

# Leaching of ashes from co-combustion of sewage sludge and wood

## Part II: The mobility of metals during phosphorus extraction.

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### Abstract

Sewage sludge and its ashes after combustion are contaminated with metals in various concentrations. In the work described in this paper, the mobility of metals during recovery of phosphorus by acid leaching of fly-ashes from co-combustion of sewage sludge with wood was investigated. The metal concentrations in two sewage sludges, fly ashes and leachates from acid phosphorus extraction were compared with phosphorus rock and different fertilisers used in the agriculture.

The secondary cyclone ashes were found to be less contaminated with trace elements than the bag filter ashes. The largest problem is cadmium, which in all ashes studied has a too high level to meet the legislative limits for the maximum dosage in Sweden and the proposed limits in the European Union. The legislation includes limits for cadmium (Cd), mercury (Hg), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) calculated for an amendment of X kg of fertiliser per year and ha of land.

The solubility of the trace metals in the cyclone ash, with Cd as an exception, is in general much lower than the solubility of phosphorus. A decrease in pH results in an increased release of Cd but has just a slight influence on the other metals analysed in this study. The Cd yield increases by 30% when pH is lowered from 2.5 to 1.0 whereas the Hg release is not affected at all. The trace element concentrations in the leachates are far below the European and Swedish limitations of metal concentrations in fertilisers. The leachates thus fit as fertilisers and also as raw material to the industry, if the Cd is removed. In part I of the project [1] focus was on the phosphorus recovery only.

Sludge, biofuel, phosphorus, leaching, co-combustion, fluidized bed, metals, fertiliser

## 1. Introduction

Phosphorus, being a limited natural resource, is used in the industry in many different applications. As an alternative to the phosphorus rock, phosphorus can be recycled from phosphorus rich residues, such as meat and bone meal (MBM), municipal sewage sludge, phosphorus rich ashes, agricultural residues etc. In EU alone, the consumption of  $P_2O_5$  was 3 620 000 tonnes in 1996 [2]. Part I of this research project [1] was focused on phosphorus recovery by acid leaching of ashes remaining after co-combustion of municipal sewage sludge and wood. The phosphorous, as well as most trace metals, is enriched in the ashes after combustion, especially in the fly ashes. The ash flows that are produced in a combustion facility differ in elemental composition as well as in element speciation due to the different environments and temperatures prevailing in the zones where the ashes are formed and collected. Some ashes might be suitable as fertilisers whereas others have to be treated as waste due to their concentrations of toxic metals. Cadmium is a metal of great concern since it is toxic to humans, animals and plants in very low concentrations, as well as it is one of the most difficult metals to separate from other elements.

The aim of this work was to investigate the metal concentrations in sewage sludge and its ashes as well as the mobility of the metals during phosphorus extraction by acid leaching. This investigation was one part of a research project concerning the combustion of sewage sludge in a fluidized bed boiler. Two sewage sludges with different compositions were used in the study.

## 2. Experimental background

In this study the same combustion tests and ash extraction method was used as in part I [1] where all experimental details can be found. However, in this study not only the main components of the fuels are of concern, but also the trace metals, Table 1, and also if there is some additional metals added together with the lime supplied for sulphur capture, Table 2.

**Table 1:** Trace elements calculated on dry fuel. Comparison of the sludge in this study and average Swedish sludge [5].

Unit		Sewage sludge <sup>1</sup>	Sewage sludge <sup>2</sup>	Wood pellets	Sewage sludge <sup>3</sup>	Sewage sludge <sup>4</sup>
Precipitation agent		$Fe_2(SO_4)_3$	$Al_2(SO_4)_3$	—	average	average
<b>Trace elements</b>						
Hg	mg kg <sup>-1</sup> dry fuel	1.2	0.78	0.02	1.1	1.2
Cd	mg kg <sup>-1</sup> dry fuel	0.86	0.53	0.11	1.2	1.4
Pb	mg kg <sup>-1</sup> dry fuel	38.0	17	0.35	33	42
Cr	mg kg <sup>-1</sup> dry fuel	31	43	0.64	33	39
Cu	mg kg <sup>-1</sup> dry fuel	400	270	2.6	390	430
Mn	mg kg <sup>-1</sup> dry fuel	300	300	120	280	280
Co	mg kg <sup>-1</sup> dry fuel	6.9	2.8	0.04	6.2	8.3
Ni	mg kg <sup>-1</sup> dry fuel	22	13	0.20	20	22
As	mg kg <sup>-1</sup> dry fuel	5.9	5.2	0.12	4.7	5.5
Sb	mg kg <sup>-1</sup> dry fuel	14	15	0.06	2.4	3.4
V	mg kg <sup>-1</sup> dry fuel	23	23	0.06	18	18
Tl	mg kg <sup>-1</sup> dry fuel	10	10	0.06	0.15	0.16
Zn	mg kg <sup>-1</sup> dry fuel	650	390	15	550	680
Se	mg kg <sup>-1</sup> dry fuel	14	15	n.a.	1.3	1.6

n.a.: not analysed, n.r.: not reported.(1)= large plant; (2)= small plant.

