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

Part I: Recovery of phosphorus

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Abstract

Combustion of sewage sludge with subsequent recovery of phosphorous is a relatively new sludge treatment option. In the work described in this paper, recovery of phosphorus by acid leaching of fly-ashes from co-combustion of sewage sludge with wood in a circulating fluidized bed combustor was investigated. The results showed that it is possible to find a pH range (0.5-1) in which it is possible to extract a significant fraction of the phosphorous from these ashes without precipitation of secondary phosphates. The type of flocculation agent used in the waste water treatment plant where the sludge is formed has a significant effect on the phosphorous recovery. Ashes from combustion of sewage sludge that was formed using aluminium sulphate as flocculating agent released nearly all phosphorus at a pH-value of 1. When iron sulphate was used as flocculating agent, this affected the chemistry of the resulting ashes, making phosphorous recovery more difficult. The yield of phosphorous from those ashes was 50-80%. In part II of the project [1] focus is on the trace element release to the leachate. This determines if the leachate can be used directly as a fertiliser or if further removal of trace elements is necessary.

Sludge, biofuel, phosphorus, leaching, co-combustion and fluidized bed

1 Introduction

Apatite minerals are the main raw materials used in the manufacturing of fertilisers. However, the resources of apatite in the world are estimated to last only for about 200 years [2]. Therefore, sustainable methods to recycle the phosphorus used in the society are needed. One way of recycling could be to use the sewage sludge as fertiliser on arable land after a digestion step. The sludge contains considerable amounts of phosphorus, together with organic matter and other plant nutrients such as nitrogen, sulphur and potassium. However, it also contains residues formed from the addition of precipitating agents in the water treatment, organic contaminants and potentially toxic trace elements, such as arsenic (As), mercury (Hg) and cadmium (Cd). These metals may get enriched in the soil in the long run if the sludge is used directly as fertiliser [3].

Another option may be to incinerate the digested sludge and use the ash for fertiliser production. Incineration with heat recovery will lead to a destruction of potentially harmful organic components. The inorganic components are transformed in various ways during combustion. Generally, the non-combustible residues resulting from a combustion unit are named bed ash and fly ash depending on the location at which the ash is collected. Variations in fuel composition, combustion technology and the conditions in the particle separation equipment affect the composition and properties of the different ash flows leaving the combustion unit. Generally, the phosphorus is enriched in the fly ash together with the trace elements. An important issue in the development of sludge ash utilisation strategies is whether the concentration of trace elements is low enough to allow the use of sludge ashes or products thereof as fertilisers [4].

Part of the energy content in the sewage sludge is utilised by digesting the sludge to form biogas (methane + carbon dioxide). However, the volume of residue remaining after biogas production is almost as large as that of the original sludge. In digestion the phosphorous remains in the residues and its recovery require an additional process to separate it. In some cases, when the original sludge has a low degree of contamination, the remaining digested sludge can be used directly for fertilizing purpose.

Recovery of phosphorous from sewage sludge can also be carried out through an extraction procedure. In the KREPRO process [5], sludge is hydrolysed at 140°C and 3.5 bar and phosphorous compounds are dissolved along with other components of the sludge. The phosphorus is recovered as iron phosphate that needs further treatment to become useful [6].

Extraction of phosphorous from the ash remaining after combustion of sewage sludge has also been suggested as a method to recover phosphorus. In the BioCon process [5; 6], the sludge is dried and incinerated with utilisation of the heat from the combustion in the drying step. The ash is ground and extracted with sulphuric acid. The recovery of phosphorus from the liquid phase is carried out using ion exchange techniques. The KREPRO process and the BioCon process both have the disadvantage that the volumes of chemicals used are rather large and none of them has been implemented in a commercial facility.

Recently, a new process has been suggested: the SEPHOS-process [7; 8]. In this process sludge ash is treated with sulphuric acid at $\text{pH} < 1.5$. The solids are separated and the pH in the remaining filtrate is step vice increased to pH 3.5 by addition of caustic soda to separate

phosphorus and heavy metals. By the increased pH the phosphorus is re-precipitated as aluminium phosphate.

The aim of the present work was to develop a simple phosphorous extraction method that could be applied to ash residues from combustion of sewage sludge. This investigation was part of a research project concerning the combustion of sewage sludge in fluidized bed boilers. Since sewage sludge has a low heating value, this was compensated for by adding a supplementary fuel. Wood is a particularly suitable supplementary fuel for sludge combustion since its low ash content causes a negligible contribution to the amount of ashes that have to be treated. The choice of sewage sludges was made with the aim to study how the precipitation agent (ferric sulphate or aluminium sulphate) influences the properties of the sludge ash and the possibility to recover phosphorous from it.

