Journal of Agricultural Sciences
Vol. 45, No 2, 2000
Pages 155-164

UDC: 546.7:666.9.014:543.51
Original scientific paper

THE APPLICATION OF ATOMIC ABSORPTION SPECTROPHOTOMETRY (AAS) FOR DETERMINING THE CONTENT OF HEAVY METALS IN PHOSPHOGYPSUM

M.B. Rajković, S.D. Blagojević, M.D. Jakovljević and M.M. Todorović*

Abstract: Phosphogypsum is formed as a by-product in the process of "green" phosphoric acid production. This is done in the so called "wet process" by the action of sulphuric acid on raw phosphate at low temperature (<100 °C). Despite the same molecular formula and marked similarity with natural gypsum, phosphogypsum contains more than 50 impurities, and this is directly connected with the type of phosphate used in the production cycle.

The aim of this paper was to consider the possibility of using phosphogypsum for amelioration of solonetz soil, bearing in mind its content of heavy metals, which are rather toxic for human organism and which can be transferred from soil to various plants used in human nutrition. On the other hand, there are very few data in the literature about the determination of heavy metals in phosphogypsum.

The content of heavy metals in phosphogypsum was determined by atomic absorption spectrophotometry because this method has broad application in analytical practice due to its high sensitivity, selectivity and precision. The results of the investigation indicate the following average content of heavy metals (in ppm): Fe-785, Pb-45, Zn-45, Cd-7, Mn-8, Co-10, Ni-20 and Cu-17. For the investigation of the effect of phosphogypsum on solonetz soil the following points were taken into consideration: maximum recommended dose of phosphogypsum (7 t/ha) for the amelioration of solonetz soil and the weight of soil layer (from 0 to 20 cm) having an area of 1 ha.

*Dr Miloš B. Rajković, Professor, Dr Srdjan D. Blagojević, Professor, Dr Miodrag D. Jakovljević, Professor, Faculty of Agriculture, 11081 Belgrade - Zemun, Nemanjina 6, FR Yugoslavia
Dr Marko M. Todorović, Assistant Professor, Faculty of Technology, Zvornik, Republic of Srpska

The results obtained indicate that the amounts of heavy metals that are introduced into the soil with 7 t/ha of phosphogypsum are in the range from 0.035 to 0.8% of their maximum permissible content for arable soils. This means that only long-term application of phosphogypsum would introduce significant amounts of these elements into the soil.

Key words: heavy metals, atomic absorption spectrophotometry, phosphogypsum, phosphoric acid, solonetz soil.

Introduction

Phosphogypsum (with a factor of 5:1 or even 8:1 relative to H_3PO_4) is formed as a by-product in the process of "green" phosphoric acid production. This is done in the so called "wet process" by the action of sulfuric acid on raw phosphate at low temperature (<100 °C).

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4{\cdot}2H_2O + 6H_3PO_4 + 2HF$$

Despite the same molecular formula, $CaSO_4{\cdot}2H_2O$, natural gypsum and phosphogypsum differ in their physico-chemical characteristics. The reason for such behaviour is that phosphogypsum is produced chemically from raw phosphates, and as a result of this it can contain even more than 50 varions impurities (Rajković et al., 1994). Phosphogypsum represents a great ballast for industrial plants and a possible threat to the environment because it is deposited in large amounts near factory facilities (Rajković et al., 1995a).

It is a common practice in the world to apply phosphogypsum in various branches of economy (civil engineering in the first place, for solidification of soil polluted with oil, agriculture etc.) in order to reduce large quantities of this material that are found in dumps. As far as agriculture is concerned, phosphogypsum can be applied without much cleaning, because some components (for example P_2O_5), that are undesirable in cement and its products, are desirable and recommended for use in agriculture (for amelioration of solonetz soil) (Rajković et al., 1995b, 1996, 1998). Significant amounts of phosphorus are introduced into the soil by the application of phosphogypsum, and it is well known that solonetz soils have low content of available phosphorus. Sodium is removed from soil ionic exchangers by applying phosphogypsum to solonetz soil. In this way, the soil obtains favorable properties.

