

# Selected heavy metals speciation in chemically stabilised sewage sludge

Ewa Wiśniowska<sup>1</sup>, and Maria Włodarczyk-Makuła<sup>1,\*</sup>

<sup>1</sup>Częstochowa University of Technology, Department of Chemistry, Water and Wastewater Technology, ul. Dąbrowskiego 69, 42-200 Częstochowa, Poland

**Abstract.** Selected heavy metals (Pb, Ni, Cd) were analysed in soil, digested sewage sludge as well as in the sludge stabilised with CaO or Fenton's reagent. The dose of Fenton's reagent was as follows:  $\text{Fe}^{2+} = 1\text{g}\cdot\text{L}^{-1}$ ,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2=1:100$ ; stabilisation lasted for 2 h. Dose of CaO was equal to  $1\text{g CaO}\cdot\text{g d.m.}^{-1}$ . Total concentration of all metals in the digested sewage sludge was higher than in the soil. Chemical stabilisation of sludge with Fenton's reagent increased total metal content in the sludge as a result of total solids removal. Opposite effect was stated when the sludge was mixed with CaO. Also chemical fractions of heavy metals were identified (exchangeable, carbonate bound, iron oxides bound, organic and residual). The results indicate that stabilisation of the sludge with Fenton's reagent increased mobility of heavy metals compared to the digested sludge. Amendment of CaO increased percent share of examined metals in residual fraction, thus immobilised them and decreased their bioavailability.

## 1 Introduction

Digested sewage sludge contains nutrients such as nitrogen or phosphorus compounds which are essential for plant growth. Because of this it can be used in agriculture or land reclamation. The main problem with agricultural use of sewage sludge is contamination of this waste material with heavy metals [1]. This problem may be aggravated if the toxic metals are mobilized in the soil [2]. Total concentration of these contaminants in the sludge may vary between several  $\text{mg}\cdot\text{kg d.m.}^{-1}$  and several thousand  $\text{mg}\cdot\text{kg d.m.}^{-1}$  [1, 3, 4]. Before land application data on heavy metals concentration in the sludge are necessary to evaluate total concentration of these pollutants according to the limit concentrations (Table 1). Permissible heavy metals concentrations in sewage sludge are, however, not suitable for assessment of metals' mobility and potential toxicity. The most suitable method for these purposes is quantification of different chemical fractions of heavy metals in the sludge. Heavy metals occur in sewage sludge and soil in various forms, e.g. soluble, adsorbed, exchangeable, precipitated, complexed [5]. The most frequently used method of heavy metals fractionation – Tessier method – distinguish five fractions of heavy metals: exchangeable, carbonate bound, iron oxides bound, organic and residual [5]. Information on the extractability and fractionation of heavy metals in sewage sludge, especially the sludge chemically stabilized are insufficient. In Polish legislation, as well as in the EU one only

---

\* Corresponding author: [mwm@is.pcz.czest.pl](mailto:mwm@is.pcz.czest.pl)

total concentration of heavy metals is limited (Table 1). No limits on individual fractions of heavy metals are set. However the knowledge on individual fractions of metals is important because they affect the bioavailability of individual compounds. It is extremely important in the case of highly toxic compounds such as Pb, Ni or Cd.

**Table 1.** Permissible total heavy metals concentration in sewage sludge according to the Polish and EU legislation (including proposals of changes in it).

Legal act	Limit concentration [mg·kg d.m. <sup>-1</sup> ]						
	Zn	Cu	Ni	Cd	Pb	Hg	Cr
Polish law [6]	2500 <sup>1)</sup> 3500 <sup>2)</sup> 5000 <sup>3)</sup>	1000 <sup>1)</sup> 1200 <sup>2)</sup> 2000 <sup>3)</sup>	300 <sup>1)</sup> 400 <sup>2)</sup> 500 <sup>3)</sup>	20 <sup>1)</sup> 25 <sup>2)</sup> 50 <sup>3)</sup>	750 <sup>1)</sup> 1000 <sup>2)</sup> 1500 <sup>3)</sup>	16 <sup>1)</sup> 20 <sup>2)</sup> 25 <sup>3)</sup>	500 <sup>1)</sup> 1000 <sup>2)</sup> 2500 <sup>3)</sup>
European Union law [7]	2500–4000	1000–1750	300–400	20–40	750–1200	16–25	-
New proposal for a directive, 2000 [8]	2500	1000	300	10	750	10	1000
New proposal for a directive, 2010 [9]	2500	1000	300	10	500	10	1000

