Investigation on the Properties of Cement Mortars with Fluid Petroleum Catalyst Residue (FPCR)

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Abstract. Fluid petroleum catalyst residue (FPCR) is a by-product material produced in the industry of petroleum. This research presents an experimental work to investigate the effect of FPCR as a partial replacement for Ordinary Portland Cement (OPC) in five replacement levels of 10%, 20%, 30%, 40%, and 50% from the dry weight of cement. For this purpose, the setting times and compressive strength were examined at ages of 3, 7, and 28 days to assess the performance of mortar samples concerning reference mix (mix with zero replacement). The findings exhibited that the compressive strengths of mortar with 10% FPCR replacement at early and later ages increased compared with the control OPC. The 10% replacement level of FPCR has almost the same initial setting time to that of OPC, while there was a slight reduction in the final setting time. The developed mortars had significant changes in their microstructures with time, as observed by the imaging from SEM. The cost of the cement industry and its negative impacts, including CO2 emissions, can be reduced considerably as a result of this study.

Keywords: Cement mortar, compressive strength, setting time, SEM, FPCR, waste recycling.

1. Introduction

Global warming, greenhouse gases and waste management have become extremely significant concerns globally. Cement manufacturing generates around 7% of CO2 emissions, worldwide [1]. It was reported by O’Rourke et al. [2] that one ton of CO2 is generated to produce the same amount of cement. In the same regard, the construction industry can consume resources and materials; thus, there is a potential to use waste and by-products produced by its activities [3, 4]. The reuse of waste and by-products in cement-based materials can decrease the demand for the extraction of raw materials and can also decrease the pressure on landfills [5-7]. Furthermore, the use of pozzolanic materials from industrial by-products can decrease cement consumption in mortars and concrete, which is becoming a wide-spread practice [8, 9]. Cementitious material, such as metakaolin, fly ash, silica fume, and rice husk ash are considered as the most used pozzolanic materials [7, 10-14] as they can increase the mechanical strength as well as enhance the long-term features of mortars and concrete.
The waste fluid petroleum catalyst residue (FPCR), which is produced from the industry of petrochemical, is a zeolite material, and it primarily comprises of silica and alumina in which there is around 50% SiO2 and 40% Al2O3 [15, 16]. FPCR displays pozzolanic activity as it has a comparable chemical composition of other pozzolanic materials, such as fly ashes [17] or metakaolin [18-20] that are used for concrete and cement mortars modification. Up to now, most of the waste catalysts are classified as nonhazardous materials [21]. Previous investigations have confirmed that FPCR showed comparable pozzolanic activity to metakaolin [16, 22, 23]. Nevertheless, the potential use of FPCR in the field of construction materials as a filler for asphalt and/or a component in brick and/or mortar manufacturing has been recommended [9, 24-27]. Interest in the consumption FPCR as a construction material has been growing in the latest years. Pacewska et al. [28] investigated the pozzolanic nature of FPCR, and they revealed that it could react with CH in a similar way to microsilica. Several other studies showed that these FPCR catalysts could partially replace cement or fine aggregate without sacrificing the quality of cementitious materials [29-31]. Mármol et al. [32] stated that FPCR has similar pozzolanic activity and chemical structure to metakaolin and synthetic pozzolan.

To sum up, this study summarises an experimental work finding of the influence of partial replacing of OPC by FPCR, to produce a binder with low carbon and comparable properties. For this purpose, several mortars were prepared with various replacing levels (10%, 20%, 30%, 40% and 50%) to investigate the properties of the prepared mortars (the initial and final setting time and the compressive strength).

2. Materials and methodology

2.1. Materials

2.1.1. Fine aggregate

Natural sand that passed from a 3.35 mm sieve with a 2.62 as specific gravity and has the particle size distribution shown in Figure 1.

![Figure 1. The particle size distribution of the fine aggregates.](image)

2.1.2. Water

Tap water was used to prepare all mixes.

