

# PHOSPHORUS RECOVERY FROM SEWAGE SLUDGE – TWO-STEP LEACHING PROCESS WITH ACID AND BASE

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## ABSTRACT

In earlier studies sludge incineration ash and SCWO-residues have been leached with acid and base. Acid leaching gives a high degree of recovery but releases besides phosphate also the main part of other metals (including heavy metals). Leaching with base (NaOH) gives a less dissolution of metals however with lower degree of recovery (up to about 50 %). When leaching with base, the calcium content in the sludge probably binds phosphorus as calcium phosphate.

In this study a two-step leaching process has been tested. Ash and SCWO-residues are in the first step leached with acid, with the main purpose to dissolve calcium. After leaching experiments with hydrochloric acid and acetic acid at different pH-levels from 3 to 6 leaching with acetic acid at pH-level 4 was chosen as the first leaching step. With a weak acid the dissolution reaction can occur at the desired pH-level without limitation caused by insufficient amount of acid. In the second leaching step the solid products was leached with 1 M sodium hydroxide. Two-step leaching gave for SCWO-residue 23% higher leaching of phosphate and for sludge incineration ash 11 % higher leaching. However, aluminium was also dissolved in the second leaching step, and has to be separated from the phosphate in a third process step.

## KEYWORDS

Acid, Base, Leaching, Phosphorus recovery, Sewage sludge

## INTRODUCTION

Leaching with acid and base is a promising method for phosphorus recovery from waste water treatment of sewage sludge. Phosphorus recovery from SCWO, Super Critical Water Oxidation, residues by leaching with acid and base in order to recover phosphorus from sludge has been studied in experimental works (Hultman et al, 2002, Hultman and Löwén, 2001, Levlin et al., 2002, 2004a, 2004b, Stark, 2002, Stark and Hultman, 2003) at the department of Land and Water resources Engineering, KTH.

Alkaline leaching is a good alternative since it gives a phosphorus product with a lower metal contamination. Leaching with acid dissolves efficiently most metals and phosphorus. Most metals are more insoluble in bases than in acids, and leaching with base gives a phosphorus product with a lower contamination of metal. However, leaching with acid gives a higher release of phosphorus than leaching with base. When leaching with base, the calcium content in the sludge binds phosphorus as calcium phosphate, decreasing the degree of phosphorus release. At leaching SCWO-

residues with sodium hydroxide residues from Karlskoga sludge with 3% calcium released 90% of the phosphorus content, while residues from Stockholm sludge with 8% calcium only released 65% (Stendahl and Jäfverström, 2003). To increase the amount of leached phosphate at alkaline leaching the calcium can in a 2-step process be dissolved by acid at about pH-level 4 before the alkaline leaching (Levlin and Hultman, 2005).

In a two-step process the solid products are in the first step leached with acid at a pH-level 4, with the main purpose to dissolve calcium. For this step sulphuric acid ( $H_2SO_4$ ) cannot be used since calcium sulphate has a very low solubility. Acids that have been used in this study are hydrochloric acid (HCl) and acetic acid ( $CH_3COOH$ ). The acid constants ( $pK_a$ ) for these acids (Hägg, 1969) are:

Sulfuric acid ( $H_2SO_4$ ):	$pK_a = 1.99$
Hydrochloric acid (HCl):	$pK_a = -7$
Acetic acid ( $CH_3COOH$ ):	$pK_a = 4.76$

The leaching result is determined by two parameters, the pH-level and the amount of acid. The pH-level decides which compounds that are soluble and therefore dissolved and the amount of acid how much of the compound that is dissolved. To achieve a pH-level of 4 only 0.0001 M acid is needed, which is a too small amount of acid to dissolve all calcium in the sample. A much higher amount of acid is needed for dissolution than for creating the pH-level. The best way to perform the dissolution with a strong acid, as HCl, would be to use a pH-state. A pH-state is an instrument, which measures the pH-level continuous and maintains the pH-level by adding acid in the same rate as the acid is consumed. In this work a given amount of acid is added and the pH level is measured after the dissolving reactions has occurred. By using different amount of acid this is a possible way to measure the dissolution at different pH-level. Figure 1 shows a sketch of the influence of pH on adding strong acid (HCl) and weak acid (acetic acid). The amount of added HCl acid minus the amount of acid for making the pH-level will be the amount of acid used for dissolution reactions. However if the calcium dissolution rate is slow the pH-level will first be very low and increase as the acid is consumed by dissolving calcium. Other reactions may thereby occur initially before the pH-level increases. By using acetic acid, which is a week acid, a large amount of acid can be added without an initial decrease of the pH-level. The acid will release hydrogen ions until the pH-level drops below the  $pK_a$  value. The larger amount of acid will make that the dissolution reaction can occur at the desired pH-level without limitation due to insufficient amount of acid. With weak acid, is the amount of added acid minus the amount of acid for making the pH-level, not the amount of acid used for dissolution reactions.

