

PHOSPHORUS RECOVERY FROM SLUDGE INCINERATION ASH AND SUPERCRITICAL WATER OXIDATION RESIDUES WITH USE OF ACID AND BASE.

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ABSTRACT

Phosphorus recovery from sludge incineration ash and 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 in the Water Chemistry Laboratory at KTH. Samples of ash taken from a sludge incineration plant and SCWO residues have been leached with acid, hydrochloric acid and base, sodium hydroxide. The metal and phosphorus content before leaching have been analyzed as well as the metal and phosphorus content in the leachate. Leaching with acid gives a higher release of phosphorus compared to leaching with base. The largest degree of leached phosphorus (80 - 100 % at acid concentrations below 0,5 M) was obtained by leaching SCWO residue with acid. Acid leaching of sludge incineration ash gave 75 – 90 % leached phosphorus at the concentration 1 M. Alkaline leaching of sludge incineration ash and SCWO-residue gave 50 – 70 % leached phosphorus at the concentration 1 M. When leaching with base, the calcium content in the sludge binds phosphorus as calcium phosphate. On leaching with acid it is difficult to recover phosphorus as other products than iron phosphate. However, iron phosphate has no commercial value as raw material for the phosphate industry, and the low solubility makes it less favourable to use as fertilizer. The possibility to recover phosphate by precipitation as calcium phosphate from the leachate achieved by leaching with base was studied. However, at increasing the base concentration the phosphorus recovery from the leachate decreased, decreasing the amount of phosphorus recovery.

KEYWORDS

Phosphorus recovery; Sludge incineration ash; Super Critical Water Oxidation

INTRODUCTION

Leaching with acid and base is a promising method for phosphorus recovery from waste water treatment 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 in the Water Chemistry Laboratory at KTH (Hultman and Löwén, 2001, Levlin et al., 2000, Stark, 2002, Stark and Hultman, 2003). Samples of ash taken from the co-incineration of sludge with municipal waste, sludge incineration plant and SCWO residues have been leached with acid, hydrochloric acid and base, sodium hydroxide. The metal and phosphorus content before leaching has been analyzed as well as the metal and phosphorus content in the leachate.

Figure 1 and 2 shows the solubility of metal hydroxide phosphates as a function of pH. Leaching with acid dissolves efficiently most metals and phosphorus. Most metals are more insoluble in bases than in acids, and leaching with base should therefore give a phosphorus product with a lower contamination of metal. However, some calcium phosphate compounds are also insoluble in bases, which also will reduce the degree of phosphorus recovery. At leaching SCWO-residues with sodium hydroxide Stendahl and Järfverström (2003) found that residues from Karlskoga sludge with 3 % calcium released 90 % of the phosphorus content, while residues from Stockholm sludge with 8 % calcium only released 65 %.

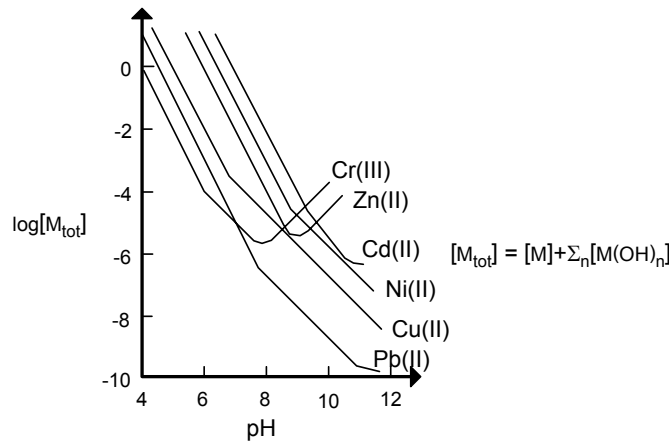


Figure 1. Solubility for pure metal hydroxide as a function of pH (Nilsson 1971).

