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Impact of thermal treatment on metal in sewage sludge from the Psittalias wastewater treatment plant, Athens, Greece

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Abstract

This paper describes a laboratory study that examined the effect of thermal treatment at four different temperatures on the behavior of heavy metals in the anaerobically treated primary sludge from the Psittalias wastewater treatment plant. The sewage sludge was found to contain significant amounts of heavy metals (Cr, Cu, Fe, Ni, Pb and Zn). The metal form distribution in the sludge samples which was determining by the application of a sequential extraction procedure revealed that a significant portion of metals was embodied in the organic and reducible fractions. Treatment at 105, 250, 650 and 900°C demonstrated significant conversions of the metals to a less mobile form as well as removal by vaporization. By applying sequential analysis, it was found that most of the metals were removed from the initial mobile phases to more stable ones. Also, significant amounts were transformed to the gaseous phase. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The disposal of huge quantities of sludge produced by municipal wastewater treatment plants is a major environmental problem. This problem is especially significant in cities [1–3]. One sludge disposal option, according to Karlsson and Giransson [4] and Esteinle [5], is thermal treatment.

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A wide variety of sequential chemical extraction (SCE) schemes has been developed for the determination of heavy metal forms in sewage sludge [6,7]. The scheme of Tessier [8], with some modifications as described by Zorpas [3] was chosen for this study.

According to this scheme (Zorpas scheme) [3], heavy metals are associated with five fractions: (1) exchangeable; (2) carbonate fraction; (3) reducible fraction; (4) organic fraction; (5) residual fraction.

In order to determine the toxicity of the sludge samples, the generalized acid neutralization capacity (GANC) procedure was utilized. This procedure is used for the identification of the chemistry of neutralization, speciation and mobility during the leaching of toxic metals from sediments, sewage sludge and stabilized wastes.

As described by Zorpas [3], in the greater Athens region, which has almost 4,500,000 residents, the main wastewater treatment plant operating is Psittalias producing a substantial amount of sludge. At Psittalia, $\sim$750,000 m^3 per day of mainly municipal wastewater along with industrial wastes are subjected to primary treatment, producing $\sim$250 tonnes per day of sludge (91,000–95,000 tonnes per year). The sludge is classified as a difficult solid waste that requires special treatment before disposal because of its noxious properties. The sludge contains salts, organic pollutants and heavy metals. Knowledge of heavy metal content and its form in the sludge are the most important factors in selecting disposal alternatives [1,2,9].

Landfilling is still the main disposal method for sewage sludge at present in Athens. Landfilling poses a potential environmental hazard, including the production of odor and releasion methane gas, as well as contamination of groundwater by leachate. Until now, sludge is processed to be disposed of at Ano Liosia's landfill (Attica region), which has a limited operation [3].

All the different methods of sludge utilization (i.e. thermal sludge treatment and disposal or dumping), create major environmental problems. There may be serious levels not only of salts and organic pollutants, but also of heavy metals in the leachate. These pollutants may cause environmental damage to soil, plants, groundwater and in the air.

In the total sludge generating, handling and disposal process, from thickening to controlled dumping, sludge incineration is one of the most important steps in reducing sludge volume. For the thermal treatment of sludge, knowledge of the salt and heavy metal content is important for the choice of the right flue gas cleaning system.

The advantage of thermal sludge treatment as opposed to dumping and utilization systems must be seen in the thermal destruction of the organic pollutants. At the same time, a large part of the heavy metals is evaporated by the high burning temperature. These metals leave with the flue gas and can be captured by condensation on the filter — ash or in the scrubber water.

The purpose of this study was to estimate the concentration and distribution (SCE) of metals in sludge, during the thermal treatment, as well as the toxicity (GANC) of the final products.

2. Materials and methods

Anaerobically stabilized sewage sludge samples were collected from Psittalia from September 1997 until January 1998. The samples were stored at 4°C. A portion of the samples was kept at 4°C (sample W = wet), while another was dried at 105°C (sample D = dry) and a third was thermally treated up to 900°C (sample K = kilned; K1 at 250°C, K2 at 650°C and K at 900°C).

Following this preparation, a known quantity of sludge was taken from each of the three sludges and the following measured parameters: pH, conductivity, total phosphorus ($P–PO_4$), organic matter (OM), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), ammonia, boron and heavy metals (Cd, Cr, Cu, Fe, Ni, Pb and Zn) concentrations and for the wet sludge a moisture content.

The pH value, conductivity, OM, TOC, total phosphorous, ammonia, moisture and boron were measured according to the Soil Analysis [10] and Standard Methods while TKN was measured according to methods given by Adams [11].

