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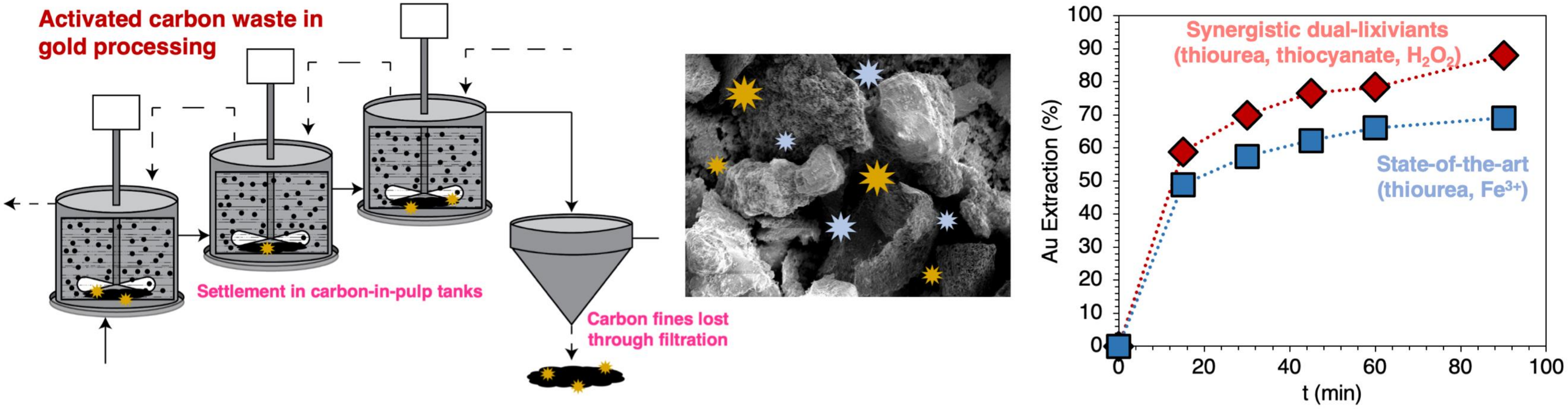
Graphical Abstract



Research Highlights

- Activated carbon ash samples contained 5960 mg·kg^{-1} of precious metals alongside numerous heavy metals
- Alkaline lixiviant treatments solubilised only 8.07% gold content of the ash
- A thiourea/thiocyanate/H_2O_2 combination improves gold extraction to 89%
- The preg-robbing ability of the waste is circumvented
- Kinetics are complicated, but tend towards a mixed-controlled process

An alternative to cyanide leaching of waste activated carbon ash for gold and silver recovery via synergistic dual-lixiviant treatment

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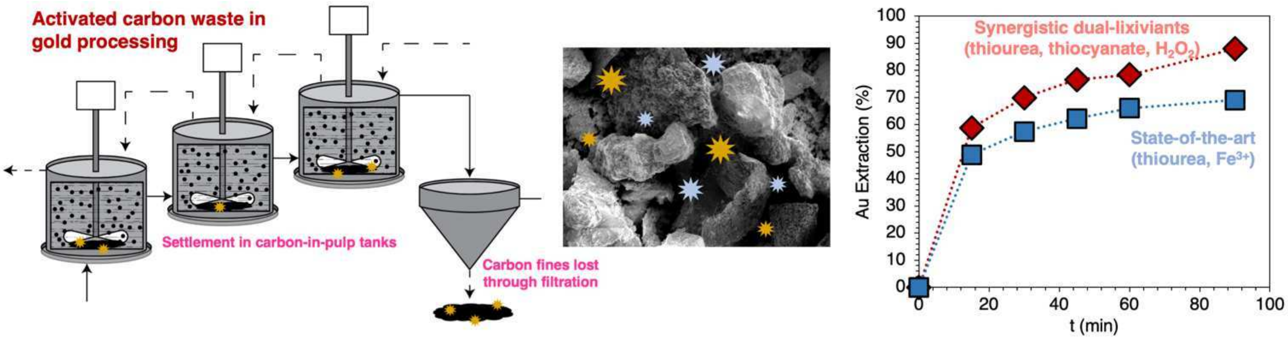

Abstract

This study reports the development of a hydrometallurgical treatment for activated carbon ash (ACA); a waste product of the carbon-in-pulp (CIP) process used in the gold mining industry, rich in adsorbed precious metals. After an initial screening of known leaching chemistries, the research focusses on dual-lixiviant (thiourea and thiocyanate) and thiourea systems, both of which have lower environmental impact than traditional cyanide leaches. Comparing ferric sulfate and hydrogen peroxide as oxidants showed that a thiourea leach is more suited to ferric sulfate whereas the dual-lixiviant leach achieved greater extraction with hydrogen peroxide. The latter demonstrated faster kinetics and improved efficiency for dissolution of gold and silver. However, both leaches had issues with silver extraction due to formation of passivating layers on the surface of the silver nanoparticles. Kinetic modelling showed both systems tended towards a mixed-controlled process. Gold extraction of 89%, with rapid kinetics using the dual-lixiviant process demonstrated that there is an alternative to cyanide leaches employed in gold recovery.

Keywords: gold recovery, leaching, activated carbon, waste valorisation, secondary metal resources

1. Introduction

Gold and silver (Au and Ag) have extensive uses in the electronics industry, as catalysts, and as luxury commodities. Present spot prices, provided by the London Metal Exchange are $54,700 (Au) and $505 (Ag) per kg respectively, having increased by ~445% and 243% in the past 20 years [1]. Globally, the majority of Au is extracted from open pit mines, where massive amounts of earth are excavated and processed for targeted metal recovery. It is estimated that to produce a single gold ring, as much as 400 tonnes of rock and soil are mined [2]. Because of the very sparse gold concentrations in most ores (for example, chalcopyrite contains <40 g·T^{-1} [3]), 99% of the extracted mass is treated as waste by mines [4], potentially releasing heavy metals and cyanide to the environment through either leaching or weathering processes [5, 6]. The concept of "green mining" has emerged in recent years as a powerful rationale for the adoption of industrial technologies and processes that minimise environmental impact and contribute to decarbonisation [7] Thus, there is a growing pressure on companies and institutions to reject precious metals produced from environmentally and socially destructive mining [8, 9]. There is a concurrent increasing interest in secondary metal resources and reprocessing, with wasteforms such as metallurgical slags [10] and dross [11] receiving recent attention from researchers. This focus has clear benefits, as part of an overall shift to a circular economy.

Initially, gold and silver bearing ores are leached for 20-40 hours in agitated tanks by sodium cyanide (NaCN) and form $[Au(CN)_2]^-$ and $[Ag(CN)_2]^-$ ions as per Equation 1.

$$4M_{(s)} + 8NaCN_{(aq)} + O_{2(g)} + 2H_2O_{(l)} \rightleftharpoons 4[M(CN)_2]^-_{(aq)} + 4NaOH_{(aq)} \qquad \textbf{(Eqn. 1)}$$

The cyanide pregnant leach solution (PLS) is commonly treated with activated carbon (AC) to selectively adsorb the metals, known as the carbon in pulp method (CIP), the main advantage being unimpaired efficiency in foul cyanide solutions [12, 13]. A typical CIP process uses a counter-current series of cascading tanks (Figure 1). The process has certain inefficiencies: loaded AC can settle at the bottom of the adsorption tanks and carbon fines (typically >20 mesh (841 µm) but otherwise chemically identical to the parent AC) can be lost in the filtration step and end up in the process tailings. Elution of the precious metals from the loaded AC (Figure 1) is achieved with various reagents, such as alkaline sodium sulfide/sodium sulphite solutions, deionised water, boiling sodium cyanide/sodium hydroxide and organic solvents [14]. None of these elution chemistries are 100% efficient and over time, loaded AC can build up in the system. A survey of 36 mines found that 0.11-0.14 kg of Au per tonne of AC remained unrecovered [15], with up to 0.525 kg of Au per tonne reported in other individual cases [16]. There is also potential for recovery from the fines passing through the filter screens (Figure 1, step 2).

