Using of Nanoparticles Extracted from Rice Husk as Cementitious Material for Sustainability Issues.

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Abstract
There are many sources of CO₂ emissions in the world. This study concentrates on two of the most important sources of CO₂ emissions. The first one is from Portland cement production as a main component of Portland cement concrete (PPC), which is the main pillar of the construction industry. The second source is due to the burning of rice husk (RH) from rice industry. Based on this information, if different types of Nanosilica particles that can be extracted from rice husk, preventing its random burning, and replace part of Portland cement (PC) in PC concrete as a pozzolanic material, which can be considered as a multiple solution for solving the previous mentioned problems of CO₂ emissions. The main objective of this study is to investigate the pozzolanic activity of these nano particles (NPs) as it can be used as cement replacement material. Also, give an important usage of rice husk by extracting the nanoparticles from rice husk instead of the random burning of it. An extensive experimental program has been conducted to examine the pozzolanic activity of different nanosilica particles extracted from rice husk using two testing methods. The first method is the electrical conductivity measurement and the second is the strength activity index according to ASTM C311, in each method there are different types of nanosilica (NS) compared to silica fume (SF), which well known as pozzolanic material and also compared to Marble Powder as an inert waste material. The results of the electrical conductivity method show that, the Nanosilica 1 has superior pozzolanic activity compared to the other materials used in this study. On the other hand, the using of the second method (strength activity index) both NS and SF almost give the same pozzolanic activity, it may be related to that, the nanoparticles didn’t disperse in the cement matrix. According to these results the nanosilica could be used as a good replacement of Portland cement due to its pozzolanic activity, which leads to lower emissions of hazards gases in cement manufacturing as well as using the rice husk as waste material.

Keywords:
Nanoparticles; Nanosilica; Rice Husk; Pozzolanic activity; Conductivity; Sustainability; Waste Materials

1. Introduction
It is well known that, huge emission of carbon dioxide and other hazards gases are produced from cement industry to the atmosphere, which leads to environmental problems. CO₂ gas represents more than 65 % of Global Greenhouse Gas Emissions [1]. There are many industrial processes that give by-products to be used as Portland cement replacement materials to reduce Portland cement usage [2-4] and achieve sustainable and durable concrete [5-8].
Rice husks (RHs) produced from the rice production are a bulky biomass with high silica content. The anticipated world rice production in 2016 is 746.1 million tons. This means that, approximately 186–260 million tons of RH biomass was generated globally in 2016 [9]. Silica and lignocellulose (LC) are two main components of RH, which lead to the usage of it in the production of silica or cellulose nanoparticles (NPs). Due to the tough nature, low nutritional value and great bulk of RH, its application has been limited [10]. The two most common RHs disposal methods are open field burning and land filling, which result in energy waste, greenhouse gas emission, air pollution, and huge landfill space occupancy due to their low bulk density [11, 12].

A pozzolan is defined as “a siliceous and aluminous material, which in itself, possesses little or no cementitious value, but which will in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties” [13-17].

Long years ago both of natural pozzolans and industrial by-products were used as supplementary cementing materials (SCMs). Using pozzolans as nanosilica extracted from RH as cementitious material provides a sustainable solution by using nanotechnology, which leads to a significant reduction in the CO₂ emissions associated with Portland clinker production. Also, the use of RH in the extraction of nanosilica will be getting rid of random burning of it. In addition to economic and environmental benefits, using of pozzolan (PZ) in the cement industry improves the durability, and mechanical properties of concrete and mortar [18-24]. Pozzolanic materials have proven to be efficient alternative materials that meet the sustainability requirements; this is because it allows using of waste in the production of PCC. In addition, the partial replacement of PC by such material will lead to reduce the amount PC, fuel consumption and CO₂ emissions.

The objective of this research is to prove that the Nanosilica extracted from rice husk can replace the cement as supplementary cementitious material or as a pozzolanic material. The main reason for replacement of cement was lowering emissions of hazards gases from both cement production and also random burning of rice husk.