(3)= Average of analysis of sludge from 48 different waste water treatment plants in Sweden [5]

(4)= Weighted average of trace elements in sludge with respect to amount of sludge produced at each waste water treatment plant, average of sludge produced in Sweden [5].

**Table 2:** Properties of the added lime.

	Unit	Hydrated lime Ca(OH) <sub>2</sub>	Lime stone CaCO <sub>3</sub>
LOI	wt-%	23.0	
Rest-CO <sub>2</sub>	wt-%	0.6	
Water at 105°C	wt-%	1.0	
K	g kg <sup>-1</sup>	0.17	2.0
Na	g kg <sup>-1</sup>	0.20	<1.0
Al	g kg <sup>-1</sup>	3.8	4.0
Si	g kg <sup>-1</sup>	7.5	2.3
Fe	g kg <sup>-1</sup>	2.4	2.0
Ca	g kg <sup>-1</sup>	520	360
Mg	g kg <sup>-1</sup>	6.0	5.0
P	g kg <sup>-1</sup>	0.10	-
As	mg kg <sup>-1</sup>	<2	-
Cd	mg kg <sup>-1</sup>	<0.05	-
Co	mg kg <sup>-1</sup>	3	-
Cr	mg kg <sup>-1</sup>	6	-
Cu	mg kg <sup>-1</sup>	2	-
Hg	mg kg <sup>-1</sup>	<0.02	-
Ni	mg kg <sup>-1</sup>	4	-
Sb	mg kg <sup>-1</sup>	<1	-
Se	mg kg <sup>-1</sup>	<1	-
Pb	mg kg <sup>-1</sup>	<1	-
V	mg kg <sup>-1</sup>	16	-
Zn	mg kg <sup>-1</sup>	5	-

### 3. Results and Discussion

#### 3.1. Ash compositions

In part I of the project [1] it was concluded that the bottom ash is not suitable for phosphorus recovery. Hence, this study only considers the fly ashes; secondary cyclone and bag filter ash. Table 3 gives the main and trace elements concentrations in the two fly ash flows. The metals are found in highest concentrations in the bag filter ash (Table 3).

**Table 3:** Trace elements in the fly ashes.

Ash analysis trace elements [mg kg <sup>-1</sup> ash]	Fe+no lime		Al+no lime		Fe+limestone		Al+limestone		Fe+hydr. lime		Al+hydr. lime	
	sec. cyclone	bag filter	sec. cyclone	bag filter	sec. cyclone	bag filter						
Hg	1.5	12	1.3	10	1.5	7.8	1.0	7.6	1.5	5.0	1.2	2.5
Cd	3.5	8.6	3.4	16	2.7	4.4	2.3	3.8	3.4	1.6	2.3	0.9
Pb	88	74	44	41	80	100	44	57	91	35	40	16
Cr	60	74	71	110	46	80	53	83	55	34	52	32
Cu	680	700	300	240	790	1000	510	900	860	420	470	200
Mn	1400	7230	1900	9830	1300	5800	1500	8300	1400	3000	1600	3000
Co	17	19	7.1	11	15	42	6.6	31	17	10	6.4	8.7
Ni	51	55	27	42	41	85	25	74	44	27	24	24
As	10	51	10	57	10	28	10	6.2	10	17	10	21
Sb	5.0	10	5.0	10	5.0	10	5.0	10	5.0	10	5.0	10
V	45	61	46	67	41	150	45	150	51	48	51	53
Zn	1600	1300	900	880	1500	780	720	840	1600	570	640	240

The concentrations of nutrients (P and K) in the ashes were high, especially in the secondary cyclone ashes. Most of the so-called macronutrients (N, P, K, Ca, Mg and S) needed by growing

crops are present, as shown in Table 4 in part I. The only one missing is nitrogen, which is emitted with the flue gas during the combustion. Also the bag filter ash contains considerable amounts of phosphorous, calcium and potassium. However, there is also a contamination of precipitation chemicals and metals in these ashes. The highest concentrations of metals are found in the bag filter ashes (Table 3). This, and the fact that the bag filter ashes only contributes to 19% of the total fly ash flow and 10% of the P-flow [1], make this ash less interesting for phosphorus recovery compared to the secondary cyclone ash.

