



Interaction of Glassy Fertilizers and Toxic Elements

IRENA WACŁAWSKA*, MAGDALENA SZUMERA, ANNA SMEREK, IZABELA SOPEL

AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Cracow, Poland

*e-mail: iwac@agh.edu.pl

Abstract

The immobilization of lead and cadmium contamination in soils by precipitation of non-assimilable for plants Pb- and Cd-phosphates was considered. A glassy fertilizer of the controlled release rate of the nutrients for plants as a source of phosphate anions was applied. Thermal analysis methods (TG/DTG/DTA) were used for the identification of components of Pb- and Cd-precipitates, which, being *in statu nascendi*, have the nonstoichiometric composition and disordered crystallographic structure difficult to identify by XRD method. The negative role of Pb and Cd complexing citric acid solution simulating the natural soil conditions, which inhibits the Pb- and Cd-phosphates formation, was stated.

Keywords: Soil environment protection, Pb and Cd immobilization, Thermal decomposition

WZAJEMNE ODDZIAŁYWANIE SZKLISTYCH NAWOZÓW SZTUCZNYCH Z PIERWIASTKAMI TOKSYCZNYMI

Rozważaniom poddano metodę immobilizacji zanieczyszczeń ołowiu i kadmu, występujących w glebie, drogą strącania odpowiednich fosforanów, które nie są wchłaniane przez rośliny. Jako źródło anionów fosforanowych zastosowano nawozy szkliste o kontrolowanej szybkości uwalniania składników pokarmowych dla roślin. Metody analizy termicznej (TG/DTG/DTA) wykorzystano do identyfikacji składników wytrąceń zawierających Pb i Cd, które - będąc *in statu nascendi* - mają skład niestechiometryczny i nieuporządkowaną strukturę krystalograficzną trudną do identyfikacji metodą XRD. Stwierdzono ujemny, wpływ kwasu cytrynowego, symulującego w roztworze naturalne warunki glebowe, który kompleksując jony ołowiu i kadmu hamował powstawanie ich fosforanów.

Słowa kluczowe: ochrona środowiska glebowego, immobilizacja Pb i Cd, rozkład termiczny

1. Introduction

The symptom of soils chemical degradation is constituted, among others, by the accumulation of toxic elements in its top layers emitted mainly by industry, pesticides, also by mineral fertilizers and liquid wastes used to fertilize soils. One method of neutralizing such a type of soil environment contamination is bonding of toxic elements into compounds difficult to dissolve, which makes them nonassimilable for plants. Phosphorus reacts with many heavy metals to form secondary phosphate precipitates that are stable over a wide range of environmental conditions. While it is true that the content of toxic elements in the soil does not undergo any change in this way, their mobility and toxic influence on living organisms are reduced.

Geochemical modelling indicates that addition of P-amendments (P-fertilizers, phosphate rocks, biosolids, manures) to Pb-contaminated soil can result in the formation of Pb-phosphate of pyromorphite type [1, 2, 3]. Pyromorphite is very stable and has extremely low solubility under the range of environmental conditions [4, 5].

Other experimental studies, in which well soluble phosphates and phosphate fertilizers were used for cadmium removal, were conducted on contaminated soils [6, 7].

This study refers to the possibilities of using chemically active silicate-phosphate glasses acting as vitreous fertilizers of controlled release rate of the nutrients (P, Ca, Mg, K, microelements) for plants [8, 9] for simultaneous bonding of lead and cadmium, constituting particularly harmful soils contamination, into the form of insoluble compounds.

The characterization of processes and products of reaction between glassy fertilizer VitroFosMaK of 42 wt% SiO₂, 12 wt% P₂O₅, 10 wt% K₂O, 22 wt% MgO, 14 wt% CaO composition and lead and cadmium chloride solutions („*ex-situ*” reactions) under soil environment simulating conditions, is the subject of the present study.

2. Experimental

2 wt% citric acid solution was used as an extractor releasing PO₄³⁻ ions from the glassy fertilizer structure. The glass to solution weight ratio was 1:100. Such conditions simula-

te the physico-chemical state similar to the natural environment of plant roots and the surrounding soil [10]. The initial concentrations of ions removed from the glassy fertilizer by the citric acid solution action were as follows: K^{1+} 380 mg/l, Mg^{2+} 350 mg/l, Ca^{2+} 435 mg/l, PO_4^{3-} 835 mg/l.

