Optimization of Phosphogypsum By-Production Using Orthophosphoric Acid as Leaching Solvent with DifferentTemperatures and Leaching Time Periods

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Abstract

Phosphoric acid production generates unavoidable calcium sulfate by product (i.e. phosphogypsum (PG)) that is usually disposed either within a nearby located gypsum stacking system. However nowadays this type of industry has been faced with two main problems; these are the formation of huge stockpiles of phosphogypsum that affects the environment due to the presence of harmful radiations that is emitted from the uranium. In addition it contains $P_2O_5>1.0$ wt% and fluorine >0.18 wt%, which makes it not suitable for the cement industry. At the same time consuming large quantity of expensive sulphuric acid that becomes a hazardous waste material too. The production ratio of PG verses marketable P_2O_5 as acid in the world is high as much as 5 tons of PG are produced for each ton of P_2O_5 ; in Jordan the ratio is around 5.0 - 5.3 ton of PG / ton of P_2O_5 produced depending on the phosphate rock composition, which means a huge amount of PG will accumulate at the Fertilizer plant in Aqaba. The major advantages of using orthophosphoric acid as leaching solvent is the decreasing ratio of the residual materials verses marketable P_2O_5 to be589 kg /ton of P_2O_5 produced. These results were obtained by utilizing the wet agitation leaching technique, compared with 5.0 - 5.3 ton of disposed PG/ton of P_2O_5 produced by Jordan Phosphate Mines Company Ltd., (JPMC). However, this alternative technique resulted in lower P_2O_5 extraction, but decrease in bulk of the residue. The disadvantage is the higher dissolution of calcium phosphate and thus considerable calcium well remain in solution.

Keywords: Phosphogypsum, Jordan, Sulpheric acid, Orthophosphoric acid, P2O5 extraction

1. Introduction

Jordan has huge reserves of phosphate deposits, the main deposits existed in the southern region of the country (Bender, 1974). The concentrations of trace elements such as U, V, Cd, Cr, and As are increasing from south to north, for example, U ranged from 40–60 mg/kg ((Jordanian Phosphate Mines Company, 1998) and 70–80 mg/kg) for samples from Esh-Shidyia and Al-Hisa mines (Khaled et al., 1990). (Ghosheh and Dodeen, 1993) had showed that other heavy metals and toxic elements in the Jordanian phosphate rocks are lower compared with several phosphate deposits from the world; this was reached by (Al-Hwaiti et al., 2001). Abed et al. 2008; found that potential toxic metals behaves as P and are enriched by a factor of more than 1.5 in the diammonium phosphate (DAP) compared with the input phosphorite. And that the trace metal content in the PG is very low. However, U sticks to the mineral francolite during upgrading of the ores, and behaves similar to Ca and P₂O₅ (Abed, 2011).

The phosphate industry is one of the most contaminating sources to the environment, which contributes to soil; water and air pollution (Vandenhove, 2002). Al-Hisaphosphate mines are heavily affecting the particulate matter in the areas around the mines, Hamaiedah and El-Hasan, 2011). The utilization of effluent mine water from the Eshidiya phosphate mines in agricultural uses was investigated; it was categorized as $C_4S_1-C_4S_2$ type, which indicates that this water cannot be used for irrigation on any type of soil (Al-Hwiti et al. 2016). Similarly, Jiries et al. (2004)has investigated the effluent water from Al-Hisa and Al-Abyad mines. And found that it can be used for irrigation of salt-tolerant plants.

According to the European Fertilizer Manufacturing Association (EFMA), there are two phosphoric acid production processes; the first, at temperature 70 -80 °C that yields 26-32% P_2O_5 , and gives acid and dehydrated phase (CaSO₄.2H₂O). The second, at temperature 90 - 110 °C, which yields 40-52% P_2O_5 , and gives acid and Hemi hydrate phase (CaSO₄.1/2H₂O) (EFMA, 2000).

The most common technique that has been employed in the world for production of phosphoric acid from the phosphate rock comprises from reacting the phosphate rock with concentrated sulphuric acid solutions as in the following equation:

$Ca_3(PO_4)_2 + 3H_2SO_4 + 2H_2O \rightarrow 2H_3PO_4 + CaSO_4.2H_2O$ (gypsum)

Contaminated gypsum which also known as PG, $CaSO_4.2H_2O$ is formed as coproduced in the production of phosphoric acid by the wet- process. Unfortunately the ratio of PG verses marketable P_2O_5 as much as 5 tons of PG were produced for each ton of P_2O_5 . This ratio is affected by the composition of the phosphate rock. In Jordan the ratio is around 5.0-5.3 ton of PG/1.0 ton P_2O_5 produced (JPMC, 2008).

Many environmental issues raised by such waste disposal problem, so it is estimated that over 40 million tons of PG was produced and accumulated in Aqaba area by Jordan Phosphate Mines Company Ltd., (JPMC) during the period 1982 – 2008. The JPMC annual disposal is approximately 2.2 million tons of dehydrate PG and 1.0 million tons of hemi hydrate. The problem is accentuated by the fact that the PG, in most of the technologies employed in the wet-process production of phosphoric acid, contains a number of serious contaminants such as radioactivity due to the presence of uranium, fluoride, heavy metals besides sulphuric and phosphoric acids and their salts. The problem is further worsened by the large volume of PG pond water which is used in most plants for scrubbing pollutants. Whereas (Abed, 2011) suggested that Uranium is concentrated in the final phosphoric acid.

