

CHEMICAL FORMS OF IRON IN THE COMPOSTS
OBTAINED FROM MUNICIPAL SOLID WASTE
CONTAMINATED WITH PULVERIZED METALLIC
Fe, Fe₂O₃ or FeS

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Keywords: municipal solid waste, composting, iron, iron oxide(III), iron sulfide(II), speciation analysis.

FORMY CHEMICZNE ŻELAZA W KOMPOSTACH
OTRZYMANÝCH Z ODPADÓW KOMUNALNYCH
ZANIECZYSZCZONYCH PYŁEM METALICZNYM Fe,
TLENKIEM Fe₂O₃ LUB SIARCZKIEM FeS

Przeprowadzono kompostowanie odpadów komunalnych z 1% dodatkiem pyłu metalicznego żelaza, tlenku żelaza(III) i siarczku żelaza(II). W otrzymanych kompostach oznaczono metodą analizy specjacyjnej udział metalu w formach bioprzyswajalnych oraz oszacowano wpływ procesu kompostowania na jego mobilność. Stwierdzono, że żelazo wprowadzone do odpadów w postaci pyłu metalicznego występuje w kompoście w formach łatwo dostępnych dla roślin, głównie we frakcji węglanowej. W odpadach zanieczyszczonych Fe₂O₃ metal jest unieruchomiony we frakcji pozostałości, a proces kompostowania praktycznie nie zwiększa jego mobilności. Przeszło połowa dodatku żelaza w formie FeS pozostaje w odpadach we frakcji pozostałości, ale po procesie kompostowania stwierdzono wzrost stężenia metalu w bioprzyswajalnej frakcji węglanowej.

Summary

Composting of municipal solid waste with a 1% addition of pulverized metallic iron, iron oxide(III) and iron sulfide(II) has been carried out. The amounts of iron in the bioavailable forms have been assayed in the composts obtained by means of speciation analysis, and the influence of composting on iron mobility has been evaluated. It has been found that pulverized metallic iron introduced into the waste occurs in the compost in the fractions easily accessible to plants, mainly the carbonate fraction. In the waste contaminated with Fe₂O₃ iron remains in the residual fraction, and composting does not practically increase its mobility. Over half of the iron from FeS remains in the waste in the residual fraction however, after composting there was an increased iron concentration in the bioavailable carbonate fraction.

INTRODUCTION

Iron is the primary raw material of modern engineering. It has been estimated that its world consumption amounts to 100 million tons per year [2]. Since iron is not toxic, its contribution to the environmental contamination has not been considered so far. It is emitted mainly by metallurgical and power industries (coal contains on average 1.5% Fe [10]). In Poland, in 1996, 1 250 000 tons of dust were emitted into the air from stationary sources, including 623 000 tons from industrial power generation and industrial engineering [15]. Large quantities of iron pass into the environment as a result of finished products corrosion.

Iron is indispensable to proper growth of living organisms. Its basic functions in plants concern photosynthesis, nitrate reduction, free nitrogen fixation and regulation of reduction and oxidation processes. 60–70% of iron present in human and animal organisms occurs in hemoglobin and myoglobin of blood. It takes part in carrying oxygen molecules with blood from lungs to muscles, where oxygen is consumed in glucose oxidation. The resulting carbon dioxide is then carried back to the lungs with iron in venous blood. Being a component of erythrocytes, iron affects acid-alkali balance, as well as reduction and oxidation mechanisms. Its deficiency or excess result in anemia and some disturbances in occurrence of other metals indispensable to life [3, 10].

Distribution and chemical forms of elements in soil depend on their biochemical properties. In soil, iron is present in two oxidation degrees, +2 and +3, in the form of oxides, hydroxides, silicates, sulfates and carbonates. Hydrated iron oxides are the most stable ones. All Fe^{+2} compounds are mobile but very unstable, whereas Fe^{+3} are stable. Under oxidizing and alkaline conditions, processes of iron compounds precipitation prevail, whereas in the wet layers of the soil the prevailing processes are those which increase the mobility of the metal as a result of its reduction [10, 17].

This paper is a continuation of the researches carried out for several years on chemical forms of metals (lead, zinc, cadmium, copper and mercury) in the composts obtained from municipal solid waste contaminated with metallic, oxide and sulfide forms of the metals [4–8]. Composting of the municipal solid waste containing specific amounts of organic elements allows its utilization with no hazard to the environment, provided the composts obtained do not contain toxic heavy metals which are harmful to people. What matters here is not only the total amount of metal but also the form it is present in the compost. Since mineralization of organic substances increases the bioavailability of metals, the research aimed at evaluating the impact of composting on the mobility of metals released into the waste in the not easily available forms of low chemical activity. This paper presents the results obtained for iron and its compounds. The municipal solid waste was mixed with pulverized metallic iron, iron oxide(III) or iron sulfide(II), and the amounts of this metal in the bioavailable forms in the mixtures obtained before and after composting were determined using speciation analysis (operational speciation) [1, 11].

