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## Influence of treated waste phosphogypsum materials on the properties of ordinary portland cement

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### Abstract

In this study, treatment of phosphogypsum (PG) with lime-water (LWT), sulphuric acid (SAT), a mixture of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (AWT), PG-water (ST), and PG-limestone (LT) was attempted to purify PG and improve its quality so that it can be used for manufacture of ordinary Portland Cement (OPC). The treatment of PG removes P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>, and MgO impurities into water-leachable phase. Chemical analysis of the treated PG and mechanical properties of OPC mortar after various treatment of PG established improvement of the quality of PG. The purified PG contain less impurities when compared with untreated PG. It was observed that the leachable of P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>, and MgO in these samples ranged from 86% to 90%, 69% to 94%, 96% to 99%, respectively, can be achieved using these treatment processes. The major phases Alite (C<sub>3</sub>S), Belite (C<sub>2</sub>S), Aluminatetricalcic(C<sub>3</sub>A), and Tetra-calcium aluminoferrite (C<sub>4</sub>AF), and control ratios Lime Saturation factor (LSF), Aluminum/Iron ratio (AR), and Silica ratio (SR) were measured. These experimental results showed that the C<sub>3</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF, C<sub>2</sub>S, LSF, AR, and SR contents fulfilled the requirement of the Jordan Standards and European Standards; hence treated PG can be replaced by natural gypsum. The X-ray diffraction analysis of OPC samples showed that C<sub>3</sub>S and C<sub>2</sub>S are major mineral phases, C<sub>3</sub>A and C<sub>4</sub>AF represent as minor constituents while the CaO and MgO represent as trace phases. The effect of treated PG on the mechanical properties of OPC mortar was investigated. The OPC produced with purified phosphogypsum were found to have strength properties similar to those produced from mineral gypsum thus fulfilling Jordan Standards and European Standards. The present study indicates that the use of PG in OPC manufacture can solve the waste disposal problem thus cleaning our environment at one hand, on the other hand it can save natural raw materials i.e gypsum.

**Keywords:** Phosphogypsum; Waste management; Treatment methods; Portland cement; Quality assessment; Compressive strengths

### Introduction

Ordinary Portland cement (OPC) is one of the most widely used material in the constructions sector. Therefore it is important to determine a complete mineralogy of clinker cement to correctly understand, interpret and predict the outcome of any plant production process (Deborah *et al.*, 2009). Every year a huge amount of OPC is produced and used for the construction of building, roads and highways and other local purposes in Jordan.

PG is a by-product of the chemical reaction called the wet process whereby sulphuric acid is reacted with phosphate rock to produce phosphoric acid, needed for fertilizer production. Approximately five tons of PG is produced for every ton of phosphoric acid manufactured (Al-Hwaiti *et al.*, 2010). Through the wet process, some impurities naturally present in the phosphate rock become concentrated in PG,

including fluoride, sulfate, phosphates, organic matter, heavy metals, radionuclides, and residual acidity (Neville, 1996). Approximately 58% of the worldwide PG by-product is stockpiled, 14% is reprocessed and 28% is dumped into water bodies (FIPR, 1998). Therefore, attempts were made to use PG in concrete (Smadi *et al.*, 1999; Al-Hwaiti *et al.*, 2013).

A large volume of natural gypsum is used by the cement industry as a set retarder for OPC. It is added to the clinker at the cement grinding stage, usually at a concentration of 5–6%, depending on its purity (Falah, 2011). The use of PG to replace natural gypsum in OPC is minimal, and the main reason for the low demand is its high moisture content and impurities, which interfere with the consistency of the cement (Van der Merwe and Strydom, 2004). The phosphorus, sulfate, fluoride, and organic impurities

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contained in PG interfere in an unpredictable way to delay the setting time, and decrease the mechanical strength development of cement (Singh *et al.*, 2002). It is, thus, clear that PG may not always be suitable for direct use in OPC. Some way has to be found to counteract the harmful influence of impurities, before it can be considered by the cement industry. To solve this problem it is required to produce PG containing few or no impurities. Some of the other methods that have been proposed or adopted for minimizing the effects of impurities in PG are described as follows: washed the PG with water using a 100- $\mu$ m sieve, then heated the PG and added calcium hydroxide to the calcined product in order to improve the setting time and compressive strength of the material produced (Al-Jabbari *et al.*, 1988); investigated the effect of washed PG with water and milk of lime  $\text{Ca}(\text{OH})_2$ , with and without preceding thermal treatment (Erdogan *et al.*, 1994). He reported that the untreated PG retarded the setting times of OPC and also reduced its strength, but it can be used to control the hydration of cement if washed with milk of lime; another method involves treatment of PG with aqueous citric acid solution which converts phosphates, fluorides and organic matter into insoluble compounds (Singh, 2002). Treatment of PG with a combined thermal and sulphuric acid treatment method has purified phosphorus impurities before it can replace natural gypsum as a set retarder in OPC. These contaminants tend to delay the setting time in unpredictable way, and impair the development of mechanical strength (Van der Merwe and Strydom, 2004). Recently, Weiguo *et al.* (2012) showed that OPC using PG as retarder has delayed the setting time

and difficulty being fed into the cement mill. The soluble phosphates in PG behave as super-retarder and bring about retarding in the setting process of cement made with PG.

PG obtained from the Indo-Jordan Chemical plants in Eshidiya Mines contains greater proportions of impurities, such as phosphate, sulfate, organic matter, fluoride, and acidity. These parameters may seriously affect strength of OPC if used in high volume. There is, therefore, a strong need to investigate preliminary properties of low volume use of (untreated and treated) PG in OPC industry.