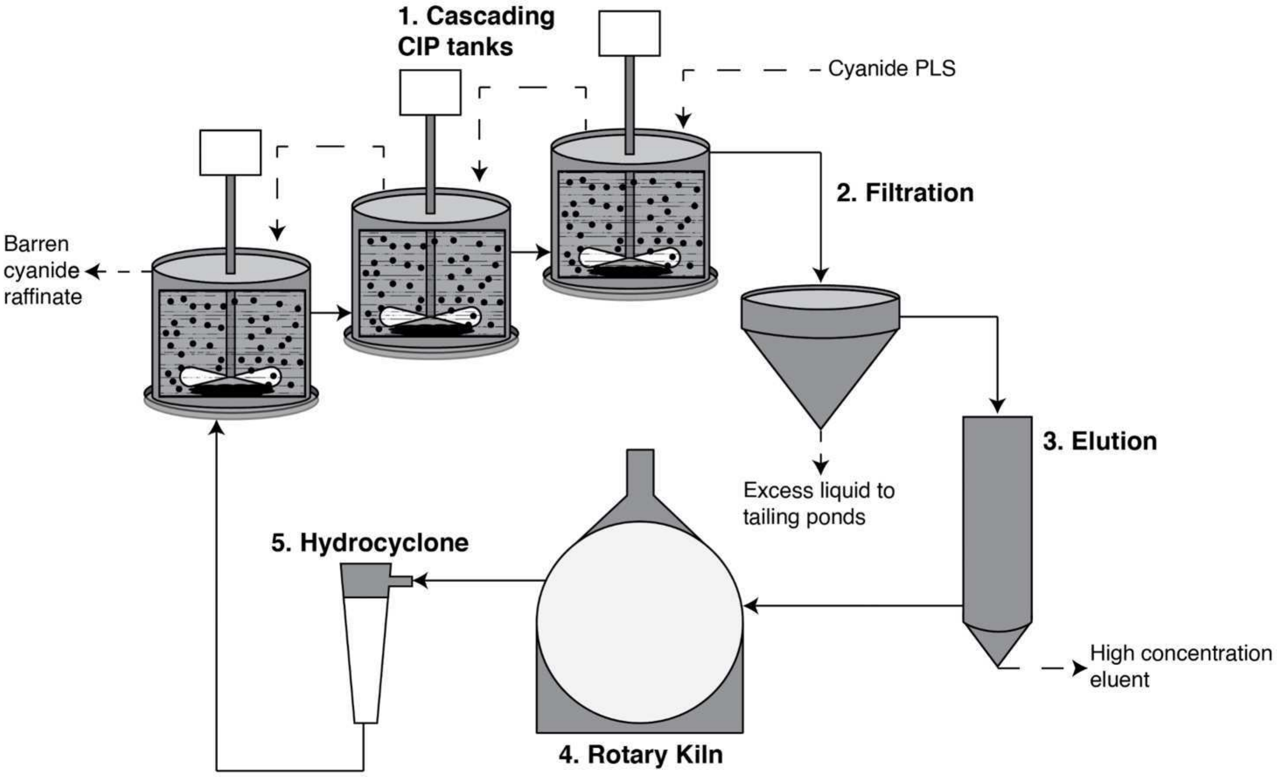

Figure 1. General CIP process for Au recovery.

Incineration is used to reduce AC waste volume and remove mercury, [17], also exposing the remaining Au and Ag present in the activated carbon ash (ACA) as electrum nanoparticles. The metals can be recovered by smelting, gravity concentration and chemical leaching [18, 19]. Due to the energy demand of smelting and slow processing times of gravity concentration the most viable technology for recovery of gold and silver from ACA is a chemical process.

Sodium cyanide has been used in gold mining since 1887 and remains the primary reagent used for Au processing, due to efficient extraction from low-grade ore [20]. It is however, highly toxic, with a mean dose of 50-200 mg causing fatality in human adults [21]. Over the past 50 years, 12 out of 67 environmental incidents in the mining sector have directly involved cyanide release [20]. Public unease about the dangers of cyanide use directly impacts decision-making in mining operations [22, 23].

Throughout the history of Au extraction, there has been a desire to find a replacement lixiviant to NaCN for leaching ores with over 100 considered by researchers [22]. Few have seen industrial application due to capital expenditure (CAPEX) of the systems and poor extraction from low grade ores. However, the concentrations of precious metals are orders of magnitude higher in ACA than most ores [3, 18, 24]. The samples investigated in this work possessed an estimated total Au and Ag value of >$153,000·T^{-1}. Thus, the potential added value of a hydrometallurgical process is much higher. Therefore, an environmentally acceptable leaching system, with more expensive reagents, but lower toxicities may be a wiser long-term business strategy. Despite this, the last significant industry survey estimated that each gold processing plant discharges ~2000 tonnes of waste carbon per year [15]

Despite its potential value, there have been few attempts to design new leaching treatments for ACA. Conventional cyanide leaching is still routinely practiced [16, 25, 26]. A review of the literature found few examples of alternative lixiviants applied to precious metal recovery from ACA, apart from the work of Amankwah *et al*. [18, 27]. We therefore examined leaching from other matrices, such as ores and waste electrical devices.

Thiourea ($SC(NH_2)_2$) is a popular and well-researched alternative lixiviant for Au, due to its complexation ability and fast kinetics. Fe^{3+} is the most commonly-used oxidant and the overall chemistry of the leaching of the metallic nanoparticles within the ACA is shown in Equation 2

$$M + 2CS(NH_2)_2 + Fe^{3+} \rightarrow M[CS(NH_2)_2]_2^{+} + Fe^{2+} \qquad (M = Ag\ or\ Au) \qquad \textbf{(Eqn. 2)}$$

For the Au half-cell reaction, $E^0 = 0.352$ V and β_2 of the thiourea complex = 2.0×10^{21} [28]. For the Ag half-cell reaction, $E^0 = 0.400$ V and β_2 of the complex = 4.07×10^{10} [29, 30] and for the Fe half-cell reaction, $E_0 = 0.771$V [28]. This is an effective system for leaching from numerous sample matrices, with >90% Au extraction routinely reported from ores [31, 32], carbon fines [18] and waste electronics [33]. Leaching durations are generally lesser than cyanide systems, at < 6 hr [29, 34]. However, a significant drawback is that thiourea itself is an oxidizable species and is converted to formamidine disulphide (FDS) and ultimately to elemental sulfur via Equations 3-5 [28].

$$2SC(NH_2)_2 \rightarrow (SC(NH)(NH_2))_2 + 2H^+ + 2e^- \qquad \textbf{(Eqn. 3)}$$
$$(SC(NH)(NH_2))_2 + {}^1/_2O_2 + H_2O \rightarrow SC(NH_2)_2 + NH_2(NH)CSOOH \qquad \textbf{(Eqn .4)}$$
$$NH_2(NH)CSOOH \rightarrow CN{\cdot}NH_2 + S^0 + {}^1/_2O_2 + H_2O \qquad \textbf{(Eqn. 5)}$$

For Equation 3, $E^0 = 0.42$ V [35]. In Equation 5, sulfur in higher oxidation states (sulfate) may also be formed, depending on solution ORP [36].

The subsequent thiourea consumption and considerable expense of the reagent is one of the main drawbacks of Au leaching by thiourea (the “freight on board” price for technical grade thiourea was >$1500·T^{-1} from most merchants at time of writing). There is however a complexation reaction with Fe^{3+} (Equation 6), which retards the rate of thiourea oxidation.

$$Fe^{3+} + 2SC(NH_2)_2 \rightarrow [Fe(SC(NH_2)_2)]^{3+}\ (\beta_2 = 2.75 \times 10^8\ [28]) \qquad \textbf{(Eqn. 6)}$$

For this reason, Fe^{3+} is historically favoured over stronger oxidants like H_2O_2 [22, 28, 36], the leaching chemistry for which is shown in Equation 7.

$$M + 4CS(NH_2)_2 + {}^1/_2H_2O_2 + H^+ \rightarrow M[CS(NH_2)_2]_2^+ + H_2O \qquad (\textbf{Eqn. 7})$$

Although H_2O_2 offers potentially faster kinetics, it also accelerates the thiourea oxidation [3, 22], as there is no competing complexation reaction, and is more costly than $Fe_2(SO_4)_3$. It should be noted that not all experimental data show that H_2O_2 systems consume more thiourea. Tremblay *et al.* found that using Fe^{3+}, rather than H_2O_2 increased thiourea consumption rate by a factor of ~2, although this study used acid mine drainage, of mainly unknown chemistry, as a source of Fe^{3+} [24].

The dissolution of Ag nanoparticles essentially follows the same REDOX mechanism as for Au and similar thiourea complexes are formed in solution. However, the literature demonstrates that Ag extraction and kinetics are always inferior to Au [3, 33, 37]. The difference is often considerable (28% verses 94% [29]). The reasoning given is that the oxidant present in the lixiviant invariably oxidises some thiourea to elemental sulfur/sulfate in colloidal form [29] (Equation 5). This readily reacts with Ag^+ (Ag_2S $k_{sp} = 6.31 \times 10^{-50}$; Ag_2SO_4 $k_{sp} = 1.20 \times 10^{-5}$), forming a tarnishing layer, which has extremely slow leaching kinetics [38]. Furthermore, excessive $Fe_2(SO_4)_3$ in the system forms a solid $Ag_2SO_2{\cdot}thiourea{\cdot}H_2O$ complex, which causes further passivation [28]. There are similar processes for the retardation of Au leaching, though not to the same degree [39].

Aside from thiourea, other alternative lixiviants studied have included thiocyanate. This also forms highly stable Au complexes, according to Equation 8 (again showing Fe^{3+} as the oxidant)

$$Fe(SCN)_4^- + M \rightarrow Fe^{2+} + M(SCN)_2^- + 2SCN^- \qquad (M = Ag \text{ or } Au) \qquad (\textbf{Eqn. 8})$$

For the Au half-cell reaction, $E_0 = 0.659$ V and $\beta_2 = 1.47 \times 10^{19}$ [40]. For the Ag half-cell reaction, $\beta_2 = 3.72 \times 10^7$ [41]. However, the solubility of AgSCN is actually low and precipitation is favourable in solutions where $[SCN^-] < 1.5$ M [42, 43], which is a drawback of these leaching systems for Ag. Aside from this, thiocyanate leaches bear some similarities to thiourea, in that thiocyanate ions become oxidised to $(SCN)_2$ and $(SCN)_3^-$ and the presence of Fe^{3+} retards the rate of oxidation (although not to the same degree as thiourea, as the complexes formed are not as stable) [40].

