**PRODUCTION OF TECHNICAL GRADE PHOSPHORIC ACID FROM INCINERATOR
SEWAGE SLUDGE ASH (ISSA)**

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ABSTRACT

The recovery of phosphorus from sewage sludge ash samples obtained from 7 operating sludge incinerators in the UK using a sulfuric acid washing procedure to produce a technical grade phosphoric acid product has been investigated. The influences of reaction time, sulfuric acid concentration, liquid to solid ratio and source of ISSA on P recovery have been examined. The optimised conditions were the minimum stoichiometric acid requirement, a reaction time of 120 minutes and a liquid to solid ratio of 20. Under these conditions, average recoveries of between 72 and 91% of total phosphorus were obtained. Product filtrate was purified by passing through a cation exchange column, concentrated to 80% H_3PO_4 and compared with technical grade H_3PO_4 specifications. The economics of phosphate recovery by this method are briefly discussed.

Keywords: Phosphate; Recovery; Whitlockite; Sulfuric acid; Acid washing; Incineration; Sewage Sludge Ash.

1. Introduction

Although phosphorus is the 11th most abundant element in the earth's crust, with an average concentration of 1180ppm, economically extractable P is essentially a finite resource (Smil, 2000). Economical extraction requires phosphate rocks, with P₂O₅ contents between 5 and 40% and these rocks only occur in a limited number of geological deposits around the world. At current rates of consumption, it has been predicted that only 50-100 years of economical P resources remain (Cordell et al., 2009; Franz, 2008; Steen, 1998). A reduction in the quality of phosphate rock has been reported as lower grade rocks are progressively exploited (Driver et al., 1999). Peak phosphate, the point at which production of a finite resource begins to decline, and where significant and irreversible price increases of the commodity arise, has been predicted to occur around 2034 (Cordell et al., 2009). In the light of these facts, the Western European phosphate industry has an objective of recovered phosphates accounting for 25% of market capacity by 2012 (Levlin et al., 2002).

A number of waste materials have been identified as potentially useful sources of P including poultry litter (Kaikake et al., 2009; Szogi and Vanotti, 2009), dairy manure (Jin et al., 2009) and meat and bone meal (Coutrand et al., 2008). However, most research into P recovery has been focused on sewage sludge. The average human excretion of P to sewage works in developed countries has been reported as 1.2-1.4g/day/capita (Smil, 2000). Averaged over a European population of 307 million in the year 2000 (Eurostat - EU 15 countries), human excretions would represent an annual input of around 146,000 tonnes of P to the sewerage system. The use of sodium tri-polyphosphates, primarily as a sequestering agent in detergents, also represents a significant input of P to the sewerage system, with some 300,000 tonnes of sodium tri-polyphosphate (Na₅P₃O₁₀) used in Europe in 2000, equivalent to around 76,000 tonnes per year as P (Raskovic, 2007). Smil (2000) considers the input of P to sewerage systems from detergents to be as significant as human excretions. The majority of P is retained in primary, secondary and tertiary sewage sludge. Application of sewage sludge to agricultural land is generally regarded as the BPEO (Best Practicable Environmental Option) as inorganic nutrients are returned to the land and organic matter can help improve soil structure. However, concerns with the heavy metal content and certain organic pollutants in sewage sludge and their potential accumulation in soils have led to an increase in the incineration of sewage sludge.

The incineration process requires sludge to be dewatered to >25% dry solids content before it is fed to a fluidised sand bed reactor maintained at 800-900°C in an aerobic environment. Under these conditions water is instantly vaporised and organic matter oxidised to CO₂, NO_x and SO_x gases. However, incineration cannot be

