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

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Phosphoric acid is one of the most important products of the inorganic chemical industry. Indeed, there are two main production processes of phosphoric acid from phosphate ores: the thermal process and the wet process. 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. Open-pit mining mainly exploits phosphate deposits in 40 countries, 12 of which supply as much as 92% of world production. Wet phosphoric acid (WPA) obtained during extraction of PRs with sulphuric acid contains impurities, the type of which depends mainly on the chemical composition and physical properties of the raw material, the type of mineral acid used for phosphate rock solution (contact, metallurgical, waste) and the applied technology. Mined PRs are assessed for P_2O_5 content and unwanted contaminants, the level of which depends on the origin and location of the mining and can be up to several wt.%.

Methods

- PRs were characterized by the WDXRF method (X'Unique II, Philips) to determine the concentration of main components,
- Ca, Si, Mg, Na, K, Fe, Al, Sr, Mn, Cu, Zn, Cr, Ni, Ti, V, Cd, As, Pb, and U content was determined by the ICP-OES technique (Varian 720-ES, Mulgrave, Australia) after microwave digestion in a closed system (Mars 5 CEM, USA) using 9 ml HNO_3 (65% Suprapur®, Merck), 3 ml HCl (30% Suprapur®, Merck),
- Determination of Cr(VI) as CrO_4^{2-} ion was made by IC technique with UV-VIS detection based on an ICS-3000 high-performance ion chromatography system (Dionex, USA),
- Hg analysis was performed by the CVAAS method using a DMA-80 evo mercury analyzer (Milestone, Italy), and P_2O_5 and SO_3 content were determined by gravimetric methods.

Materials

- Phosphate rocks PR1, PR2, and PR3 were obtained from mines Djebel Onk (Tébessa, eastern Algeria), Khunayfis (Syria), and Negev Desert (Israel), respectively,
- Certified reference material SRM 694, Western Phosphate Rock (NIST).

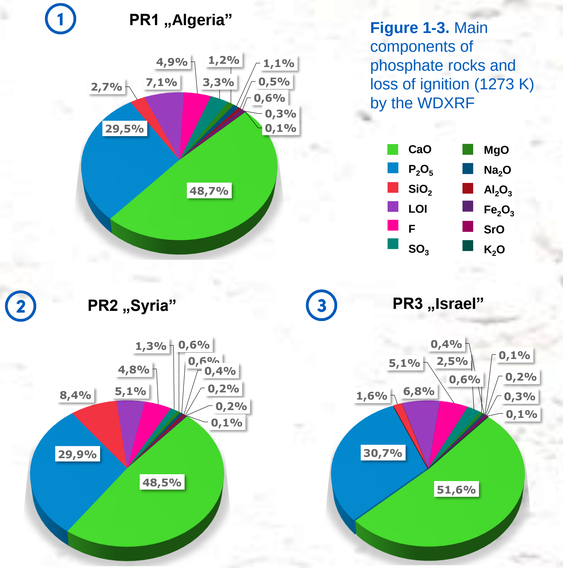

Figure 1-3. Main components of phosphate rocks and loss of ignition (1273 K) by the WDXRF

Results

Analysis of the composition of the PRs showed that the most abundant compounds in all samples were P, Ca, S, and Si. In addition, contaminants of Na, Mg, Fe, Al, K, Sr, F at the level of wt % and Mn, Cu, Zn, Ti, V, U, Ni, As, Hg, Cr, and Cr(VI) at the ppm were found. The contents of selected elements are given in terms of oxide forms.

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

	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
SrO	0.267	0.187	0.251
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

Accuracy

The accuracy of the determination of P_2O_5 by gravimetric method and of Ca, Cd, Al, Fe, K, Mg, Mn, Na, Si, U, and V by ICP-OES was found by SRM 694 analysis. The accuracy expressed as a recovery factor ranged from 85.9% for Fe_2O_3 to 112% for K_2O.

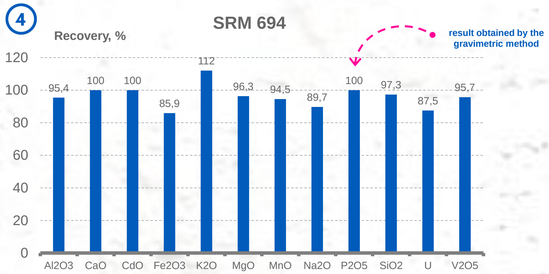

Figure 4. Recovery of constituents from SRM by ICP-OES method

Conclusions

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.

- Mineral and organic contaminants of PR determine their suitability for the WPA production process and significantly reduce their commercial value.
- There is increasing demand for purified wet-process phosphoric acid (WPA) for the enhancement of crop production and improving the quality of food products.
- Developing an effective purification method will improve the quality of phosphoric acid.

References

1. M.F. Cheira, M.N. Rashed, A.E. Mohamed, G.M. Hussein, M.A. Awadallah, Materials Today Chemistry, 14 (2019) 100176.
2. S. Kouzbour, B. Gourich, F. Gros, C. Vial, F. Allam, Y. Stiriba, Hydrometallurgy, 188 (2019) 222.
3. A. A. Elzoghby, Journal of Radioanalytical and Nuclear Chemistry, 329 (2021) 899.
4. M.H. Taha, A. M. Masoud, Y. M. Khawassek, E. A. Hussein, H. F Aly, E. Guibal, Environmental Science and Pollution Research, 27 (2020) 31278.
5. S. S. Mar, M. Okazaki, Microchemical Journal, 104 (2012) 17.

9th International Conference on Sustainable Solid Waste Management 15-18 June 2022, Corfu, Greece