

Flue Dust Behaviour in FSF - Arsenic Condensation in Off-gas Line Conditions

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Abstract. The suspension smelting oxidation step has favourable conditions to generate chemical flue dust from the low-boiling elements of the feed mixture due to the high particle temperatures in the reaction shaft where combusting sulphide mineral particles reach temperatures above the melting point of magnetite. Arsenic, antimony, lead, and zinc are common impurity elements of high volatility in copper concentrates. They tend to accumulate in the flue dust due to the high volatility and closed mode of the flue dust circulation practiced in most industrial smelting-converting processes. Then, the only outlets for the volatile impurities are the anodes and the discard slag. A separate flue dust treatment for impurity removal is an option but it creates an additional step for the smelting plant and cost in the processing. When the concentrate grades decrease, and their impurity levels rise this outlet for the trace elements may become necessary. The arsenic condensation mechanisms in dust-free conditions in the copper flash smelting process gas train have been recently studied in SO₂-air-N₂ gas mixtures. It seems that the formation mechanism of arsenic-containing dust deposits is kinetically constrained, and their chemistries are influenced by the condensation temperature and atmosphere.

INTRODUCTION

The high-temperature smelting and refining processes generate flue dust either as entrainment of fines from the feed mixture or as chemical dust vapourised from the raw materials. The chemical dust is result of low-boiling or sublimating substances in the smelting and their vapours' deportment in the off-gas train of the smelting vessel [1]. There, the volatilised species cool down and have opportunity to react with the surrounding atmosphere. Highly volatile elements in the copper smelting are arsenic, zinc and mercury but also antimony, lead and bismuth have moderate tendency for vaporisation [2-4]. The volatilisation is a spontaneous, thermally activated process.

A vaporisation-condensation cycle of such elements may exist inside the smelting vessel, like zinc and alkali metals circulation in blast furnace, but also form a continuous solids stream from the furnace, along with the off-gas. In FSF/FCF (Flash Smelting Furnace/Flash Converting Furnace) environments the off gas is led to sulphur fixing and sulphuric acid manufacturing where it

will be cleaned from all solids. In the waste heat boiler (WHB) the off-gas carries a mixed flue dust of the smelter, containing the mechanical and chemical fractions. Depending on the minor and trace element concentrations in the feed mixture, the flue dust assay varies from one smelter to another [5-6]. Recovering elements from various flue dusts, not commonly practiced industrially, has been studied a lot and hydrometallurgical or combined pyro-hydrometallurgical techniques seem to be most flexible due to easy leaching of various sulphates [7-8].

The condensation mechanisms and product phases in various conditions of the cooling gas flow have been studied in the literature only in rare cases. Most of the studies are dealing with formation of nanostructures and -powders in well-controlled laboratory conditions [e.g., 9].

WHB

In the past, the normal practice in FSF/FCF operations was to lead the flue dust back to the smelting step, due to its high copper concentration [10-11]. The impact of flue dust in the feed mixture can be taken into consideration in the operational point, and its decomposition products do not harm the basic procedures on the smelter. The increasing impurity element concentrations, in particular arsenic, have changed this picture a lot. Many custom smelters are today facing the problem of increasing impurity levels in their discard slag and the anode quality. This has increased concerns about the closed flue dust circulation mode [7, 12].

In FSF/FCF, the behaviour of flue dust in WHB, Figure 1, and electrostatic precipitator (ESP) is controlled by the adjustments of the gas phase and its free oxygen [13]. That is why most flash smelters operate in slightly oxidising mode in their off-gas train, trying at the same time to avoid weak acid formation as much as possible.

