ENVIRONMENTAL IMPACT OF SEWAGE SLUDGE ASH ASSESSED THROUGH LEACHING

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Abstract:

As part of a wider feasibility study on the possible reuse potential of Croatian sewage sludge ash, ash has been produced by laboratory incineration of sewage sludge from two Croatian wastewater treatment plants. The Croatian sewage sludge ash was tested for soluble heavy metals according to EN 12457 and the results were considered in the context of EU landfill Waste Acceptance Criteria. With sewage sludge ash alone, the main soluble elements/ions of concern were (in decreasing order): Mo, SO_4, Cr and Cl. When obtained ash was incorporated into cement mortars at cement replacement rates of 20%, EN 12457 leaching of the crushed mortars demonstrated compliance with the strictest limits for inert landfill Waste Acceptance Criteria and well within other limits specified for use in road bases. However, much of the reduction in leaching levels can be attributed to the dilution effect of sand used in mortars. In the cases of Se, Cr, F and Cl, results imply that the cement used in the mortars actually represents a more significant source of soluble Se, Cr, F and Cl than the produced ash. Regardless, the overall results reveal that leaching of heavy metals and other ions were not a significant concern that would prevent the potential reuse of Croatian sewage sludge ash in cement mortars or concretes should Croatian wastewater treatment plants opt for sewage sludge incineration as an alternative sludge disposal and management option.

1 Introduction

Sewage sludge generation from wastewater treatment plants (WWTP) is unavoidable and the quantity of sludge generated per volume of sewage treated will increase as secondary and tertiary treatment levels are introduced to meet ever more stringent quality requirements for final effluent discharges.

Following the recent entry of Croatia into the EU in 2013, there is a need to align with the myriad European Directives and Regulations within a certain

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timeframe. One major challenge will be to upgrade wastewater treatment plants to meet the same minimum requirements as set out by the Urban Wastewater Treatment Directive 91/271/EEC. One obvious consequence of this will be the production of much larger quantities of sewage sludge. Sewage sludge is composed of organic and inorganic solids accumulated during the physical (sedimentation, filtration), biological (microbial activity) and chemical treatment (coagulation, flocculation) of sewage. It may contain pathogens, parasites, viruses and many harmful and dangerous substances (heavy metals, toxins, radionuclides, etc.).

1.1 Sewage sludge disposal considerations

As a general rule of thumb, around 50% of operating costs for any municipal WWTP are due to sewage sludge management and disposal. Eurostat data [1] shows that land spreading (use in agriculture and horticulture) of sludge remains the dominant disposal method. Nevertheless, incineration has become a significant alternative option while land filling of sewage sludge has been kept at more or less the same levels since 2004 (see Fig. 1) and is expected to become relatively less important in the future. Although not explicitly banned by the Landfill Directive (99/31/EC), landfilling of sewage sludge is clearly at odds with the goals set out in that Directive of reducing the quantities of biodegradable waste sent to landfill.

The land spreading of sewage sludge is currently controlled by the Sludge Directive (86/278/EEC) and sets maximum limits for the following heavy metals: cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), mercury (Hg) and chromium (Cr). It is uncertain whether the Sludge Directive will be revised in the next few years or not, because since its implementation many Member States have adopted much stricter requirements for the landspreading of sewage sludge.

Across the EU, incineration has arisen as an alternative approach to sewage sludge disposal which provides water utilities a great deal of stability and control over sludge management. Incineration effectively converts 1 tone of dewatered sewage sludge containing pathogens and heavy metals into around 100 kg of sterile sewage sludge ash (SSA). It has been estimated that around 1.7 Mt per annum of SSA is produced globally in the incineration of sewage sludge (mostly in the US, EU and Japan) [2].

1.2 SSA disposal considerations

Analyses of SSA with X-ray fluorescence spectrometer (XRF) consistently reveal that the main elements (besides oxygen) are: silicon (Si), iron (Fe), aluminium (Al), calcium (Ca) and phosphorus (P), but also may contain significant amounts of heavy metals that are concentrated in the ash following sludge incineration [3].

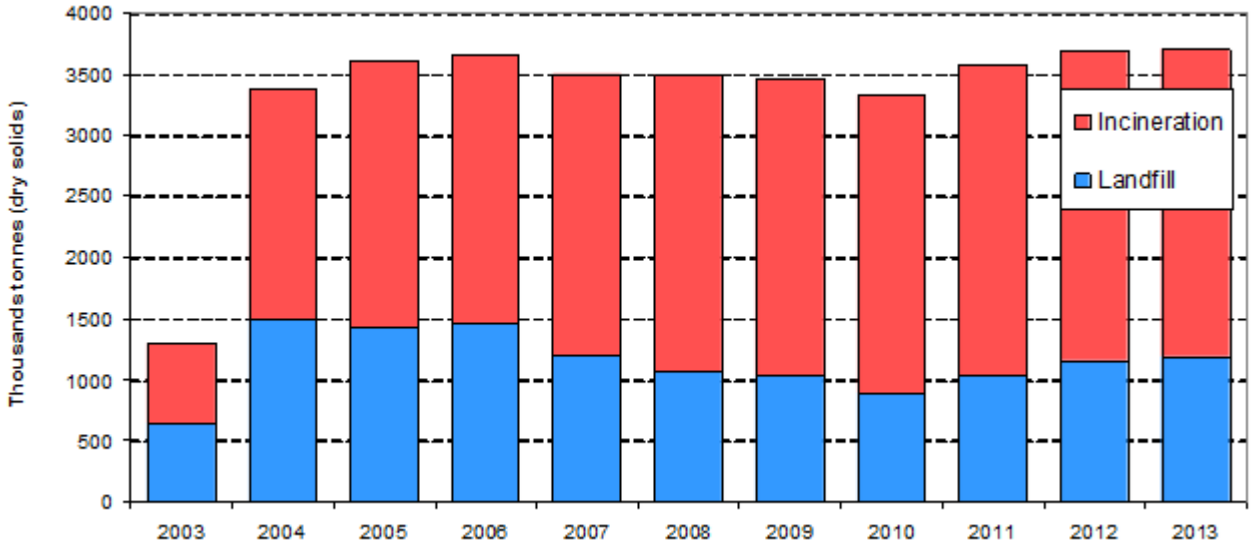

Figure 1. Eurostat data [1] reported for EU countries during the period 2003-2013. (Note that 2014 data was not well collected and that where gaps in data for individual countries appeared e.g. in 2007, it was assumed to be halfway between the data reported in 2006 and 2008).