Experiments were conducted applying the following procedure:

- Dissolution of 1 g of VitroFosMaK (0.1-0.3 mm) in 100 ml of 2 % citric acid by shaken for 1/2 h;
- Filtration of the reacted solution;
- Adding 50 ml 0.05 M $PbCl_2$ / 50 ml 0.0125 M $CdCl_2$ to 100 ml of filtrate;
- Filtration of the precipitate after different time intervals;
- Determination of Pb, Cd and PO_4 content in solution by ICP-AES method,
- Precipitate characterization by TG/DTG/DTA, XRD, FTIR, SEM-EDS analysis

Thermal analysis was carried out with Derivatograph-C (Hungarian Optical Works). Experiments conditions were: samples mass 80 mg, heating rate $10^\circ C \cdot min^{-1}$, air atmosphere. To identify the solid products of reactions diffractometer Philips X' Pert Pro with $CuK\alpha$ source was applied. The FTIR and SEM-EDS studies of precipitates were carried out on the Digilab FTS 60v Spectrometer with samples prepared in the form of KBr pellets and JSM 5400 Jeol scanning electron microscope equipped with an energy dispersive X-ray analysis respectively.

3. Results and discussion

The course of the lead and cadmium ions reaction with the phosphate ions extracted from the glassy fertilizer under the citric acid action was presented in Table 1.

Table 1. Evolution of lead, cadmium and phosphates concentrations in the chloride solution in the presence of citric acid with the reaction time.

Time [day]	pH	[Pb^{2+}] [mg/l]	[PO_4^{3-}] [mg/l]	Time [day]	pH	[Cd^{2+}] [mg/l]	[PO_4^{3-}] [mg/l]
0	3.5	8786	835	0	3.5	1403	872
2	3.5	1086	625	22		577	468
7	3.5	869	445	0	5.0	1403	872
14	3.5	203	282	6		60	249
21	3.5	146	490	29	7.0	8.5	264
				0		1403	872
				22	137	370	
				43	179	229	

The obtained results show that the most effective process of lead ions immobilization from the solution (~65 %) took place in the initial stage of the reaction, after 2 days. Together with the reaction time elongation, the amount of lead ions in the examined solution was gradually decreasing after 21 days, achieving the amount of 146 mg/l, resulting in 98 % immobilization of this chemical element in the precipitate. At the same time the reduction of phosphate concentration was less effective (~60 %). Simultaneously, it was found that the cadmium removal process was influenced by pH conditions. The most effective (~96 %) process of cad-

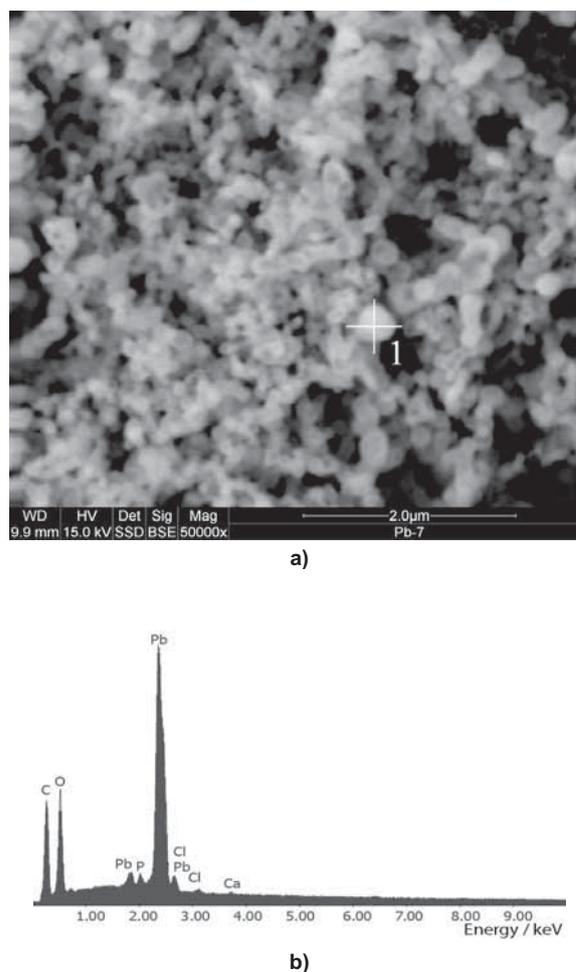


Fig. 1. Analysis of Pb-precipitate after 7 days of reaction in citric acid solution: a) SEM image, b)EDS spectrum.

