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Mineralogy and leachability of gasified sewage sludge solid residues

Ana Belén Hernandez[a], Jean-Henry Ferrasse[a,*], Perrine Chaurand[b], Hans Saveyn[a,c,d], Daniel Borschneck[b], Nicolas Roche[a]

[a] M2P2, Laboratoire de Mécanique, Modélisation et Procédés Propres, CNRS-Aix-Marseille University, UMR 6181, Aix-en-Provence, France
[b] CEREGE, Centre Européen de Recherche et d'Enseignement des Géosciences de l'Environnement, CNRS-Aix-Marseille University, UMR 6635, ECCOREV, Aix-en-Provence, France
[c] Institute for Prospective Technological Studies – IPTS, Joint Research Centre (JRC), European Commission, Spain
[d] Particle and Interfacial Technology Group, Ghent University, Belgium

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ABSTRACT

Gasification of sewage sludge produces combustible gases as well as tar and a solid residue as by-products. This must be taken into account when determining the optimal thermal conditions for the gasification process. In this study, the influence of temperature, heating atmosphere and residence time on the characteristics of the gasified sewage sludge residues is investigated. ICP-AES analyses reveal that the major chemical elements in the char residues are phosphorus, calcium, iron and silicon. Heavy metals such as copper, zinc, chromium, nickel and lead are also present at relatively high levels – from 50 to more than 1000 mg/kg of dry matter. The major mineral phases' identification – before and after heating – as well as their morphology and approximate chemistry (XRD and SEM-EDX) demonstrate that a number of transformations take place during gasification. These are influenced by the reactor's temperature and the oxidative degree of its internal atmosphere. The copper-, zinc- and chromium-bearing phases are studied using chemometric tools, showing that the distribution of those metals among the mineral phases is considerably different. Finally, batch-leaching tests reveal that metals retained in the residue are significantly stabilized after thermal treatment to a higher or lower extent, depending on the thermal conditions applied.

1. Introduction

About 10 million tonnes dry matter (d.m.) of sewage sludge (SS) were produced each year in the EU for the period 2003–2006 [1]. Currently, the main disposal methods are landfilling, agricultural recycling and incineration. Due to growing sludge production, landfilling cannot be considered as a sustainable approach to sludge management. Also, agricultural recycling is strongly regulated at EU level by the sludge directive, prohibiting the use of untreated sludge on agricultural land, unless it is injected or incorporated into the soil (directive 86/278/EEC) [2]. This directive also sets limit values for heavy metals and organic compounds contents – these limits are expected to be stringently reviewed in the next years. In this context, thermal conversion is an attractive way for SS disposal. This alternative, not only enables the removal of organic pollutants and pathogenic organisms, but also leads to a remarkable volume reduction of waste and allows for the recovery of the sludge energy content [3].

The most established thermal technology is incineration [4], which can provide energy by heat recovery from hot exhaust gases. Nevertheless, incineration requires two major treatment operations: extensive gas cleaning – to match the emission limit values set for air pollutants (directive 2000/76/EC) [5] – and safe disposal of ashes, containing considerable concentrations in potentially toxic metals such as Zn, Cu, Cr, Ni, Cd, Pb, As, Hg, Mo, Se and Sb [6,7]. Depending on their distribution in the incinerator, ashes present different physical characteristics and heavy metals contents and so they are classified as bottom ashes, fly ashes and slurries [8]. Over the last years increasing attention has been given to incinerated sewage sludge ashes (ISSAs) management and some studies have focused on its chemical, physical, leaching and ecotoxicological characterizations [6,8–10], phosphorus recovery [11], metals recovery [12] as well as its reuse [13].

Lately, several advanced thermal technologies have been introduced as a clear alternative to incineration [14], e.g. thermal gasification, consisting in cracking and converting the volatiles and carbon contained in the biomass at high temperatures – typically between 700 and 900 °C – and low oxidative atmosphere. The organic content of biomass is converted into combustible gases such as H_2, CO, CH_4, which after tar and ash cleaning, can be combusted to generate electricity and heat. Until now, research on SS gasification has focused on gas production yield and gas composition [3,15–21] as well as on power generation [22], but there is still a lack of knowledge on the mineralogy and leachability of the

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[*] Corresponding author. Tel.: +33 4 42 90 85 05.
E-mail address: jean-henry.ferrasse@univ-cezanne.fr (J.-H. Ferrasse).

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Table 1
Sewage sludge proximate analysis: average and standard deviation (in brackets) values of five repetitions.

Moisture, wt%	Volatile content, wt% d.m.	Fixed carbon, wt% d.m.	Ash content, wt% d.m.
83 (3)	63 (3)	11 (5)	32.5 (0.4)

d.m.: dry matter.

solid gasified sewage sludge residues (GSSRs), which represents approximately 30% of the solids initial dry mass [14].

The presence of heavy metals is one of the major problems related to sewage sludge and sewage sludge ashes [6,9,23–26]. For instance, if those are disposed of by landfilling, metals can be solubilized by rainwater and then leach and accumulate in topsoil or contaminate groundwater. Therefore, the European Directive 99/31/ED on landfilling [27] requires a detailed knowledge on the composition and leaching behavior of residues, in order to allow for their classification and to set compliance procedures. Research shows that metals in the SS are mainly contained in the leachable organic fractions, but heating convert them into less soluble forms [28,29]. Also, metals solubility is influenced by the oxidative degree of the atmosphere in the reactor during heating [30]: chromium is more soluble under oxidative incineration conditions than reductive pyrolysis conditions whereas copper, zinc and lead show the opposite trend. Recently, Saveyn et al. [31] examined the fate of heavy metals during gasification of SS and determined that Cu, Cr, Ni, Pb and Zn were present in the GSSR in concentrations from less than 50 mg/kg (Pb) to more than 1000 mg/kg (Cu). Since those previous works do not determine the mineralogical characteristics of residues, metals distribution among the mineral phases remains uncertain and so the study of their leaching behavior remains incomplete.