The cost of landfill disposal of SSA can vary widely between different countries but it is often a sensitive question to which type of landfill it is deemed suitable for. Total landfill cost is composed of three elements; transport to site, gate fees and taxes. The only true comparison that can be made between different countries is in terms of applicable taxes. According to a review by Fischer et al. [4], tax levels can range from 1-2 €/t to up to 200 €/t. In the city of Zagreb (Croatia) the tax for the disposal of non-hazardous waste is about 50 €/t, while the inert waste tax is less than 2 €/t. A similar approach occurs in the UK where inert waste landfill tax is about 2.5 £/t, while tax for non-hazardous and hazardous wastes is around 80 £/t. It is clear that viewed from a purely economic perspective, it is important to understand the characteristics of SSA prior to considering its landfill disposal.

The Landfill Directive sets out provisions for waste acceptance criteria (WAC) to inert landfill, non-hazardous landfill and hazardous landfill. As detailed by EU landfill waste acceptance criteria and EU Hazardous Waste Directive compliance testing of incinerated sewage sludge, SSA would be classified as a mirror entry 19 01 13* in the European Waste Catalogue. This simply means that the waste may be considered as hazardous or non-hazardous depending upon results of further analyses. Consequently, it is necessary to obtain results of a leaching test based on WAC set out in Decision 2003/33/EC following the Landfill Directive.

The results of Donatello et al. [5] revealed that the leaching of fluoride, sulphate and several other ions was too high for SSA to be accepted in inert waste landfill. The same paper also revealed that the elements of most concern in relation to maximum allowable limits for non-hazardous waste landfill were Selenium (Se), Molybdenum (Mo) and Antimony (Sb).

In the interests of diverting SSA from landfill, substantial research has been published that focuses on the reuse of SSA in construction materials such as cement mortars, concrete, bricks and tiles [1, 3, 6]. However, due to concerns about metal cations and other anions leaching from SSA, it is important to know what effect SSA has on the leaching of heavy metals from construction materials in which it is incorporated. This subject is of particular relevance in light of European Commission Mandate 366 concerning the emission of dangerous substances from construction products.

This paper will give an overview of leaching of heavy metals from the SSA in the context of WAC set out under the Landfill Directive (99/31/EC) and consider the leaching of heavy metals from SSA-containing mortars using different standard leaching tests mentioned in the literature. With the aim of assessing the potential implications of the future installation of sewage sludge incineration capacity in Croatia, samples of Croatian sewage sludge as well as Croatian SSA produced by laboratory scale incineration are analysed for leachable heavy metals, thereby enabling the degree of enrichment of heavy metals during incineration to be evaluated. The use of Croatian SSA in cement mortars will simultaneously permit an investigation of the degree of immobilization of heavy metals from SSA in cement mortars as well as assessing the suitability of such mortars to be used as construction products.

1.3 Leaching

Leaching can be defined as the process of release of inorganic or organic substances or ions from the solid phase to a surrounding liquid phase. Leaching processes can be controlled by dissolution, desorption and other mechanisms, which are directly affected by variables such as: pH, redox potential, ionic strength of the liquid phase, temperature, dissolved organic matter and (micro) biological activity [7].

Furthermore, for a given liquid phase, the final concentration of the dissolved substances in that liquid phase will be strongly influenced by factors such as: time; the liquid to solid ratio; the amount of solid surface area that is exposed to the fluid and whether the tests are static (liquid phase is not replenished periodically) or dynamic (liquid phase is replenished periodically).

Leaching tests are used for determining the concentration of elements (mainly heavy metals) that are released within a certain time from the solid phase into the liquid phase, which are then considered to be potentially dangerous and bioavailable.

Examples of situations where leaching is of utmost importance include: landfills; road bases; stabilized blocks (especially for nuclear waste containment purposes), in spoil heaps or in geotechnical applications. Tests can be designed to analyze leachate concentrations at different times during a defined period or to provide a snapshot of leachate concentration after one given time period. In addition to the EN 12457 standards that link directly to the EU Landfill Directive, other widely published leaching tests include: the German DEV S4, the Dutch NEN

7341, 7343, 7345 and 7349, the French X31 -210, American TCLP, Swiss VAT, etc. [8].

2 Materials and methods

2.1 Materials

The sewage sludge that was used in this study was sourced from two Croatian WWTPs. Karlovac WWTP is sized to treat a population equivalent of 98.500 and provides tertiary treatment (conventional activated sludge technology plus nitrification and biological and chemical phosphorus removal stages) whilst WWTP Zagreb operates with secondary treatment (conventional activated sludge technology). Sludge treatment on both WWTPs includes anaerobic stabilization and dewatering with some lime addition.
Sludge was collected from both WWTPs and dried at 105°C for at least 24-36 hours and until constant mass. The laboratory incineration procedure involved placing in a furnace at 800°C (for 3 hours) or 1000°C for 2.5 hours. After incineration, the granular ashes were ground to a fine powder prior to further testing.