2.1.3. Binder materials

Ordinary Portland cement Type I (CEM I) was used produced by Lafarge in Iraq, and it is known commercially as Al Jeser. This cement complies with the requirement of (EN 197-1:2011) [33], and has a density of 2913 kg/m³; the pH of the aqueous solution was found to be 12.9.
Fluid petroleum catalyst residue (FPCR), which is a high alumino-silicate waste material, was also used. It is chiefly composed of alumina and inorganic silica, and it shows pozzolanic activity [34]. Mineralogical and chemical analyses were conducted to make a qualitative assessment of the geometric features of both OPC and FPCR particles. First, FPCR was milled for 45 minutes to decrease its mean particle size to 15.88 μm, and, accordingly, improve its pozzolanic reactivity [35]. From the microstructural studies (SEM provided in Figure 2), the OPC particles appeared with irregular shapes after the process of clinker grinding. However, the grinded FPCR particles appeared agglomerated with regular shape. It can be observed from the distribution of the particle size of OPC shown in Figure 3 that the majority of particles is falling in the range of 4-60 μm, while most FPCR particles (after grinding) are in the region of 0.8-60 μm. The measured pH of the FPCR was 6.03, while 2.46 was the specific gravity.

Figure 2. SEM view of OPC and FPCR particles.
The Energy-dispersive X-ray fluorescence (EDXRF) spectrometer was used to obtain the chemical compositions of OPC and FPCR (see Table 1). It can be concluded that the principal oxides in the FPCR were Al₂O₃ and SiO₂, which is agreed with the results stated by Mármol, Savastano, Bonilla, Borrachero, Monzó, Soriano and Payá [32], Mas et al. [36] and Dulaimi et al. [37]. The calcium hydroxide reacts with SiO₂ and Al₂O₃ in the existence of moisture to produce calcium silicate hydrate (CSH) gel [38]. Besides, the principal OPC oxides resulted from EDXRF were Ca, Si and Al and Fe with 2.62% as SO₃ content. These findings were consistent with those concluded by Sadique, Al Nageim, Atherton, Seton and Dempster [11], Corinaldesi and Moriconi [39], Sadique et al. [40]. In the same regard, the X-ray diffraction (XRD) method was used to assess the mineralogy of the two materials. It can be noticed that OPC was crystalline and includes sharp peaks (Figure 4). The prominent identified crystal peaks were: alite (3CaOSiO₂), periclase (MgO), ferrite (4CaOAl₂O₃ fe₂O₃), belite (2CaOSiO₂), and calcite (CaCO₃). However, the diffraction pattern of FPCR (Figure 5) showed an amorphous nature with shallow crystalline peaks, which will provide high reactivity during the hydration process.

| Oxide   | OPC    | FPCR  |
|---------|--------|-------|
| CaO, %  | 61.92  | 0.04  |
| SiO₂, % | 25.12  | 40.32 |
| Al₂O₃, % | 2.34  | 46.52 |
| Fe₂O₃, % | 1.68  | 0.37  |
| MgO, %  | 1.56   | 0.58  |
| Na₂O, % | 1.55   | 0     |
| K₂O, %  | 0.71   | 0.04  |
| SO₃, %  | 2.62   | 0     |
| TiO₂, % | 0.41   | 0     |
| LOI, %  | 0.23   | 1.25  |
2.2. Mix proportion

The mortars' mix proportion was 1:3 (cement or binder: sand) (by weight) with constant water to cement or binder ratio of 0.40. The content of binder, which involves OPC and FPCR, was kept fixed for all mixes. The various samples of mortar were cast in 5×5×5 cm cubes with FPCR as cement replacement by 10%, 20%, 30%, 40%, and 50%. Specimens were compacted in three layers using a vibrating table. After 24 h, all specimens were de-moulded and placed in a water tank till the ages of testing (3, 7, and 28 days). Table 2 provides the mix proportions details of the tested mortar specimens.

Table 2. Details of all mix proportions of the tested mortar specimens

| Mix Designation | OPC, % | FPCR, % | w/b |
|-----------------|--------|---------|-----|
| OPC             | 100    | 0       |     |
| OF10            | 90     | 10      |     |
| OF20            | 80     | 20      | 0.4 |
| OF30            | 70     | 30      |     |
| OF40            | 60     | 40      |     |
| OF50            | 50     | 50      |     |
2.3. Testing procedure

2.3.1. Setting time

Setting time test was performed on both OPC and OPC-FPCR specimens using Vicat device according to BS EN 196–3 [41].

2.3.2. Compression testing

The test of the compressive strength was performed on 5 cm cubes to examine the development strength of mortars that include different quantities of FPCR as OPC substitution at various curing ages. Three specimens were examined at each age of 3, 7, and 28-day of curing for every single mix under a loading rate of 0.35 MPa/min using a digital compression machine. The compression test was performed following BS EN 196-1[42].