The PG is found to be radioactive due to the presence of naturally occurring uranium and radium in the phosphate ore (Dippel, 2004). Thus, PG is classified as a hazardous waste and is currently being disposed and stockpiled on sandy soil (Berish, 1990), (Azouazi et al., 2001) and (Dueñas et al., 2007). There are various storage processes of PG wastes, such as ocean disposal (Wissa, 2001), dry stacking on land, which is the common practice (EPA, 1999), and wet stacking on basins (Anon, 1998), as well as the use of PG as mine backfill disposal as suggested by (Dippel, 2004). (Al-Hwaiti et al., 2005) reported that trace elements in the PG stacks are stable with time, which indicates that trace elements were not leached from the stacks in any significant amount.

An associated problem is the production of sludge produced in the neutralization of gypsum pond water by liming. The sludge produced is another solid waste which is a mixture of complex compounds of phosphates and fluorides and is disposed of on the gypsum stacks.

Some technologies attempted at minimizing the pollutants in the PG. One of these attempts was used by (Nabulsi, 1999). He carried out several tests on specimens that were prepared from the PG in Jordan; the results showed that it can be used as a gypsum binder in the building industry. It can be also for producing precast units of low density and acceptable thermal insulation properties. However, the problem here is the radioactivity that still presents in the tested PG samples.

Other attempt was done by Industrial Chemistry Center in Royal Scientific Society, 1994. The team in the center prepared several samples from PG that brought from JPMC-Industrial Complex in Aqaba-Jordan and washing these samples up to five times using Tap water and sea waterto reduce the impurities that present in the tested PG samples such as H₃PO₄, HF, H₂SO₄ and P₂O₅. The results of washing revealed that the P₂O₅ content decreased 13%, but the SO₄ increased in the tested samples.

(Abdelhadi et al., 2014) demonstrated experimentally the use of raw PG without treatment (heating) in cement production, which will eliminate a serious environmental source of pollution; besides, decreases the cost of cement production.

(Smadi et al., 1999) studied the behavior of the compressive strength of cement with different replacement ratios of purified (PG) and calcined temperature up to 900 °C, he found an increasing trend in compressive strength which improved the initial and final setting time. (Bhadauria andThakare, 2006) utilized the PG wastes in cement additive as past or mortar in concrete; it was found that it is suitable for concrete in terms of workability and compressive strength. PG is also known worldwide for its applications as a binder or cement, (Gutt, 1978); Ouyang et al., 1978); (Ghafoori, 1986); (Akın &Yesim, 2004); (Degirmenci, 2008); (Lysandrou&Pashalidis, 2008); and (Yang et al., 2009).

Other possibilities exist, but as yet not considered economical, for example the production of sulphuric acid from the PG or use it in cement clinker. At the same time the expensive sulphuric acid raw material consumed will produce a large pile of waste material (e.g. PG) near the plant is considered as another problem facing the

production of phosphoric acid by using the sulphuric acid and phosphate ore. The estimated amount of sulphuric acid that consumed is about 2.7 ton /1.0 ton of P_2O_5 produced. (Rabba, 1993) had carried out a metallurgical test work on the phosphate shale copper ore (Cambrian) at Wadi Khalid, at northern Wadi Araba region. He concluded that the most sufficient and economic acid should be used for extraction the copper and P_2O_5 from the ore is the phosphoric acid to avoid the formation of PG.

The aim of this research is to find alternative technique by using the orthophosphoric acid for leaching the Jordanian phosphate ore instead of sulphuric acid. Therefore, the main objective of this study is to estimate the maximum acid extractable percent of P_2O_5 from the phosphate oreto determine the amount of insoluble minerals in the phosphate ore by using various acids/water ratios, and to investigate the release of P_2O_5 with various temperatures and duration of leaching using orthophosphoric acid as solvent. In addition this work aimed to prevent the formation of huge amounts of PG rich in uranium, fluorine and P_2O_5 .

2. Sampling and Analytical methodology

2.1 Leaching Test:

Nine representative samples prepared from the phosphate ore sample labeled as Ph-1, each of 10 g in weight, ground to -20 microns. One representative sample from the phosphate ore (Ph-1) was digested with concentrated nitric perchloric solutions. The solutions were analyzed using an A.A.S. technique, different standards contain increasing amount of P₂O₅ were employed to analyze the digestion filtrates. This technique was performed to remove errors in P₂O₅ estimation of the samples due to dilution of solutions for analysis. Eight representative samples from the phosphate ore (Ph-1), each of 10 g in weight were previously ground to -20 microns. Four samples (IR-5, IR-6, IR-7 and IR-8) were leached with orthophosphoric acid (90% concentration which contains 65.29% P₂O₅ concentration), it should be noted that each 1.0 ml of acid is equivalent to 1.75 g H₃PO₄ (90% Conc.). Two of them were performed at temperature of 30°C for 1.0 and 2.0 hours leaching time and the other two samples were treated at temperature 50°C for 1.0 and 2.0 hours leach times using magnetic stir techniques for agitating the phosphate components in the leach solutions, employing an acid strength of 17.5 % phosphoric acid on a weight basis, the strength being equivalent to 10.0 ml of acid per 100ml of solvent used for leaching. The remaining four samples (IR-1, IR-2, IR-3 and IR-4) were leached with concentrated sulphuric acid (90% Conc.). Two of them were performed at temperature of 30°C for 1.0 and 2.0 hours leach times and the other two samples were treated at temperature of 50°C for 1.0 and 2.0 hours leach times, utilizing an acid strength of 18.35 % sulphuric acid on a weight basis, the strength being equivalent to 10 ml of acid per 100ml of solvent used for leaching. It should be noted that each 1.0 ml of acid is equivalent to 1.835 gm H₂SO₄. Samples of the leached solution were being taken at intervals of 1.0 and 2.0 hours for analysis.