1) in agriculture

2) for not agricultural purposes

3) for other purposes permitted by law acts

Concentration of Pb in sewage sludge can reach even 370 mg·kg d.m.<sup>-1</sup>. It is mainly present in the sludge in the residual fraction and adsorbed by Fe oxides and organic matter [3]. Thus it is not susceptible for release [5]. Intake of Pb in soil and sludge is also affected by carbonates. It's exchangeability in these materials is rather low. Nickel concentration in sewage sludge can reach even 4000 mg·kg d.m.<sup>-1</sup> [3]. The content of this metal in sewage sludge rarely is higher than set by law standards [5, 6], however it is more bioavailable for plants and even at allowable concentrations can be toxic for plants and living organisms. Ni is mainly bound by Fe oxides [3]. Cd is also strongly toxic. Its concentration in the sludge is usually not higher than 100 mg·kg d.m.<sup>-1</sup> [3]. This compound is however well soluble and it can be present practically in all fractions. It indicates that not only total concentration of heavy metals but also individual fractions are important during assessment of environmental risk of heavy metals [3, 5]. Chemical stabilisation is an interesting alternative to conventional stabilisation methods of sewage sludge. Usually advanced oxidation methods (e.g. Fenton's reagent, peracetic acid etc.) are used for this purpose. They can be used both for improvement of sewage sludge degradability (as pre-treatment method) [10] and for stabilisation of sewage sludge [11]. Because use of strong oxidants usually needs low pH removal of heavy metals from solid phase to reject water may occur [12]. As it was stated by Azhdarpoor et al. [13] leaching of heavy metals from sewage sludge is the most effective under pH of 2–3, at dose of hydrogen peroxide 3 g·L<sup>-1</sup> and Fe<sup>2+</sup> 2 g·L<sup>-1</sup>. During 15 minutes about 80–100% of heavy metals can be leached from the sludge. Cd and Pb leachability was under these conditions comparable. In the studies done

by Ito et al. [14] effective leaching of heavy metals from sewage sludge was observed at dose of H<sub>2</sub>O<sub>2</sub> equal to 0.2 g·L<sup>-1</sup> when Fe<sup>3+</sup> was present in the reaction environment (at pH = 2.5). Use of H<sub>2</sub>O<sub>2</sub> alone needed dose of this oxidant equal to 1–5 g·L<sup>-1</sup>. Use of strong oxidants for sewage sludge is considered mainly as a tool for heavy metals leaching and also for improvement of sludge dewatering [12, 15]. However heavy metals leaching by oxidants is well documented, no detailed study on the changes of the metal fractions in the sewage sludge has been done.

The aim of the study was examination of soil, digested sludge and chemically stabilized (with Fenton’s reagent and CaO) sewage sludge for total concentrations of Pb, Cd and Ni and chemical fractions (I-exchangeable, II-carbonates, III-iron oxides bound, IV-organic, V-residual) of the metals.

## 2 Materials and methods

**Soil.** Soil samples were collected from the plough layer (0–20 cm) from the farm placed near Częstochowa. They were air-dried and sieved through a 3 mm sieve. In the soil samples grain size analysis, pH in water, pH in KCl (potentiometrically), sorption capacity (by Kappen method), humidity, total suspended solids (TSS) (by owen dry-method, at 105°C), humus concentration (by Tiurin method) were primary analyzed. The measurements were done according to standard methods [16].

**Sewage sludge. Chemical stabilization.** Raw sewage sludge samples were taken from primary sedimentation tank of municipal wastewater treatment plant. Sewage sludge samples were passed through a 3 mm sieve. Sewage sludge was chemically stabilized with Fenton’s reagent (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>=1:100; dose of Fe<sup>2+</sup> = 1g·L<sup>-1</sup>) for 2 h, at 20±1°C. CaO was introduced into the sludge at the dose of 1 gCaO·g d.m.<sup>-1</sup>.

**Analysis of chemical properties.** pH was analysed potentiometrically according to PN EN 12176. Total suspended solids in the sludge (TSS) was analysed according to the PN-EN 12880 :2004.