EXPERIMENTAL

APPARATUS AND REAGENTS

– Atomic absorption spectrometer Perkin Elmer 3300. The sample was introduced in an acetylene-air flame, and the measurement conditions were set according to the instruction manual;

– A 2 dm³ Dewar flask with a thermometer and aeration system;

– Municipal solid waste from Gliwice, dried at 105°C and ground in an impact mill (\varnothing less than 1 mm);

– Pulverized metallic iron, minimum 96%, prod. Chemische Produkte GmbH;

– Iron oxide Fe₂O₃, prod. POCh;

– Iron sulfide FeS, prod. PARK;

– Redistilled water;

– Potassium nitrate (KNO₃), analytically pure, prod. POCh;

– Potassium fluoride (KF), analytically pure, prod. POCh;

– Sodium pyrophosphate (Na₄P₂O₇), analytically pure, prod. POCh;

– Sodium versenate (EDTA), analytically pure, prod. POCh;

– Nitric acid (HNO₃) conc., analytically pure, prod. ZA Tarnów;

– Chloric acid (HClO₄) 70%, analytically pure, prod. Merck Germany;

– Hydrofluoric acid (HF) conc., analytically pure, prod. Merck Germany.

COMPOSITING OF MUNICIPAL SOLID WASTE

The composting mixture contained: 311.5 g of municipal solid waste, 175 g of redistilled water, 35 g of compost (leaven) and 3.5 g of additives (pulverized metallic iron, iron oxide or sulfide per pure element). All the components were thoroughly mechanically mixed during two hours, put into Dewar flask and the aeration system was started. The waste for composting without iron was prepared in the same way. The process was carried out for eight days.

During the composting process, the temperature of the waste was measured. An increase in temperature was found during the initial 40 hours of the process. After reaching the maximum point ($t > 45^\circ\text{C}$), the temperature was gradually decreasing. On the fourth day, the compost was taken out of the flask, mixed and reintroduced into the flask to continue the process. After the aeration, an increase in temperature of the compost was found, but not so high (up to 35°C). On the eighth day, the temperature of the compost equaled the room temperature.

The content of organic matter in the waste was assayed from mass decrement of the sample, after it was roasted in a furnace under aerobic conditions, at the temperature of 550°C, using the gravimetric method [14].

IRON SPECIATION IN THE WASTE

1.0000 g of the waste (dry weight) before and after composting was taken for analysis. Humidity of the compost was determined by means of the gravimetric method. Speciation analysis was conducted according to Rudd [16]. Table 1 shows the fractions determined and the extractants applied. The sample was treated with 20 cm³ of the extractant solution and shaken for 24 hours. Then, the sediment was separated from the solution by centrifuging and treated with another extractant. The solution was transferred into a volumetric flask ($V = 50 \text{ cm}^3$) which was filled with redistilled water to volume. The contribution of iron to the residual fraction was calculated from the weight difference of the addition and the total iron weight determined in the fractions 1–6 (without the background).

Table 1. Classification of iron fraction in the waste according to Rudd [16]

Forms	Extractant
1. Soluble	redistilled water
2. Exchangeable	1 mol/dm ³ KNO ₃
3. Adsorbed	0.5 mol/dm ³ KF
4. Organically bound	0.1 mol/dm ³ Na ₄ P ₂ O ₇
5. Carbonate	0.1 mol/dm ³ EDTA
6. Sulfide	6 mol/dm ³ HNO ₃
7. Residual	Difference between the total iron mass and the sum of iron mass in fractions 1–6, or extraction with HNO _{3conc.} , HClO _{4conc.} , HF _{conc.}

The total iron content in the waste was determined, applying mineralization of the sample in the mixtures of HClO₄ + HNO₃ or HF + HNO₃ [14]. Iron content in the extracts was measured by means of atomic absorption spectrometry.

MEASUREMENTS AND RESULTS

Four composting processes were conducted on:

- waste without the addition of iron,
- waste with a 1% addition of pulverized metallic iron,
- waste with a 1% addition of iron oxide(III),
- waste with a 1% addition of iron sulfide(II).

In each measurement, the speciation of iron in the waste was carried out twice, before and after composting. Extraction was repeated for four parallel waste samples. The results (mean values) are presented in Tables 3–9.