Other lixiviants investigated for extraction of precious metals include thiosulfate [44], glycine [37] and aqua regia [45]. An aspect of Au hydrometallurgy more rarely considered is the use of synergistic dual-lixiviants. Improved extraction has been found with iodine/thiocyanate [46] and particularly thiourea/thiocyanate systems. Yang *et al.* studied the kinetics of Au leaching with varying lixiviant molar ratios and suggested the formation of a mixed-ligand $Au(SC(NH_2)_2)_2(SCN)$ complex [47]. Zhang *et al.* identified the role of thiocyanate in reducing free thiourea consumption in the system [48]. This may represent a pathway towards reducing the working-CAPEX of thiourea leaching, though initial cost may be higher.

However, dual lixiviant treatments remain poorly understood. They have only been employed with Fe^{3+} as the oxidising species. Ag extraction has not been studied, athough a dual-lixiviant system could potentially negate the low solubility of AgSCN via mixed-ligand complex formation [47]. The kinetics of solubilisation are sparsely investigated. They have never been applied to ACA materials and there is no evidence of efficacy in the presence of "preg-robbing" species (those which retain some affinity for the target metals and can re-adsorb them from the PLS), such as unincinerated AC particles. These are the challenges addressed in this study, which aims to effect a step change in gold mining sustainability via alternative leaching chemistries, applied for the first time to waste ACA, and exploring process optimisation and dissolution mechanisms.

2. Experimental

2.1. Materials and reagents

H_2O_2 (30% w/v solution), HNO_3 (70% v/v, 99.999%), $Fe_2(SO_4)_3$ (≥97%), glycine (≥99%) and thiourea (≥99%) were purchased from Sigma Aldrich (Gillingham, UK). H_2SO_4 (>95%) and NaOH (98%) was purchased from Fisher Scientific (Loughborough, UK). NaSCN (≥98%) was purchased from Fluka (Gillingham, UK). Deionised water (>18 MΩ) was used throughout.

Activated carbon ash (ACA) was kindly provided by R.S. Bruce and was a composite of samples of spent AC from a number of gold mines in the United States (Cortez, Hycroft, Marigold and Round Mountain). The composite sample was ashed by incineration at 900°C (Carbolite AAF 12/18 chamber furnace, Hope, UK) and took the form of a fine powder. Particle size was not investigated on this occasion.

2.2 Solid state analysis of activated carbon ash

Powder XRD (PXRD) spectra were attained using an X-ray diffractometer (Bruker D2 PHASER, Coventry, UK) using dual Ni kβ filters. Samples were prepared by grinding with a mortar and pestle, then passing the particles through the appropriate international standard sieve. Spectra were matched using the ICDD PDF-4+ crystallographic database and semi-quantitative analysis performed using the Sieve+ computer programme, by the ICDD [49]. Visualisation of the ash was achieved using an analytical scanning electron microscope (Jeol JSM-6010LA, Tokyo, Japan). Samples (as received) were mounted onto carbon tape. Energy-dispersive X-ray spectroscopy (EDX) analysis was carried out on the same instrument, operated in point analysis mode.

2.3. Materials assay

The absolute concentrations of Ag, Au and other metals in the ACA parent sample were determined as follows. ACA was milled to a particle size of <250 μm via grinding with a mortar and pestle and passing the particles through the appropriate international standard sieve. Samples were then weighed, placed in a Zr crucible and fused with nitrogen-flushed sodium peroxide at 700°C for a minimum of 15 min, using a meker burner. Samples were then dissolved in deionised water and HCl and diluted appropriately for ICP-OES analysis.

2.4. Leaching studies

All leaching experiments were conducted in Nalgene® 1L jars, fitted with baffles and PTFE magnetic stirrers. Except when removing samples, the lids were sealed to prevent atmospheric O_2 from affecting the ORP. Magnetic stirring was fixed at 300 rpm. A typical leach was conducted over a period of 6 hours with temperature controlled at 25°C. Each experiment used 25.0 g activated carbon ash and the initial volume of solution used was fixed at 250 mL. Leaching solutions were made up using deionised water and the required quantities of lixiviant (aqua regia, glycine, thiocyanate, thiosulfate and thiourea) and oxidant ($CuSO_4$, $Fe_2(SO_4)_3$, H_2O_2 and Na_2SO_3) in volumetric flasks. For most experiments, [thiourea] was set at 0.13 M and [thiocyanate] at 0.78 M, as per optimum reported concentrations for Au dissolution [48]. $[Fe^{3+}]$ was varied between 0.006 M and 0.18 M. $[H_2O_2]$ was varied between 0.0147 and 0.147 M. The suspension pH was set and maintained throughout leaching experiments within ±0.5 units using a standard Ag/AgCl electrode (Mettler-Toledo DGi115-SC, Leicester, UK). For lixiviant screening, this was done with HNO_3/NaOH and for all other experiments, H_2SO_4/NaOH was used. Periodically, 4 mL "thief" samples were removed from the leaching vessel, which were immediately added to aliquots of 9 mL HNO_3 (1% v/v), to prevent any precipitation, then filtered, using Corning 0.2 μm syringe filters. Concentrations of Ag and Au were determined using ICP-OES (Spectro Arcos FHS12, Kleve, Germany).

2.5. Fitting of leaching data to kinetic models

Data were fitted to the “shrinking core model” [50], which is commonly-used to describe heterogeneous leaching reactions [51, 52]. This model considers a simple reaction system A + B ⟶ products, where A is the reactive aqueous species and B is the leached species. Reacting particles of B are considered to be spheres. At the outset of the reaction, the whole reactive outer layer of the particles is exposed to the leaching solution and as the reaction proceeds, the reactive portion shrinks, forming a gelatinous product layer [50]. Three variants of the model are shown in Equations 9-11.

$$\frac{t}{\tau} = 1 - (1 - \mathrm{X_b})^{\frac{1}{3}} \qquad \textbf{(Eqn. 9)}$$

$$\frac{t}{\tau} = 1 - 3(1 - \mathrm{X_b})^{\frac{2}{3}} + 2(1 - \mathrm{X_b}) \qquad \textbf{(Eqn. 10)}$$

$$\frac{t}{\tau} = \left[(1 - \mathrm{X_b})^{-\frac{1}{3}} - 1\right] + \frac{1}{3}\ln(1 - \mathrm{X_b}) \qquad \textbf{(Eqn. 11)}$$

In these equations, t is the time that the leaching experiment has progressed for at the point a given sample is taken (min), τ is the total leaching time (min) and X_b is the reacted fraction of the leached species. If a dataset agrees with Equation 9, the reaction is rate-controlled by the diffusion of A across the particle boundary layer (diffusion-controlled). If Equation 10 describes the data, the kinetics are dominated by the chemical REDOX reaction (reaction-controlled). If Equation 11 fits the data accurately, both stages are influential to the rate (mixed-controlled). These models were fitted to leaching data using linear regression.

3. Results and Discussion

3.1. Solid state analysis of activated carbon ash

A PXRD spectrum of the untreated ACA sample (Figure 2) revealed a number of crystalline phases, mostly varieties of SiO_2 (~26% mass). Also present were $NaAlS_3O_8$ (albite, ~54%) and graphite (~20%). The latter indicated that a small proportion of the original activated carbon is graphitised and survives the incineration process. Apart from changes in the ratios of the three species present, there was no change to the apparent minerology of the ACA after the leaching treatment, as any leached crystalline species were not present at high enough concentrations to be detected by PXRD.

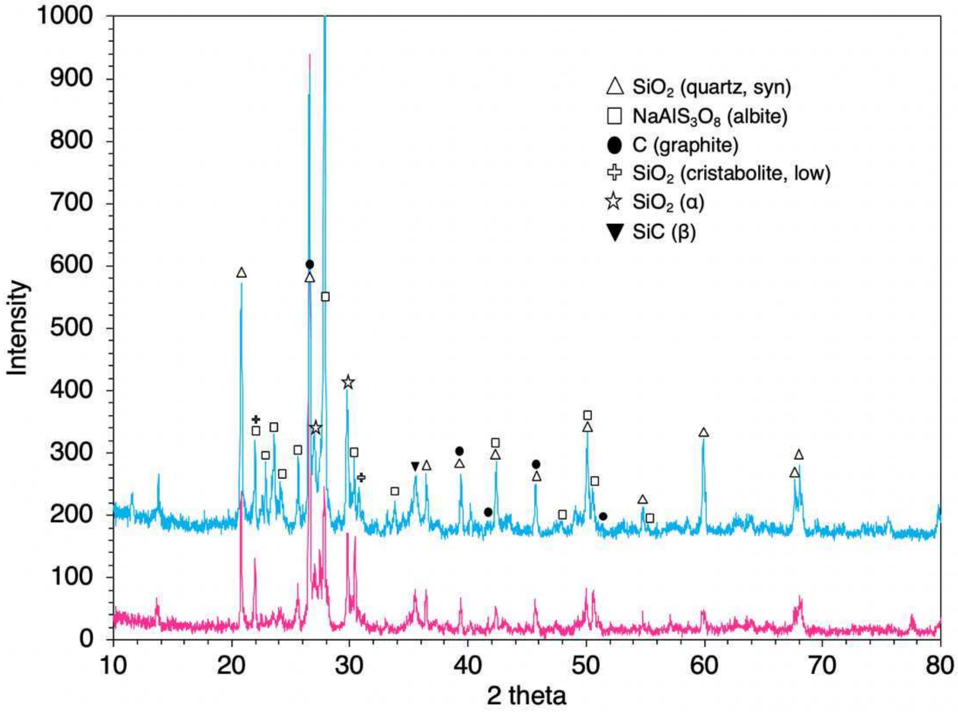

Fig. 2. [in colour] PXRD spectra of ACA before leaching treatment (pink line) and ACA after 0.13 M thiourea, 0.78 M thiourea and 0.06 M Fe^{3+} leach (blue line). Other lixiviant and oxidant combinations produced very similar spectra and are not presented.