2.2 Agitation Experiment

Twenty nine representative samples have been prepared from the phosphate ore sample numbered Ph-1 were treated using an acid strength of 100, 150, 200 and 300 ml of H₃PO₄ (90%conc.)/1000 ml of solutions. The samples were 100gm in weight each. Nine samples leached for a period of 1.0, 2.0 and 3.0 hours, were performed at atemperature of $30C^{\circ}$, $50C^{\circ}$ and $80C^{\circ}$ using an acid strength of 100 ml of H₃PO₄ (90%conc.) /1000 ml of solutions. Other nine samples were leached under similar conditions that used in the previous samples (similar weights, leach times and leaching temperature) but different in acid strengths. The acid strength that used was 150 ml of H₃PO₄ (90%conc.) /1000 ml of solutions that used in the previous eighteen samples but employing an acid strength of 200 ml of H₃PO₄ (90%conc.) /1000 ml of solutions that used in the previous eighteen samples but employing an acid strength of 200 ml of H₃PO₄ (90%conc.) /1000 ml of solutions. The last three samples were leached for one hour at a temperature of $30C^{\circ}$, $50C^{\circ}$ and $80C^{\circ}$ using an acid strength of 300 ml of H₃PO₄ (90%conc.) /1000 ml of solutions. The leach residue after each interval was analyzed by X.R.F and Calcimeter for P₂O₅, CaO, other extractable elements and calcite respectively.

The chemical composition of PG was investigated through X-Ray Fluorescence analysis. It was done using the machine (XRF-Pioneer F4), manufactured by Broker at the labs of Natural Resources Authority (NRA), Amman. The machine comes with an attached 72-position sample changer. Pellets were made by fusing 0.8 g of sample powder and 7.2 g of L2B4O7 in Au/Pt crucible using a flexor machine (Leco 2000) for 3 - 4 minutes at 1200 °C. The melt was poured in a mold and left to cool to form a glass disc; trace elements were analyzed. The machine was calibrated with international standards, particularly the Geological Survey of Japan (GSJ) geochemical standards (i.e., Japanese slate JSI-1 and JSI-2). The analytical error was within 5%. Moreover, mineral constituents were determined using X-Ray Diffraction analysis. It was executed using the machine (XRD-Philips Expert MPD) at the labs of Natural Resources Authority (NRA), Amman. The samples were scanned between 2° and 65° 20, using Ni-filtered Co K α radiation, 40 kV/40mA, divergent and scattering slits of 0.02°mm, a receiving slit of

0.15mm, with stepping of 0.01° and scanning speed of 3°/min.

3. Results and Discussion:

3.1 Treatment of Phosphate Ore Using concentrated H₂SO₄and H₃PO₄

The results showed that the P_2O_5 extraction obtained from two samples that were treated at temperatures 30C° and 50C° was 89.6% and 93.05% in 1.0 hour of leaching, with an acid consumption of 851 and 877 kg H_2SO_4 /ton of ore respectively. The calculated amounts of H_2SO_4 that consumed to produce 1.0 ton of H_3PO_4 (concentration 99.5%) were 2.29 and 2.26 tons respectively. The chemical results obtained for the residue from X.R.F. analysis showed that it contained 30.0, 29.94% CaO, and 42.54, 43.26 %SO₃, using these figures the amount of gypsum precipitated in the leach residue (PG) was estimated to be 91.37 % and 92.97 % of the residue weight which are equivalent to 16.33 and 16.37 g respectively, while the original weights of the ore samples that used in the tests were 10.0gr each, this increase in weight being due to the formation of gypsum inthe residual samples.

The P_2O_5 extraction obtained from the other two samples that were treated at temperatures 30C° and 50C° was 100 % for both tested samples in 2.0 hours of leaching, with an acid consumption of 896 and 897 kg H₂SO₄/ton of ore respectively. The calculated amounts of H₂SO₄ that consumed to produce 1.0 ton of H₃PO₄ (concentration 99.5%) were 2.15 and 2.16 tons respectively. From the analysis of the leach residue for CaO and SO₃ that was 94.63 and 95.07 wt% respectively, these figures are equivalent to 15.85 gr with 23% loss of ignition and 15.59 gr weight with 21% loss of weight respectively. It should be noted that the original ore samples used in the tests were 10 gr weight each, the increase in weight being due to the formation of gypsum in the residual samples.

It should be noted that the samples used in these tests were leached under similar conditions of the previous tests (similar weights, leaching temperature and acid strengths), but different in leaching time periods. The complete results of these tests are presented in Tables 1.

