Analysis of the cement clinker produced with incorporation of petroleum sludge

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Abstract. Very limited researches have been conducted on the incorporation of petroleum sludge waste into cement clinker production even though this waste may contain similar components to those of clinker raw materials. In this research, petroleum sludge was integrated into cement plant as raw material to produce the cement clinker. As results, incorporation of 5% of this waste was able to produce an acceptable quality of cement. Despite the use of petroleum sludge has decreased the properties of the produced clinker, but it still fit the requirements.

1. Introduction
Due to the high demand of cement in the international markets, companies are doubling their production in this important substance, which is resulted in the depletion of the natural resources. Through literature, incorporation of different types of waste into cement plants has been studied widely by researchers as a mean of minimizing the amount of raw materials consumption (Fang et al., 2015; Rodríguez et al., 2013; Lin et al., 2012; Lairaksa et al., 2013). It could be noted that the possibility to incorporate the waste into cement production is related mainly to the similarity of its composition to the cement raw material. Petroleum sludge is one of these wastes, which is considered toxic and very harmful to the environment; moreover, it is resulted in the occupancy of large areas (Ling & Isa, 2006). However, researches regarding incorporation of petroleum sludge into cement plants are very scarce even though this type of sludge contains very similar components to those of cement as mentioned by Lechtenberg (Lechtenberg, 2010).

This research aims to determine whether it is possible to incorporate petroleum sludge as raw material into cement clinker production by investigating the quality of the produced clinker in terms of structural and morphological analysis.

2. Materials and methods
The raw materials (limestone marl and iron ore) were collected from the Cement Company of Ain EL-Kebira (SCAEK), situated in Setif province, Algeria. The samples of petroleum sludge (PS) waste were
from the oil drilling field of Hassi Messaoud, Algeria. After drying the materials under a temperature of 105°C to constant weights, they were subjected to grinding to pass through the sieve of 75µm. Two samples were formulated according to the ratios of the cement clinker produced by SCAEK, which are the silica ratio (SM=2.3), the lime saturation factor (LSF=0.9) and the alumina ratio (AM=0.9). The control sample that was labelled PS0 does not contain any percentage of PS, and the other sample contains 5% of PS and labelled PS5. Then, the samples were formulated within a cylindrical mould and pressed to be enough stable; then, clinkerized for 30 minutes in a furnace under a temperature of 1450°C with 10°C/min as heat rate, after that, they were cooled to room temperature. After that, the samples were subjected to the structural characterization using Bogue’s formulas and the morphological analysis using the scanning electron microscopy (SEM) and the Energy-dispersive X-ray spectroscopy (EDX).

3. Results and discussion

3.1. Molecular structure analysis

Bogue’s potential calculation gave the results for alite and belite for sample 1 (PS5) as well as for the control sample (PS0) as presented in table 1.

| Tricalcium silicate (alite) C₃S (%) | Control (PS=0%) | Sample 1 (PS=5%) |
|-------------------------------------|-----------------|------------------|
|                                     | 52.44           | 48.76            |
| Dicalcium silicate (belite) C₂S (%) | 23.94           | 26.88            |

From the table, it is clear that all the percentage are within the ranges that are (45-65%) for the alite and (10-30%) for the belite. Nevertheless, there was a decrease in alite content and an increase in belite content for PS5 compared to PS0. These results are in line with the results of Lin et al. (2012), who have concluded that addition of sewage sludge into cement raw materials decreases the C₃S percentage. In addition to that, Xu et al., (2014) have reported that the belite percentage increases with the excessive addition of lime dried sludge into the cement raw materials.

3.2. Morphological analysis

Figure 2 presents the phases that constitute the different samples by using SEM technique. For PS0 (figure 4.9-a), it is observed a presence of many prismatic shapes crystals with very clear edges and distinct boundaries, one of these crystals is labeled (A). These crystals are designated to the alite (C₃S) as described by Xu et al. (2014). For PS5 (figure 4.9-b), the addition of 5% of petroleum sludge was resulted in a slight change of the alite crystals, which is correspond to the unclarity of the crystals edges. This change in the shapes was not much and some crystals were appeared and are labeled (B). These results are in line with
the mineralogical analysis that gave the C:\textit{S} value of 48.76\% for PS5 lower than that of PS0, which was 52.44\%.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{morphological_characteristics_of_the_samples}
\caption{Morphological characteristics of the samples.}
\end{figure}
3.3. **Analysis of the clinker contents by EDX**

The results of SEM-EDX are presented in table 2 and figure 2. As the study was focused on the identification of the main minerals that constitute the cement clinker, which are alite (Ca$_3$SiO$_5$) and belite (Ca$_2$SiO$_4$), the analysis were also focused on the main constituent of alite and belite that are the calcium oxide (CaO) and the silica (SiO$_2$). Figure 2 shows close results for PS5 (figure 2-b) compared to PS0 (figure 2-a) with high picks for the elements Ca and Si and lower picks for the other elements, which indicates that the most important components in the different samples are those associated to Ca and Si.

Table 2 shows that the highest contents are those of CaO and SiO$_2$, which represent around 90% of the total samples contents. The CaO contents were 71.44% and 70.26% for PS0 and PS5, respectively, where the SiO$_2$ contents were 20.36% and 19.03% for PS0 and PS5, respectively. These results are in correspondence with the results of figure 2. These findings are in line with those of the molecular structure analysis (Bogue’s calculation) that showed percentages of C$_3$S and C$_2$S within the normal ranges even though there was a slight change in the values due to the incorporation of petroleum sludge.

|       | CaO (%) | SiO$_2$ (%) | Al$_2$O$_3$ (%) | FeO (%) |
|-------|---------|-------------|-----------------|---------|
| PS0   | 71.44   | 20.36       | 3.20            | 3.88    |
| PS5   | 70.26   | 19.03       | 3.15            | 3.80    |

Table 2. The EDX values of the samples' main contents.
Figure 2. EDX of the different samples.
4. Conclusion
Incorporation of petroleum sludge (PS) waste into cement clinker production was successfully achieved in this research. As results, 5% of this waste provided very acceptable quality of cement clinker with close findings to those of clinker without PS. Consequently, this research provides a sustainable elimination of petroleum sludge from the environment as well as a decrease in the use of cement raw materials to be saved for longer period of time.

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