



Investigation of Cd contents in several phosphate rocks used for the production of fertilizer

Swe Swe Mar ^{a,*}, Masanori Okazaki ^b

^a Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24-16, Nakacho, Koganei, Tokyo 184-8588, Japan

^b Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, 2-24-16, Nakacho, Koganei, Tokyo 184-8588 Japan

ARTICLE INFO

Article history:

Received 5 March 2012

Accepted 23 March 2012

Available online 30 March 2012

Keywords:

Cadmium
Minerals
Phosphate rocks

ABSTRACT

Phosphate rocks (PRs) can be a source of cadmium pollution in soil and food chain. PRs are mainly used for the manufacturing of phosphate fertilizers. The characteristics of PRs with special reference to cadmium, which are important phosphate fertilizer source, were investigated. In my field of study, PR of USA (PR1: from Wyoming, PR2: from Florida PR3: from Idaho), Morocco (PR4: from Qued Zem), Russia (PR5 from Slyudanka), and Japan (PR6: from Okinawa) were selected and compared using X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray diffraction (XRD). Elemental analysis results of PR samples showed that they were mainly composed of Ca, P, Si, Al, S and Fe. Total phosphate concentration in all PRs was 6 to 38% on the average. The Cd concentration levels in all PR samples ranged from 0.15 to 507 mg kg⁻¹. PR4 sample exhibited about two times higher Cd concentration than those of the literatures so far published. XRD analysis revealed that; fluorapatite ((Ca₅(PO₄)₃F), hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) and carbonate fluorapatite (Ca₅(PO₄CO₃)₃F) were the dominant minerals. This study also confirmed that PR3 and PR4 exhibited higher Cd content and prominent mineral component was carbonate fluorapatite, suggesting that Cd might be exchanged to Ca and/or occluded in carbonate fluorapatite during its formation by sedimentation.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Phosphate rock is a general term which refers to rock which is most commonly of the apatite group {Ca₅(PO₄)₃[F, OH or Cl]}. Phosphate minerals occurring in the primary environment include: 1) fluorapatite (Ca₁₀(PO₄)₆F₂), found mainly in igneous and metamorphic environments, e.g., in carbonatites, and mica-pyroxenites, 2) hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂), found not only in igneous, metamorphic environments but also in biogenic deposits, for example, in bone deposits, 3) carbonate hydroxyapatites (Ca₁₀(PO₄CO₃)₆(OH)₂), found mainly on islands and in caves, as part of bird and bat excrements, guano. Members of the apatite family are the most common phosphate minerals. Apatites in igneous and metamorphic rocks generally approach fluorapatite in composition [1]. The principal phosphate mineral in sedimentary phosphorites is carbonate fluorapatite [2]. Carbonate fluorapatite is typically secondary origin of phosphorite.

Phosphate rock (PR) is naturally occurring mineral assemblages containing high concentration of phosphate minerals, which can be commercially exploited, either directly or after processing [3,4]. It is a natural mineral deposit of phosphorus and calcium, which belongs to the species of the apatite family. About 95% of the world PR production,

which approach 150 million tons annually, is consumed for manufacturing of phosphate fertilizer [5]. The world phosphate resources are distributed, according to their type, approximately as follows: 75% from sedimentary marine deposits, 15–20% from igneous, metamorphic and weathered deposits, and 2–3% from biogenic sources (bird and bat guano deposits) [6,7]. Seventy percent of the known world phosphate rock reserves are located in sedimentary marine deposits of the Upper Cretaceous and Eocene ages of the Mediterranean phosphogenic province covering Morocco, Spain, Sahara, Algeria, Tunisia, Egypt, Israel, Jordan, Syria, Saudi Arabia, Turkey and Iraq, which is formed in deposits laid down in the ancient Tethys Sea of the Mesozoic and Tertiary ages [8]. Sedimentary rocks contain high concentration of heavy metals [9]. About 90% of these deposits are used as raw material for manufacturing of phosphate fertilizer [10]. More than 40 countries all over the world produce PRs. Most important of these countries, arranged in descending order of their production capacities, are: USA, Morocco, China, Russia, Tunisia, Jordan, Brazil, Israel, Syria, South Africa, Egypt, Australia, Senegal, India, Togo, and Canada. The United States is the world's largest producer and consumer of PRs and the leader in fertilizer production and exports [11]. PR of commercial grade has been exploited in several countries in Middle East and in North Africa. Morocco is the major phosphate producer and has the greatest reserve, followed by South Africa and US.

