Proc. Estonian Acad. Sci. Chem., 1990, 39, N 1, 1—4
https://doi.org/10.3176/chem.1990.1.01

УДК 661.63.014 : 577.118

Mihkel VEIDERMA, Ludmilla VIISIMAA

TRACE ELEMENTS IN PHOSPHATE ROCK AND FERTILIZERS*

Introduction

Apart from the elements contained in phosphate rock in macroquantities (P, Ca, O, F, C, Mg, Fe, Al, S), it also contains trace elements in big varieties. Most of them are connected with phosphate mineral isomorphously replacing the constituent parts of apatite $Ca_{10}(PO_4)_6F_2$. That is why trace elements concentrate at the enrichment of rock and their content in the concentrates is 1.5—3 times higher than in rock. In chemical processing the trace elements are distributed between phases and partially go over to the product (fertilizers etc.), partially to solid waste, sewage and exhaust gases. Penetrating into the soil, water, plants, animal and human organisms, they can harmfully influence natural ecosystems and organisms. Especially it concerns Cd, Pb, Hg, As, radioactive isotopes, but at a higher content also Sr, rare earth and other heavy elements.

In the present paper the content of toxic and radioactive elements in the Baltic phosphorites has been determined (of the deposits of Maardu, Kingissepp, Toolse, Rakvere) and our data and those obtained from literature on other deposits of the USSR and of the world have been compared [1—4]. The distribution of those elements in the chemical processes and their content in fertilizers have been studied, the amounts penetrating with fertilizers into the soil have been estimated.

Results and discussion

By content the trace elements in the Baltic phosphorites are divided into three groups (Table 1). The content of Cd, Pb, U and Th in various phosphate rocks is presented in Table 2. The differences in their content in phosphorites of various Baltic deposits being insignificant, the results of determination have been given together.

The Baltic phosphorites differ from other phosphorites in a smaller content of Cd, radioactive elements and in a sligthly increased content of Pb. Less Cd and U is found in the Kola apatite, but its Th content is higher than in other phosphate rocks. The content of Hg and As in the Baltic phosphorites is usually not higher than 0.5 and 1 ppm, respectively.

Table 1

Microelements in the Baltic phosphorite concentrates

	Content, ppm	Elements
I	10^2—10^3 and more	Na, K, Mn, Ti, Cl, Br, Sr, Ce, Y, La, Nd
II	10—10^2	V, Cr, Ni, Sc, Pb, Mo, Zn, Sb, Rb, U, Ra, W, Cu, Zr, Hf, Ca, Ge, Sm, Pr, Gd, Dy, Er, Yb, I
III	less than 10	Cd, Hg, Co, As, Ta, Th, Tb, Ho, Tm, Eu a. o.

* Presented at the 32nd IUPAC Congress, Stockholm, 1989.

Table 2

Content of Cd, Pb, U and Th in phosphate rocks, ppm

	Cd*	Pb*	U	Th
Phosphorites				
Baltic	1.0—6.3	7.3—61	38—50	5—14
Karatau	0.3—6.6	4.6—64		
Marocco	7—25	2—39	100—150	8
Tunis	34—50	2	48	23
Senegal	70—75	4	105	17
Florida	5—13	12	100—180	11—19
Apatites				
Kola	0.2—0.8	1.5—14	6—10	23
Kovdor	5	20—32	10—20	

* For the USSR determined by H. Hödrejärv

In the pyrite containing phosphorite varieties the content of As can amount to 3 ppm. The content of Sr and rare earth elements is relatively high for phosphorites (0.2—0.4% and 0.15—0.25%, respectively) and is lower to apatites (for example, in the Kola apatite 2.3 and 1.1%). From the rare earth elements Ce (30% of the total amount), Y (22%), Nd (17%) and La (14%) are prevailing [5].

As apatite is not water-soluble, the trace elements contained in phosphate rock do not present any direct danger to the environment. However, in mining and enrichment phosphate rock can penetrate into waters in the form of suspension and pass over to bottom sediments in which it can be dissolved by the excretion phosphates, microcomponents, etc. If phosphates in the form of dust penetrate into the digestive tract of animals and people, the solution of apatite takes place in gastric juice.

In chemical processing trace elements are distributed between phases differently, but, as a rule, pass over to more soluble compounds. In producing single superphosphate practically all heavy and radioactive metals pass over to the product (Table 3). In the process of obtaining phosphoric acid they are distributed between acid and phosphogypsum.

Table 3

Content of Cd, Pb, U and Th in fertilizers, ppm per product and P_2O_5 (mean)

Fertilizer	Rock	Cd	Pb	U	Th
Single superphosphate	Kola apatite	0.1—0.7	1.0—6.0	0.9—5.1	10.8—16.0
		2	17.5	15	67
	N.-Africa phosphorite	10—21	2	24—80	
		86	11.1	266	
Triple superphosphate	Kola apatite + Baltic phosphorite	0.4—2.0	6.0—23	14.3—17.3	7.0—16.5
		2.6	32.2	35.1	26.1
	Florida phosphorite	7			
		15.5			
Ammophos	Kola apatite	0.3—1.5	0.9—12.9	2.2—3.7	8.0—14.4
		1.8	13.8	5.9	22.4
	Florida phosphorite	2—15	4—6		
		17	10		

According to different data the transition into the phosphoric acid in per cent is the following: Cd 16—35, Pb 17—32, Sr 60—70, U 80—95, Th 75—80 [1, 4].

That is why the fertilizers obtained through the stage of producing phosphoric acid (ammophos, triple superphosphate etc.) contain less metals mentioned above (with regard to P_2O_5).