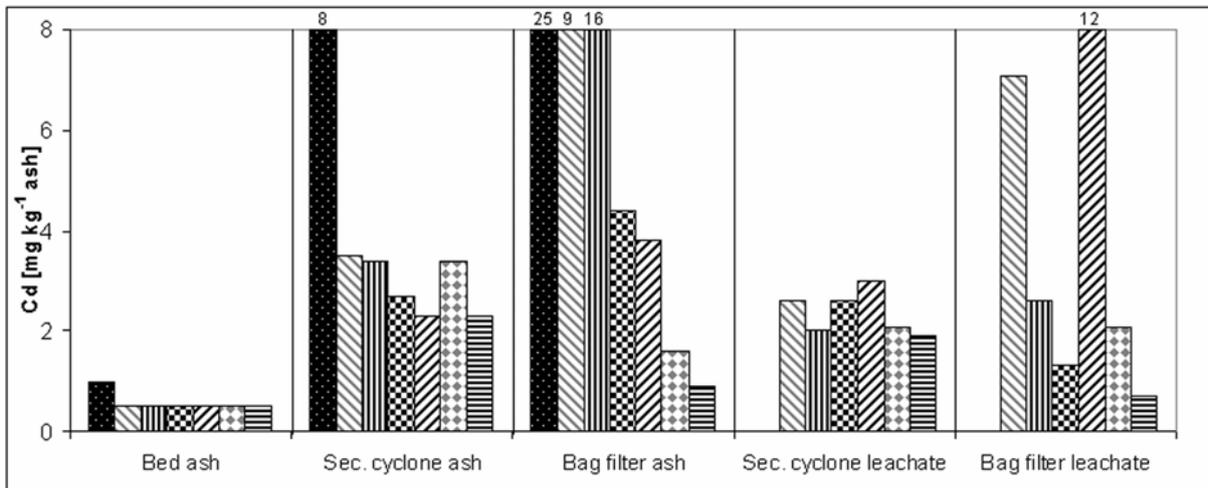
### 3.2. Leachate

The concentrations of trace elements in the leachates are much lower than in the ashes (Tables 3 and 4). Cadmium is the only exception, having a concentration similar to that in the ashes. The Cd/P ratio becomes smaller as pH decreases, since a lower pH favours the release of phosphates. Due to a maximum release of phosphorus at pH 1 [1] the discussion of the mobility of metals are concentrated to this pH. The macronutrients are dissolved to a larger extent than the metals. Nearly all phosphorus and calcium is released from the ashes of aluminium rich sewage sludge at pH 1, whereas 50-80% is released from the iron rich ashes. About 40-50% of the other nutrients are also found in the leachate, see Table 5 Part I.

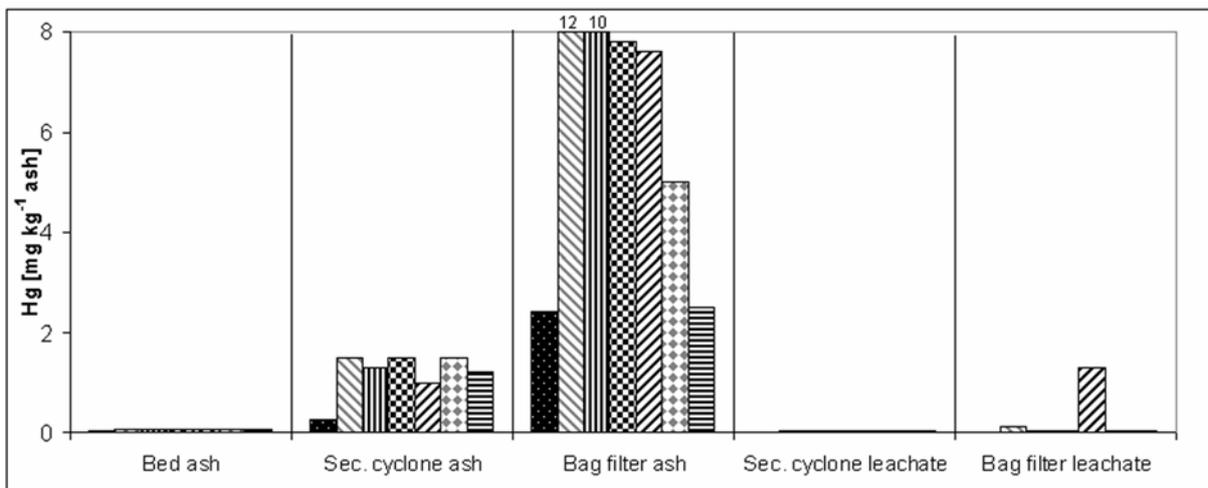
**Table 4:** Trace elements calculated on dry ash leached. Results from pH 1.