Cadmium (Cd) is one of the trace elements highly enriched in PR. Sedimentary rocks have higher Cd concentrations than the igneous

* Corresponding author. Tel.: +81 39084972195; fax: +81 423887276.
E-mail address: swesmooth@gmail.com (S.S. Mar).

deposits, typically in the range of 3–150 mg kg⁻¹ can be found in some rocks. Igneous deposits are generally very low in cadmium content. The average Cd concentration in PR (18 mg kg⁻¹) is 60 times its average content in shale's (0.3 mg kg⁻¹) [12]. The amounts of Cd vary widely not only among various PR sources but also even in the same deposit [13]. Composition of phosphate rocks largely depends on its type and origin. As there is currently no commercial means of removing Cd completely during fertilizer manufacturing process, the only measure to reduce Cd in product is to use relatively low Cd concentration PR to make fertilizer. The studies reported by several researchers revealed the high toxicity of Cd and that the major route of Cd addition to soils is through phosphate fertilizers [14–16]. Therefore, it is important to know the PR cadmium assemblages not only for reasons of agronomic or fertilizer technology, but also for environmental issues. Chemical composition of phosphate rock as a raw material for fertilizer is necessary to be checked for heavy metals, especially Cd because Cd is a hazardous material for human health when it is contained in foods from agricultural product. Although the phosphate fertilizers are generally the major source of trace metals among all mineral fertilizers only a limited fraction of the metals is lost to the by-products during manufacture of soluble phosphate fertilizers. For example, the final Cd concentration in fertilizers, expressed on a unit phosphorus basis, was not very different from that in the rock phosphate, and the Cd:P ratio in the rock phosphate determined the fertilizer Cd concentration [17]. As far as we searched, there are no papers available concerning Cd contents and mineral component of PRs. The objectives of this study are to investigate cadmium contents of PRs from different countries and to elucidate the relationship between the Cd content and carbonate fluorapatite.

2. Materials and methods

2.1. Sample collection and preparation

Samples of PR1, PR2, PR3, PR4, PR5 and PR6 were collected from Wyoming (United State of America), Florida (United State of America), Idaho (United State of America), Qued Zem (Morocco), Slyudanka (Russia) and Okinawa (Japan), respectively. The sample was crushed, ground to powder, homogenized and kept in an oven at 105 °C for 1 day to remove moisture if any. The 6 samples of PRs were analyzed in order to estimate elemental composition, the concentration of Cd and mineral contents.

2.2. Elemental analysis

Quality control was assured by the use of four replicate analyses performed on all samples. The use of reagent blanks, standard reference (JSAC 0402) and internal control samples were also analyzed in order to monitor analytical accuracy and precision. All the samples were analyzed for their major elements (CaO, P₂O₅, SiO₂, Al₂O₃, SO₃, Fe₂O₃, Na₂O, MgO, Cl, K₂O, TiO₂, V₂O₅, MnO) by X-ray fluorescence analysis (PANalytical, Axios). The sample to cellulose ratio was 1:3.

2.3. Digestion procedure for Cd determination

For the analysis of total Cd, 1 g of each powdered sample was placed in a 200 mL conical flask; 10 mL of concentrated HNO₃ was added to each sample. The flask was heated below boiling temperature and 5 mL HClO₄ was poured and the sample was again heated. When the brown vapor no longer appears, additional HClO₄ was added once more and the sample mixture was reheated. This step was repeated until emission of white vapor. The solution was boiled for evaporation to near dryness and 15 mL of 2 mol L⁻¹ HNO₃ was added onto the residues to dissolve all the digested salts. Digestate was cooled and filtered with No.5C Advantec filter paper. Residue

was washed with deionized water to get the final concentration of 0.3 mol L⁻¹ HNO₃ by filling 100 mL volumetric flask.