DISCUSSION

Composting is a biochemical process which consists in mineralization of organic matter with concomitant microorganisms and emits heat. Although in the soil composting is very slow, it can be intensified in a laboratory, ensuring optimum conditions for metabolism (sufficient amounts of fractions in the waste which are susceptible to biochemical degradation, activity of microorganisms and their capability to degrade specific substances, waste humidity, room temperature, aeration velocity, and the like) [12].

The research was carried out under model conditions. The measurements were conducted on ground municipal solid waste homogenized by mixing. The ratio of carbon to nitrogen in the waste (C:N = 25:1) and its humidity (50% on average) were optimum. Composting was carried out in the thermally insulated flask, thus limiting the exchange of heat with the environment, but sufficient aeration of the composted matter was ensured. The addition of iron and its compounds neither caused the microorganisms to be poisoned nor hindered the process. After the first 20 hours, a considerable increase in temperature was observed, until it reached the maximum value between 25th–35th hours of composting (Fig. 1). Both the temperature at its maximum (47–52°C), as well as its width are comparable with the graph obtained when composting the waste alone.

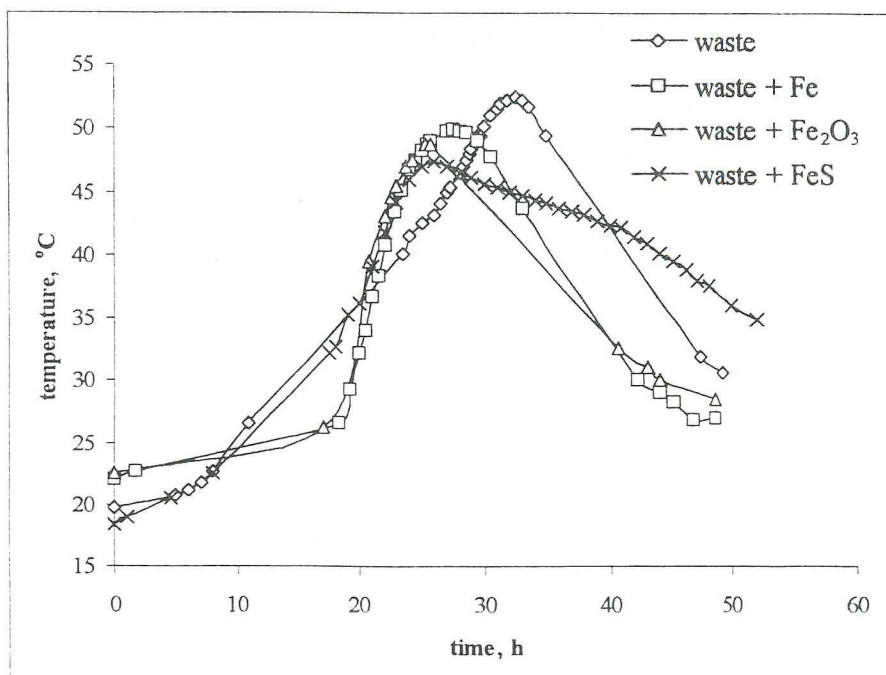


Fig. 1. Temperature of the waste during the composting process

It has also been found that the process caused a decrease in the content of organic matter by 8–9% on average. The decrement of organic matter and self-heating of the composted matter to the temperature over 45°C indicate that the waste had been partially mineralized.

Speciation analysis was conducted according to Rudd [16] who regarded the following fractions as extremely hazardous to the environment:

- soluble, including compounds soluble in the soil solution, and thus very mobile;
- exchangeable, including metals retained by soil and leached by other positive ions;
- and carbonate, including metals occurring in the forms of carbonates or precipitated with carbonates. Those elements may pass into the soil solution when pH is lowered (acid rains).

Metals occurring in the organically bound and sulfide fractions are regarded as relatively poorly available and poorly available. However, under suitable oxidation and reduction conditions, they may even change their forms into soluble in water. The residual fraction comprises metals strongly bound with the materials present in the compost.