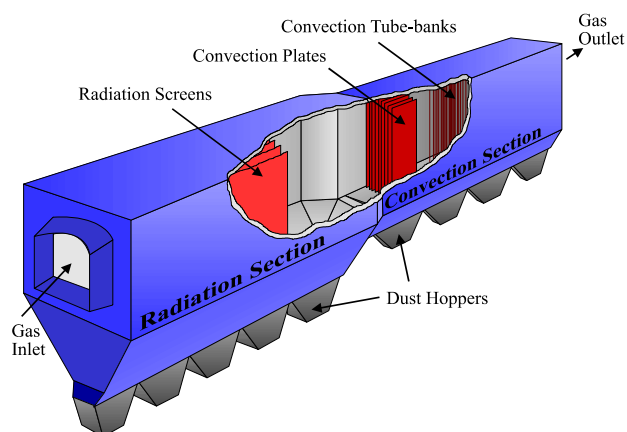


Figure 1. A typical horizontal WHB and its structure for collecting heat values from FSF/FCF process gas and treating flue dust in a form that it can be handled in pneumatic conveying.

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In many bath smelting technologies, the recovery of process heat from the off-gas has been regarded as less important and the gas cooling is arranged by excessive (secondary) air so that the radiation section of WHB is no more used [14-15]. At the same time, no accurate control of the gas composition and its oxygen activity is any more possible. This indicates how the flue dust management and the options for managing its chemistry may also vary from one technology to another.

The internal flue dust circulation

In the conventional closed flue dust circulation, the smelting and converting flue dusts are mixed with the smelter feed. It enriches the amounts of volatile elements in the flue dust until a stationary condition has been achieved and then the total concentrate feed amounts of the impurities correspond to their amounts in the anode and discard slag streams i.e., the system is in the stationary condition.

The circulating flue dust assay, however, is very different from the feed and contains in addition to copper also high concentrations of the volatile elements depending on, whether the circulation is closed or open. Their concentrations may exceed 10-100× the concentration in the concentrate mixture [16] in stationary conditions, see Figure 2. This means that e.g., most arsenic in the feed mixture comes from the circulating flue dust.

As a first approximation, if the circulating load of arsenic is diminished by 90 %, a similar decrease is expected in the arsenic levels in the FSF slag and matte. This has significant impacts on the downstream processing of the smelting slag, its utilisation, and the converting product assays.

Depending on the technologies in the smelting, the reverts at the smelter, slag concentrate, and the slag cleaning furnace matte may generate additional material circulations internally in the smelter as well. They are consumed as parts of the smelting or converter feeds, in a similar way as the flue dusts in the closed circulation mode. However, the impact of reverts on the oxygen balance is less than that of the flue dust but the impact on the heat balance may be significant [17].

Internal load of volatile impurities in FSF

Based on the reports and public information about the flue dust assays and mineralogies in various smelters, the closed flue dust circulation generates dust assays very rich in arsenic and other volatile elements [18]. The closed flue dust circuit is visualised schematically in Figure 2. In those cases, the degree of volatilisation of e.g., arsenic, in the smelting vessel is impossible to estimate from the published plant data.

FLUE DUST CHEMISTRY AND MINERALOGY

Particle size

The formation of chemical dust in cooling smelter off-gas flow means that various metals precipitate at temperatures specific to each forming substance. Thus, the phase composition in the presence of several volatile metals is complex, and the particle size is small if the precipitation is homogenous and not taking place on another dust particle. This is confirmed by several sampling studies and the bi-modal character of the material is due to the mixture of mechanical dust ($d_{50} = 10-20 \mu\text{m}$) and chemical dust ($d_{50} = 0.1-1 \mu\text{m}$) [8, 19]. It is also evident that ESP dusts are much finer than WHB dusts [20].

Most of the coarse material is either settled down in the WHB or the ESP [3, 13]. The gas cooling from typical 1300 °C to less than 200 °C is a simultaneous process with the chemical reactions in the gas train, and it has a major impact on the thermodynamic stabilities of metal sulphates and SO_3 .