1 considered as a complete disposal process, as an inorganic sewage sludge ash is generated from the exhaust gas
2 that requires disposal. Characterisation and potential re-use applications for this incinerated sewage sludge ash
3 (ISSA) has been the subject of significant research. Excluding oxygen, the major elements present in ISSA are
4 Si, Fe, Al, Ca and P (Cyr et al., 2007). Significant quantities of heavy metals exist in ISSA with the most
5 common being Zn, Cu, Pb and Cr. The P_2O_5 content of ISSA has been reported to be as high as 26%, although
6 the average figure is around 15% (Cyr et al., 2007). This is comparable to a low grade phosphate rock.
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8 The majority of ISSA is currently sent to landfill, although there is uncertainty if the ash should be
9 considered as inert, non-hazardous or hazardous waste. Recent leaching tests reported by the authors show that
10 ISSA cannot qualify for inert landfill according to EU landfill waste acceptance criteria (Donatello et al., 2010a).
11 Re-use applications have included use as a clay or sand substitute in the manufacture of bricks (Anderson et al.,
12 1996; Okuno and Takahashi 1997; Tay and Show 1997; Wiebusch and Seyfried 1997), tiles (Lin et al., 2008;
13 Chen and Lin 2009), ceramics (Merino et al., 2007; Park et al., 2003) and lightweight aggregates (Wainwright
14 and Cresswell 2001; Cheeseman and Virdi, 2005). Considerable work has also evaluated the use of ISSA as a
15 cement replacement material and as a potential pozzolanic additive to cement mortars (Garces et al., 2008;
16 Donatello et al., 2010b in press; Pan et al., 2003; Monzo et al., 1996; Cyr et al., 2007; Paya et al., 2002).
17 However, these re-use applications represent a waste of a potentially valuable P resource.
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19 Reported work in the literature regarding P recovery from ISSA is either related to thermo-chemical
20 treatment or acid leaching processes. With thermo-chemical treatment, the aim is to mix ISSA with NaCl, KCl,
21 $MgCl_2$ or $CaCl_2$ salts and subject the mixture to temperatures between 900 and 1100°C (Mattenberger et al.,
22 2008; Adam et al., 2009). Under these conditions, metal chlorides are volatilised and P is converted to a more
23 bio-available form so that treated ISSA can be used directly as a fertiliser even in compliance with the strict
24 German fertiliser standards (Adam et al., 2009). However, there are concerns over the operating costs of thermo-
25 chemical treatment and with equipment lifetime due to the highly corrosive conditions generated.
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27 Acid washing processes have the benefit of potentially lower energy consumption and the production of a
28 phosphoric acid product that could be tailored to niche products with potentially higher market prices. Oliver and
29 Carey (1976) dissolved >90% of phosphate by refluxing ISSA with 10% H_2SO_4 ($\sim 1.8 \text{ mol.l}^{-1}$) at a liquid to solid
30 (L/S) ratio of 25:1. Franz (2008) showed that between 66 and 99% of total phosphate could be dissolved by
31 washing ISSA with 14% H_2SO_4 ($\sim 2.5 \text{ mol.l}^{-1}$) for 10 minutes at L/S ratio of 2. Stark et al. (2006) reported that up
32 to 87% of total phosphate in ISSA could be extracted with 1 mol.l^{-1} HCl at L/S ratio of 50 for 2 hours. Takahashi
33 et al. (2001) showed 89-93% dissolution of phosphate by reacting ISSA with 0.5 mol.l^{-1} H_2SO_4 at a L/S ratio of
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10 for 1 hour. A major problem with acid washing of ISSA is the co-dissolution of heavy metals and major cations such as Fe, Al and Ca. Proposed solutions have included pH adjustment (Franz, 2008; Takahashi et al., 2001), sulfide precipitation (Franz, 2008) and cation exchange (Franz, 2008; Svensson, 2000) to achieve an uncontaminated phosphate precipitate.

After sulfuric acid, phosphoric acid represents the largest global market for acids with some 50×10^6 tonnes/yr of phosphate as P_2O_5 produced globally. Around 80% of global phosphate demand is for fertiliser manufacture, 12% for laundry detergents, 5% for animal feeds and 3% for other speciality applications (Driver et al., 1999; Smil, 2000; Steen, 1998). Assuming that the estimated 1.7 million tonnes ISSA produced globally each year contains 15% as P_2O_5 , then some 255,000 tonnes P_2O_5 /yr could be reclaimed from ISSA, representing just over 0.5% of the global market (Donatello, 2009 PhD Thesis). Therefore recovered phosphate from ISSA should be targeted at speciality applications, where a significant market share could be achieved. The speciality market uses technical, food and beverage or electronic grade phosphoric acid at 85% H_3PO_4 concentration and attracts significantly higher revenues than merchant grade 50% H_3PO_4 that is generally used in fertiliser manufacture. Based on supplier quotations, typical market prices for technical grade 85% H_3PO_4 varied between US \$750 and US \$2000 per metric tonne between 2007 and 2009. From the estimated 255,000 tonnes/yr of P_2O_5 from global ISSA sources, up to 414,000 tonnes of 85% concentration H_3PO_4 could be produced. Assuming that a viable process can be developed to produce technical grade phosphoric acid from ISSA, this waste material could be used to generate revenues of between US \$310 and US \$828 million per year while re-using a finite resource.

The aim of this work was to optimise the experimental variables that control phosphate extraction from ISSA by sulfuric acid leaching and to investigate the technical feasibility of producing a technical grade phosphoric acid from ISSA by a purification and concentration process.

2. Experimental

2.1. Materials

Samples of ISSA were obtained from each of the seven currently operational sewage sludge incinerators in England. Blackburn Meadows (BBM), Esholt (Esh), Calder Valley (CVI) and Knostrop (Knos) are operated by Yorkshire Water with a combined capacity to treat around 84,000 tds (tonnes dry solids)/yr of sewage sludge. Shell Green (SG) incinerator operated by United Utilities is currently being expanded and will be able to treat

~100,000 tds/yr from 2010. The remaining two incinerators, Beckton (Beck) and Crossness (XN) are operated by Thames Water and between them can treat up to 180,000 tds/yr. If all incinerators were to operate at full capacity and sewage sludge solids were 35% inorganic by mass, approximately 130,000 t/yr of ISSA would be produced in the UK. All of the incinerators operate fluidised sand bed furnaces in excess O₂ atmospheres at 800 to 900°C to achieve complete water evaporation and combustion of organic matter. The ISSA is separated from exhaust gases by bag filters, electrostatic precipitators and/or cyclone separators.