2.4. Cadmium analysis

Standard solutions of cadmium were prepared using high purity standard liquid solution of 0, 0.01, 0.1, 1.0, and 10 µg L⁻¹. These standard solutions were used for making a standard calibration curve for Cd to be determined. Analysis of PR for Cd concentration in the digested solutions was carried out with inductively coupled plasma mass spectrophotometry (ICP-MS Thermo, X Series II, Thermo Scientific, Winsford, U.K). Certified reference standard material JSAC 0402 was used to check the analytical method and the instrument accuracy. Deionized-water was used throughout and was directly obtained from a Milli-Q system for ICP-MS analysis. All reagents were of analytical grade (Wako Pure Chemical Industries, Osaka, Japan).

2.5. X-ray diffraction analysis

To identify PRs, the samples were analyzed by X-ray diffraction (XRD). For XRD analysis, the samples were dried and pulverized to less than 75 µm using a mixer mill (MM 301, Retsch, Haan, Germany) in order to induce the preferred orientation of particles horizontally loaded to the sample holder. The XRD (Rigaku, Ultima IV, USA) was operated at 40 kV and 30 mA and the CuK_α radiation (0.543088 nm) was selected as a primary beam. The goniometer was operated under the following conditions: start angle 10°, end angle 70°, and step size 0.02° with a scan speed of 2° m⁻¹ at room temperature.

2.6. Statistical methodology

Cd concentrations in different PRs are reported by computing a 95% confidence interval for the mean. In order to compare Cd concentration among different PRs, means were also analyzed using a Tukey's (HSD) test at 0.05 probability level. Data analysis was done using standard packages of the JMP 8.01 procedure in the Statistical Analysis System [18].

3. Results and discussion

3.1. Elemental composition of phosphate rocks

The major elemental composition did not differ much among different phosphate rocks. CaO, P₂O₅, and SiO₂ were the most abundant species in all phosphate rock samples of which values were as high as 39 to 71%, 6.1 to 38%, and 0.85 to 37%, respectively (Table 1). The lowest concentration of calcium (CaO) was detected in PR3 and the highest (71%) in PR4. Concentrations over 40% of calcium were found in PR1,

Table 1
Elemental analysis (wt.%) in phosphate rocks from different countries by X-ray fluorescence.

Elements	PR1	PR2	PR3	PR4	PR5	PR6
CaO	44.8	52.1	39.3	71.0	60.1	55.4
P ₂ O ₅	28.4	32.7	6.12	24.4	37.7	33.6
SiO ₂	9.27	8.48	36.5	0.895	0.847	0.930
Al ₂ O ₃	7.29	1.81	8.15	0.285	0.0647	5.94
SO ₃	0.795	1.08	0.233	1.19	0.337	0.305
Fe ₂ O ₃	6.39	169	3.09	0.353	0.0835	1.53
Na ₂ O	2.15	1.06	1.81	1.05	0.203	0.656
MgO	0.165	0.462	2.23	0.304	0.0525	0.408
Cl	0.0606	0.0355	0.0085	0.0236	0.219	0.123
K ₂ O	0.173	0.159	1.16	0.0304	0.0023	0.288
TiO ₂	0.0765	0.0745	0.583	0.0133	0	0.128
V ₂ O ₅	0	0.0176	0.069	0.0361	0.0032	0.005
MnO	0.0805	0.0435	0.116	0.0051	0.0223	0.0751
Total	99.7	99.7	99.4	99.6	99.6	99.4

Download English Version:

<https://daneshyari.com/en/article/7644305>

Download Persian Version:

<https://daneshyari.com/article/7644305>

[Daneshyari.com](https://daneshyari.com)