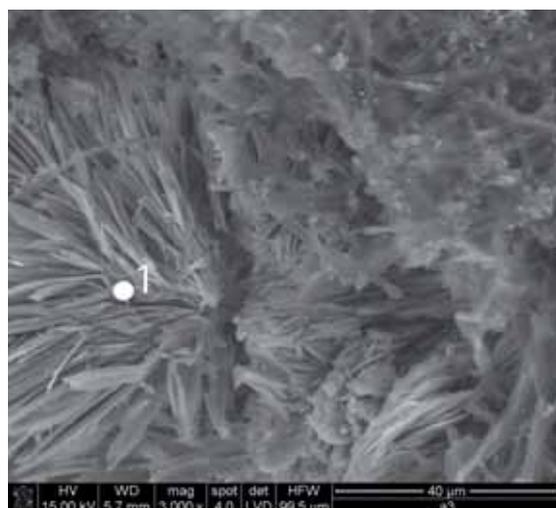
mium ions immobilization from the solution at pH = 5, took place after 6 days.

Together with the time elongation, the amount of cadmium ions was gradually decreasing, achieving after 29 days the amount of 8.5 mg/l resulting in 99.5 % immobilization of this chemical element in the precipitate. At the same time the reduction of phosphate concentration was less effective (~70 %). SEM image (Fig. 1a) showed the precipitated reaction products of lead ions and phosphate ions after 7 days of the reaction, with the morphology of the amorphous compound.

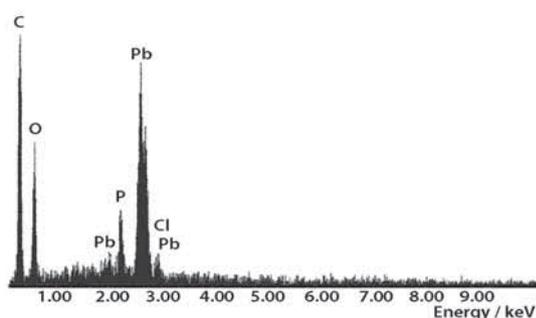
According to EDS analysis (Fig. 1b), the precipitate contains 62 at.% of carbon, 28 at.% of oxygen, 7 at.% of lead and 1 at.% of phosphorus. This composition leads to an atomic ratio of Pb/P ~7.0 which is different from pyromorphite (Pb/P = 1.67).

On the other hand, SEM image of precipitate after 21 days of the reaction (Fig. 2a) demonstrates its more crystalline form and the EDS analysis (Fig. 2b) of the chosen point of precipitate showed that it contains insoluble lead phosphate of the pyromorphite composition (atomic ratio Pb/P close to 1.67).

SEM image (Fig. 3a) showed the precipitated reaction products of cadmium ions and phosphate ions after 6 days of the reaction, with the morphology of the amorphous compound.



a)



b)

Fig. 2. Analysis of Pb-precipitate after 21 days of reaction in citric acid solution: a) SEM image, b) EDS spectrum.

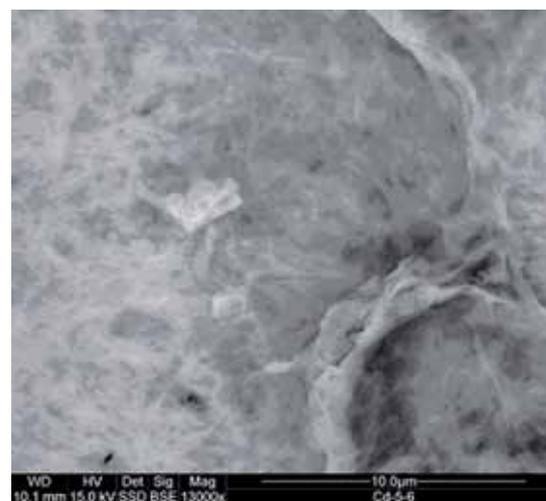
According to EDS analysis (Fig. 3b), the precipitate contains 52 at.% of carbon, 30 at.% of oxygen, 7 at.% of cadmium and 0.1 at.% of phosphorus. This composition leads to an atomic ratio of Cd/P \sim 70.0 which is different from any cadmium phosphates.

Since it is impossible to identify the precipitates phase composition using the XRD method, they were subjected to thermal analysis (Figs. 4a and 4b).

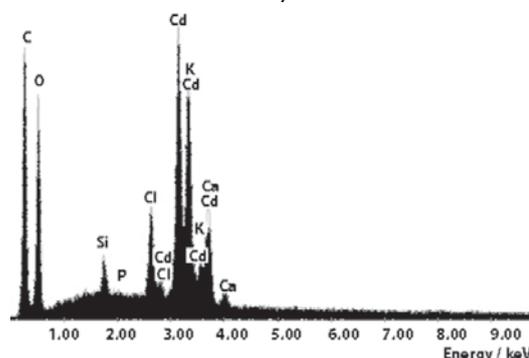
According to the TG/DTG/DTA results, the endothermic effects up to 250°C can be interpreted as the dehydration of lead and cadmium citrates. In the case of lead citrate and in the interval temperature of 250-360°C the dehydration continues as an intermolecular process with a formation of double C=C bond, *i.e.*, with transformation of the citrate into aconitate.