The application of atomic absorption spectrophotometry for determination of heavy metals in phosphogypsum (taken from a dump that is located in Prahovo) is presented in the present paper, because in the existing literature there are very few data on the content of heavy metals in this kind of material. The content of heavy metals in phosphogypsum was determined by atomic absorption spectrophotometry (AAS) because this method has wide application in practice due to its high sensitivity (many elements can be determined in concentrations of 10^{-6} g or less), precision (around 1%), selectivity and the possibility to be applied for the determination of a large number of elements (more than 20 elements can be determined by AAS) (Kirkbright et al, 1974; Welz, 1980; Pantović and coworkers, 1989; Jakovljević and Blagojević, 1998).

The aim of the present paper was to consider the possibility of using phosphogypsum for amelioration of solonetz soil, bearing in mind its content of heavy metals, and taking into consideration maximum recommended dose of phosphogypsum (7 t/ha) for such a soil amelioration and the weight of soil layer (from 0 to 20 cm) having an area of 1 ha. Namely, the purpose was to determine whether its application can cause contamination of the soil with heavy metals, which are extremely toxic for human organism. This is important from the viewpoint of possible pollution of agricultural crops with heavy metals and negative effects of polluted crops on human and animal health when they are used in nutrition.

Material and Methods

Investigations were performed with phosphogypsum obtained from chemical industry in Prahovo (IHP Prahovo) by a technological procedure in which raw phosphates are treated with sulfuric acid. Before determination of the investigated heavy metals, phosphogypsum was digested according to the following procedure.

Digestion procedure: One gram of fine ground phosphogypsum was weighed into Erlenmeyer flask (100 or 150 cm^3), 20 cm^3 of concentrated nitric acid was then added and the content of the flask was gently boiled for 2 to 3 hours. There was a small funnel on the top of the flask. After boiling with conc. HNO_3, the vessel was removed from the hot plate for the sake of cooling. Hydrogen peroxide (3 cm^3 of 30% solution) was then added and boiling was continued for 15 minutes. The digested material was transferred into volumetric flask (50 cm^3) using distilled water. The volume of the liquid in the flask was adjusted to exactly 50.00 cm^3 with distilled water. In the end, the liquid in the flask was filtered through filter paper and the filtrate was collected in a suitable reagent bottle. The solution obtained after the digestion was used for the determination of heavy metals in phosphogypsum. The following heavy metals were determined: iron, lead, zinc, cadmium, manganese, chromium, nickel and copper. The concentrations of the investigated elements in standard solutions were within the followmg limits (in µg/ml): Fe 0-20; Mn 0-10; Zn 0-2; Cu 0-5; Co 0-3; Pb 0-5; Cd 0-2; Ni 0-4; (Rajković et al., 1999).

All determinations were performed by using atomic absorption spectrophotometer Varian Spectr AA-10/20 Spectrophotometer Plus (Varian Australia Pty, Ltd., Mulgrave, Victoria, Australia).

The determination of other phosphogypsum components was carried out by using dried samples. The following analytical methods (Manual, 1977) were used for the determination of analyzed components:

- P_2O_5 - spectrophotometric method with ammonium molybdate reagent;
- CaO - gravimetric method;

- Mg - gravimetric method;
- Al - spectrophotometric method with 8-hydroxyquinoline (oxime).

Results and Discussion

Raw phosphate, whose quality is presented in Table 1, and sulfuric acid were used as starting raw materials for the production of "green" phosphoric acid by "wet" dihydrate procedure that is applied in Chemical Industry Prahovo. The presence of other compounds in phosphate (besides $Ca_3(PO_4)_2$) very often determines its suitability for the production of phosphorus fertilizers. Compounds of other elements impose their influence on chemical and physical properties of the product.