A medium-resolution SEM image of a non-homogenised sample (Figure 3a) shows particles of the three main minerals present within the sample. A point EDX analysis on the particles designated with Greek symbols was used to identify the species (Table S1-S4). In addition to the crystalline materials, the micrographs showed a small fraction of amorphous, porous AC, which had survived incineration, remained with the ash (Figures 3a and 3b). This suggested the ACA might retain preg-robbing capabilities. Elemental mapping of a particle of AC (Figures 3c and 3d) showed that Ag nanoparticles were distributed very evenly over the surface. Au distribution was similar, but appeared also to feature a number of sites of richer concentrations. This cannot be related to liquefication of nanoparticles during incineration, because of the higher melting point of Au, but previous work has identified larger deposits of Au in carbon fines [53]. Au mapping was also performed on a silicate particle, which showed the metal was also present in the non-carbonaceous fraction of the ash (Figure S1).

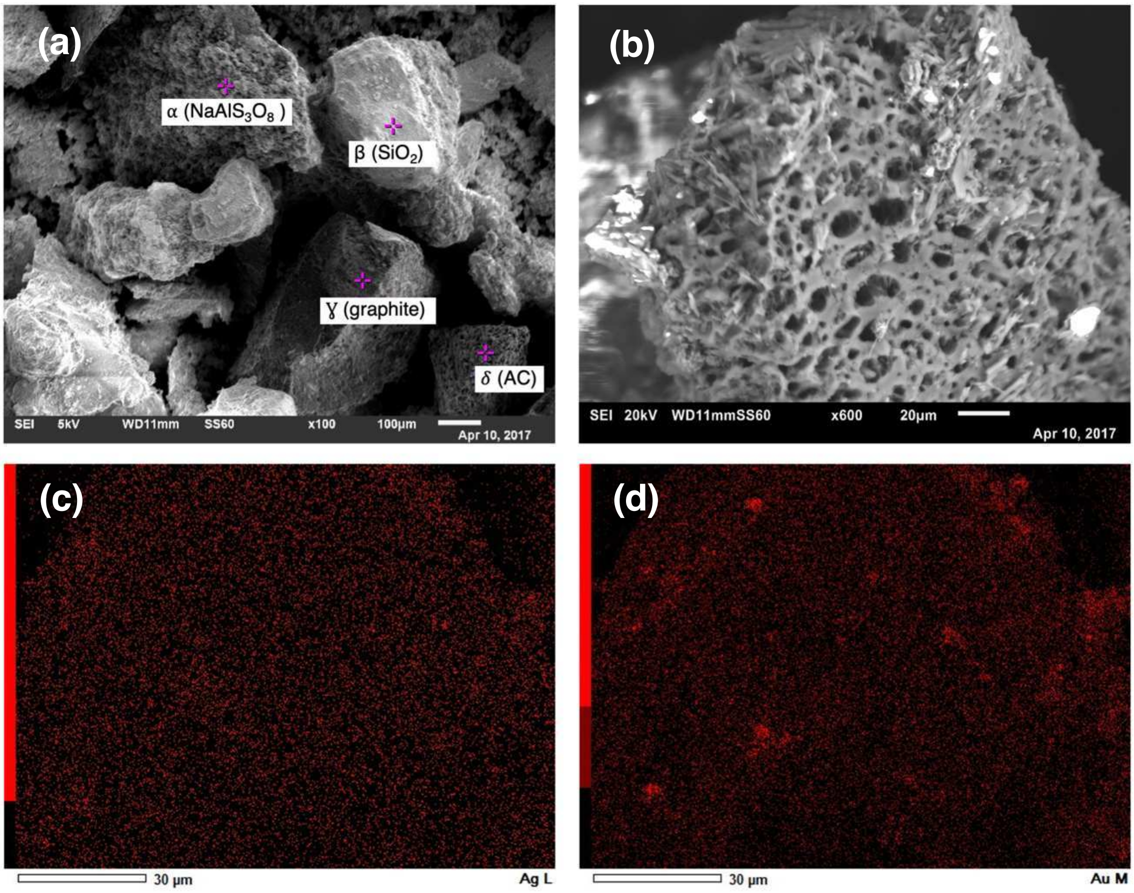

Fig. 3. [in colour] SEM images of ACA samples. **(a)** Showing the variety of mineral particles in the ash, with different phases (confirmed by EDX) indicated. **(b)** An unincinerated AC particle. **(c)** Ag elemental mapping of an AC particle. **(d)** Au elemental mapping of an AC particle.

3.2. Materials assay

The quantification of metals present in the ACA is shown in Table 1. As can be seen, the ACA was a rich source of precious, transition and heavy metals, in particular, having a remarkably high Sn concentration. It follows that a number of solubilisation and complexation reactions are possible, which could complicate Au and Ag recovery. For example Cu^{2+} is known to decrease Au extraction in thiourea media [35, 54], likely due to favourable REDOX reactions, similarly to Fe^{3+} [55]. It also has a high affinity for thiocyanate (K_{sp} for $CuSCN_{(s)}$ formation = 5.75×10^{12} [40]). Thiocyanate is known to readily adsorb and deposit sulfur on a variety of metallic surfaces, such as Cr, Fe and Ni [56, 57]. Additionally, Sn thiourea and thiocyanate complexes are readily formed in aqueous, acidic conditions [58, 59], although nothing is reported as to their interference in Ag and Au leaching. Although an acidic pre-treatment is seemingly a good option to try and improve Au and Ag extraction [3, 35], this would also add the cost of an additional leaching stage to a proposed process. Subsequent results (section 3.4) demonstrate that under the correct experimental conditions, a high efficiency of Au extraction was possible without acid pre-treatment.

Table 1. Concentrations of Ag, Au and other metals present in the ACA bulk sample.

Element	Concentration (mg·kg)
Ag	2,910
As	501
Au	2,780
Cr	178
Cu	822
Fe	1,710
Mn	1270
Ni	1070
Pb	427
Sn	87,000
Ti	407
Zn	2,160

3.3. Lixiviant screening

Initial investigations focussed on identifying the most appropriate lixiviant(s) for the leaching of ACA, using chemistries reported previously in the literature for the solubilisation of Ag and Au, but keeping temperature, time and solid:liquid ratio constant. All these initial leaches proceeded for 300 min. The efficiency of the leaching was calculated by mass-balancing. Results (Table 2) showed that alkaline systems were less suitable for the leaching of Ag and Au from ACA. The effectiveness of the alkaline thiosulfate system is known to be very sensitive to [Cu^{2+}] [44] and the leached Cu from the ACA may have accelerated thiosulfate consumption [60]. The alkaline glycine and alkaline thiosulfate studies referenced were based on leaching from a pure Au source and so did not account for other species that might solubilise and affect the extraction [37, 61].

Table 2. Ag and Au leaching from ACA achieved by different literature lixiviant treatments. 25 g ACA in 250 mL solution. Contact time = 300 min. T = 20°C.

Leaching conditions	pH	Ag % extraction	Au % extraction	Reference
0.5 M thiosulfate + 0.2 M $CuSO_4$ + 1 M NH_3	9.5	0.400	8.07	[44]
0.5 M Na_2SO_3 + 0.1 M thiourea	12.5	0.103	0.379	[61]
0.5 M glycine + 1% H_2O_2 (0.29 M)	11.0	0.0531	0.0303	[37]
0.13 M thiourea + 0.09 M $Fe_2(SO_4)_3$	1.25	2.00	28.6	[33]
0.13 M thiourea + 0.78 M thiocyanate + 0.03 M $Fe_2(SO_4)_3$	1.25	1.65	27.0	[48]
1HNO_3:3HCl (v:v, conc.)	-	1.12	2.69	

The relative leaching efficiencies for Ag were similar to Au. However, in nearly all cases, the extent of solubilisation was much lower. It is notable that, for the systems with a large disparity between Ag and Au leaching, there was a source of sulfate ions in the lixiviant, which could reflect the formation of the insoluble Ag_2S/Ag_2SO_4 layer on the surface of the nanoparticles [29]. From screening results, the two most promising lixiviants were carried forward for kinetic studies and optimisation of conditions, these being the acidic thiourea and the thiourea/thiocyanate (dual-lixiviant) treatments. It was thought that the latter system, in conjunction with H_2O_2 as an alternative oxidant, could boost Ag extraction, by negating the formation of the sulfurous layer. At the same time, it was hoped that the thiocyanate would reduce the oxidation of thiourea, resulting in higher extraction than the thiourea-only system.

3.4. Effect of oxidants and concentrations

The effect of both oxidants on the Ag and Au extraction and leaching kinetics was examined for both the thiourea and dual-lixiviant systems. A range of oxidant concentrations was studied (Figure 4).