In the temperature interval of 320-400°C the deesterification and decarboxilation of COOH groups existed or formed as a result of the deesterification is masked by the exothermic effects of the burning of H in the air [11, 12]. According to [13], after this step the formation of lead and cadmium carbonates should take place. Taking into account that in the temperature interval of 250-400°C the thermal decomposition process of lead carbonate takes place [14], the newly formed lead carbonate decomposes and PbO as the final product is obtained.

XRD examinations of the precipitates after heating to 500°C showed (Fig. 5) that their thermal decomposition solid products are lead oxide and carbon, which are in accor-

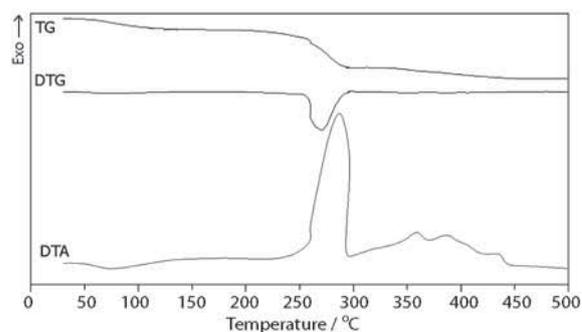


a)

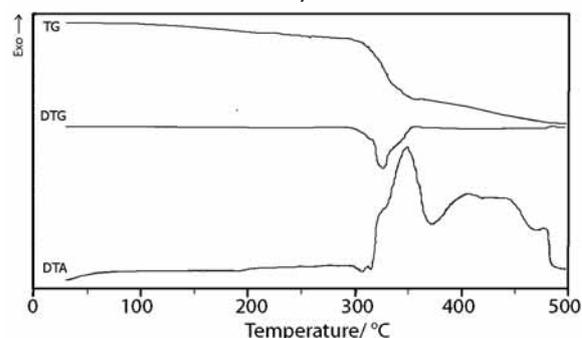


b)

Fig. 3. Analysis of Cd-precipitate after 6 days of reaction in citric acid solution: a) SEM image, b) EDS spectrum.



a)



b)

Fig. 4. TG/DTG/DTA analyses of precipitate: a) (0.05 M PbCl₂) after 7 days and b) (0.0125 M CdCl₂) after 6 days of reaction.

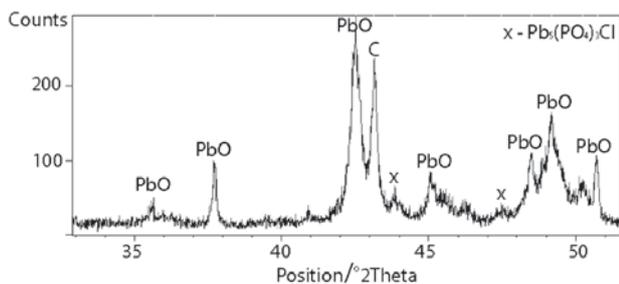


Fig. 5. XRD analysis of Pb-precipitate after 21 days of reaction heated up to 500°C.

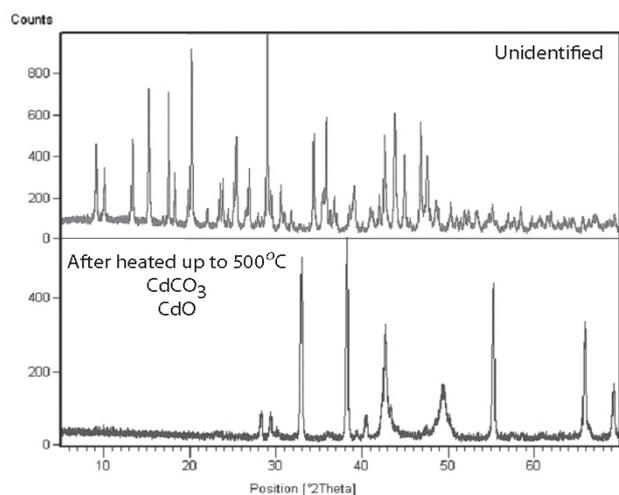


Fig. 6. XRD analysis of Cd-precipitate after 6 days of reaction heated up to 500°C.

dance with thermal decomposition products of lead citrate [15] and cadmium carbonate and cadmium oxide, which are in accordance with thermal decomposition products of cadmium citrate (Fig. 6).