Tab. 1. - Chemical analysis of raw phosphate used in the production of phosphoric acid by "wet procedure" (Chemical Industry Prahovo, unpublished data)

Chemical composition	Phosphate (content in wt. %)
P_2O_5 total	31.6%
CaO	50.6 %
SiO_2	8%
Fe_2O_3	0.5 %
Al_2O_3	0.5 %
MgO	0.7 %
Na_2O	0.35 %
K_2O	0.025 %
F	4%
F/P_2O_5	0.1356
Cl	0.15%
CO_2	7%
loss on ignition	11%
moisture (H_2O)	up to 3 %
uranium	100 ppm
Cr	117 ppm
Ni	30 ppm
Pb	50 ppm
Cd	7 ppm
V	10 ppm
As	8 ppm
organic carbon	0.20 ppm

Compounds of iron and aluminium are the most important. The content of Fe_2O_3 and Al_2O_3 which is higher than 3% is detrimental, and this is chiefly due to possible transformation of soluble into insoluble phosphates. It is considered that each % of Fe_2O_3 transforms 2% of P_2O_5 into insoluble form, while each % of Al_2O_3 transforms 1% of P_2O_5. Increased content of these oxides is also undesirable from the standpoint of physical properties of the product (Popović, 1989). In the case of phosphate, used for the production of the investigated phosphogypsum, the content of Fe_2O_3 and Al_2O_3 is satisfactory (0.5%). The content of CO_2 in phosphate from 1-3% is considered favourable. However, the phosphate used for the production of the investigated phosphogypsum had 7% of CO_2 and this is not desirable from the standpoint of super phosphate production (due to the consumption of acid for neutralization of carbonates). This higher content of carbonates has no effect on the quality of phosphogypsum. Fluorine is one of the more important components and it has a significant role in determining the solubility of phosphorus from raw phosphates. The content of fluorine in the investigated phosphate is within usual values. When raw phosphates are treated with sulfuric acid, fluorine is removed in the form of HF. As far as the content of heavy metals in the raw phosphate is concerned, it can be seen that chromium is present in highest amounts (117 ppm), while the content of cadmium is lowest (7 ppm). Values for the content of organic carbon (0.20 ppm) indicate very low content of organic matter in the phosphate.

The problem of heavy metals in phosphogypsum has not been considered enough in literature. It is known that they are transferred from raw phosphate to phosphoric acid and phosphogypsum in the production of the mentioned acid by "wet" dihydrate procedure. When phosphogypsum is applied for amelioration of solonetz soil, there is a possibility of soil contamination with heavy metals, and the latter can have a rather negative effect on nutrition cycle. Phosphogypsum can contain 20-30% of moisture, variable amounts of organic compounds, soluble and insoluble phosphates, compounds of fluorine, small amounts of sodium compounds, rare earth and even radioactive elements.

In the production of phosphoric acid in Chemical Industry Prahovo, the following products were obtained: 30% and 50% phosphoric acid, and phosphogypsum as their by - product. The quality of phosphogypsum is presented in Table 2. The content of phosphorus, calcium, magnesium and aluminium was determined by methods, aforementioned in this paper, while presented values for the content of other components are the result of previous unpublished investigations.

Tab. 2. - Quality of phosphogypsum formed as a by-product in the production of phosphoric acid in Chemical Industry Prahovo

Chemical composition	Phosphogypsum	
	sample taken from filter	sample taken from dump
P_2O_5 total %	1.04	1.33
P_2O_5 water %	0.24	0.16
P_2O_5 insoluble %	0.80	1.17
P_2O_5 crystall. %	0.52	0.83
CaO %	40.26	39.97
H_2SO_4 %	-	54.48
Mg %	$0.47 \cdot 10^{-2}$	0.41
MgO %	$0.78 \cdot 10^{-2}$	-
Fe ppm	785	410
Al %	-	1.12
Si %	-	0.71
Na %	-	0.054
Cl %	-	0.00579
solid matter at 60 °C	63.40	85.78
solid matter at 120 °C	51.40	69.86
H_2O %	-	30.94

As can be seen from the results presented in Table 2, the composition of phosphogypsum changes during its storage in dump. In other words, it "proceedes the aging process". Phosphogypsum from filter cannot be directly used. One of the reasons is that starting phosphate contains uranium, which can be transferred to phosphogypsum. However, ^{222}Rn (uranium's radioactive descendant), which has a short half-time of decomposition (3.825 days), is for more significant for phosphogypsum. The amount of this radioactive element decreases during storage of phosphogypsum in dumps and as a result the danger of soil contamination is significantly reduced. Because of these reasons, amelioration of solonetz soil is usually carried out with phosphogypsum stored in dumps.