**Heavy metals speciation.** In order to study the forms of Pb, Cd and Ni in soil and sewage sludge the modified Tessier extraction procedure was used [5]. It consisted of five steps which give rise to five different fractions – Table 2. The extraction was carried out in glass centrifuge tubes of 50 mL capacity with an initial mass of 1 g oven dried (105°C) fine fraction (< 1mm) of the samples. Supernatants were analysed by atomic absorption spectroscopy. Analyses were performed in triplicate.

**Table 2.** Method of metal speciation in sewage sludge and soil [5].

Fraction	Form of metal	Parameters of fractionation	Time of extraction, h
I	Exchangeable	1.0 M CH <sub>3</sub> COONH <sub>4</sub> , pH = 7.0, T = 20°C	2.0
II	Carbonate bound	1.0 M CH <sub>3</sub> COONa, pH = 5.0, T = 20°C	4.0
III	Iron oxides bound	0.04 M NH <sub>2</sub> OH·HCl in 25% CH <sub>3</sub> COOH (v/v), T = 95°C	4.0
IV	Organic	0.02 M HNO <sub>3</sub> + 30% H <sub>2</sub> O <sub>2</sub> + 3.2 M CH <sub>3</sub> COONH <sub>2</sub> in 20% HNO <sub>3</sub> (v/v), pH = 2.0, T = 85°C	5.5
V	Residual	10 M HNO <sub>3</sub> + 30% H <sub>2</sub> O <sub>2</sub> , T = 100°C	1.5

### 3 Results and discussion

Total concentrations of selected heavy metals in soil, digested sludge and chemically stabilized sewage sludge are listed in Table 3.

**Table 3.** Total heavy metals concentrations [ $\text{mg}\cdot\text{kg d.m.}^{-1}$ ] in soil, digested sewage sludge and chemically stabilized sewage sludge.

Metal	Digested sludge	Sludge stabilised with CaO	Sludge stabilised with Fenton's reagent	Soil
Pb	$103.5 \pm 11.2$	$63.0 \pm 9.7$	$190.7 \pm 15.1$	$31.8 \pm 3.2$
Cd	$14.4 \pm 1.3$	$13.0 \pm 2.3$	$39.1 \pm 19.1$	$4.3 \pm 0.7$
Ni	$113.2 \pm 18.2$	$64.1 \pm 14.1$	$173.8 \pm 22.9$	$19.3 \pm 1.8$

Total concentration of all examined heavy metals in digested sludge was higher than in soil. Concentrations of Pb and Cd were about three times higher, whereas Ni content in the sewage sludge was about 6 times higher than in the soil. The studied soil was qualified as sandy (sand light-clay). There was a light soil with the low humus concentration (1.5%), acid ( $\text{pH KCl} = 5,2$ ), with the low sorption capacity ( $13.6 \text{ cmol}(+)\cdot\text{kg}^{-1}$ ) and low humidity (24%). Stabilization of sludge with CaO decreased total content of heavy metals in sewage sludge. It was probably associated with the fact that amendment of CaO increased total solids concentration in the sample, whereas concentration of metals did not change. As a result apparent decrease of heavy metals concentration in sewage sludge occurred. Contrary to stabilization with CaO use of Fenton's reagent increased total concentration of examined heavy metals in sewage sludge. Pb concentration increased from 103.5 to 190.7  $\text{mg}\cdot\text{kg d.m.}^{-1}$ . Concentration of Cd from 14.4 to 39.1  $\text{mg}\cdot\text{kg d.m.}^{-1}$ , whereas Ni from 113.2 to 173.8  $\text{mg}\cdot\text{kg d.m.}^{-1}$ . During stabilisation of sewage sludge with Fenton's reagent decrease of total solids occurred. Because use of Fenton's reagent did not affect concentration of heavy metals, but decreased TSS content, concentration of these compounds in the sludge after stabilisation apparently increased (Table 4). Thus it can be stated that fates of heavy metals in sewage sludge during chemical stabilisation are connected with the changes of total solids concentration. In all samples the less abundant contaminant was cadmium.

