Petroleum Sludge as gypsum replacement in cement plants: Its Impact on Cement Strength

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Abstract. Due to high cost of cement manufacturing and the huge amount of resources exhaustion, companies are trying to incorporate alternative raw materials or by-products into cement production so as to produce alternative sustainable cement. Petroleum sludge is a dangerous waste that poses serious imputs on soil and groundwater. Given that this sludge contains a high percentage of anhydrite (CaSO₄), which is the main component of gypsum (CaSO₄·2H₂O), it may play the same gypsum role in strength development. In this research, a total replacement of gypsum (100%) has been substituted by petroleum sludge in cement production and has led to an increase of 28.8% in UCS values after 28 curing days. Nevertheless, the burning of this waste has emitted a considerable amount of carbon monoxide (CO) gas that needs to be carefully considered prior to use petroleum sludge within cement plants.

1. Introduction

Due to high cost of cement manufacturing and the huge amount of resources exhaustion, companies are trying to incorporate alternative raw materials or by-products into cement production so as to produce alternative sustainable cement. Gypsum (CaSO₄·2H₂O), which is the hydration product of anhydrite (CaSO₄), is an important additive component in cement production since it has a role to regulate the setting time. Usually, cement companies buy gypsum from other suppliers, because the companies are installed nearby limestone careers and/or clay source careers, thus, the whole cement cost would be increased.

Many gypsum by-products are generated by the chemical industries and are commonly disposed to the landfill. As results, a source of danger to the environment is presented, mainly to the groundwater. Some of these are being used in building constructions such as pastes, mortars, components (plasterboards, masonry blocks and ceilings) and decorative elements [1]. Others are being incorporated into cement production for environmental reasons. Japan has used gypsum by-products in cement production long time ago, in addition to South Africa, Brazil and Russia [2]. Since they are considered as wastes that are generated throughout industrials processing, gypsum by-products may contain different sources of danger such as chloride content, insoluble residues, organic content, and
others. Thus, they are not suitable for direct use in cement production before being cleaned up or treated.

However, Algerian petroleum sludge contains a considerable amount of anhydrite, which is the main component of gypsum; thus, it may give promised results when it is incorporated into cement plants. Nevertheless, petroleum sludge is one of the hazardous wastes [3] that has high volatile content and organic matters that may affect the cement quality or it may cause problem to the production process. For that, necessary precautions should be taken prior to use this waste into cement production.

The current study is an attempt to examine the possibility to incorporate petroleum sludge into cement production as gypsum replacement by executing the unconfined compressive strength on the new cement produced.

2. Materials and methods

2.1. Materials Collection

2.1.1. Clinker. The clinker was collected from SCAEK (Cement Company of Ain EL- Kebira) Subsidiary of the group GICA (Industrial Group of Algerian Cement) situated in Ain El-Kebira, Setif, Algeria. Then, it was 105°C oven dried until it lost its moisture, grinded to pass through 1mm pore diameter metallic sieve and stocked in a polyethylene bag prior to be analyzed.

2.1.2. Gypsum. Gypsum has been collected from the career of The GRANU EAST Company Subsidiary also of the group GICA based in the municipality of Beni Fouda, State of Setif, Algeria. This gypsum, which is also supplied to SCAEK, was dried under a temperature of 50°C, grinded to pass through 1mm pore diameter metallic sieve and stocked in a polyethylene bag prior to be analyzed.

2.1.3. Petroleum Sludge. Petroleum Sludge was collected from the oil drilling field of Hassi Messaoud, Algeria. It was then burned in an industrial kiln to eliminate the organic matter and to measure the gases emitted through burning. After that, it was also grinded to pass through 1mm pore diameter metallic sieve and stocked in a polyethylene bag prior to be analyzed.

2.2. Petroleum Sludge Analysis

Previous study by the same authors has given some data about petroleum sludge characterization like its efficiency to play the same role of gypsum as setting retarder. In addition to that, it contains 54% of anhydrite, which is the main component of gypsum, thus, it may play also the same role of gypsum in strength development. More information about petroleum sludge is that its content in heavy metals is fit to the cement requirements if its incorporation doesn’t exceed 50%.

17 kg of petroleum sludge was put in a small industrial kiln made to burn different types of wastes and was burned under a temperature of 600°C until the disappearance of the total organic matter. Few minutes after putting the sludge, a measurement of the gases emitted was performed using an electric probe detector. After being cooled, the residue of sludge was collected in a metallic container and kept for future laboratory use.

2.3. Cement Preparation

Different percentages of clinker, gypsum and PS have been determined according to cement production requirement obtained from the production unit of SCAEK in order to emulate the cement produced there. As they use 2.5% to 5% of gypsum added to 97.5% to 95% of clinker, respectively, 2.5% and 5% of petroleum sludge have been chosen as replacement of 50% and 100% of gypsum, respectively. Table 1 represents the samples percentages. It should be noted that the choice of these percentages is based on the percentage of SO3 in cement that should not exceed 2.5% [4].
Table 1: Different percentages of samples preparation

| Samples | Petroleum Sludge (%) | Gypsum (%) | Clinker (%) |
|---------|----------------------|------------|-------------|
| Reference | 0                     | 5          | 95          |
| 1       | 2.5                   | 2.5        | 95          |
| 3       | 5                     | 0          | 95          |

Each sample has been prepared separately and blended within a grinder for 30 minutes. The blending operation should be continued until 95-97% of the obtained cement could pass through 90µm pore size diameter metallic sieve in order to obtain a finesse of 3700 -4200 cm²/g. After that, the samples were kept in polyethylene bags to prevent any source of moisture prior to be tested.

2.4. Unconfined Compressive Strength
Compressive strength test was carried out according to NF EN196-1 [5]. Mortars were prepared by mixing cement, sand and distilled water with the ratios: water to cement of 0.24 and cement to sand of 0.33. The mortars were mixed separately within a mixture, cast in 40 mm * 40 mm * 160 mm moulds, left cured under a temperature of 22 °C and a relative humidity of 95.0% for 24 hours and then removed from the moulds prior to be tested for the Unconfined Compressive Strength (UCS) for 2, 7 and 28 days. After the designated curing age of each specimen was reached, it was subjected to UCS test, and the values were recorded.

3. Results and discussion

3.1. Gases Emission
The burning procedure of petroleum sludge is an effective way to eliminate totally its organic content, but the gases emitted should be analyzed carefully to prevent any source of danger opposed to the cement plant by this waste. Table 2 and table 3 presents the threshold emission of the gases emitted through cement plants, and the gases emitted from petroleum sludge at 21.0 % of O_2 as reference, respectively.

Table 2: The threshold emission of the gases emitted through cement plants

| Gases | thresholds |
|-------|------------|
| CO₂   | N/A        |
| NOₓ   | 878.0 ppm  |
| SO₂   | 266 ppm    |
| CO    | 162 ppm    |
Table 3: The gases emitted from petroleum sludge burning at 21.0% of O2 as reference

| Gases | values  |
|-------|---------|
| CO₂   | 0.0 %   |
| NOₓ   | 0.0 ppm |
| SO₂   | 0.0 ppm |
| CO    | 392.0 ppm |

No detection was noticed for almost all the gases except for carbon monoxide (CO) with an amount of 392.0 ppm. This last value is undoubtedly a concern since it exceeds the threshold emission for cement plants, which is 162 ppm. [6]. Thus, preliminary precaution should be taken prior to burn this waste within cement factories.

3.2. Unconfined Compressive Strength (UCS)
Table 4 and Figure 1 show the results of UCS for all the samples in MPa.

Table 4: The UCS values for all the samples

| Samples | Curing ages |
|---------|-------------|
|         | 2d | 7d | 28d |
| Reference | 24.5 | 44 | 54.5 |
| 1       | 35 | 56.2 | 70.2 |
| 2       | 22.8 | 45.6 | 56.7 |
It is clear that the UCS values were increased significantly with the curing ages for all the samples even for 100% replacement for gypsum by petroleum sludge (samples 2). These results, which may refer to the role of curing time in increasing the strength, are explained by the water that is still existed within the samples and needs enough time to be evaporated. In addition to that, the UCS values after 28 curing ages exceeded the limit strength for cement CEM I 42.5 produced by SCAEK, which is 40.0 MPa [4]. Thus, replacement for gypsum by petroleum sludge is effective and played the same role of gypsum as additive for cement clinker in achieving high strength values according to the standard.

In the other hand, it can be seen that the UCS values of sample 1 with 50% replacement of gypsum showed a significant increase with percentages of 42.9%, 27.7% and 28.8% for 2, 7 and 28 days, respectively compared to the reference sample. Lower than these percentages are marked also for samples 2 with 100% replacement of gypsum, where there was a slight increase of 3.6% and 4.0% for 7 and 28 curing days. Nevertheless, there was a slight decrease with 6.9% for 2 curing days but the result still fir to the standard value, which is 10 MPa. These results conduct to the advantage of using petroleum sludge in increasing the cement strength.

These results are better than those obtained by Singh and Garg (2002) [7] who have studied the incorporation of phosphogypsum, which is a by-product from the phosphoric acid industries, as a source of gypsum into cement plants. They have concluded that a 5% of phosphogypsum could be used as an additive replacing the natural selenite gypsum in cement production. Nevertheless, they have noted that the UCS values have been reduced as a result of this replacement.

4. Conclusion
From the above results, gypsum could be replaced by petroleum sludge as a sustainable low cost disposing method for this waste and that provide a free raw material for cement production. The main conclusions are expressed as follow:

1. Gypsum has been totally substituted by petroleum sludge in cement production and has led to an increase of 28.8% of UCS values after 28 curing days.
2. Cement industries may use petroleum sludge in their production offering therefore a sustainable complete disposal of this waste.

3. Petroleum sludge contains high amount of carbon monoxide (CO), which is a dangerous gas, thus, it should be considered prior any burning operation of this waste within cement plants.

**Acknowledgment**
The authors want to thank C.E.T.I.M laboratories, Algeria and UTHM University for their support to execute this work.

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