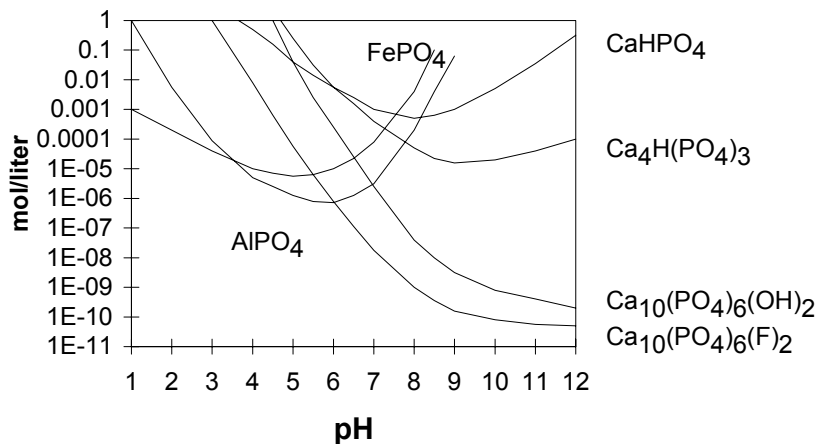


Figure 2. The solubility of metal phosphates (Stumm and Morgan, 1981).

On leaching with acid it is difficult to recover phosphorus as other products than iron phosphate, which is dissolved together with the phosphorus. Without removing iron from the leachate, phosphate will preferentially be recovered as iron phosphate, which has a lower solubility than for instance calcium phosphate. Recovery of the phosphate as other product than iron phosphate requires that iron has to be removed from the leachate before the phosphate can be recovered. However, iron phosphate has no commercial value as raw material for the phosphate industry, and

the low solubility makes it less favourable to use as fertilizer. The global deposits of economically mineable phosphate are estimated to be 10^9 ton phosphorus and the total amount in the sediments is estimated to be 10^{15} ton phosphorus (Butcher et al., 1994). Many different phosphate minerals are available, but only apatite (calciumphosphate, $\text{Ca}_3(\text{PO}_4)_2$) is used for phosphate production (Corbridge, 1995). Since the phosphate in the sludge originate from phosphorus products produced from calcium phosphate ore, recovering the phosphate as iron phosphate will not preserve the limited calcium phosphate resources.

In the proposed BioCon process ash from sludge incineration would be leached with acid and the content in the leachate separated with ion exchange technology (Levlin, 2001). However in the sludge incineration plant built by the BioCon Company in Falun and Mora, the phosphate recovery process based on ion exchange has been abandoned (NyTeknik, 2002). The proposed phosphate recovery process is to leach the ash with sulphuric acid and recover the phosphate as iron phosphate.

In leaching with a base such as sodium hydroxide, NaOH, it will be possible to recover phosphate from the leachate as calcium phosphate by precipitation with calcium. In the Aqua Reci process ash from SCWO is leached with sodium hydroxide and precipitated with lime (Stendahl and Jäfverström, 2003). An other proposal is to leach the metals from the sludge with calcium hydroxide at high pressure, without leaching the phosphate and use the metal free sludge as fertilizer (NyTeknik, 2003).

LEACHING ASH AND SUPERCRITICAL WATER OXIDATION RESIDUES WITH ACID

Leaching experiment

Comparison of the results from leaching residues from supercritical water oxidation of sludge and from co-incineration of waste water treatment sludge together with household waste or re-cycled wood, are shown in Figure 3.

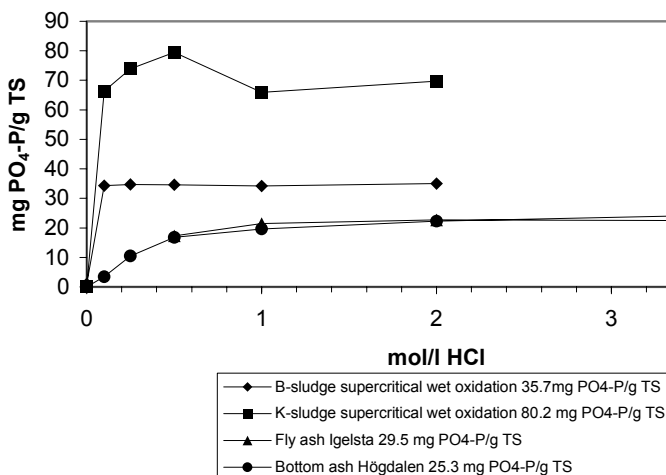


Figure 3. Phosphorus leaching ash and SCWO-residues by HCl (Hultman and Löwén, 2001).

