B. Chambers*, C. A. Pickles and J. G. Peacey

Thermodynamic Analysis of the Sulphation Roasting of Enargite Concentrates

Abstract: The mining industry is under increasing pressure to assess the extraction of value from complex copper ores, such as those containing enargite (Cu_3AsS_4), due to the rising demand for copper and gold. A sulphation roast, weak acid leach, and electrowinning process flowsheet has been studied to address the treatment of copper concentrates containing significant amounts of enargite. Copper is recovered from the calcine by acid leaching, with most of the arsenic being fixed in the leach residue after gold extraction by cyanidation. The relative simplicity of roasting combined with proven hydrometallurgical technologies has the potential to be economically advantageous and readily scaled for commercial operation. Based on a proposed reaction mechanism, a thermodynamic analysis has been performed using HSC Chemistry® 6.1 in order to establish an operating window and assess the overall potential feasibility of the proposed flowsheet.

Keywords: thermodynamic analysis, sulphation roasting, enargite

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Introduction

Enargite (Cu_3AsS_4) is a sulphosalt mineral, often associated with high gold and silver values. Deposits occur throughout the world, especially in Chile where they are often located in the vicinity of large-scale copper porphyry-mining operations, such as Chuquicamata. Enargite concentrates can be smelted directly by a few copper smelters that have adapted to be able to process high arsenic inputs, however most custom copper smelters limit their arsenic input for environmental reasons and only process clean copper concentrates, containing less than about 0.3% arsenic. Consequently, most smelters charge a penalty of approximately US$2.50 to US$3.00 per 0.1% over 0.1% or 0.2% arsenic and likely will not treat significant concentrates with greater than 0.3% arsenic, as outlined by Peacey et al [1].

Future copper supply growth is necessary to meet the increasing demand from China and other developing nations; however, the long development periods and rapidly increasing capital costs for large-scale copper mining projects have constrained the rate with which new mined copper supply can be brought on-stream. At the same time, the industry average copper grades have been decreasing over the past 20 years as outlined by Codelco, from 0.95% Cu in 1985 to a projected 0.65% Cu in 2020 [2]. Due to market fundamentals, more challenging deposits, such as those containing enargite, are now being considered as potentially productive properties.

The increasing demand for copper and gold has motivated research into developing more effective methods of extracting value metals from enargite concentrates. The methods proposed for treating enargite concentrates are similar to those used commercially for pre-treating sulphidic refractory gold ores and concentrates. These processes are:

- Pyrometallurgical oxidation with air and/or oxygen in roasters;
- High temperature pressure oxidation (HTPOX) using tonnage oxygen in autoclaves;
- Biological oxidation in stirred tank reactors.

The gold and silver values are recovered from the oxidized product by conventional cyanidation. Currently, there is only one commercially-proven treatment process for high arsenic-bearing concentrates; partial roasting of the concentrate at 923 to 1023 K produces a low arsenic calcine and an arsenic trioxide off-gas.

A paucity of information exists in the literature regarding the sulphation roasting of enargite or other similar arsenic-containing concentrates. Nakazawa et al developed a thermodynamic model of the removal of arsenic during partial roasting [3]. This study did not

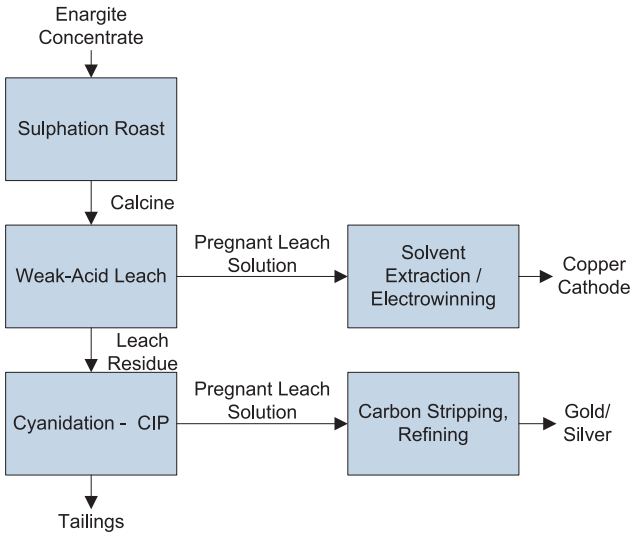

Fig. 1: Simplified process flowsheet for enargite or high arsenic containing concentrates.

involve sulphation roasting using sulphur dioxide gas. The model indicated that at 973 K in an inert atmosphere, 60% desulphurization could be achieved with an arsenic removal of 80 to 90%. Experimental work on partial roasting by Padilla et al suggested that arsenic removals of greater than 98% could be achieved at 993 K [4]. However, Holmstrom showed that at these roasting temperatures sintering would occur and this would likely prevent the calcine from being effectively leached [5].

In the current research, a process consisting of a sulphation roast, followed by a weak-acid leach and subsequent electrowinning is proposed as an alternative treatment method for enargite or similar high arsenic concentrates. The proposed process flowsheet is shown in Figure 1. The concentrate undergoes a sulphation roast under optimized conditions to maximize production of soluble copper sulphate and insoluble iron oxide. During sulphation roasting, the arsenic would be ideally fixed as stable ferric arsenate, which is disposed of in the final leach residue following cyanidation to recover the gold and silver values. The roast calcine undergoes a weak acid leach and the pregnant leach solution would then be processed through conventional solvent extraction and electrowinning processes to produce copper cathode. The leach residue should be amenable to cyanidation due to the decomposition of enargite and other sulphide minerals during the sulphation roast. The final residue would be stored in a lined tailings pond.

This proposed flowsheet may be economically advantageous when compared to a partial roasting pre-treatment and the selling of the resultant de-arsenized calcine to copper smelters. This flowsheet would be particularly advantageous if existing SX/EW facilities are available, for example, at an existing heap leach copper operation that has exhausted its heap leachable ore. Electrowinning allows for on-site processing of copper cathode and the operations are easily scaled without compromising efficiency. The relative simplicity and efficiency of roasting, when combined with hydrometallurgical technologies, provides an opportunity to address the arsenic problem at improved project economics.

In this research, firstly a reaction mechanism is developed for the proposed sulphation roasting process, based on the information available in the literature. In order to determine if the process is feasible, a thermodynamic study has been performed using the equilibrium program of HSC Chemistry® 6.1. The equilibrium product compositions were determined as a function of the important variables. Based on these results a detailed flowsheet is proposed.

Reaction mechanism

The reaction mechanisms for the sulphation roasting of an enargite concentrate have been previously studied. Yoshimura, Luganov et al, Smith, and Secco et al have described the decomposition of both enargite and the associated pyrite as outlined in the following reactions [6–9]:

$$2Cu_3AsS_4(s) = 3Cu_2S(s) + A_2S_3(g) + S_2(g) \quad (1)$$

$$2FeS_2(s) = 2FeS(s) + S_2(g) \quad (2)$$

Padilla et al suggested that enargite first converts to tennantite ($Cu_{12}As_4S_{13}$) and subsequently to digenite (Cu_9S_5) and then to chalcocite (Cu_2S) [4]. At low oxygen partial pressures, Smith reports that in the presence of pyrite, enargite converts to chalcopyrite ($CuFeS_2$) and chalcopyrite–like compounds according to the following reaction [8]:

$$2Cu_3AsS_4(s) + 6FeS_2(s) = 6CuFeS_2(s) + A_2S_3(g) + 2.5S_2(g) \quad (3)$$

Peretti, McCabe & Morgan, and Ferron & De Cuyper have described the oxidization of the iron and copper metal sulphides produced in reactions (1) to (3) [10–12]. These metal sulphides are designated by MS in the following reaction:

$$MS(s) + O_2(g) = MO(s) + SO_2(g) \quad (4)$$

During the conversion of copper sulphide to oxide, chalcocite converts to copper (I) oxide (Cu_2O) before forming

copper (II) oxide (CuO). In the presence of oxygen, the gases oxidize based on the following equations according to Padilla et al and Smith [4, 8]:

$$S_2(g) + 2O_2(g) = 2SO_2(g) \quad (5)$$

$$2SO_2(g) + O_2(g) = 2SO_3(g) \quad (6)$$

$$2As_2S_3(g) + 9O_2(g) = As_4O_6(g) + 6SO_2(g) \quad (7)$$

The production of sulphur trioxide (SO_3) gas as outlined in reaction (6) is critical to the formation of sulphates. The sulphation of metal oxides by sulphur trioxide has been described by Ferron & De Cuyper according to the following reactions [12]:

$$MO(s) + SO_3(g) = MSO_4(s) \quad (8)$$

$$2MO(s) + SO_3(g) = MO \cdot MSO_4(s) \quad (9)$$

$$MO \cdot MSO_4(s) + SO_3(g) = 2MSO_4(s) \quad (10)$$

The sulphation reaction can proceed directly as outlined in reaction (8), based on the prior oxidization of the sulphides as given by reaction (4) and the formation of the sulphating sulphur trioxide gas in reaction (6). Alternatively, the formation of an intermediate oxy-sulphate as presented in reaction (9) followed by the sulphation of the oxy-sulphate as shown in reaction (10), can occur. As the roasting temperature increases beyond 800 K, these reactions begin to reverse and the sulphates decompose. At temperatures above 923 K, the formation of ferrites is expected as outlined by Shirts et al according to the following reaction [13]:

$$CuO(s) + Fe_2O_3(s) = CuO \cdot Fe_2O_3(s) \quad (11)$$

Holmstrom and Downey et al suggested that arsenic trioxide gas ($As_4O_{6(g)}$) will oxidize to arsenic pentoxide (As_2O_5) in the calcine, under highly sulphating conditions between 773 and 923 K, according to the reaction [5, 14]:

$$As_4O_6(g) + 2O_2(g) = 2As_2O_5(s) \quad (12)$$

Chakraborti & Lynch noted that above approximately 1000 K, arsenic pentoxide will decompose, forming arsenic trioxide vapour and oxygen [15]. Alternatively, assuming fast reaction kinetics, it is suggested that arsenates will form in lieu of arsenic pentoxide, as follows:

$$As_4O_6(g) + 2Fe_2O_3(s) + 2O_2(g) = 4FeAsO_4(s) \quad (13)$$

$$As_4O_6(g) + 6CuO(s) + 3.5O_2(g) = 2Cu_3(AsO_4)_2(s) \quad (14)$$

Based on reactions (1) to (14), the following overall reaction for the roasting of enargite is proposed:

$$Cu_3AsS_4(s) + 3FeS_2(s) + 11O_2(g) = 3CuSO_4(s) + Fe_2O_3(s) + FeAsO_4(s) + 3.5SO_2(g) \quad (15)$$

The production of water-soluble copper sulphate, insoluble iron oxide, and arsenic fixed in the calcine, represents the ideal sulphation reaction products. The formation of ferric arsenate ($FeAsO_4$) is more beneficial than the formation of cupric ferrite ($Cu_3(AsO_4)_2$) as copper recovery would be unaffected and ferric arsenate has high-long term stability. Thermodynamically this reaction is highly favourable and it would be expected that the reaction rate would increase with temperature and be proportional to the surface area of the sulphide. Ferron & De Cuyper suggested that the diffusion of sulphur trioxide through the product layer of increasing thickness is the rate-determining step in the sulphation reactions [12].

Materials and methods

Raw materials

The enargite concentrate used in this research was from Kinross's La Coipa Mine in Chile. With regards to the mineralogy, X-Ray Diffraction (XRD) analysis, showed the presence of mainly enargite (Cu_3AsS_4), pyrite (FeS_2), covellite (CuS) and silica (SiO_2). The composition of the concentrate utilized in the calculations is given in Table 1. The gold and silver contents in this particular concentrate were 21 g/t and 745 g/t, respectively, but these were not considered in the thermodynamic study. Other minor constituents will be present and these were added to the silica content.

Equilibrium calculations

The Equilibrium module of HSC Chemistry® 6.1 was utilized to calculate the multi-component equilibrium composition using the Gibbs free energy minimization method

Mineral	Enargite (Cu_3AsS_4)	Pyrite (FeS_2)	Covellite (CuS)	Silica (SiO_2)
Mass	30%	40%	14%	16%

Table 1: Composition of the concentrate as determined by Inductively Coupled Plasma (ICP) analysis.

as developed by Roine [16]. Selection of the relevant elements involved in the equilibrium calculations resulted in the generation of a list of potentially stable elements and compounds. Unstable species can be eliminated to facilitate the calculations and the species are grouped into various phases. The input data consists of the amounts and temperatures of the raw materials. The program determines the amounts of the various stable species at constant temperature and constant pressure. The amount of a given raw material, the temperature and the pressure can be varied in predetermined increments. For species in condensed solutions, ideal behavior is assumed and therefore the default value of the activity coefficient is unity. If a species of interest is not included in the database, then it can be added along with the known thermodynamic properties. This method has been applied previously to the roasting of arsenic containing concentrates by Nakazawa et al and Chakraborti & Lynch [3, 15].

Inputting of the elements Fe, Cu, As, Si, S and O into the program resulted in the generation of a list of 154 possible species. However, many of these would not be present in significant amounts under the present equilibrium conditions and as a result, the list was simplified to the 38 species shown in Table 2. The species were grouped into five phases: gases, oxides, sulphides, sulphates and arsenates. Silica was assumed to be inert and the formation of copper silicates was not considered because of the slow kinetics of the solid-solid reactions. The thermodynamic data for enargite was added and the values utilized are given in Table 3. The control conditions for the calculations are given in Table 4. The temperature was varied from 600 to 1200 K. Roasting would not be considered below 600 K, due to the slow kinetics of the reactions. Above 1200 K, sintering and dead roasting would occur, which is not discussed in this paper. The input gas is initially set at 19% oxygen at a 20:1 gas to solid molar ratio.

In the present thermodynamic study, the desired products are copper sulphates, iron oxides, and arsenates. The optimized operating window will reflect the balance between these species, which maximizes both the copper recovery and arsenic fixation. It is important to note that since roasting involves gas-solid reactions, equilibrium products may not exist under actual operating conditions due to kinetic factors. The thermodynamic predictions

Gases	Sulphides	Oxides	Sulphates	Arsenite/Arsenates
N_2	AsS	As_2O_3	$CuO \cdot CuSO_4$	$Cu(AsO_2)_2$
As_2	As_2S_2	As_2O_4	$CuSO_4$	Cu_3AsO_4
As_4	As_2S_3	As_2O_5	Cu_2SO_4	$Cu_3(AsO_4)_2$
As_4O_6	Cu_3AsS_4	CuO	$FeSO_4$	$FeAsO_4$
AsS	$CuFeS_2$	Cu_2O	$Fe_2(SO_4)_3$	$Fe_3(AsO_4)_2$
As_2S_3	Cu_5FeS_4	$CuO \cdot Fe_2O_3$		
O_2	CuS	$Cu_2O \cdot Fe_2O_3$		
S_2	Cu_2S	Fe_2O_3		
SO_2	FeAsS	Fe_3O_4		
SO_3	FeS_2			

Table 2: Input species for the sulphation roasting of an enargite concentrate.