Mineralogy

As chemical flue dust precipitates as characteristic substances, they typically are pure phases without any solubility. For maintaining flowability, the FSF/FCF flue dusts are oxidised for eliminating the residual sulphides, and further on in the WHB radiation section sulphatised for eliminating stickiness. The WHB atmosphere and its high SO_2 concentration has tendency for generating sulphates

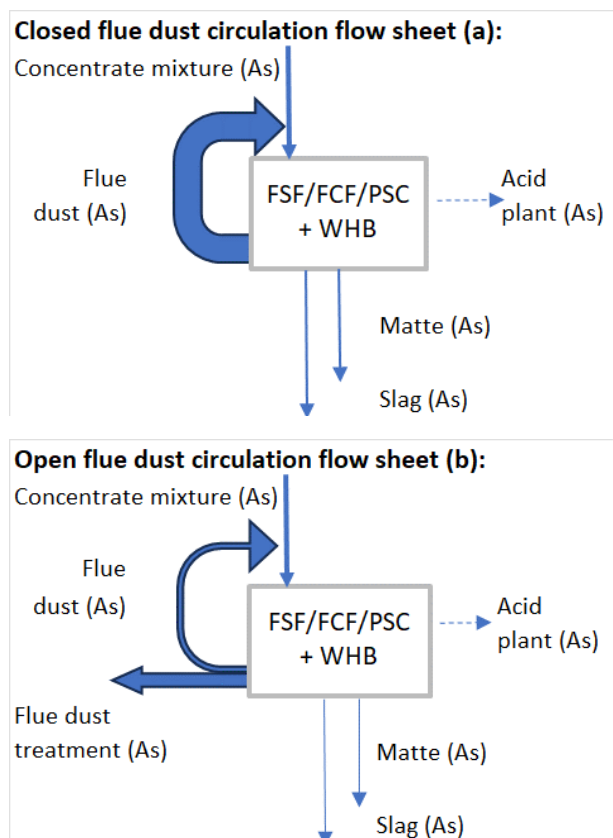
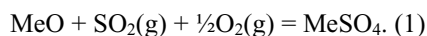


Figure 2. A schematic impact of flue dust circulation on the arsenic department - the circulating arsenic amount in copper smelter (a) decreases when the open mode (b) is adopted, resulting in lower arsenic departments in the slag and matte.

from copper oxides in the flue dust provided there is free oxygen available [21]. Thus, in the outlet most flue dust particles are coated with MeSO₄ scales (Me =Cu, Pb, Zn) and sulphate sulphur is a major component of the dust forming in WHB conditions by reactions:



The presence of sulphates makes the dust hygroscopic which impairs its handling, and storage in the smelter.

Speciation of metals in WHB - the case of arsenic

The speciation of sulphur in the WHB dust varies from one operational practice to another [16, 19]. In addition to arsenic (III) oxide also arsenates and arsenic sulphide have been detected in various smelters and one reason for the different observations is also the smelting technology used. Typically, the smelters based on the suspension smelting technology tend to avoid sulphides in the WHB due to their stickiness and bad flowability, and all sulphur in the FSF/FCF dusts is preferentially found as sulphates [21-22].

FLUE DUST FORMATION

Thermodynamic equilibria in gas cooling

The FSF/FCF off-gas in WHB is very strong in SO₂ containing typically >40-50 vol% when it starts the cooling process from 1300 °C in the radiation section. In the junction of the radiation and convection section it has cooled down to 600-700 °C and beyond that, it is assumed that the forming dust is solid, not sticky anymore, and flows freely in the dust hoppers and further on, during the pneumatic conveying. Thus, the interesting temperature window in WHB for generating SO₃ is between 1300 and 700 °C in the radiation section and 700 to 300 °C in the convection section.

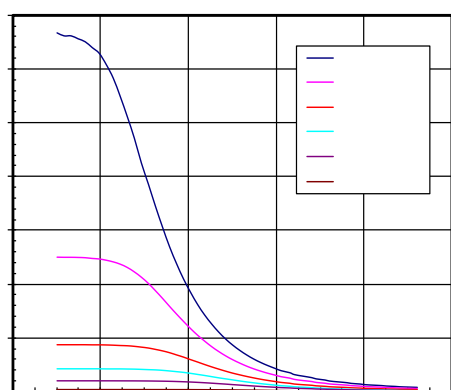
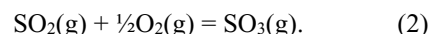


Figure 3. The SO₂-SO₃ equilibrium at constant initial oxygen partial pressures between 1300 and 500 °C.