Laboratory reagent grade sulfuric and hydrochloric acids (Fischer Scientific) were used with concentrations of 98% (s.g. 1.84) and 36% (s.g. 1.18) respectively. All water used was of distilled purity.

2.2. ISSA characterisation

The methods used to measure the particle size distribution, BET specific surface area, major elements by x-ray fluorescence (XRF) and crystalline phases by x-ray diffraction (XRD) have previously been described by the authors (Donatello et al., 2010a). Total phosphate (expressed as P₂O₅) in as-received ISSA samples was measured by Kjeldahl digestion of ~1.0 g samples in 25 ml of 98% H₂SO₄ (s.g. 1.84). The mixture was heated at 140°C for 1 hour and then 365°C for 3 hours to achieve reflux conditions. The mixture was then allowed to cool, diluted to 1 litre in DI water and filtered to remove any siliceous solids prior to analysis by molybdenum blue colorimetry at 880 nm using a Skalar Sans⁺⁺ automated wet chemistry analyser.

2.3. Acid leaching experiments

The acid leaching process was only optimised for one ISSA sample and the optimal conditions were applied to the other six ISSA samples. It was decided to carry out process optimisation with BBM ISSA as this sample had relatively high P content and had been the subject of previous work (Tong, 2008). Unpublished previous work had shown a slight negative effect of gypsum doping and elevated temperatures on P dissolution and so these factors were not investigated. The influence of the following variables on P dissolution were examined for BBM ISSA; reaction time, acid concentration and liquid to solid ratio. The aim of the experiments was to reduce each of these variables to the minimum practical limit while achieving satisfactory P dissolution and minimal Al, Ca, Fe, Mg and Zn dissolution.

An outline of the experimental process is illustrated in Figure 1. Following filtration, the filtrate was diluted 1 in 100 with 0.1 mol.l⁻¹ HCl to prevent phosphate or sulfate salt precipitation and to dilute the solution P concentration to within the linear range of 0 – 160 mg/l achievable with the automated wet chemistry analyser (Skalar San⁺⁺) using the molybdenum blue colorimetric method. The diluted filtrate was also analysed for Al, Ca, Fe, Mg and Zn by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) to determine the extent of co-dissolution of these cations with P.

Due to possible sample heterogeneity, residual solids retained on the filter from each set of 4 replicates were combined and oven dried at 105°C. The average P concentration of the acid insoluble solids was measured by Kjeldahl digestion of ~1.0 g samples in 25 ml of 98% H₂SO₄ and dilution to 250 ml before being filtered and analysed for P by molybdenum blue colorimetry. The total P in each sample was calculated as the quantity of P in filtrate plus the average P content in retained solids. The percentage P extraction was calculated as the filtrate P content divided by the total P content.

For the purposes of calculating the extraction efficiencies of Al, Ca, Fe, Mg and Zn, XRF data or ICP-AES data in Table 1 was used to assume the total elemental content in ISSA.

2.3.1. Stoichiometric acid determination

To ensure that sufficient acid was added to dissolve all phosphate as phosphoric acid, it was necessary to consider reaction stoichiometry. The ISSA samples used in this study have been shown to contain phosphate in the form of the tri-calcium phosphate mineral, whitlockite (Figure 2). The following stoichiometric equation applies to whitlockite dissolution;

If we assume that the total P measured in ISSA exists as Ca₃(PO₄)₂ it can be concluded that 20 ml of 0.184 mol.l⁻¹ H₂SO₄ would be required for every 1 g of BBM ISSA. However, analysis of XRF data in Table 1 shows that there is insufficient Ca present in ISSA for all P to exist as Ca₃(PO₄)₂. In reality it is likely that some Ca is substituted for Fe, Mg or Al.

There is the possibility that other constituents in ISSA could also react with acid and increase the effective stoichiometric acid requirement. A different approach, previously described by Franz (2008), follows a method

used by the US Department of Agriculture for calculating the quantity of sulfuric acid required in superphosphate fertiliser manufacture where;

$$\frac{g \text{ } H_2SO_4}{100g \text{ ISSA}} = (1.749 \times CaO\%) + (0.962 \times Al_2O_3\%) + (0.614 \times Fe_2O_3\%) + (2.433 \times MgO\%) \\ + (1.582 \times Na_2O\%) + (1.041 \times K_2O\%) - (0.691 \times P_2O_5) - (1.225 \times SO_3)$$

Franz added an additional 10% H_2SO_4 to that calculated from the above equation to ensure that phosphate was present as the H_3PO_4 species. Applying the equation to BBM ISSA, with the reported XRF results in Table 1 showed that 20 ml of 0.24 mol.l⁻¹ H_2SO_4 would be required for 1 g of BBM ISSA, including the additional 10% acid.

