine, and 60 hit to be imported. After the second layer is poured and then hit 60 the mixture is set to air leak. Then templates is put for 24 hours in a humidity bath (θ =30°C and ω =90%) and open it, and in the absence of water in the pool water 20°C period (3, 7 and 28 days) put. Unlike concrete composite showed better resistance in absence of water that TABLE 2 shown its results.

Compressive strength test

The UK test standard BS EN 12390-1: 2000 and BS EN 12390-2: 2000 are performed. The samples oftentimes after drying placed on the compressive strength that are divided into two pieces. Which \( t_1 \) and \( t_2 \) are the initial and final time respectively, compressive strength is calculated:

\[
\text{Compressive strength} = \frac{1}{2} (t_1 + t_2)
\]

TABLE 1: The formulation of composition of artificial stone base

<table>
<thead>
<tr>
<th>Material</th>
<th>% Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSCF</td>
<td>Same as mold</td>
</tr>
<tr>
<td>Cement</td>
<td>50% Wt. of SSCF</td>
</tr>
<tr>
<td>Unsaturated polyester resins (UPR)</td>
<td>1-15% Wt. of Cement</td>
</tr>
<tr>
<td>H₂O</td>
<td>20-30% Wt. of Cement</td>
</tr>
<tr>
<td>Micro Si or CaCO₃</td>
<td>7% Wt. of Cement</td>
</tr>
</tbody>
</table>

with ACI 211.1-91 Standard America[14].

TABLE 2: The physicochemical properties of artificial stone from SSCF in different combination

<table>
<thead>
<tr>
<th>Sludge of stone cutting factory (SSCF)</th>
<th>Cement (C)</th>
<th>Water</th>
<th>Unsaturated Polystyrene resin (UPR)</th>
<th>Compression Strength testing</th>
<th>Flexural strength testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>gr</td>
<td>% Wt. to SSCF</td>
<td>gr % Wt. to C</td>
<td>gr % Wt. to C</td>
<td>gr % Wt. to C</td>
<td>gr</td>
</tr>
<tr>
<td>177</td>
<td>50</td>
<td>88.5</td>
<td>30</td>
<td>26.55</td>
<td>10</td>
</tr>
<tr>
<td>177</td>
<td>50</td>
<td>88.5</td>
<td>25</td>
<td>22.13</td>
<td>12</td>
</tr>
<tr>
<td>177</td>
<td>50</td>
<td>88.5</td>
<td>20</td>
<td>17.70</td>
<td>15</td>
</tr>
</tbody>
</table>
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Unit of compressive strength is kN and for conversion kN to bar (kg/cm²), units are multiplied in 6.37 constant.

\[ P(kN) = t_1 - t_2 \]

Flexural strength test

The tensile strength test, applies axial tension were taken the samples. Due to the shape of templates is problem the force exerted In line with the axis. Therefore the tensile strength calculated by indirect methods, in the bending test and the splitting (split-half) as per standard BS EN 12390-5: 2000 was conducted using the flexural strength \[ P \text{ (kg/cm}^2 \text{)} = \frac{t_1 - t_2}{2} \times 6.37 \]

RESULTS AND DISCUSSIONS

The sludge of natural stones like rock powder and need not sieve. The best samples given according to results of TABLE 2 are thirds of the sample that their compressive and flexural strength are most other samples. In this sample was prepared by formulation basic: the 177 gr of SSCF, cement is 50% Wt. of SSCF, water is 20% Wt. of cement and UPRs are 12% Wt. of cement. Figure 3 is the optical microscope images of the artificial stone are produced with formations of TABLE 3. As is visible in Figure 3, the dark areas show porosity in artificial stone and the artificial stone of 25% Wt. of water and 12% Wt. of UPRs relates to cement is less porous (part of b in Figure 3).

To reduce the porosity of this sample, the fillers (micro Si and CaCO₃) are added them to 7% Wt. of cement. In TABLE 3 is shown their formulation and the samples were dried in the absence of pool water, samples containing calcium carbonate (unlike concrete) are been soft and disintegrated. But samples containing micro Si are with a porosity of less and strength.

According to the results in TABLE 3, the physicochemical properties of this formulation are not satisfactory. To enhance its properties to micro-silica, are added nanoparticles of \( \alpha \text{TiO}_2 \) in % Wt. of different.