The ESP operates at around 300-380 °C, depending on its construction. No SO₃ formation is generally expected to take place there [14]. In those conditions, the SO₂-SO₃

equilibrium (2) is strongly on the SO₃ side in the off-gas cooling, but the kinetics is very slow. Its driving force in WHB is constrained by the residual oxygen partial pressure, as shown in Figure 3, according to reaction:



The thermodynamic stability of SO₃ is greatly enhanced in the temperature gradient from about 1000 °C down to 500 °C. It can be assumed that sulphur dioxide and oxygen are at copper smelting and converting temperatures 1200-1300 °C predominantly as individual molecules and the thermodynamic driving force for the formation of sulphur trioxide is very small [23]. The SO₂-rich off-gas produces weak acid in the end of the gas train, at acid plant. The gas may reach the dewpoint of sulphuric acid at the surface temperature of the WHB tubes when reacting with water and causing wet corrosion scales and deterioration on the boiler tube surfaces [11].

Phase assemblies in the As-S-O equilibria

Most authors dealing with the condensation of metal vapours in industrial gas streams assume, in lack of experimental evidence, that they react according to the substances' thermodynamic stabilities. As to arsenic compounds, this simplification is common e.g., in combustion engineering [24-25], extractive metallurgy [26], and environmental science [27].

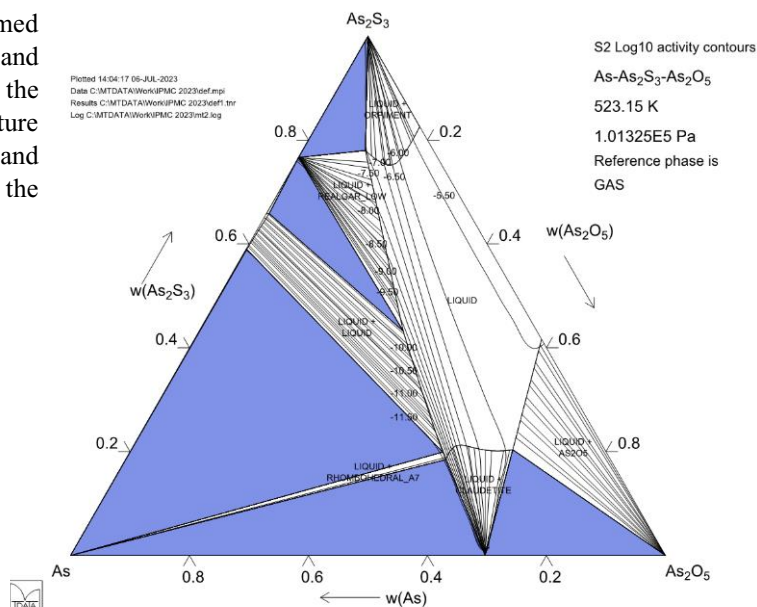


Figure 4. Isothermal section at 250 °C and sulphur iso-activity contours of the system As-S-O; standard state S₂(g, 1 bar); MTDATA vers. 7.4 and MTOX database vers. 8.2 [30].

The arsenic-oxygen-sulphur (As-O-S) ternary system is composed of several pure substances and a low-temperature molten oxy-sulphide domain, see Figure 4. The phase relations in the binaries are known to some accuracy and even recent thermodynamic assessments exist about the As-O and As-S binary systems and the As-S-O ternary [28-29]. The tendency to form glassy sulphide

mixtures [28], however, may harm e.g., the XRD (X-ray diffraction) phase analyses.