Species	$\Delta H_{298\,K}$ (kJ mol^{-1})	$S^0_{298\,K}$ (J mol^{-1} K^{-1})	$C_p(T) = a + 0.001bT + 10^5c(1/T^{-2})$ (J mol^{-1} K^{-1}, for T in K)		
			a	b	c
Enargite (Cu_3AsS_4)	–179.0	257.6	196.7 ± 1.2	49.9 ± 1.6	–19.18 ± 0.84

Table 3: Data utilized for enargite; heat capacity, enthalpy and entropy [20, 21].

Feed Temperature	Gas Feed Amount (kmole)			Solid Feed Amount (kg)				Gas:Solid Molar Ratio
	N_2(g)	O_2(g)	SO_2(g)	Cu_3AsS_4	CuS	FeS_2	SiO_2	
298 K	7.881	2.109	1.110	30	14	40	16	20:1

Table 4: Control parameters for the thermodynamic study of enargite concentrates.

may indicate trends but bench-scale experimentation will be required to confirm the calculations.

Results and discussion

Figure 2 shows the effect of temperature on the equilibrium composition of the incoming gas stream for the S-O system in the absence of the calcine. At low temperatures, sulphur trioxide predominates with oxygen. At higher temperatures sulphur trioxide is not stable, sulphur dioxide forms and the amount of oxygen increases. Therefore, the sulphating reactions are more favourable at lower temperatures.

Figure 3 shows the effect of temperature on the equilibrium composition of the Fe-Cu-As-S-O species for the control feed and gas compositions at a gas to solid ratio of 20:1. At low temperatures, ferrous sulphate ($FeSO_4$) and copper sulphate ($CuSO_4$) predominate. As the temperature increases further, the ferrous sulphate converts to ferric sulphate ($Fe_2(SO_4)_3$) and subsequently to hematite (Fe_2O_3), while the copper sulphate becomes oxysulphate ($CuO \cdot CuSO_4$) then cupric oxide (CuO). At even higher temperatures, copper ferrites ($CuO \cdot Fe_2O_3$ or $Cu_2O \cdot Fe_2O_3$) form as hematite and copper oxide react.

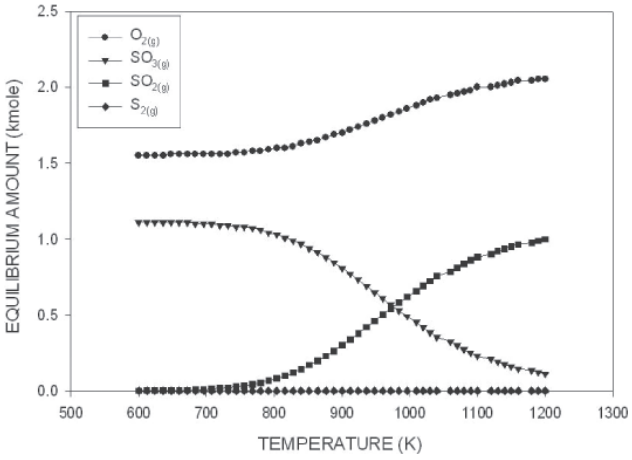

Fig. 2: The effect of temperature on the equilibrium amounts of gaseous species in the S-O system for the control conditions in the absence of calcine.

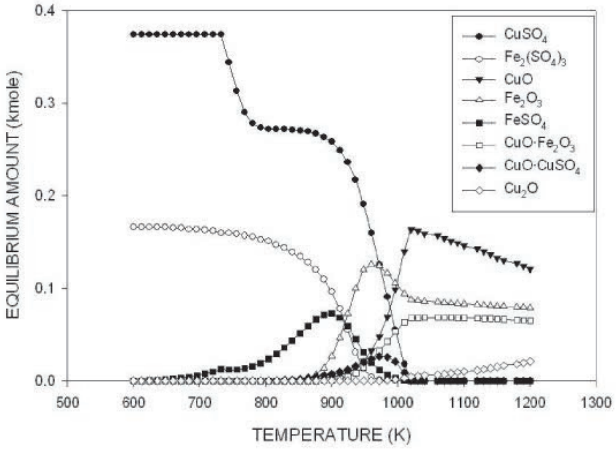

Fig. 3: The effect of temperature on the equilibrium amounts of Cu-Fe-O species for the control conditions.

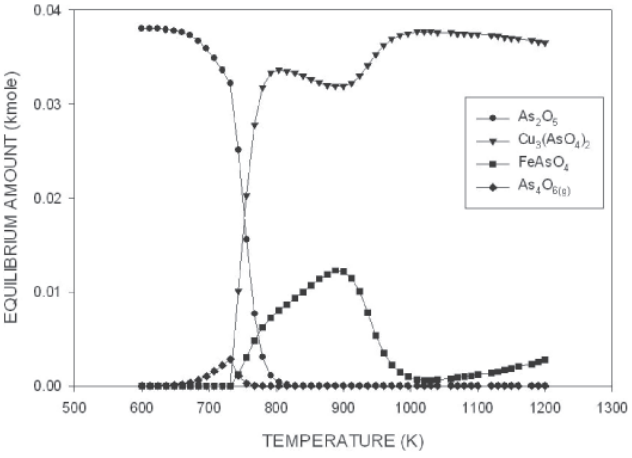

Fig. 4: The effect of temperature on the equilibrium amounts of arsenic-containing species for the control conditions.

Figure 4 shows the behaviour of the arsenic-containing species as a function of temperature for the control conditions. At low temperatures the majority of the arsenic is present as solid arsenic pentoxide with some gaseous arsenic trioxide. As the temperature increases, copper arsenate forms very rapidly with increasing temperature and then ferric arsenate. At even higher temperatures, the ferric arsenate decreases to very low levels while the copper arsenate increases and levels off. Figure 5 shows the vapour pressures of the gaseous arsenic-containing species. Arsenic will volatilize at low temperatures due to the high vapour pressure of arsenic trioxide ($As_4O_{6(g)}$) and will consequently be removed from the system as described by Nakazawa et al and Holmstrom [3, 5]. Arsenic gas needs to be retained in the calcine in order to react. The production of arsenic pentoxide (As_2O_5) through the oxidation of arsenic trioxide is thermodynamically favourable as follows:

$$As_4O_{6(g)} + 2O_{2(g)} = 2As_2O_{5(s)} \quad (16)$$

Downey et al proposed that arsenic pentoxide will form in the calcine, under highly sulphating conditions between 773 and 923 K [14]. On the other hand, Chakraborti & Lynch suggested that arsenates will form in lieu of arsenic

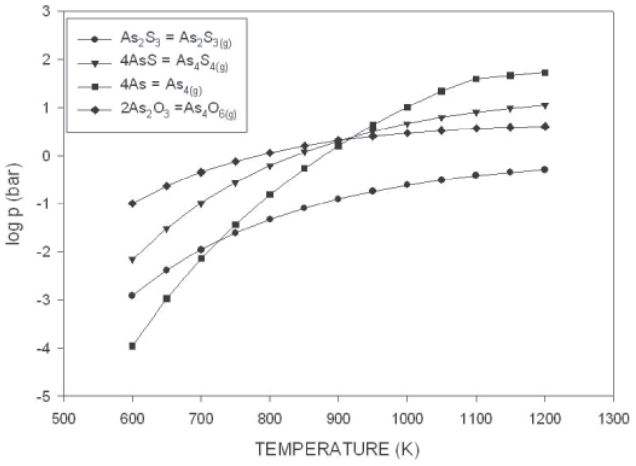

Fig. 5: The effect of temperature on the partial pressures of gaseous arsenic species in the As-S-O system.