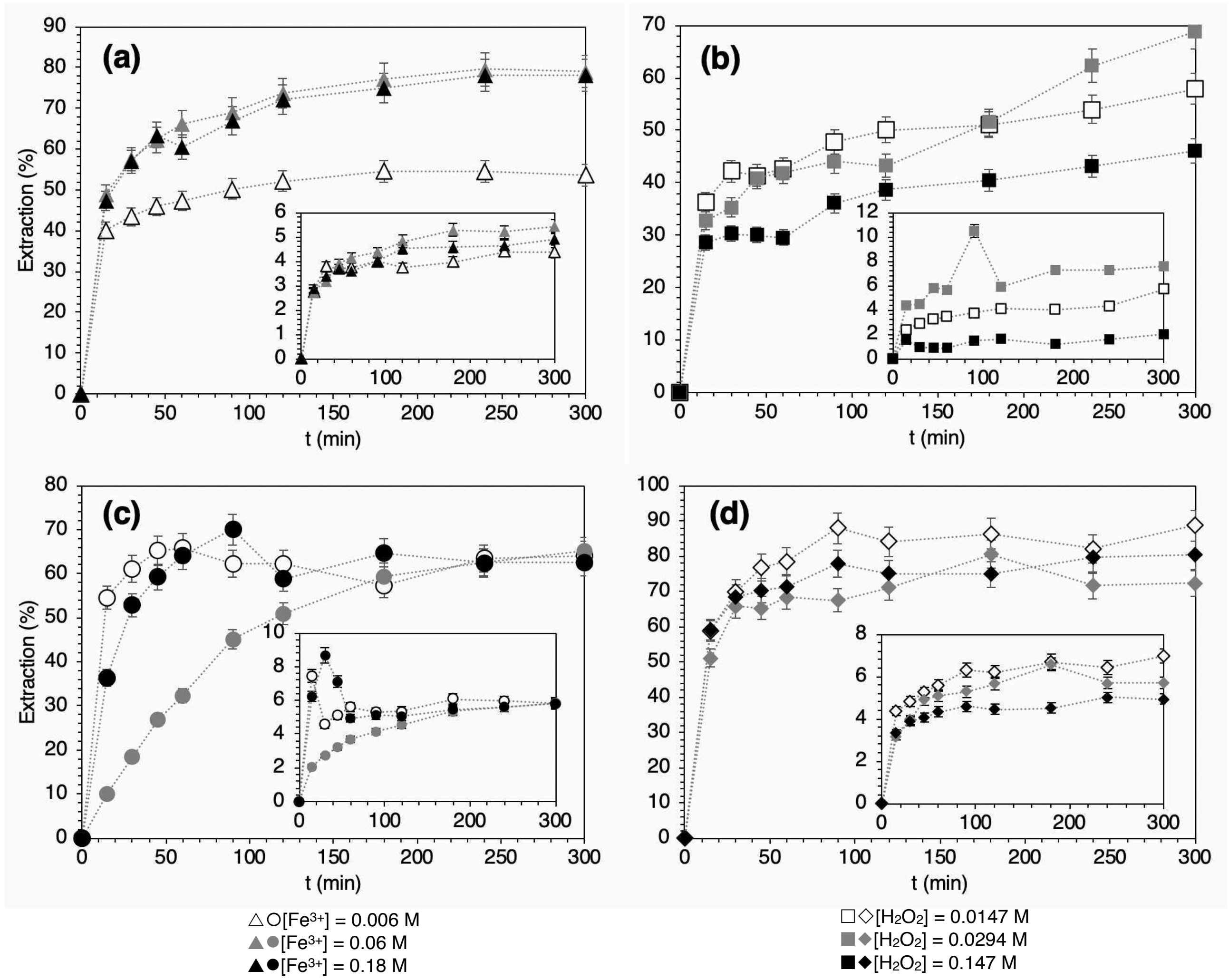

Fig. 4. Leaching of Ag and Au from ACA, using various lixiviants and conditions. Main graphs show Au leaching. Insets show Ag leaching. **(a)** Thiourea with $Fe_2(SO_4)_3$. **(b)** Thiourea with H_2O_2. **(c)** Dual-lixiviant with $Fe_2(SO_4)_3$. **(d)** Dual-lixiviant with H_2O_2. Error bars are derived from the RSD of the ICP instrument. All experiments used 25 g ACA in 250 mL solution. [thiourea] = 0.13 M. [thiocyanate] = 0.78 M. Contact time = 300 min. T = 20°C. pH = 1.5.

3.4.1. Thiourea system

In all experiments, the initial dissolution of metals was rapid for the first 15 min, then proceeded more gradually, similarly to previous literature [3]. For the thiourea system, $Fe_2(SO_4)_3$ was the superior oxidant, with a peak Au extraction of 78.2%. The H_2O_2 leaches achieved an Au extraction of only 68.8%. This appears to confirm that H_2O_2 oxidises thiourea to FDS and elemental sulfur at a faster rate than Fe^{3+}, without the presence of a stabilising species [3, 62]. Solubilisation of Ag was comparatively poor in all experiments, with a maximum extraction of 7.6% achieved with H_2O_2 and 5.4% with $Fe_2(SO_4)_3$. This could indicate that formation of AgS passivating layers around the nanoparticles is indeed reduced with H_2O_2 as the oxidant, though only moderately. The apparent suppression of Ag dissolution was possibly due, in part, to the H_2SO_4 used to adjust experimental pH, which would act as a source of sulfate ions, detrimental to Ag dissolution [63]. However, comparison of leaching efficiency to lixiviant screening results show it was still a better choice than

HNO_3. H_2O_2 was also not ideal for Ag leaching in thiourea systems because, as the more powerful oxidant, it would oxidise thiourea to FDS rapidly, which promotes the precipitation of insoluble Ag salts previously mentioned [29]. These are leached very slowly in thiourea solutions, via Equation 12 [43] (Figure 4b).

$$Ag_2S + (SCN_2H_3)_2 + 2H^+ + 4SC(NH_2)_2 \rightarrow 2Ag(SCNH_2)_2)_3^+ + S^0 \qquad \textbf{(Eqn. 12)}$$

The programme HySS2008 was used to model the speciation of Ag and Au complexes for leaching experiments (Supporting Information p2). It should be noted this is applicable only to the thiourea/H_2O_2 experiments, as in $Fe_2(SO_4)_3$ leaches, excess thiourea would have been complexed by Fe^{3+} [31, 48]. From this data, it may be seen that, contrary to Equation 2, the dominant Ag species in solution are probably $[Ag(CS(NH_2)_2)_3]^+$ and $[Ag(CS(NH_2)_2)_4]^+$ (Figure S2), which may be of interest from the perspective of thiourea consumption in future Ag extraction studies. In the initial leaching stages, the dominant Au species is, as expected, $[Au(CS(NH_2)_2)_2]^+$, but as more Au is solubilised and thiourea is oxidised, the concentration of $[Au(CS(NH_2)_2)]^+$ increases sharply (Figure S3). This liberates some thiourea and explains why Au extraction continued to increase slowly over the experimental timeframe (Figure 4b).

Increasing $[Fe^{3+}]$ increased the Au extraction up to 0.06 M. But the improvement beyond this concentration was minimal and there was also no increase in the kinetics (Figure 4a). This is broadly in agreement with the literature, which has reported an optimal thiourea/Fe^{3+} ratio in thiourea systems of ~1.5-2.9 [3, 33] The precise optimum for this ratio is probably quite sensitive to the leached material, in terms of co-extraction of many other species, which could readily interact with thiourea in solution [64], particularly Cu [35] (Table 1). Additionally, a considerable quantity of Fe would have been leached from the ACA, which would affect the Fe^{2+}/Fe^{3+} equilibrium. This work also confirmed that when [thiourea] < 0.158 M and $[Fe^{3+}]$ > 0.00178 M, the Au leaching rate is independent of $[Fe^{3+}]$ [28]. For the H_2O_2-assisted leaches, a $[H_2O_2]$ of 0.0294 M was found to be optimal for Au recovery (Figure 4b). For the 0.15 M sample, a yellow precipitate was clearly observed in the leaching vessel, confirming that Equation 5 was proceeding. This would obviously be deleterious to the metal extraction. For the H_2O_2 experiments, the Au extraction continued to rise slowly over 1-6 hr. This could indicate slow dissolution of the tarnishing sulfurous layer, which has been reported in acidic thiourea media [43, 65].

For the thiourea system, the Au dissolution is somewhat lower than reported in certain other studies. Deschênes and Ghali, using thiourea/H_2O_2 leaching from chalcopyrite in equivalent conditions, reported 89% Au solubilisation after 8 hr. Li *et al.* attained 90% Au and 50% Ag extraction from mobile phone waste, using 0.0537 M $Fe_2(SO_4)_3$ (but with a greater [thiourea] of 0.315 M [33]. This indicates the preg-robbing abilities of the unincinerated AC in the material.

3.4.2. Dual-lixiviant system

The dual-lixiviant leach responded quite differently to the varying oxidant concentrations. H_2O_2 was a significantly better oxidant than $Fe_2(SO_4)_3$, with a maximum extraction of 88.7% verses 70.0%. Economically, this was achieved with the lowest $[H_2O_2]$ tested. Kinetics were also much improved over the thiourea system. The H_2O_2-assisted leach was essentially complete after 90 min, verses 300 min for the equivalent thiourea experiment, which we attribute to the stronger oxidant and the fact that the lixiviants are not tied up in relatively stable Fe^{3+} complexes. The results therefore did not replicate the beneficial effect of thiocyanate on thiourea/$Fe_2(SO_4)_3$ systems seen previously [48]. The Ag extraction remained poor, with $Fe_2(SO_4)_3$ giving marginally better extraction at 8.7%, compared to 7.0% for H_2O_2.