Leaching solution	Sample	Leach Time (hr)	Temp (°C)	Residue Weight (gr)	CaO %	P ₂ O ₅ %	SiO ₂ %	MgO %
H_2SO4	IR-1	1.0	30	16.33	30.0	1.92	3.63	0.04
	IR-2	2.0	30	16.75	29.4	0.00	4.00	0.04
	IR-3	1.0	50	16.37	29.94	1.28	3.68	0.03
	IR-4	2.0	50	16.4	30.8	0.00	3.5	0.00
H ₃ PO4	IR-5	1.0	30	4.93	38.91	23.27	14.43	0.34
	IR-6	2.0	30	3.85	40.31	23.87	13.41	0.34
	IR-7	1.0	50	4.00	41.8	24.10	12.26	0.25
	IR-8	2.0	50	3.21	42.37	25.45	11.11	0.18
XRF ana	alysis o	f ore sam	ple (Ph-1	1)	49.13	30.16	7.61	0.35

Table 1a. X.R.F analysis and leaching results of the Ph-1 samples utilizing H₂SO₄ and H₃PO₄

Table1b.X.R.F analysis and leaching results of the Ph-1 samples utilizing H₂SO₄ and H₃PO₄

Leaching solution	Sample	Al ₂ O ₃ %	Fe2O3 %	Na20 %	K20 %	SO ₃ %	%IOT	U (ppm)	P2O5 extraction
	IR-1	0.19	0.16	0.06	0.03	42.54	21.0	40	89.6
H_2SO4	IR-2	0.16	0.135	0.06	0.03	43.26	23.0	NA	100
	IR-3	0.14	0.137	0.05	0.02	43.26	NA	35	93.05
	IR-4	0.08	0.11	0.03	0.003	44.2	21.0	NA	100
	IR-5	0.77	0.67	0.03	0.07	0.05	15.71	53	62.0
H ₃ PO4	IR-6	0.60	0.57	0.07	0.07	0.04	6.041	55	69.53
	IR-7	0.55	0.52	0.08	0.8	0.04	6	48	68.4
	IR-8	0.51	0.46	0.07	0.07	0.04	.5614	44	72.91

						.30	
XRF analysis of ore sample Ph-1 sample (Ph-1)	0.53	0.26	0.60	0.03	1.23	8.15	

3.2 Treatment of Phosphate Ore Using 10.0 ml of Concentrated H₃PO₄/90 ml Distilled Water

Leaching results have shown that P_2O_5 is released from phosphate using dilute orthophosphoric acid. The P_2O_5 extraction results obtained range from 62.0% using 10.0 ml of H_3PO_4 (99.5% Conc.) /100 ml of solvent after 1.0 hour leaching to 69.53% using the same acid strength after 2.0 hours leaching at 30C° Table (2). The maximum P_2O_5 extraction obtained from phosphate ore samples after 2.0 hours leaching at 50°C with orthophosphoric acid was 72.91-%. This was produced using acid solution of 10.0 ml H₃PO₄ (90% Conc.) /100 ml of solvent. Extraction from this material dropped to 68.04% when the lowest leach time periods were employed. Similarly, CaO extraction from the phosphate ore was also leach time periods dependent. The CaO and P_2O_5 extraction values obtained matched each other closely, indicating that all components of the apatite in the samples leached were being taken into solution. The calculated amounts of H_3PO_4 that generated from the tested samples after 2.0 hours leaching at 30°C and 50°C were 289.1 and 303.14 kg (concentration100%) /1.0 ton of phosphate respectively, while the generated phosphoric acid from the tested samples after 1.0 hour leaching at 30°C and 50°C were257.8 and 282.9 kg/ ton of ore respectively.

No precipitation was observed from the leach solutions once they were filtered, indicating that CaO and P_2O_5 were stable in the leached solutions. Weight losses in the residues were recorded for the four samples tested. These weight losses in the leached samples were related to the apatite and calcite content of the ore samples and the leach time periods employed. They varied from 50.70 % at 30C° to 60.0 % at 50C° after 1.0 hour leaching, while weight losses in the remaining two samples were ranged from 61.5 to 68.0 % at 30C° and 50C° respectively after 2.0 hours leaching. The summary of the results of residue production, acid consumption and extracted P_2O_5 % by using the two acids are presented in Tables 2a and b.

Acids		H ₂ SO ₄									
Leach. T °C		30 °C	30 °C				50 °C				
		Oresamples	Residue	Acid Consumed	P ₂ O ₅ % Extracted	Oresamples	Residue	Acid Consumed	P2O5 % Extracted		
Leach.	1	3.704	6.049	2.29	89.6	3.564	5.834	2.26	93.05		
Time (hr)	2	3.316	5.554	2.15	100	3.316	5.438	2.16	100		

Table 2a. Extracted P2O5 utilizing Sulphuric acid as the leaching solvent

Table 2b. Extracted P ₂ O ₅ utilizing	Orthophosphoric acid	as the leaching solvent
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Acids	H ₃ P	O ₄
Leach. T °C	30 °C	50 °C

		Oresamples	Residue	Acid Consumed	P ₂ O ₅ % Extracted	Oresamples	Residue	Acid Consumed	P ₂ O ₅ % Extracted
Leach.	1	10	4.93	2.58	62.0	10	4.0	2.84	68.4
Time (hr)	2	10	3.85	2.89	69.53	10	3.21	3.03	72.9

Although the use of H₃PO₄ resulted in lower P₂O₅ extraction, but also reduces the residue weight Fig. 1.