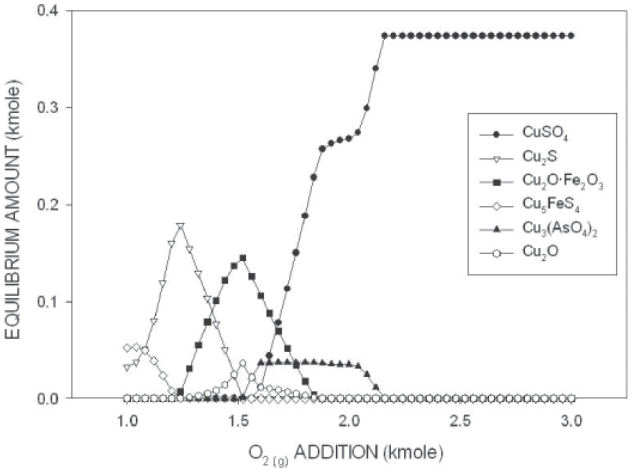

Fig. 6: The effect of oxygen addition on the equilibrium amounts of copper-containing species at 750 K for the control conditions.

pentoxide assuming fast reaction kinetics, which fits the thermodynamic results more accurately [15]. It was also noted in their study that high arsenic trioxide vapour pressures at high temperatures will cause high removal rates unless the system is pressurized to retain arsenic in the calcine. Therefore it is expected that at temperatures below 923 K some arsenic will be retained in the calcine, while at temperatures above 973 K, arsenic will be largely volatilized and the arsenate species in the calcine will be stable but only as minor components. It is possible that, under highly oxidizing conditions and at high temperatures, some arsenic pentoxide product forms in the off-gas. However, arsenic trioxide is the primary product collected industrially in smelting and also in partial roasting operations as described by Filippou et al and Riveros et al; there is little indication that arsenic pentoxide is produced [17, 18]. The above discussion demonstrates that in the proposed roasting process (750 to 1000 K) the arsenic would be fixed mainly as copper arsenate and some iron arsenate with a significant amount of arsenic being volatilized as arsenic trioxide.

Figure 6 shows the copper-containing species at a fixed temperature of 750 K and the control conditions for varying oxygen additions. At low oxygen additions, copper and copper-iron sulfides are present as a result of the decomposition of enargite. At intermediate oxygen levels, copper oxides and arsenates form and finally copper sulphate, at high oxygen additions. Figure 7 shows the iron-containing species and it can be seen that hematite and magnetite and iron sulphides predominate at low oxygen additions. At intermediate oxygen additions, cuprous ferrite ($Cu_2O \cdot Fe_2O_3$) is favourable and with increasing oxygen additions ferrous sulphate and subsequently ferric sulphate predominate. The arsenic-

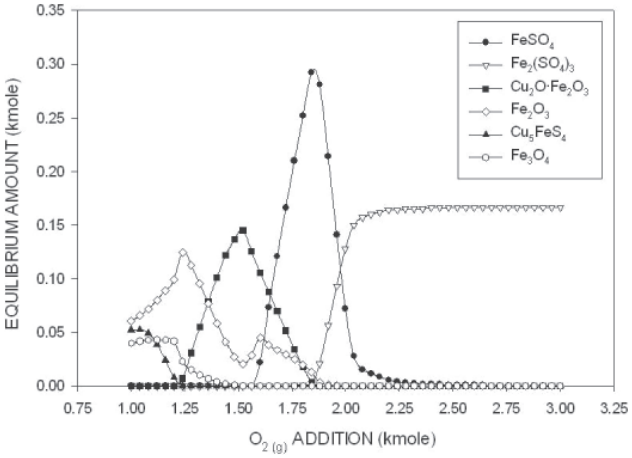

Fig. 7: The effect of oxygen addition on the equilibrium amounts of iron-containing species at 750 K for the control conditions.

containing species are shown in Figure 8 and it can be seen that at low oxygen levels, arsenic trioxide prevails. As the oxygen addition increases, copper arsenate forms in significant amounts and subsequently some iron arsenate is produced. At very high oxygen levels, only arsenic pentoxide is present. In terms of the roasting process, the maximum amount of iron arsenate occurs at an oxygen addition of about 2 kmoles. As discussed previously, since the formation of arsenates is more kinetically favourable, the formation of arsenic pentoxide would not be expected at high oxygen additions.

Figure 9 shows the copper-containing species as a function of the oxygen addition at 1000 K. Again at low oxygen additions, the sulphides are stable and as the oxygen increases, cuprous oxide and cuprous ferrites form. However, in contrast to 750 K, as the oxygen addi-

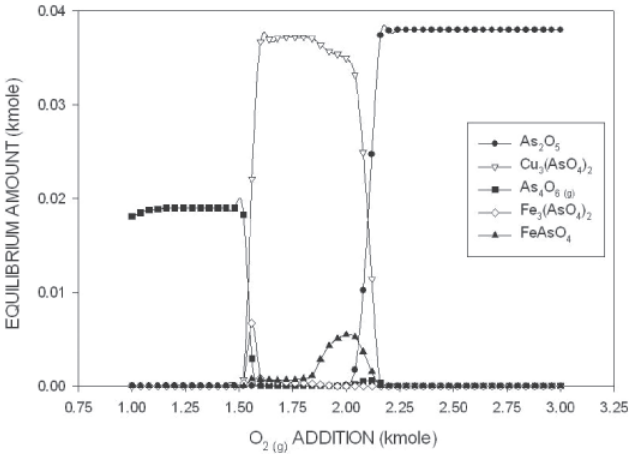

Fig. 8: The effect of oxygen additions on the equilibrium amounts of arsenic-containing species at 750 K for the control conditions.

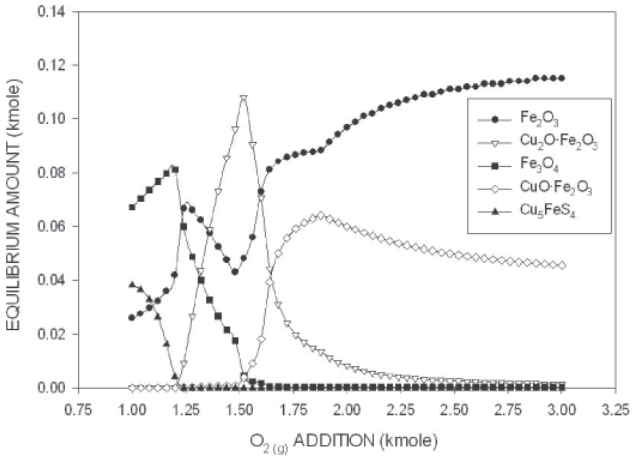

Fig. 10: The effect of oxygen additions on the equilibrium amounts of iron-containing species at 1000 K for the control conditions.

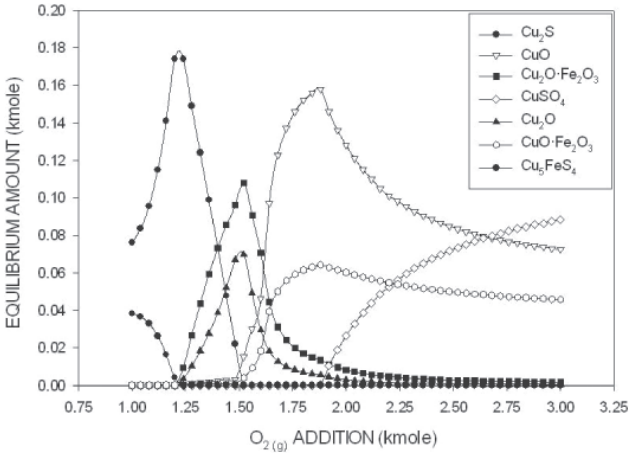

Fig. 9: The effect of oxygen additions on the equilibrium amounts of copper-containing species at 1000 K for the control conditions.