Now a days, Jordan PG has not yet been utilized in OPC (Al-Hwaiti *et al.*, 2013). The aim of this study is to: (1) treat PG waste with lime-water (LWT), sulphuric acid (SAT),  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  mixture (AWT), PG-water (ST), and PG-limestone (LT), in order to reduce chemical oxides such as  $\text{MgO}$ ,  $\text{SO}_3$ , and  $\text{P}_2\text{O}_5$  content in the studied samples; (2) to investigate the various chemical compounds  $\text{C}_3\text{S}$ ,  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$ ,  $\text{C}_2\text{S}$ , LSF, AR, and SR in order to assess the hardening of cement and setting time, and the quality of OPC; (3) to evaluate the physical and mechanical properties, in order to improve the hardening of cement and compressive strengths.

## Materials and methods

### Materials

The raw materials were collected from Rashidiya area at Tafila, south Jordan. The raw materials needed to produce cement are generally extracted from limestone rock, clay, and natural gypsum. They are then crushed and transported to the

**Table I. The chemical compositions (%) of the raw materials required for the production of clinker**

	Limestone	Clay	Pozzolana	Natural gypsum
CaO	52.95	23.70	11.36	30.01
SiO <sub>2</sub>	3.32	47.19	40.97	2.02
Al <sub>2</sub> O <sub>3</sub>	1.16	7.67	13.95	0.32
Fe <sub>2</sub> O <sub>3</sub>	0.67	4.14	15.11	-
MgO	0.50	1.69	7.55	0.06
MnO	0.02	0.02	-	-
TiO <sub>2</sub>	1.20	1.70	-	-
Na <sub>2</sub> O	0.02	0.33	0.36	-
K <sub>2</sub> O	0.18	0.76	0.04	-
SO <sub>3</sub>	0.04	0.10	0.09	45.56
P <sub>2</sub> O <sub>5</sub>	0.03	0.12	-	0.01
F	0.00	0.00	-	0.01
LOI	41.35	13.62	12.70	20.26
Sum	101.44	101.04	102.13	98.25

Rashidiya cement plant where they are stored and homogenized. The chemical compositions of raw materials: limestone, clay, pozzolana and natural gypsum are listed in Table I. The mixing percentage contents of the raw materials required for the production of clinker is 70%, 25%, 5% and 5%, respectively. The moisture contents of the raw mixture

supplied to the mills ranged from 4.1% to 7.6%. Fifteen PG samples were collected from Indo-Jordan Chemicals Company (Fig. 1), weighted 10 Kg each. For every 5 samples, one composite samples were selected, weighted 1 kg each, ground, dried overnight at 45°C, and then stored for several treatment methods.

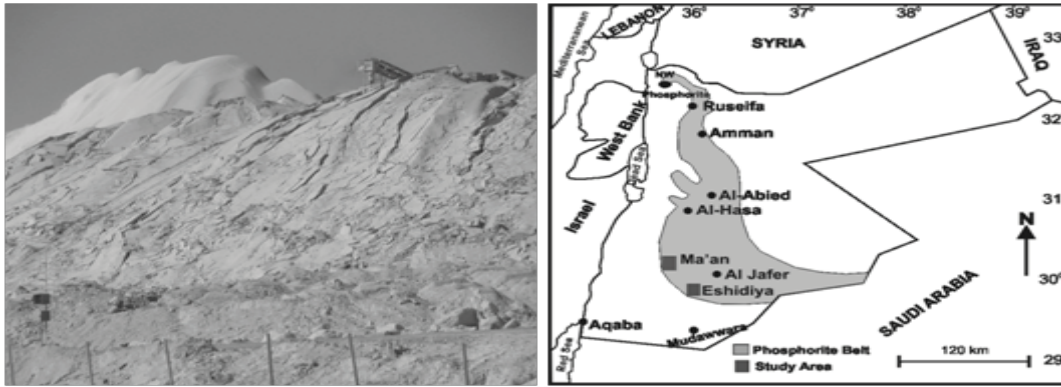


Fig. 1. Samples site and location map of the study area.

Table II. The mix proportions of varying percentage of reagent and PG

Code	PG	Reagent	Reaction Time	T	Filtered	Dried
	g		hour	°C		°C
PG-1	200	-	-	-	-	85
PG-2	200	-	-	-	-	85
PG-3	200	-	-	-	-	85
PG-4	200	-	-	-	-	65
PG-5	200	-	-	-	-	65
Lime-Water Treatment						
LWT1	200	Lime water + Sea water (v/v) (100ml: 700ml)	24	25	A Büchner funnel	65
LWT2	200	Lime water + Sea water (v/v) (125ml: 675ml)	24	25	A Büchner funnel	65
LWT3	200	Lime water + Sea water (v/v) (150ml: 650ml)	24	25	A Büchner funnel	65
LWT4	200	Lime water + Tap water (v/v) (100ml: 700ml)	24	25	A Büchner funnel	65
LWT5	200	Lime water + Tap water (v/v) (100ml: 700ml)	24	25	A Büchner funnel	65
LWT6	200	Lime water + Distilled water (v/v) (100ml: 700ml)	24	25	A Büchner funnel	65
LWT7	200	Lime water + Distilled water (v/v) (1250ml: 675ml)	24	25	A Büchner funnel	65
Sulphuric acid + Water Treatment						
SAT1	200	5 %Sulphuric acid + Sea water (v/v) (12ml: 88ml)	24	25	A Büchner funnel	65
SAT2	200	5 %Sulphuric acid+ Tap water (v/v) (12ml: 88ml)	24	25	A Büchner funnel	65
SAT3	200	5 %Sulphuric acid + Distiled water (v/v) (12ml: 88ml)	24	25	A Büchner funnel	65
SAT4	200	5 %Sulphuric acid + Limewater (v/v) (12ml: 88ml)	24	25	A Büchner funnel	65
(H <sub>2</sub> SO <sub>4</sub> + 4 ml 2% HNO <sub>3</sub> ) + Water Treatment						
AWT1	200	300 ml 5%H <sub>2</sub> SO <sub>4</sub> + 4 ml 2% HNO <sub>3</sub> + Distilled water (v/v) (250ml: 750ml)	24	25	A Büchner funnel	65
AWT2	200	300 ml 5%H <sub>2</sub> SO <sub>4</sub> + 4 ml 2% HNO <sub>3</sub> + Distilled water (v/v) (300ml: 700ml)	24	25	A Büchner funnel	65
PG + Water Treatment						
ST1	200	Tap water (100 ml)	24	25	A Büchner funnel	65
ST2	200	Distilled water (200 ml)	24	25	A Büchner funnel	65
PG + Limestone Treatment						
LT1	200	Limestone (5 g)	-	-	-	-
LT2	200	Limestone (10 g)	-	-	-	-
LT3	200	Limestone (25 g)	-	-	-	-
LT4	200	Limestone (50 g)	-	-	-	-
LT5	200	Limestone (75 g)	-	-	-	-