2.2 Methods

The 4 SSA samples (Karlovac-800; Karlovac-1000; Zagreb-800 and Zagreb-1000) were digested and analyzed for major elements with Inductively Coupled Plasma optical emission spectroscopy (ICP-OES) by a commercial accredited laboratory using methodology set out in EN ISO 11885.2010.
Heavy metals in both sewage sludge and SSA were analyzed by a commercial accredited laboratory using methodology set out in EN 13657 for Cr, Cu, Pb, Cd, Zn and Ni, according to EN ISO 11969 for As, EN ISO 12846 for Hg and EN ISO 15586 for Mo.
Mortars were prepared using CEM II/B-M (S-V) 42.5N, dolomite sand (0/4 mm) and ordinary tap water with a water-binder ratio of 0.50. SSA was used as a 20% replacement for the cement. Batches were prepared in a 5 litre mixing bowl, with 2027 g of cement, 507 g of SSA, 1267 g of water and 7508 g of sand. Batches were mechanically mixed, placed in moulds, demoulded after 24 hours, cured for a further 27 days, then crushed and subjected to leaching tests.
Leaching tests were performed in compliance with EN 12457-2 on the total of 4 samples of SSA and 4 samples of crushed cement mortar with built-in SSA (mortar debris) as shown in Fig. 2. SSA was obtained by incineration of sewage sludge collected from two WWTP in Croatia (KA-Karlovac and ZG-Zagreb) at two different temperatures 800°C and 1000°C.
Approximately 90 g of SSA, or mortar fragments from specimens after strength testing, was placed in a glass vessel of volume 1 L, and a specific amount of leachant (demineralised water) was added in order to attain a desired ratio of liquid/solid (L/S=10). The glass bottle was agitated for 24 hours at a rate of 2 rpm (rotations per minute). After agitation, the sample was allowed to settle for 15 ± 5 minutes. The eluate was then filtered through a 0.45 μm pore size membrane filter under vacuum.
The eluate was divided into the required number of samples for chemical analysis.
Prior to analysis for heavy metals by Atomic Absorption spectrometry (Perkin Elmer Analyst 800), the filtrate was acidified with 1 mL of 65% nitric acid per 100 mL of filtrate sample to prevent any unwanted precipitation during sample storage. Chloride and fluoride ion concentrations in the filtrates were analyzed by colorimetry using a Hach Lange DR 5000 spectrophotometer.

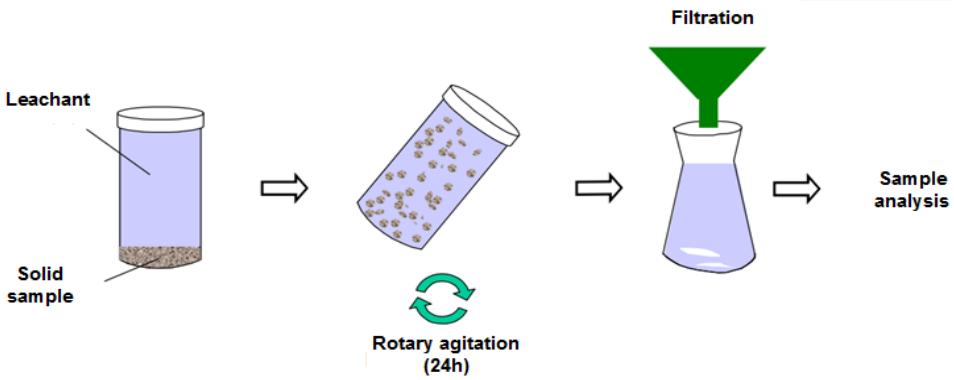

Figure 2. Schematic diagram of the leaching test [7] *that was performed on samples of SSA and crushed mortars with built-in SSA.*

3 Results and discussion

3.1 Major elements in SSA

The results of the digestion and ICP-OES analyses of the four SSA samples are shown below in Table 1.
Table 1 confirms that both samples (K and Z) contained high quantities of Ca due to the lime stabilization of sludge at the WWTP sites and that the Ca content is enriched in samples incinerated at 1000°C instead of 800°C.
The Karlovac SSA was significantly richer in Ca, Al and P than the Zagreb SSA, which suggests (i) that $Al_2(SO_4)_3$ and $Ca(OH)_2$ is used as a chemical precipitation agent for phosphate recovery during tertiary treatment at the Karlovac site and (ii) that the tertiary sludge was combined with the primary and secondary sludges in the collected samples. This is further supported by the extremely low SiO_2:Al_2O_3 ratio in Karlovac SSA compared to Zagreb SSA. The Zagreb SSA shows a much more normal SiO_2:Al_2O_3 ratio of approximately 2.5:1 while that of Karlovac SSA is less than 0.5:1.
All other major elements are within the normal ranges expected for SSA although it must be noted that a significant quantity of "other" elements are unaccounted for in the Zagreb SSA and that these decrease significantly when the incineration temperature is increased from 800 to 1000°C.

Table 1. Major elements present in Karlovac (K) and Zagreb (Z) SSA (%)

Sample	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	TiO_2	Na_2O	K_2O	SO_3	P_2O_5	Remaining
K-800	8.0	16.5	37.6	8.2	4.2	0.8	0.3	1.3	5.8	16.0	1.3
K-1000	2.9	11.7	42.1	9.4	4.5	1.0	0.3	1.3	7.7	17.2	1.9
Z-800	20.8	7.5	23.5	5.7	2.5	0.4	0.15	0.5	4.75	10.4	23.8
Z-1000	25.7	8.5	27.0	7.0	3.0	0.5	0.1	0.6	5.9	12.0	9.7

3.2 Total metals in sewage sludge and SSA

Heavy metal concentrations are greatly influenced by industrial discharges sent to the sewerage network and the degree of pre-treatment carried out on industrial sites prior to any discharge. For example, the extremely high upper limit for Cr in Table 2 reported by Metcalf and Eddy [9] is likely to be due to discharges from small tanneries which discharge directly to the mains sewerage network with little pre-treatment.
From Table 2 it is clear that heavy metal concentrations in sewage sludge can easily vary by several orders of magnitude - especially considering the ranges of concentrations reported by Metcalf and Eddy [9].
A significant difference in sludge characteristics can be expected between primary and secondary sludges (which have high organic matter content) and tertiary sludge from chemical phosphate stripping, which will be predominantly inorganic. Anaerobic stabilization of combined sludges will reduce the organic content of sludge and lime stabilization will reduce the organic content further still, increase Ca content and potentially immobilize heavy metals in the high pH sludge.
With the exception of As and Se, the heavy metal concentrations in Croatian sewage sludge are very similar to mean values reported for Swedish and German sewage sludge. Values for As were 2-3 times higher than the Swedish mean value but were still at the lower end of the range of values reported by Metcalf and Eddy [9].
However, the range of Se values reported for Croatian sewage sludge has an extremely high upper limit of 710 mg/kg dry matter, which is around 40 times higher than the upper limit reported by Metcalf and Eddy [9].
Table 3 compares the concentrations of certain heavy metals in 4 samples obtained by laboratory
scale incineration of Croatian SSA with the results from the literature.
The results in Table 3 show that the levels of heavy metals in the laboratory produced CroatianSSA are significantly lower than mean values reported in the literature. This can in part be attributed to the relatively low degree of industrial activity in Croatia although it must be noted that the laboratory incineration process provides a substantially longer residence time than the process in industrial scale incinerators and this may be the reason for low results for heavy metals that can be volatilised at temperatures around 800 to 1000°C such as As, Hg and Pb.
During incineration, virtually all organic matter, which typically accounts for two thirds of all solids in sewage sludge (dry matter), is combusted to gases, thus reducing sludge solids mass by around 67%. The