Figure 1. Agitation leaching test results using sulphuric and Orthophosphoric acid.

3.3 Results Obtained Using Different Orthophosphoricacid/Tap Water.

A total of 29 samples with weight 100 gr were treated with different orthophosphoric acid (H_3PO_4). Four acid/tap water ratios were performed (i.e. 100ml/900ml; 150/850; 200/800 and 300/700 respectively). Each mixture was investigated with variable temperature ($30C^\circ$, $50C^\circ$ and $80C^\circ$) and leaching time (1, 2 and 3 hours). The results obtained are summarized in Tables (3 &4).

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Sample ID & Mixing Ratios		T °C	Residue Wt.(gr)	Leach time (hr)	Ca0%	$P_2O_5\%$	SiO ₂ %	Mg0%
100/900	IR-9	30	54.0	1.0	44.80	27.91	11.84	0.20
	IR-10	30	46.0	2.0	42.7	27.60	13.74	0.15
	IR-11	30	43.16	3.0	41.69	24.25	17.56	0.15
	IR-12	50	46.34	1.0	45.71	29.38	11.39	0.19
	IR-13	50	38.70	2.0	45.18	28.73	11.84	0.12
	IR-14	50	32.5	3.0	44.50	27.58	13.96	0.10

	IR-15	80	44.5	1.0	32.08	13.00	39.18	0.30
	IR-16	80	47.1	2.0	47.85	32.0	8.84	0.12
	IR-17	80	64.0	3.0	48.18	35.20	6.53	0.13
150/850	IR-18	30	28.4	1.0	37.72	19.62	23.08	0.20
	IR-19	30	26.0	2.0	33.14	16.02	28.97	0.26
	IR-20	30	25.3	3.0	30.97	12.64	29.15	0.29
	IR-21	50	27.0	1.0	38.25	18.32	24.78	0.24
	IR-22	50	24.1	2.0	34.22	15.00	27.80	0.18
	IR-23	50	27.8	3.0	30.26	11.65	33.68	0.16
	IR-24	80	37.5	1.0	45.21	29.0	12.74	0.09
	IR-25	80	39.8	2.0	42.38	26.44	15.38	0.07
	IR-26	80	38.8	3.0	41.92	26.23	14.79	0.08
200/800	IR-27	30	17.1	1.0	27.15	10.99	22.88	0.28
	IR-28	30	16.8	2.0	30.55	9.90	17.87	0.24
	IR-29	30	15.16	3.0	20.5	9.87	31.70	0.21
	IR-30	50	15.73	1.0	27.33	9.33	25.15	0.27
	IR-31	50	15.76	2.0	27.56	9.00	24.82	0.25
	IR-32	50	14.66	3.0	20.60	10.0	34.40	0.27
	IR-33	80	22.0	1.0	35.75	16.37	29.72	0.08
	IR-34	80	24.0	2.0	34.95	17.38	30.83	0.02
300/700	IR-35	30	20.3	1.0	23.7	15.86	19.82	0.16
	IR-36	50	13.14	1.0	17.39	5.00	42.97	0.26
	IR-37	80	11.8	1.0	11.7	3.28	59.5	0.25
XRF analy	vsis of hea	dore sar	nple (Ph-1)		49.13	30.16	7.61	0.35

Table 3b. X.R.F. analysis of the leached samples treated with various H₃PO₄ acid concentrations

iample ID & Aixing Ratios		M2O3%	¹ e2O3%	Va20%	ζ 20%	0 ₃ %	• %		205% xtracted
100/900	IR-9	0.51	0.47	0.12	0.06	ND	5.60	7.62	50.03
	IR-10	0.55	0.54	0.24	0.07	ND	4.20	9.29	57.90
	IR-11	0.73	0.66	0.19	0.085	ND	4.80	9.11	65.30
	IR-12	0.43	0.48	0.49	0.075	ND	3.50	7.02	54.85
	IR-13	0.45	0.45	0.26	0.05	ND	4.94	7.05	63.00
	IR-14	0.49	0.44	0.17	0.05	ND	3.90	7.79	70.30
	IR-15	2.01	1.32	0.09	0.17	ND	3.30	5.76	80.82
	IR-16	0.13	0.12	0.39	0.02	ND	4.7	6.31	50.03
	IR-17	0.05	0.09	0.41	0.005	ND	4.2	5.38	25.3
150/850	IR-18	1.03	0.83	0.22	0.11	ND	6.42	10.77	81.5
	IR-19	1.45	1.09	0.24	0.14	ND	7.00	12.26	86.2
	IR-20	1.49	1.07	0.13	0.13	ND	9.87	14.10	89.4
	IR-21	1.01	0.77	0.26	0.10	ND	7.86	9.74	83.6
	IR-22	1.30	1.00	0.15	0.11	ND	5.1	11.13	88.01
	IR-23	1.61	1.02	0.20	0.14	ND	3.4	15.7	89.26
	IR-24	0.20	0.11	0.43	0.05	ND	4.5	7.10	63.94
	IR-25	0.17	0.08	0.17	0.01	ND	4.3	11.07	65.11
	IR-26	0.22	0.09	0.41	0.04	ND	4.8	10.98	66.13
200/800	IR-27	2.32	1.18	0.19	0.15	1.42	18.75	14.31	93.77
	IR-28	1.93	1.13	0.17	0.12	1.66	22.63	12.73	94.5
	IR-29	3.17	1.16	0.21	0.21	1.04	21.50	14.4	95.04
	IR-30	2.49	1.16	0.16	0.15	1.22	19.24	13.12	95.13
	IR-31	2.29	1.13	0.22	0.14	1.25	19.0	13.92	95.3
	IR-32	2.87	1.07	0.22	0.19	0.89	14.94	13.5	95.14