Table 2 shows the results of statistical calculations. The total iron content (including the background) in the soluble, exchangeable and adsorbed fractions was very low (below 100 $\mu\text{gFe/g}$ dry wt.). The table includes the results for the organically bound and carbonate fractions. Iron concentration for the first fraction – depending on type of the addition – varies from 200 to 1150 $\mu\text{gFe/g}$ dry wt., whereas for the latter, it is 1400 $\mu\text{gFe/g}$ dry wt. for the waste alone, and 11 200 $\mu\text{gFe/g}$ dry wt. for the waste with the addition of pulverized Fe. The table also contains a number of repetitions (N) of parallel iron concentration determinations in individual fractions, mean arithmetic value of iron concentration (\bar{m} $\mu\text{gFe/g}$ dry wt.), sample variance (S^2) and standard deviation in the sample (S). The coefficient of variation „ v ”, which is of relative character and is defined by the equation: $v = s/\bar{m}$, was applied as a measure of dispersion [9]. The results collated in Table 2 range from 0.009 to 0.298, however, they do not exceed the value of 0.15 in most cases. Speciation analysis is very time consuming and poses a lot of problems of technical nature, thereby allowing many mistakes to happen. The source of mistakes may be the analyzed material itself. The municipal solid waste is a mixture of various refuse e.g. food, plants, paper, cardboard, glass, plastics, metals, ashes, slag, and, although it is ground and mixed very thoroughly, it is impossible to obtain its perfect homogeneity. Mixing the waste with iron or its compounds at a ratio of 1:100 created an additional difficulty. Despite the problems mentioned above, it may be stated that the repeatability of the results obtained under those conditions was satisfactory and allows for an evaluation of changes in iron bioavailability in composting.

In the municipal solid waste used the total iron content was 9500 $\mu\text{gFe/g}$ dry wt. on average and mainly the carbonate, sulfide and residual fractions

Table 2. Statistical evaluation of the results on determination of iron concentration in the organically bound and carbonate fractions in the waste without any additions and contaminated with iron or its compounds

	Organically bound fraction		Carbonate fraction	
	before composting	after composting	before composting	after composting
WASTE				
N	4	4	3	4
\bar{m} [$\mu\text{gFe/g dry wt.}$]	192	223	1365	1508
S^2	806	242	5047	2287
S	28	16	71	48
v	0,148	0,070	0,052	0,032
WASTE WITH ADDITION OF Fe				
N	4	4	4	4
\bar{m} [$\mu\text{gFe/g dry wt.}$]	601	1149	11119	11183
S^2	32060	21674	1230909	1922295
S	179	147	1109	1386
v	0,298	0,128	0,100	0,124
WASTE WITH ADDITION OF Fe_2O_3				
N	4	4	4	4
\bar{m} [$\mu\text{gFe/g dry wt.}$]	270	299	1824	2440
S^2	530	3062	21227	24355
S	23	55	146	156
v	0,085	0,185	0,080	0,064
WASTE WITH ADDITION OF FeS				
N	3	4	4	4
\bar{m} [$\mu\text{gFe/g dry wt.}$]	276	560	2904	4860
S^2	85	286	16438	2084
S	9	17	128	46
v	0,033	0,030	0,044	0,009

dominated (Table 3). The concentration of iron in the residual fraction was calculated from the difference between the total iron content in the waste (assayed using mineralization in the mixture of concentrated acids $\text{HClO}_4 + \text{HNO}_3$) and the total of its concentrations in fractions 1–6. The iron addition entered into the waste in the form of pulverized metallic Fe or FeS was 10000 $\mu\text{gFe/g dry wt.}$ It shows that the background contribution was substantial and was reflected in the results by subtracting the iron concentration in specific fractions by the value assayed in the waste alone.

Table 3. Iron concentration in the waste without the addition of Fe_{met} , FeS , Fe_2O_3 ; [$\mu\text{gFe/g}$ dry wt.]

Forms	Iron concentration in the waste before composting [$\mu\text{gFe/g}$ dry wt.]	Iron concentration in the waste after composting [$\mu\text{gFe/g}$ dry wt.]
1. Soluble	36	35
2. Exchangeable	51	30
3. Adsorbed	29	48
4. Organically bound	186	253
5. Carbonate	1398	1605
6. Sulfide	1877	3179
Total iron content (mineralization $\text{HClO}_4 + \text{HNO}_3$)	9500	
7. Residual*	5923	4350

* Calculated value.

Iron introduced into the waste in the form of pulverized metallic Fe was bound in the composts mostly with carbonates (89%) (Table 4). The contribution of iron to the soluble, exchangeable and adsorbed fractions does not exceed 3% and can be omitted. In the waste before composting, iron was also present in the sulfide and organically bound fractions. After composting, however, iron was not found in the sulfide fraction. It should be emphasized that there was a complete lack of iron in the residual fraction, inaccessible to plants. The balance of iron achieved in the waste was confirmed by the results of the sample mineralization (10985 $\mu\text{gFe/g}$ dry wt., without the background) (Table 5). The high contribution (70%) of iron to the carbonate fraction was also found for the smaller addition of pulverized metallic Fe (3000 $\mu\text{gFe/g}$ dry wt.) [13].