Zhang *et al.* reported optimal dual-lixiviant conditions at 0.13 M thiourea, 0.78 M thiocyanate and 0.056 M Fe^{3+}. The Au extraction from ore decreased quite sharply at both higher and lower [thiocyanate] [48]. Our leaching conditions were almost identical and it therefore again follows that the species co-leached from the ACA are significant to performance of the dual-lixiviant. The non-oxidative complexation reactions of Fe^{3+} with the two lixiviants are as follows:

$Fe^{3+} + 4SCN^{-} \longrightarrow [Fe(SCN)_4]^{-}$ (**Eqn. 13**)

$Fe^{3+} + 2SC(NH_2)_2 \longrightarrow [Fe(SC(NH_2)_2)_2]^{3+}$ (**Eqn. 14**)

For Equation 13, $\beta_4 = 2.5 \times 10^6$ [40] and for Equation 14, $\beta_2 = 2.75 \times 10^8$ [28]. It can be seen that the ratio of relative stability of $[Fe(SC(NH_2)_2)_2]^{3+}/[Fe(SCN)_4]^{-}$ is large (~1 x 10^2). However, the equivalent ratio for stability of $[Au(SC(NH_2)_2)]^{+}/[Au(SCN)_2]^{-}$ is much greater (~2 x 10^5). Zhang *et al.* therefore proposed that when [thiocyanate] exceeds [thiourea], thiocyanate will react with $Fe(SC(NH_2)_2)_2$ and liberate thiourea into solution [48]. It should be noted that this explanation does not take into account the possible existence of mixed-ligand complexes, which may have very high stability constants [47] (for example, $Fe(SC(NH_2)_2)_2(SCN)_2$ is readily formed in solution [66]). As discussed in 3.2, the ACA sample used in this work had higher concentrations of potentially interfering leachable metals (Table 1). Therefore, it is feasible that the actual [thiourea]/[thiocyanate] ratio in the work of Zhang *et al.* [48] would have been different to that of our study. This would be true even assuming mixed-ligand complexes are present. Future work by this research group will identify the optimum ratio for ACA leaching with Fe^{3+} as the oxidant.

There are several considerations to explain why the dual-lixiviant/H_2O_2 system was the most efficient for Au extraction in this study. The first is that thiocyanate alone is known to be an effective Au lixiviant [46], although this does not seem to be the case for our dual-lixiviant/$Fe_2(SO_4)_3$ system, so could enhance leaching as per Equation 8. There is also the consideration that the possible mixed-ligand Au and Ag complexes could have stability constants in excess of even the equivalent thiourea complexes, which could aid the dissolution of oxidised Au^{+} and increase the quantity of Au leached via thermodynamic favourability. It should be noted however that this is by no means certain. Dhuley and Dongre investigated mixed-ligand Cd complexes and found that for $[Cd(SC(NH_2)_2)_2]^{2+}$, $\beta_2 = 2.51 \times 10^3$, whereas for the most stable mixed-ligand species $[Cd(SC(NH_2)_2)_2(SCN)]^{+}$, $\beta_{21} = 1.55 \times 10^3$ [67] (no data available for Ag or Au equivalents). Also, it is not clear why this is would not be the case for the dual-lixiviant/Fe^{3+} experiments. Speciation diagrams cannot be used for guidance because of the absence of data on the mixed-ligand complexes.

The second reason is that thiocyanate could react with the variety of metal cations solubilised by the leaching conditions and either precipitate them or form stable aqueous species. Thiocyanate is a versatile ligand, capable of coordinating via N- or S-donation, according to hardness of metal ion. As mentioned previously, it has high affinity for Cu^{2+}, moderate affinity for Fe^{2+} [40] and can complex with Sn [59]. As a result, these and other leached transition metal species would be passivated, leaving a greater concentration of available thiourea to participate in Equations 2 and 7. This for example, negates the formation of $Cu(SC(NH_2)_2)^{+}$ ($\beta_2 = 1.26 \times 10^{11}$ [55])Therefore, the thiocyanate presence could overcome the need for acid pre-treatment in the leaching of ACA that is often cited as necessary [28, 35].

The final point and a possible explanation of the optimum [H_2O_2] comes from a consideration of the kinetics of the competing oxidation reactions. It is known that the rate law for oxidation of thiourea, thiocyanate and many other electron pair-donating molecules by H_2O_2 is of the form:

$R_0 = k_2[H_2O_2][thio] + k_3[H_2O_2][thio][H^{+}]$ (**Eqn. 15**)

Where "thio" represents the electron donor. However, in aqueous solution, $k_3 >> k_2$ [68], so Equation 15 approximates to:

$R_0 = k_3[H_2O_2][thio][H^{+}]$ (**Eqn. 16**)

For thiocyanate oxidation to formamidine disulfate at 20°C, $k_3 = 1.3\ M^{-2}\cdot min^{-1}$ [69]. Data for thiourea at 20°C was not available, but at 25°C, $k_3 = 85.2\ M^{-2}\cdot min^{-1}$ [68]. Under our experimental conditions, the oxidation of thiourea is approximately an order of magnitude faster than that of thiocyanate. However, the oxidation rate of FDS is of similar magnitude (Table S6). The kinetics here are more complicated, as there is a competing hydrolysis reaction, but Hu *et al.* reported k_{obs} at pH 1.5 as

0.342 min^{-1} [70]. Even assuming all the thiourea in the system is quickly oxidised to FDS our initial experimental rate of FDS oxidation was calculated to be slower than thiocyanate oxidation (Table S5).

We propose that at low [H_2O_2] (0.0147 and 0.0294 M), a proportion of the thiourea is quickly oxidised to FDS. The thiocyanate in the system acts sacrificially to prevent the second oxidation of FDS to $CN{\cdot}NH_2$ and S^0. The H_2O_2 will be consumed in the reactions and the actual oxidants, which effectively promote the leaching of Au will be FDS itself [48, 71] and $(SNC)_3^-$ / $(SNC)_2$ [72]. When [H_2O_2] = 0.147 M, the thiocyanate in the system is not sufficient to prevent some complete oxidation of the thiourea and formation of $CN{\cdot}NH_2/S^0$. This would not only irreversibly consume excessive thiourea, but also promote the formation of the experimentally-observed sulfurous layer on the Au and Ag nanoparticles, preventing further leaching [65]. This is probably why recovery at higher [H_2O_2] is poorer. The synergistic behaviour is not observed with Fe^{3+} as the oxidant, because the rate of oxidation of thiourea and thiosulfate and consumption of oxidant is much lesser. Even with a large excess of thiourea in the system, most Fe^{3+} would not be consumed over our experimental timeframe [34]. Interestingly, Deschênes and Ghali also reported an optimum [H_2O_2] of 0.0147 M in their Au leaching investigations, though for a thiourea only system [3]. To validate this proposal, a chromatographic study will be carried out in the future, to monitor [thiourea], [thiocyanate] and [FDS] during the progressing leaches.

It is clear that the synergism of the dual-lixiviant for Au leaching is not replicated for Ag leaching. There are two possible reasons for this. The first being that the oxidation product of thiocyanate $(SNC)_2$ rapidly hydrolyses, according to Equation 17 [42]:

$$3(SCN)_2 + 4H_2O \longrightarrow 5SCN^- + HCN + 7H^+ + SO_4^{2-} \qquad \textbf{(Eqn. 17)}$$

Hence providing a source of sulfate in the system, to react with unleached Ag. The second reason is the low solubility of AgSCN in solutions where [SCN^-] < 1.5 M [42, 43]. This may explain why, for some experiments, Ag in solution decreased after an initial spike in extraction (Figure 4c).

Overall, despite the poor Ag extraction, the combination of thiourea, thiocyanate and low concentrations of H_2O_2 produce a synergistic effect, which seems able to mainly overcome the difficulties in Au leaching from preg-robbing materials [73]. This is contrary to the popular belief [43] that H_2O_2 is an unsuitable oxidant for such processes. The insoluble passivating salts, preventing Ag solubilisation, would be almost entirely Ag, rather than Au species, because the great majority of Au is solubilised under optimal experimental conditions. Due to the much higher value of Au there would at present (without further investigations into the seeming recalcitrance of Ag) be little point in attempting a salt-separation process.

3.5. Data fitting to kinetic models

It was found that the data for Ag leaching could not be described well by any of the kinetic models (low R^2 values) and fitting is not presenting. This is probably because, as discussed previously, the rapid formation of tarnishing sulfurous layers of mixed speciation on the surface of the Ag nanoparticles means that multiple dissolution processes take place simultaneously over the experimental timeframe [29, 38]. For Au leaching, the fitting of the three models to selected data are shown in Figure 5. The full range of R^2 values for the fitting are shown in Table 3.

Table 3. Agreement of kinetic models to Au leaching data. Experimental conditions as per Figure 4.