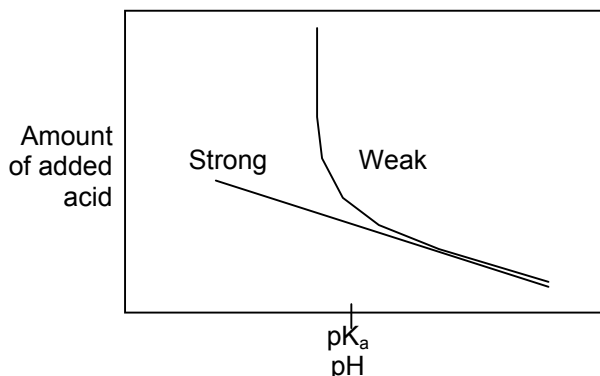


Figure 1. Achieved pH-level by adding different amount of strong or weak acid.

## EXPERIMENTAL

### Leaching experiments at pH-levels 3-6

In order to evaluate the first step of the two-step leaching process, 5 ml SCWO-residue (from SYVAB) and 0.5 g sludge incineration ash (from Mora) was leached with HCl and acetic acid at different pH-levels (3, 4, 5 and 6). (5 ml SCWO-residue with 122 g SS/l gives 0.61 g SS). The ash was mixed with 5 ml distilled water. After mixing for two hours was the sludge centrifuged for 20 min at 4000 rpm and the liquid phase was filtered through a 0.45  $\mu\text{m}$  filter. The dissolved amount of phosphorus was analysed with a Flow Injection Analyse instrument (Aquatec Tecator) and dissolved calcium, aluminium and iron was analysed with Atomic absorption spectrometry (Varian SpectraAA 55).

Figure 2 shows the achieved pH-level by adding different amount of acid to SCWO-residue and sludge incineration ash. With HCl lower pH-level was achieved than with acetic acid. For the same pH-level the acid consumption was higher for SCWO-residue than for ash with exception for an addition of 0.0045 mole acetic acid to the ash gave a pH-level of 3.9. This shows that more acid has been consumed by dissolution reaction with the SCWO-residue and that the ash is less reactive than the SCWO-residue. The differences in reactivity can be caused by different heating temperature 600  $^{\circ}\text{C}$  for the SCWO-process compared to 800  $^{\circ}\text{C}$  for the incineration. This will cause that the phosphate in the SCWO-residue is in a metastable phase compared to a stable phase in the incineration ash (Glaum, 2004).

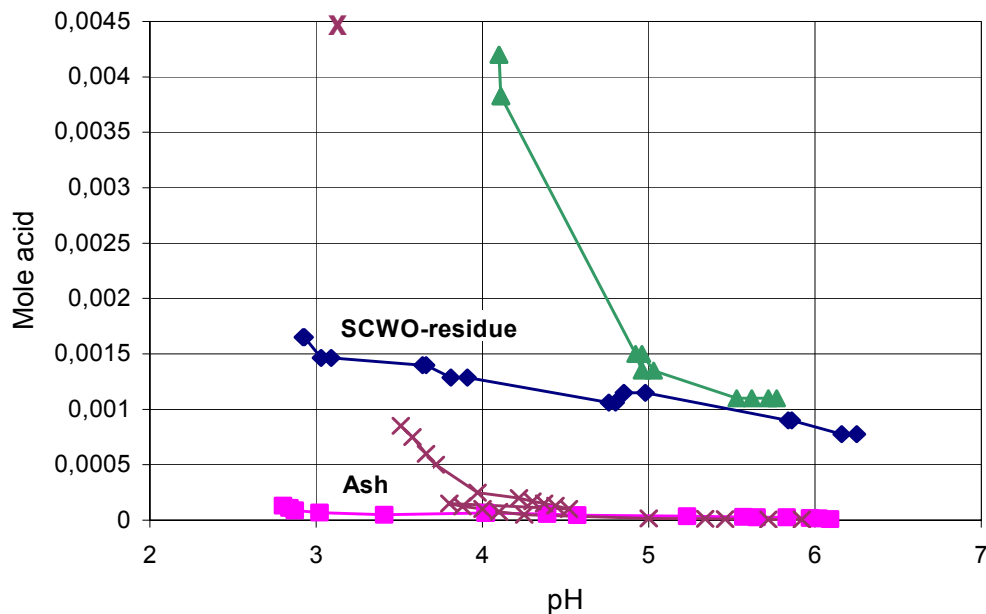


Figure 2. Achieved pH-level by adding different amount of acid (■, ♦) HCl and (x, ▲) CH<sub>3</sub>COOH to (♦, ▲) 0.61 g SCWO-residue (SYVAB) and (■, x) 0.5 g sludge incineration ash (Mora).