Table 4. Speciation results of iron in the waste with the addition of pulverized metallic iron (without the background)

Forms	Iron concentration in the waste before composting [$\mu\text{gFe/g}$ dry wt.]	Iron concentration in the waste after composting [$\mu\text{gFe/g}$ dry wt.]
ADDITION	10 000	
1. Soluble	205	61
2. Exchangeable	65	144
3. Adsorbed	83	52
4. Organically bound	415	896
5. Carbonate	9 721	9 578
6. Sulfide	1 002	0
Total in forms 1–6	11 491	10 731

Table 5. Total iron concentration in compost [$\mu\text{gFe/g}$ dry wt.]

Addition	Total value of iron addition [$\mu\text{gFe/g}$ dry wt.]	Total iron concentration in the compost [$\mu\text{gFe/g}$ dry wt.]	Total iron concentration in the compost without the background [$\mu\text{gFe/g}$ dry wt.]
Without the addition (background)	—	9 500	0
Fe_{met}	10 000	20 485	10 985
Fe_2O_3	10 000	19 223	9 723
FeS	11 000	22 655	13 155

Completely different composting results were obtained after introducing Fe_2O_3 into the waste (Table 6). Using the extractants mentioned above (mainly EDTA solution), it was possible to leach a mere $540 \mu\text{gFe/g}$ dry wt. from the waste and $890 \mu\text{gFe/g}$ dry wt. from the composts. Over 90% of the addition remained in the residual fraction, inaccessible to plants. In addition, speciation analysis of the waste and composts according to Tessier was carried out [19].

Table 6. Iron concentration in the waste with the addition of iron oxide(III) (without the background)

Forms	Iron concentration in the waste before composting [$\mu\text{gFe/g}$ dry wt.]	Iron concentration in the waste after composting [$\mu\text{gFe/g}$ dry wt.]
ADDITION	10 000	
1. Soluble	0	7
2. Exchangeable	0	0
3. Adsorbed	32	2
4. Organically bound	84	46
5. Carbonate	426	835
6. Sulfide	0	0
Total in forms 1–6	542	890

Table 7 shows the fractions determined by this author, suggested extractants and the analysis results obtained. Although the operational speciation analysis defines fractions by the extractants used, and the results obtained by means of Rudd's and Tessier's methods cannot be compared directly, it should be emphasized that also in this case the amount of the iron addition leached was less than 20%. The total iron concentration in the compost determined by mineralization, without the background, was $9723 \mu\text{gFe/g}$ dry wt. and is consistent with the value of the addition (within error limits) (Table 5). Poor mobility of iron introduced into the waste in this form confirms earlier reports on the stability of Fe^{3+} compounds [10, 17].

Table 7. Results of speciation iron according to Tessier in the waste with the addition of iron oxide(III) (without the background)

Forms	Extractant	Iron concentration in the waste before composting [$\mu\text{gFe/g}$ dry wt.]	Iron concentration in the waste after composting [$\mu\text{gFe/g}$ dry wt.]
ADDITION		10 000	
1. Exchangeable	1.0 mol/dm ³ MgCl ₂	40	12
2. Carbonate	1.0 mol/dm ³ NaOAc, pH = 5.0	26	0
3. Bound with Mn and Fe oxides	0.04 mol/dm ³ NH ₂ OH · HCl in 25% CH ₃ COOH solution, $t = 96 \pm 3^\circ\text{C}$	528	528
4. Organic	0.02 mol/dm ³ HNO ₃ + 30% H ₂ O ₂ , pH = 2, $t = 85 \pm 2^\circ\text{C}$	1132	974
Total in forms 1–4		1726	1518

Table 8 shows results on speciation of the waste and composts with the addition of FeS. Since the sulfide used contained more iron than it contained according to the stoichiometric composition, the amount of the addition was not 10 000 but 11 000 $\mu\text{gFe/g}$ dry wt. In the waste before composting, the total amount assayed in fractions 1–6 was 3300 $\mu\text{gFe/g}$ dry wt., whereas in the waste after composting, it equaled 5200 $\mu\text{gFe/g}$ dry wt. Thus, it may be estimated that composting slightly increases the mobility of iron, and that the element leached concentrates in the carbonate fraction, classified as easily accessible. The remaining iron (70% in the waste and 50% in the composts) is present in the residual fraction.