2 Experimental background

2.1 The Boiler.

The 12 MW_{th} circulating fluidized bed (CFB) boiler at Chalmers University of Technology (Göteborg, Sweden) was used for the combustion tests, Figure 1.

Figure 1: The 12-MW_{th} FBC boiler at Chalmers University of Technology. (1) combustion chamber, (2) bottom bed sampling location, (3) hot primary cyclone, (4) particle return leg, (5) cyclone exit duct, (6) secondary cyclone, (7) bag filter.

The combustion chamber (1) has a square cross-section of about 2.25 m² and a height of 13.6 m. The supplementary fuel (wood pellets) is fed to the bottom of the combustion chamber through a fuel chute and the sewage sludge through the particle return leg (4). The mechanically dewatered sludge was supplied by a special sludge pump (rebuilt cement pump) to the particle seal where it was mixed with the hot particles coming from the primary cyclone before it entered into the combustion chamber. Part of the solids carried by the flue gas are separated in the primary cyclone and recirculated back to the combustion chamber (3) through the particle return leg (4) back into the combustion chamber. Primary combustion air is supplied to the bottom of the combustion chamber, and secondary air is injected through a nozzle register located just above the fuel chute. After passing the exit duct of the cyclone (5), the flue gases are cooled to 150°C in the convection path and about 80 % of the coarsest size fraction of the fly ashes are separated from the flue gases in a secondary cyclone (6) and the remaining fraction of fines is captured in a textile bag filter (7). This is not a common arrangement in commercial CFB boilers, but it has the advantage of giving fly ash samples with different size distributions depending on the collection point. This gives the opportunity to study how the particle size distribution influences the characteristics of the ash.

2.2 *The Fuels.*

The base fuel was wood pellets, produced from sawdust from Swedish domestic trees like pine and birch. Wood pellets were chosen as base fuel in the tests because it is a well defined bio fuel with constant properties and low ash content. The additional fuels were two different municipal sewage sludges. In the first set of tests mechanically dewatered sludge from a large waste water treatment plant was used. This plant treats the waste water from a city with 775 000 inhabitants. The second set of tests involved dewatered sludge from a smaller waste water treatment plant in a town of 35 000 inhabitants. Both plants treat waste water from mainly households. On top of this household waste water, various industries are also connected to the sewage system. The two waste water treatment plants produce digested sludge, but employ different precipitation chemicals for phosphorus removal. The large plant utilizes ferric sulphate and the smaller plant aluminium sulphate. Table 1 shows the fuel analyses.

The co-combustion tests were performed with the same boiler load as during monofuel-combustion operation. Since the heating value of sludge is lower than that of wood, the mass flow of sludge was correspondingly larger than that of wood for the same thermal load. With a moisture content of 72-79% and an ash content of 42-46% on dry bases the lower heating value of the sludge becomes too low for mono-combustion. Co-firing with a fuel with higher heating value becomes necessary. Despite the dry and ash-free wood pellets a mixing ratio of 15% (on dry fuel) is an upper limit without sacrificing the same bottom bed temperature for all the tests. Pre-drying of the sludge would allow higher mixing ratios up to 100% sludge.

Table 1: Properties of the sewage sludge and wood pellets.

	Unit	Sewage sludge ¹	Sewage sludge ²	Wood pellets
Precipitation agent		Fe ₂ (SO ₄) ₃	Al ₂ (SO ₄) ₃	—
Proximate analysis				
Water	wt-%, raw	72.0	77.8	8.0
Ash	wt-%, dry	46.0	42.6	0.4
Combustibles	wt-%, dry	54.0	57.4	99.6
Volatiles	wt-%, daf	94.4	85.3	81.7
Ultimate analysis				
C	wt-%, daf	52.6	50.2	50.3
H	wt-%, daf	7.2	7.3	6.1
N	wt-%, daf	5.4	5.0	0.8
S	wt-%, daf	1.4	1.3	0.01
Cl	wt-%, daf	0.1	0.1	0.01
O	wt-%, daf	33.3	36.2	43.5
Heating value (MJ kg⁻¹)				
HHV, daf	MJ kg ⁻¹	20.5	19.5	18.8
LHV, raw	MJ kg ⁻¹	2.78	2.24	17.2
Ash analysis				
K	g kg ⁻¹ dry ash	13.3	10.7	82.0
Na	g kg ⁻¹ dry ash	7.28	6.9	6.7
Al	g kg ⁻¹ dry ash	73.3	193	12.2
Si	g kg ⁻¹ dry ash	127	115	79.7
Fe	g kg ⁻¹ dry ash	160	42.1	20.9
Ca	g kg ⁻¹ dry ash	40.0	38.0	164
Mg	g kg ⁻¹ dry ash	9.9	5.3	26.4
P	g kg ⁻¹ dry ash	58.6	61.3	12.7
Ti	g kg ⁻¹ dry ash	4.4	9.6	0.7