**Table 4.** Selected chemical properties of sewage sludge used in the study.

Parameter	Unit	Digested sewage sludge	Sludge stabilised with CaO	Sludge stabilised with Fenton's reagent
pH	-	6.9	10.8	4.5
TSS	$\text{g}\cdot\text{L}^{-1}$	215.1	389.2	189.8
VSS	%	48.6	32.1	42.5

Chemical stabilisation of the sludge also affected chemical fractions of individual heavy metals. Fractions of Pb, Ni and Cd in sewage sludge, chemically stabilised (with CaO and Fenton's reagent) sewage sludge compared to fractions in soil are presented in Figures 1–3. In relation to Pb, the series followed for soil, digested sewage sludge, sewage sludge stabilised with Fenton's reagent, sludge stabilized with CaO were:

Carbonate bound > organic > iron oxides bound > residual > exchangeable,  
Carbonate bound > organic > iron oxides bound > residual > exchangeable,

Carbonate bound > iron oxides bound > exchangeable > organic > residual  
 Residual > organic > carbonate bound > iron oxides bound > exchangeable.

According to the data presented by Wilk and Gworek [3] Pb in sewage sludge is mainly adsorbed by Fe oxides and organic compounds. It is also present in residual fraction. During the study we have found that Pb was not present in exchangeable fraction of sewage sludge, and the dominant fraction of Pb in digested sewage sludge was the carbonate bound one.

For the Cd the series were followed:

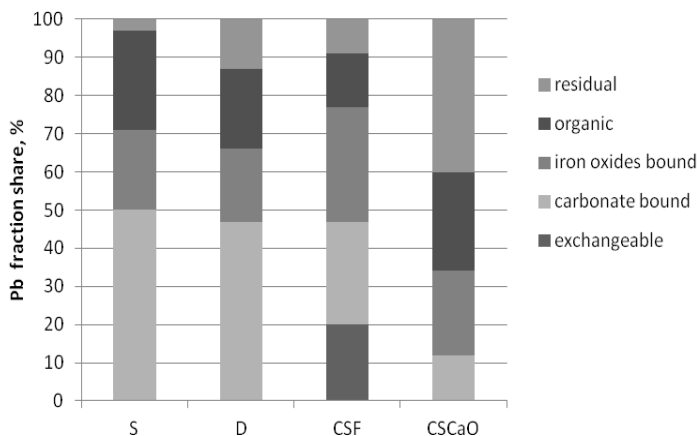
Residual > iron oxides bound > carbonate bound > organic = exchangeable,  
 Residual > iron oxides bound > exchangeable > organic > carbonate bound,  
 Residual > iron oxides bound > exchangeable > carbonate bound > organic,  
 Residual > iron oxides bound > exchangeable > organic > carbonate bound.

Compared to the results obtained by other authors [3] it can be stated that high content of Cd in residual fraction is typical. By the mentioned authors this metal compound percent share is usually the less in exchangeable fraction, whereas in carbonate bound one is usually relatively high. In this study percent share of exchangeable fraction of Cd in the sludge was higher than carbonate bound one. This was probably associated with the diversity of sewage sludge between various wastewater treatment plants.

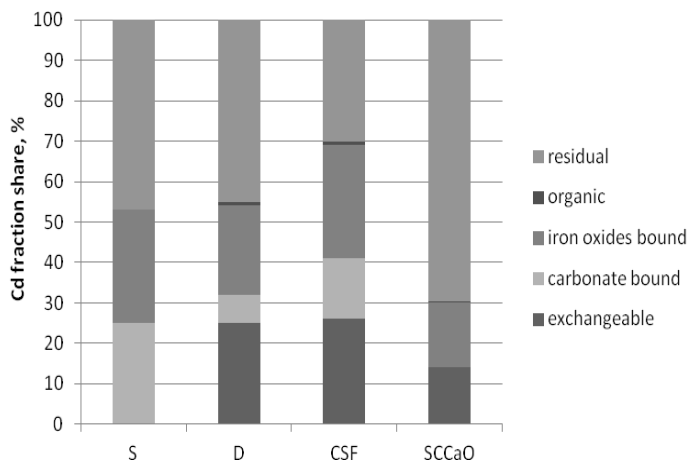
In the case of Ni the series were:

Carbonate bound > residual = exchangeable > organic > iron oxides bound,  
 Iron oxides bound > organic > exchangeable > residual > carbonate bound,  
 Iron oxides bound > exchangeable > carbonate bound > organic > residual,  
 Residual > iron oxides bound, exchangeable > organic > carbonate bound.