mass reduction with the Croatian SSA during incineration was calculated to be within the range of 42-48%, being slightly higher at higher incineration temperatures. The lower than typical mass loss in Croatian sludge incineration can be explained by the fact that the sludge was lime stabilised.

Assuming metal volatilisation losses negligible, incineration should result in a 2-fold increase in heavy metals concentrations in the remaining inorganic SSA compared to sludge dry matter. A comparison of the concentrations in the Croatian sludge and the Croatian SSA for selected heavy metals is given by CF values included above in Table 4.

Any CF value of around 2 or more is indicative that the metal has not volatilised. The lower the CF, the greater extent to which the metal has volatilised.

Table 2. The content of heavy metals in Croatian sewage sludge compared to results reported in the literature (mg/kg of dry matter)

Heavy metal	Typical metal content in sewage sludge [9]	Average of analysis of sludge from 48 WWTPs in Sweeden [10]	Average of analysis of 6800 sludge samples from Germany [10]	Metal content in sewage sludge from 10 WWTP in Croatia [11]	WWTP Karlovac	WWTP Zagreb
As	1.1 - 230	4.7	-	<0.001 - 9.815	-	14.59
Cd	1 - 3410	1.2	3.8	<0.001 - 1.483	<0.001	<2.0
Cr	10 - 99000	33	91	0.009 - 78.841	93	29.5
Cu	84 - 17000	390	330	<0.001 – 598	-	314
Pb	13 - 26000	33	159	<0.001 - 108.5	112	73.8
Hg	0.6 - 56	1.1	2.7	<0.001 - 2.579	-	1.49
Mo	0.1 - 214	-	-	<0.01 - 3.78	-	2.66
Ni	2 - 5300	20	39	<0.001 - 38.48	-	31.1
Se	1.7 - 17.2	1.3	-	<10 – 710	-	-
Zn	101- 49000	550	1318	<0.001 -1137	835	693

Table 3. The content of heavy metals (mg/kg) in Croatian SSA compared to results reported in the literature [5, 12-21]

Metal	Litterature review			SSA from WWTP Karlovac		SSA from WWTP Zagreb	
	Min	Max	Mean	800°C	1000°C	800°C	1000°C
As	0.4	726	26.5	9.4	11.6	5.1	5.4
Cd	0.3	94	10.0	2.4	0.9	<DL	<DL
Cr	16	2636	491.9	21.9	20.2	42.5	43.0
Cu	118	5420	1226.5	207.4	142.3	532.5	470.0
Ni	4	2000	173.7	89.0	52.3	83.0	85.5
Pb	21	2055	430.2	70.4	94.5	28.2	70.7
Sb	4	137	39.0	-	-	-	-
Zn	644	10000	2360.8	243.0	920.0	655.0	770.0
Hg	0	7	2.0	<DL	<DL	<DL	<DL
Mo	5.9	42.5	18.2	16.9	14.2	15.1	16.2
Se	0.5	600	76.0	8.1	6.3	1.1	1.0

Table 4. Concentration factors (CF) as the ratio of concentrations of certain heavy metals in Croatian sewage sludge and in SSA after laboratory incineration

Metal	As	Cr	Cu	Pb	Hg	Mo	Ni	Zn
CF-800	0.4	0.8	1.7	0.5	<0.01	5.7	2.7	0.6
CF-1000	0.4	0.9	1.5	0.9	<0.01	6.1	2.8	1.1

From the results in Table 4, it is clear that only Mo and Ni did not volatilise to any significant degree during sludge incineration at both temperatures. The results also indicate that Cr and Cu volatilisation is significantly higher when the incineration temperature is raised from 800 to 1000°C. Mercury, as can be expected, showed an extremely high degree of volatilisation at both temperatures.
The behaviour of heavy metals during the sludge incineration has been previously reported in the literature in some detail [22-25]. A complete vaporization of metals such as Hg, Cd, As and significant vaporization of Pb occurs during the combustion of the sludge at temperatures over 800°C. However, in industrial scale incinerators with much shorter residence times, Cd, Pb and As may be contained in the SSA in significant concentrations due to their vapour condensation on the particles during the cooling of SSA [25].

3.3 EN 12457 soluble metals in sewage sludge and SSA

The results from EN 12457 leaching help determine what type of landfill a particular waste can be sent to (i.e. hazardous, non-hazardous or inert). The results of leaching from samples of SSA are compared to the relevant waste acceptance criteria as per the EU Landfill Directive in Fig. 3.
In the context of WAC limits, the leaching results for SSA fell into one of three categories:

- Contaminants of very low concern with concentrations well below the maximum limits for inert waste landfill (i.e. Cu, Cd, Ni, Pb, Zn, Hg and As)
- Contaminants of intermediate concern with concentrations close to or exceeding the maximum limits for inert waste landfill (i.e. Cr, SO_4, Cl, F and arguably Se)
- Contaminants of high concern with concentrations close to or exceeding the maximum limits for non-hazardous waste landfill (i.e. Mo).