### Batch Purification of phosphogypsum

Three composite PG samples were subjected for each treatment: lime-Water treatment (LWT), sulphuric acid treatment (SAT), H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> mixing treatment (AWT), PG-Water treatment (ST), PG-Limestone treatment (LT) reagent process. The mix proportions were composed of varying percentage of reagent and PG are summarized in Table II. The PG samples were thoroughly shaken with aqueous solution in a mechanical shaker for 24 hours at ambient temperature, filtered through a Buckner funnel and then dried overnight at 65°C. Batch purification experiments were conducted in polyethylene bottles.

### Ordinary portland cement (OPC) tests

Sixty six purified PG samples produced from batch experiments were mixed with clinker from Rashidiya cement plant. OPC was produced by mixing of 95% of clinker and 5% of purified PG. The grindability or crushing is determined by comparing the increase in fineness in material and the energy spent for such increase. Approximately 95% of OPC particles are smaller than 45 μ with average of particle size about 15 μ. The initial setting time ranged from 110 to 120 min, whereas the final setting ranged from 580 to 600 min. Good quality cement requires adequate fineness corresponding to a specific surface ranging from 3200 and 3500 Blaine (cm<sup>2</sup>/g). The monitoring of quality control of cement is pre-requisite to start the study of the PG based cement. The physical properties of the OPC were determined by measuring specific surface area, specific gravity, and bulk density of OPC was performed according to the ASTM C597, ASTM C39 and ASTM C188. Specific surface area of OPC ranges between 300 m<sup>2</sup>/kg and 320 m<sup>2</sup>/kg. Specific gravity of OPC is found to be in the range of 3.10 to 3.25. Bulk density of OPC ranges from 830 kg/m<sup>3</sup> to 1650 kg/m<sup>3</sup>.

### Chemical analysis

#### X-ray fluorescence (XRF)

Eight PG samples were analyzed for major and minor oxides of CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, and SO<sub>3</sub> by using X-ray fluorescence (SIM XRF ARL 8405) at the Research Department, Jordan Phosphate Mines Company (JPMC). Sixty six OPC samples for major oxides CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, Na<sub>2</sub>O, K<sub>2</sub>O, and SO<sub>3</sub> were analyzed by using X-ray analyzer (ARL WIN XRF V3.1-2) at Rashidiya cement plant. C<sub>2</sub>S, C<sub>3</sub>A, C<sub>4</sub>AF, C<sub>3</sub>S, and LOI for OPC were measured by using ARL win XRF V 3.1-2. The SO<sub>3</sub> content of each gypsum sample was first determined by a wet chemical method, and each of the gypsum samples was then mixed with the clinker to achieve a final SO<sub>3</sub> content of 3.1% in the cement.

### Preparation of specimens and testing

Sixty six OPC mixes were made for each type of PG purified. Each mix was prepared to produce mortar specimens that are needed to assess the compressive strength in addition to other tests that might be needed for SEM and XRD tests. All OPC specimens were cast in 16 × 4 × 4 cm molds for testing compressive strength of cement mortar. Measurements were made for 2 and 28 days. The compressive strength tests were carried out according to EN 196-1.

### Quality assessment of OPC

The principal constituents of OPC are tricalcium silicate (3CaO.SiO<sub>2</sub>), dicalcium silicate (2CaO.SiO<sub>2</sub>), tricalcium aluminate (3CaO.Al<sub>2</sub>O<sub>3</sub>) and tetracalcium aluminoferrite (4CaO.Al<sub>2</sub>O<sub>3</sub>.Fe<sub>2</sub>O<sub>3</sub>) and they are designated as C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A, and C<sub>4</sub>AF respectively (Lobthenbach *et al.* 2006). C<sub>3</sub>S and C<sub>2</sub>S are responsible for strength development. C<sub>3</sub>A and C<sub>4</sub>AF control setting and heat evolution during hydration (Natalya, 2003). The properties of the cement, such as its setting time and strength, are adjusted by the addition of gypsum and by grinding to specific degrees of fineness (Wagner and Vassilopoulos, 2000). The compositions of the constituents are used to determine the quality of the OPC. The quality of the cement products were calculated from the oxide concentrations of the cement using Bogue formulae (Ali *et al.*, 2008). The lime saturation factor, the silica and aluminum ratios were calculated from the percentage oxide compositions (Charles *et al.*, 2010). The formulae for the calculation are as follows:

$$\text{Lime Saturation factor (LSF)} = \{(\text{CaO}) / [(2.8\text{SiO}_2) + (1.2\text{Al}_2\text{O}_3) + (0.65\text{Fe}_2\text{O}_3)]\} \quad (6)$$

$$\text{Aluminum/iron ratio (AR)} = [(\text{Al}_2\text{O}_3) / (\text{Fe}_2\text{O}_3)] \quad (7)$$

$$\text{Silica ratio (SR)} = [(\text{SiO}_2) / (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)] \quad (8)$$