Effect of the off-gas composition - arsenic speciation in gas phase

The low-temperature oxy-sulphide melt forming above ≈ 100 °C is stable according to the recent assessment from metallic arsenic to both sulphide and oxide primary phase fields, saturated at ambient pressure by solid As_2S_3 and AsS (As_2S_2) as well as As_2O_3 and As_2O_5 . The isothermal section at 250 °C is shown in Figure 4. It also depicts the sulphur iso-activity contours, defined as $p(\text{S}_2)$ with $\text{S}_2(\text{g}, 1 \text{ atm})$ as standard state. A gas phase equilibrium in the conditions of the experimental set up by Wan et al. [31] is depicted in Figure 5.

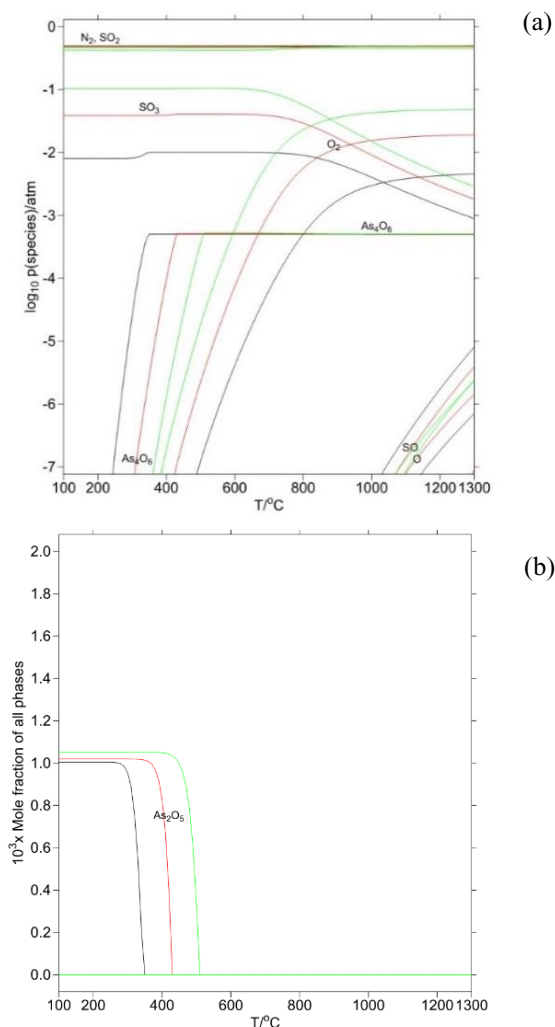


Figure 5. The gas phase speciation of arsenic and sulphur in cooling gas (a) as a function of temperature from 1300 to 100 °C with initial $p(\text{O}_2) = 0.05\text{-}0.02\text{-}0.005 \text{ atm}$ and $p(\text{SO}_2) = 0.5 \text{ atm}$ and (b) solid precipitate mass (calculated using MTDATA and MTOX 8.2 database).

The saturation temperatures of the condensed phase, As_2O_5 in these cases, are easily identified on the graph as the sudden decrease of $\text{As}_4\text{O}_6(\text{g})$ partial pressure at different oxygen partial pressures between 200-400 °C. The predominant arsenic species in the gas phase is dimer

of arsenic trioxide $\text{As}_4\text{O}_6(\text{g})$. The formation of SO_3 has a clear impact on the oxygen partial pressure, but the precipitation of As_2O_5 also extracts oxygen from the gaseous SO_3 , as shown in Figure 5 and its $\text{SO}_3(\text{g})$ contours.

Chemistry of condensed arsenic in $\text{SO}_2\text{-O}_2$ mixtures

Arsenic metal, arsenic sulphides, and arsenic trioxide (As_2O_3) were identified in the condensed deposits formed in flowing gas streams with 50 vol% SO_2 and 0.5-5.0 vol% O_2 in a controlled temperature gradient between about 300 and 50 °C [31-32]. Outside that temperature widow, no arsenic precipitation was detected. The speciation of arsenic and sulphur were ascertained by XPS (X-ray photoelectron spectroscopy) and EDS/EPMA (energy dispersive spectroscopy/electron probe X-ray microanalysis) in the deposits formed on a fused quartz tube. The observations indicate strong interactions between the gas mixture and condensing arsenic species in gas. From the gas phase speciation equilibria in Figure 5, can be concluded that a strong non-equilibrium state prevails during the condensation process when the arsenic-bearing substances in liquid or solid form generate the condensed deposit.

