Communication

PETROLEUM SLUDGE AS RAW MATERIAL FOR CEMENT CLINKER PRODUCTION

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Abstract: The objective of this study is to investigate the performance of incorporating petroleum sludge waste as raw materials into the cement clinker production. The burnability and the structural analysis of the produced clinker were studied. The results showed that the addition of petroleum sludge into the clinker matrices improved the burnability of the clinker by lowering the free lime content. Moreover, 2.5% and 5% of this waste was effective and did not affect the quality of the cement clinker negatively. This study, which is the first to investigate the incorporation of petroleum sludge into cement production, provides also a complete elimination of this waste from the environment.

Keywords: Petroleum sludge; Cement clinker; Free lime content; Burnability

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11. Introduction

Petroleum sludge (PS) is referring to a thick, viscous [1] intractable mixture encountered during the crude petroleum exploration, production, transportation, storage and refining processes [1,2]. This sludge is considered as one of the hazardous wastes according to Resources Conservation and Recovery Act (RCRA) [3]. Simultaneously, it leads to occupation of hundreds of hectares and presenting significant danger zones [4]. Various types of treatment methods were investigated to solve the PS danger, but they have shown limited effects on the removal of heavy metals from this waste [5]. Moreover, the expensive cost associated to majority of the methods encourages the move toward a sustainable treatment of this waste.

On the other hand, the cement demand in the markets knows an increase during the last years due to the importance of this material in building and construction. In 2015, it was reported that the worldwide cement production was estimated to 4.1 billion tons [6]. In Algeria, the first company of cement, which named GICA (Cement Industry Group of Algeria) produces more than 10 Million tons of cement in 2016 [7]. This production is associated to several issues like the natural resources depletion, and carbon dioxide (CO_2) emission. However, it is required to provide 1.7 to 1.8 tons of raw materials in order to produce 1 ton of cement. In addition to that, cement production is considered as one of the largest producers of CO_2 [8]. For example, 1 ton of cement is resulted in the emission of almost 0.7 tons of CO_2 [9]. These disadvantages and others are making the call to move towards sustainability of cement production.

One of the alternative improvements to produce cement by offering a sustainable amendment to the treatment of PS is to incorporate this waste within the cement production plant kiln ([10-12]. The combination of this waste with the cement raw materials is leading to encapsulation of the heavy metals in the cement matrices and remains them stable. Furthermore, the sludge does not require a significant heat or fuel to treat it since it contains a considerable amount of oil, thus, it should lead to lowering the CO2 emission [13].

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Nevertheless, incorporation of PS as raw material into cement production is not yet studied. Towards that, objective of this research is to determine the efficiency of incorporating PS as raw material to produce cement by examining its free lime content (F-CaO) and its mineralogical characterization compared to the ordinary Portland cement.

2. Materials and Methods

Limestone, marl and iron, which are the main raw materials that are used to produce the clinker, were collected from the Cement Company of Ain EL- Kebira (SCAEK), Subsidiary of the group GICA (Industrial Group of Algerian Cement) situated in Setif province, Algeria. Petroleum sludge (PS) was collected from the oil drilling field of Hassi Messaoud, Algeria, from the well coded OMF-46. All the materials were oven dried separately under a temperature of 105°C to constant weights. After that, they were grinded to pass through 75µm pore diameter metallic sieve and stocked in polyethylene bags prior to be analyzed. All the raw meals were chosen and blended with simulation to the modulus of the cement clinker produced by SCAEK that are lime saturation factor (LSF=0.9), silica modulus (SM=2.3) and alumina modulus (AM=0.9). 15 to 25 g of the different raw meals were pressed into a cylindrical mould of 2 cm diameter; then, they were clinkerized within a furnace for 30-min under 1450°C with a heat rate of 10°C/min; and then cooled to room temperature. After that, the samples were grinded prior to be analysed for the free lime content (f-CaO) using the glycerol-ethanol method; then, they were subjected to a structural analysis using Bogue's potential compositions that are alite (tricalcium silicate, C_3S), belite (dicalcium silicate, C_2S), aluminate (tricalcium aluminate, C_3A) and ferrite (tetracalcium aluminoferrite, C_4AF) that are calculated according to the following equations [14]:

$$C_3S = 4.0710*CaO-7.6024*SiO_2-1.4297*Fe_2O_3-6.7187*Al_2O_3 \quad (1)$$

$$C_2S = 8.6024*SiO_2+1.0785*Fe_2O_3+5.0683*Al_2O_3-3.0710*CaO \quad (2)$$

$$C_3A = 2.6504*Al_2O_3-1.6920*Fe_2O_3 \quad (3)$$

$$C_4AF = 3.0432*Fe_2O_3 \quad (4)$$

3. Results and discussion

5% of PS was the maximum percentage that was able to produce an acceptable raw meal because of the high content of SO_3, for that, the investigation was conducted on four different samples, which are PS0 (with 0% of PS), PS1 (with 1% of PS), PS2.5 (with 2.5% of PS) and PS5 (with 5% of PS). Figure 1 shows the free lime content (f-CaO) in all the samples, which were 1.5%, 1% and 0.8% for PS0, PS1 and both of PS2.5 and PS5, respectively. All the percentages were regular and did not exceed the maximum content for the normal clinker, which is 1.5% [11]. The graph shows a dramatic decrease in f-CaO for PS1 with a percentage of 33%, followed by 47% for both of the other samples, by referring to PS0. This decrease was due mainly to the decrease in limestone content within the matrices since the limestone is the main source of f-CaO. However, the limestone content changed from 85% in PS0 to 81%, 80% and 79% for PS1, PS2.5 and PS5, respectively.

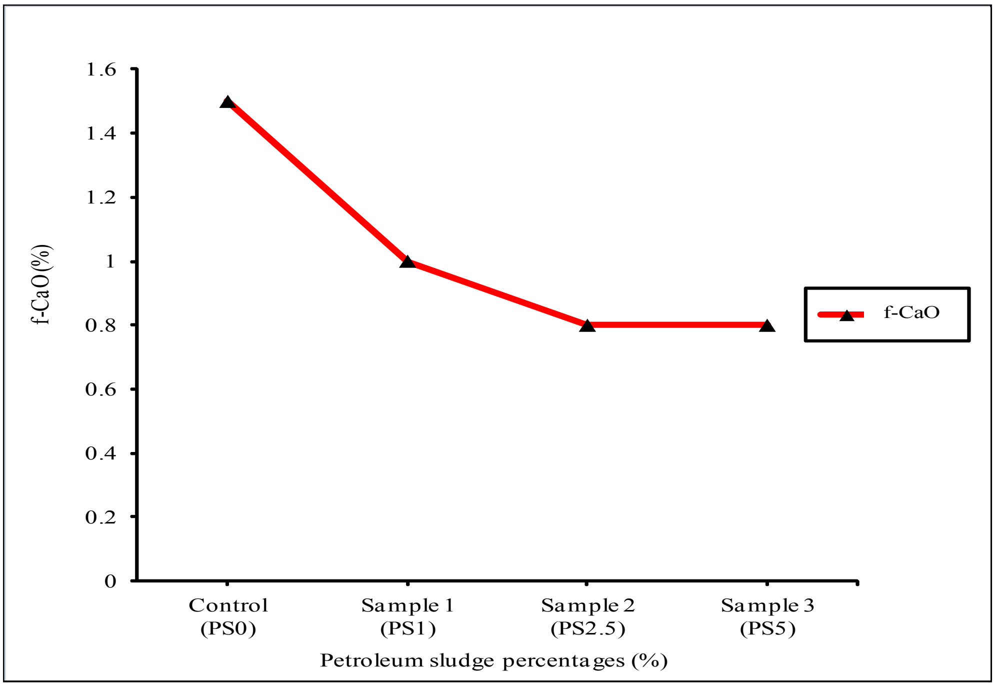

Figure 1. Free lime content of the cement clinker samples

The graph of Figure 1 is appeared in decreasing manner for PS1 and PS2.5 by referring to PS0; then, it shows almost stabilization after that. This result is explained with the different percentages of PS added to the raw materials as prescribed by previous researchers. It was reported that a small percentage of sludge added to the raw materials improves the burnability of clinker and makes it easy to sinter, but the addition of an excessive amount may increase the impurities within the materials and thus limit the function of the sludge to improve the clinker burnability [11].

The structural analysis was performed by calculating Bogue's potential composition using different equations; and the results are presented in Table 1.

Table 1. Main clinker mineral components in the different matrices

Samples / Parameters	Control (PS0)	Sample 1 (PS1)	Sample 2 (PS2.5)	Sample 3 (PS5)
Alite (C_3S) (%)	52.44	38.02	48.97	48.76
Belite (C_2S) (%)	23.94	36.67	26.18	26.88
Aluminate (C_3A) (%)	3.83	4.38	4.31	3.85
Ferrite (C_4AF) (%)	15.02	15.32	14.11	11.28

The percentages shown in table 1 are for the main crystals that constitute the cement clinker, based on which a final decision on the performance of raw materials burning and the quality of cement was taken. These crystals are tricalcium silicate or alite (C_3S), dicalcium silicate or belite (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). As general observation, the addition of PS into the raw materials has led to some changes in the structures of PS1, PS2.5 and PS5 compared to PS0, but the changes were differentiated from one sample to another.