Considering the effect of incineration temperature, the data suggest that raising the temperature from 800 to 1000°C caused the levels of water soluble Cr, Cl, F and Mo to increase for both types of Croatian SSA while causing levels of water soluble Se to decrease. Regardless, it is clear that Croatian SSA should not be considered as an inert waste due to the concentrations of soluble Cr, SO_4, Cl and/or Mo. Similar conclusions have been drawn from other studies in the literature.
The results for leaching of the elements of most concern in Croatian SSA (i.e. SO_4, Cl, F, Cr, Se and Mo) are compared with other results from different SSA samples reported in the literature in Fig. 4.
Despite the significant number of publications about SSA in the academic literature, there are only a few studies that report on leaching of elements from SSA in terms of WAC for European landfills.
From the limited studies available, Fig. 4 shows that the results for EN 12457 soluble SO_4, Cl, Cr and Mo from Croatian SSA were within the ranges of values reported by other studies. However, the results for Se and F were much lower in Croatian SSA than the British or French SSA studied. The very low values for soluble Se may be linked to the experimental conditions used to generate the SSA in the first place. The UK and French SSAs were sourced from fluidised bed incinerators where sludge is rapidly combusted in the order of seconds at temperatures of 750-900°C and is quickly cooled as it goes through the heat exchanger and then ash recovery stage. On the other hand, the Croatian SSA was incinerated in a laboratory furnace at 800 or 1000°C for 2.5 to 3 hours. Although the chemical speciation of Se in sewage sludge and SSA cannot be determined, it is worth noting that the boiling point of the pure element is approximately 685°C. This fact, in combination with the much longer combustion time for Croatian SSA, would suggest that much of the Se present in Croatian sludge has volatilised. A study of Brazilian SSA by Fontes et al. [16] followed a similar approach to this study where the ash was incinerated in a laboratory furnace (at 950°C for 3 hours). Unfortunately, they followed a different leaching test according to a Brazilian standard (NBR 10004/10005/10006) and did not analyse for Mo although they also noted very low levels of soluble Se. In comparison to the applicable Brazilian standard, they found that SSA should not be considered as an inert waste due to soluble Mn and SO_4.
Unlike Se, the same effect was not observed for Mo, which is not a volatile metal at all under these conditions (the melting point around 2600°C). Indeed, the levels of soluble Mo are a consistent concern for SSA in other studies too, despite the fact that Mo is never one of the main heavy metals present in SSA in terms of total concentrations.
By comparing results from leaching tests and from aqua regia or lithium metaborate digestion tests, which attempts to measure the total content of metals present, an approximate idea of the relative solubility of each of the heavy metals analysed in SSA can be

obtained. This data is compared with those from the literature in Table 5.

The relative solubilities of different heavy metals in SSA vary widely. Although not included in Table 5, the Zn and Pb in SSA are confirmed to have an extremely low solubility (less than 0.1%). From the metals included in Table 5, As has a low relative solubility (average 0.9%) and Cr has a small but notable degree of solubility (average 1.3%) although this is significantly increased by two results for the Croatian SSA at 1000°C, which appear significantly higher than the other equivalent data. In contrast, Mo shows a consistently high degree of relative solubility in SSA from different studies (average 40.9%). With Se, there is also a high degree of solubility (average 22.0%) although this would be significantly higher if the Croatian results were excluded, which appear to be abnormally low. As alluded to earlier, it is possible that any soluble forms of Se are volatilised during the longer combustion periods that the Croatian SSA has been subjected to.

Due to the concerns with leaching of certain elements from Croatian SSA, it is necessary to investigate how the solubility of these elements is affected when SSA is used in blended cement mortars in order to understand the potential for stabilised SSA to meet requirements for inert landfill or to be considered as a possible supplementary cementitious material in construction products.

