Characterization of The Marble Sludge of The Shaq El Thoaban Industrial Zone, Egypt and Its Compatibility for Various Recycling Applications

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Abstract: The marble industry in Egypt showed a remarkable progress in the last few years as witnessed from the rates of production which reached 4.5 million tons in year 2011. Huge wastes result from the quarrying and the processing of marble; these wastes have negative impacts on the environment and the sustainable development. The marble cutting wastes are mainly generated in the form of solid parts and aqueous sludge. Water content, size analysis distribution, whiteness index, and chemical characteristics were determined for the marble sludge samples to evaluate its computability for various recycling applications.

Key words: Sludge, Filter press, Whiteness, Recycling, Compatibility.

INTRODUCTION

The marble industry in Egypt showed a tremendous development in the last 16 years, Investments of more than 1.5 billion $ were inducted in this industry and the result is that Egypt occupies the Fifth position among the stone producing countries and has the fourth world ranked marble and granite industrial zone (Shaq El Thoaban, East of Cairo).

The great demand of the Egyptian stones in the export markets led to produce the required amounts regardless of their quality and that could only be possible through using conventional quarrying methods (explosion), which has a destructive effect on the quarry sites and cause huge wastes (> 66 %) estimated as 6.4 million tons yearly (Egyptian marble strategy study, 2005), which are accumulated in the quarrying areas and has a negative effect on the sustainable development of these areas as new quarry sites.

Marble processing lines in the factories (marble is a commercial name for all types of hard compact carbonate rocks that are capable to attain surface polishing), produce also huge amounts of wastes either solid wastes (result from shaping of the irregular blocks and cutting slabs, fractured blocks and the rejection of broken or damaged slabs and tiles), and liquid wastes (slurry, resulted from sawing the blocks to slabs and grinding and polishing processes). The random disposal of these wastes, estimated as one million tons yearly, (Egyptian marble strategy study, 2005), in the areas near the factories (irrespective of their possible economic values) and with the increasing production cause severe environmental problems, such as land degradation, increase wastage of minerals, air pollution, water pollution, dust, damage to flora and fauna and human resources displacement.

Establishment of a thorough waste management plan generates a multitude of advantages for the marble industry, these include the following:

• Improved health and safety: Decreasing the amount of scrap piles, airborne particulates, and general trash creates a healthier and safer environment for employees.
• Reduced storage, transport, and disposal costs: With less waste to store and transport, the costs of handling waste are diminished.
• Potential generation of revenue: Scrap stone, sludge, and other waste products can be sold on an array of markets, creating a secondary company revenue stream.
• Increased Efficiency: Decreasing the amount of material lost during the quarrying, crushing, and cutting processes increases efficiency and the quantity of profitable product.
• Enhancement of industry reputation: Comprehensive, proactive waste management practices can result in not only a socially responsible reputation but in greater community acceptance of the quarrying operation, Natural stone council, (2009).

Regarding the value of the wastes and their negative impact on the environment it is very important to study in detail their characteristics and their suitability for recycling in different products, which will increase the investments in the Egyptian marble industry and hence its development as a key player of the world marble producing countries.

Sampling:

Twenty five marble sludge samples were collected from 25 selected factories using filter press for recycling water, (Fig. 1), the samples were collected periodically within a period of 6 months to monitor all the variations
in the sludge composition. For each factory, a representative sample was prepared through mixing and homogenizing equal weights of the collected sludge samples.

Fig. 1: Accumulation of sludge resulted from the water recycling using filter press.

Methodology:
The marble sludge representative samples were analyzed in order to determine their characteristics, the analyses include: Water content percentage (humidity), size distribution using laser size analyzer, the whiteness index. The chemical analysis by gravimetric method was applied to determine CaO and MgO and hence calculation of the CaCO3 and MgCO3.

Sludge Characteristics:
1- Water Content:
The water content of the marble sludge samples was determined by heating the samples for two hours at 105°C (until reaching constant weight), the results are shown in Table (1), the average water content of the marble sludge samples is 17.26%, the variation of water content from 1.25 to 44.12 %, reflects the sludge condition at the time of sampling whether almost dry or having more water content due to dysfunction of the filter press process.

Table 1: Water content, Whiteness and size analyses of the studied sludge samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Water content %</th>
<th>Whiteness</th>
<th>Size analyses</th>
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<td></td>
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Average 17.26 74.75 3.4 84.93 11.67 100
2- Size Analysis:
The results of the size analysis of 18 marble sludge samples are shown in Table (1). The results of the size analysis show that, the dominant size of the marble sludge samples is the silt size (63-2 µm), which forms 84.9% of the marble sludge samples as a result of the friction between the diamond beads and the marble blocks. The clay size fraction (<2µm) form about 11.6% of the marble sludge samples. Sand fraction (µm > 63) in the marble sludge represents about 3.4%, Fig. (2).