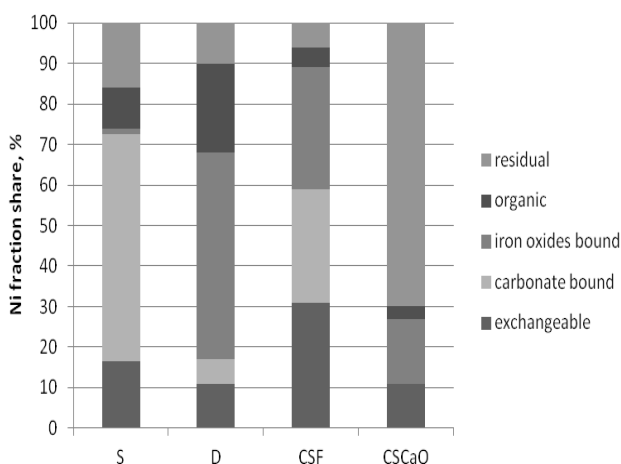
The results obtained in the study for sewage sludge are typical for sewage sludge. As it was stated by Wilk and Gworek [3] Ni in sewage sludge is mainly present in connections with Fe and Mn oxides and organic fraction, as well as in the residual one.



**Fig. 1.** Speciation of Pb in examined samples: S – soil, D – digested sludge, CSF – sludge stabilized with Fenton’s reagent, CSCaO – sludge stabilised with CaO.



**Fig. 2.** Speciation of Cd in examined samples: S – soil, D – digested sludge, CSF – sludge stabilized with Fenton’s reagent, CSCaO – sludge stabilised with CaO.



**Fig. 3.** Speciation of Ni in examined samples: S – soil, D – digested sludge, CSF – sludge stabilized with Fenton’s reagent, CSCaO – sludge stabilised with CaO.

Chemical fractions of heavy metals in sewage sludge can be affected by origin of sewage sludge, pH, organic matter content [3]. It is the reason for the differences observed between the results obtained in this study compared to the ones observed by other authors [3, 5].

As can be seen from Fig. 1–3 amendment of CaO increased residual fraction of examined heavy metals in the sludge both compared to the soil and digested sewage sludge. The increase was especially visible in the case of Pb and Ni. Amendment of Ca simultaneously decreased exchangeable fraction of the sludge. Whereas Fenton’s reagent increased this fraction percent share in the case of all metals. Percent share of exchangeable fraction was the lowest in the soil (only Ni was present in this fraction in soil). Ni in soil was present mainly as carbonate bound compounds (> 50%). Fraction of iron oxides bound Ni was negligible. Over 10% were residual and exchangeable fractions. Less than 10% were the organic compounds of Ni (Fig. 3). Percent shares of Ni in the digested sewage sludge differed from the ones in soil. The dominant fraction were iron

oxides bound and organic. It can be connected with the fact that during sewage sludge treatment ferrous salts are used as coagulants, and the flocks which are formed during the process catch the Ni ions on its surface. Reach organic fraction of the sludge also can adsorb heavy metals present in the sludge. This fraction is significantly less in the soil. As it was mentioned above chemical stabilisation of sewage sludge with Fenton's reagent increased exchangeable fractions of Ni in the sludge. Simultaneously decrease of Ni content in residual and organic fraction occurred. It could be connected with the destruction of solids during chemical stabilisation of the sludge. During 2 h chemical stabilisation of sewage sludge with Fenton's reagent decrease of total suspended solids by about 12% occurred. It doubtless moved persistent compounds of Ni bounded to suspended solids. As a result increase of exchangeable fraction occurred simultaneously with the decrease of Ni content in residual and organic fractions. Amendment of CaO immobilised Ni in the sludge which was with no doubt connected with pH increase (Table 4). Simultaneously percent share of exchangeable fraction of Ni decreased from more than 20% to less than 15%. Iron oxides bound fraction of Ni decreased slightly compared to digested sewage sludge. The residual fraction of Ni stayed the dominant one in the sludge amended with CaO.