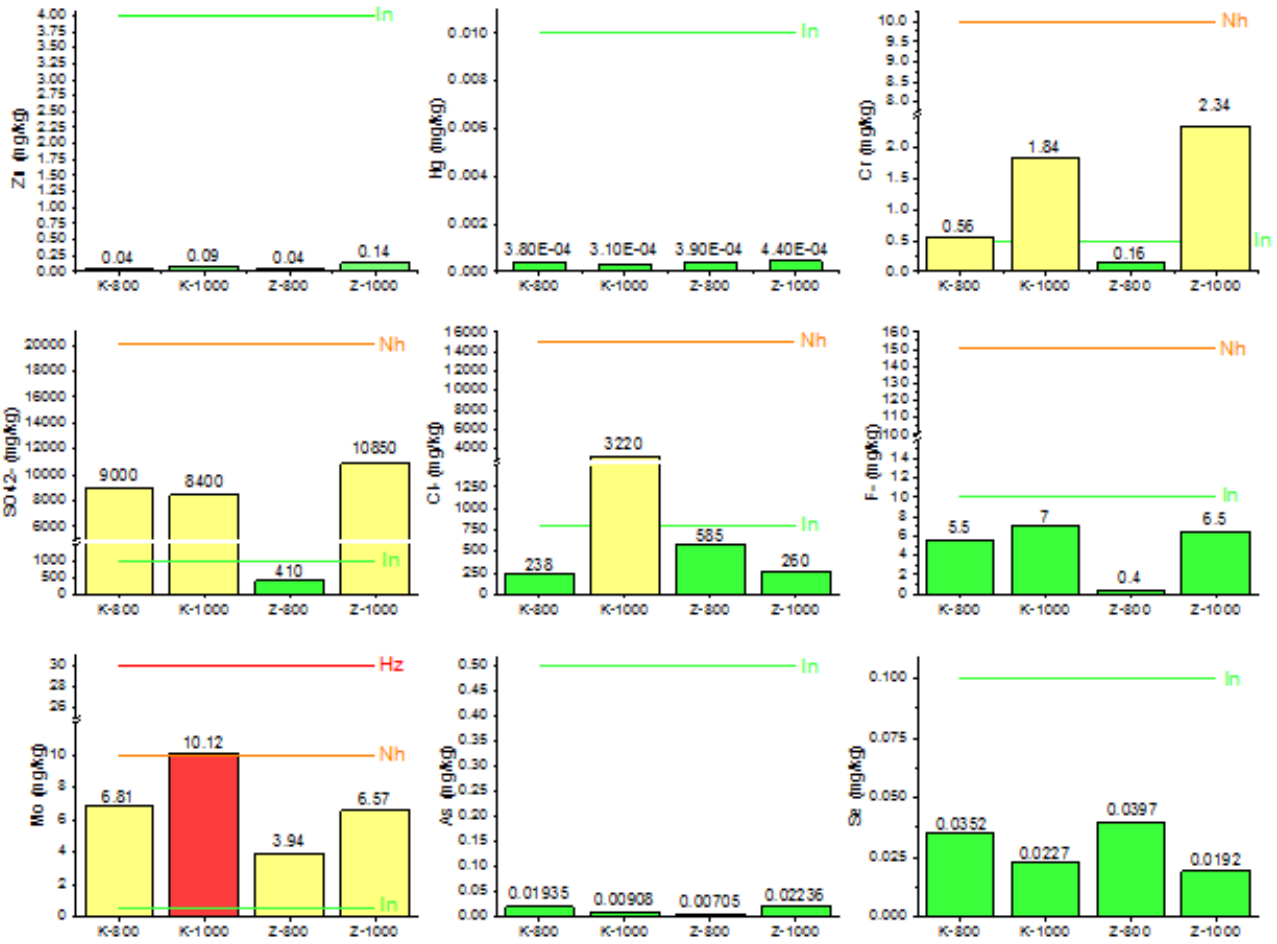

Figure 3. Comparison of EN 12457 leaching test results for Croatian SSA with relevant WAC limits for European landfills (Results for Ni, Cd and Cu not included because they were below the limit of detection. In = maximum limit for inert waste landfill; Nh = maximum limit for non-hazardous waste landfill; Hz = maximum limit for hazardous waste landfill).

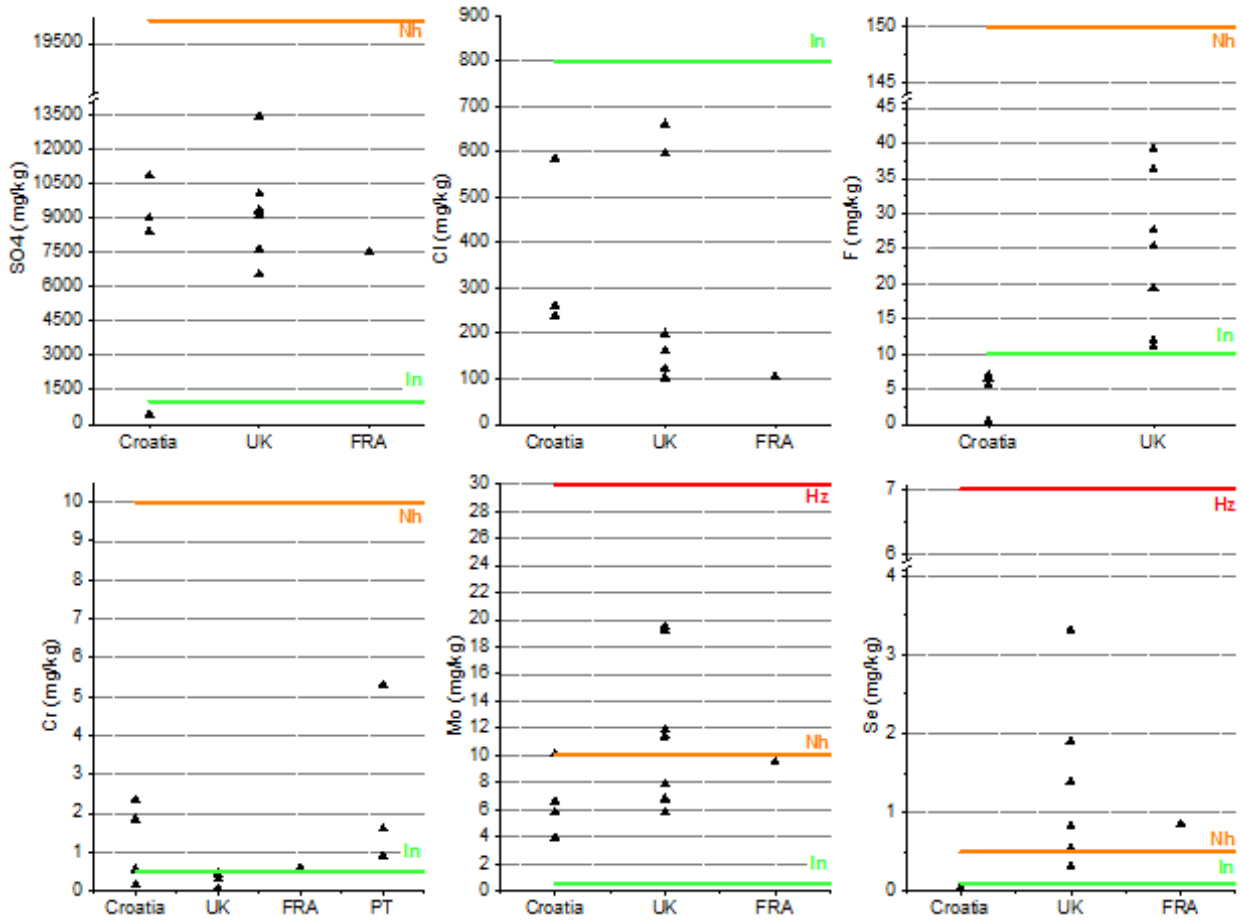

Figure 4. Leaching test results for selected elements from Croatian SSA in the context of other EN 12457 results reported in the literature (UK refers to [5]; FRA refers to [26] and PT refers to [27]. Lines refer to maximum limits for Inert (In), Non-hazardous (Nh) and Hazardous (Hz) waste landfills.

3.4 Leaching from SSA containing mortars

The next step in the evaluation of SSA was to examine how the solubility of elements of concern identified in section 3 is affected when SSA is immobilised within an alkaline Portland cement matrix. A series of mortars were prepared with a binder (cement + SSA) to sand ratio of 1:3 and with 20% of the cement fraction replaced by SSA. After curing for 28 days, the mortars were crushed to particle size <4 mm and tested according to the EN 12457 leaching method. The results of leachate analysis of selected elements of interest are plotted in Fig. 5.