The analysis of heavy metals in phosphogypsum afforded results, which were comparable with values defined by the regulations (1990), and are presented in Table 3. Calculation of the amounts of heavy metals introduced into the solonetz soil by phosphogypsum was done in the following way. There will be used zinc to illustrate this calculation. It was found that the content of Zn in phosphogypsum is 45 ppm (mg/kg). Thus, with each ton of applied phosphogypsum 45x1000 = 45,000 mg of zinc is introduced into the soil. Since standard value for the amount of applied gypsum is between 6 and 7 t/ha (Наркевич, Печковский, 1984), we shall take the upper limit of 7 tons and with this amount of phosphogypsum 7x45000 mg (315,000 mg) of zinc are introduced per each hectare of soil. Now it is necessary to calculate the amount of zinc added per kg of soil. To do so, we have to calculate the mass of soil represented by an area of 1 ha and the depth of 20 cm. This mass = $20 \cdot 10^8 \cdot 1.5$ g = $3 \cdot 10^6$ kg, where 20 = depth of plow layer in cm; 10^8 = area in cm^2 equivalent to 1 ha and 1.5 is the soil volume mass in g/cm^3. So, the amount of zinc added per kg of soil = $315{,}000/3 \cdot 10^6$ = 0.105 mg. The data for other metals were calculated in the same manner and the obtained results were compared with maximum permissible values defined by the (Regulations, 1990).

Tab. 3. - Analysis of heavy metals present (in ppm) in phosphogypsum and analysis of their addition to the soil by the application of phosphogypsum to solonetz

Heavy metal	Content of heavy metals in phosphogysum (ppm or mg/kg)	Addition of heavy metals to the soil per 1 ton of phosphogypsum	Quantities of heavy metals that are added per 1 ha of soil	Addition of heavy metals with phosphogypsum per 1 kg of soil (mg)	Maximum permissible contents for soil (ppm or mg/kg) Regulations, 1990
Fe	785	785,000 mg/l t	5,495,000 mg/ha	1.8317	-
Pb	45	45,000 mg/l t	315,000 mg/ha	0.105	up to 100
Zn	45	45,000 mg/l t	315,000 mg/ha	0.105	up to 300
Cd	7	7,000 mg/l t	7,000 mg/ha	0.016	up to 2
Mn	8	8,000 mg/l t	56,000 mg/ha	0.0186	-
Co	10	10,000 mg/l t	70,000 mg/ha	0.0233	up to 50
Ni	20	20,000 mg/l t	140,000 mg/ha	0.0467	up to 50
Cu	17	17,000 mg/l t	119,000 kg/ha	0.03967	up to 100

The investigated metals can be arranged in the following order with respect to the amount in which they are added per kg of the soil:

$$Fe > Pb \geq Zn > Ni > Cu > Co > Mn > Cd$$

Iron is introduced into the soil in the highest amount (around 2 mg/kg), but it belongs to metals whose total content in soil is legally unlimited. In addition one should bear in mind the fact that iron is an element which plays an important physiological role in plants.

The calculated quantities of heavy metals (in mg/kg), which should be introduced into solonetz soil by the application of phosphogypsum, were compared with recommended maximum contents (Regulations, 1990). The following values (in % of maximum permissible contents) were obtained:

Pb (0.105%), Zn (0.035%), Cd (0.8%), Co (0.0466%), Ni (0.09%) and Cu (0.04%)

Hence, in relation to maximum permissible contents, zinc is added in lowest amount (0.035% of legally defined limit for the total content of this element in the soil) and cadmium in highest (0.8%). This means that only through a long-term application of phosphogypsum to solonetz soil, the content of heavy metals would significantly increase and in this way decrease the quality of soil.