## Results and discussion

### Influence of chemical composition in OPC products

The eight major oxides P<sub>2</sub>O<sub>5</sub>, SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, SO<sub>3</sub>, and L.O.I in the PG from Eshidiya are summarized in Table III. Examination of the data in Table III showed that the major oxides concentration in the samples less varied considerably, most notably, SO<sub>3</sub> concentrations in PG-1, PG-2, PG-3, PG-4, PG-5, PG-6, PG-7, PG-8 were 41.42%, 42.50%, 43.20%, 42.40%, 41.76%, 41.80%, 41.80% and 42.70%, respectively. Chemical analysis of major oxides of treated PG is shown in Table V. The mean percentage of CaO content in the LWT, SAT, AWT, ST, and LT are 63.89%, 63.77%, 63.70%, 64.00%, and 64.38%, respectively. Amount

**Table III. Chemical composition (%) of PG from Indo-Jordan chemical at Eshidiya Mines**

	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	L.O.I	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>
PG-1	4.89	11.29	10.10	33.30	0.73	0.34	0.27	41.42
PG-2	4.64	11.27	10.12	33.20	0.48	0.20	0.10	42.50
PG-3	5.02	11.55	10.40	32.20	0.45	0.26	0.09	43.20
PG-4	4.57	15.15	10.70	30.65	0.45	0.22	0.08	42.40
PG-5	4.37	11.62	10.88	31.50	0.42	0.18	0.07	41.76
PG-6	4.52	10.66	10.10	31.90	0.50	0.20	0.09	41.86
PG-7	4.95	11.63	10.90	32.12	0.69	0.29	0.13	41.80
PG-8	4.80	10.41	10.65	32.27	0.44	0.17	0.08	42.70
Average	4.72	12.45	10.48	32.14	0.52	0.23	0.11	42.20
STD	0.23	2.44	0.35	0.86	0.12	0.06	0.07	2.75

**Table IV. Chemical analysis of major oxides (%) of treated PG**

	SO <sub>3</sub>			MgO			P <sub>2</sub> O <sub>5</sub>		
	T	Cx	L %	T	Cx	L %	T	Cx	L %
LWT-1	42.2	40.91	96.94	0.11	0.108	98.18	4.72	4.18	88.56
LWT-2	42.2	34.82	82.51	0.11	0.109	99.09	4.72	4.13	87.50
LWT-3	42.2	35.68	84.55	0.11	0.108	98.18	4.72	4.15	87.92
LWT-4	42.2	34.66	82.13	0.11	0.109	99.09	4.72	4.17	88.35
LWT-5	42.2	37.85	89.69	0.11	0.109	99.09	4.72	4.15	87.92
LWT-6	42.2	38.99	92.39	0.11	0.109	99.09	4.72	4.16	88.14
LWT-7	42.2	35.86	84.98	0.11	0.109	99.09	4.72	4.15	87.92
Average	42.20	36.97	87.60	0.11	0.11	98.83	4.72	4.16	88.04
SAT-1	42.2	41.13	97.46	0.11	0.107	97.27	4.72	4.22	89.41
SAT-2	42.2	37.96	89.95	0.11	0.109	99.09	4.72	4.23	89.62
SAT-3	42.2	41.3	97.87	0.11	0.108	98.18	4.72	4.20	88.98
SAT-4	42.2	37.29	88.36	0.11	0.107	97.27	4.72	4.18	88.56
Average	42.20	39.42	93.41	0.11	0.11	97.95	4.72	4.21	89.14
AWT-1	42.2	41.05	97.27	0.11	0.108	98.18	4.72	4.13	87.50
AWT-2	42.2	38.6	91.47	0.11	0.109	99.09	4.72	4.15	87.92
AWT-3	42.2	38.23	90.59	0.11	0.107	97.27	4.72	4.14	87.71
Average	42.20	39.29	93.11	0.11	0.11	98.18	4.72	4.14	87.71
ST-1	42.2	39.38	93.32	0.11	0.108	98.18	4.72	4.22	89.41
ST-2	42.2	39.97	94.72	0.11	0.108	98.18	4.72	4.25	90.04
ST-3	42.2	39.27	93.06	0.11	0.11	99.09	4.72	4.26	90.25
Average	42.20	39.54	93.70	0.11	0.11	98.48	4.72	4.24	89.90
LT-1	42.2	30.43	72.11	0.11	0.105	95.45	4.72	4.10	86.86
LT-2	42.2	29.53	69.98	0.11	0.106	96.36	4.72	4.11	87.08
LT-3	42.2	30.87	73.15	0.11	0.107	97.27	4.72	4.08	86.44
LT-4	42.2	30.34	71.90	0.11	0.106	96.36	4.72	4.04	85.59
LT-5	42.2	24.96	59.15	0.11	0.105	95.45	4.72	4.08	86.44
Average	42.20	29.23	69.26	0.11	0.11	96.18	4.72	4.08	86.48