(1)= large plant; (2)= small plant.

daf= dry and ash free, raw= as received

2.3 Experimental Procedure.

Six combustion test series were carried out, each consisting of three cases. Each series included a reference case when only wood pellets were fired. In the second series, 7% of the total dry mass of the fuel was sludge, and in the third series the sludge fraction was 15%. The investigation about recovery of phosphorous was focussed on the ashes from the tests with 15% sludge. In this paper, the tests are named after the origin of the sludge: Fe for sludge precipitated with ferric sulphate and Al for sludge precipitated with aluminium sulphate, with a suffix relating to the lime addition strategy. In the series “Fe+no lime” and “Al+no lime”, no lime was added to the combustion chamber and the emissions of sulphur dioxide (SO₂) and hydrogen chloride (HCl) reached values that reflect the concentrations of sulphur and chlorine in the fuel. In the series “Fe+limestone” and “Al+limestone”, limestone (CaCO₃) was added to the bed to capture sulphur as CaSO₄, and in the series “Fe+hydr. lime” and “Al+hydr. lime”, hydrated lime (Ca(OH)₂) was injected into the flue gas upstream of the bag filter to investigate its effect on ash composition and emissions of HCl and SO₂. Table 2 summarizes the test conditions.

Table 2: Test matrix.

Test names	Precipitation agent	No Lime	Lime to bed	Hydrated lime to bag filter
Fe+no lime	Fe ₂ (SO ₄) ₃	X		
Al+no lime	Al ₂ (SO ₄) ₃	X		
Fe+limestone	Fe ₂ (SO ₄) ₃		X	
Al+limestone	Al ₂ (SO ₄) ₃		X	
Fe+hydr. lime	Fe ₂ (SO ₄) ₃			X
Al+hydr. lime	Al ₂ (SO ₄) ₃			X

The boiler operating conditions are presented in Table 3. They were chosen to represent a typical CFB boiler and kept similar in all tests. After each change of fuel composition and lime addition method an equilibration time of 12 hours [4] was allowed before the solid samples for analysis were collected, in order to establish steady-state concentrations of the trace elements. In each test the following samples were taken (for locations see Figure 1); wood pellets and sludge before entering the boiler, bottom bed material (2), ash from the cyclone leg (4), ash collected in the secondary cyclone (6) and bag filter ash (7).

Table 3: Operating conditions [9].

	Unit	Wood/Sludge ¹ Fe+no lime	Wood/Sludge ² Al+no lime	Wood/Sludge ¹ Fe+limestone	Wood/Sludge ² Al+limestone	Wood/Sludge ¹ Fe+hydr. lime	Wood/Sludge ² Al+hydr. lime
Load, MW _{th}	MW _{th}	6.1	6.0	6.0	6.4	6.0	6.0
Bed temp.	°C (bottom)	848	843	852	850	850	848
Bed temp.	°C (top)	866	880	852	856	882	870
Exit temp. of after combustion chamber	°C	849	855	865	861	828	834
Total riser pressure drop	kPa	6.4	6.4	6.5	6.3	6.6	6.3
Calcium addition molar ratio Ca/S		0.0	0.0	1.7	2.7	4.6	5.0
Ca/S with Ca in fuel included		1.9	1.9	3.7	4.7	6.3	7.2
Excess air ratio		1.2	1.2	1.2	1.2	1.2	1.3
Primary air flow/total air flow	%	57	50	59	59	57	57
Superficial flue gas velocity at top of riser U _{top}	m s ⁻¹	5.3	5.2	5.2	5.4	4.9	5.0

(1)= Large plant; (2)= Small plant.

2.4 Chemical analyse.

The contents of moisture and combustibles in the fuels and ash samples were determined using a LECO MAC 400 Proximate Analyzer 785-700 system. Ultimate analysis was performed by using an external accredited laboratory (SP, Swedish Testing and Research Institute). X-ray Fluorescence (XRF) was used for the determination of the main ash elements.

2.5 Ash extraction procedure.

All ash extraction experiments were carried out at room temperature in a 718 pH-STAT Titration unit (Metrohm Ltd.) with continuous pH measurement and automatic compensation for the release of alkaline components by addition of sulphuric acid. The investigated pH-range was pH 0.5-2.5. Each experiment was started with 0.4 g of ash and 60 ml of water, i.e. a mass ratio of solid to liquid of 1:150. The additions of acid required to keep the pH at the chosen level was logged. The experiments had duration of 90 minutes, based on experience from pre-tests. In

addition, the length of this extraction time was considered relevant for real processes. After the leaching experiment, the slurries were separated into a solid part and a leachate by filtering through a membrane filter with a pore size of 45 μm . A second series of experiments were carried out in the same way as described above but with less liquid giving a mass ratio of solids to liquid of 1:8.