	IR-33	0.72	0.13	0.30	0.06	0.72	6.3	10.07	88.1
	IR-34	0.56	0.09	0.24	0.05	0.6	5.2	10.09	86.17
300/700	IR-35	2.13	1.10	0.13	0.14	1.32	15.04	20.18	89.33
	IR-36	2.72	1.55	0.17	0.19		15.0	12.18	98.0
	IR-37	2.77	0.10	0.00	0.0	1.49	6.8	12.4	98.72
						1.18			
XRF at	nalysis of	0.53	0.26	0.6	0.03	1.23	3.90	8.15	-
headore an	mple (Ph-1)								



Figure 2. CaO% accumulation and the extracted $P_2O_5\%$ at differentOrthophosphoric%

Sample ID & Mixing ratio		Leaching Temp. (C°)	Leach Time	Residue Weight, (gr)	XRF analysis for CaO of residue of leaches samples		
8		- F (-)	(hr)		Estimated %	Computed%CaOcontent	
					CaO	(gm)	
	IR-9	30	1.0	54.0	44.8	24.19	
	IR-	30	2.0	46.0	42.7	19.64	
100/900	10	30	3.0	43.16	41.69	17.99	
	IR-	50	1.0	46.34	45.71	21.18	
	11	50	2.0	38.7	45.17	17.48	
	IR-	50	3.0	32.5	44.5	14.46	
	12	80	1.0	44.5	32.08	14.28	
	IR-	80	2.0	47.1	47.85	22.54	
	13	80	3.0	64.0	48.15	30.82	
	IR-						
	14						
	IR-						
	15						
	IR-						
	16						
	IR-						
	17						
	IR-	30	1.0	27.4	37.72	10.71	
	18	30	2.0	25.0	33.14	8.62	
150/850	IR-	30	3.0	23.8	30.97	7.84	

Table 1a	Decults of V D L	analyzia for (CoO of residue	of loophad com	place with differen	t U DO avid strongth
1able 4a.	RESULTS OF A.R.I	'. allalysis loi v	CaO of festure	of leached sam	pies with differen	IL H3F O4 actu suengui
		2			1	J . U

	19	50	1.0	26.0	38.25	10.33
	IR-	50	2.0	23.1	34.22	8.25
	20	50	3.0	21.3	30.26	8.41
	IR-	80	1.0	37.5	45.21	16.95
	21	80	2.0	39.8	42.38	16.88
	IR-	80	3.0	38.8	41.92	16.26
	22					
	IR-					
	23					
	IR-					
	24					
	IR-					
	25					
	IR-					
	26					
	IR-	30	1.0	17.1	27.15	4 64
	27	30	2.0	16.8	30.55	5 13
200/800		30	2.0	15.16	20.5	3 11
200/000	28	50	5.0 1.0	15.10	20.5	1 3
	20 ID	50	1.0	15.75	27.33	т.5
	20					
	29 ID					
	1K- 20					
	50 ID	50	2.0	15 76	27.56	4.24
	1K- 21	50	2.0	13.70	27.50	4.54
	51 ID	30	5.0 1.0	14.00	20.0	5.02 7.96
	1K- 22	80 80	1.0	22.0	55.75 24.05	/.80
	52 ID	00	2.0	∠4.0	34.93	0.37
	1K-					
	33					
	1K-					
200/502	34 ID	20	1.0	20.2	22.7	4.01
300/700	IR-	30	1.0	20.3	23.7	4.81
	35	50	1.0	13.14	17.39	2.29
	IR-	80	1.0	11.8	11.7	1.38
	36					
	IR-					
	37					

Table 4b. X.R.F. analysis of the estimated and computed escaped CO_2 % and extracted CaO% from the ore sample as obtained from the Calciminer analysis with various H₃PO₄acid strength

Sample ID &	Leaching Temp. (C°)	Calcimeteranaly leached samples	sis for residues of	% CO ₂ escaped from ore sample	% CaO extracted from ore sample
Mixing	1 ()	Estimated %	Computed CO ₂	1	•
ratio		CO ₂	content (gr)		
100/900	IR-9	2.67	1.44	77.91	50.03
	IR-10	2.30	1.06	83.74	57.9
	IR-11	2.00	0.86	86.81	65.3
	IR-12	2.35	1.09	83.28	54.85
	IR-13	2.28	0.88	86.50	63.0
	IR-14	2.24	0.73	88.80	70.3
	IR-15	ND	ND	ND	70.94
	IR-16	2.26	1.06	83.74	54.13
	IR-17	2.79	1.79	72.55	37.24
150/180	IR-18	1.35	0.37	94.33	78.20
	IR-19	0.96	0.24	96.32	83.46