Figure 3 shows dissolution of phosphorus versus addition of acid for 0.61 g SCWO-residue (SYVAB) and 0.5 g sludge incineration ash (Mora) and figure 4 shows the dissolution versus pH. These diagrams shows that more phosphorus have been leached from the SCWO-residue than from the ash. With addition of 0.0045 mole acetic acid the same amount of phosphorus (1.5 mg) were leached from the ash and from the SCWO-residue. With use of HCl the phosphorus release

increased at pH-levels below 3. Figure 5 shows percentage of acid used for phosphorus leaching and creating pH-value versus pH. At leaching of the more reactive SCWO-residue less of the acid was used for these purposes than at leaching the ash. The SCWO-residue has a phosphorus content of 8.8 %, which with used amount of 0.61 g the gives 54 g and the ash has a phosphorus content of 8 %, which with used amount of 0.5 g gives 40 g.

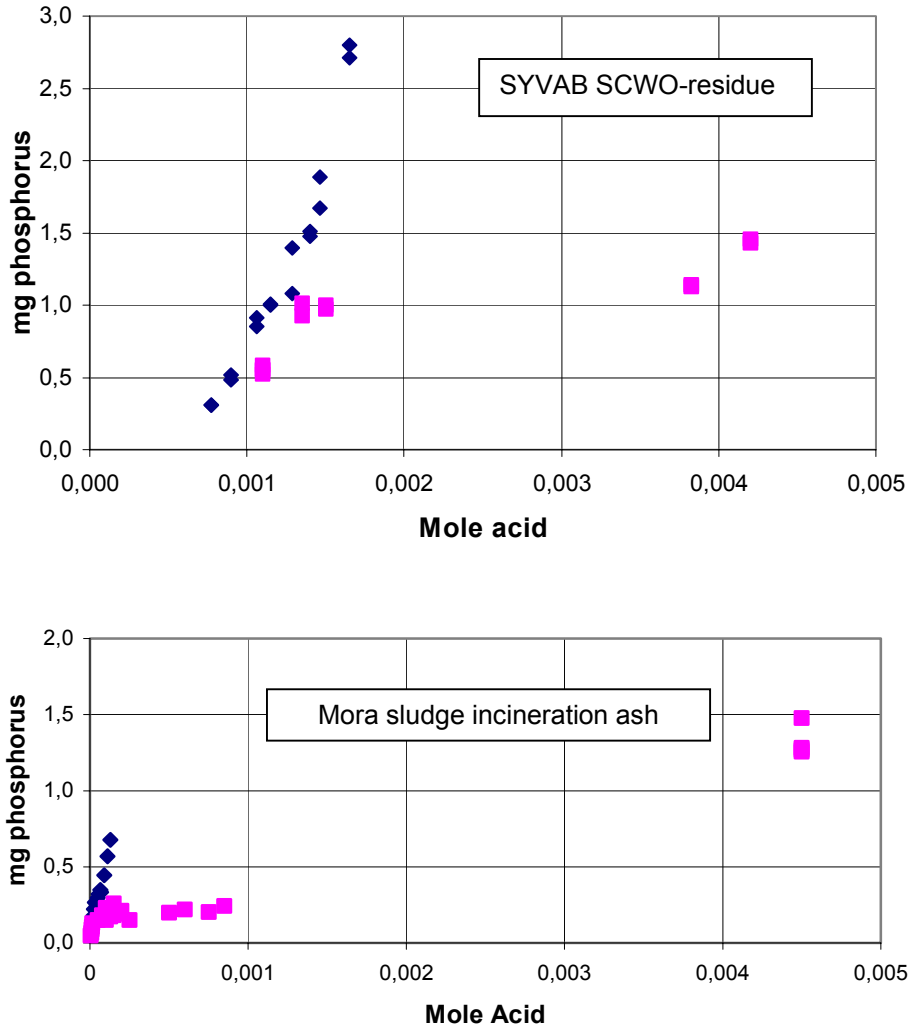


Figure 3. Dissolution of phosphorus versus addition of acid  $\blacklozenge$  HCl and  $\blacksquare$  CH<sub>3</sub>COOH for 0.61 g SCWO-residue (SYVAB) and 0.5 g sludge incineration ash (Mora).