2.3.2. Reaction time optimisation

Reaction time was varied from 5 to 720 minutes. To ensure that acid concentration was not a factor, 0.50 mol.l⁻¹ H_2SO_4 was used. This was more than double the stoichiometric requirement, to allow for any competing acid reactions with ISSA. For each reaction time, 4 replicates were prepared by adding accurately but approximately 1.0 g BBM ISSA and 20 ml of 0.50 mol.l⁻¹ H_2SO_4 before shaking for 5, 10, 30, 60, 120, 240 or 720 minutes. After shaking, slurries were vacuum filtered through Whatman no. 542 paper and the filtrate and retained solids prepared and analysed as described in section 2.3.

2.3.3. Sulfuric acid requirement

The minimum sulfuric acid requirement for a system with a liquid to solid ratio of 20 ml: 1 g has been calculated to be between 0.18 and 0.24 mol.l⁻¹ H_2SO_4 . It is desirable to identify the minimum acid concentration to reduce the costs of the operation and to minimise unwanted SO_4^{2-} in the filtrate. All samples were prepared with approximately 1.0 g BBM ISSA and 20 ml of 0.0, 0.10, 0.19, 0.30 or 0.50 mol.l⁻¹ H_2SO_4 and then shaken for a pre-determined optimal reaction time. Filtrates and retained solids were then prepared and tested as described in section 2.3.

2.3.4. Liquid to solid (L/S) ratio optimisation

1 The system under investigation is far more dilute than industrial processes which produce a product
2 containing around 30% H_3PO_4 . This implies a significant energy cost when the acid filtrate has to be
3 concentrated up to 50% or 85% H_3PO_4 to produce a saleable product. The lower the original L/S ratio, the lower
4 the later evaporation energy costs. L/S ratios of 20, 15, 10 and 5 were tested.
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6 The volume of liquid used in each sample was kept constant at 20 ml and the weight of solids changed from
7 1 g, 1.33 g, 2 g and 4 g to produce samples with L/S ratios of 20, 15, 10 and 5 ml/g respectively. As the liquid
8 volume was constant, the acid concentration had to be varied to achieve the same optimum acid: ISSA ratio. For
9 example, if the optimum acid concentration was 0.20 mol.l^{-1} at an L/S of 20, when the L/S changes to 10, the
10 acid concentration must also change to 0.40 mol.l^{-1} to compensate. All reactions were carried out at the
11 previously chosen optimum reaction time and optimum acid: ISSA ratio. Filtrates and retained solids were then
12 treated as described in section 2.3.
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24 2.3.5. *Source of ISSA*

25 The optimised reaction time (120 minutes), sulfuric acid concentration (0.19 mol.l^{-1}) and L/S ratio (20) for
26 BBM ISSA were then applied to the other six ISSA samples to determine P recovery data. Filtrates and retained
27 solids were treated as described in section 2.3.
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34 2.4. *Filtrate purification and concentration*

35 After determining the optimal acid leaching procedure, the process was repeated at a larger scale (x20) and
36 the filtrate was purified by cation exchange and concentrated up to around 85% H_3PO_4 concentration by
37 evaporating excess water. Pure H_3PO_4 boils at around 158°C so it is possible to concentrate H_3PO_4 by
38 evaporating water. Cation exchange represents the logical choice for removing cation impurities, the resin used
39 was Purolite C-100x10, a gel type polystyrenic strong acid cation exchange resin in the H^+ form with a minimum
40 guaranteed exchange capacity of 2.2 eq.l^{-1} . Columns containing approximately 100 ml of resin were set up which
41 should be able to process more than 10 l of filtrate before regeneration is required. Before first use, the resin was
42 rinsed with 250 ml of 1 mol.l^{-1} HCl and flushed with DI water. Sample filtrate volumes of 1 l were then passed
43 through the resin. To prevent possible dilution from any rinsing acid liquid present among the resin beads, the
44 first 100 ml of eluate were discarded. Resin was regenerated by plugging the top of the column with glass wool,
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inverting the column 180° and flushing with excessive quantities of 1 mol.l⁻¹ HCl to achieve counter-current regeneration. The overall process is illustrated in Figure 3.