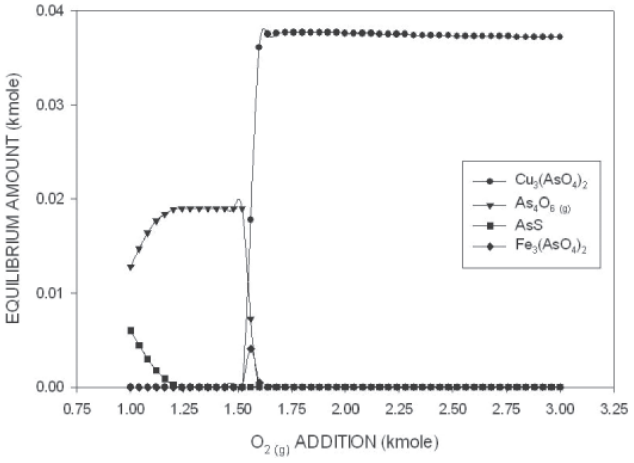

Fig. 11: The effect of oxygen additions on the equilibrium amounts of arsenic-containing species at 1000 K for the control conditions.

tion increases above 1.5 kmole, cupric oxide, cupric ferrite and copper arsenate are produced instead of copper sulphates. The copper sulphates are not produced until an oxygen addition of almost 1.9 kmole, in comparison to 1.6 kmole at 750 K. Figure 10 shows the iron-containing species at 1000 K as a function of the oxygen addition. Again, hematite, magnetite and sulphides prevail at low oxygen additions. For oxygen additions from 1.2 to 1.5 kmole the amounts of hematite and magnetite decrease as cuprous ferrite forms. Just above 1.5 kmole, the cuprous ferrite is converted to cupric ferrite ($CuO \cdot Fe_2O_3$) and as a result the amount of hematite increases. At about 1.9 kmole, the cupric ferrite begins to decompose into cupric oxide and hematite. Iron sulphates only form in relatively small amounts at 1000 K in comparison to the relatively large amounts at 750 K. Figure 11 shows the effect of oxygen on the arsenic-containing species at 1000 K. At low oxygen additions, arsenic trioxide gas predominates and at an oxygen addition of 1.5 kmole, the arsenic trioxide vapour is consumed and copper arsenate forms. In comparison to 750 K (Figure 8), only a small amount of iron arsenate is present and arsenic pentoxide is absent. These results demonstrate that additional oxygen is required to form sulphates at higher temperatures. At temperatures above 1000 K, copper sulphates cannot form even in the presence of considerable excess oxygen.

Figure 12 shows the effect of the gas/solid molar ratio and temperature on the amounts of gaseous species in the S-O system in equilibrium with the calcine, for the control conditions. As the gas/solid molar ratio increases from 0 to 20, the equilibrium amount of sulphur dioxide increases but is independent of temperature. Above a ratio of 20,

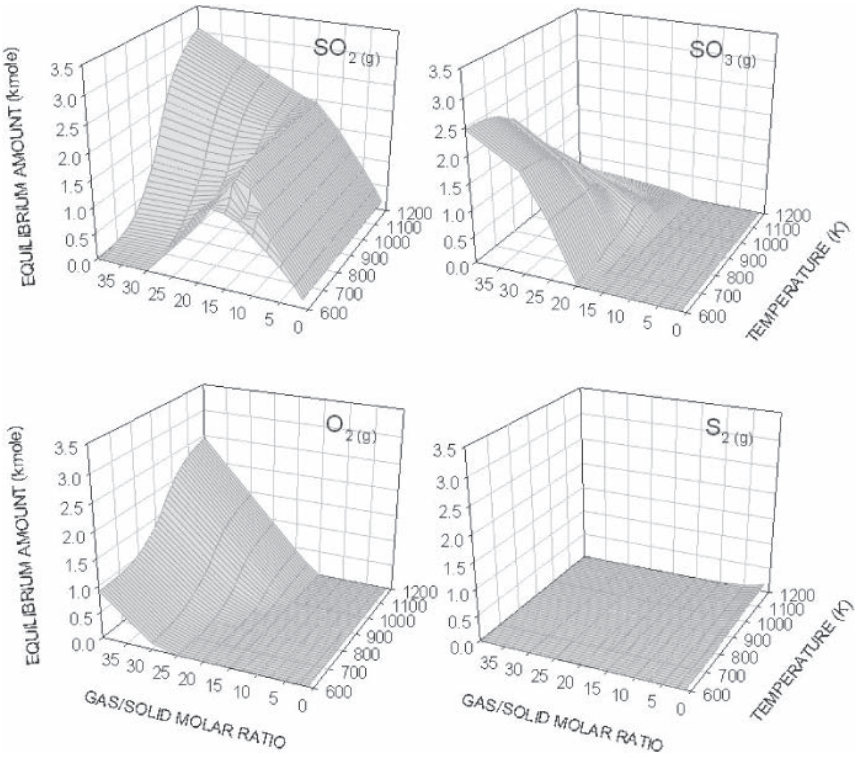

Fig. 12: The effect of gas/solid molar ratio and temperature on the equilibrium amounts of $SO_{2(g)}$, $SO_{3(g)}$, $O_{2(g)}$ and $S_{2(g)}$ in equilibrium with the calcine for the control conditions.

excess oxygen is available and this results in the production of sulphur trioxide at low temperatures. However, at high temperatures, sulphur trioxide is unstable and as a result, oxygen and sulphur dioxide predominate. Sulphur gas only forms in small amounts at high temperatures and low gas/solid ratios.

Figure 13 shows the amounts of the major copper-bearing species produced as a function of the gas/solid molar ratio and temperature for the control conditions. At low gas/solid molar ratios, only sulphides exist and roasting has not occurred. Above gas/solid molar ratios of about 12, roasting begins and copper sulphides are completely eliminated at a gas/solid molar ratio of 20. Subsequently, the amounts of the copper-containing species are independent of the gas/solid molar ratio. At low temperatures, copper sulphate is the primary species, simplifying copper recovery. Above 800 K, copper arsenate begins to form and is present even at high temperatures. Above 900 K, copper sulphate becomes unstable and copper oxide and cuprous ferrite are produced. Copper recovery from calcines produced at high temperatures would therefore require higher acid concentrations during leaching, due to the presence of these three copper-containing species.

Figure 14 shows the effect of gas/solid molar ratio and temperature on the iron-containing species for the control conditions. At low ratios, some hematite is produced across the whole temperature range. At temperatures below 700 K and molar ratios beyond 5, ferrous sulphate forms rapidly. At a molar ratio of about 20, excess oxygen is produced and ferric sulphate becomes the predominant species at low temperatures. Some ferric arsenate forms between 800 and 1000 K, but only in minor quantities. The amount of hematite reaches a maximum at about 900 K and then decreases due to the presence of copper oxides and the formation of cuprous ferrite. Insoluble iron, as hematite, can only be produced over a narrow temperature range and at high gas/solid ratios. At lower temperatures, iron becomes soluble, whereas at higher temperatures, copper recovery is reduced due to the formation of ferrites.