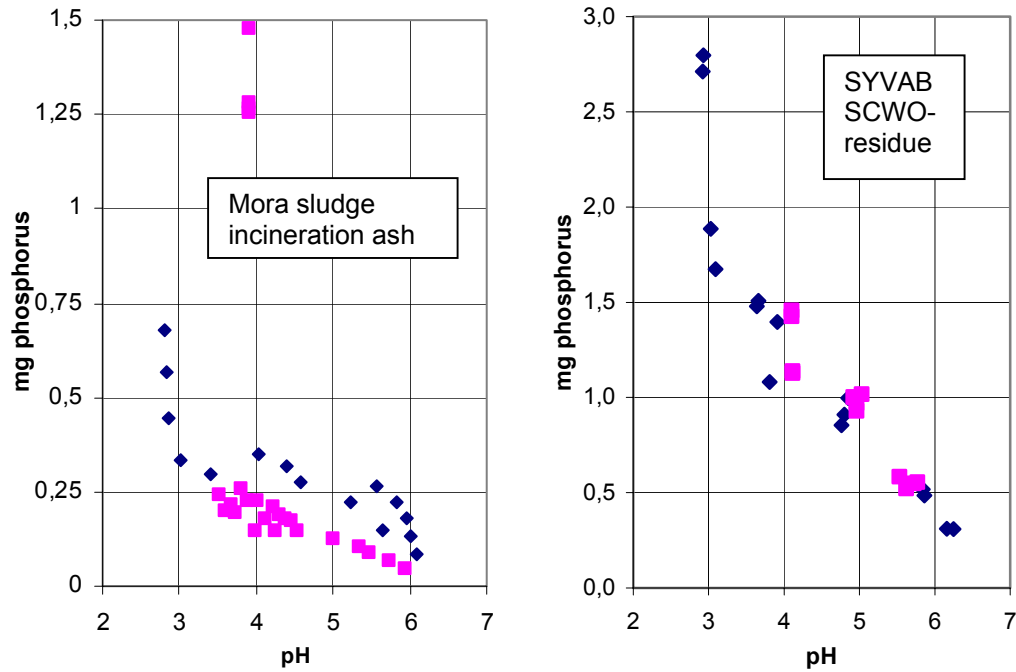


Figure 4. Dissolution of phosphorus versus pH for  $\blacklozenge$  HCl and  $\blacksquare$   $\text{CH}_3\text{COOH}$  for 0.61 g SCWO-residue (SYVAB) and 0.5 g sludge incineration ash (Mora).