The Zn, Fe, Mg, Ca, Al, P and SO₄²⁻ content of the filtrate produced from the optimised process for BBM ISSA was measured before and after cation exchange purification. Sulfate concentration was measured indirectly by reaction with a known excess of barium and colorimetric determination of unreacted barium using a Skalar Sans⁺⁺ automated wet chemistry analyser. After concentration to around 85% H₃PO₄, it would be inaccurate to determine the elemental concentrations in concentrated acid due to large dilution factors, the viscosity of the acid and uncertainty of the exact specific gravity of the acid. Therefore the elemental concentrations were extrapolated from the change in mass of the initial dilute phosphoric acid with known elemental concentrations, assuming that all lost mass was due to water evaporation. Condensate was analysed for dissolved P to ensure that no P was lost during the concentration stage.

3. Results

3.1. As-received ISSA characterisation

The chemical characteristics of ISSA samples are summarised in Table 1. X-ray fluorescence analysis showed that with the exception of oxygen, the five major elements present in ISSA were Si, Fe, Al, Ca and P, as also reported by Cyr et al. (2007). The orange/red colour of BBM, CVI and SG ISSA was probably due to the elevated levels of Fe in these ash samples. Beckton and Crossness ISSA from Thames Water showed elevated levels of Ca which may be attributable to the different method of ash separation used at these incinerators, where partial blending with spent lime/coke from the flue gas abatement system occurs. Other elements present at lower but significant concentrations were Mg, K, Na, Ti and S. Total P results from colorimetric analysis broadly agreed with XRF results and ranged from 12.3 to 17.5% P₂O₅. Previous work has shown that Zn is the most significant heavy metal present in ISSA, at levels that ranged between 1200 and 2800 mg/kg ISSA (Donatello et al., 2010a).

Particle size varied considerably between samples with the Knostrop ISSA being around 4 times larger on average than Beckton and Crossness ISSA, which were the finest samples. The specific surface area of ISSA was also much higher for Beckton and Crossness ISSA and, along with the finer particle size distribution, is attributed to the partial blending of spent activated lignite coke with these samples.

X-ray diffraction data in Figure 2 shows that quartz was the dominant crystalline phase present in all samples. Haematite was also observed in samples with high Fe content (BBM, CVI and SG). All samples showed peaks corresponding to various types of whitlockite. Due to very similar diffraction patterns, it was not possible to conclude if the whitlockite was the pure tri-calcium variety or with partial Fe or Al substitution for Ca. It is assumed that a mixture of different forms exist in each ISSA sample.

3.2. *Effect of reaction time*

The effect of reaction time on P and cation dissolution is summarised in Figure 4, with data expressed as % of total element dissolved. Total P was calculated as the sum of soluble P, plus P extracted from the remaining solids by Kjeldahl digestion. This was calculated for each reaction time and varied between 67,000 and 78,000 mg/kg due to heterogeneity in the 1 g ISSA samples.

Total Al, Fe, Mg and Ca were assumed to be approximately 71,000, 116,000, 23,500 and 85,000 mg/kg respectively by reference to XRF data in Table 1. Total Zn was assumed to be the average Zn extracted by lithium metaborate fusion (2737 mg/kg for BBM ISSA in Table 1). Percentage cation extraction efficiencies should be viewed as approximate because the same total value is assumed for all 1 g sub-samples.

From Figure 4 it is clear that 0.5 mol.l⁻¹ H₂SO₄ is capable of dissolving approximately 85% of P present within 30 minutes. This increases up to around 91% P dissolution after 120 minutes of reaction time and then only slowly up to 100% dissolution after 720 minutes. Major cations simultaneously dissolve with P, but to lower extents. Aluminium and Mg ions were the most soluble, whereas Fe and Ca had limited solubility. The apparently low acid solubility of Ca is misleading because simultaneous CaSO₄.2H₂O precipitation occurs in the reaction system.

Dissolution of P from whitlockite in ISSA is characterised by rapid dissolution of over 80% of total P during the first 30 minutes, as acid readily dissolves P from the whitlockite particles present in ISSA. This is followed by gradual dissolution of the remaining extractable P. The lower dissolution rate may be due to steric hindrance caused by the formation of gypsum crystals on the original whitlockite particle surfaces and/or by acid insoluble haematite and quartz phases restricting acid contact with some whitlockite crystals.

The optimum reaction rate in terms of P dissolved per minute occurred at 5 minutes. However it is important for the economics of the process that a high percentage of P is removed. Achieving 85% removal after 30 minutes appears to be the optimum and has the advantage of dissolving relatively low quantities of cations. However, considering that ideally a lower H₂SO₄ concentration closer to the stoichiometric requirement of 0.18

to 0.24 mol.l⁻¹ should be used, and that other ISSA samples may require more time to extract P, 120 minutes was chosen as the optimum reaction time.

3.3. *Effect of H₂SO₄ concentration*

Previous studies by the authors with an equivalent whitlockite-sulfuric acid system showed that insufficient P dissolution occurred below 0.10 mol.l⁻¹ H₂SO₄ (Donatello, thesis 2009). Therefore the H₂SO₄ concentrations were limited to 0.0 mol.l⁻¹ (DI water), 0.10 mol.l⁻¹, 0.19 mol.l⁻¹ (the stoichiometric acid requirement at L/S of 20), 0.30 mol.l⁻¹ and 0.50 mol.l⁻¹, which is a repeat of the 120 minute reaction time condition from the previous experiment.