B-sludge and K-sludge from Borlänge and Karlskoga, Sweden, was incinerated by supercritical water oxidation in a pilot plant in Karlskoga. The SCWO reactions take place at a pressure of 275 bars and a temperature between 400 and 600 °C. A complete destruction is obtained of organic material in wastewater and sludge (Gidner et al, 2000). Two incineration plants in the Stockholm area, Högdalen and Igelsta, was used for full-scale co-incineration studies with sludge. In Högdalen incineration plant, there municipal solids wastes from Stockholm is incinerated in a grate oven, the solid wastes were mixed with 10 % sludge (Älvesand, 1998). Most of the ashes are obtained as bottom ash, which was used for the leaching experiments. At the Igelsta plant, where biofuels are incinerated in a fluidised bed reactor, incineration were performed with a mixture of 80 % biofuel (recirculated wood) and 20 % sludge (VAI VA-Projekt AB, 1998). Most of the Igelsta ashes are obtained as fly ash, which was used in the leaching experiments.

The difference in recovered phosphorus depends mainly on the phosphorus content. Figure 4 shows that the degree of phosphorus release is high. However, a higher acid concentration is needed for reaching the same degree of recovery of phosphorus from ash than from supercritical water oxidation residues.

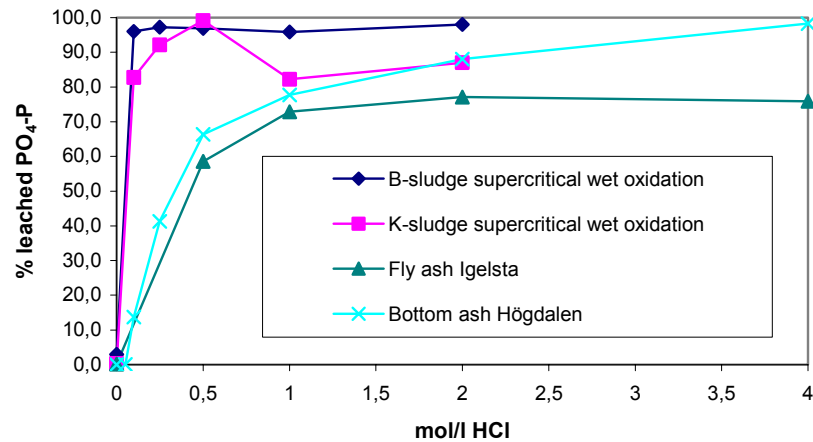


Figure 4. Release of phosphorus from leaching ash (Igelsta fly ash and Högdalen bottom ash) and SCWO-residues (B-sludge, Borlänge and K-sludge, Karlskoga) with HCl.

Metal contamination of the leachate

The degree of phosphorus recovery is high, but especially the phosphorus from co-incineration has a very high metal/phosphorus ratio. Table 2 shows the quota metal/phosphorus in the leachate (with 2 M HCl) from ashes from co-incineration and in sludge approved for agricultural use (Levlin et al., 2000). The produced ashes during co-incineration showed often a much higher quotient of metal to phosphorus than the supplied wastewater sludge and the quotient in the leachate is normally higher than for the sludge and also higher than in approved sludge.