3- The Whiteness Index:
Most of the marble sludge samples are the powder of limestone and the colour of their dry powder is almost white. The whiteness index of the marble sludge samples is shown in Table (1), it ranges from 60.04 to 85.18 % with an average of 74.75 %, which is far less than the calcium carbonate whiteness requirements for paints and fillers. The variation of the whiteness value reflects the variation in the chemical composition of the processed marble samples.

4- Chemical Analysis:
The sludge samples were analysed chemically to determine the percentages of their different constituents. Gravimetric method was used to determine CaO and MgO and then estimating the CaCO\textsubscript{3} and the MgCO\textsubscript{3} values, which are the main constituents of the marble sludge resulting from sawing, cutting and polishing marble, limestone and dolomites, (Table. 2). The calcium carbonate content of the marble sludge samples varies from 82.58% to 98.84% with an average of 91.53%. Magnesium carbonates are not dominant as most of the sludge is produced from marble sawing; the magnesium carbonate ranges from 0 to 11.44 % with an average of 1.48%. The acid insoluble residue varies from 1.15 % to 22.27% with an average of 7.34%. This residue represents all the clays and sands encountered in the processed marbles and all contaminants that could be added to the sludge during the processing.

RESULTS AND DISCUSSIONS
The discussion of the previously obtained data will be focussed on the averages and the overall compositions and sizes of the collected sludge samples, form the selected 25 marble factories in Shaque Al Thoaban industrial zone. The previously mentioned analyses illustrate some important characteristics of the studied marble sludge wastes which affects, greatly, its utilization as a raw materials in some industries.

The chemistry of the limestone sludge shows that, the main bulk composition is CaCO\textsubscript{3} (average 91.53 %), while MgCO\textsubscript{3} and AIR (acid insoluble residues) are present in minor amounts, Fig. (3).

The percentage of sludge whiteness is, to great extent, affected by the amount of CaCO\textsubscript{3} content as the whiteness increases with the increasing the content of CaCO\textsubscript{3}, Fig. (4). The relation is inverted between whiteness and MgCO\textsubscript{3} content, as the whiteness decreases as the MgCO\textsubscript{3} content increases, due to the presence of grey coloured dolomite, Fig. (5).

The content of CaCO\textsubscript{3} and MgCO\textsubscript{3} greatly affects the size of the produced powder, The high content of CaCO\textsubscript{3} in the processed stone, the finer produced powder and vice versa, Fig. (6), on the otherhand, this relation is inverted with the MgCO\textsubscript{3} content, as the size of the produced powder decreases as the content of MgCO\textsubscript{3} increases, Fig. (7).
Table 2: Chemical analysis results of the marble sludge samples.

<table>
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<tr>
<th>Sample No.</th>
<th>Ca %</th>
<th>Mg %</th>
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<th>MgCO₃</th>
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Average 36.765 0.426 91.534 1.4792 7.3416 100.03

Fig. 3: Histogram showing the distribution of CaCO₃, MgCO₃ and A.I.R in the studied sludge samples.

Fig. 4: The relationship between whiteness % and the CaCO₃ content.
Uses of Wastes:

It can be apparently seen that the waste materials of marble industry reach millions of tons. Stocking of these waste materials is impossible; these waste materials should be inactivated properly without polluting the environment. The most suitable inactivating method nowadays is recycling. Recycling provides with some advantages such as protecting the natural resources, energy saving, contributing to economy, decreasing the waste materials and investing for the future.

Compatibility of the present marble sludge for recycling in alternative applications:
The following applications are suitable for recycling the present marble sludge samples taking into consideration their chemical composition, whiteness, humidity, and grain size.

Compatibility of Marble Sludge for Recycling in Some Applications:
1- Cement Manufacture:
Cement is made by fusing ground mixtures of limestone and clay and Variable amounts of pyrite, bauxite and sand in special furnaces and then adding gypsum. The mixture should contain 78 % CaCO₃. SiO₂ around 13 %, iron oxide around 2 %, aluminum oxide about 3.5 %. The production processes can either be “dry” or “wet”. The wet process is not frequently used as it has remarkable energy problems due to the evaporation of the watery solution containing up to 35 % humidity.
Sludge compatibility: As to its composition, sludge made of marble has an average CaCO₃ content of 91.35 %. Magnesium (average content is 0.43%) is less than the upper permutable limit of magnesium which is 2.5 %. As for humidity, the humidity content of the sludge is incompatible with the “dry process” since before firing, the humidity content of the dust should be approximately 6-7 %, and so the average 17.2% humidity of the sludge would be incompatible in terms of energy. In addition, there would be problems with the sludge transport and storage systems. The humidity of the sludge is fit for the “wet process”, and the costs would only involve the transport and handling of the sludge. The cement industry can consume high sludge amounts.

2- Paper Industry:
In the production of paper, limestone (4 % and 10 %), is added to the mixture of fillers and pigments, and the same ratios are added again during the polishing stage. The CaCO₃ content must be at least 95 %, and contain low amounts of silica, aluminium silicate, iron, sulphur, and should have 60 % of its particles under 2 microns and should have a high whiteness.
Sludge compatibility: the marble sludge must be carefully selected regarding its colour, and purity as dark sludge samples must be excluded hence they have low calcium carbonate content and have negative impact on the average calcium carbonate of the sludge (91.53%) and its whiteness. They should therefore be ground beforehand to produce particle sizes that are 100 % smaller than 50 microns. Humidity should not be a problem since the finished product is sold as slurry. In conclusion, white marble sludge seems perfectly suitable for the paper industry.