$$T = \text{Total}, CX = \text{Leaching}, L = \text{Leaching } (\%L) = (Cx * CaO / TCaO) * 100\%$$

of CaO as specified in OPC by the British standards, Jordan Standards, and European Standards should be within the range 63% to 67%, 61% to 65%, 61% to 67%, respectively (Ali *et al.*, 2008). According to Neville (1996) the proper lime content is limited due to the lower early strength produced when lime content of OPC is too low, and unsoundness when it is too high. High CaO content is associated with early strength whereas; slightly lower content of lime favors ultimate strength which develops gradually over a long period of time (Pandey and Shukla, 1980). In

order to increase the strength it is necessary to increase the lime content, or grind finer. But higher temperatures are required to burn the high lime mixtures (Neville, 1996). The mean concentrations of SiO<sub>2</sub> in the LWT, SAT, AWT, ST, and LT are 21.39%, 21.42%, 21.00%, 21.30%, and 21.60%, respectively (Table V). British Standards, Jordan Standards, and European standards specify amounts of SiO<sub>2</sub> in Portland cement within the range of 21% to 22%, 18% to 21%, and 19% to 21%, respectively. Hence treated PG could be replaced by natural gypsum.

The mean concentrations of  $\text{Al}_2\text{O}_3$  in the LWT, SAT, AWT, ST, and LT are 5.07%, 5.08%, 5.10%, 5.07%, and 4.72%, respectively. The Jordan standards and European standards specify amounts of  $\text{Al}_2\text{O}_3$  in OPC within the range of 4% to 6% and 2% to 6% (Tamas, 2010). The mean concentrations of  $\text{Fe}_2\text{O}_3$  in the LWT, SAT, AWT, ST, and LT are 3.28%, 3.27%, 3.30%, 3.29%, and 3.32%, respectively. However, the amount of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in OPC are within the specified limit, indicating that the CaO content is specified limit, and the silica becomes specified limit, which may be accompanied by a specified limit in alumina and ferric oxide, the temperature of burning will not be raised and the special influence of the high lime will not be lost, which appear to be of high value for their cementing qualities. This results is confirmed by

(Neville, 1996), if the CaO content is fixed, and the silica becomes too high, which may be accompanied by a decrease in alumina and ferric oxide, the temperature of burning will be raised and the special influence of the high lime will be lost. If the lime content is too low, which means an increase in the alumina and ferric oxide, the cement may become quick-setting and contain a larger amount of alumina compounds, which appear to be of little value for their cementing qualities. Rapid setting is undesirable, and is not permitted by the standard specifications, because the cement sets up so rapidly that it cannot properly be worked in the forms before stiffening occurs.

The mean concentrations of MgO in the LWT, SAT, AWT, ST, and LT are 2.52%, 2.98%, 2.20%, 2.48%, and 2.19%, respectively. According to Jordan standard and EU specification the MgO content in OPC would be <5%. MgO contents have a detrimental effect on the soundness of the coarse, especially at late ages. Austin (1985) showed that high magnesium oxide reacts with water to form  $\text{Mg}(\text{OH})_2$ , and this is the slowest reaction among all other hardening reactions. Since  $\text{Mg}(\text{OH})_2$  occupies a larger volume than the MgO and is formed on the same spot where the MgO particle is located, it can split apart the binding of the hardened cement paste, resulting in expansion cracks commonly known as magnesia expansion. In this study, the average percentage leach of MgO was found to be 98%, 98%, 98%, 98%, and 96% from original MgO present in LWT, SAT, AWT, ST, and LT, respectively (Table IV), indicating that the leach of MgO showed that low magnesium oxide reacts with water to form  $\text{Mg}(\text{OH})_2$ .

The mean concentrations of  $\text{SO}_3$  in the LWT, SAT, AWT, ST, and LT are 2.98 %, 3.32%, 3.60%, 3.13%, and 3.29%, respectively. According to Jordan standard and EU specification the  $\text{SO}_3$  content in OPC ranged from 2.70% to 3.50%, from 1.50% to 2.50% respectively, (Faleye *et al.*, 2009), indicating that the allowable  $\text{SO}_3$  content in the cement

will prevent sulfate expansion. In this study, the average percentage leach of  $\text{SO}_3$  was found to be 88%, 93%, 93%, 94%, 69% from original  $\text{SO}_3$  present in LWT, SAT, AWT, ST, and LT, respectively (Table IV), indicating that the leach of  $\text{SO}_3$  showed that setting time effectively decreased and then improved OPC standard specification.

The mean concentrations of loss on ignition (LOI) in the LWT, SAT, AWT, ST, and LT are 3.01 %, 3.13%, 3.15%, 3.11%, and 3.23%, respectively. LOI of the all samples were found to conform as specified by the Jordan standards and EU Standards. It can be concluded that the allowable LOI indicates non-hydration and non-carbonation, which may be caused by appropriate storage or adulteration of OPC during transport or transfer. The possible reasons of variations are specification of raw mix, uniformity of mixture, and decrease impurities from various stages of processing, and intentional alteration. Variations in chemical constituents affect the OPC properties like, hardening/hydration, setting time, corrosion resistance, color, etc (Pandey and Shukla, 1980). The OPC produced with purified PG were found to have CaO,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , MgO,  $\text{SO}_3$ , and LOI chemical compositions similar to those produced from mineral gypsum thus fulfilling Jordan Standards and European Standards.