2.3.3. Scanning electron microscopy (SEM)

SEM observation was utilised to evaluate the morphology of various raw material after 3 and 28 days. An Inspect S and a Quanta 200 model was used to perform this observation. The samples were first coated with a gold layer to increase visibility. Various mortar mixes were prepared (Table 2).

3. Results and discussion

3.1. Results of the setting times

The setting time results of OPC, OF10, OF20, OF30, OF40 and OF50 mixes are given in Table 3. The outcomes from the results of the setting time showed a decrease in the initial and final setting times of OF10, OF20, OF30, OF40 and OF50 relative to OPC. Initial and final setting times of the OF10 were 102 and 211 min, respectively, while it was 106 and 215 min for OPC. As more OPC is being substituted by FPCR, lower setting time is being obtained, due to the higher surface area and porous nature of FPCR [16, 43]. Consequently, when the proportion of OPC replacement increases lead to reduce the water content and thus shortens the required setting time. These results are in agreement with that of Su, Fang, Chen and Liu [31], Payá et al. [44].

| Test                      | OPC | OF10 | OF20 | OF30 | OF40 | OF50 |
|---------------------------|-----|------|------|------|------|------|
| Initial Setting Time (min)| 106 | 102  | 100  | 93   | 88   | 83   |
| Final Setting Time (min)  | 215 | 211  | 204  | 199  | 186  | 179  |

3.2 Results of the compressive strength

Figure 6 summarizes the results of the compressive strength of various mortars that were tested at 3, 7, and 28 curing days. In general, increasing the replacement level of FPCR resulted in a modest decrease in the mortars compressive strength at all ages except the lowest replacement level (10%). Comparing the results of the control mortar (100% OPC) with the corresponding mortars with 10% and 20% of FPCR replacement shows that for earlier compressive strength values (i.e. three days) were lower. However, mortars with a higher replacement level of FPCR exhibited the inverse trend as their earlier compressive strength were lower than the control mortar.

The high reactivity at an early age due to the use of FPCR with the presence of 10% and 20% of FPCR improved the strength development significantly at 3 and 7-day. This tendency is kept for 28-day of
curing. These findings were in good agreement with the results of Wu, Wu and Hsu [29] and Chen, Tseng and Hsu [30].

Figure 6. Compressive strength results.

3.3 Scanning Electron Microscopy (SEM)

SEM is a scanning technique that offers high-resolution and detailed images for the surfaces of the scanned sample. SEM can evaluate the hydration products that are produced in each sample. The progress in the microstructure and morphology changes of OF10 are shown in Figures 7 and 8. The generation of cementitious products, like Calcium Silicate Hydrate (C-S-H), Portlandite (CH), and Ettringite happened during the first 7-day of curing (early age) is evidence as all FPCR particles were covered by hydration products (Figure 7). The Ettringite can be simply recognised as well as the C-S-H gel and CH, which means that all FPCR particles were completely dissolved. Furthermore, Figure 8 shows that there was vast growth in the hydration products and cementitious C-S-H gel that happened over the curing age. This reflects the pozzolanic reaction growth over curing time, even with the substantial part of CH that have previously reacted at early ages into FPCR particles.

The SEM images at 28 days revealed a dense microstructure and less noticed Ettringite for the OF10. Both OPC and FPCR particles were converted into hydration products because of the strong hydration reaction. The glass phase of the pozzolanic materials contain soluble SiO₂ and Al₂O₃ that react with the released Ca(OH)₂ from the cement hydration generating additional C-S-H gel, which enhances the strength [45].
4. Conclusions

This research can draw several concluded points:

1. The analysis indicates that FPCR is mainly composed of SiO₂ and Al₂O₃.
2. Results showed that replacing more OPC producing lower setting times of mortars.
3. The early compressive strength of mortar with 10% FPCR as a replacement was higher than others due to the pozzolanic reaction of FPCR. Furthermore, the compressive strengths of mortar with 10% FPCR at 3, 7 and 28 days were increased compared with the control OPC.
4. The suitability of preparing blended cement using FPCR has been demonstrated. Mortars with 10% of replacement exhibited better compressive strengths in comparison with OPC, while 20% replacement still showed comparable compressive strengths, which demonstrates the influential role of this pozzolan material.
5. More research and development mainly on optimum mix design and durability cement mortar should be investigated.
6. Various cementitious products were noticed from the binary microstructure system of (OPC/ FPCR), such as Calcium Silicate Hydrate (C-S-H), Portlandite (CH) and Ettringite. This means that FPCR developed an early age pozzolanic effect, which results in high strengths.
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