From the results in Fig. 5 it is clear that the leaching of the elements of concern that were flagged with pure SSA are all well in compliance with the stricter limits for inert waste landfill when the SSA is mixed in a cement mortar.

The reduction in leaching of elements of concern can be due to simple dilution in the mortar matrix or due to a chemical immobilization of the elements within the alkaline cement mortar matrix. Taking the 3:1 mortar mix of 3 parts sand: 1 part cement (0.8 parts PC + 0.2 parts SSA) but ignoring the content of mixing water, an approximate dilution factor of 1 in 20 applies (i.e. a factor of 0.05). A comparison of the SSA-mortar and ash-SSA leaching data is provided in Table 6 and the net differences compared with the hypothetical dilution factor.

Looking at the average dilution factors in the bottom row of Table 6, it is clear that the reductions in As and Mo are very close to the hypothetical dilution factor, implying that there is little or no significant immobilization of these metals in the cementitious matrix (assuming that the cement and sand do not introduce additional sources of soluble As and Mo).

Results from Coutand et al. [13] suggest that SSA is a much more significant source of As than cement

because soluble concentrations increased by a factor of 5 when 25% of cement was replaced with SSA. The observation for Mo is not supported by the results of Maozhe et al. [26] who did not detect any Mo in leachates from SSA-concretes. However, it must be added that their leaching test was carried out using complete monolithic samples (according to EN 15863), whereas here the mortars were crushed prior to leaching tests according to EN 12457. As a general rule with SSA-mortars, the results of leaching tests carried out by Cyr et al., (2007) suggest that crushed mortars will leach 3-6 times more As, Ba, Cd, Cr, Cu, Ni, Sb, Pb, Ti, V, Zn, expressed as a cumulative total, than equivalent monolithic samples.

Assuming a simple dilution scenario with Cr and Cl, there were 5-10 times more soluble concentrations in SSA-containing mortars than would be expected.. The only explanation for this is that the cement used is a more significant source of additional soluble Cr and Cl than SSA. This idea is strongly supported by data from Maozhe et al. [26], who showed that results of soluble Cr and Cl in reference concretes were 2-10 times higher than those of SSA-concretes. However, Coutand et al. [13] showed the opposite effect, with soluble Cr levels being increased by a factor of 2 when SSA replaced 25% of cement in mortars. Leaching of Cr (especially Cr VI) has been a concern with Portland cement during many years, as reflected by Directive 2003/53/EC, which bans the supply or use of cement with soluble Cr(VI) concentrations greater than 2 mg/kg. The clay and limestone raw materials used in cement manufacture may contain traces of Cr and Cr may be inadvertently transferred to cement from stainless steel balls used during milling operations. Under typical conditions in the kiln, most Cr can be oxidized to the more toxic Cr(VI) form [28, 29]. Leaching of Cr (VI) from Portland cement clinkers can reach 20 mg/kg [30, 31]. For this reason, it is necessary to add reducing agents to Portland cement prior to its placing on the market [31]. Nevertheless, in hydrated cement materials, Yu et al. [8] state that leaching of chromium (Cr), and Cr (VI) from mortars and concrete is mainly associated with the process of decomposition or dissolving C-S-H gel caused by carbonization.

Finally, with F and Se, the leachate concentrations are around 50 times higher than would be expected in a simple dilution scenario. This strongly implies that the cement is a significant source of additional soluble F and Se and that any possible immobilization of these elements in the cementitious matrix does not compensate for these additional sources.

Regardless of the different behaviours of these 6 elements in SSA-mortars, the results in Fig. 5 make it clear that SSA-mortars when crushed at their End-of-Life could realistically be sent to inert waste landfill or used as aggregates in road bases.

Table 5. Relative solubility of selected heavy metals in SSA from different sources [5, 2, 27]

	As			Cr			Mo			Se		
Sample	Total	Leach	% sol.	Total	Leach	% sol.	Total	Leach	% sol.	Total	Leach	% sol.
K-800	9.4	0.0194	**0.2**	21.9	0.56	**2.6**	16.9	6.81	**40.3**	8.1	0.0352	**0.4**
K-1000	11.6	0.0091	**0.1**	20.2	1.84	**9.1**	14.2	10.12	**71.3**	6.9	0.0227	**0.4**
Z-800	5.1	0.0071	**0.1**	42.5	0.16	**0.4**	15.1	3.94	**26.1**	1.1	0.0397	**3.6**
Z-1000	5.4	0.0224	**0.4**	43.0	2.34	**5.5**	16.2	6.57	**40.6**	1.0	0.0192	**1.9**
UK1	21.7	0.13	**0.6**	1031	0.45	**0.0**	66.3	19.2	**29.0**	2.0	0.32	**16.0**
UK2	20.5	0.23	**1.1**	250	0.04	**0.0**	27.3	11.4	**41.8**	4.0	1.9	**47.5**
UK3	42.5	0.27	**0.6**	366	0.06	**0.0**	25.0	6.8	**27.2**	1.6	0.52	**32.5**
UK4	11.4	0.20	**1.8**	409	0.04	**0.0**	19.3	7.9	**40.9**	2.5	1.39	**55.6**
UK5	235	0.71	**0.3**	257	0.02	**0.0**	20.2	5.8	**28.7**	2.6	0.82	**31.5**
UK6	7.1	0.26	**3.7**	917	0.02	**0.0**	22.6	19.5	**86.3**	5.8	3.31	**57.1**
UK7	9.8	0.1	**1.0**	100	0.31	**0.3**	45.7	11.9	**26.0**	7.1	0.54	**7.6**
FRA				600	0.6	**0.1**	26.0	8.7	**33.5**	8.1	0.87	**10.7**
PT-A2				435	1.6	**0.4**						
PT-A3				719	5.3	**0.7**						
PT-B3				307	0.91	**0.3**						
Max.			**3.7**			**5.5**			**86.3**			**0.4**
Min.			**0.1**			**0.0**			**24.3**			**57.1**
Avg.			**0.9**			**1.3**			**40.9**			**22.0**