The choice of sulphuric acid as the extraction medium was based on the fact that there are not many soluble sulphate complexes of trace metals formed. Hydrochloric acid would add chloride ions to the leachate and these could form soluble complexes with most heavy metals, thus increasing the amount of metals in solution. Yoshizaki and Tomida [10], studied removal of trace metals from sewage sludge by both hydrochloric acid and sulphuric acid in the pH-range 0.8-1.5. They found that at room temperature, leaching during 1 hour gave a larger release of trace metals with hydrochloric acid than with sulphuric acid. The most significant difference concerned Pb, where HCl released 100% and H_2SO_4 just 37% of the available Pb in the sludge [10].

The content of PO_4^{3-} ions in the leachate was determined by a colorimetric method with a molybdenum reagent as well as by an Ion Chromatographic (IC) method. The total phosphorus content was determined by means of Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES). The contents of main elements in the leachates were also determined by using ICP-OES.

2.6 Chemical equilibrium calculations.

Calculations of solubility equilibria in conditions similar to those applied in the leaching experiments were made using the Medusa/ Hydra program and the database version 31 [11]. The components considered were: aluminium, iron, phosphorus, calcium and potassium. All soluble and non-soluble complexes available in the database were allowed, provided that the chemistry behind their presence was reasonable.

2.7 Electron Scanning Microscopy.

The appearance and element distributions of ash samples and solid residues remaining after leaching and filtration were examined by Scanning Electron Microscopy (SEM) including Energy Dispersive X-ray Fluorescence analysis (EDX). The electron beam induces emission of element specific X-ray wave lengths and by programming the detector to scan the specimen surface, element “maps” can be obtained.

2.8 Mineralogical analyses by X-ray powder diffractometry.

The mineralogy of the ash samples was studied by X-ray Powder Diffraction (XRD), for the identification of the crystalline components. The instrument used in this work was a Siemens D5000 Powder Diffractometer applying Cu characteristic radiation and a scintillation detector. The Joint Committee of Powder Diffraction Standards database was used for identification of crystalline compounds. This method allows the identification of crystalline components present in amounts larger than 1-2% (w/w).

3 Results and Discussion

3.1 Influence of sludge type and lime addition strategy on the ash flows

The accuracy of the ash mass flow measurements was estimated by a total mass balance of solid material over the fluidized bed combustor under steady-state operating conditions. The input mass flow of fuel ash, lime and silica sand was compared with the exiting mass flows of bed and fly ash [12]. The release of volatiles from the ashes was neglected, but the conversion of lime and unburned char in the exit flows was taken into account. The resulting ash recovery fraction (ash out ash in⁻¹) varied between 0.90 and 1.20, which is good, considering the size of the boiler, see Table 4.

Table 4: The ash flows and ash recovery fraction for the different tests.

Unit	Bed ash kg h ⁻¹	Sec. cyclone ash kg h ⁻¹	Bag filter ash kg h ⁻¹	Ash recovery Fraction ash out ash in ⁻¹
Wood	17.4	4.9	3.6	0.87
Fe+no lime	19.7	79.2	8.4	1.04
Fe+limestone	27.5	94.3	10.7	1.05
Fe+hydr.lime	11.3	80.7	36.0	1.22
Al+no lime	46.9	45.8	5.7	1.03
Al+limestone	37.4	71.9	9.2	1.12
Al+hydr.lime	30.2	52.4	27.5	0.90

The distribution of non-combustibles between bed and fly ash fractions in the combustion tests included in this work is given in Table 4. The bed ash flow is higher when combusting sludge precipitated with aluminium sulphate than when sludge precipitated with iron sulphate was used. The increased amount of ash introduced by the iron based sludge ends up in the cyclone ash, a fact that indicates formation of smaller ash particles than in case with the aluminium based sludge. The particle size distributions of typical ash samples are shown in Figure 2 [13]. The much smaller particle sizes of ash collected from the bag filter (about 1/10th of the sizes of secondary cyclone ash particles) is clearly seen. The dominant ash flow in all tests is collected in the secondary cyclone, except for the test “Al+no lime” Table 4, in which the bed ash flow is similar to the flow of cyclone ash, and in the reference test “wood” in which the bed ash flow is dominating. The addition of hydrated lime to the bag filter increases the bag-filter ash flow by approximately a factor three.

Figure 2: Particle size distribution (% by number) for typical ashes from combustion cases Fe+no lime. (A) secondary cyclone ash, (B) bag filter ash. Lines- cumulative, bars – fractional distribution [13].