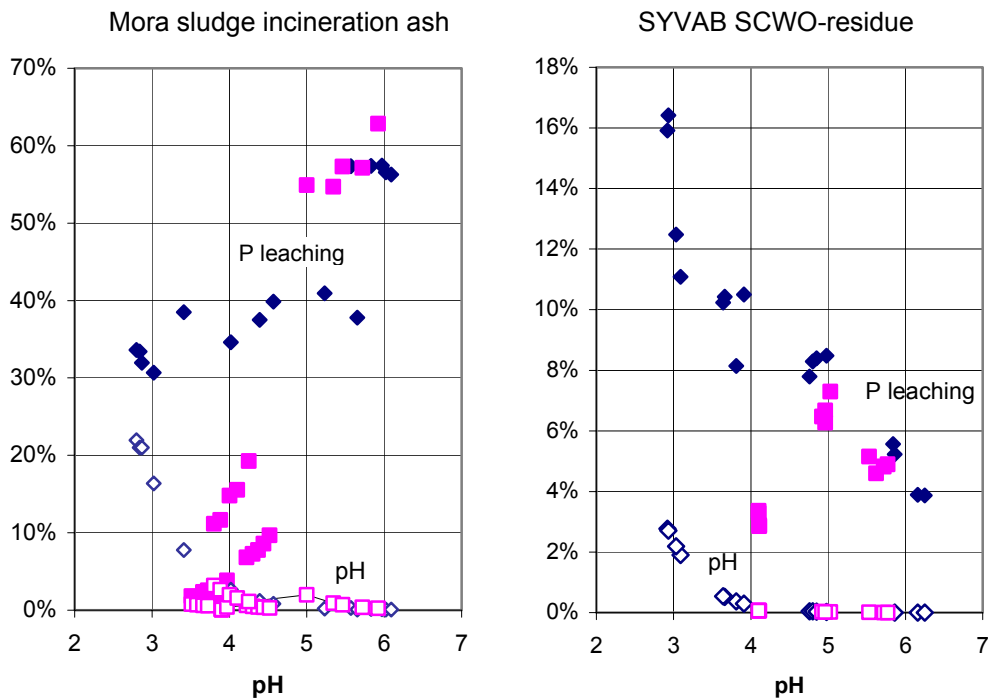


Figure 5. Percentage of acid used for phosphorus leaching ( $\blacklozenge$ ,  $\blacksquare$ ) and pH-value ( $\diamond$ ,  $\square$ ) versus pH for HCl ( $\blacklozenge$ ,  $\diamond$ ),  $\text{CH}_3\text{COOH}$  ( $\blacksquare$ ,  $\square$ ), 0.61 g SCWO-residue (SYVAB) and 0.5 g sludge incineration ash (Mora).

Figure 6 shows dissolution of calcium and aluminium versus addition of acid and pH-value for 0.61 g SCWO-residue (SYVAB) and figure 7 shows the same for 0.5 g sludge incineration ash (Mora). The aluminium dissolution is high below pH-level 3. The dissolution of calcium is highest from the SCWO-residue, varying from 25 mg at pH-level 3 to 10 mg at pH-level 6. The dissolution of calcium is higher from SCWO-residue than from the less reactive sludge incineration ash there the dissolution is smaller, below 2 mg. However, at using a larger amount of acidic acid 12.7 mg calcium was dissolved. At leaching the SCWO-residue no difference was noted between using a strong acid as HCl and a weak acid as acetic acid. The SCWO-residue reacts fast with the acid and a pH-level is achieved, which is determined by the dissolution reactions. For the less reactive ash is the pH-level determined by a small amount of added acid, which gives a smaller dissolution of calcium. However the higher dissolution of calcium that was achieved with a large addition of acetic acid shows that calcium can be selectively dissolved from the ash with use of a weak acid.