Table 8. Iron concentration in the waste with the addition of iron sulfide(II) (without the background)

Forms	Iron concentration in the waste before composting [$\mu\text{gFe/g}$ dry wt.]	Iron concentration in the waste after composting [$\mu\text{gFe/g}$ dry wt.]
ADDITION		11 000
1. Soluble	3	5
1. Exchangeable	14	0
3. Adsorbed	14	2
4. Organically bound	86	267
5. Carbonate	2339	4171
6. Sulfide	799	776
Total in forms 1–6		5221

Mineralization of the waste with the addition of FeS carried out by means of the mixture of $\text{HClO}_4 + \text{HNO}_3$ before and after its composting produced different results. Therefore, mineralization of the waste and the compost was carried out also after sequential extraction (residual fraction). It has been found that in the waste before composting, the mixture of the concentrated acids applied did not leach all introduced FeS from the residual fraction (analysis – 3100 $\mu\text{gFe/g}$ dry wt.; calculations – 7745 $\mu\text{gFe/g}$ dry wt.), whereas after composting, the results were very close to the calculated value (analysis – 5570 $\mu\text{gFe/g}$ dry wt.; calculations – 5780 $\mu\text{gFe/g}$ dry wt.). In order to leach the whole addition of iron, mineralization should be carried out in the mixture of $\text{HF} + \text{HNO}_3$ (13 155 $\mu\text{gFe/g}$ dry wt. – without the background) (Table 5).

For comparison, we carried out an analysis of the waste with the addition of iron sulfide(II) according to Tessier. The results are shown in Table 9. An application of hydrogen peroxide and elevated temperature to the acid solution resulted in leaching much larger amounts of iron from the sample of both the waste (8097 $\mu\text{gFe/g}$ dry wt.) as well as the compost (13 287 $\mu\text{gFe/g}$ dry wt.). This may indicate that part of the iron introduced into the waste in the form of FeS is permanently bound with organic matter (organically bound fraction).

Table 9. Results of speciation iron according to Tessier in the waste with the addition of iron sulfide(II) (without the background).

Forms	Iron concentration in the waste before composting [$\mu\text{gFe/g}$ dry wt.]	Iron concentration in the waste after composting [$\mu\text{gFe/g}$ dry wt.]
ADDITION	11 000	
1. Exchangeable	40	33
5. Carbonate	135	219
3. Bound with Mn and Fe oxides	966	2009
4. organic	6956	11 026
Total in forms 1–4	8097	13 287

In the above experiments, the addition of iron was introduced into the waste in the pulverized metallic form and of specific chemical compounds. As it was mentioned herein, metallurgical dust containing this element mainly in the forms of Fe_{met} , FeS, FeS_2 , FeO, Fe_2O_3 is one of the main sources of environmental contamination [18]. Therefore, it was extremely interesting to compare the composition of the composts obtained in the research with the composition of the waste contaminated with industrial dust. In the tests, metallurgical dust deposited on the electrofilters of an induction furnace was used. Iron content in the dust determined by its mineralization in a mixture of $\text{HClO}_4 + \text{HNO}_3$ was 0.282 gFe/g dry wt. Iron leaching from the metallurgical dust was additionally conducted with a solution of nitric acid of incrementing acidity. The results obtained are shown on Figure 2. It has been found that iron occurred in the

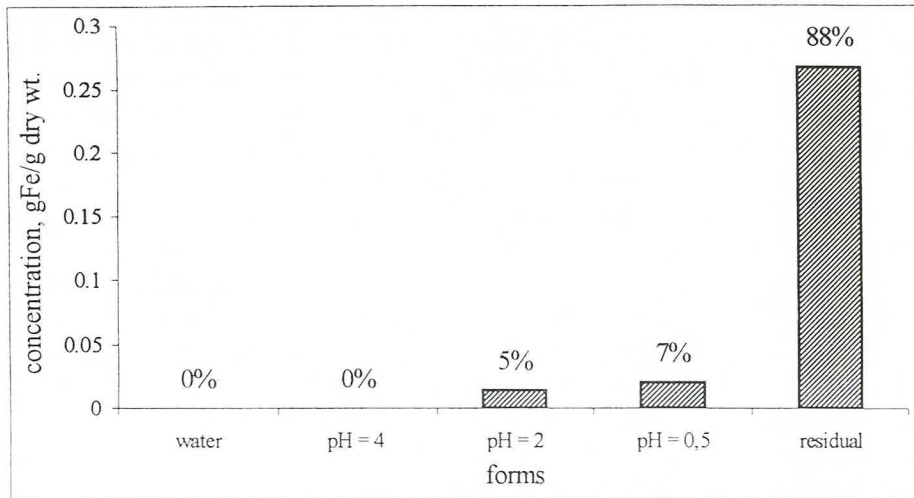


Fig. 2. Results of iron leaching from the metallurgical dust with a solution of nitric acid of incrementing acidity

dust in the compounds of low chemical activity. The dust did not contain iron compounds soluble in water or dilute nitric acid (pH = 4), and only 2% and 7% of iron, respectively, passed into the solution at extractants' pH = 2 and 0.5. Only the mixture of $\text{HClO}_4 + \text{HNO}_3$ caused complete leaching of the remaining iron.