Several methods have been developed to determine the pozzolanic activity; many of these methods are based on the measurement of a property that is directly related to concrete applications [25]. These methods can be divided into direct and indirect methods. The direct methods related to the presence of Ca(OH)₂ and its reduction with time as the reaction between calcium hydroxide and silica occurs, using analytical methods such as X-ray diffraction (XRD), thermo-gravimetric analysis (TGA) and other methods. The indirect test methods measure a physical property of a test sample that indicates the extent of pozzolanic activity. This may involve measurement of properties such as compressive strength, electrical conductivity and other methods. Compressive strength test methods have been used to assess the pozzolanic activity of coal bottom ash, glass powders, crushed bricks, silica fume and sewage sludge ash [26]. Electrical conductivity and pH measurements were used to determine the pozzolanic activity of the fluid catalytic cracking (FCC) in aqueous suspensions of pozzolan/calcium hydroxide [25]. Results from an indirect pozzolanic activity test are often corroborated using direct tests to confirm that pozzolanic reactions are occurring [26].
Nanotechnology is one of the frontiers of science today. As a matter of fact, nanotechnology could affect us all, beyond nanoparticles, critical length scales and nano-tools [27]. There are many methods used for nanoparticles production, an approach for comprehensive utilization of RHs have been developed to obtain both lignocellulose and high quality porous silica nanoparticles from RHs. Most of the lignocellulose in RHs was first extracted by dissolving in ionic liquids. The dissolved lignocellulose was subsequently separated and collected. The remaining RH residue after extraction that contains a high concentration of silica was thermally treated to synthesize amorphous porous silica nanoparticles with a high purity and surface area [27].

The main aim of this research is to examine the pozzolanic activity of nano-silica extracted from rice husk waste with no value material with different production techniques, this will allow us to replace the cement as supplementary cementitious material for better environmental sustainability. In addition to compare the efficiency of different types of nano-silica with other well-known pozzolanic material such as “silica fume”. To achieve this goal an experimental program has been conducted to examine the Pozzolanic activity of Nanosilica 1 and Nanosilica 2 extracted from rice husk, using two different method of extraction compared to SF, which have highly pozzolanic activity and Marble Powder as an well-known waste inert material. The testing of the pozzolanic activity for all materials in this study through two methods, the electrical conductivity measurement and the second method is the strength activity index according to ASTM C311.

2. Materials and Experimental Test

2.1 Materials

The aggregate used is clean siliceous sand with 0.6 mm of maximum aggregate and also was graded sand that’s satisfying the ASTM C618. Cement (OPC Type 1 32.5N). %95 Pure calcium hydroxide (CH) form MORGAN SPECIALITY CHEMICALS CO. Silica fume (SF) from Sika Company, contains extremely fine (0.1 mm) reactive silicon dioxide with bulk density = 300 kg/m$^3$ and TEM images as shown in Fig 1. Nanosilica 1 (NS 1) from NanoTech Company with mean particle size= 40 nm and TEM images as shown in Fig 2. Nanosilica 2 (NS 2) from NanoTech production Company with mean particle size= 20 nm and TEM images as shown in Fig 3, both of them produced by NanoTech Company as in Fig 4. Commercial Marble powder was produced from local source in Cairo (Shak El Taban).

Fig. 1: TEM image for SF Fig. 2: TEM image for NS1 Fig. 3: TEM image for NS2
2.2 Pozzolanic Activity Measuring Methods

The pozzolanic activity has been measured in this study through two methods one of them was the electrical conductivity method and the other was strength activity index method (SAI) as in the ASTM C311.