The comparison of FTIR spectra of precipitates before and after heating up to 500°C (Figs. 7 and 8) confirms that the products of the lead ions and cadmium ions reaction with phosphate ions in the presence of citric acid simulating soil environment are lead and cadmium citrates, identified with the use of thermal methods.

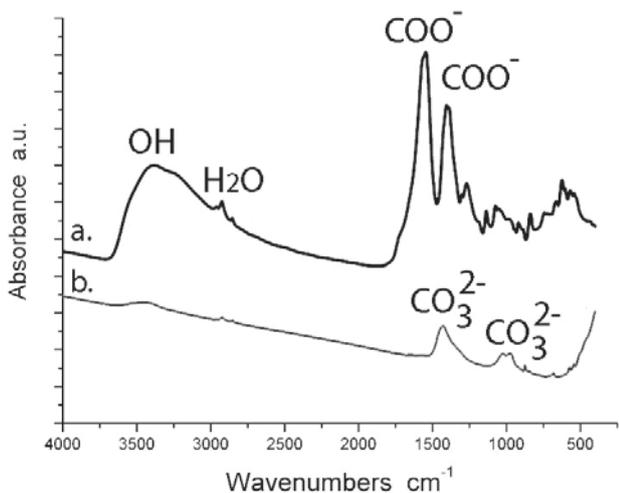


Fig. 7. FTIR spectra of Pb-precipitate after 22 days of reaction: a. before and b. after heated up to 500°C.

The FTIR spectra of non heated precipitates are characterized by three groups of bands related to the vibrational frequencies of the COO^- , H_2O and OH [16, 17]. The symmetric stretching vibrations ν_s (COO^-) are observed at 1403 cm^{-1} . The asymmetric stretching vibrations ν_{as} (COO^-) appear at 1548 cm^{-1} . The presence of water in the precipitate is confirmed by the bands at $3500\text{--}2800\text{ cm}^{-1}$. The removal of organic compounds from the precipitate structure was significantly manifested in the FTIR spectrum.

The bands related to carboxylate groups and water molecules disappear, while the bands characteristic of stretching vibrations of CO_3^{2-} groups probably originated from calcium carbonate, which is the product of the calcium citrate decomposition, present also in the precipitate, appear at 1429 cm^{-1} (Ca ion is the product of glassy fertilizer dissolution in the citric acid) and cadmium carbonate which is a product of cadmium citrate decomposition.

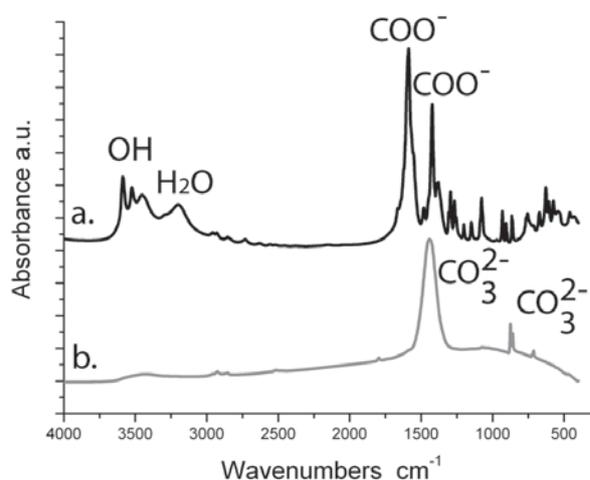


Fig. 8. FTIR spectra of Cd-precipitate after 6 days of reaction: a. before and b. after heated up to 500°C.

From the research carried out it results that the presence of the citric acid solution simulating soil environment conditions has an inhibiting effect on the process of lead and cadmium bonding into the form of insoluble phosphates. Citric acid is a polycarboxylic organic acid, which in the presence of alkaline cations and alkaline earth cations forms salts (citrates) characterized by high solubility, whereas in the presence of non-metals (P, Si), it activates the dissolution process of their compounds, which are usually insoluble or hardly soluble in water. So, the presence of citric acid as a compound strongly complexing metals, including lead and cadmium, causes the formation of soluble lead and cadmium citrate complexes.

4. Conclusions

The presented research demonstrated that the VitroFo-sMaK glassy fertilizer was effective in lead and cadmium immobilizing under soluble lead and cadmium citrate complexes in the presence of citric acid solution. A higher effectiveness of lead ions elimination from the examined chloride solutions in relation to cadmium ions has been observed. The presence of citric acid solution simulating natural soils environment has an inhibiting effect on the process of bonding lead and cadmium into the form of insoluble phosphates.

Acknowledgements

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