Leachate analysis													
trace elements	Fe+no lime		Al+no lime		Fe+limestone		Al+limestone		Fe+hydr. lime		Al+hydr. lime		
[mg kg <sup>-1</sup> dry ash]	sec. cyclone	bag filter	sec. cyclone	bag filter	sec. cyclone	bag filter							
Hg	0.017	0.097	0.017	0.017	0.017	0.018	0.017	1.3	0.017	0.017	0.017	0.018	
Cd	2.6	7.1	2.0	2.6	2.6	1.3	3.0	12	2.1	2.1	1.9	0.7	
Pb	7.7	8.9	8.4	6.5	9.2	6.6	5.6	8.4	7.7	6.6	6.7	3.6	
Cr	2.0	12	2.2	8.0	1.9	7.3	7.0	21	7.8	8.2	8.8	8.7	
Cu	152	103	185	148	221	64	89	71	191	143	164	61	
Mn	666	3480	639	3070	630	1240	978	5340	817	4020	759	1480	
Co	2.7	3.7	2.7	6.0	2.6	2.3	1.2	3.6	0.9	3.8	1.0	2.4	
Ni	4.3	4.9	3.0	8.7	3.6	2.1	3.0	7.5	0.9	4.4	2.9	5.1	
As	7.7	59	7.9	31	5.4	23	7.2	61	8.5	37	10	23	
Sb	1.7	2.1	1.7	2.2	1.7	1.8	1.7	2.5	1.7	2.8	1.7	1.8	
V	31	70	35	118	37	67	54	82	52	108	52	51	
Zn	324	244	269	133	238	73	84	134	52	52	50	27	

Figures 1 and 2 shows the distributions of Cd and Hg in the bed ash, sec. cyclone and bag filter ash (Table 3) and in the leachates from the sec. cyclone and bag filter ashes (Table 4). The bed ash has only low concentrations of the metals, but in addition, nutrient concentrations are low as well [1] and the bed ash mostly consists of bed sand. Most Hg is found in the bag filter ashes after combustion, Figure 2, whereas, Cd, Pb and Cu are more evenly distributed between the secondary cyclone and bag filter, see Figure 1 and Tables 3 and 4. The lower concentrations in the bag filter ashes from the tests Al/Fe+ hydr. lime is due to dilution by the hydrated lime added. Nearly all Hg and most Pb remains in the solid residue after the acid leaching of the ash.



**Figure 1:** Hg concentration in the bed, secondary cyclone and bag filter ashes compared with leachates recalculated on amount of leached ash. Ashes from the test with pure wood were not leached. ■ Wood □ Fe+no lime ▨ Al+no lime ▩ Fe+limestone ▪ Al+limestone ▫ Fe+hydr. lime ▬ Al+hydr. lime



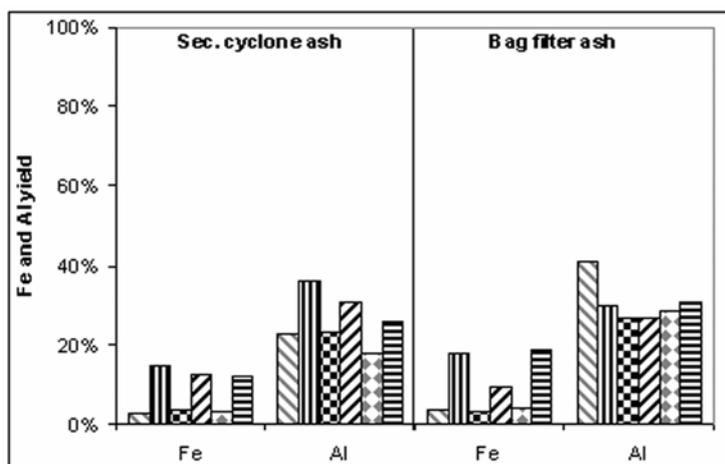
**Figure 2:** Cd concentration in the bed, secondary cyclone and bag filter ashes compared with leachates recalculated on amount of leached ash. Ashes from the test with pure wood were not leached. ■ Wood □ Fe+no lime ▨ Al+no lime ▩ Fe+limestone ▪ Al+limestone ▫ Fe+hydr. lime ▬ Al+hydr. lime

The results for Cd are quite different than for Hg, as shown in Figure 1. There is no big difference between the concentrations of Cd in the different fly ashes studied and most of the Cd is dissolved and found in the leachates. Thus, the leachate has to be treated in order to decrease its concentrations of Cd. However, the benefit is that the solid residue is cleansed from Cd but the aim is to receive leachates that do not contain any trace metals not to clean the solid residue from trace elements.

The different lime addition strategies used in the study did not have any considerable impact on the ash composition besides dilution of the bag filter ash in the tests Fe+hydr. lime and Al+hydr. lime, which had no impact on the leaching results.

The Al in the leachate may be a problem considering the use as fertiliser. Aluminium is known to be highly toxic to plant growth. It is the cation ( $Al^{3+}$ ) that causes poor nutrient and water uptake by inhibiting the root elongation [3; 4]. A fraction of 20-40% of the Al content in the ashes is dissolved in the leachate, Figure 3, and the molar ratio of Al/P extracted per kg of ash are 1 for all the Al-rich ashes and 0.5 for the Fe-rich. Results from X-ray powder diffractometry (XRD) presented in part I [1] show that the Al in the Al-rich ashes is found as  $Ca_9Al(PO_4)_7$  and  $AlPO_4$  and as  $MgFeAlO_4$  in the Fe-rich ashes.