2.2.1 Electrical Conductivity Testing Method

The electrical conductivity was used to determine the pozzolanic activity of the different types of nano silica and other materials in aqueous suspensions of pozzolan/calcium hydroxide. The electrical conductivity of aqueous suspensions of Nano silica 1 (NS 1), Nanosilica 2 (NS 2), Silica fume (SF) and Marble Powder (MP) in the absence of calcium hydroxide were measured which indicated by C0 using one gram of pozzolan was added to 50 mL of distilled water into a sealed beaker at 40 °C. Then, the electrical conductivity measurements were recorded for a total period of 10,000 second at 40 °C by using HACH (HQ430d flexi) electrical conductivity meter [24]. The electrical conductivity of dissolved lime in the distilled water in the absence of pozzolan indicated by CL and the electrical conductivity of the aqueous suspension of the pozzolan with of calcium hydroxide indicated by CF was measured as follows: an unsaturated solution of calcium hydroxide was prepared by dissolving 40 mg of CH with 50 mL of distilled water in a closed sealed beaker to prevent carbonation, and then raising the temperature to 80 °C to accelerate dissolution by using a heater. Subsequently, the temperature was decreased to 40 °C, and 1 g of the mineral under study was added (SF, NS 1, NS 2 or MP). Next, the electrical conductivity of the solution was immediately measured for a total time of 10,000 s. But for the calculation of the loss in the conductivity in percentage %LC as in equation 1, the electrical conductivity of dissolved lime in the distilled water in the absence of pozzolan must be also measured.

\[
%LC = \frac{CL-((CF)-(C0))}{CL} * 100
\]  

The assessment of the pozzolanic activity of materials by measuring the electrical conductivity in aqueous suspensions takes into account the fact that the OH⁻ and Ca²⁺ dissolved in water react with the silica from the pozzolan to produce insoluble products, such as calcium silicate hydrate (CSH). The decline of these ions in solution decreases the electrical conductivity of the solution, if the solution is unsaturated with respect to CH. Because the pozzolanic reaction causes a reduction in the concentration of OH⁻, a decrease in the pH of the system also occurs;
this means that the relation between the % loss in conductivity and the pozzolanic activity of materials under test is directly proportional [24].

2.2.2 Strength Activity index

Strength activity index is a standard test in ASTM C311 and the test is based on measuring the compressive strength values of test mortar and control cement mortar by using compressive testing machine. The weights for the mixture of the control sample given in the standard to make six cubes (50mm*50mm*50mm) are cement (500 g), water (242 g), and sand (1375 g). In accordance with ASTM C311 [12], 20% by weight of the cement used in the control mortar was replaced with the tested material to prepare the test mortar, while the mix designs used in this study as shown in Table 1.

Table 1: Mix Design for all tested materials.

<table>
<thead>
<tr>
<th>Name of Sample</th>
<th>Cement (Kg)</th>
<th>Water/Binder Ratio</th>
<th>Sand (Kg)</th>
<th>SF (%)</th>
<th>NS1 (%)</th>
<th>NS2 (%)</th>
<th>MP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.5</td>
<td>0.484</td>
<td>1.375</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SF</td>
<td>0.4</td>
<td>0.564</td>
<td>1.375</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NS1</td>
<td>0.4</td>
<td>0.58</td>
<td>1.375</td>
<td>18</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NS2</td>
<td>0.4</td>
<td>0.6</td>
<td>1.375</td>
<td>18</td>
<td>-</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Marble Powder</td>
<td>0.4</td>
<td>0.6</td>
<td>1.375</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
</tbody>
</table>

The Flow was constant for all Mixtures

It has been indicated that, water content of the test mortar should be adjusted according to the required flow according to that of the control mix flow. Since Specification C 618 specifies that “meeting the 7 day or 28 day Strength Activity Index will indicate specification compliance” only one age might be required. At the option of the producer or the user after preparing six-cube batches, only three cubes of control and test mixtures need to be molded for either 7 or 28 day testing [28]. To determine the compressive strength, as specified in Test Method C 109/C 109M, is depending upon how many specimens were molded as prescribed in the section on Number of Specimens [29]. Calculation of the strength activity index with Portland cement is done as follows:

Strength activity index with Portland cement = (A/B) *100

Where:
A = average compressive strength of test mixture cubes, MPA, and
B = average compressive strength of control mix cubes, MPA.

3. Results and Discussion

In this section the results of both conductivity test and SAI test for all tested materials will be represented and discussed.

3.1 Conductivity Results
The relation between the conductivity in (µs/Cm) and time in (sec) for lime and other tested materials is shown in Fig. 5, from this figure it was clear that Co must be measured before the calculation of % of loss in conductivity. This means that, the conductivity of the solution can increase, due to the presence of soluble salts in the tested materials.