3- Manufacture of Water Paints:
Limestone is used in the production of paints both as filler and as pigment. The limestone used must has more than 90 % CaCO₃ and 1 % impurities it should has a particle size of less than 2 microns and containing 1% humidity, white sludge is appreciated as they have high whiteness.
Sludge compatibility: The average CaCO₃ of the marble sludge is compatible with that required for the production of water paints, white sludge samples have to be carefully selected since dark sludges can alter the whiteness Consumption of the marble sludge could be really high, since water paints are largely used in the building industry.

4- Plastic industry:
a- Polypropylene:
Polypropylene production involves mixing with varying amounts of fillers depending on the finished products, for packaging films it must have a particle size (less than 2 microns) and a filler percentage of 30-40 %, while this ratio reach about 60 %. In the polypropylene for packages and it must has particles (less than 10 microns). Humidity must not exceed 0.1 %.
Sludge compatibility: The particle size may be a problem and it could be reduced by grinding, also the sludge needs drying.

b- Polyvinyl Chloride (PVC):
CaCO₃ is largely used as filler; its particle size depends on the finished product, although its upper limit is 40 microns.
Sludge compatibility: Remarkable amounts can be used, since PVC can be filled with remarkable amounts (as much as 60 %) but the marble sludge must undergo grinding and drying.
5- Fertilizers Manufacture:
Calcium nitrate Ca(NO₃)₂ is commonly used as a fertilizer as a source of calcium and nitrogen and is made by direct reaction between a solution of nitric acid and calcium carbonate.

Sludge compatibility: The particle size of these sludge seems to be fine enough (under 300 microns) for the intended use, and the humidity content of filter pressed materials should not cause any problem since the above reaction takes place in the aqueous state. Sludge transport seems to be the more restrictive one.

6- Desulphurisation of Fumes From Thermoelectric Plants:
High amounts of sulphur oxides are produced in high-power thermoelectric plants and are very harmful both the health and to the environment. To control these problems, desulphurisation process is applied using CaCO₃ and gypsum is produced.

Sludge compatibility: marble sludge can be used without any restrictions regarding its composition or humidity.

7 - Production of Animal Food:
Calcium carbonate makes up 7 to 10 % of the components of animal food, it must contain no heavy metals, have a suitable particle size and low humidity content. In addition, the calcium content must be at least 38% and it must not contain any toxic substance.

Sludge compatibility: Sludge made of selected white marble could be used but should be checked for purity, low metal pollutants and toxicity.

8 - Bituminous Mixes:
Bituminous mixes are used to make road surfaces. The formulation of such mixes is approximately 6 % bitumen and 94 % inert materials.

Sludge compatibility: Only the larger fraction of marble dust (and only after drying) could be used, so a selection would be required. In addition, since marble sludge must be dried before it is used the extra energy costs must be also be taken into account.

9 - Marble Resin Products:
Marble resin decorative plates, are manufactured by mixing calcium carbonate made of 25 % white dust with grain sizes less than 200 microns and 75 % with grain sizes between 0.6 and 0.35 mm with polyester resin.

Sludge compatibility: The grain size of the marble sludge seems fit for the above process. Humidity level should be adjusted (no greater than 6-7 %).

10- Recovery of Lead From Flat Batteries:
Marble sludge can be used in the recovery of lead from car batteries as replacing soda ash.

Sludge compatibility: Marble sludge is suitable for this application as no restrictions regarding its composition, size or humidity are required.

11-Production of Solvay Soda:
In this process, calcium carbonate is the basic reagent. It is calcined at approximately 1000 °C, Then, CO₂ with water, NH₃ and NaCl causes sodium bicarbonate to precipitate and, by heating at approximately 200 °C, to produce sodium carbonate.

Sludge compatibility: The sludge must be selected in order to ensure they have a CaCO₃ % in the range of 90-99 %; MgCO₃ % = 0-6 %, Fe₂O₃-SiO₂-Al₂O₃ % = 0-3 %. Humidity is not a problem since it could be removed during calcination. The usable amounts would be very high.

12 - Iron and Steel Manufacture:
Iron and steel manufacture involves adding flux (limestone) for an easier smelting and forming scraps or slag.

Sludge compatibility: The chemical composition of marble sludge is compatible with that of the flux, while its particle size and humidity content (which should be low) are not suitable. Marble sludge should be submitted to adequate treatments.

13- Ceramics Industry:
The use of marble sludge in the production of structural ceramics is an option from re-use that is reported in the CORDIS "ReWaStone project" (1998), showed that the use of marble mud in the production of structural ceramics would be both technically and economically feasible and would imply a massive use of the marble wastes.
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