3.2 Ash compositions.

Table 5 gives the main elements concentrations in the three ash flows. Combining these concentrations with the ash flows of Table 4 gives the outgoing P-flows, Figure 3. From Figure 3 it is evident that the dominating outgoing P-flow is that with the secondary cyclone ash. Leaching of the bed ashes is therefore not relevant. This means that if phosphorous recovery is the focus then the secondary fly ash should be studied in more detail with the bag filter ash as a comparison.

Table 5: Main elements in the fly ashes.

Ash analysis main elements [g kg ⁻¹ dry 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	sec. cyclone	bag filter	sec. cyclone	bag filter	sec. cyclone	bag filter
K	22	36	41	48	13	19	17	15	16	8.4	16	5.0
Na	8.1	7.3	10	8.0	7.3	7.0	7.0	5.0	7.0	3.0	8.0	3.0
Al	83	63	170	120	73	83	180	130	79	36	210	58
Si	130	95	130	88	130	110	11	92	130	560	120	45
Fe	180	180	41	29	160	190	46	77	180	81	47	21
Ca	49	99	51	130	40	100	81	140	65	330	55	380
Mg	10	24	18	28	9.4	19	7.0	18	11	14	8.2	13
P	66	57	60	39	60	56	59	51	66	23	63	17
Ti	5.0	4.2	9.0	9.0	4.2	5.5	9.0	6.0	4.0	20	9.3	2.1
S	2.0	18	3.0	35	12	17	4.0	22	65	16	2.0	18

The phosphorous is not retained in the bed ash, but follows the incombustible residues from the fuel to the cyclone and the filter. In addition, the results in Table 5 show that the iron and aluminium remaining from the precipitation chemicals, as well as most of the remaining main elements of the fuel ash, can be found in the cyclone and filter ashes.

Figure 3: Phosphorus flows in the different ashes as kg/h for the tests with 15% sludge as co-fuel.

▨ Fe+no lime ▨ Al+no lime ▨ Fe+limestone ▨ Al+limestone ▨ Fe+hydr. lime ▨ Al+hydr. lime

Depending on precipitation agent, the original form of phosphorus in the sludge prior to digestion is FePO_4 or AlPO_4 . According to chemical equilibrium calculations [14], the phosphorus combines with calcium to form $\text{Ca}_3(\text{PO}_4)_2$ during combustion of both sludge types, if Ca is available.

A comparison of the molar ratios between Ca and P in the ash parts of the sludges and in the ashes shows that calcium is enriched relative to phosphorous during ash formation (Table 6). However, the cyclone ash generally does not contain enough calcium to indicate that the phosphorous would be present in $\text{Ca}_3(\text{PO}_4)_2$ only. The theoretical molar Ca/P ratio would in that case have to be 1.5. The bag filter ashes, on the other hand, contain a surplus of calcium (except for the case Fe+no lime). The iron in iron sulphate treated sludge theoretically tends to form $\text{Fe}_2\text{O}_3(\text{s})$ during combustion, whereas combustion of aluminium based sludge theoretically would result in a partial transformation of the aluminium phosphate to different aluminium silicates. Some aluminium could also be associated with phosphate in the ash, especially if there is a lack of Ca [14].

Table 6: Ca to P ratios in the sludges and ashes studied

	Fe-based sludge		Fe+no lime		Fe+limestone		Fe+hydr. lime	
	Ash part of the sludge		sec. cycl.	bag filter	sec. cycl.	bag filter	sec. cycl.	bag filter
molar ratio								
Ca P ⁻¹	0.54		0.81	1.4	1.17	1.65	1.01	7.73
	Al-based sludge		Al+no lime		Al+limestone		Al+hydr. lime	
	Ash part of the sludge		sec. cycl.	bag filter	sec. cycl.	bag filter	sec. cycl.	bag filter
molar ratio								
Ca P ⁻¹	0.48		0.62	3.14	1.17	2.21	0.71	6.7

Results from the qualitative X-ray powder diffraction analysis, carried out for the original ash samples, are shown in Table 7. Haematite (Fe_2O_3) was identified in all the Fe-rich ashes but also

small amounts of MgFeAlO_4 . The phosphate found in these ashes contained both calcium and iron. This indicates that iron may not only be present as haematite after the combustion, a result given by the equilibrium calculations. Small amounts of haematite were found also in the bag filter ash “Al+limestone”. Some of the calcium was found as calcium sulphate (product of the sulphur capture) and calcium carbonate (the original limestone that has not calcinated to CaO), but most calcium was found together with the phosphate, which in this case was a calcium aluminium phosphate or calcium iron phosphate.