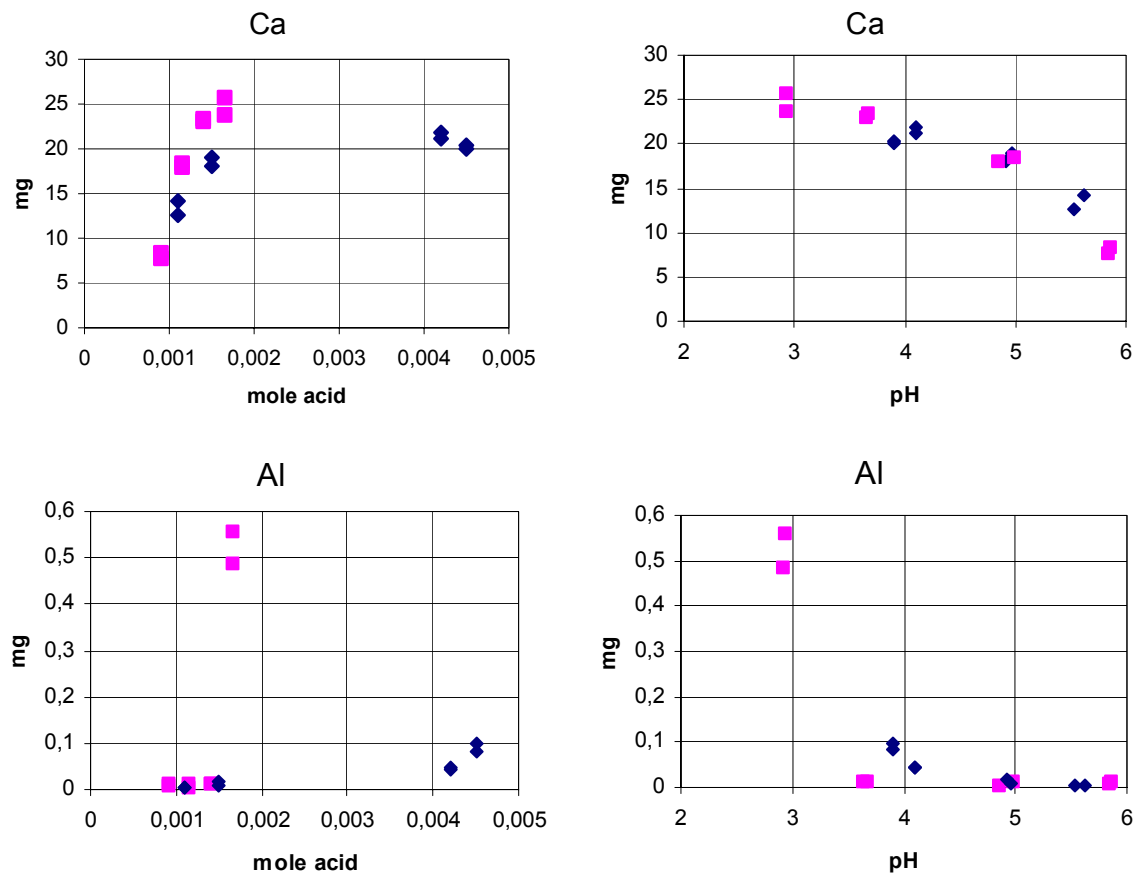


Figure 6. Calcium and aluminium dissolution at acid leaching (■) HCl and (◆) CH<sub>3</sub>COOH, from 0.61 g SYVAB SCWO-residue.

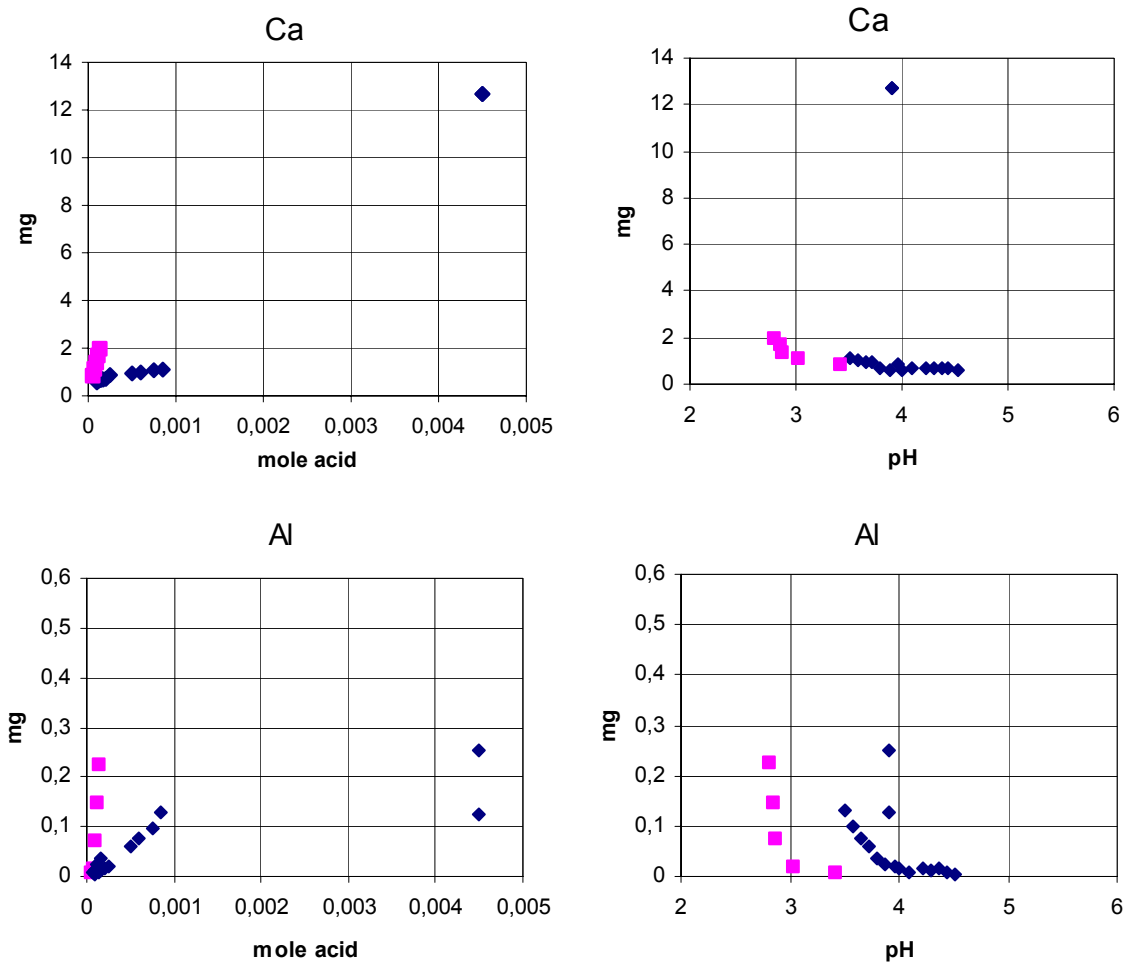


Figure 7. Calcium and aluminium dissolution at acid leaching (■) HCl and (◆) CH<sub>3</sub>COOH, from 0.5 g Mora sludge incineration ash.