For determining the total metal concentration, the sludge samples were digested (1 g with HNO_3 and H_2SO_4) vacuum filtered. The heavy metal concentration were measured by atomic absorption spectroscopy using a Perkin-Elmer 2380 spectrophotometer as described by Zorpas [3].

In order to study the forms of metals in the three categories of sludge (W, D and K), a SCE procedure was used for the partitioning of these metals into five fractions [3]. According to this scheme, heavy metals are associated with five fractions: exchangeable (extracted by 1 M CH_3COONa for 1 h at room temperature and at pH 8.2), bound to carbonates (extracted by 1 M CH_3COONa for 5 h at room temperature and at pH 5.0), bound to iron and manganese oxides (extracted by 0.04 M $NH_2OH.HCl$ in 25% v/v CH_3COOH for 6 h at 96°C), bound to OM (extracted by 0.02 M HNO_3 and 30% w/v H_2O_2 for 2 h at 85°C and pH 2.0, followed by the addition of 3.2 M CH_3COONH_4 in 20% w/v HNO_3 with 30% w/v H_2O_2 for 3 h at 85°C, diluted with distilled water and let for 30 min at room temperature) and residual (extracted by 40% w/v HF, c.HNO_3 and 0.2 M NH_4NO_3 at pH 3.0, for 1 h and at room temperature).

The GANC test procedure was used in order to estimate the sludge toxicity [3,12]. This test is a single batch procedure that utilizes a series of sludge samples extracted with increasingly acidic leachants. Leachant strength starts out at the initial pH value and is increased, by adding 2N acetic acid, until pH is below 5 for three consecutive samples.

3. Results and discussions

The physico-chemical characteristics of the raw sludge are shown in Table 1. The sludge samples had a water content of ∼70%. The pH of wet (sample W) and dry (sample D) sludge samples ranged in the neutral area while the value of the kilned (sample K) sample was alkaline. High levels in total phosphorous and the TOC content were found in both wet and dry sludge samples. This condition is due to the fact that the main load of the treatment plant is municipal. In contrast, the kilned K samples had zero TOC values due to the volatility of the organics at in high temperatures, while in K1 and K2 TOC values were 12.30 and 25.30%, respectively.

As shown in Table 2, thermal treatment of wet sludge samples up to 900°C resulted in a mass reduction of ∼84%. The mass reduction observed when dried (at 105°C) samples are

Table 1
Characteristics of anaerobicaly stabilized primary sewage sludge

Parameters	Sludge samples				
	W[a]	D[a]	K1[a]	K2[a]	K[a]
Water Content (%)	70.4	–	–	–	–
pH	7.2	7.3	8.2	9.3	12.7
P–PO_4 (mg/g)	7.8	12.3	10.2	–	–
TOC (%)	10.3	26.5	24.3	–	–
TKN (%)	5.33	1.61	1.00	–	–
Ammonia (mg/g)	3.52	0.95	0.02	–	–
Conductivity (mS/cm)	2.102	1.001	0.852	0.554	0.102
Boron (mg/g)	–	–	–	–	–

[a] For wet (W) sludge samples g refers to wet sludge, for dry (D) to dry sludge and for kilned (K) to kilned sludge.

Table 2
Mass reduction (%) of the sludge due to thermal treatment

Thermal treatment (°C)	Mass reduction (%) of sludge samples
25–105	70.4
25–900	84.0
105–250	22.0
250–650	23.0
105–650	45.0
650–900	27.6
105–900	56.4

subjected to thermal treatment up to 900°C was 56.4 and 45.0%, when samples are treated up to 650°C.

The heavy metals concentrations of the sludge samples are shown in Table 3. The sludge samples contain significant amounts of all heavy metals. However, it is worth noting the high concentration of zinc and chromium in primary sludge samples. Although the mass reduction due to thermal treatment from 105 to 900°C was ∼50% (Table 2), the concentrations of lead (Pb) and zinc (Zn), in dry and kilned sludge, were found at approximately at the same levels. This metal concentration reduction may be explained by the volatility at high

Table 3
Metals concentration in anaerobically stabilized primary sewage sludge during thermal treatment

Sludge samples	Cd (mg/g)[a]	Cr (mg/g)[a]	Cu (mg/g)[a]	Fe (mg/g)[a]	Ni (mg/g)[a]	Pb (mg/g)[a]	Zn (mg/g)[a]
W	0.001	0.390	0.102	3.260	0.021	0.182	0.996
D (105°C)	0.002	0.558	0.258	5.833	0.041	0.258	1.729
K1 (250°C)	0.002	0.698	0.328	7.478	0.052	0.260	1.729
K2 (650°C)	0.002	0.901	0.429	10.587	0.068	0.262	1.795
K (900°C)	0.003	1.113	0.591	13.210	0.098	0.265	1.820

[a] For wet (W) sludge samples g refers to wet sludge, for dry (D) to dry sludge and for kilned (K) to kilned sludge.