Composting of the waste contaminated with metallurgical dust was performed in a similar way to the composting with the addition of iron compounds. Dust was introduced into the waste. The addition of iron was $24\,200 \mu\text{gFe/g}$ dry wt. We also determined the concentrations of other metals (copper, zinc, cadmium and lead) whose amounts in the dust were considerably smaller. The results of those tests are being prepared. The toxic metals present in the dust did not poison microorganisms and the temperature of the composting increased to 48°C . The content of organic matter decreased by as much as 16%. Figure 3 compares the distribution of iron in individual fractions in the composts obtained from the waste with the addition of Fe dust, iron oxide Fe_2O_3 , iron sulfide FeS , and in the compost from the waste with the addition of metallurgical dust.

It has been found that iron does not occur in fractions 1–3, and its weight contribution to the organically bound fraction is a mere 1.8%. Similarly to the composts obtained from the waste contaminated with Fe_2O_3 and FeS , iron accumulated in the carbonate, sulfide and residual fractions. The largest amounts of iron are present in the residual fraction. The extractants applied enabled us to leach only 33% of the addition inclusive of: 19% with EDTA solution – carbonate fraction, and 12% with $6 \text{ mol/dm}^3 \text{ HNO}_3$ solution – sulfide fraction. Therefore, it may be believed that iron occurs in the metallurgical dust examined mainly in the oxide and sulfide forms and composting will cause only a negligible increase in its bioavailability.

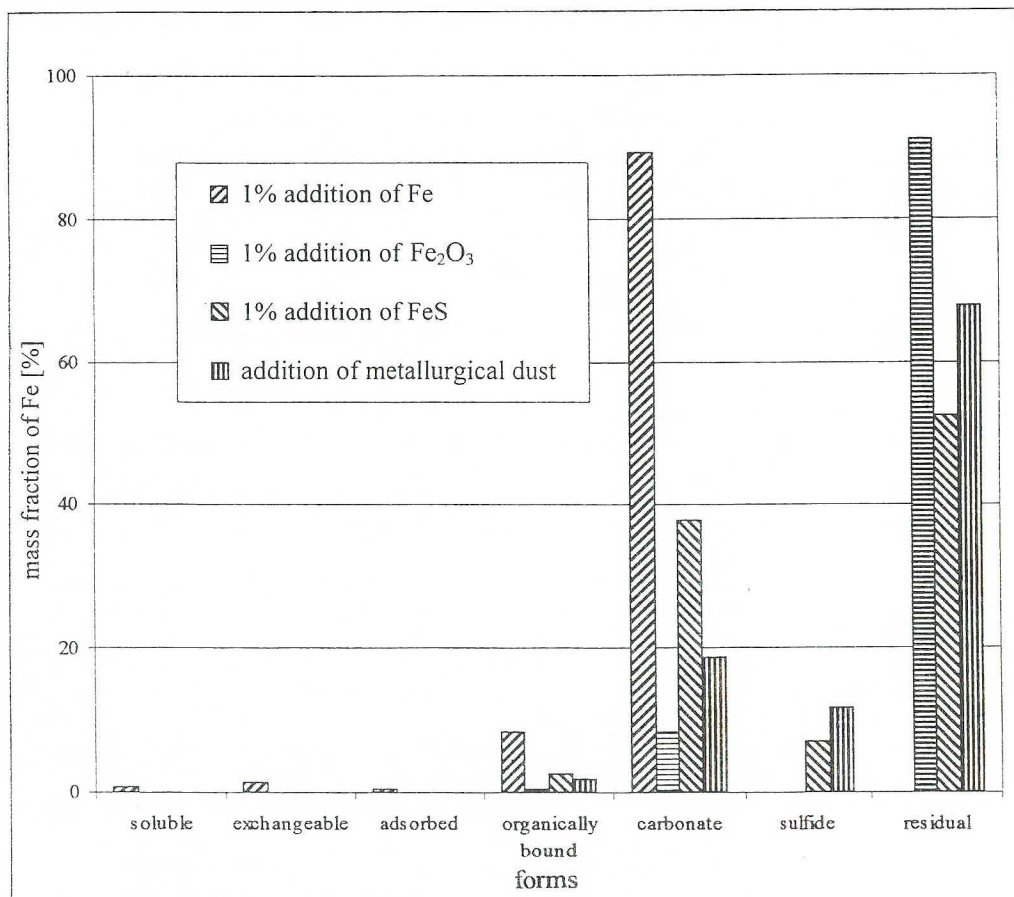


Fig. 3. Distribution of iron in individual fractions in the composts obtained from the waste with the addition of pulverized Fe, iron oxide Fe₂O₃, iron sulfide FeS or metallurgical dust

CONCLUSIONS

1. Iron introduced into the waste in the form of pulverized metallic Fe occurs in the composts obtained mainly in the carbonate fraction, easily accessible to plants, and organically bound fraction which is relatively inaccessible to plants. No amounts of iron has been found in the residual fraction.