OPC always contains phosphorus in the range 0.2 to 0.3 weight percent (wt. %)  $\text{P}_2\text{O}_5$  (Kwon *et al.*, 2005). The effect of phosphorus was studied in order to validate the use of phosphorus-rich limestone quarries, such as the phosphatic rocks, however, in this study clinkers phosphorus concentration was above 1 wt. % P. The major effect of phosphorus addition is to decrease the  $\text{C}_3\text{S}/\text{C}_2\text{S}$  ratio, with a strong deterioration of the mechanical properties of the hydrated OPC, since  $\text{C}_3\text{S}$  is the main hydraulic phase in clinker. For each additional of  $\text{P}_2\text{O}_5$  above 1 wt. %, the  $\text{C}_3\text{S}$  concentration decreases with 9.9 wt. % whereas the  $\text{C}_2\text{S}$  concentration increases with 10.9 wt. %. Above 2.25 wt. %  $\text{P}_2\text{O}_5$ , the clinker is no more acceptable for cement production. In this study, the mean concentrations of  $\text{P}_2\text{O}_5$  in the LWT, SAT, AWT, ST, and LT are 0.56 %, 0.51%, 0.58%, 0.48%, and 0.64%, respectively. All the OPC samples were found to be competent with regard to maximum  $\text{P}_2\text{O}_5$  limit range should be 0-1%, and preferable range should be 0.3- 0.5% as specified by the Jordan Standards and EU Standards. It can be concluded that the allowable  $\text{P}_2\text{O}_5$  accelerates the clinkerization reaction, reduces the intensity of internal volatile cycle, reduces the early strength, and reduces  $\text{C}_3\text{S}$  content (Taylor, 1997).

#### Quality assessment of OPC by XRD

Fig. 2. shows that the major constituents of OPC:  $\text{Ca}_3\text{SiO}_5$  ( $\text{C}_3\text{S}$ ),  $\text{Ca}_2\text{SiO}_4$  ( $\text{C}_2\text{S}$ ),  $\text{Ca}_3\text{Al}_2\text{O}_6$  ( $\text{C}_3\text{A}$ ),  $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$  ( $\text{C}_4\text{AF}$ ) (Taylor, 1997). The X-ray diffraction analysis of OPC

**Table V. Chemical compositions of natural gypsum, PG, treated PG and OPC**

Elements	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	C <sub>3</sub> S	C <sub>4</sub> AF	C <sub>3</sub> A	C <sub>2</sub> S	LSF	AR	SR
Natural gypsum	60.90	20.30	5.40	3.80	4.40	3.10	42.75	25.95	7.88	15.00	0.93	1.42	2.21
PG (untreated)	62.30	21.80	5.10	3.50	1.60	2.90	40.08	32.26	7.59	14.70	0.90	1.46	2.53
OPC (JS-STD)	65.60	21.00	5.50	3.30	1.40	2.70	57.74	26.65	8.99	10.04	0.97	1.67	2.39
OPC (EU-STD)	66.20	23.30	5.13	3.53	0.83	0.27	51.82	27.71	7.62	10.74	0.90	1.45	2.69
LWT-1	63.62	21.19	4.99	3.28	2.20	3.07	50.67	22.53	7.67	9.98	0.94	1.52	2.56
LWT-2	63.99	21.62	5.12	3.29	3.29	2.87	48.58	25.33	8.00	10.01	0.93	1.56	2.57
LWT-3	63.68	21.21	5.08	3.3	2.72	3.00	50.32	22.85	7.88	10.04	0.94	1.54	2.53
LWT-4	64.01	21.55	5.07	3.26	2.25	2.95	49.35	24.55	7.92	9.92	0.93	1.56	2.59
LWT-5	63.99	21.47	5.03	3.27	2.19	3.09	49.73	24.04	7.80	9.95	0.94	1.54	2.59
LWT-6	64.18	21.46	5.09	3.24	2.23	2.92	50.70	23.27	8.01	9.86	0.94	1.57	2.58
LWT-7	63.75	21.26	5.13	3.31	2.73	2.97	49.96	23.26	7.99	10.07	0.94	1.55	2.52
Average	63.89	21.39	5.07	3.28	2.52	2.98	49.90	23.69	7.90	9.98	0.94	1.55	2.56
SAT-1	63.98	21.46	5.10	3.18	2.23	3.31	48.80	24.71	8.13	9.68	0.94	1.60	2.59
SAT-2	63.52	21.35	5.06	3.32	2.72	3.27	47.94	25.04	7.79	10.10	0.93	1.52	2.55
SAT-3	63.95	21.42	5.05	3.27	2.2	3.38	48.99	24.45	7.85	9.95	0.94	1.54	2.57
SAT-4	63.63	21.46	5.12	3.32	4.75	3.31	47.04	26.04	7.95	10.10	0.93	1.54	2.54
Average	63.77	21.42	5.08	3.27	2.98	3.32	48.19	25.06	7.93	9.96		1.55	
AWT-1	62.5	21	5.1	3.2	2.1	3.3	50.05	22.1	7.75	9.93	0.95	1.4	2.3
AWT-2	64.9	21	5.1	3.4	2.3	3.9	50.15	22.42	7.93	10.07	0.95	1.55	2.5
AWT-3	63.8	21	5.1	3.3	2.2	3.6	50.25	22.59	8.11	10.12	0.95	1.7	2.7
Average	63.7	21	5.1	3.3	2.2	3.6	50.15	22.37	7.93	10.04	0.95	1.55	2.5
ST-1	63.86	21.22	5.04	3.3	2.71	3.26	50.51	22.73	7.77	10.04	0.94	1.53	2.54
ST-2	64.14	21.38	5.05	3.27	2.4	3.02	50.65	22.81	7.85	9.98	0.94	1.52	2.54
ST-3	64.2	21.42	5.12	3.31	2.32	3.1	50.90	22.92	7.97	9.98	0.94	1.58	2.57
Average	64	21.3	5.07	3.29	2.48	3.13	50.69	22.82	7.86	10.00	0.94	1.54	2.55
LT-1	63.73	21.06	4.78	3.2	2.08	3.08	53.62	19.93	7.25	9.74	0.95	1.49	2.64
LT-2	63.61	20.96	4.76	3.19	2.07	3.15	53.84	19.48	7.22	9.71	0.96	1.49	2.64
LT-3	63.81	20.49	4.62	3.16	2.03	3.71	57.62	15.28	6.90	9.62	0.98	1.46	2.63
LT-4	64.66	20.15	4.59	3.12	2.01	3.06	65.78	8.15	6.88	9.49	1.01	1.47	2.61
LT-5	66.10	20.36	4.85	3.92	2.76	3.45	66.02	8.56	6.22	11.93	1.01	1.24	2.32
Average	64.38	20.60	4.72	3.32	2.19	3.29	59.37	14.28	6.89	10.10	0.98	1.43	2.56