The present study deals with this lack of knowledge of the GSSR characteristics – not only essential to establish a safe final disposal for those residues, but also to determine the optimal thermal conditions for the gasification process. Hence, gasification experiments were run to investigate the influence of different operative conditions, on: 1, GSSR chemistry and mineralogy; 2, location and leaching behavior of metals concentrated on the GSSR.

2. Materials and methods

2.1. Sewage sludge samples and thermal treatment

Centrifuged SS was sampled from a municipal wastewater plant (Aix-en-Provence, France, about 200,000 p.e.). In order to avoid variations in metal contents, a large amount of well mixed sludge was sampled at once and subsequently frozen in separate portions. Elementary and proximate analyses are shown in Tables 1 and 2.

Samples (about 200 g) were placed on a metallic support, introduced in an electrically heated horizontal bench scale tubular reactor (Fig. 1) and then submitted to thermal gasification to study the effect on the residue characteristics of temperature, atmosphere, and residence time of solids at the studied temperature. Table 2 recapitulates conditions during those experiments. A heating rate of about 15 °C/min was applied until the target temperature was reached. Steam produced by a laboratory water heater was pushed by either inert gas (argon) or air to generate the corresponding heating atmospheres. The gas production yield was measured and its composition analyzed on-line by gas chromatography (GC) and Fourier transformed infra-red spectrometry (FTIR). Also, a sample of SS was dried at 105 °C for 24 h with the aim of comparing GSSR and primary dried sewage sludge (DSS).

A sufficient amount of each sample was finely crushed in an agate mortar and sampled to perform elemental analyses (CHNS), ICP-AES, XRD and μ-XRF analyses.

2.2. Characterization of residues

The chemical composition of residues (major and trace elements) was determined by ICP-AES (Horiba Ultima-C 2000), after either acid digestion by HNO_3 and H_2O_2 or alkaline hydrolysis by $LiBO_2$ [32,33]. Also C, H, N, S and O contents were measured in duplicate with an accuracy of ±0.2% using a Thermo Finnigan EA 1112.

The major mineral phases were determined with an X-ray θ–θ diffractometer (X'Pert Pro MPD, Panalytical) using Co Kα radiation (λ = 1.79 Å) and running at 40 kV and 40 mA, with a linear detector X'Celerator and a secondary flat monochromator. Samples were placed on a zero-background silicon plate and spinned at 15 rpm. A counting time of 22 s per 0.033° step was used for 2θ in the 5–80° range. The International Center of Diffraction Data PDF-2 database and the X'Pert Highscore plus software (Panalytical) were used to identify the mineral phases from the obtained X-ray diffraction (XRD) patterns.

SEM-EDX analyses were performed to examine the morphology (phase's shape and size) and chemistry of the mineral phases. Non-crushed samples were cast in Epoxy, polished and carbon-coated before being placed in the SEM (Phillips XL30 SFEG). Different areas of samples were investigated by SEM running at 20 keV and using backscattered electron images. The element distribution in GSSRA&C samples was examined by punctual analyses using EDX (5 μm diameter on 100 randomly chosen points for each sample).

The location of metals among the mineral phases was examined by more sensitive micro-analyses, using a XGT7000 spectrometer (Horiba Jobin Yvon) equipped with a Rh X-ray tube and running at 30 kV power in partial vacuum. Samples (100 mg) were pressed in the form of 13 mm diameter pellets. For each sample, μ-XRF punctual measurements (10 μm) were performed on 40 randomly chosen points during a counting time of 600 s/point. As the X-ray beam penetrated within the matrix, the obtained spectral data corresponded to the mixture of all the chemical elements detected (Mg, Al, Si, P, S, K, Ca, Ti, Cr, Fe, Cu and Zn), which constituted several mineral phases. Data was arranged in a [nm] matrix containing the intensity values for each n emission line (named variables) and for the m points analyzed. The mixture spectra matrix was treated with the SIMPLe-to-use Interactive Self-modeling Mixture Analysis algorithm (SIMPLISMA) [34]. This specific approach was previously used, with μ-XRF spectral data, to investigate the Cr- and V-bearing phases in steel slag [35] and the copper speciation in pig slurry [36]. SIMPLISMA is based on the presence of so-called pure variables – i.e. variables with a significant standard deviation of intensity for the m points. Assuming validity of the Beer Lambert law and comparing the pure variable's mean intensity with the standard deviation of the intensity for the other variables, SIMPLISMA calculates a spectrum associated with this pure variable (resolved spectrum) – formed by the elements which "vary" identically to the pure variable for the m points – and its relative weight to the mixture spectrum. Elements which "vary" identically are located together in samples and so each resolved spectrum represents the mixture of bearing phases for its pure variable. The initial spectral data can be reconstructed by the sum of the resolved spectra multiplied by the relative average weight – concentration in arbitrary units.

2.3. Leaching tests

The solubility of elements in DSS and GSSR samples was studied by a one-stage batch leaching test at a liquid to solid ratio