Table 1. The quota metal/phosphorus in leachate (with 2 M HCl) from ashes from co-incineration in Högdalen and Igelsta, and in sludge approved for agricultural use (Levlin et al., 2000).

| | | Högdalen ash, mg Me/g P | Igelsta ash, mg Me/g P | Approved sludge, mg Me/g P |
|----------|----|-------------------------|------------------------|----------------------------|
| Cadmium | Cd | 0.08 | 1.63 | 0.0667 |
| Chromium | Cr | 1.17 | 16.3 | 3.33 |
| Copper | Cu | 43.4 | 43.1 | 20 |
| Lead | Pb | 9.86 | 96.9 | 3.33 |
| Mercury | Hg | --- | --- | 0.0833 |
| Nickel | Ni | 0.904 | 1.63 | 1.67 |
| Zinc | Zn | 51.6 | 466.7 | 26.7 |

LEACHING SUPERCRITICAL WATER OXIDATION RESIDUES WITH BASE

Leaching experiment

Results of phosphorus leaching from SCWO-residues using base (NaOH) are presented in Figure 5 (Stark and Hultman, 2003). Run 1-3 are performed with sludge from Karlskoga WWTP, while Run 4 are using another sludge type from Bromma WWTP (Stark, 2002). The results show that the amount of phosphorus release increase, with increasing concentration of base. The release of phosphorus is much dependent of the origin of the sludge. In run 1-3 the phosphorus leaching increases more between the concentration of 0 M and 0.5 M NaOH than when the concentration is above 0.5 M.

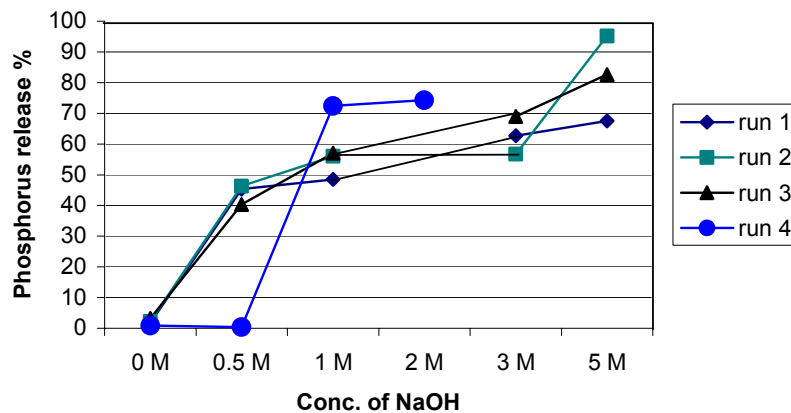


Figure 5. Release of phosphorus from leaching SCWO-residues with NaOH (Stark and Hultman, 2003).

Phosphorus recovery by precipitation with calcium

To recover phosphorus, phosphorus in the leachate can be precipitated with addition of calcium. Figure 6 shows the degree of phosphorus recovery under different concentration of NaOH and Ca^{2+} . It is found that the phosphorus recovery increased, when concentration of NaOH increased from 0 M to 1 M. Thereafter, the phosphorus recovery decreases, when concentration of NaOH increases from 1 M to 5 M. Therefore, the maximum phosphorus recovery occurs between 0.5 M and 1 M NaOH. When the concentration of NaOH is around 1 M, approximate 50 % of total phosphorus is

recovered. However, over 98 % of the soluble phosphorus can be recovered from the leachate by adding calcium chloride (CaCl_2). High concentration of NaOH might have a negative impact for phosphorus recovery, because high concentration of NaOH might cause that the calcium ion to precipitated as calcium aluminium components or other species rather than calcium phosphate. Therefore, depending on the consideration of economic for obtaining more phosphorus recovery, the best concentration of NaOH for recovering phosphorus will be between 0.5 M and 1 M NaOH. Meanwhile, the best dose of calcium ion would be between 35 mg/L to 265 mg/L or controlling the molar ratio of Ca/P as 1.35.