**Table VI. Physical characteristics of OPC tests containing treated PG**

Physical property	LWT	SAT	AWT	ST	LT	
Blaine surface area (cm <sup>2</sup> /g)	3200	3500	3200	3300	3200	
Specific gravity	3.15	3.10	3.12	3.17	3.25	
Unit weight (kg/m <sup>3</sup> )	2400	2480	2300	2250	2500	
Initial setting time (min)	-Final setting time (min)	115 -600	112 -590	108 -596	110 -580	120 -600

samples showed that  $C_3S$  and  $C_2S$ , as a major mineral phase,  $C_3A$  and  $C_4AF$  are represents as minor constituents while the free lime  $CaO$  and Periclase  $MgO$  present as trace phases. The mean percentage proportions of  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$

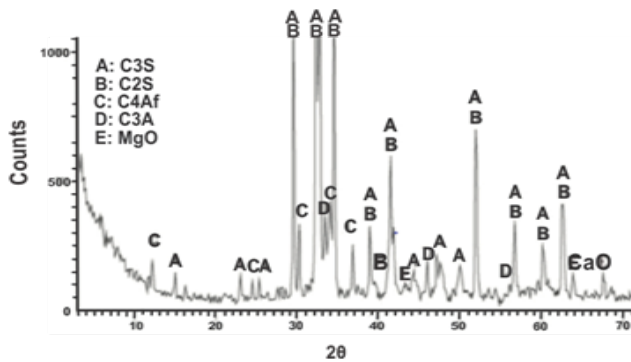


Fig. 2. X-ray diffraction of OPC

in OPC are shown in Table V. The mean concentrations of  $C_3A$  in the LWT, SAT, AWT, ST, and LT are 50%, 48%, 50%, 50%, and 60%, respectively. These results indicate that  $C_3A$  content lies within the range recommended by Jordan Standard (50%-64%) (JS 30-1:2007) (Falah, 2011) and European Standard (50%-64%) (EN 197-1, 2000) specifications for ordinary OPC purposes. Hence, treated PG could be replaced by natural gypsum. The mean percentage proportions of  $C_4AF$  in the LWT, SAT, AWT, ST, and LT are 24%, 25%, 22%, 23%, and 14%, respectively. These results indicate that  $C_4AF$  content agree with the result recommended by Jordan Standard (26%) and European Standard (27%) specifications for OPC purposes (Falah, 2011; EN 197-1, 2000). Therefore, treated PG could be replaced by natural gypsum. The mean percentage proportions of  $C_3S$  in the LWT, SAT, AWT, ST, and LT are 8%, 8%, 8%, 8%, and 7%, respectively. These results indicated that  $C_3S$  content lies with the result recommended by Jordan Standard (6%- 9.5%) and European Standard (6 % - 9.5%) specifications for OPC purposes. Thus, treated PG could be replaced by natural gypsum. However, concrete made with OPC having a relatively high  $C_3S$  content will tend to gain more strength and produce more heat of hydration at earlier ages, usually within the first week of placement (EN 197-1, 2000). The mean percentage proportions of  $C_2S$  in the LWT, SAT, AWT, ST, and LT are 10%, 10%, 10%, 10%, and 10%, respectively. These results indicated that  $C_2S$  content conform with the result recommended by Jordan Standard (10%) and European Standard (10%) specifications for OPC purposes (Falah, 2011; EN 197-1, 2000). Treated PG could be replaced by natural gypsum. Chandra (1997), specified concrete made with OPC having a relatively high  $C_2S$  content tends to gain more of its strength at later ages, perhaps up to four weeks

after placing. Overall, variation in the chemical constituent of cement affects the hardening/hydration, setting time, corrosion resistance, color of cement (Pandey and Shukla, 1980). The mean ratio of LSF, AR, and SR in OPC is shown in Table V. The mean ratios of LSF in the LWT, SAT, AWT, ST, and LT are 0.94, 0.93, 0.95, 0.94, and 0.98, respectively. These results indicate that LSF content lies within the range recommended by (Noor-ul-Amin, 2010) (0.9-0.98) as specified OPC purposes. Treated PG when replaced by a natural gypsum, can be used in OPC manufacturing process. The mean ratios of AR in the LWT, SAT, AWT, ST, and LT are 1.55, 1.55, 1.55, 1.54, and 1.43, respectively. These results indicate that AR content is within the range recommended by Sam *et al.* (2013) (1.3-2.5) specifications for OPC purposes. However, AR ratio above 2.5, can develop high early strength and low early strength and low heat of hydration occur if it goes below 1.3 (Sam *et al.*, 2013). It can be concluded that treated PG could be replaced by natural gypsum, and it does not create any problem in cement manufacturing process and OPC strength. The mean ratios of SR in the LWT, SAT, AWT, ST, and LT are 2.56, 2.56, 2.50, 2.55, and 2.56, respectively, and lies within the range recommended by (Noor-ul-Amin, 2010). However, if SR less than 2, burning become very easy but excessive liquid phase and low strength cement is obtained. On the other hand if the SR reaches up to 3, then the high strength OPC is obtained, therefore the burning become very difficult. For SR more than 3, no clinkerization takes place. This indicates that treated PG can be replaced by natural gypsum.