Table 7: Crystalline compounds found in ash samples from the different tests. X= more and x=less.

Ash sample	SiO_2	Feldspars	CaCO_3	Ca(OH)_2	CaSO_4	Fe_2O_3	MgFeAlO_4	Phosphates	Others
Sec. cyclone ash									
Fe+no lime	X	x				X	x	$\text{Ca}_9\text{Fe(PO}_4)_7$	
Fe+limestone	X	x	x		x	X	x	$\text{Ca}_9\text{Fe(PO}_4)_7$	
Fe+hydr. lime	X	x				X		$\text{Ca}_9\text{Fe(PO}_4)_7$ trace	MgSiO_3
Al+no lime	X	x	x						
Al+limestone	X	x	x		x			Possibly AlPO_4	
Al+hydr. lime	X	x			x			$\text{Ca}_9\text{Al(PO}_4)_7$	
Bag filter ash									
Fe+no lime	x				x	X	x	$\text{Ca}_9\text{Fe(PO}_4)_7$	$\text{K}_{0.4}\text{Na}_{0.6}\text{Cl}$
Fe+limestone	x		x		x	X	x	$\text{Ca}_9\text{Fe(PO}_4)_7$	
Fe+hydr. lime	x			X	x	X	x	$\text{Ca}_9\text{Fe(PO}_4)_7$ trace	MgSiO_3 , $\text{K}_{0.4}\text{Na}_{0.6}\text{Cl}$
Al+no lime	x		x		X			$\text{Ca}_9\text{Al(PO}_4)_7$	
Al+limestone	x	x	x		X	x		$\text{Ca}_9\text{Al(PO}_4)_7$	
Al+hydr. lime	x		x	X	x			$\text{Ca}_9\text{Al(PO}_4)_7$ trace	$\text{Ca}_3\text{Al}_2\text{O}_3$

3.3 Release of phosphorous to the liquid phase in acid extraction.

When the ashes were leached at pH 2.5 only 22-30% of the phosphorus in the secondary cyclone ashes and 35-60% of that in the bag filter ashes was dissolved (Figure 4). By decreasing the pH to 1, the phosphorus yield in the leachate of the secondary cyclone ash from sludge precipitated with aluminium sulphate increased to 74-95%, whereas 49-65% of the phosphorous in ashes from iron based sludge could be extracted. Generally, at pH 1, the phosphorus was easier extracted from the Al-rich ashes than from the Fe-rich ashes. At pH 2.5 there was no significant difference observed between the ashes from the different cases.

Figure 4: P-yield in leachate from secondary cyclone and bag filter ashes leached at different pH. Only the ashes from iron based sludge were extracted at pH 0.5. ■ Fe+no lime ▨ Al+no lime ▩ Fe+limestone ▪ Al+limestone ▫ Fe+hydr. lime ▬ Al+hydr. lime

The results from analysis of the leachate produced by extraction of both cyclone ash and bag filter ash at pH 1 are presented in Table 8.

Table 8: Main elements calculated on dry ash leached. Results from pH 1.

Leachate analysis												
main elements	Fe+no lime		Al+no lime		Fe+limestone		Al+limestone		Fe+hydr. lime		Al+hydr. lime	
(g/kg dry ash)	sec. cyclone	bag filter	sec. cyclone	bag filter	sec. cyclone	bag filter	sec. cyclone	bag filter	sec. cyclone	bag filter	sec. cyclone	bag filter
K	10	26	31	45	7.7	10	9.0	7.2	7.0	11	6.6	9.8
Na	1.9	3.8	3.7	4.1	1.4	2.6	1.9	1.6	2.2	1.2	1.9	1.5
Al	19	26	63	37	17	22	56	35	14	10	53	18
Si	4.3	13	26	34	3.9	11	14	19	3.6	8.2	14	13
Fe	5.1	6.4	6.1	5.2	5.7	5.8	5.7	7.2	5.8	3.2	5.7	4.0
Ca	43	85	45	134	59	77	85	115	42	154	43	125
Mg	5.1	10	4.0	15	5.4	7.5	3.0	5.9	6.0	6.9	3.1	6.9
P	41	47	56	32	39	36	56	42	32	15	47	15
Ti	0.15	0.24	0.28	0.55	0.12	0.24	0.15	0.26	0.11	0.20	0.15	0.33

In order to investigate whether the phosphorus could be extracted to a greater extent from iron based sludge ashes even more acidic conditions were used in some additional leaching tests where the pH-value was decreased to only 0.5. In Figure 4 these results are included. Only the bag filter ash “Fe+hydr. lime” gave an increased phosphorus yield, 85% as compared to 68% at pH 1 (Figure 4). For the secondary cyclone ashes the release of phosphorous was still fairly poor using the lower pH-value. This is consistent with the results obtained by Matsuo [15] when investigating how an addition of ferric chloride, FeCl_3 , to the sludge, prior to combustion, could be used to prevent phosphorus release from the sludge ash in a land fill. However, it was not reported by Matsuo [15], how the iron chemically stabilized the phosphorus.