For C_3S, it is clear that all samples have their percentages within the normal range, which is from 45% to 66% except for PS1 with 1% of PS that shows a value of 38.02%. The graph also shows decreases of 27.5%, 6.6% and 7.0% for PS1, PS2.5 and PS5, respectively compared to PS0, which is due to the addition of PS that is considered as the main source of impurities. This result is supported by Chen et al. (2010) [14] who have reported that the addition of some percentages of sludge into the

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raw materials may affect C_3S formation due to the impurities, but a controlled amount may be beneficial for the C_3S formation. The results obtained are also in line with those of Rodriguez et al. (2013) [10], who have declared the slight reduction in the alite formation when incorporating the dried sewage sludge into the clinker raw materials.

However, the addition of 1% of PS affected the alite formation negatively; and this may be because of the insufficient amount of PS, which is resulted in the decrease of CaO. However, incorporation of 1% of PS only could not provide the sufficient amount of CaO that is necessary to formulate the alit. On the other hand, PS5 showed slightly more decrease in alite percentage than PS2.5, and this is due to the excess of impurities within PS5. This result is supported by Xu et al. (2014) [11] who have concluded that lime dried sludge (LDS) up to 15% has improved the alite formation, but the addition of 18% of LDS have resulted in reducing the alite percentage. Other studies conducted by Lin et al. (2012) [16] have also concluded that addition of sewage sludge into cement raw materials may decreased the C_3S percentage. Their conclusion is in agreement with the results of this study.

Based on the results of alite, 2.5% and 5% of PS, which correspond to PS2.5 and PS5, respectively could be considered as applicable percentages that could be incorporated into cement clinker formation. Contrary, PS1 with 1% of PS should be eliminated or less considered to replace the cement clinker since its alite content is out of the range. However, the study of the other crystal phases, mainly the belite should be performed so as to take an ultimate decision about the applicability of these percentages.

Table 1 shows that PS1with a value of 36.67% is the only sample that is beyond the range, which is 10% to 30% for normal content of C_2S. Contrary to the alite, this figure shows an increase in belite percentages by addition of different amount of PS compared to PS0. This is mainly due to one character of this crystal, which is the capacity to combine large amounts of other elements more than the alite. It was reported that the belite has the ability to contain foreign elements in its structure [17]. This may explain the increase of alite percentages. On the other hand, the increases in belite percentages were 53.2%, 9.4% and 12.3% for PS1, PS2.5 and PS5, respectively. By using the same explanation for the alite but reversing the role of PS to increase the belite percentage, the content of PS should be stringently adapted for better results. The results of belite found in this study are in accordance with those of previous researchers [10, 11, 16]. In the study of Xu et al., (2014) [11], on the reuse of lime dried sewage sludge (LDS), they reported that the belite percentage increased with the excessive addition of LDS into the cement raw materials.

Based on the results of alite and belite, it could be concluded that the usage of 2.5% and 5% of PS is more efficient compared to the usage of 1% of PS into the cement raw materials.

For tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF), which present supplementary results for the quality of the produced clinker, it appears that no strange comments for almost all the results. However, there was no significant change in the C_3A values in the samples that incorporate PS compared to PS0. It was reported that the C_3A value should not exceed 5% for the Portland cement class one (CEMI) [18]. Moreover, the change in the results of C_4AF was not significant after addition of PS for PS1 and PS2.5 compared to PS0. But a clear decrease for PS5, which is mainly due to the excess amount of PS.

The ratio C_3A/C_4AF has shown increase values from 0.25 in PS0 to 0.29, 0.31 then 0.34 for PS1, PS2.5 PS5, respectively. Same results were obtained by Xu et al. (2014) [11] who have proved that this ratio increases with the increase of LDS percentages.

 doi:10.20944/preprints201806.0053.v1

5. Conclusions

This research provides a sustainable free cost treatment method of petroleum sludge (PS) waste and offers the ultimate elimination of this waste by providing a decrease in the cement raw materials consumption. However, the addition of this waste is an effective solution for decreasing the free lime content (f-CaO) up to 47% of the cement production, thus improving the clinker burnability. Moreover, incorporation of a controlled percentage of PS into cement production (2.5% of 5% in this study) is considered effective and did not highly affect the quality of cement.

Funding: This research is funded by Research & Development division of CRD/ SONATRACH, Boumerdes, Algeria and postgraduate research grant (GPPS) under the vote number: U581.

Acknowledgments: The authors would like to thank Research & Development division of CRD/ SONATRACH, Boumerdes, Algeria, for the help to achieve this work. Special thanks are expressed also to office for Research, Innovation, Commercialization and consultancy (ORICC) in UTHM University who offered the postgraduate research grant (GPPS) under the vote number: U581, as kind of support for this research.

Conflicts of Interest: The authors declare no conflict of interest.

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