Leaching system	**Kinetic model R^2 values**		
	Diffusion-controlled	**Reaction-controlled**	**Mixed-controlled**
Thiourea, 0.006 M Fe^{3+}	0.415	0.601	0.902
Thiourea, 0.06 M Fe^{3+}	0.613	0.791	0.675
Thiourea, 0.18 M Fe^{3+}	0.627	0.884	0.920
Thiourea, 0.0147 M H_2O_2	0.632	0.870	0.932
Thiourea, 0.0294 M H_2O_2	0.765	0.858	0.820
Thiourea, 0.147 M H_2O_2	0.610	0.827	0.864
Dual-lixiviant, 0.006 M Fe^{3+}	0.269	0.350	0.421
Dual-lixiviant, 0.06 M Fe^{3+}	0.873	0.945	0.980
Dual-lixiviant, 0.18 M Fe^{3+}	0.519	0.513	0.529
Dual-lixiviant, 0.0147 M H_2O_2	0.507	0.419	0.562
Dual-lixiviant, 0.0294 M H_2O_2	0.287	0.332	0.303
Dual-lixiviant, 0.147 M H_2O_2	0.400	0.546	0.689

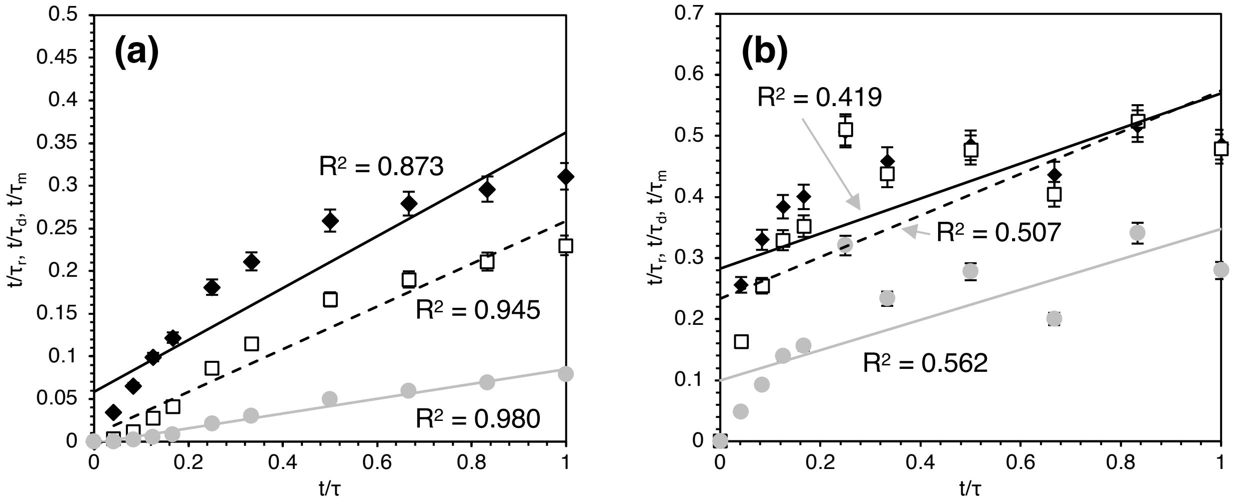

Fig. 5. Fitting of Au leaching data to kinetic models. **(a)** Dual-lixiviant system with 0.006 M Fe^{3+} oxidant. **(b)** Dual-lixiviant system and 0.0147 M H_2O_2 oxidant. ◆ = diffusion-controlled model (d). □ = reaction-controlled model (r). ● = mixed-controlled model (m). Experimental conditions as per Figure 4.

The mixed-controlled model produced the best fit to the data for almost every experiment. In the case of the few exceptions, all models described the data quite poorly and the superiority of one over the other carries little relevance (Table 3). Results imply that both diffusion of lixiviant through a gelatinous product layer around the Au particles and chemical reactions were influential to the leaching rate [50]. It is not possible to state with any certainty what the overall rate-limiting step of the process is, because leaching rates (at least in thiourea-only systems) are known to be dependent on both thiourea concentration and oxidant concentration [22] and altering either parameter affects not just the oxidation of Au (Equation 2), but all chemical interactions between lixiviant, oxidant and metal (Equations 3-7).

Perhaps surprisingly, the dual-lixiviant system with Fe^{3+} as the oxidant (0.06 M) gave the best fitting to the model (R^2 = 0.980, Figure 5a). This indicates that the processes for thiourea and thiocyanate leaching of the metals produce an empirically homogeneous mechanism, which is supported by the literature evidence for the mixed-ligand complex formation [47]. Yang *et al.* also concluded that dual-lixiviant/Fe^{3+} system had mixed-controlled kinetics [47]. The thiourea/Fe^{3+} system is claimed to be diffusion-controlled at low [Fe^{3+}] and reaction-controlled at high [Fe^{3+}] [28], but there was no evidence of this switch in our dataset. The H_2O_2 systems gave comparatively poor fits to the data (Table 3, Figure 5b) and again, no strong conclusions can be drawn on the rate-limiting process for metal dissolution. This is in agreement with the proposed mechanisms, because, the rates of chemical reaction would be dictated by the concentrations of H_2O_2, FDS and possibly $(SCN)_3^-$ and $(SCN)_2$ at different points in time, whereas for the Fe^{3+} experiments, there would have been a source of Fe^{3+} in the solution throughout the experimental timeframe [34], so the dominant mechanism would be assumed to change more gradually, if at all.

3.6. Considerations for industrial implementation

The hydrometallurgical treatment of ACA is challenging. Because the waste is partially derived from carbon fines, endowing it with a small particle size, treatment via existing CIP technology seems feasible. Research has been carried out demonstrating the successful transfer of Au from carbon fines to coarse AC particles [26]. However, this was achieved using a conventional cyanide lixiviant. A promising alternative may be a resin-in-pulp (RIP) process, in which the functionality of the chosen ion-exchange resin can be tailored to complement the alternative leaching chemistry. It is known for example that in weak acid (acetate) media, the analogous iminodiacetate resins are highly effective at adsorbing metals as acetate complexes [74, 75]. Thiourea resins are commercially available and known for high gold extraction capabilities [76]. A simple static RIP system would consist of first, the gold extraction vessel, followed by a guard vessel, containing mixed-bed resins to remove the remaining heavy metals and detoxify the barren leachate [77]. After this step, the leachate could potentially be recycled, which negates any release of thiourea (which still possesses significant toxicity [22]) to the environment. Control of ORP would be important to the process, as oxidation of the lixiviants could occur at every process stage [22, 28]. This research group is currently investigating RIP technology with a view to developing a more contiguous approach to ACA treatment. The kinetic data produced in this initial study suggests that leaching residency times in both batch and battery counter-current system could be reduced by a factor of ~3 with the use of a dual-lixiviant/H_2O_2 system, compared to a thiourea system (Figure 4), so the potential benefits to plant throughput are significant. This would need to be confirmed in a lab-scale RIP simulation, before scale-up work.

4. Conclusions

We have assessed a dual-lixiviant system (thiourea/thiocyanate) and a common thiourea system for the recovery of Ag and Au from activated carbon ash (ACA). The material contained a proportion of unincinerated activated carbon, presenting a challenge to successful leaching in terms of preg-robbing abilities. The leaching of Au was successful, with an optimum extraction of 79% attained via thiourea leaching and 89% achieved with the dual-lixiviant system. The choice and concentration of oxidant was influential to the success of the treatment. The optimum for thiourea leaching was 0.06 M Fe^{3+}, but 0.0147 M H_2O_2 was the preferred choice for the dual-lixiviant system. The synergy between thiourea, thiocyanate and H_2O_2 was thought to be due to the rapid oxidation of a proportion of thiourea to formamidine disulphide, with thiocyanate suppressing the further irreversible oxidation step, thus creating favourable conditions for Au dissolution. The extraction of Ag was poor (<10%) across all experiments, suggesting poorly-soluble passivating layers were formed in all the conditions studied. Kinetics of uptake were reasonably described by the mixed-controlled model, meaning no overall rate-limiting step could be defined. Under optimum conditions, maximal Au extraction was achieved within 100 min. Despite the additional up-front cost of the dual lixiviants, the proposed thiourea/thiocyanate/H_2O_2 system effectively and rapidly extracts Au from the highly preg-robbing ACA, without the need for an acidic pre-treatment step. The extra value generated from the waste, over thiourea/Fe^{3+} leaching, was calculated as >\$14,000·T^{-1}. These results suggest that the addition of thiocyanate could help to address the excessive thiourea consumption, which is a barrier to the widespread succession of thiourea leaching to the established cyanidation process. This is especially pertinent to precious metal recovery from ACA, which has significantly higher valorisation potential than ores and electronics waste.

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Alternatives to cyanide leaching of waste activated carbon ash for recovery of precious metals

SUPPORTING INFORMATION

Charlie R. Adams, Christopher P. Porter, Thomas J. Robshaw, James P. Bezzina, Victoria R. Shields, Alan Hides, Richard Bruce, Mark D. Ogden[1]

Table S1. Point EDX analysis of position α (assigned as mainly $NaAlS_3O_8$) from Figure 2 in the main article.

Element	Mass %	Atomic %	Sigma	Net	K ratio	Line
C	5.39	10.42	0.02	4971	0.003988	K
O	39.38	57.14	0.14	43180	0.1019	K
Na	6.66	5.77	0.28	2547	0.002295	K
Al	7.52	6.52	0.48	3351	0.002994	K
S	32.36	20.15	0.17	15290	0.01744	K

Table S2. Point EDX analysis of position β (assigned as mainly SiO_2) from Figure 2 in the main article.

Element	Mass %	Atomic %	Sigma	Net	K ratio	Line
O	53.07	68.22	0.09	158000	0.3728	K
Na	3.04	2.72	0.05	10720	0.02279	K
Mg	5.01	4.24	0.08	16090	0.03456	K
Al	1.47	1.12	0.25	3976	0.009513	K
Si	26.18	19.18	0.19	58860	0.1614	K
Ca	6.18	3.17	0.48	1180	0.009144	K
As	2.91	0.80	0.19	5088	0.01784	L

Table S3. Point EDX analysis of position γ (assigned as mainly graphite) from Figure 2 in the main article.