### Experiments with the complete Two-step leaching process

Evaluation of the leaching experiments at pH-levels 3-6 gave that leaching with 0.0045 mole acetic was chosen for the first leaching step the in further experiments with the two-step leaching process. Leaching at pH 4 of 1.5 g phosphorus (consumes 0.00015 mole acid) gives that the largest part of the phosphorus remains unleached and can thereby be leached with base in the second process step in a two-step leaching process. That this amount of acetic acid gives the same result with ash as with SCWO-residue indicates that it may be possible to use acetic acid for the first leaching step also with sludge incineration ash. In this experiments sludge incineration ash (Mora) and SCWO-residue from SYVAB and Karlskoga sludge was used. (5 ml Karlskoga SCWO-residue with 200 g SS/l gives 1 g SS)

In the two-step process Ca is first leached with 30 ml 0.15 M acetic acid at pH 4. In this leaching 5 ml SCWO-residue samples is used or 0.5 g ash mixed with 5 ml distilled water. After the first leaching the samples are centrifuged and the liquid is separated. To remove the remaining acid distilled water is added to the solid phase, which is centrifuged followed by separation the liquid. Phosphate is thereafter leached in second leaching with 25 ml 1 M NaOH. 5 ml distilled water is added before the NaOH leaching. For comparison samples of SCWO-residue and sludge incineration ash is leached with NaOH without the first leaching step with acetic acid. The

dissolved amount of phosphorus, calcium, aluminium and iron was analysed on samples from the two-step leaching, samples leached only with NaOH and also on samples from the first leaching step.

Table 1 shows dissolved phosphate from two-step leaching SCWO-residue (SYVAB and Karlskoga) and sludge incineration ash (Mora). The column “2 step” shows leaching with NaOH of four samples which have first have been leached with acetic acid and the column “NaOH only” leaching with NaOH of four samples without the first leaching with acetic acid. The column “2 step” shows for all samples a higher dissolution of phosphate than the column “NaOH only”. The column “Increase” shows how much higher the dissolution with “2 step” is compared with “NaOH only”. Two-step leaching gives for SCWO-residue 23% higher leaching of phosphate and for sludge incineration ash 11% higher leaching compared to leaching only with NaOH. The column “NaOH used for P leach” shows how much of the added NaOH that has been consumed by leaching phosphate. The column “Leached P of total” is the percentage of phosphate in the solid material that has been leached.

Table 1. Dissolved phosphate from two-step leaching SCWO-residue (SYVAB and Karlskoga) and sludge incineration ash (Mora).

	Dissolved P (mg/l)		Dissolved P (mg)		Increase	NaOH used for P leach		Leached P of total	
	2 step	NaOH only	2 step	NaOH only		2 step	NaOH only	2 step	NaOH only
SCWO-residue	1028.90	823.67	30.87	24.71	<b>25%</b>	12%	10%	54.81%	43.87%
	971.90	819.15	29.16	24.57	<b>19%</b>	11%	10%	51.77%	43.63%
SYVAB	1025.30	814.67	30.76	24.44	<b>26%</b>	12%	9%	54.61%	43.40%
	985.20	803.70	29.56	24.11	<b>23%</b>	11%	9%	52.48%	42.81%
Mean:	1002.83	815.30	30.08	24.46	<b>23%</b>	12%	9%	53.42%	43.43%
Total:	56.32 = 88 mg P/g SS x 128 g SS/liter x 0.005 liter								
SCWO-residue	584.76	526.29	17.54	15.79	<b>11%</b>	7%	6%	64.26%	57.83%
	556.27	437.09	16.69	13.11	<b>27%</b>	6%	5%	61.13%	48.03%
Karlskoga	553.83	440.23	16.61	13.21	<b>26%</b>	6%	5%	60.86%	48.38%
	573.07	419.27	17.19	12.58	<b>37%</b>	7%	5%	62.97%	46.07%
Mean:	566.98	455.72	17.01	13.67	<b>24%</b>	7%	5%	62.31%	50.08%
Total:	27.30 = 27.30 mg P/g SS x 200 g SS/liter x 0.005 liter								
Ash	839.61	735.41	25.19	22.06	<b>14%</b>	10%	9%	62.97%	55.16%
Mora	784.13	735.70	23.52	22.07	<b>7%</b>	9%	9%	58.81%	55.18%
	792.20	726.83	23.77	21.80	<b>9%</b>	9%	8%	59.42%	54.51%
	841.07	733.99	25.23	22.02	<b>15%</b>	10%	9%	63.08%	55.05%
Mean:	814.25	732.98	24.43	21.99	<b>11%</b>	9%	9%	61.07%	54.97%
Total:	40.00 = 80 mg P/g ash x 0.5 g ash								

Table 2 shows dissolved calcium, aluminium and iron from two-step leaching SCWO-residue (SYVAB and Karlskoga) and sludge incineration ash (Mora). The table show mean values of two samples analysed with atomic absorption spectroscopy. The column “Acid” shows how much that has been dissolved by acetic acid. The column “2 step” shows how much that has been dissolved by the NaOH in the second leaching step after leaching with acetic acid. The column “Only NaOH” shows how much that has been leached by NaOH without the first leaching step with acetic acid.