Results for the effect of different H₂SO₄ concentrations on P dissolution after 120 minutes at ambient temperature and L/S ratio of 20 are shown in Figure 5. From the results it is clear that the H₂SO₄ concentration can be reduced as low as the stoichiometric requirement (0.19 mol.l⁻¹) with little adverse impact on P extraction efficiency. Below the stoichiometric acid requirement, there is a directly proportional decrease in P extraction efficiency with decreasing acid concentration.

The dissolution of major cations from BBM ISSA was highly variable between individual samples. Reducing the H₂SO₄ concentration to 0.19 mol.l⁻¹ does not significantly decrease the levels of major cations in the filtrate and these are still present at problematic levels for Al and Mg with 30-40% dissolution. To minimise the concentration of sulfate anions in the filtrate, it was decided that future experiments should use 0.19 mol.l⁻¹ of H₂SO₄, at L/S ratio of 20.

3.4. *Effect of L/S ratio*

The optimised H₂SO₄ concentration of 0.19 mol.l⁻¹ chosen at L/S of 20 is equivalent to 0.0038 moles H₂SO₄ per gram ISSA. Samples were prepared with L/S ratios of 5, 10, 15 or 20. To maintain the ratio of 0.0038 moles H₂SO₄ per g ISSA, 0.76 mol.l⁻¹ solution was used in L/S = 5 systems, 0.38 mol.l⁻¹ H₂SO₄ at L/S = 10 and 0.25 mol.l⁻¹ at L/S = 15. Figure 6 below illustrates the extraction efficiency of P, Al, Fe, Ca, Mg and Zn relative to the total quantities present in BBM ISSA.

The results in Figure 6 indicate how important it is for there to be sufficient contact between solid particles and the leaching solution. Samples with L/S ratios of 10 and 5 dissolve on average only around 61% and 25% of total P respectively, despite there being sufficient time and acid available to dissolve >80% of total P. As the L/S

ratio decreases, contact efficiency is reduced along with the extraction efficiency of P and all major cations.

However there was no significant decrease in P extraction between L/S ratios of 15 and 20.

L/S ratio of 20 was chosen as the optimum condition due to the fact that P extraction was slightly higher and more consistent than at L/S 15 for P extraction.

3.5. *Effect of ISSA source*

Following from the results of the previous three experiments, the optimised conditions for P extraction were; reaction time of 120 minutes, H_2SO_4 concentration of 0.19 mol.l^{-1} and L/S ratio of 20. Figure 7 shows the average P extraction efficiencies for each of the seven ISSA samples under these conditions.

It is evident that all ISSA samples release the majority of total phosphate under these optimised conditions. Replicate samples were quite consistent with the exceptions of SG and Esholt ISSA. Average P extraction varied from 72 to 91%, indicating the similarity of ISSA samples in terms of P availability.

In general, Mg and Al have the highest degree of co-dissolution with phosphorus for any given sample (Figure 8). Esholt and CVI ISSA showed the lowest overall cation co-dissolution and the two Thames ISSA samples (Beckton and Crossness) showed the highest cation dissolution. The solubility of Zn was generally below 10% except with the Thames ISSA samples, which showed much higher dissolution of between 30 and 60%. The same effect was noted with Fe, Mg, and Al to differing extents. The reason for the higher cation dissolution from Thames ISSA samples must be related to the different ash collection mechanisms used on these plants. The Thames incinerators use cyclonic separators to remove the majority of ISSA and blend ISSA with spent lignite coke from downstream flue gas abatement. Other incinerators use electrostatic precipitators or bag filters to remove ISSA and do not blend any spent activated coke material with ISSA.

Cation exchange treatment will ultimately produce an acidic waste solution from resin regeneration that requires disposal. An interesting approach to dealing with cation exchange was described by Svensson (2000) where by staging cation and anion exchangers in a certain formation and using different solutions to regenerate the resins, it was proposed that separable products such as $\text{Fe}_2(\text{SO}_4)_3$, KHSO_4 and H_3PO_4 could be produced from a mixed filtrate. Alternatively the different metals could be selectively precipitated by controlled sulfide dosing (Tokuda et al., 2008) or sodium decanoate addition (Mauchauffee and Meux, 2007) to the spent cation regeneration acid. This is however outside the scope of the work, which was focussed primarily on obtaining a high purity H_3PO_4 product.

3.6. Filtrate purification and concentration

Zinc, Fe, Ca, Mg, Al, P and SO_4^{2-} concentrations in the filtrate before and after cation exchange and assumed concentrations after concentration are shown in Table 2 in comparison to the technical grade H_3PO_4 specification from a commercial supplier.