In TABLE 4 are the physicochemical properties of this samples that the micro Si filler content is 7% Wt. of cement with different combining the percentages of \( \alpha \text{TiO}_2 \)-NP.

Samples obtained have a smoother surface and glossier surface than before samples and the compressive strength of samples with different % Wt. \( \alpha \text{TiO}_2 \)-NPs are better and time of coherence of

Figure 3: The optical microscope images of the artificial stone with: a) water is 30% Wt. of cement and UPRs are 10% Wt. of cement, b) water is 25% Wt. of cement and UPRs are 12% Wt. of cement and c) water is 20% Wt. of cement and UPRs are 15% Wt. of cement.
TABLE 3: The physicochemical properties of artificial stone from SSCF with 7% of filler equal 6.19 gr

<table>
<thead>
<tr>
<th>Kind of filler</th>
<th>sludge of stone cutting factory (SSCF)</th>
<th>Cement (C)</th>
<th>Water</th>
<th>Resin polystyrene unsaturated</th>
<th>Compression strength testing</th>
<th>Flexural strength testing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gr %Wt. to SSCF gr %Wt. to C gr %Wt. to C gr</td>
<td>kN MP kN MP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micro Si</td>
<td>177 50 88.5 25 22.13 12 10.62 39.00 15.51</td>
<td>8.55 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO₃</td>
<td>177 50 88.5 25 22.13 12 10.62 0 0</td>
<td>0 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 4: The physicochemical properties of artificial stone from SSCF with % Wts. of αTiO₂-NP filler

<table>
<thead>
<tr>
<th>αTiO₂-NP</th>
<th>sludge of stone cutting factory (SSCF)</th>
<th>Cement (C)</th>
<th>Water</th>
<th>Resin polystyrene unsaturated</th>
<th>Compression strength testing</th>
<th>Flexural strength testing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%Wt gr %Wt. to SSCF gr %Wt. to C gr %Wt. to C gr</td>
<td>kN MP kN MP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.45 177 50 88.5 25 22.13 12 10.62 43.12 2.68</td>
<td>9.09 2.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>13.28 177 50 88.5 25 22.13 12 10.62 49.00 3.06</td>
<td>10.33 2.52</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>22.13 177 50 88.5 25 22.13 12 10.62 60.25 4.12</td>
<td>12.70 3.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>30.98 177 50 88.5 25 22.13 12 10.62 81.15 5.23</td>
<td>17.11 4.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>39.83 177 50 88.5 25 22.13 12 10.62 88.36 6.34</td>
<td>18.63 4.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4: The optical microscope images of the artificial stone with: a) 5%, b) 15%, c) 25%, d) 35% and e) 45% Wt. of αTiO₂-NP filler. The combination is lower than other samples. Figure 4 shown, higher percentage of αTiO₂-NP in artificial stone production are decrease porosity and linkage between the particles increases.
As is visible in Figure 4 of part (d) and (e), porosity of samples are less and have smooth surface. The physicochemical properties of samples are more (TABLE 4). Comparing the TABLES 3 and 4, the compressive and flexural strength add with increasing these fillers.

All artificial stones produced by the percentage combination of \( \text{aTiO}_2 \)-NPs have hydrophobic properties. By placing the samples in water, their surfaces do not absorb water. And the amount of fatty oil was spread across on the surface of the sample (45% Wt. of \( \text{aTiO}_2 \)-NP), oil was analyzed in the light of sun and did not have any effect on its level.

CONCLUSION

The aim of this study is conversion of sludge of stone cutting factory (SSCF) to artificial stone and the recovery of natural resources. The results show, the physicochemical properties of artificial stone prepared from sludge of stone cutting factory (SSCF) of Doroud city in Iran are better because the percentage of lesions of travertine stone is more at waste of factory; properties of this kind of artificial stone have improved.

Unlike concrete, the compressive and tensile strength of artificial stone is been better in exposed to air and without the presence of water pool and fillers of CaCO\(_3\) would be prepared to soften artificial stone. The \( \text{aTiO}_2 \)-NP fillers are increasing the physicochemical properties of them and the porosity of samples is been less. With increasing it, artificial stone properties prepared show a significant increase and these properties are increased in the passage of time.

Crystal of anatase titanium dioxide nanoparticles have excellent expansion of surface, therefore, increasing this filler to artificial stone is caused, its surface is been smooth and glossy and show properties of water and dust escaping.

REFERENCE

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