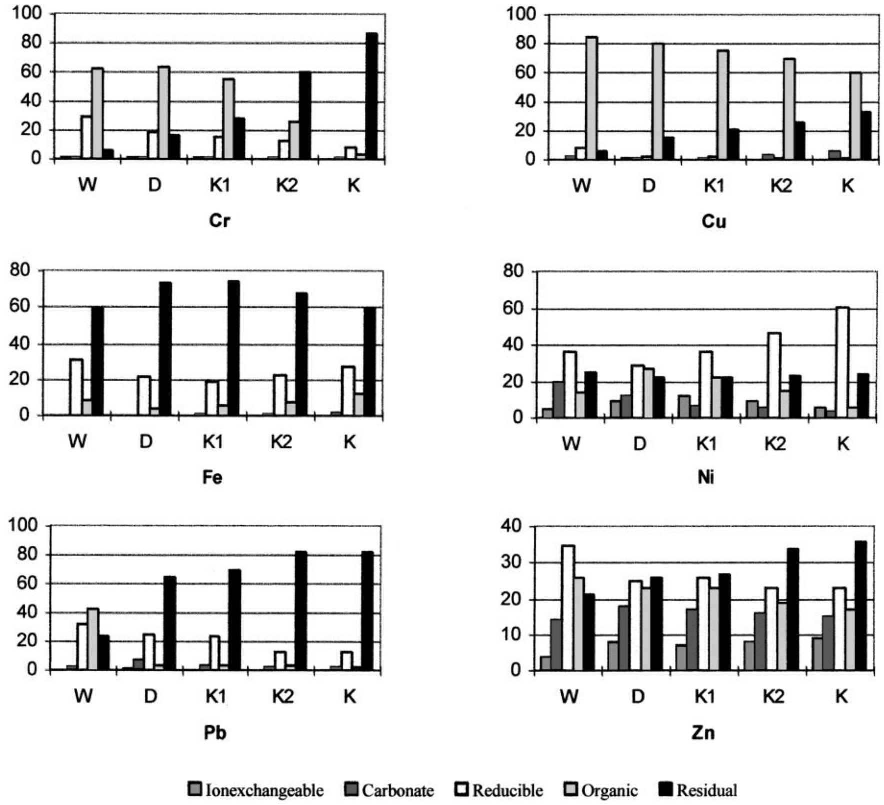

Fig. 1. Metal partitioning in primary sludge samples.

temperature of metals, such as cadmium, lead and zinc, as also been observed elsewhere [13].

The metal partitioning in the sludge samples as determined by SCE is shown in Fig. 1. In primary wet sludge samples, almost all of the chromium, copper and zinc were bound to the organic and reducible fractions with <8% being removed during the other three steps of the extraction sequence. Only nickel and lead had substantial proportions of metal in all phases, although lead was not found in the exchangeable fraction. In the case of iron, 9% was removed from the exchangeable, carbonate and organic phases and 31% from the reducible. Most of the metal was bound to the residual fraction.

As shown in Fig. 1, the thermal treatment caused significant changes in the partitioning of the metals. For chromium and lead, it is obvious that there was a significant increase in the proportion of metals in the residual phase, up to 87%, during thermal treatment while the percentage amount of these metals in the organic fraction decreased enormously. Copper was mainly bound to the organic and residual phases with <10% in the other three phases. In the case of primary sludge samples, the metal's percentage in the organic phase reduced from 84 to 60% as the residual fraction increased from 5 to 31%. In contrast the metal's percentage of these phases in the secondary sludge samples during thermal treating, remained at the initial levels. The major proportion of nickel and zinc was associated with the residual and reducible phases with very low concentrations in the other three fractions for each of the three categories of sludge samples.

Comparing these results with studies carried out previously [14–17], we note chromium and copper were found in similar proportions in all fractions while iron was mainly associated with the residual and reducible fractions. Nickel has been observed to have substantial proportions in all phases, whereas zinc was mostly found in the organic and reducible fractions. As far as lead is concerned, its concentrations in the organic and residual fractions were >90%.