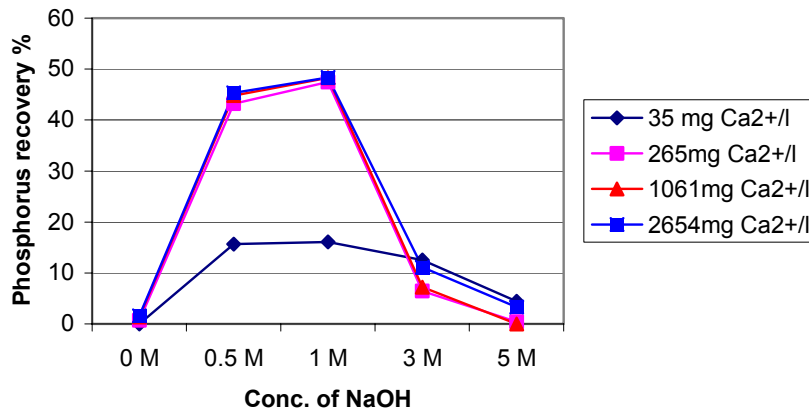


Figure 6. Results of phosphorus recovery by precipitation from leachate with calcium under different concentrations of NaOH (Stark and Hultman, 2003).

LEACHING ASH FROM SLUDGE INCINERATION WITH ACID AND BASE

Leaching experiment

Ash from the sludge incineration plant in M ora was leached with both acid HCl and base NaOH, at different concentrations up to 1 M acid/base concentration. An ash sample of 500 mg was leached in 25 ml leaching solution. The concentration of phosphate in the leachate was analysed and the phosphorus release from the ash was calculated. Figure 7 shows the achieved phosphorus release from the M ora ash at different concentrations of HCl (0 M, 0.25 M, 0.5 M and 1 M) and NaOH (0 M, 0.2 M, 0.5 M and 1 M) in five leaching experiments. The phosphorus content of the ash is 80 mg/g ash and 80 mg/g leached phosphorus is thereby equal to 100 % released phosphorus. The phosphate release leaching with base varies from 60 % to 70 % and with acid from 75 % to 90 %.

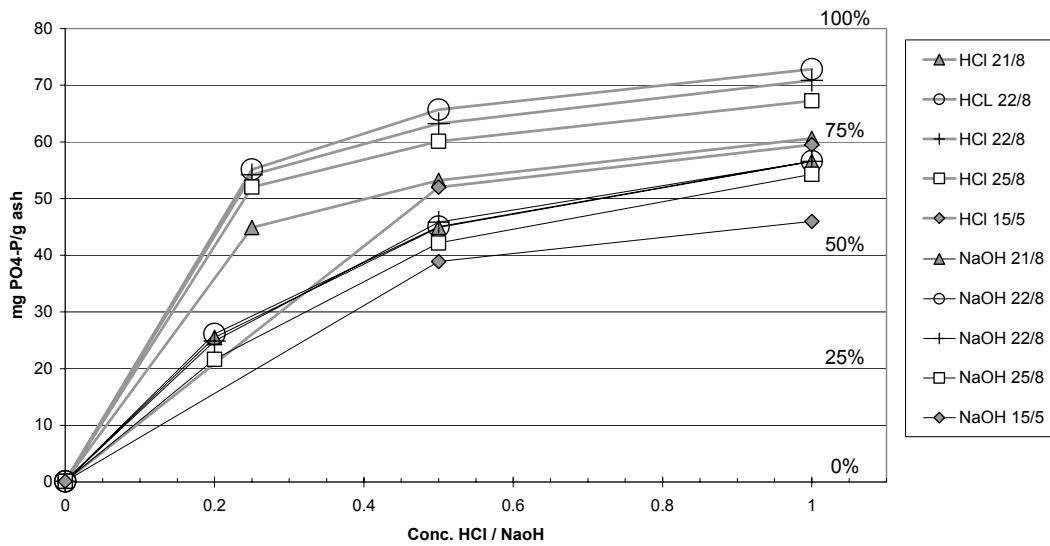


Figure 7. Phosphorus release from leaching five samples of M ora ash, versus concentrations of HCl and NaOH.