2. Iron bound in the iron oxide(III) is stable and occurs in the waste in the residual fraction. Composting has not made iron change into more mobile forms.

3. The addition of iron sulfide(II) to the waste accumulates mainly in the residual and carbonate fractions. Composting increases slightly iron bioavailability; an increase in iron concentration in the carbonate fraction has been observed.

4. In the composts obtained from the municipal solid waste contaminated with metallurgical dust, 67% of iron was present in the residual fraction inaccessible to plants. The remaining 33% of the addition's mass accumulates in the carbonate and sulfide fractions. The distribution of iron to particular fractions is similar to that in the compost obtained from the waste contaminated with iron sulfide(II) and iron oxide(III).

REFERENCES

- [1] *Speciation analysis of metals*, multi-author work edited by Siepak J., Oficyna Wydawnicza Uniwersytetu Adama Mickiewicza, Poznań 1998 (in Polish).
- [2] Bartecki A.: *Chemistry of transition elements*, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 1996 (in Polish).
- [3] *Clinical biochemistry in medical practice*, multi-author work edited by Sznajda J., PZWL, Warszawa 1983 (in Polish).
- [4] Ciba J., M. Zołotajkin, J. Cebula: *Changes of chemical forms of lead and trilead tetroxide (minium) during the composting process of municipal solid waste*, *Pollutants in Environment*, 4/5, 117–120 (1994/1995).
- [5] Ciba J., M. Zołotajkin, J. Cebula: *Changes of chemical forms of zinc and zinc sulfide during the composting process of municipal solid waste*, *Water, Air, and Soil Pollution*, 93, 167–173 (1997).
- [6] Ciba J., M. Zołotajkin, J. Cebula: *Chemical forms of cadmium in the composts from the municipal solid waste with the addition of metallic cadmium, cadmium oxide and sulfide*, *Arch. Ochr. Środ.*, 2, 131–140 (1998) (in Polish).
- [7] Ciba J., J. Kluczka, M. Zołotajkin: *The composting process effect on the chemical changes of mercury(II) sulphide in the municipal solid waste*, *Arch. Ochr. Środ.*, 1, 125–132 (1999).
- [8] Ciba J., M. Zołotajkin: *Changes in copper forms while composting municipal solid waste*, *Arch. Ochr. Środ.*, 2, 121–129 (1999) (in Polish).
- [9] Czermiński J.B., A. Iwasiewicz, Z. Paszek, A. Sikorski: *Statistical methods for chemists*, PWN, Warszawa 1992 (in Polish).
- [10] Kabata-Pendias A., H. Pendias: *Biogeochemistry of trace elements*, PWN, Warszawa 1993 (in Polish).
- [11] Kabata-Pendias A., B. Szteke: *Quality problems in trace analysis in environmental studies*, Wydawnictwo Edukacyjne Zofii Dobkowskiej, Warszawa 1998 (in Polish).
- [12] Kempa E.: *Management of municipal solid waste*, Arkady, Warszawa 1983 (in Polish).
- [13] Połec D.: *Chemical changes in pulverized iron in composting of municipal solid waste*, MSc thesis, The Technical University of Silesia, 1997 (in Polish).
- [14] Ostrowska A., S. Gawliński, Z. Szczubiałka: *Methods for analysis and evaluation of soils and plants characteristics*, Inst. Ochr. Środ., Warszawa 1999 (in Polish).
- [15] *Polish Statistical Yearbook 1998*, GUS Zakład Wydawnictw Statystycznych, Warszawa 1999 (in Polish).
- [16] Rudd T., D.L. Lake, I. Mehrotra, R.M. Sterritt, P.W.W. Kirk, J. A. Campbell, J.N. Lester: *Characterisation of metal forms in sewage sludge by chemical extraction and progressive acidification*, *The Science of the Total Environment*, 74, 149–175 (1988).
- [17] Sadowski Z.: *Biochemistry of iron and manganese*, *Wiadomości Chemiczne*, 51, 11–12, 758–770 (1997) (in Polish).
- [18] Suwińska T., J. Ciba: *Chemical forms of iron, zinc and lead in different metallurgical dusts*, *Materiały Zjazdu PTChem i SITChem*, Wrocław 1998, S4, P37 (in Polish).
- [19] Tessier A., P.G.C. Campbell, M. Bisson: *Sequential Extraction Procedure for the Speciation of Particulate Trace Metals*, *Anal. Chem.*, 51, 7, 844–850 (1979).