The arsenic-containing species produced as a function of gas/solid molar ratio and temperature, are shown in Figure 15. At gas/solid ratios below 15, arsenic volatilizes as arsenic trioxide across the whole temperature range. At high ratios and low temperatures, arsenic pentoxide is the only species present. At temperatures between 800 to 1000 K, copper arsenate and minor amounts of iron arsenate coexist. However, above this temperature range, copper arsenate is the dominant species. Therefore, at low gas/solid ratios, arsenic can be removed through volatilization, while at high gas/solid ratios, arsenic is retained

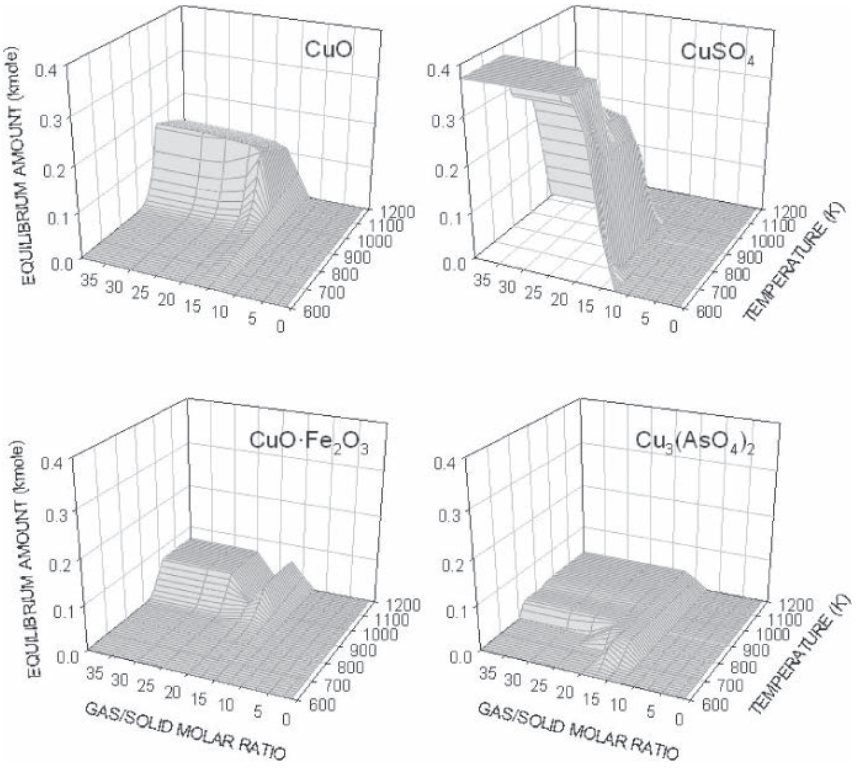

Fig. 13: The effect of gas/solid molar ratio and temperature on the equilibrium amounts of CuO, $CuSO_4$, $CuO \cdot Fe_2O_3$ and $Cu_3(AsO_4)_2$ for the control conditions.

in the calcine. The amount of iron arsenate produced is insufficient and therefore arsenic would have to be leached from the calcine and subsequently precipitated from the pregnant leach solution, in order to ensure adequate arsenic sequestration.

Figure 16 displays the effect of p_{SO2}/p_{O2} and temperature on the equilibrium amounts of the arsenic-bearing species. At high ratios, gaseous arsenic trioxide is the only species present. At low temperatures and low ratios, arsenic pentoxide forms. Above about 750 K, copper arsenate predominates with minor amounts of ferric arsenate being produced between 750 and 1000 K. At high ratios, arsenic will be volatilized from the calcine as arsenic trioxide, however, at low ratios, arsenic will be retained in the calcine and subsequently leached in order to ensure stability. These results can be compared with those for the effect of gas/solid molar ratio on the behavior of the arsenic-containing species in Figure 15. It can be seen that copper arsenate forms at high temperatures and high gas/solid molar ratios and low p_{SO2}/p_{O2} ratios. Iron arsenate forms at intermediate temperatures and high gas/solid molar ratios and low p_{SO2}/p_{O2} ratios. Additionally, a comparison of the results based on p_{SO2}/p_{O2} ratios with the gas solid molar ratio for the iron and copper species, demonstrates that they exhibit similar behaviour. This indicates that the major factor affecting the sulphation roasting process is the amount of oxygen in the input gas.

Industrial application

Based on this thermodynamic analysis, the optimum operating parameters have been determined and a more detailed process flowsheet has been developed as outlined in Figure 17. An operating window for sulphation roasting in a fluidized bed between 800 and 925 K at a gas to solid ratio above 20 in an atmosphere of about 10% sulphur dioxide and 10% oxygen is proposed. At 800 K under these conditions, copper sulphate, iron sulphate and arsenic pentoxide are all expected to form in the calcine; these species are water soluble during subsequent leaching operations. As the roasting temperature increases to 925 K some copper sulphates are converted into oxy-sulphates, and hematite formation becomes more favourable than iron sulphate. At these temperatures, copper and iron arsenates are more stable than arsenic pentoxide and are similarly retained in the calcine. All the dust in the off-gas will be recycled back to the fluidized bed and a wet-gas scrubber will be utilized to remove any volatilized arsenic. The remaining off-gas will contain high amounts of

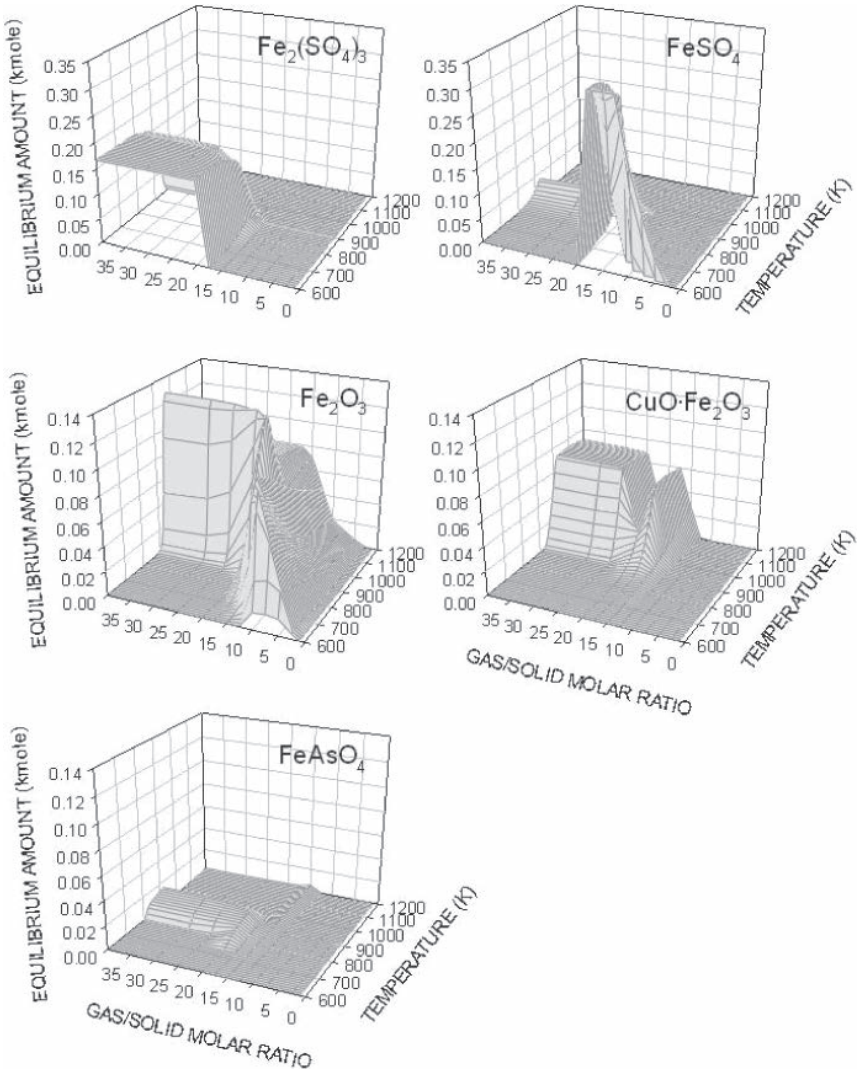

Fig. 14: The effect of gas/solid molar ratio and temperature on the equilibrium amounts of $Fe_2(SO_4)_3$, $FeSO_4$, Fe_2O_3, $CuO \cdot Fe_2O_3$ and $FeAsO_4$ for the control conditions.

sulphur dioxide which can be converted to sulphuric acid in the acid plant. A summary of the expected calcine products under the optimum roasting conditions and their acid solubility is presented in Table 5.