Only 3-4% of the Fe in the Fe-rich ashes is dissolved in the leachate, hence, the iron concentrations are of no concern.



**Figure 3:** Fe and Al yield in leachate from secondary cyclone and bag filter ashes.

▫ Fe+no lime ▨ Al+no lime ▩ Fe+limestone ▪ Al+limestone ▤ Fe+hydr. lime ▥ Al+hydr. lime

### 3.3. Comparison of manure, artificial fertilisers, sewage sludge and ashes as sources of phosphorous to agricultural soil.

Normal contents of trace elements in common fertilisers (liquid and solid manure from pigs, liquid manure from cows, two different artificial fertilisers) are compared with the contents in sludges, ashes and leachates from the present investigation in Table 5, including comparison of an average of 48 Swedish sludges [5; 6].

**Table 5:** Trace element concentrations in various P-sources as g/(ha, year) calculated on a P-supply of 22 kg P (ha, year)<sup>-1</sup>.

Trace elements g (ha,year) <sup>1</sup>	Hg	Cd	Pb	Cr	Cu	Ni
Limits*	1.5	0.75	25	40	300	25
Limits EU**	100	150	15 000	15 000	12 000	300
Sewage sludge series Al	0.61	0.42	13	34	212	10
Sewage sludge series Fe	0.94	0.68	30	24	310	17
Sewage sludge average <sup>1</sup>	0.90	0.98	27	27	320	16
Liquid manure from pigs <sup>2</sup>	0.009	0.28	1.2	6.8	150	4.5
Solid manure from pigs <sup>2</sup>	0.02	0.26	2.1	12	120	6.4
Liquid manure from cattle <sup>3</sup>	0.013	0.11	0.90	2.1	22	4.2
Artificial fertiliser <sup>4</sup>	0.0009	0.005	0.04	0.81	0.15	0.48
Artificial fertiliser <sup>5</sup>	0.031	0.35	0.55	3.3	6.8	1.43
<b>Sec. Cyclone ashes</b>						
Fe+no lime	0.50	1.2	30	20	230	17
Fe+limestone	0.55	0.99	29	17	290	15
Fe+hydr. lime	0.50	1.1	30	18	290	15
Al+no lime	0.48	1.3	16	26	110	10
Al+limestone	0.37	0.85	16	20	190	9.3
Al+hydr. lime	0.42	0.90	14	18	170	8.4
<b>Bag filter ashes</b>						
Fe+no lime	4.5	3.3	29	29	270	21
Fe+limestone	3.1	1.7	39	31	390	33
Fe+hydr. lime	4.8	1.5	34	34	400	26
Al+no lime	5.6	9.0	23	62	130	24
Al+limestone	3.3	1.6	25	25	390	32
Al+hydr. lime	3.3	1.2	21	42	260	31
<b>Leachates from sec. cyclone ashes</b>						
Fe+no lime	0.009	1.4	4.1	1.1	82	2.3
Fe+limestone	0.012	1.1	4.8	1.2	105	1.7
Fe+hydr. lime	0.012	1.7	6.3	1.3	150	2.4
Al+no lime	0.007	1.2	2.2	2.8	35	1.2
Al+limestone	0.007	0.83	3.0	3.1	76	0.34
Al+hydr. lime	0.008	0.90	3.2	4.2	77	1.4
<b>Leachates from bag filter ashes</b>						
Fe+no lime	0.046	3.3	4.2	5.9	48	2.3
Fe+limestone	0.010	1.6	4.0	4.9	91	5.3
Fe+hydr. lime	0.025	1.8	9.4	10	91	3.0
Al+no lime	0.93	8.6	5.7	15	49	5.1
Al+limestone	0.009	1.1	3.5	4.2	75	2.3
Al+hydr. lime	0.026	0.94	5.2	13	89	7.3

<sup>1</sup>Limits, for trace element supply by sludge to farmland, by the Swedish environment protection agency code of statutes 1994:2 (changed 1998:4 and 2001:5)[7].

\*\*Eu Concil direktive of 12 June 1986, 86/278/EEC.

<sup>2</sup>Average of sludge from 48 different wastewater treatment plants in Sweden [5].

<sup>3</sup>[5]

<sup>4</sup>milk producing cows [5].

<sup>5</sup>NPK-S 21-4-7 from Hydro Agri [5].

<sup>6</sup>P20 from Hydro Agri [5].