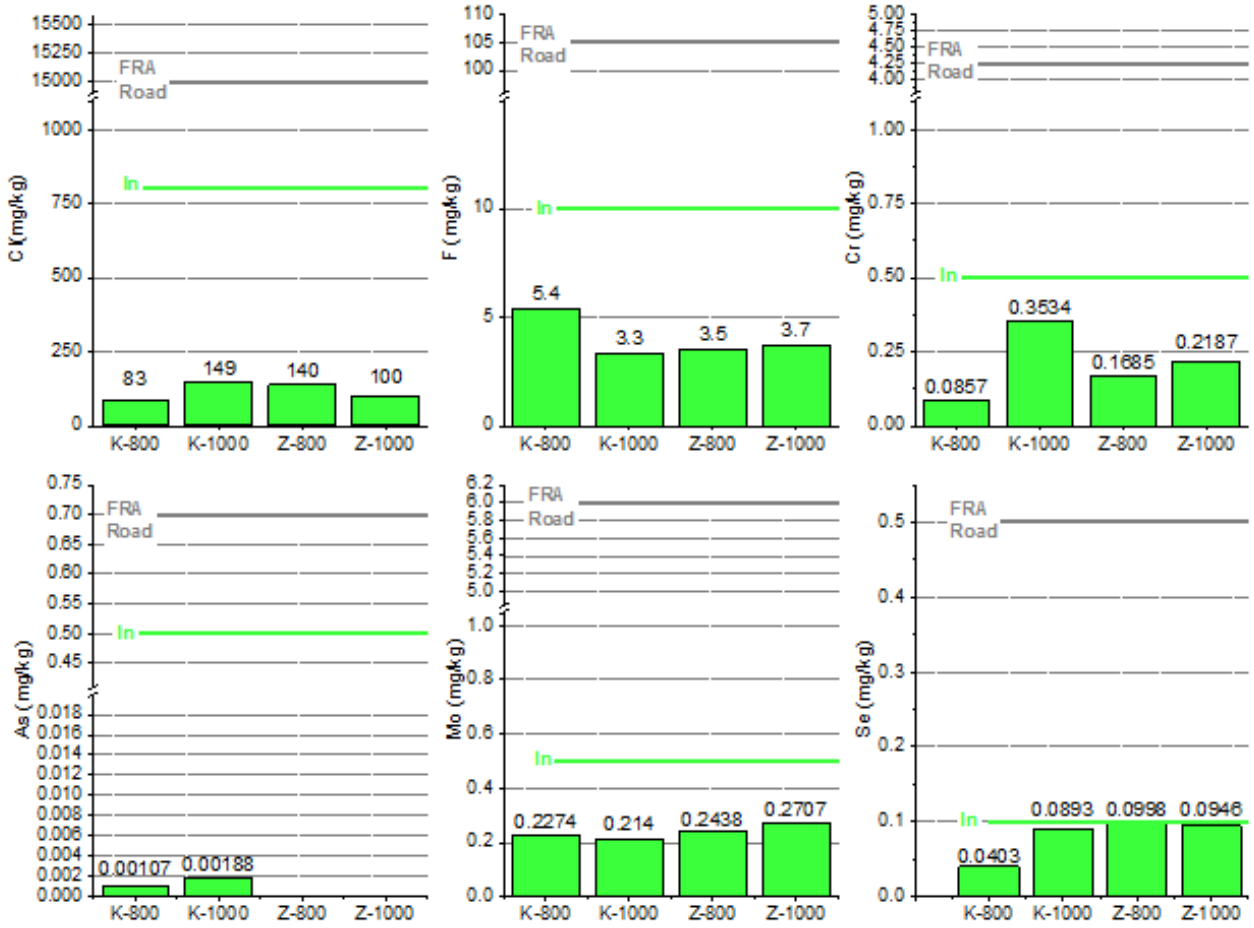

Figure 5. Leaching of elements of concern from crushed cement mortars with 20% of cement replaced by Croatian SSA (In = WAC maximum limit for inert waste landfill; FRA Road = maximum limits for leaching in order to be considered as suitable for use in road base materials).

Table 6. Comparison of ash and mortar leaching data for Croatian SSA

Sample	Cl	F	Cr	As	Mo	Se
K-800	0.28	0.62	0.34	0.13	0.04	0.64
K-1000	0.03	0.77	0.05	0.12	0.02	1.78
Z-800	0.24	8.75	1.05	0	0.06	2.51
Z-1000	0.38	0.57	0.09	0	0.04	4.93
Average	**0.23**	**2.68**	**0.38**	**0.06**	**0.04**	**2.46**

4 Conclusions

In order to evaluate the likely leaching characteristics of Croatian SSA that would be produced if WWTPs in Zagreb or Karlovac were to use sewage sludge incineration as an alternative sludge disposal and management option, SSA has been produced by laboratory scale incineration of Croatian sewage sludge. A comparison of total metal levels in the sludge before incineration and the SSA remaining after incineration revealed that the following metals volatilised to some extent during the incineration process: (in descending order) Hg > As > Pb > Cr > Zn > Cu meanwhile Ni and especially Mo were effectively concentrated in the SSA.

The leaching characteristics of Croatian SSA are within the ranges of other studies reported in the literature for SSA from different sources.

In the context of landfill WAC, the main elements/ions of concern were: Mo, SO_4, Cr and Cl, in order of decreasing levels of concern. The soluble Se results were extremely low compared to literature

values and this was attributed to the longer residence times in the laboratory furnace compared to industrial fluidised bed systems, which facilitated the volatilisation of most of the soluble fraction of Se.
When Croatian SSA was used in cement mortars, at cement substitution rates of 20%, the mortars all complied with the strictest limits set out for inert waste landfill WAC. However, in the cases of Mo and As, the reduction in leaching can be attributed to the dilution effect of cement and sand from the mortars. Conversely, results for soluble Cr, Cl, F and Se imply that the Portland cement used is a much more significant source of these contaminants than the Croatian SSA.

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