The gas phase speciation in equilibrium conditions in the FSF/FCF vessel, Settler and Uptake, can be estimated in a straightforward way based on the general composition of the gas phase, arsenic concentration of the feed mixture, and estimated enrichment of arsenic-bearing species. With a dust generation of 5 wt% of the feed mixture concentrate content and closed flue dust circulation, the molar concentration of arsenic-bearing gaseous substances can be assumed to be at least $10\times$ the stationary inlet and outlet concentrations. In open flue dust circulation mode, the concentration is about 0.4 vol % As in the gas (with about 0.3 wt% As in the concentrate feed) and in closed circulation correspondingly about $>4 \text{ vol } \%$.

The deposit formation mechanism

When oxygen partial pressure of the gas is slightly reduced from the lowest experimental value of the study by Wan et al. [31-32], $p(\text{O}_2) = 0.5 \text{ vol}\%$, the arsenic oxy-sulphide phase appears in the equilibrium assemblage at low temperatures, along with arsenic oxide. At the same time, the speciation of arsenic is modified significantly as shown in Figure 6.

The partial pressures of arsenic and arsenic sulphide species are increased several orders of magnitude but that of arsenic trioxide dimer stays essentially constant. In the calculations arsenic trioxide was present in the gas phase in a similar way as in Figure 5. The equilibrium calculations indicate how sensitive the atmosphere is to relatively small perturbations in its composition and in particular the prevailing $p(\text{O}_2)$.

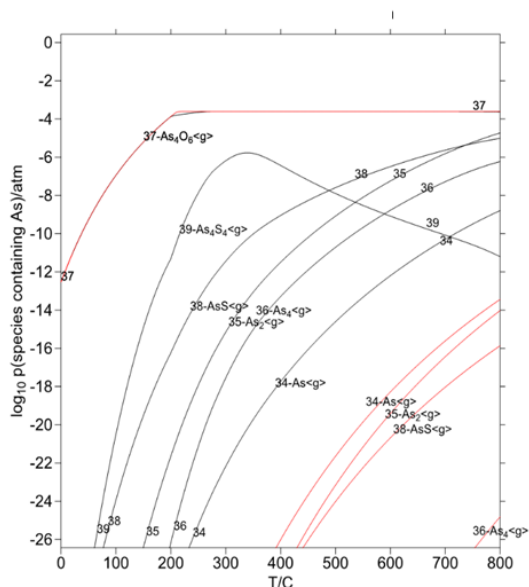


Figure 6. Equilibrium speciation of the gas phase arsenic species when cooling from 800 °C to room temperature; the mixtures contain initially 50 vol% SO₂ and traces of oxygen (— 0.1 and —0.05 vol% O₂).

Such substances can be formed because of the strong tendency of SO₂(g) to oxidise at low temperatures to SO₃(g). The arsenic sulphides formed in the precipitation were mostly glassy and did not allow identification by XRD. A short thermodynamic approach to the conditions where arsenic in metallic form, as sulphides and oxides exist was made using predominance area diagrams, as shown in Figure 7. The diagram was constructed with HSC Chemistry software (vers. 9.9) [33], by defining the SO₃ species dormant and fixing the partial pressure of sulphur (p(S₂)). It is significant that the HSC databases only contain pure substances and no solution phases, like the As-O-S alloy melt described earlier, are included in Figure 7. In this sense, the predominance area diagram in Figure 7 just approximates the true phase assembly of the As-O-S system but gives an illustration of the stabilities of its oxide and sulphide substances at low temperatures.