	IR-20	0.59	0.14	97.85	84.05
	IR-21	1.62	0.42	93.56	78.98
	IR-22	1.39	0.32	95.10	83.21
	IR-23	0.94	0.20	97.0	82.88
	IR-24	2.59	0.97	85.12	65.49
	IR-25	ND	ND	ND	65.67
200/800	IR-26	2.40	0.93	85.74	66.89
	IR-27	0.82	0.15	97.7	90.55
	IR-28	0.74	0.12	98.16	89.55
	IR-29	0.00	0.00	0.00	93.67
	IR-30	0.7	0.11	98.31	91.25
	IR-31	0.00	0.00	0.00	91.16
	IR-32	0.00	0.00	0.00	93.85
	IR-33	1.23	0.27	96.0	83.99
	IR-34	1.33	0.32	95.1	82.93
300/500	IR-35	0.89	0.18	97.24	90.21
	IR-36	0.00	0.00	100.0	95.34
	IR-37	0.00	0.00	100.0	97.2

4. Discussion

4.1 Results of the Agitation Leaching with Sulphuric Acid

The calcium phosphate which may be dissolved during the leaching of phosphate ore with orthophosphoric acid is not necessarily a problem. The calcium may be precipitated by the addition of stoichiometric amounts of sulphuric acid and this correspondingly results in the increase of phosphoric acid in the leach solutions. The produced calcium sulphate is of an excellent quality and in itself represents a possible commercial product.

According to Table(2)each 1.0 ton P_2O_5 produced needs 3.52 ton of phosphate ore to produce 4.30 ton of precipitate with gypsum content about 98%, this quantity of the produced gypsum will consume 1.96 ton of concentrated sulphuric acid as shown in Fig (1).

The estimated amount of residue (pure gypsum) for each 1.0ton of P_2O_5 produced was 0.626ton, compared with 4.5-5.0 ton of PG residue produced by JPMC-IND COMPLEX in Aqaba/Jordan. The whiteness of the precipitated sample was measured, the results revealed that the whiteness was 97.5%. Compared with 56.5 the whiteness of the PG that produced by JPMC-IND COMPLEX in Aqaba/Jordan.Furthermore, washing the precipitate with diluted sulphuric acidat a temperature of 40 °C for 10minutes agitation will raise the gypsum mineral to more than 99.5% with 0.00% P_2O_5 content. No impurities such as uranium and fluoride were recorded in the new product. Adding natural gypsum to this precipitate that washed by water with 1:1 ratio will reduce the P_2O_5 to 0.5% instead of 1.0% and raised SO₄ in the new product. This will give the quality of the product to be more commercial and more suitable for cement industry and at the same time reduce the costs of washing the product by diluted sulphuric acid.

4.2 Results of the Agitation Leaching with Orthophosphoric Acid

The presence of apatite $(Ca_5 (PO_4)_3.OH, F)$ in the Jordanian phosphate ore and its dissolution in the orthophosphoric acid solutions resulted in the presence of phosphor in solution. The form of the major reactions which occur during phosphate ore leaching are illustrated by the following equations:

 $\blacksquare Ca_5 (PO_4)_3 (OH) F+ H_3PO_4 + 5H_2O \rightarrow 5CaO + 4H_3PO_4 + H_2O + F$

■Ca₅ (PO₄)₃ (OH) F + Phosphoric Acid +Water \rightarrow Calcium oxide + Phosphoric Acid

■5CaO + $4H_3PO_4 + H_2O \rightarrow H_3PO_4 + Ca (H_2PO_4)_2$ (Mono-Calcium phosphate) Liquid

■Apatite + H_3PO_4 + SiO_2 +Fluorine (F) → H_3PO_4 + (Mono-Calcium phosphate) + HF (v)

$$\blacksquare HF(v) + SiO_2 \rightarrow Si F_4(v)$$

■Si $F_4(v)$ + Scrubbing by water → H_2SiF_6 (Liq.) Floro-silicic Acid

The other minor reactions that may be formed and resulted in formations of solid materials associated with the cake of residue samples. These reactions are:

1-Reaction between Na₂O and SiO₂ to produce Sodium silicates (Na₂SiO₃)

2-Reaction between CaO and SiO₂ to produce Calcium silicates Ca₂SiO₃

3-Reaction between CaO and F to produce Calcium fluoride CaF2

Employing 10% ratio of solid to solution the leaching results have shown that P_2O_5 is released from phosphate ore samples using concentrated orthophosphoric acid (300ml of $H_3PO_4/1000$ ml of Tap water). The highest P_2O_5 extraction result obtained was 98.72% in 1.0 hour leaching time using a temperature of 80C°, comparing with 98.0% when employing a temperature of 50C°. Extraction of the P_2O_5 that obtained from this material dropped to 80.82% using a temperature of 80C° and 54.85% at a temperature of 50C° when the lowest acid strength (100ml of $H_3PO_4/900$ ml of Tap water) was employed, Table 3.

Dissolution of the calcium phosphate content of the phosphate ore with orthophosphoric acid was mirrored by a weight loss of the leaching residue. This ranged from 46.0-88.20 % depending on the leaching time, acid concentration and temperature used in leaching process.