The highest ratios of Cd/P and U/P are in the fertilizers obtained from the North African phosphorites, the products from the Kola apatite have high ratio of Th/P. The content of Sr, Hg and As in single superphosphate from the Kola apatite is 1.1%, 0.1 and 0.75 ppm., respectively.

If we take from Table 3 the maximum contents of elements in fertilizers and use a dose of P_2O_5 100 kg/ha, then up to 8.6 g of Cd, 3.2 g of Pb, 26.6 g of U and 6.7 g of Th is also carried into the soil per ha. As to Cd it is more than permitted in a number of countries (in ČSSR 3 g/ha a year).

Table 4

Specific activities of phosphate rock and fertilizers, nCi per kg of the product and P_2O_5 (mean)

Rock, fertilizer	U_{nat}	276_{Ra}	Th_{nat}
Phosphorites			
Baltic	15.0—16.5	14.0—16.2	1.1—1.9
	56.2	53.9	5.3
Marocco	45	41.9	0.4
	132.3	123.1	1.1
Florida	35.2	34.4	0.8
	103.2	101.2	2.4
Apatite (Kola)	0.7—1.2	0.6—1.0	1.6—2.1
	2.3	2.0	4.7
Single superphosphate (Kola)	0.7	0.6	1.2
	3.3	2.8	5.7
„ „ (Florida)	27.1	21.3	0.6
	150	118	3.3
Triple superphosphate (Kola + Baltic)	6.5	5.9	1.1
	14.4	13.1	2.4
Triple superphosphate (Florida)	58.0	21.0	1.3
	145	52.5	3.2
Ammophos (Kola)	1.1	0.1	1.0
	2.2	0.2	2.0
„ (Florida)	55.0	5.0	1.7
	110	10.0	3.4

Radioactive nuclei (Table 4) are in phosphate rock in the state of natural equilibrium. U and Ra pass over into the single superphosphate in the same proportion as in rock. However, in producing phosphoric acid, U and Th pass over mainly to the acid, whereas Ra goes to phosphogypsum. That is why there is much less Ra than U in ammophos. The specific activity of Ra in phosphogypsum from phosphorites can amount to 20 nCi/kg (in building materials for dwellings it must not exceed 10 nCi/kg). By preliminary estimation natural radioactive nuclei in phosphoric fertilizers have an insignificant influence on the soil radiation state, but can influence people working in mines, plants and storehouses of phosphate rock and fertilizers [6–8].

Conclusion

The content of trace elements, particularly of heavy and radioactive metals, is an important component in the characteristics of phosphate rock and fertilizers. In case of a higher content of Cd and radioactive nuclei in phosphate rock the phosphorus containing fertilizers can exert harmful influence on natural ecosystems and organisms.

REFERENCES

1. *Вейдерма М. А., Пуура В. А.* Месторождения фосфоритов // Итоги науки и техники. Неметаллические полезные ископаемые, **6**. М., 1988, 119—128.
2. *Вийсимаа Л., Хёдреярв Х.* Микроэлементы в фосфоритах Эстонии // Тр. Таллинн. политехн. ин-та, 1988, № 658, 62—67.
3. *Пелекис Л., Киррет О., Тауре И. и др.* Нейтронно-активационный анализ фосфоритов, продуктов их обогащения и концентрата глауконита // Изв. АН ЭССР. Хим., 1988, **37**, № 4, 282—284.
4. *Кириллова Н. К., Петрова Р. Т., Зинюк Р. Ю.* Распределение микропримесей свинца и кадмия при сернокислотной экстракции фосфатов и нейтрализации фосфорной кислоты // Исследования в области технологии фосфорсодержащих продуктов и сульфитных солей. Л., 1988, 19—26.
5. *Вийсимаа Л., Вейдерма М.* Выделение редкоземельных элементов при переработке эстонских фосфоритов // Изв. АН ЭССР. Хим., 1987, **36**, № 2, 98—102.
6. *Алексеев Ю. В.* Охрана почв Ленинградской области от загрязнения тяжелыми металлами // Бюл. Почв. ин-та им. В. В. Докучаева, 1986, № 38, 10—12.
7. *Гращенко С. М.* К нормированию концентрации естественных радионуклидов в фосфорных удобрениях // Гигиена и санитария, 1981, № 1, 84—86.
8. *Pfister, H., Philipp, G., Pauly, H.* Population doze from natural radionuclides in phosphate fertilizers // Radiat. Environ. Biophys., 1976, **13**, 247—261.

Tallinn Technical University

Received
Sept. 11, 1989

Mihkel VEIDERMA, Ludmilla VIISIMAA

MIKROELEMENTIDEST FOSFAATTOORMES JA VÄETISTES

Katsetulemuste ja kirjandusandmete põhjal on iseloomustatud looduslikke fosfaate erinevaist leiukohtadest, sealhulgas ka Eesti fosforiite, toksiliste ja radioaktiivsete elementide — Cd, Pb, Sr, As, U, Th — sisalduse põhjal. On näidatud elementide jaotumus faaside vahel fosfaatide töötlemisel mineraalväetisteks ning antud neile hinnang keskkonnaohtlikkuse seisukohast.

Михкель ВЕЙДЕРМА, Людмила ВИЙСИМАА

МИКРОЭЛЕМЕНТЫ В ФОСФАТНОМ СЫРЬЕ И УДОБРЕНИЯХ

С использованием экспериментальных и литературных данных представлена характеристика природных фосфатов различных месторождений (в том числе эстонских фосфоритов) по содержанию некоторых токсичных и радиоактивных элементов — Cd, Pb, Sr, As, V, Th. Показано фазовое распределение микроэлементов при переработке фосфатного сырья на удобрения, дана оценка их экологического влияния.