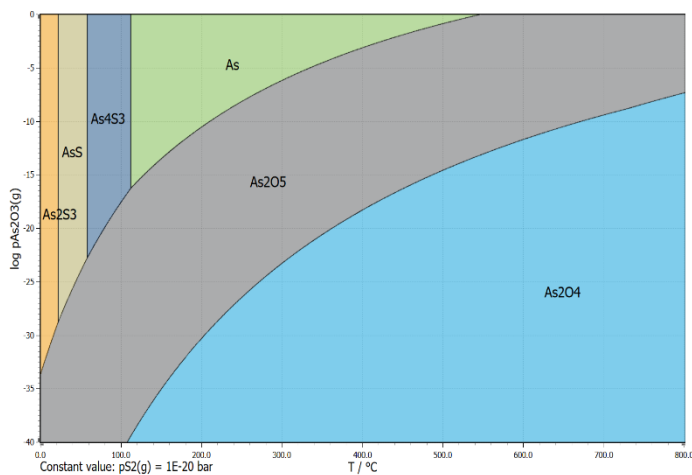


Figure 7. A predominance area diagram of the system As-O-S with fixed p(S₂) of 10⁻²⁰ bar (≈atm).

Recent experimental observations in dust-free SO₂-O₂ atmospheres indicate that arsenic-bearing deposits contain several oxidation degrees, from metallic arsenic to arsenic (III) and arsenic (V) oxides and sulphides [31-32]. In XPS measurements, sulphate sulphur, or (VI)-sulphur, was also found in some samples indicating the formation of SO₃ in the experimental conditions and its subsequent reaction to sulphuric acid in ambient air.

Is this reaction sequence Wan et al. [32] have identified a trace of some kind of inability for oxygen to adsorb on As-O-S alloys. An explanation for this may be a similar feature as with Fe and Ni sulphides which have been identified as very good catalysts for the oxygen and hydrogen generation in aqueous systems [24, 34]. In this kind of catalysed process of the SO₃ formation on As-S-O alloys, the generation of low-valence species of arsenic is possible when it is supersaturated and condensing from the gas phase.

Such a reaction sequence is evidently facilitated by the availability of multiple oxidation states of arsenic and sulphur in the deposits, as was pointed out recently by Wan et al. [32] in their XPS observations of the deposits. With this kind of electrocatalytic feature, electron transfer between the condensing species is taking place over a small activation barrier, and the formation of low-valence arsenic species is possible along with the formation of gaseous sulphur trioxide on the deposit. They all were identified in the deposits in a certain temperature zone by Wan et al. [32].

The actual nucleation process on the fused silica tube may progress without major barriers due to the surface energy relations in the silica-As-O-S deposit systems. According to Wan et al. [32], the wetting angle of liquid arsenic on silica was found to be close to zero (after solidification) which facilitates the nucleation and formation of the new phase [35-36].

CONCLUSIONS

A selective element separation from condensed particles to gas phase is effective in the reaction shaft suspension oxidation step of the flash smelting technology [37-38]. Therefore, it should be beneficial for the element deportment in the smelting to adjust the process flowsheet towards the open flue dust circulation mode. In that case, the volatile elements, gasified in early stages of the matte making process, would be separated from the main material stream, thus discontinuing their passage along with the other feed components to the downstream steps.

The mechanism of arsenic condensation in dust-free conditions of the smelter gas, at gas temperatures in ESP and beyond, towards the acid plant, produces very complex, non-equilibrium deposits on the gas duct walls, containing arsenic compounds. Instead of generating the stable arsenic(V)oxide, the precipitate was composed of

metallic arsenic and arsenic sulphide, along with arsenic (III)oxide. The reason for such a behaviour may be the surface properties of As-O-S alloys with electrocatalytic features. They would allow deposition of reduced species of SO₂(g) and As₄O₆(g) on the duct surface and nucleation of metal and sulphides. The liquid oxy-sulphide mixture phase would be subsequently formed due to its stability, lowering spontaneously the total energy of the system.

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