Using a temperature of 80°C for leaching the phosphate ore that employing 1.0 and 2.0 hour leaching periods, the weight loss recorded was lower compared with the previous tests that employed a temperatures of 30°C and 50°C, this differences may be related to the amount of phosphate mineral formed in the residues of the leached samples that being treated at 80°C only. The extraction of P_2O_5 did not increase further even though the test was running for a period of 2.0 hours. However, residue weight continued to rise after 1.0 hour leaching. The result suggests that the extraction of P_2O_5 may be limited after 1.0 hour leaching at a temperature of 80°Cand strength of the acid that less than 30% is not capable of dissolving further P_2O_5 from the ore or even preventing the formation of calcium phosphate hydrate from the leach solutions at this temperature, Fig. (2).

Examining the leaching residues after 1.0 hour treatment using different acid concentration revealed that the main chemical differences observed between them is the CaO content. As the acid strength increased, it was observed that CaO values decreased in the residues. This was evident from the decrease in the residue weights Table 4 and Fig. (2).

It is interesting to note that in case of using an acid concentration of 200ml $H_3PO_4/800ml$ of water, the fluoride content in the leached ore sample that treated at 30C° was 22.63% after 2.0 leaching time. However, the lowest fluoride extraction value 3.30 % was noticed at the 100ml ml $H_3PO_4/900ml$ leaching at 80 °C. Generally the fluoride extraction is increasing with increasing acid concentration, and decreasing with increasing temperatures of leaching, thus 30 °C yields always higher fluoride in residue in the form of fluorite mineral (CaF₂), as shown in Fig. (3).

Analysis of the leached samples revealed that in all cases the maximum extraction of fluorine was obtained after 2.0 hour from the tested samples that being used with acid strength of 200ml of phosphoric acid/ 800 ml of solvent. It reaches 22.63 wt% at lower temperature (30 °C); meanwhile, the lowest fluorine extraction was found at 100ml of phosphoric acid/900 ml at higher temperature (i.e. 80 °C). There is a positive correlation to some extent between higher extraction of P_2O_5 and F; Table (3).

Employing 10% ratio of solid to solution the leaching results have shown that P_2O_5 is readily released from phosphate ore samples using diluted orthophosphoric acid (200ml of $H_3PO_4/800$ ml of solvent). The highest P_2O_5 extraction results obtained was 95.04% in 3.0 hours leaching time using a temperature of 30C°, comparing with 94.5% when employing a temperature of 30C° and 2.0 hours leaching time. Consequently, we can conclude that employing a leaching temperature of 30C° for 3.0 hours leaching time with acid strength 20% for leaching the phosphate ore, the extraction of P_2O_5 was 95.04% and this will remain constant even though an extra hour of leaching was added. This might be attributed to the fact that carbonate minerals (apatite and calcite minerals) in the phosphate ore sample were completely dissolved. This was confirmed by the absence of CO_2 contents in the residue, Table (4). The remaining 5%P_2O_5 in the residue could be presented in the form of crystalline phosphoric acid. Thus, no need for further use of higher acid strength or longer leaching time. It is interesting to note that the fluoride content in the leached ore sample that treated at 30C° was 22.63% after 2.0 leaching. The decreases in extraction of fluoride may be due to the increase of fluorite mineral (CaF₂) formation in the residue sample which is estimated to be about 44.5% of the residue. X.R.D analysis for the leach residue of phosphate ore sample number IR-27(-2mm) that treated for 3.0 hour leaching at 30°C and acid strength of 200ml H₃PO₄/800ml of water is shown in Figure (3).

Dissolution of the calcium phosphate content of the phosphate ore with orthophosphoric acid was mirrored by a weight loss of the leaching residue. This ranged from 82.0-84.84 % depending on the leach time used for leaching.



Figure 3. X.R.D analysis for the leach residue of phosphate ore sample number IR-27

5. Conclusions

In this work phosphoric acid has been investigated as a possible solvent for the recovery of P_2O_5 from Jordanian phosphate ores. The idea was initiated depending on bases that phosphoric acid composition is similar to the composition of the apatite phosphate mineral, so the acid will dissolve the apatite without any reaction between the dissolved components of the apatite and the phosphoric acid and no precipitations will be formed during the agitation leaching process as seen in the following equations:

$$Ca_5 (PO_4)_3 (OH) F + H_3PO_4 + 5H_2O \rightarrow 5CaO + 4H_3PO_4 + H_2O + F$$

Apatite + Phosphoric Acid + Water \rightarrow Calcium oxide + Phosphoric Acid

One of the assumed advantages in the use of orthophosphoric acid in leaching the phosphate ore would be pregnant solutions identical in acidic character which could be combined together for further treatment. The data confirms that P_2O_5 can be extracted from the Jordanian phosphate ores utilizing orthophosphoric acid solutions, and revealed the increase solubility of apatite in this solvent. The results show that dilute sulphuric acid was capable of leaching slightly more of all the elements measured under the leaching conditions employed at low temperature. Dissolution of the calcium phosphate content of the Jordanian phosphate ore with orthophosphoric acid caused a weight loss of the leaching residue ranged from 50.7-68.0 % depending upon the leaching time.

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