Table 2. Dissolved calcium, aluminium and iron from two-step leaching SCWO-residue (SYVAB and Karlskoga) and ash (Mora).

		Dissolved Ca			Dissolved Al			Dissolved Fe		
		Acid	2 step	Only NaOH	Acid	2 step	Only NaOH	Acid	2 step	Only NaOH
SCWO-residue	(mg/l)	576.5	0	0	2.6	867	883	0	0	0
SYVAB	(mg)	20.2	0	0	0.09	26	26	0	0	0
SCWO-residue	(mg/l)	57.1	0	0	20	755	687	0	0	0
Karlskoga	(mg)	2.0	0	0	0.7	23	21	0	0	0
Sludge incineration ash	(mg/l)	362	0	0	5.4	506	507	0	0	0
Mora	(mg)	12.7	0	0	0.19	15	15	0	0	0

Figure 8 shows a scheme for separation of species at two-step leaching. Calcium is insoluble in NaOH and is dissolved the first leaching step with acetic acid. Aluminium is partly dissolved with acetic acid but more soluble at leaching with NaOH. Iron is insoluble both in acetic acid and NaOH.

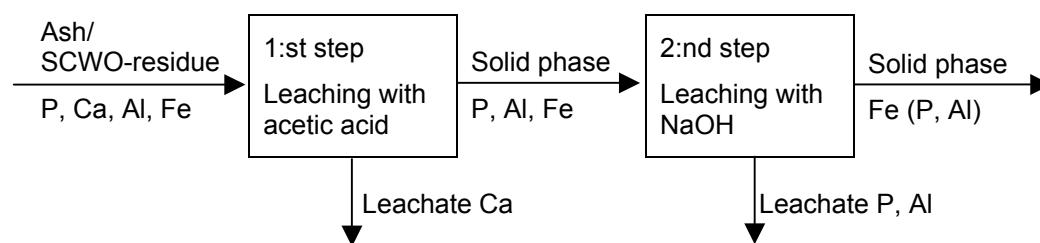


Figure 8. Scheme for separation of species at two-step leaching.

## DISCUSSION

In a two-step process the solid products are in the first step leached with acid at a pH-level 4, with the main purpose to dissolve calcium. The leaching experiments with hydrochloric acid and acetic acid at different pH-levels from 3 to 6 showed that only calcium was leached. With a weak acid the dissolution reaction can occur at the desired pH-level without limitation caused by insufficient amount of acid. The dissolution of calcium is higher from SCWO-residue (20 mg at pH-level 3), than from the less reactive sludge incineration ash there the small addition of acid required to achieve the determined pH-level, gave dissolution below 2 mg. With sludge incineration ash 0.001 to 0.0001 mole acid was used compared to 0.01 to 0.04 moles with the SCWO-residue. However, at using 0.045 moles of acidic acid 12.7 mg calcium was dissolved from the ash. At leaching the SCWO-residue no difference was noted between using a strong acid as HCl and a weak acid as acetic acid. Leaching with acetic acid at pH-level 4 was therefore chosen for the first leaching step.

In the second leaching step the solid products was leached with 1 M sodium hydroxide. Two-step leaching gave for SCWO-residue 23% higher leaching of phosphate and for sludge incineration ash 11 % higher leaching, compared to leaching only with sodium hydroxide. The leached amount of phosphorus was about 60%. To get a higher degree of phosphorus recovery the second leaching step with base can be made at higher temperatures. Stendahl and Jäferström (2003) dissolved up to 90% of the phosphorus at temperatures between 80-90 °C. However, aluminium was also dissolved at leaching with base, and has to be separated from the phosphate in a third process step. To improve the process less aluminium and more phosphorus has to be leached in the second step. If iron is used as precipitation chemicals there will be less aluminium that can be dissolved in the

second process step. Alternatively if aluminium is chosen as precipitation chemicals aluminium separated from phosphorus in a third process step can be used as precipitation chemical and the treatment plant can be self supplied with precipitation chemicals.

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