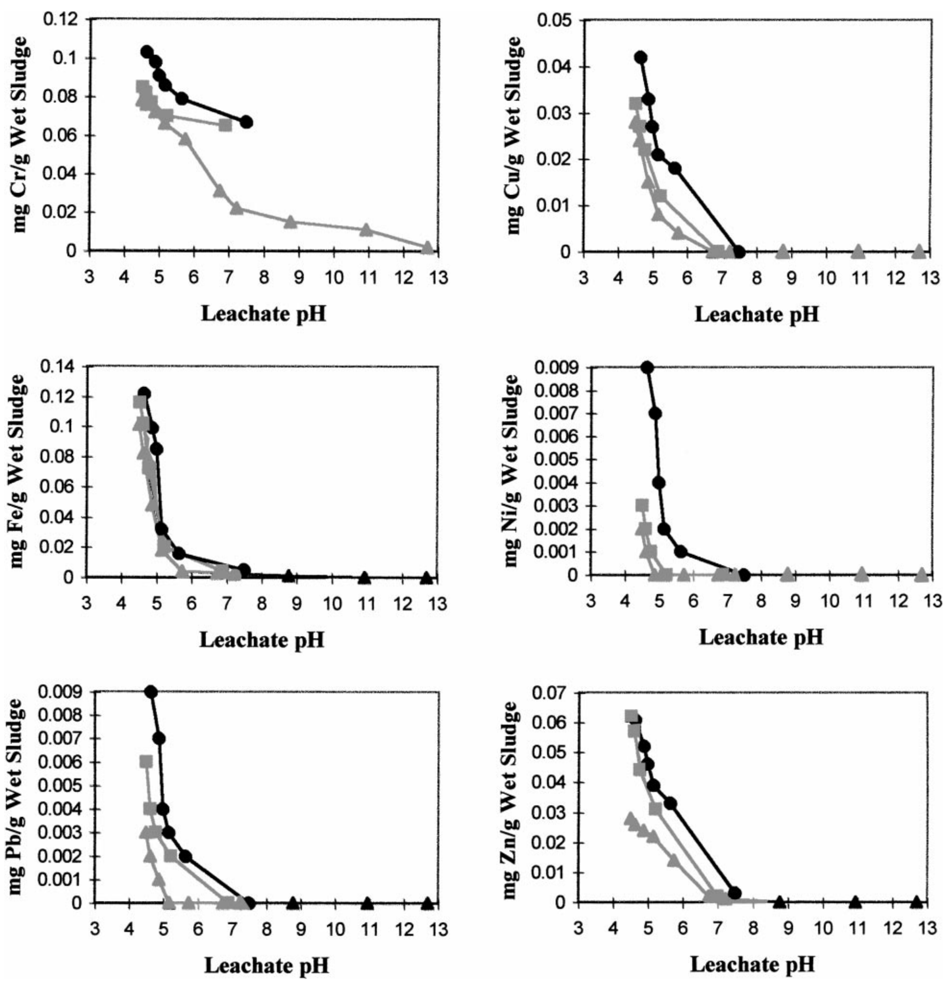

Fig. 2. Generalized acid neutralization capacity (GANC) metals releases to leachates from primary sludge samples as a function of pH of leachate.

In conclusion from our work with SCE, we observed an increase of reducible, organic and residual fractions due to drying up to 105°C. The organic fraction was reduced and the residual was increased due to thermal treatment up to 900°C.

Using the GANC test, Fig. 2, we found that the pH of leachates from thermally treated sludge samples increased while the heavy metal concentration decreased. We also observed that as the temperature of the thermal treatment increased, the metal contents of the leachates from GANC tests for the same pH values, decreased. This finding can be explained by the results of the sequential extraction scheme where the metals were mobilized to more stable fractions with the increase of the temperature of the treatment.

Of the two thermal processes (105 and 900°C) drying utilized less energy and has lower operational costs and does not yield volatile constituents. Drying also produced smaller values of less reachable product.

4. Conclusions

1. Heavy metal concentrations, in thermally treated sludge samples increased, because the mass reduction of the sludge samples was 56.4%.
2. Heavy metals are transported from the labile phases in the wet sludge samples to more stable fractions in the dry and kilned sludge samples as determined by the SCE scheme. This transformation of metal content due to thermal treatment at 105°C was not as significant as it was due to thermal treatment at 900°C.
3. The metal content is not expected to be easily released under conditions encountered in nature a finding, which was verified by the GANC leach test.
4. For the thermal treatment of the wet sludge samples up to 105°C, the required energy is not high and the biogas produced from the anaerobic digestion can be used. For the thermal treatment, up to 900°C, the energy cost is higher.
5. Thermal treatment appears to be an efficient method of stabilization and improvement of sewage sludge before the final disposal, but it needs further examination.

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