Element	Mass %	Atomic %	Sigma	Net	K ratio	Line
C	93.13	94.75	0.10	37960	0.03045	K
O	6.87	5.25	0.11	2286	0.05394	K

Table S4. Point EDX analysis of position δ (assigned as mainly activated carbon) from Figure 2 in the main article.

Element	Mass %	Atomic %	Sigma	Net	K ratio	Line
C	66.75	83.77	0.06	62210	0.04991	K
O	8.59	8.09	0.06	9881	0.02331	K
Na	1.46	0.95	0.06	2601	0.005527	K
Mg	3.29	2.04	0.09	5309	0.01140	K
Si	1.99	1.07	0.11	2259	0.006195	K
S	6.98	3.28	0.16	4541	0.01497	K
Pb	10.94	0.80	0.83	2535	0.01384	M

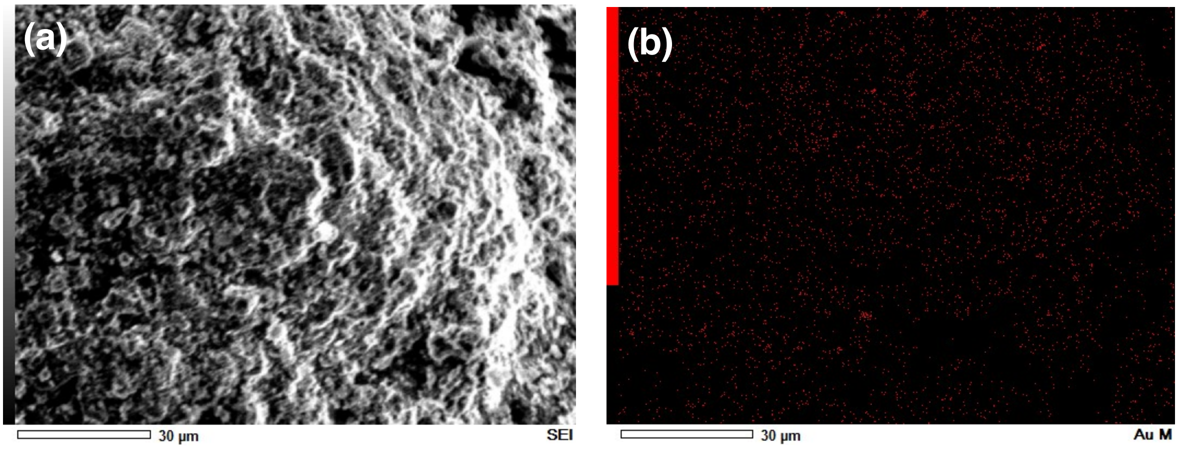

Fig. S1. (a) SEM image of a silicate particle and (b) accompanying Au elemental mapping.

Modelling of predicted Ag and Au speciation data in thiourea solutions

Speciation modelling was undertaken using the HySS2008 software [1]. All stability constants for the complexes and hydrolysis products modelled were obtained from the NIST database [2] or the literature [3, 4]. From these sources, stability constants are given at 25°C and at constant ionic strength. The concentrations of Ag and Au were calculated from the maxima present in solution, taken from the relevant leaching experiments. Although this would of course change over the experiment duration, it can be seen that the thiourea concentration would always be in a large excess.

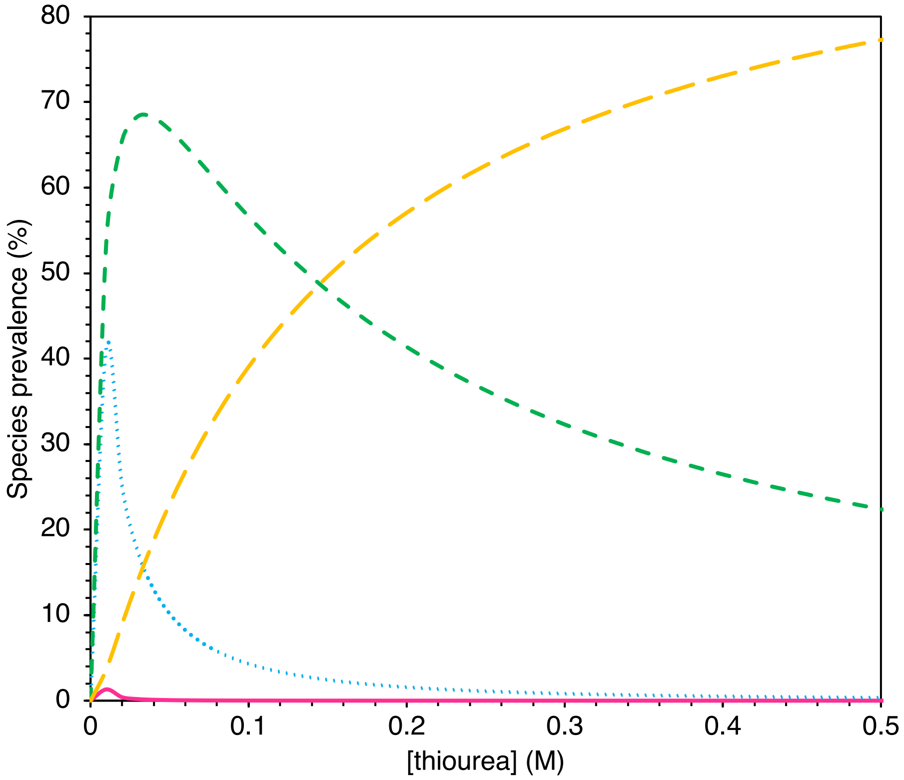

Fig. S2. HySS Ag speciation in thiourea leaching system. [Ag] = 4.08 x 10^{-5} M. Pink line = $[AgTu]^+$. Dotted blue line = $[AgTu_2]^+$. Dashed green line = $[AgTu_3]^+$. Dashed yellow line = $[AgTu_4]^+$.

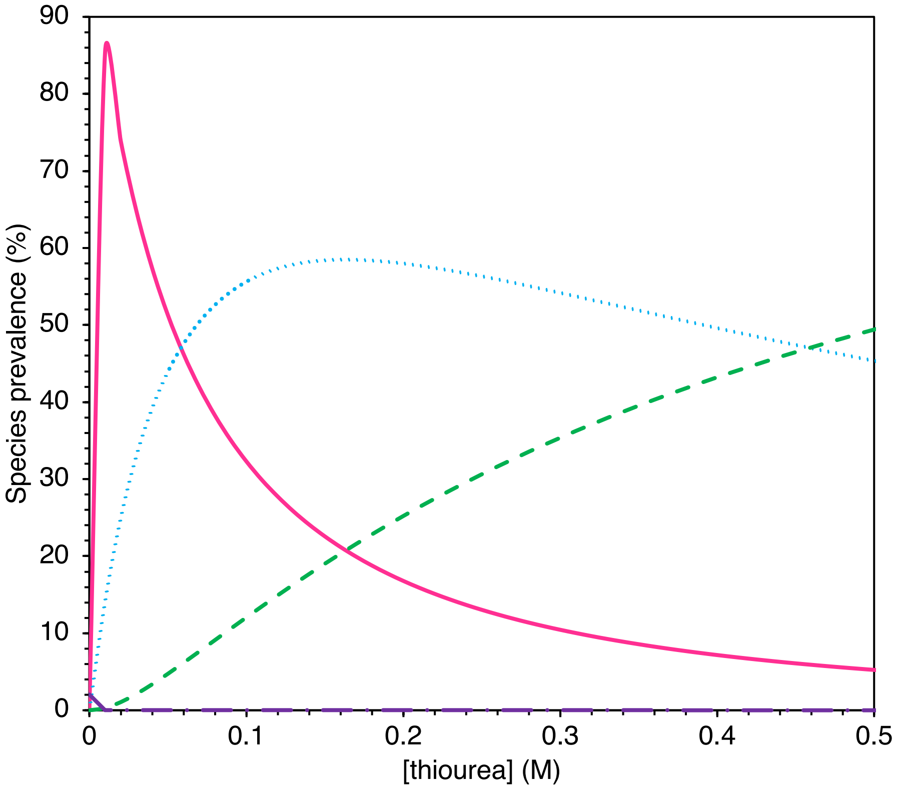

Fig. S3. HySS Au speciation in thiourea leaching system. [Au] = 4.26 x 10-4 M. Pink line = $[AuTu]^+$. Dotted blue line = $[AuTu_2]^+$. Dashed green line = $[AuTu_3]^+$. Dashed purple line = [AuOH].

Estimation of experimental rates of thiourea, thiocyanate and formamidine disulphide (FDS), with H_2O_2 as the oxidant

For thiourea and thiocyanate, the initial experimental reaction rates were estimated from the rate law $R_0 = k_3[H_2O_2][thio][H^+]$ where "thio" is the oxidised species. The value of k_3 for thiourea was taken from Hoffmann and Edwards at 25°C [5]. For thiocyanate, the value was taken from Wilson and Harris at 20°C [6]. For FDS, the pseudo-second-order rate constant calculated by Hu *et al.* at 20°C and pH 1.5 was used [7]. [FDS] was taken as 0.065 M (the maximum theoretical concentration that could exist in the system).

Table S5. Calculation of initial experimental rates of oxidation of thiourea, thiocyanate and FDS.

$[H_2O_2]$ (M)	**Estimated rate of reagent oxidation ($mol \cdot min^{-1}$ x 10^{-4})**		
	Thiourea	**Thiocyanate**	**FDS**
0.0147	51.5	4.71	3.27
0.0294	103	9.43	6.54
0.147	515	47.1	32.7

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Declaration of Interest Statement

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: