Petroleum sludge treatment and reuse for cement production as setting retarder

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Abstract. Petroleum sludge is a dangerous waste that needs to be treated to avoid any contamination of soil and groundwater due to its disposal. As an attempt to treat this waste, it has been incorporated into cement production as substitution for gypsum. As results, 5% of petroleum sludge has shown effective results and could play the same role of gypsum in delaying the flash setting of cement clinker.

Keywords: Petroleum sludge, cement, setting time, gypsum replacement, heavy metals.

1. Introduction

The unavoidable outcome to the different petroleum production processes is the generation of a considerable amount of waste called petroleum sludge (PS). This last is referring to a thick, viscous [1] intractable mixture encountered during the crude petroleum exploration, production, transportation, storage and refining processes [1, 2]. The PS is constituted predominantly of water, solids of the crossed geological formations during the drilling operation and hydrocarbons that are deduced from both the drilled petroleum itself and the substances used for the drilling operation. According to Resources Conservation and Recovery Act (RCRA), sludge is a hazardous waste [3] that affects the environment and the living things if it is disposed improperly. However, abundance, Intractability and harmful impacts of PS have made it a source of danger that attracted various types of treatment methods like centrifugation, solidification/stabilization, solvent extraction, landfarming, pyrolysis, biodegradation, photodegradation, ultrasonic treatment, incineration and others. Researchers have concluded that it is ineffective to implement a typical method to get rid fully of the PS danger without any side effects. However, all the methods are associated with advantages and disadvantages that may prompt implementing such method for some purposes and not for others. Incineration is a promised treatment method that has attracted many researchers since long time ago for the treatment of wastes generated from industries. Nevertheless, this method is much expensive (130- 150 USD/ ton) and needs further treatment for the ash produced [4].

As a new sustainable treatment, in 2006, MVW Lechtenberg & Partner have concluded that the PS is feasible to be implemented into cement plants, but as a fuel only [4]. The study has not shown a
complete data about the whole process such as the raw materials substitution, destination of ash, impact of the project and others.

While gypsum is a main component in cement production since it has a role to regulate the setting time, the XRD of PS shows that is contains a considerable amount of anhydrite, which is the main component of gypsum. Thus, it may play the same role of gypsum in cement production.

The current study aims to incorporate PS into cement production as gypsum replacement by examining the impact of this waste on the setting time.

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.

All materials: clinker, gypsum and petroleum sludge were analyzed by using the X-Ray Fluorescence (XRF) in order to identify their chemical components.

2.2. Petroleum Sludge Analysis

2.2.1. Loss of Ignition (LOI). This test was conducted according to ASTM D7348 by weighing 2g of petroleum sludge in a crucible, placing it in a furnace with an air atmosphere and heating it under a temperature of 950°C for 2h. The fired sample would be then cooled down to room temperature in a desiccator and weighed again. The weight loss associated with firing the sample is known as the loss of ignition (LOI) [5].

2.2.2. Leaching. This test was conducted by extraction using Toxicity Characteristics Leaching Procedure (TCLP) according to EPA Method 1311 and analysis using inductively coupled plasma mass spectrometry (ICP-MS). For that, 5g of PS was extracted with 20:1 liquid to solid ratio in an acetate solution in 2L bottles and was rotary agitated at 30 rpm for 18 hours using the rotary system [6]. After that, the solid and liquid phases were separated by filtration through 0.45-mm-pore-size membrane filters. The pH was measured, then; the extract was acidified to 2% HNO3 prior to analysis for metals using ICP-MS. Then, the heavy metals quantities in the solutions obtained would be compared with the regulatory cited by the United States Environmental Protection Agency (USEPA).

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 emulate the cement produced there. As they use 2.5% to 5% of gypsum added to 97.5% to 95% of clinker, respectively,
1%, 3.5% and 5% of petroleum sludge have been chosen as replacement of 20% 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 SO\(_3\) in cement that should not exceed 2.5% [7].

| Samples | Petroleum Sludge (%) | Gypsum (%) | Clinker (%) |
|---------|----------------------|------------|-------------|
| Reference | 0                    | 5          | 95          |
| 1        | 1                    | 4          | 95          |
| 2        | 3.5                  | 0          | 96.5        |
| 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 cm\(^2\)/g. After that, the samples were kept in polyethylene bags to prevent any source of moisture prior to be tested.

2.4. Setting Time
This test has been performed through two steps: consistency and Vicat needle

Consistency was performed by mixing 500g of dried cement with a measured amount of distilled water, then; the paste was put quickly into the conical Vicat ring, completely filled by leveling it with the upper tight edge of the ring and the excess paste was removed by using a trowel [8]. After that, the ring was centered under the rod which was brought in contact with the surface of the paste, the set screw was tightened to the upper zero mark of the scale, and then; it was released immediately to read the value indicator below the origin surface of the paste. For normal consistency, a value of 6 ± 2 mm should be obtained after making trials by mixing fresh cement each time. From mixing of paste until releasing of the rod, 30 seconds should not be exceeded [8].

Time of Setting Determination was effecting by putting the previous prepared paste in a mould and remained in a moist cabinet in the automatic Vicat apparatus (adapted to a computer) prior to start measurements. After 30 minutes, the automatic Vicat was starting penetrating every 15 minutes until a penetration of 25 mm was obtained. The elapsed time between the initial contact of cement and water and the penetration of 25 mm is the initial time setting [9]. But the final setting time was the measure when the needle did not mark the specimen surface with a complete circular impression [9]. The calculation of initial and final setting time was made automatically by the apparatus and the results were shown on the screen of the computer.