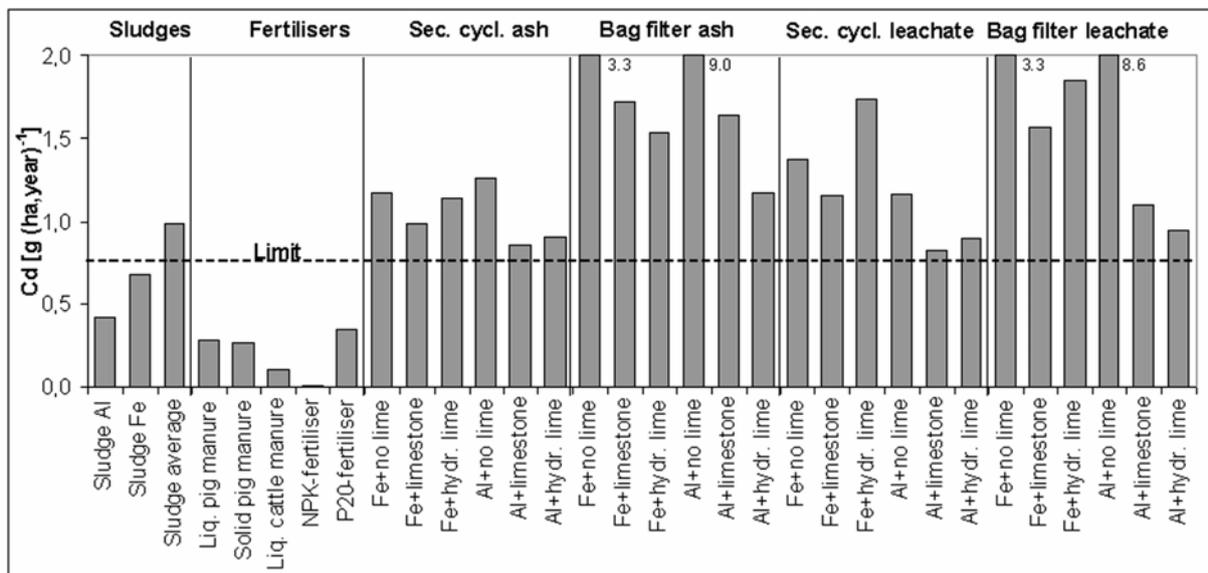
The limits on Cd for artificial fertilisers in Sweden is 44 mg Cd/ kg P<sub>2</sub>O<sub>5</sub> (100 mg Cd/kg P) [2]. There is also a voluntary limit of 22 mg Cd/kg P<sub>2</sub>O<sub>5</sub>, (50 mg Cd/kg P). According to a report to the European Commission [2], the first limitation for Cd in artificial fertilisers in the European Union is proposed to be 60 mg Cd/ kg P<sub>2</sub>O<sub>5</sub>, and a future target limitation is 20 mg Cd/ kg P<sub>2</sub>O<sub>5</sub>. Cadmium standards in EU Member States currently range from 21 to 90 mg Cd/ kg P<sub>2</sub>O<sub>5</sub> [2]. The Cd guaranteed for the fertiliser NPK from Hydro Agri included in Table 5 corresponds to 2.2 mg Cd/kg P<sub>2</sub>O<sub>5</sub> (5 mg Cd/kg P). By Swedish legislation, the maximum dosage of phosphorus per hectare (10,000 m<sup>2</sup>) and year on the most common types of farmland in Sweden is 22 kg, using sewage sludge or stable manure as fertiliser [5; 7]. To prevent long term contamination of the soil, limits have been set for absolute concentrations of some trace elements (Cd, Hg, Cr, Cu, Ni, Pb and Zn) for direct use of sludge, see Table 5. The limit for Cd is 0.75 g/(ha, year). The European Commission have legislations on the same elements, but the permitted concentrations are much more generous, see Table 5.