#### Physical properties of OPC

The blaine surface area, specific gravity, and unit weight test results are presented in Table VI. All samples were milled to a fineness of approximately 3200  $cm^2/g$  Blaine surface area. The average specific gravity and unit weight of the OPC contains LWR, SAT, AWT, ST, and LT is 2.35 and 2400  $kg/m^3$ , 2.40 and 2480  $kg/m^3$ , 2.32 and 2300  $kg/m^3$ , 2.27 and 2250  $kg/m^3$ , 2.50 and 2500  $kg/m^3$ , respectively. The increase in density of OPC can be attributed to increase specific gravity of additives as compared to that of LT. Unit weight of OPC increased from 2250  $kg/m^3$  ST to 2500  $kg/m^3$  LT was used as fine additives in OPC. However, substantial increases in viscosity and unit weight occur at the concentration at which close packing is reached. The increase of viscosity beyond this limit may be explained by an increase in inter-particle friction due to increased solid-solid contact.

#### The compressive strengths of the (OPC)

The compressive strength values of the 2-days and 28-days OPC samples containing the treated PG conform to the corresponding value using natural gypsum and untreated PG are given in Table VII. The average compressive strength



results of OPC at 2-days and 28-days in the natural gypsum, PG, LWR, SAT, AWT, ST, and LT is 10 and 42.5 N/mm<sup>2</sup>, 8.2 and 30.1 N/mm<sup>2</sup>, 13.6 and 35.3 N/mm<sup>2</sup>, 10.7 and 31.5 N/mm<sup>2</sup>, 12.8 and 35.8 N/mm<sup>2</sup>, 10.7 and 35.1 N/mm<sup>2</sup>, and 9.5 and 34.5 N/mm<sup>2</sup>, respectively. It can be concluded that the

**Table VII. Compressing strength tests of OPC containing untreated and treated PG and natural gypsum**

	2-days (N/mm <sup>2</sup> )	28-days (N/mm <sup>2</sup> )
Natural gypsum	10	42.5
Phosphogypsum	8.2	30.1
LWT-1	14.1	35.6
LWT-2	13.8	35.2
LWT-3	13.7	35.6
LWT-4	14.0	34.9
LWT-5	14.2	35.4
LWT-6	12.0	35.1
LWT-7	13.1	35.1
Average	13.6	35.3
SAT-1	10.2	31.5
SAT-2	11.1	32.4
SAT-3	10.5	31.4
SAT-4	10.8	30.8
Average	10.7	31.5
AWT-1	12.3	38.0
AWT-2	13.0	38.1
AWT-	13.2	39.5
Average	12.8	38.5
ST-1	10.9	35.5
ST-2	10.7	34.9
ST-3	10.5	34.7
Average	10.7	35.1
LT-1	10.0	35.1
LT-2	9.0	34.2
LT-3	9.4	34.5
LT-4	9.8	34.8
LT-5	9.2	34.6
Average	9.5	34.6

compressive strengths of treated PG at 2-days and 28-days have sufficient strength for OPC applications. These results were confirmed and fulfilled the requirement with the specification of OPC obtained in the Jordan standard (JS 30-1:2007) and according to European standard (EN 197-1, 2000) for the compressive strengths.

### Conclusion

The industrial and laboratory tests performed in this study indicate that PG can be replaced by gypsum as a set retainer. The various treatment process of the PG in the laboratory and industrial tests indicate the influence of the product, on the parameters illustrating the quality of the OPC. All the parameters are in accordance with the standards Jordan standards and European standards; the PG appears as a substitute of the gypsum at level up to 5% of constituents.

Nevertheless, times of setting hardening of OPC containing natural gypsum are high compared to those whom obtained with the treated PG; conform to the Jordan standards and European standards. This can be attributed due to the effectiveness of various treatment process that remove the undesirable MgO, SO<sub>3</sub>, and P<sub>2</sub>O<sub>5</sub> in OPC products. It is observed that the various treatment process of PG in the laboratory and the tests carried in the industry influence the properties of OPC. The chemical and mineralogical analyses for studied OPC samples after addition of treated PG show that the dominant phases composition are C<sub>3</sub>S and C<sub>2</sub>S while the C<sub>3</sub>A and C<sub>4</sub>AF are less abundant, whereas CaO and MgO exhibits as trace phase. These experimental results also showed that the C<sub>3</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF, C<sub>2</sub>S, LSF, AR, and SR contents achieved the requirement of the Jordan standards and European standards; hence treated PG can be replaced by natural gypsum. Several treatment of PG with LWT, SAT, AWT, ST, LT used in cement mortar mixture has resulted in improvement in the 28-days mechanical properties compared to those of mortars prepared with untreated PG. The percentage improvement in compressive strengths was higher with AWT, whereas the LT compressive strength showed the lowest. Treated PG improves the strength development when used in OPC and hence it can be used in construction industry for preparation of OPC replacing natural gypsum, which is a valuable ingredient of OPC, to achieve economy.

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