3. Results and discussion

3.1. Chemical Analysis
The chemical components of clinker, gypsum and petroleum sludge are shown in table 2.
It is seen that petroleum sludge and gypsum have high content of Sulfur trioxide (SO₃) which is in charge of delaying the cement setting by controlling the early reactions of tricalcium aluminate [10]. Indeed, without existence of a required amount of SO₃ in cement, it can lead to flash setting [11]. GICA produces cement with SO₃ requirement between 2 and 5%, and in this study the XRF showed that the clinker has only 0.18 % of SO₃, thus, it should be regulated with a sufficient and adequate amount of gypsum and/or petroleum sludge.

3.2. The loss on ignition (LOI)
LOI of petroleum sludge was made by a muffle furnace at a temperature of 900°C; the results gave an average loss value of 20.80%. This value describes water, the organic content like onentalkanes, aermatics, asphaltenes and resin [51] and even some percentages of carbonate matters. It may also contain volatile organic carbons (VOCs) and semi-volatile organic carbons (SVOCs) like polycyclic aromatic hydrocarbons (PAH) [12, 13]. Thus, this value should be eliminated prior to use the petroleum sludge as gypsum replacement.

The ash (or mineral matter) content is the value of the residue remaining after the loss on ignition is achieved, and therefore the result is expressed as ash% = 100% - LOI = 100-20.80= 79.20%. Thus, the ash content of the petroleum sludge is 79.20%. This amount of ash may be beneficial as replacement for gypsum in cement production.

3.3. Leaching
The analysis of the leachate by using the ICP-MS is presented in table 3.

This analysis shows that the heavy metals have not exceeded the regulatory limits for cement for all the elements except for lead (Pb), which is 149.02ppm compared to the maximum percentage in cement, which is 75ppm Table 4 shows the maximum concentrations of some heavy metals from a number of cement plants throughout the world. Thus; incorporation of petroleum sludge in cement plants should take in consideration this value to prevent any danger comes from this waste. In the current study, the maximum amount of PS incorporated would not exceed 50% of any raw material used for cement production.

| Components | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | K₂O | Na₂O | PAF | TOT |
|------------|------|-------|-------|-----|-----|-----|-----|------|-----|-----|
| Clinker    | 21.15| 4.34  | 5.70  | 66.49| 1.33| 0.18| 0.08| <0.05| 0.32| 99.59|
| Gypsum     | 10.74| 3.35  | 1.30  | 27.90| 3.83| 29.51| 0.44| 0.93 | 21.76| 99.76|
| Petroleum Sludge | 5.47 | 1.29  | 0.56  | 25.05| 3.47| 38.41| 0.27| 3.29 | 20.80| 100.00|

| Elements | Mn | Ni | Zn | Fe | Cu | Pb | Cd | Cr |
|----------|----|----|----|----|----|----|----|----|
| Concentration (ppm) | 25.77 | 0.34 | 0.20 | 37.40 | 3.43 | 149.02 | 0.44 | 0.48 |

Table 2. Chemical compositions of clinker, gypsum and petroleum sludge

Table 3. Heavy metals content of petroleum sludge
Table 4. Maximum concentrations of some heavy metals from a number of cement plants throughout the world

| Heavy metals  | Maximum concentrations (ppm) |
|--------------|-------------------------------|
| Manganese (Mn) | 2366                          |
| Nickel (Ni)    | 129                           |
| Zinc (Zn)      | 321                           |
| Iron (Fe)      | N/A                           |
| Copper (Cu)    | N/A                           |
| Lead (Pb)      | 75                            |
| Cadmium (Cd)   | 1.12                          |
| Chromium (Cr)  | 422                           |

3.4. Setting time
Table 5 shows the initial and the final setting times for all samples.

Table 5. Initial and final setting times for the different samples

| Samples (CK/GY/SL) | Initial setting time | Final setting time |
|--------------------|----------------------|--------------------|
| Reference          | 1h55min              | 4h05min            |
| 1                  | 1h55min              | 4h00min            |
| 2                  | 2h10min              | 3h45min            |
| 3                  | >2h10min             | >3h45min           |

It is noticed that all samples respond to the minimum initial setting time for cement, which is 75 minutes [14].

Sample 1, where 20% of gypsum was substituted by PS, showed the same results of initial setting time compared to the reference, and a slight increase (5 minutes) in the final setting time. These results are explained with the non-negative impacts of PS in substituting gypsum at lower percentage.

For sample 2 and sample 3, substitution of gypsum with the different percentages showed an increase in initial setting time and a decrease in the final setting time compared to the reference sample, but the differences are not that much. These results can’t be explained only with the efficiency.
of using petroleum sludge in slowing down the early hydration of tricalcium aluminate ($C_3A$) and preventing the flash setting of the cement clinker [10].

4. Conclusion

From the above results, cement plants could offer a sustainable disposal of petroleum sludge could be treated within by offering. The main conclusions are expressed as follow:

1. Petroleum sludge contains a high amount of Sulfur trioxide ($SO_3$) that helps in delaying the flash setting once added to the cement clinker, thus, it is worth to be used as a substitute for gypsum.
2. Petroleum sludge plays the same role of gypsum as setting retarder.
3. The heavy metals constitution of petroleum sludge even though they are lower than the acceptance limits except the lead (Pb), but the incorporation percentage should be controlled to prevent any source of danger comes from this heavy metal.

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