Experimental study on the composition of phosphate rocks for wet phosphoric acid production

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Phosphoric acid and its manufacturing industries play a crucial role in ensuring the availability of phosphorous for the world's food needs as it is economically and sustainably produced (Cheira et al, 2019). Indeed, there are two main production processes of phosphoric acid from phosphate ores: the thermal process and the wet process (Kouzbour et al, 2019). In industry, the extraction (wet) process is more commonly used due to its lower energy requirements compared to the thermal process and thus greater economic viability. Phosphate rocks (PR) which are sedimentary or igneous rocks mined from clay deposits are mainly mined and processed to form phosphoric acid as well as elemental phosphorus. The level of potentially toxic metals in the phosphate rock depends on the type and the origin of the PR whereas; sedimentary phosphate deposits possess much higher concentrations of potentially hazardous elements than igneous rock phosphate deposits (Elzoghby, 2021). The origin of PR is thus of critical importance since some areas are reputed for the presence of high concentrations of hazardous metals that decrease substantially the commercial value of produced phosphoric acid. The production of phosphoric acid by the wet process frequently gives a product that inevitably contains several impurities (Kouzbour et al, 2019), In addition, the high concentration of impurities affect negatively the filtration of phosphoric acid, and the solubility of the produced fertilizers and has a harmful impact on the environment as well as human health. Cadmium occurs naturally in phosphate rocks, and its concentration ranged from 3–150 mg/kg (Mar and Okazaki, 2012) with an average concentration of 18 mg/kg. This element is classified as carcinogenic, non-biodegradable, bioaccumulative in the environment. During the wet production process, most of the cadmium is transferred into the phosphoric acid and in turn in the phosphate fertilizers. The long-term application of phosphate fertilizers results in the accumulation of cadmium in the soil and subsequently to the human body via the food chain. (Taha et al, 2020). There is increasing demand for purified wet-process phosphoric acid (WPA) for the enhancement of crop production and improvement the quality of food products. (Cheira et al, 2019). Thus, developing an effective purification method will improve the quality of phosphoric acid and prevents the spreading of cadmium on agricultural land.

This paper presents the test result of phosphate rock's chemical composition from various origins, with special reference to cadmium. The different analytical methods were applied, such as inductively coupled plasma optical emission spectrometry (ICP-OES), cold vapor atomic absorption spectrometry (CVAAS), ion chromatography (IC), and gravimetric methods. Samples of PR1, PR2, and PR3 were obtained from mines Djebel Onk (Algiers), Khunayfis (Syria), and Negev (Israel), respectively. Total major elements CaO, SiO_2, Na_2O, MgO, Fe_2O_3, Al_2O_3, K_2O as well Cd, Mn, Cu, Zn, Ti, V, Cr, Ni, U, As, and Pb content were determined using ICP-OES spectrometer with an axial view (Varian 720-ES, Mulgrave, Australia) after microwave digestion in a closed system (Mars, CEM), using a mixture of HNO_3 and HCl acids. In the case of SiO_2, a mixture of HF, HNO_3, and HCl acids was used. For the selective determination of Cr(VI) as CrO_4^{2-} ion, an ion chromatography technique with UV-VIS detection based on an ICS-3000 high-performance ion chromatography system from Dionex (USA) was used. After elution, the Cr(VI)-complex was formed using a post-column derivatization reaction with 1.5-diphenylcarbazide through a reaction coil. The Hg content was analyzed by the CVAAS method using a DMA-80 *evo* mercury analyzer (Milestone, Italy), while P_2O_5 and SO_3 content were determined by gravimetric methods. All procedures were performed in triplicate, and then the average value has been set.

Analysis of the composition of PRs revealed that CaO, P_2O_5, SO_3, and SiO_2 were the most abundant species in all samples of which values were as high as 53.2 to 57.1%, 28.7 to 30.4%, 1.46 to 3.36%, and 1.67 to 8.67% respectively. The major element contents showed no significant differences between the PR samples, regardless of their origin, excluding SiO_2. Other major components of PRs were Na_2O, MgO, Fe_2O_3, Al_2O_3, K_2O present to a lesser extent. These results are similar to those published by Mar and Okazaki (2012) who have studied phosphate rock's chemical composition. The cadmium concentration in PR1, PR2, and PR3 was 14.3; 7.52; 24.8 mg/kg, respectively. The results from this study show a good agreement with the literature. In addition, in the composition of the analyzed phosphate rocks the occurrence of impurities such as Mn, Cu, Zn, Ti, V, U, Ni, As, Hg, Cr, and its speciation form Cr(VI) were found. The impurities present in all PRs at the lowest level are Hg and Pb which is below the LOQ of the ICP-OES method. The accuracy of the ICP-OES method was confirmed through the analysis of the SRM 694, *Phosphate Rock, Western* (NIST), and the results are shown in Table 2.

Table 1. The concentration of major elements and impurities in phosphate rocks from various sources.

Constituents	PR1	PR2	PR3
Concentration wt., %			
P_2O_5	29.0	28.7	30.4
CaO	53.2	53.4	57.1
SO_3	3.36	1.46	2.68
SiO_2	2.93	8.67	1.67
Na_2O	1.54	0.611	0.521
MgO	1.31	0.341	0.348
Fe_2O_3	0.635	0.205	0.269
Al_2O_3	0.507	0.327	0.131
K_2O	0.202	0.104	0.220
Concentration, ppm			
Mn	72.9	10.7	15.3
Cu	10.6	26.5	28.9
Zn	161	302	475
Ti	109	67.2	32.4
V	63.5	125	99.4
Cr_{total}	187	124	77.5
Cr(VI)	0.418	0.575	0.783
Ni	14.9	23.5	54.4
Cd	14.3	7.52	24.8
U	40.5	72.1	110
As	12.8	5.24	10.8
Pb	<8.0	<8.0	<8.0
Hg	0.0201	0.0227	0.0525

Table 2. Analytical results for SRM 694 by ICP-OES method and their comparison with certified values.

Constituents	Certified value ± U, wt.%	Obtained value, wt. %	Recovery, %
Al_2O_3	1.8 ± 0.1	1.8	100
CaO	43.8 ± 0.4	43.9	101
CdO	0.015 ± 0.003	0.0152	101
Fe_2O_3	0.79 ± 0.06	0.70	88.1
K_2O	0.51 ± 0.02	0.57	113
MgO	0.33 ± 0.02	0.32	97.1
MnO	0.0116 ± 0.0012	0.0115	99.2
Na_2O	0.86 ± 0.04	0.81	94.1
SiO_2	11.2 ± 0.4	10.3	92.0
U	0.01414 ± 0.00006	0.01230	87.0
V_2O_5	0.31 ± 0.07	0.30	95.7

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