Cation exchange greatly reduced the levels of cations in the dilute acid, by factors of ~100 for Ca, ~500 for Fe and Zn, ~2000 for Al and 10,000 for Mg. It is also important to note that around 6% of total filtrate P was lost during cation exchange, due to PO_4^{3-} anions being tightly associated with bound multivalent cations on the surface of the resin beads.

When attempting to concentrate the un-purified filtrate, the solution eventually turned into a white slurry as the solubility product of various sulfate and phosphate salts was exceeded. However, concentration of the purified filtrate showed no precipitation problems up to around 80% as H_3PO_4 . One major problem with the concentrated acid product is the high sulfate content. To meet existing specifications it would be necessary to remove excess sulfate anions to below 100ppm. Although this could be achieved by proven techniques such as precipitation with Ba salts, the low solubility product of $\text{Ba}_3(\text{PO}_4)_2$ would mean losses of P.

4. Discussion

The dissolution of 80-100% of phosphate from ISSA by sulfuric acid is feasible, as previously demonstrated by other researchers (Oliver and Carey, 1976; Stark et al., 2006; Takahashi et al., 2001; Franz, 2008). However a different approach has been taken in this work that has attempted to produce a technical grade phosphoric acid from ISSA. The major costs of the proposed process are the sulfuric acid to dissolve the phosphate, hydrochloric acid to regenerate the cation exchange resin and the energy to evaporate the excess water from the dilute filtrate.

Using the optimised process, it has been calculated that from 1 tonne of ISSA, 368 kg of 98% H_2SO_4 , 426 kg of 36% HCl and energy to evaporate about 987 kg of water would be required to produce at least 195kg of 85% technical grade H_3PO_4 (Donatello, 2009). Clearly the most significant cost is the energy required to evaporate water. Ideally any potential pilot scale or commercial scale plant would be located adjacent to an abundant source of waste heat such as steam cycle power plants, so that waste heat could be used to evaporate excess water. In hindsight, it is evident that the horizontal motion shaker used in this study, although advantageous in processing large numbers of samples simultaneously, was not sufficiently aggressive to create

optimum contact at low L/S ratios (<15 ml/g). If a similar mixing regime as to that described by Franz (2008) were to be employed, it is feasible that a L/S ratio as low as 2 ml/g could be used to produce a filtrate with around 10 times less water to be evaporated (98 kg water/tonne ISSA).

The high level of sulfate in the concentrated phosphoric acid product fails to comply with product specifications. If a valid product is to be developed for speciality applications, it would be necessary to treat the filtrate at some stage with a highly selective solvent extraction process, using a solvent such as tri-butyl phosphate which is widely used in the wet process phosphoric acid industry. Otherwise, it would be recommended to only concentrate the purified filtrate to merchant grade 50% H₃PO₄ for use in fertiliser manufacture.

Another important consideration is the ultimate fate of the acid insoluble residue that remains after filtration. If this material is sent to landfill without further treatment, it is possible that high levels of leachable sulfate would require acid treated ISSA to be sent to hazardous waste landfill at high cost. The potential for re-use of the acid insoluble residue in Portland cement (CEM-I) based mortars is therefore the subject of ongoing research.

5. Conclusions

A number of conclusions can be drawn from the work carried out;

- Phosphorus is present in ISSA in the form of the tri-calcium phosphate mineral, whitlockite, with varying degrees of Ca substitution by Fe, Al and/or Mg.
- From current global ISSA production of $\sim 1.7 \times 10^6$ tonnes/yr, approximately 250,000 tonnes of P₂O₅ could be recovered. With the speciality phosphate market representing around 1,500,000 tonnes of P₂O₅, it is recommended that ISSA recovered phosphate is targeted at these applications.
- Up to 100% of phosphate can be recovered from ISSA by acid leaching if sufficient contact and reaction time is allowed (up to 720 minutes). However around 80% of phosphate is dissolved in the first 30 minutes.
- Below the stoichiometric acid requirement, P dissolution was directly proportional to acid concentration.
- Above the stoichiometric acid requirement, very little additional P dissolution was noted.
- The horizontal motion mixing procedure used in this work was insufficient to achieve adequate acid to phosphate contact below L/S ratios of 15. Using a more aggressive mixing procedure could lower the L/S ratio as low as 2, greatly reducing later energy costs for acid concentration.

- Cation exchange proved a useful technique for removing Al, Fe, Mg, Ca and Zn impurities that co-dissolve with P. However, around 6% of dissolved P was retained in the resin bed due to association with multivalent cations adsorbed onto resin surfaces.
- A high degree of sulfate removal is required before the acid product could be sold as technical grade H_3PO_4 .

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Fig. 1. Process for P extraction from BBM ISSA.

Fig. 2. XRD patterns for ISSA samples.

Fig. 3. Overall acid leaching, purification and concentration process.