Metal contamination of the leachate

The metal content of unleached ash (table 2) and the metal content of the leachate (table 3) was analysed with ICP, Inductive Coupled Plasma, emission spectrometry (ICP-AES) for the higher concentrations and ICP mass spectrometry (ICP-QMS, ICP-SMS) for the lower concentrations. Mercury was analysed with a special emission spectrometry method (AFS). The high aluminium content in the ash compared to iron, shows that aluminium is used as precipitation agent in the M ora wastewater treatment plant. The metal content is higher in the leachate from leaching with acid than in the leachate from leaching with base. When leaching with base, the metal content was so small that the concentrations were lower than the detection level. The high molybdenum and tin concentration in the leachate makes it difficult to detect cadmium.

Table 2. Elementary composition of M ora ash (99.8 % DS).

| Element | % DS | Element | % DS | mg/g DS | Element | mg/kg DS |
|--------------------------------|-------|---------|-------|---------|---------|----------|
| Al ₂ O ₃ | 41.1 | Al | 21.75 | 217.51 | Cd | 0.351 |
| CaO | 6.91 | Ca | 4.94 | 49.39 | Co | 13.3 |
| Fe ₂ O ₃ | 11.9 | Fe | 8.32 | 83.23 | Cr | 136 |
| MgO | 0.99 | Mg | 0.60 | 5.97 | Cu | 436 |
| MnO | 0.135 | Mn | 0.105 | 1.046 | Hg | 0.134 |
| P ₂ O ₅ | 18.5 | P | 8.07 | 80.73 | Ni | 58.3 |
| SiO ₂ | 20.1 | Si | 9.39 | 93.94 | Pb | 18.4 |
| | | | | | Zn | 448 |

Table 3. Metal content in leachate (test 22/8) from leaching M ora ash with HCl and NaOH.

| Element | 0M | 0.25M | 0.5M | 1M | 0M | 0.2M | 0.5M | 1M |
|---------|--------|--------|-------|-------|--------|--------|--------|--------|
| | HCl | HCl | HCl | HCl | NaOH | NaOH | NaOH | NaOH |
| Ca mg/l | 3.47 | 814 | 826 | 847 | 3.7 | <2* | <2* | <2* |
| Fe mg/l | 0.123 | 85.6 | 95 | 104 | 0.0996 | 0.35 | 1.14 | 0.7 |
| Mg mg/l | 0.462 | 56.6 | 58.9 | 62.1 | 0.466 | <0.9* | <0.9* | <0.9* |
| Al mg/l | 0.782 | 836 | 955 | 1070 | 0.633 | 439 | 970 | 861 |
| Cd µg/l | <0.12* | <1.9* | <2.9* | <3.4* | <0.16* | <0.55* | <0.90* | <0.55* |
| Co µg/l | 0.0806 | 27.2 | 31 | 36.8 | <0.05* | <0.5* | <0.5* | <0.5* |
| Cr µg/l | <0.5* | 25.2 | 25.8 | 28.1 | <0.5* | <5* | <5* | <5* |
| Cu µg/l | 5.87 | 3500 | 3690 | 3880 | 2.6 | 51.7 | 621 | 259 |
| Hg µg/l | <0.02* | 0.0329 | 0.14 | 0.518 | <0.02* | <0.02 | <0.02* | <0.02* |
| Mn µg/l | 9.15 | 6010 | 6300 | 6570 | 9.02 | 21.4 | 37.6 | 25 |
| Ni µg/l | <0.5* | 58.8 | 72.4 | 71.5 | <0.5* | <5* | <5* | <5* |
| Pb µg/l | 0.531 | 251 | 285 | 309 | 0.515 | 8.77 | 84.3 | 33.1 |
| Zn µg/l | 3.53 | 2390 | 2630 | 3340 | 5.09 | 135 | 996 | 563 |

Mercury was analysed with AFS. Other values below 0.5 mg/l and Al at 0M NaOH was analysed with ICP-SMS and the other values above 0.5 mg/l with was analysed ICP AES.

* Values below the detection level is marked with "<" and the detection level.