![Graph showing conductivity values over time for different materials](image)

**Fig. 5: Conductivity values (µs/Cm)**

Fig. 6 shows the relation between the percentage of loss in conductivity and time for different materials; NS1, NS2, SF and MP, from this figure it can be shown this NS1 compared to other materials. The rate of loss in conductivity for nanosilica compared to other materials in the first 30 min of the test was very high which it could speed the rate of the pozzolanic reaction.

![Graph showing % loss of conductivity over time](image)

**Fig. 6: The % of Loss in Conductivity for all materials**

The results are summarized in Fig. 7, from this figure it can be indicated that, % of loss in conductivity for NS 1 has the superior % of loss in conductivity at 90% compared to other material. Also indicate that NS 1 can be used as cement replacement material with more pozzolanic activity than silica fume by 100% greater enhancement than NS2 and MP. This may be related to the large difference between the surface area between Nano silica and micro silica.
(silica fume), which directly proportional with the reaction between silica particles and Calcium hydroxide. While the large difference in pozzolanic activity between two types of nanosilica may be related to differences in both the properties of surface and also the contact angles between them.

![Graph showing % of loss in conductivity for different materials](image)

**Fig. 7: The Maximum % of Loss in Conductivity for all materials**

### 3.2 Strength Activity Index Results

The SAI test was performed according to ASTM C311 to NS1, NS2, SF and MP with ratios as shown in Table 1. The results for the water to binder ratios for all mix are shown in Fig. 8. From this figure the mixes contains NS1 and NS2 needed more water than the mix contains SF, this may due to the large difference between nanosilica and silica fume.

![Graph showing W/C Ratio for different materials](image)

**Fig. 8: W/C Ratio for different mixtures in the SAI**
Fig. 9 shows SAI for different mixes; NS1, NS2, SF and MP, from this figure it is clearly shown that replacing cement by other pozzolanic material slightly decreases the S.A.I. In addition, the results of the SAI showed that the used NS1 and NS2 in addition to silica fume almost decrease the SAI by 3 and 11% respectively, while the marble have 15 % decreased than the silica fume replacement. This decrease of SAI when adding nanosilica to silica fume may be related to adding the mixture of nanosilica with silica fume in the cement mixture without dispersion.

**Fig. 9: The Results of SAI**

It concluded that, in spite of the enormous increase for consumption of Ca(OH)$_2$ in the conductivity method for NS1 than SF, it is shown that the SAI of NS1 is reduced than SF. This difference in comparing the pozzolanic activity using both methods may be due to two factors, first; the real chemical reaction between silica components in the tested materials and Ca(OH)$_2$ in the absence of cement matrix in the first measurement method, while in the second method the dispersion of this nanoparticle in the mixture is a main factor affecting the compressive strength of the tested materials for avoiding agglomeration of this nanoparticles and loss its main advantage “nano-dimension”. The second factor; in the strength activity index method the flow must be constant for all tested mixture which leads to change the quantity of water in each test which can lead also to the reduction of compressive strength of the cubes as shown in Fig. 8.

**4. Conclusions**

The main problem that has been studied in this research was how to reduce the large emissions of CO$_2$ due to not only by reducing the amount of cement used in construction but also by using of nanosilica that can be extracted from Rice husk instead of random burning of it. While the main objective of this study was to investigate the pozzolanic activity of nanosilica particle extracted from rice husk to be used as cementitious material. From this study it can be concluded that:

- NS 1 has shown that it has the lead in the pozzolanic activity compared to any other materials used in this research.
• NS 1 gives greatest % of loss in conductivity which is doubles that of SF.
• NS 1 show a very high rate of loss in conductivity in the first 30 minutes which leads to accelerate the pozzolanic reaction.
• It was shown that in the SAI the water to binder ratio was not constant to achieve the constant flow, which means that NS1 needs more water than SF.
• The results of SAI shows that there are a reduction of the pozzolanic activity of NS 1 compared to SF.
• The dispersion of nanoparticle is main problem affecting the SAI results.

By proving the pozzolanic activity of the nanosilica extracted from rice husk can lead the future work in the environmental phase of lowering the % of CO₂ emissions, other hazard gases, also their bad effect on the environment and for better sustainability. Recommendations for future work are to make the SAI with constant water to binder ratio.

5. REFERENCES


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