There are no clear tendencies in the results showing that the solubility of phosphorus can be related to the supply of limestone to the bed or to hydrated lime added to the bag filter; only

minor effects of the lime were observed. This means that active sulphur capture strategies (limestone to the bed or hydrated lime to a bag filter) can be adopted without disturbing an active phosphorous recovery strategy such as leaching at low pH-values using aluminium sulphate as precipitation agent at the waste water treatment plant.

3.4 *Equilibrium calculations.*

Equilibrium calculations using the Hydra/Medusa program package [11] showed that three solid compounds may influence the recovery of phosphorus in the liquid phase: $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaHAl}(\text{PO}_4)_2$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. These compounds may precipitate from the solution in different pH intervals, thus preventing the phosphorus from ending up in the extraction product. The ferric phosphate could form at a pH below 4.2, the calcium aluminium phosphate in the pH range 4.2 to 6 and hydroxyl apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) at a pH level over 6. This means that, theoretically, there is no pH window where the phosphorous extraction would not be disturbed by precipitation of a solid phosphate. The amount of phosphorous bound in these solid compounds depends on the amounts of Fe^{3+} , Al^{3+} and Ca^{2+} available in the water phase and pH. The interference from precipitation would be most serious for ash from iron based sludge, but the ash from aluminium based sludge would also be affected since it contains significant amounts of iron as well (Table 1). However, the experimental results showed that phosphorous could actually be extracted and kept in solution. In addition, the amount of ferric iron released to the leachate was very low in all experiments: less than 5% for ashes from iron based sludge and less than 20% for the aluminium based.

In the present case, the dominant iron compound in the ashes is haematite (Fe_2O_3). Haematite is theoretically not soluble at pH above 1.5, but it is soluble at lower pH. The low concentration of iron in the leachates indicates that the dissolution kinetics of the hematite present in the ashes is too slow and consequently the amount of ferric ions available for formation of solid $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ is small. This is favourable for the extraction of phosphorous.

This is illustrated in Figure 5, where theoretically possible concentrations of dissolved Al, Fe, Ca and P are compared with those found in experiments on the “Fe+no lime” secondary cyclone ash at pH 0.5, 1 and 2.5.

Figure 5: Comparison of the calculated (equilibrium) and experimental (measured) concentrations of dissolved compounds at pH 0.5, 1 and 2.5. Ash sample “Fe+no lime” secondary cyclone.

■ Calc pH 0.5 ▨ Exp pH 0.5 ▩ Calc pH 1.0 ▤ Exp pH 1.0 ▦ Calc pH 2.5 ▧ Exp pH 2.5

Both iron and aluminium were found in much lower amounts than the theoretical in the leachates, whereas the calcium content approximately corresponded to the equilibrium content and the phosphate content was much higher than theoretically expected.

The solubility of aluminium compounds present in the ashes is important, not only for its possible reactions with phosphate, but also for its possible effect on the environment. Aluminium ions (Al^{3+}) released to a soil could have detrimental effects on plants growing on that soil. The aluminium ions will probably be bound in different minerals or precipitate as aluminium hydroxide in suitable pH ranges, but there is a risk of plant uptake at certain conditions [16].

The investigation of the untreated and extracted ashes with the electron microscope indicated both physical and chemical transformations during leaching. Figure 6a shows the electron microscopy pictures of the original ash “Fe+limestone” and Figure 6b the ash after leaching. The corresponding element maps are given in Figure 7a and 7b. From both these sets of figures it is evident that the original ash consists of well defined, individual particles whereas the leached ash contains agglomerated clusters of small particles sticking to the surfaces of the larger ones.

a) Original ash

b) Leached ash

Figure 6: Electron microscopy pictures comparing the cyclone ash (a) “Fe+limestone” in its original form and (b) after leaching.

Figure 7a: SEM-EDX element maps for the cyclone ash “Fe+limestone”.

Figure 7b: SEM-EDX element maps for the solid residue after leaching of the cyclone ash “Fe+limestone” at pH 2.

The element maps support the findings of iron oxide and calcium iron phosphate using XRD analysis (Table 7). These compounds seem to survive the leaching procedure (Figure 7b) to some extent. This makes sense in the light of the low leachability of Fe showed in Figure 5. The experimental results show that combustion of the sewage sludge followed by extraction of the ashes to recover phosphorous is a better procedure than using the sludge directly as a soil fertiliser considering the possibility to exclude aluminium from the flow of metals to the agricultural soil. The chemistry of trace metals in ash from sewage sludge and wood will be further discussed in part 2 [1] of the project.