Table 4 shows the metal/phosphorus ratio in the ash, in the leachate from leaching with acid and base and the quota from leaching with acid and with base. The metal/phosphorus quota is highest in the ash and lowest in the leachate achieved from leaching with base. One exception is aluminium there the metal/phosphorus ratio is higher then leaching with base than with acid. Aluminium is a metal that is dissolved with both acid and base. However, since aluminium is used as precipitation agent, dissolving aluminium together with phosphorus can be used for recovery of precipitation agent by separating aluminium and phosphorus in a second process step.

Table 4. Ratio metal/phosphorus in the ash, in the leachate and the quota acid/base.

| | Me/P ash | Me/P HCl-leachate | | | Me/P NaOH-leachate | | | Me/P HCl Me/P NaOH | |
|----------|----------|-------------------|-------|-------|------------------------|------------------------|------------------------|------------------------|------------------------|
| | | 0.25M | 0.5M | 1M | 0.2M | 0.5M | 1M | 0.5M | 1M |
| | | Ca g/gP | 0.612 | 0.699 | 0.627 | 0.579 | $<3.87 \times 10^{-3}$ | $<2.12 \times 10^{-3}$ | $<1.71 \times 10^{-3}$ |
| Fe g/gP | 1.031 | 0.073 | 0.072 | 0.071 | 6.77×10^{-4} | 1.21×10^{-3} | 5.98×10^{-4} | 59.692 | 118.8 |
| Mg g/gP | 0.074 | 0.049 | 0.045 | 0.042 | $<1.74 \times 10^{-3}$ | $<9.54 \times 10^{-4}$ | $<7.69 \times 10^{-4}$ | >46.9 | >55.2 |
| Al g/gP | 2.694 | 0.718 | 0.725 | 0.731 | 0.849 | 1.028 | 0.735 | 0.705 | 0.994 |
| Co mg/gP | 0.165 | 0.023 | 0.024 | 0.025 | $<9.68 \times 10^{-4}$ | $<5.30 \times 10^{-4}$ | $<4.27 \times 10^{-4}$ | >44.4 | >58.9 |
| Cr mg/gP | 1.685 | 0.022 | 0.020 | 0.019 | $<9.68 \times 10^{-3}$ | $<5.30 \times 10^{-3}$ | $<4.27 \times 10^{-3}$ | >3.70 | >4.50 |
| Cu mg/gP | 5.401 | 3.004 | 2.802 | 2.651 | 0.100 | 0.658 | 0.221 | 4.256 | 11.981 |
| Hg µg/gP | 1.66 | 0.028 | 0.106 | 0.354 | <0.039 | <0.021 | <0.017 | >5.01 | >20.7 |
| Mn mg/gP | 12.95 | 5.159 | 4.785 | 4.489 | 0.041 | 0.040 | 0.021 | 120.0 | 210.2 |
| Ni mg/gP | 0.722 | 0.050 | 0.055 | 0.049 | $<9.68 \times 10^{-3}$ | $<5.30 \times 10^{-3}$ | $<4.27 \times 10^{-3}$ | >10.4 | >11.4 |
| Pb mg/gP | 0.228 | 0.215 | 0.216 | 0.211 | 0.017 | 0.089 | 0.028 | 2.422 | 7.466 |
| Zn mg/gP | 5.549 | 2.051 | 1.997 | 2.282 | 0.261 | 1.056 | 0.481 | 1.891 | 4.745 |

DISCUSSION

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. However leaching with acid gives a higher metal contamination of the leachate than leaching with base. Leaching with base will preferentially dissolve phosphorus and the metal contamination of the phosphorus can be decreased.

To recover phosphorus from the leachate by leaching with base, phosphorus in the leachate can be precipitated with addition of calcium. By precipitation as calcium phosphate it will be possible to recover phosphate from the leachate as calcium phosphate. However, at increasing the base concentration the phosphorus recovery from the leachate decreased, decreasing the amount of phosphorus recovery.

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