### 3.4. Ash and leachates as fertiliser

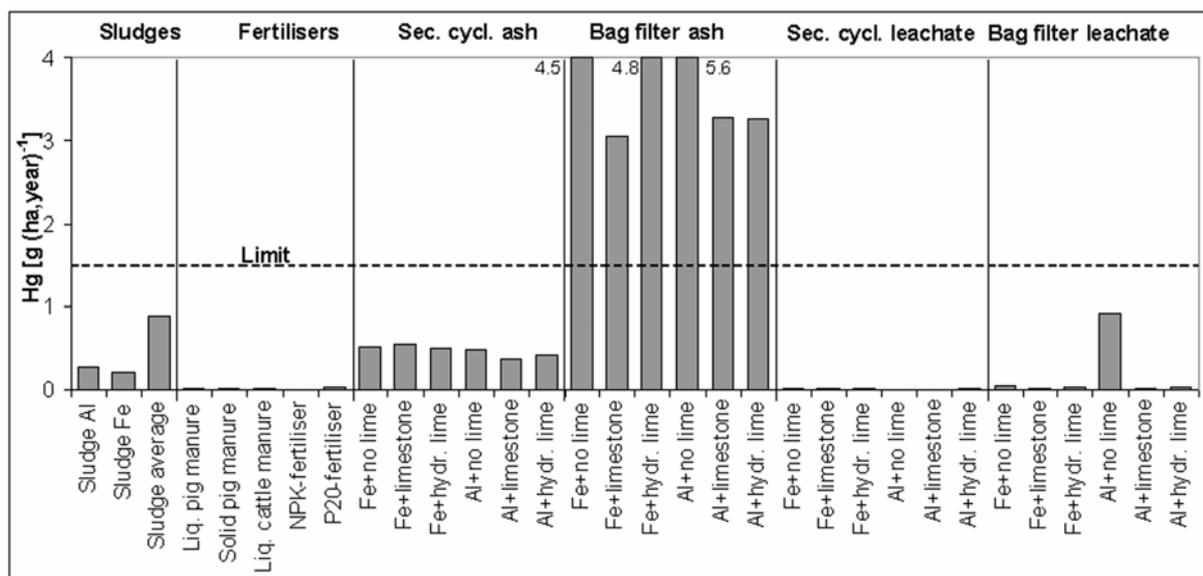
If the ashes studied in this work were to be used directly as a mineral fertiliser on agricultural soil, their Cd contents would be the principal limiting factor based on the limitations (Table 5). All ashes had too high levels of Cd to make a dosage of phosphorous of 22 kg/(ha, year) possible, see Figure 4. If, instead, the Cd concentration in the ashes is taken as a limitation for the amount of ash that could be used, a phosphorus dosage between 13 and 19 kg phosphorus/(ha, year) is possible, using the secondary cyclone ashes, and between 2 and 13 kg phosphorus/(ha, year), using the bag filter ashes in which the Cd concentration varies considerably.

In addition, the contents of Hg, Pb, Cr, Cu and Ni in bag-filter ashes seriously limit their use as mineral fertilisers. For the cyclone ashes Pb is the only metal, besides Cd, that has a content that, in some case, exceeds the limit value. Zinc is not of any concern and excluded from the comparison in Table 5.

The concentrations of trace elements are much lower in the leachates than in the ashes. The results in Table 5 show that the leachates have nearly as low concentrations of trace elements as the traditional fertilisers, cadmium being the only exception. Hence, a decadmiation process is necessary if the leachate is to be used as fertiliser. Figures 4 and 5 illustrates the Cd and Hg supplied to farmland if using sludge, fertilisers, ashes or leachates as phosphorus source. Hg is a good example of the low concentrations of metals in leachates. As seen in Figure 5, only the bag filter ashes have Hg concentrations exceeding the limitations for applications as fertilisers on farmland and the leachates concentrations of Hg is as low as in commercial fertilisers. The results for Pb and Cu are nearly as good as for Hg, Table 5.



**Figure 4:** Concentrations of Cd in sludge, fertilisers, ashes and leachates when supplying 22 kg P (ha, year)<sup>-1</sup>.



**Figure 5:** Concentrations of Hg in sludge, fertilisers, ashes and leachates when supplying 22 kg P (ha, year)<sup>-1</sup>.

The low pH-value of the leachate is a major problem. One way to deal with this would be to lime the soil when spreading the leachate. Liming is anyway necessary on many soils, such as the typical Swedish farmland [7], and it would be possible to increase the limestone dosage. By supplying 5 kg of limestone (CaCO<sub>3</sub>) or 2.8 kg CaO per m<sup>3</sup> leachate, the pH would increase from 1 to approximately 5.5. The increased pH would make the Al<sup>3+</sup> precipitate as insoluble Al(OH)<sub>3</sub>, making the Al content in the leachate less harmful.

### 3.5. Leachate as raw material to the phosphorus industry

The leachate contains dissolved phosphorous in various forms. This phosphorous can be used in the phosphate industry as raw material instead of sedimentary phosphorus rock. The concentrations of trace elements in the leachate are low (Table 4). Most of the Cd is dissolved in the leachates, but still the Cd-concentration is low compared to the concentrations in most phosphate rocks (Table 6) [2]. In the leachates from the secondary cyclone ashes the concentration varies between 16 and 35 mg Cd/kg P<sub>2</sub>O<sub>5</sub> and the leachates from the bag filter ashes are in the same range. Only the leachates from the tests with no lime addition have higher concentrations. In addition, Table 6 also shows that only a minor part of the phosphorus minerals actually are suitable for fertiliser production. In 10% of the available phosphate rocks used as raw material in the fertiliser industry, the Cd concentration is lower than 13 mg/kg P<sub>2</sub>O<sub>5</sub>, and this type of rock is used for the production of low-Cd fertilisers. This type of phosphorus rock is igneous and is only found in Russia, South Africa, Finland and South America. The remaining 90% of the phosphate rocks are sedimentary rocks containing Cd in concentrations ranging from less than 25 to more than 245 mg Cd/kg P<sub>2</sub>O<sub>5</sub> [2]. These rocks, that have to be utilised in a near future, will need some kind of decadmiation process. Consequently, from a raw material point of view, less Cd would have to be removed in a process where the leachates from sewage sludge ash were used as phosphorous source compared to what would be necessary when the sedimentary rocks is to be utilised.