3.5 Comparison with other methods of phosphorous recovery from sewage sludge.

As mentioned in the introduction, there are a few other processes proposed for recovery of phosphorus from sewage sludge or from ashes from combustion of sludge: the BioCon-process recovering phosphorus and iron sulphate from incinerated sewage sludge and the KREPRO and Cambi/KREPRO processes in which phosphorous is extracted by acid from hydrolysed sludge [5; 6]. Due to large consumption of chemicals in combination with high energy demand, none of these processes are economically feasible at present. Hultman and co-workers [17] made a theoretical comparison of different techniques for recovery of phosphorus applied to a specific waste-water plant. They suggested solutions and compared estimated consumptions of chemicals, based on data from pilot-plants where the BioCon and KREPRO processes have been tested. In these processes most compounds in the ash or sludge are dissolved, in contrary to the method used in the present study, where the purpose is to find a pH at which only the phosphorus compounds dissolve. The sludges compared in the present study and in the study of Hultman et al. have approximately the same concentration of phosphorus and the recovery is estimated to

80% in both cases. The calculations of Hultman et al. allow a comparison of BioCon and the method used here, as presented in Figure 8. The figure shows the amount of chemicals, based on the number of acid equivalents (represented by H^+), required to neutralise the alkalinity of a certain mass of ash and to transfer the cat ions in Table 9 into the water phase.

Table 9: The H^+ required for dissolving (hydrolysis) of different compounds containing Fe, Al, Ca and Mg represented by the corresponding hydroxides.

	ekv. H^+ /mol		ekv. H^+ /mol
$Fe(OH)_3$	3	$Ca(OH)_2$	2
$Al(OH)_3$	3	$Mg(OH)_2$	2

Figure 8: Calculated chemical consumption for Henriksdal ash [17] and calculated chemical consumption for the ashes in this study if using the BioCon-process (Black symbols) compared with the actual chemical demand in this study (Open symbols). One equivalent is one mole of H^+ .

Hultman et al. estimated the amount of chemicals needed to dissolve Ca, Fe, Al and Mg for Henriksdal [17]. This case, completed by the cases with Fe-rich ash and Al-rich ash from the present study, is shown by the black squares in Figure 8. The corresponding consumption of chemicals for the present technique is shown as open triangles. The final products obtained with the BioCon-process are phosphoric acid, iron chloride, potassium bisulphate and sand, whereas the products of the present technique are not refined to that extent.

If applying the ion-exchange technology of the BioCon-process on the leachate from the present technique, the amount of chemicals needed would still be much lower than in the BioCon process.

Recently, a new process has been suggested: the SEPHOS-process [7; 8]. That process is the one most corresponding to the present work. In the SEPHOS-process sewage sludge ash is treated with sulphuric acid at $pH < 1.5$, both parameters similar to what is tested in this study. The solid residues are separated and the pH of the filtrate is stepwise increased to 3.5 by addition of caustic soda. The elevated pH causes a precipitation of aluminium phosphate diluted with most of the trace metals dissolved in the initial step. Due to lack of information about this process a comparison with the other processes in Figure 8 is not possible.

4 Conclusions

The results obtained in this work showed that the phosphorus is more concentrated in the fly ash than in the bed ash. Generally, 75-98% of the phosphorous leaving the CFB boiler is retained in the fly ash. Therefore, the development of a process for recovery of phosphorous should be focused on fly ash.

The phosphorus in the ash is easier to extract if the precipitation agent in the water treatment plant is aluminium sulphate instead of iron sulphate. The pH-value has to be low (about 1) to achieve above 50% yield of phosphorus in the leachate from ashes of sludge precipitated by Fe in short-time leaching, suitable for an industrial process. A similar pH gives a phosphorus yield of 75 to 95% from ash originating from Al-precipitated sludge. The low pH suitable for leaching has to be increased if the leachate is to be used as fertiliser.

The benefits of the present method are 1) co-combustion of sewage sludge and wood that makes it possible to use the calorific value of the sewage sludge for heat production, 2) the destruction of organic toxic compounds and 3) the phosphorus recovery technique with low consumption of chemicals that allows utilisation of the phosphorus in the ashes.

Moreover, the performance of this method is not affected by the common sulphur capture strategies employed in fluidized bed boilers.

Acknowledgments

This work was performed with financial support from the Swedish Energy Administration and the KK-Foundation. The practical performance of the tests were carried out with support from the operating staff of Akademiska Hus AB and the research staff at the Department of Energy and Environment division of Energy Technology Chalmers University of Technology which is gratefully acknowledged.

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