It should be emphasized that special attention has to be paid to the content of cadmium whose presence depends on the type of phosphate used in the technological process. During the production of phosphoric acid by "wet" dihydrate procedure, 2/3 of cadmium present in phosphate goes into phosphoric acid and 1/3 into phosphogypsum. This fact should have to be kept in mind, because, besides natural sources, phosphorus fertilizers and phosphogypsum are also the sources of cadmium. The results of previous investigations (Kastori, 1997) indicate that an increase of cadmium content in soil occurs through long-term application of phosphorus fertilizers, but many years are necessary for the content of this metal to reach maximum permissible level. As far as phosphogypsum is concerned, the results of our investigation indicate that with 7 tons of this material per hectare (maximum dose) 0.8% of maximum permissible cadmium content in soil is introduced into the solonetz soil. Since melioration of solonetz with this amount of phosphogypsum is carried out with in the interval from 5 to 6 years, we can certainly say that addition of cadmium is small and is not a danger to the environment.

Conclusion

Application of phosphogypsum in various fields, especially in agriculture and civil engineering, is of essential significance, because in this way large amounts of this material are removed from dumps. Phosphogypsum represents a ballast for factories producing phosphoric acid and for the environment (actual ISO standards must be taken into consideration).

Phosphogypsum is used in agriculture for amelioration of solonetz soils. Through its application sodium is removed from adsorptive complex of solonetz soil, so that it obtains favourable properties. In addition significant amounts of phosphorus are added to the soil. Results of previous investigations (Rajković et al., 1995a) indicate that productive potential of solonetz soil becomes significantly improved within five to six years after complex amelioration. Increased nitrogen doses in the form of physiologically acid ammonium nitrate enhances both the effect of phosphogypsum and harvest index.

The obtained results, regarding phosphogypsum application for amelioration of solonetz soil, have shown that with maximum recommended dose of 7 t/ha heavy metals are added in amounts ranging from 0.035% to 0.8% of their maximum permissible content for various soils. This means that only through long-term continual application of phosphogypsum heavy metals would be introduced in appreciable amounts. Since the process of solonetz amelioration is most often performed in an interval from 5 to 6 years, addition of heavy metals could be considered negligible and without any adverse effect on the environment. In other words, there is no danger of excessive soil contamination with heavy metals when phosphogypsum is applied for amelioration of solonetz soils.

REFERENCES

1. Jakovljević, M.D. i Blagojević, S.D. (1998): Određivanje sadržaja teških metala u prehrambenim proizvodima, III Jugoslovenski simpozijum prehrambene tehnologije, Poljoprivredni fakultet, Zemun, 04.-06.februar 1998. god., Zbornik radova, Sveska V: Analitika u prehrambenoj tehnologiji. Podsekcija: Teški metali u namirnicama prehrambene tehnologije, s. 185-190.
2. Kastori, R. (1997): Teški metali u životnoj sredini. Naučni institut za ratarstvo i povrtarstvo, Novi Sad.
3. Kirkbright, G.F and Sargent, M. (1974): Atomic Absorption and Fluorescence Spectrometry. Academic Press, London.
4. Наркевич, И.П. и Печковский, В.В. (1984): Утилизация и ликвидация отходов в технологии неорганических веществ. Москва. Химия.
5. Pantović, M., Džamić, R., Petrović, M. i Jakovljević, M. (1989): Praktikum iz agrohemije. Naučna knjiga, Beograd.
6. Popović, Ž. (1989): Agrohemija, Naučna knjiga, Beograd.
7. Pravilnik o dozvoljenim količinama teških metala i organskih materija u zemljištu (1990), Službeni glasnik Republike Srbije, broj 11.
8. Priručnik (1977): Metode odredivanja mineralnih dubriva, fosforne kiseline i njihovih sirovina, IHP Prahovo.
9. Raikovich, M.B., Karlikovich-Raich, K. and Chirich, I. (1994): Comparative - Studies of Phosphogypsum and Rock Properties. Russ. J. Appl. Chem., Vol. 67(3) p. 454.
10. Rajković, M.B., Hadžić, V. i Molnar, I. (1995a): Otpadni fosfogips iz hemijske industrije - pojam, primena, perspektiva - (monografija) Naučni institut za ratarstvo i povrtarstvo, Novi Sad.
11. Rajković, M.B. i Karljiković-Rajić, K. (1995b): Hemijski gips-fosfogips: primena u poljoprivredi i za dobijanje amonijum-sulfata. Hem. Ind. (Beograd), 49(2), s. 73-77.