Similar phenomenon was observed in the case of Cd (Figure 2). Amendment of CaO also caused the residual fraction of this metal as dominant. Simultaneously percent shares of exchangeable and iron oxides bound fractions of Cd decreased compared to the digested sludge. Carbonate bound fraction of Cd practically did not exist in sludge stabilised with CaO. Contrary to the stabilisation with CaO treatment of the sludge with Fenton's reagent slightly decreased exchangeable fraction of Cd in the sludge. However it must be emphasised that Cd in sewage sludge was more exchangeable in all samples of the sludge than in soil. Percent share of residual fraction of Cd was however comparable both in soil and sewage sludge, in the last sample content of carbonate bound Cd was lower.

Also in the case of Pb (Fig. 1) treatment of sludge with Fenton's reagent increased the mobility of the examined heavy metals. Chemical stabilisation of the sludge with Fenton's reagent also decreased carbonate bound fraction of Pb. Simultaneously percent share of iron oxides bound fraction of Pb increased. It is connected with the changes of sludge properties during stabilisation with strong oxidants under low pH values (pH of chemically stabilised sludge was equal to 4.5). Introduction of Fe (as catalyst in Fenton's reaction) could enrich iron oxides bound fraction compared to the digested sludge. Destruction of residual and organic fractions caused release of not bioavailable Pb to the supernatant and to other fractions of metals, particularly to the exchangeable one.

As in the case of Cd and Ni also Pb percent share in residual fraction increased as a result of CaO stabilisation. Organic fraction was comparable to the one observed in the sludge before chemical stabilisation.

Based on the results obtained during the study it can be stated that use of strong oxidant mobilises heavy metals in sewage sludge, probably as a result of suspended solids destruction as well as a result of pH drop. Contrary to this treatment method amendment of CaO decreases the mobility of heavy metals in sewage sludge, simultaneously decrease apparent decrease of total heavy metals concentration occurs.

## 4 Conclusions

1. Heavy metals concentrations in chemically stabilized sewage sludge was higher than permissible limits for this kind of waste material established by Polish law standards. Concentration of heavy metals in the sludge was higher than in soil.

2. Amendment of sewage sludge with CaO decreased total concentration of heavy metals in the sludge, as well as decreased their mobility. The dominant chemical fraction of metals in the sludge amended with CaO was the residual one.
3. Chemical stabilization of sewage sludge by Fenton's reagent increased total concentration of heavy metals in sewage sludge. It also mobilised them by increase of percent share of heavy metals in exchangeable fraction.

*Funding for this project was provided by BS-PB-402-301/11*

## References

1. J. Bernacka, L. Pawłowska, A. Krobski, Publishing House of Institute of Environmental Protection, Warsaw (2002) (in Polish)
2. A. Fuentez, M. Loréns, J. Sáez, M. Aguilar, J. Ortuño, V. Mesequer, *Bioresour. Technol.* **99** (2008)
3. M. Wilk, B. Gworek, *Environ.* **39** (2009) (in Polish)
4. E. Wisniowska, M. Włodarczyk-Makuła, R. Nowak, *Rocz. Ochr. Sr.* **18**, 2 (2016)
5. L. Dąbrowska, *Chem. Pap.* **66**, 3 (2012)
6. Ordinance of the Minister of the Environment on sewage sludge, 06. 02. 2015
7. Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture
8. Working document on sludge 3rd draft, Brussels 27 April 2000
9. Working document on sludge and biowaste, Brussels 21. 09. 2010
10. I. Zawieja, L. Wolny, M. Próba M., *Environ. Res.* **156** (2017)
11. K. Barbusiński, K. Filipek, *Pol. J. Environ. Stud.* **9**, 3 (2000)
12. M. Janosz-Rajczyk, E. Wiśniowska, *Chem. Pap.* **59**, 6b (2005)
13. A. Azhdarpoor, R. Hoseini, M. Dehghani, *JHSS* **3**, 4 (2015)
14. A. Ito, K. Takahashi, J. Suzuki, T. Umita, *J. Water Environ. Technol.* **11**, 4 (2013)
15. R. Devil, J. Baeyens, E. Neyens, *Environ. Eng. Sci.* **23**, 6 (2006)
16. A. Mocek, S. Drzymała, Publishing House of University of Life Science, Poznań (2010)