After sulphation roasting under the optimum conditions, the process will utilize sulphuric acid from the acid plant, SX leachate or spent electrolyte, to perform a 10 g/L weak acid leach, ensuring that all the copper values are recovered. Arsenic in the form of copper arsenate will be leached and will need to be fixed in an effluent treatment plant along with arsenic in the wet-gas scrubber bleed solution; any ferric arsenate will remain in the leach residue. It is expected that enough ferric ions will be leached from the calcine to maintain a 1:1 iron to arsenic ratio in the pregnant leach solution, while the iron will remain as hematite in the leach residue. A 1:1 iron to arsenic ratio is required in the pregnant leach solution in order to perform the atmospheric scorodite process to fix arsenic as described by Demopoulos et al [19]. Scorodite will be removed during solid/liquid separation and the neutralized pregnant leach solution will undergo SX/EW to produce a copper cathode. The raffinate from SX would be recycled back into the leaching process with part being bled to heap leaching or neutralized and disposed of in lined tailings ponds. The weak-acid leach residue will be washed and filtered before being subjected to cyanidation in order to recover gold and silver. The cyanidation leach residue, as well as the arsenic fixed as scorodite and the neutralized leachate will all be disposed of in lined tailings ponds.

This process would be particularly useful for operations with existing copper SX/EW facilities. High copper,

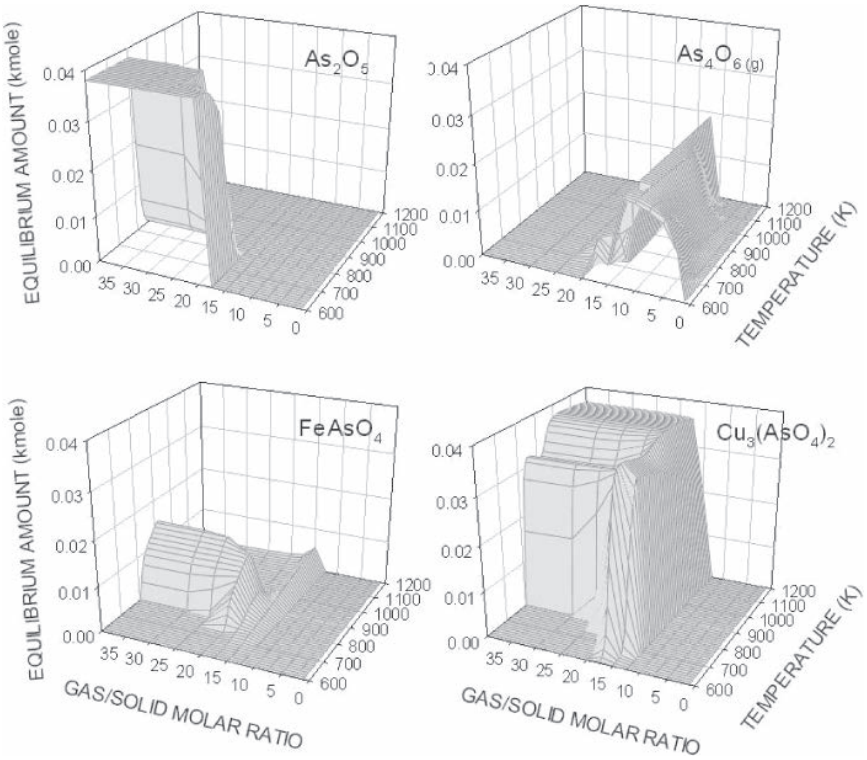

Fig. 15: The effect of gas/solid molar ratio and temperature on the equilibrium amounts of $As_4O_{6(g)}$, $Cu_3(AsO_4)_2$, As_2O_5 and $FeAsO_4$ for the control conditions.

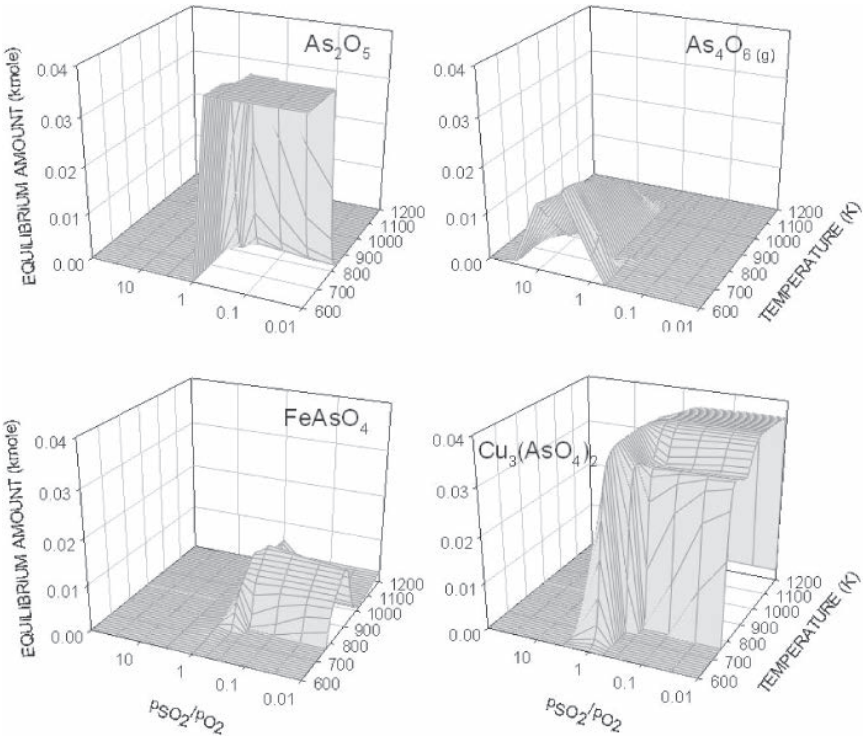

Fig. 16: The effect of pSO_2/pO_2 and temperature on the equilibrium amounts of As_2O_5, $As_4O_{6(g)}$, $FeAsO_4$ and $Cu_3(AsO_4)_2$ for the control conditions.