12. Rajković, M.B., Karljiković-Rajić, K. (1996): Otpadni fosfogips iz industrije. Deo IV. Tehnološka rešenja prerade sekundarnog fosfogipsa na industrijskom nivou radi upotrebe kao primarnog proizvoda. Arh. Farm. Beograd, 46(1-2) s. 69-82.

13. Rajković, M.B., Karljiković-Rajić, K. (1998): Possibilities for Application of Phosphogypsum in Agriculture. Rev. Res. Work Fac. Agr., Vol. 43(1) pp. 133-142.

14. Rajković, M.B., Blagojević, S.D., Jakovljević, M.D. i Vladisavljević, G.T. (1999): Primena metode atomske apsorpcione spektrofotometrije (AAS) za određivanje sadržaja teških metala u fosfogipsu. XXXIX Savetovanje Srpskog hemijskog društva, Beograd, 15-17. oktobar 1999. god., Sekcija za zaštitu životne sredine, ZS 12p, Izvodi radova, s. 263.

15. Welz, B. (1985): Atomic Absorption Spectrofotometry. Sec. Ed., VCH, New York.

Received July 4, 2000
Accepted October 13, 2000

PRIMENA METODE ATOMSKE APSORPCIONE SPEKTROFOTOMETRIJE (AAS) ZA ODREĐIVANJE SADRŽAJA TEŠKIH METALA U FOSFOGIPSU

M.B. Rajković, S.D. Blagojević, M.D. Jakovljević i M.M. Todorović*

Rezime

Procesom dobijanja "zelene" fosforne kiseline tzv. "mokrim postupkom", dejstvom sumporne kiseline na sirovi fosfat na niskoj temperaturi (<100 ^{0}C) kao nus-proizvod nastaje - fosfogips (sa faktorom 5:1, u odnosu na H_3PO_4). Uprkos istoj molekulskoj formuli i izraženoj sličnosti sa prirodnim gipsom, fosfogips sadrži preko 50 vrsta nečistoća, što je u direktnoj vezi sa vrstom fosfata koji je korišćen u proizvodnom ciklusu.

Cilj rada bio je razmatranje mogućnosti primene fosfogipsa za melioraciju soloneca, sa aspekta sadržaja teških metala, koji su izuzetno toksični i kumulativni za čovekov organizam, a iz zemljišta prelaze u biljke, kojima se čovek hrani. Sa druge strane, u literaturi se nalaze veoma oskudni podaci o ispitivanju sadržaja teških metala u fosfogipsu.

Sadržaj teških metala u fosfogipsu odredivan je metodom atomske apsorpcione spektrofotometrije (AAS), budući da je to metoda koja je našla veliku primenu u praksi usled visoke osetljivosti, selektivnosti i preciznosti. Rezultati ispitivanja su pokazali sledeći sadržaj teških metala (u ppm): Fe - 785, Pb - 45, Zn - 45, Cd - 7, Mn - 8, Co - 10, Ni - 20, Cu - 17. Za ispitivanje

*Dr Miloš B. Rajković, van. prof., dr Srđan D. Blagojević, van. prof. i dr Miodrag D. Jakovljević, red. prof., Poljoprivredni fakultet, 11081 Beograd - Zemun, Nemanjina 6, SR Jugoslavija
Dr Marko M. Todorović, docent, Tehnološki fakultet, Zvornik, Republika Srpska

uticaja primene fosfogipsa za melioraciju soloneca, uzeta je u obzir preporučena maksimalna norma za gipsovanje soloneca od 7 t/ha zemljišta i težina sloja debljine od 0 do 20 cm a površine 1 ha.

Dobijeni rezultati su pokazali da se preporučenom maksimalnom normom za gipsovanje soloneca fosfogipsom unosi po 1 ha zemljišta od 0,035 do 0,8% od maksimalno dozvoljenog sadržaja teških metala - MDK vrednosti, što znači da bi tek višegodišnjom upotrebom fosfogipsa došlo do unošenja značajnijih količina ovih elemenata u zemljište. Kako se proces melioracije soloneca najčešće vrši u intervalu od 5 do 6 godina, unošenje teških metala bilo bi u zanemarljivoj količini i bez uticaja na životnu sredinu.

Primljeno 4. jula 2000.
Odobreno 13. oktobra 2000.