**Table 6:** Cadmium content in leachate analysis in this study and main commercial phosphorus rocks according to different sources [2].

Leachate analysis	Cadmium content [ $\text{mg kg}^{-1} \text{P}_2\text{O}_5$ ]		
	No lime	Limestone	Hydr. lime
Fe Sec. cyclone	27.1	22.6	34.2
Fe Bag filter	65.8	31.0	36.4
Al Sec. cyclone	23.0	16.3	17.7
Al Bag filter	169	21.7	18.6
<b>Phosphate rock</b>			
<b>Igneous</b>	<b>(1)</b>	<b>(2)</b>	<b>(3)</b>
Kola (Russia)	<13	0.3	0.25
Pharlaborwa (South Africa)	<13	0.1	0.38
<b>Sedimentary</b>			
Florida (USA)	23	19.8-32.7	24
Jordan	<30	12.1-28	18
Khouribga (Morocco)	46	17-63	55
Syria	52	13-46	22
Algeria	60	42-62.6	
Egypt	74		
Bu-Cra (Morocco)	100	101-115	97
Nahal Zin (Israel)	100	81-112	61
Youssoufia (Morocco)	121	164.7	120
Gafsa (Tunisia)	137	94	173
Togo	162	164-179	147
North Carolina (USA)	166	125	120
Taiba (Senegal)	203	165-180.6	221
Nauru	243	-	-

Sources:(1) Davister (1996); (2) Botschek and Van Balken (1999); (3)Demandt (1999).

There are several decadmiation processes under development, but none of them are yet commercially viable on an industrial level. For igneous phosphorus rock several methods of calcinations with different additives are presented and for phosphoric acid various processes are suggested, such as co-crystallisation, precipitation with sulphide, ion exchange, ion flotation or solvent extraction [2].

The phosphorus concentration in the pure apatite mineral, i.e.  $\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$ , is 42%  $\text{P}_2\text{O}_5 \text{ kg}^{-1}$ . The purity varies in and between different ores, and in reality the concentrations are below 36%  $\text{P}_2\text{O}_5 \text{ kg}^{-1}$ . Low grade phosphorus rock has concentrations around 10%  $\text{P}_2\text{O}_5 \text{ kg}^{-1}$  [8], i.e. lower than in the secondary cyclone ashes discussed in this work, that have phosphorus concentrations of 13,6%-15,2%  $\text{P}_2\text{O}_5 \text{ kg}^{-1}$  ash. For every tonne of  $\text{P}_2\text{O}_5$  produced from apatite ores, five tonnes of gypsum are generated as a by-product. This gypsum is contaminated with radioactive elements from the ore, such as radon and uranium [9], and hence, not useful as raw material for gypsum board or other applications. The phosphate industry has to deposit the gypsum and make sure that there is no radioactive leakage to the environment.

Recovery of phosphorus from sewage sludge ashes would give no mining costs, no additional by-products or residues. In addition, the removal of Cd that has to be applied would give a decrease of mobilized Cd in the biological system.

#### **4. Conclusions**

The bed ash has low nutrient concentrations and consists mostly of bed material (sand) making it uninteresting from a fertiliser point of view.

The fly ashes have a good nutrient composition, with the exception of N which is lost to the gas phase during combustion. However, the ashes also contain high concentrations of different metals, especially the bag filter ashes, making them unsuitable as fertilisers.

By adopting a leaching process at low pH-values most of the nutrients, such as P, Ca, K, Mg and Mn, can be dissolved and recovered in the leachate. The leachates contain very low concentrations of metals, with the exception of Cd which is fully dissolved. This makes the leachate suitable as fertiliser if the Cd is removed.

The high concentrations of Al may be a problem if the leachate is used as fertiliser. Al as precipitant of P is preferable considering the high solubility of phosphorus in the leachate [1]. Probably Al will be precipitated as insoluble hydroxide when the pH is increased, but if the Al content proves to be detrimental to plants, Fe would be a better alternative as precipitant in the waste water treatment plant.

The Cd in the leachate exceeds the concentrations in fertilisers but not the concentrations in most phosphorus rocks. The main part of the phosphorus rocks in the world contain too high levels of Cd to be used as raw material directly. This means that the phosphorus industry soon will be forced to apply decadmiation processes in the production in order to quote with the future standards of P-fertilisers. If the same decadmiation processes can be used on both phosphorous rocks and the leachate from the present process it will be possible in the future to use fly ashes from incineration of municipal sewage sludge (with leaching as a pre-treatment step). This can be an alternative raw material to sedimentary phosphorus rocks in a step towards future recycling of P-resources to the agricultural sector.

By using phosphorus rich ashes instead of phosphorus rocks there would be no mining costs, no additional rest products, such as radioactive gypsum and the Cd amount in the biological system would decrease.

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