Fig. 4. Extraction efficiency of P, Zn and major cations from BBM ISSA as a function of reaction time with $0.5 \text{ mol.l}^{-1} \text{ H}_2\text{SO}_4$ at a L/S ratio of 20 at ambient temperature. Total cations present assumed from data in Table 1. Results are averages of 4 replicates $\pm$ 1 standard deviation.

Fig. 5. Effect of H₂SO₄ concentration on P extraction efficiency and dissolution of Zn and major cations present in BBM ISSA. Reaction time was 120 minutes, L/S ratio was 20 and temperature 20°C. Results are the average of 4 replicates +/- 1 standard deviation.

Fig. 6. Effect of L/S ratio on average extraction efficiency of P, Zn and major cations present in BBM ISSA. Reaction time was 120 minutes and H₂SO₄ concentration was varied to be maintained at the equivalent of 0.0038 moles H₂SO₄ per gram ISSA. Results are the average of 4 replicates +/- 1 standard deviation.

Fig. 7. P extraction efficiencies from other ISSA samples using the optimised process for BBM ISSA. Results are averages of 3 replicates +/- 1 standard deviation.

Fig. 8. Percentage extraction of Zn, Fe, Mg, Ca and Al for different ISSA samples using the optimised P extraction process for BBM ISSA. Average filtrate concentrations are also included in text with each column. Results are averages of 3 replicates +/- 1 standard deviation.

Table 1

Summary of the physical and chemical characteristics of ISSA samples (Donatello et al., 2010a).

	BBM	Esh	CVI	Knos	SG	Beck	XN
Si (%)	15.1	15.6	13.9	12.4	15.0	16.5	15.8
Al (%)	7.1	14.5	7.8	16.6	6.9	6.8	6.3
Fe (%)	11.6	8.3	17.0	4.8	16.3	4.8	4.7
Ca (%)	8.5	5.4	6.6	6.3	7.4	12.2	13.5
P (%)	6.6	6.2	5.9	7.7	5.7	7.8	7.0
Mg (%)	2.4	1.1	1.9	1.3	1.7	2.4	2.6
K (%)	1.5	1.4	1.2	1.2	1.2	1.9	2.0
Na (%)	1.6	0.3	1.0	1.6	1.1	1.0	1.6
Ti (%)	0.8	0.7	0.7	1.1	0.7	0.7	0.6
S (%)	0.6	0.3	0.5	0.4	0.6	0.5	1.1
LOI (%)	1.8	1.1	2.1	1.6	0.9	1.4	1.6
Total P (% as P ₂ O ₅)	7.6	5.7	6.3	7.6	6.6	5.9	5.4
	(17.4)	(13.0)	(14.5)	(17.5)	(15.2)	(13.4)	(12.3)
Zn (mg/kg)	2737	1653	1878	1628	2576	1226	1536
Mean particle size (μm)	108.8	93.4	98.3	263.6	141.6	51.2	67.2
d ₁₀ (μm)	247.6	233.3	232.1	563.9	324.0	116.6	149.8
d ₅₀ (μm)	78.9	63.4	68.5	220.3	109.4	34.9	42.8
d ₉₀ (μm)	16.7	6.2	12.0	41.5	10.0	5.0	7.2
BET surface area (m ² /g)	10.4	8.4	7.5	9.3	6.4	18.0	23.8

Table 2

Levels of P and selected cation impurities in product acid before and after purification and concentration.

	Dilute ISSA	Conc. ISSA	Dilute ISSA	Conc. ISSA	*Supplier
	H ₃ PO ₄	H ₃ PO ₄ (85%)	H ₃ PO ₄	H ₃ PO ₄	specification
	without cation exchange		with cation exchange		
H ₃ PO ₄	0.98-1.07%	85%	0.92-1.01%	79.7%†	80-85%
SO ₄ ²⁻ (ppm)	943	80128	814	69171††	100††
Zn (ppm)	21.4	1819	0.031	2.6	5**
Fe (ppm)	263	22355	0.463	39.5	50
Ca (ppm)	434	36890	4.122	350	-
Mg (ppm)	372	31620	0.036	3.1	-
Al (ppm)	1451	123335	0.74	63	-

*Limit values supplied by Henan Harvest Chem. Co. Ltd, RUI Chem. Ltd and Shanghai Merry Yang Enterprise

Co. Ltd. **5ppm limit applies for all heavy metals. †It was not possible to control the laboratory process to produce a pre-determined H₃PO₄ concentration however in theory 85% is achievable by evaporating slightly more water. †† SO₄²⁻ analysis (by automated colorimetric analysis) was highly variable although average values greatly exceed the allowable limit of 100 mg/l SO₄²⁻. Based on a complete stoichiometric reaction with 0.19 mol.l⁻¹ H₂SO₄ at L/S ratio 20 (leaving 0.0625 mol.l⁻¹ of H₂SO₄ unreacted), a minimum of around 51,000 mg/l SO₄²⁻ can be expected in the concentrated, cation exchange treated acid.