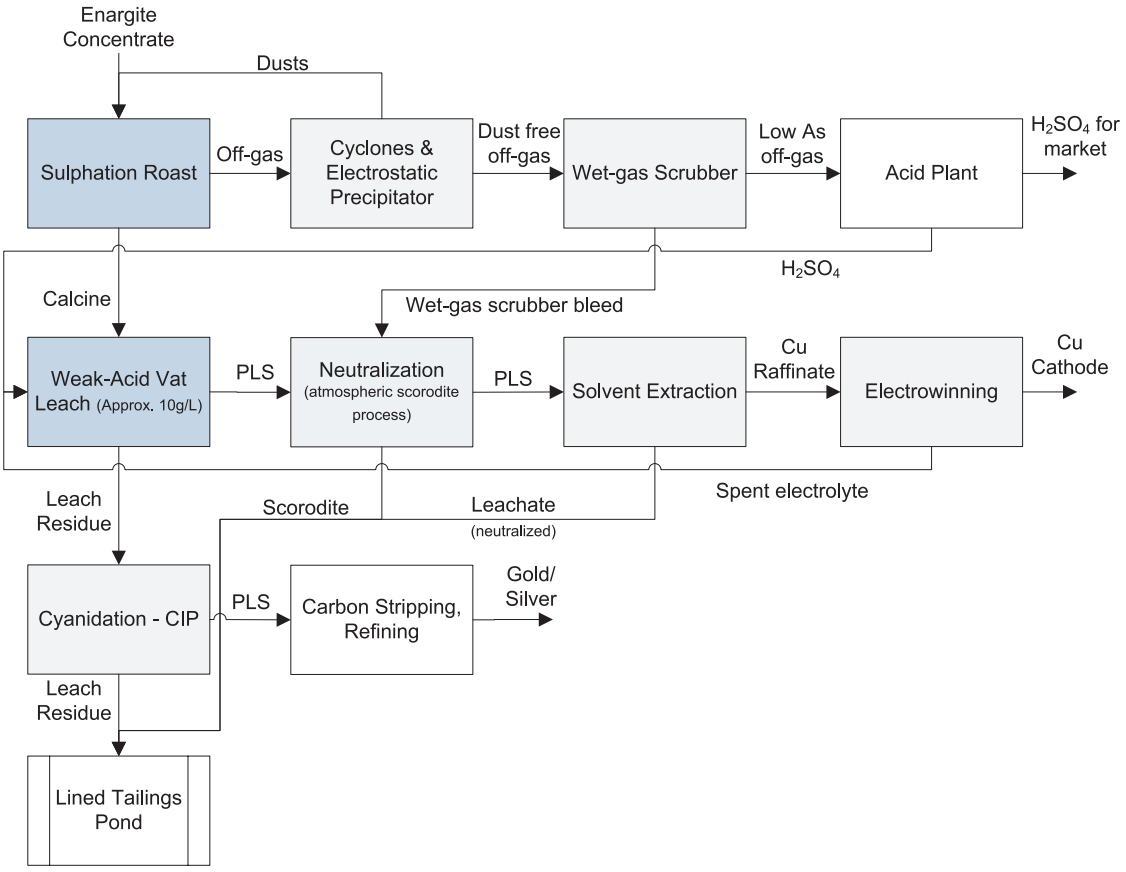

Fig. 17: Detailed flowsheet for the proposed sulphation roast, weak-acid leach, electrowinning process for the enargite concentrate.

Mineral phases in the calcine	Approximate composition (mole%)	Predicted solubility
Major species		
Copper sulphate ($CuSO_4$)	60%	Water soluble
Hematite (Fe_2O_3)	24%	Insoluble
Iron sulphate ($Fe_2(SO_4)_3$)	7%	Water soluble
Cupric arsenate ($Cu_3(AsO_4)_2$)	7%	Weak acid soluble
Ferric arsenate ($FeAsO_4$)	2%	Strong acid soluble
Total	100%	
Minor species		
Arsenic pentoxide (As_2O_5)	–	Water soluble
Copper oxysulphate ($CuO \cdot CuSO_4$)	–	Weak acid soluble
Copper oxide (CuO)	–	Weak acid soluble
Copper ferrite ($CuO \cdot Fe_2O_3$)	–	Strong acid soluble
All sulphides	–	Insoluble

Table 5: The calcine composition and the solubility of the phases for the optimum roasting conditions.

gold and silver extractions should be achieved, with the arsenic fixed in an environmentally-stable form. However a variety of potential disadvantages exist which need to be further investigated. The proposed roasting reaction is exothermic and significant cooling would be required to maintain roasting temperatures. In order to control the temperature, water injection will be necessary, resulting in downstream gas handing issues and increased capital cost due to the higher roaster gas flows. Furthermore, a significant amount of sulphate is produced, forming weak acid, which will need to be recycled on-site or neutralized.

Conclusions

A thermodynamic study of the sulphation roasting of an enargite concentrate has been performed. The following reaction mechanism was proposed:

$$Cu_3AsS_4(s) + 3FeS_2(s) + 11O_2(g) = 3CuSO_4(s) + Fe_2O_3(s) + FeAsO_4(s) + 3.5SO_2(g)$$

Based on this reaction, the calcine would consist of water soluble copper sulphate, insoluble hematite and arsenic fixed as ferric arsenate and/or scorodite. HSC Chemistry® 6.1 was utilized to study the effects of temperature, oxygen additions, gas to solid ratio and p_{SO2}/p_{O2} ratio on the equilibrium composition of both the off-gas and the calcine. The optimum roasting temperature should be between 800 and 925 K where excess oxygen is the major factor affecting the composition of the products. The calculations demonstrate that the process is technically feasible and a detailed process flowsheet has been developed. Further experimental work and heat balances will need to be performed in order to determine if this process can be commercially viable.

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References

[1] J.G. Peacey, M. Gupta and K. Ford, *Proceedings of Copper 2010*, **3**, Hamburg, Germany, (2010), pp. 1035–1050.
[2] Codelco (D. Hernandez – Presenter), Presentation at Metal Bulletin Copper Conference 2010, Santiago, Chile, (June 2010).
[3] S. Nakazawa, A. Yazawa and F.R.A. Jorgensen, *Metallurgical and Materials Transactions*, **30**B, pp. 393–401 (1999).
[4] R. Padilla, Y. Fan, M. Sanchez and I. Wilkomirsky, *TMS*, EPD Congress 1997, Orlando, Florida, (1997), pp. 73–83.
[5] A. Holmstrom, *Scandinavian Journal of Metallugy*, **18**, pp. 12–30 (1989).
[6] Z. Yoshimura, *MMIJ*, **78**, 447–453 (1962).
[7] V.A. Luganov, V.I. Shabalin and O.V. Vasilevskiyi, *Journal of Chemistry and Technology of Chalcogenes and Chalcogenides*, **65**, pp. 249–251 (1982).
[8] E.H. Smith, *Mining Engineering*, **38**, pp. 971–979 (1986).
[9] A.C. Secco, G.A. Riveros and A.A. Luraschi, *Proceedings of Copper 87*, Viña del Mar, Chile, (1987), pp. 225–238.
[10] E.A. Peretti, *Disussions of the Faraday Society,* **4**, 174–179 (1948).
[11] C.L. McCabe and J.A. Morgan, *Journal of Metals*, **8**, 800A (1956).
[12] C.J. Ferron and J. De Cuyper, *International Journal of Mineral Processing*, **35**, 225–238 (1992).
[13] M.B. Shirts, P.A. Bloom and W.A. McKinney, *U.S. Bureau of Mines*, Report of Investigations 7996, Salt Lake City, Utah, (1975).
[14] J.P. Downey, E.C. Eccleston and J.P. Hager, *Rewas '99, Global Symposium on Recycling, Waste Treament and Clean Technology*, San Sebástian, Spain, (1999), pp. 1675–1683.
[15] N. Chakraborti and D.C. Lynch, *Metallurgical Transactions*, **14**B, 239–251 (1983).
[16] A. Roine, *HSC Chemistry 6.0 – User's Guide.* Outokumpu Research Oy, Pori, Finland, (2006).
[17] D. Filippou, P. St-Germain and T. Grammatikopoulos, *Mineral Processing and Extractive Metallurgy Review*, **28**(4), 247–298 (2007).
[18] P.A. Riveros, J.E. Dutrizac and P. Spencer, *Canadian Metallurgical Quaterly*, **40**(4), 395–420 (2001).
[19] G.P. Demopoulos, F. Lagno, Q. Wang and S. Singhania, *Proceedings of Copper 2003*, **4**, Santiago, Chile, (2003), pp. 597–616.
[20] R.R. Seal II, R.A. Robie, B.S. Hemingway and H.T. Evans Jr., *The Journal of Chemical Thermodynamics*, **28**, 405–412 (1996).
[21] J.R. Barton and P.B. Craig, *Economic Geology*, **68**, 493–506 (1973).