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Thermal decomposition of arsenopyrite in the presence of calcium oxide [1]

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Abstract

The thermal decomposition of arsenopyrite in the presence of calcium oxide was studied using TG/FTIR. A fairly pure arsenopyrite mineral and an industrial arsenopyrite concentrate were examined in inert and oxidizing atmospheres. The decomposition takes place below 800°C with the release of arsenic and sulphur in a form that depends on the prevailing atmosphere and on the amount of CaO added. The results also indicated that, with the addition of an appropriate amount of CaO, nearly complete containment of arsenic and sulphur during the decomposition of arsenopyrite may be possible.

INTRODUCTION

In the extraction of gold from arsenical ores, several steps are involved. The ores, usually composed of quartz, arsenopyrite, pyrite, chalcopyrite and a variety of minor components, are treated by crushing and grinding followed by gravity flotation and roasting to obtain a calcine suitable for the cyanidation treatment used in the recovery of gold. The roasting process is normally conducted in two stages. The first stage is carried out in an oxygen-deficient atmosphere (distillation) where the arsenic and most of the sulphur are removed as gaseous species. Arsenic sulphide may form in this stage. Arsenic is later oxidized to As_2O_3 and captured in baghouse filters. In the second stage (roasting), the solids are subjected to oxidation to form a porous iron oxide calcine containing the gold. During this stage, the remaining sulphur reacts with oxygen and is emitted to the atmosphere as SO_2.

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Many studies on the thermal decomposition and oxidation of arsenopyrite have been reported in the literature [1–6]. Lukesh [1] reported that arsenopyrite samples sealed in evacuated silica tubes decomposed at about 650°C. He suggested that the reaction may follow a scheme such as

$$\mathrm{Fe}_x\mathrm{As}_y\mathrm{S}_z = \mathrm{Fe}_x\mathrm{S}_z + y\mathrm{As} \tag{1}$$

$\mathrm{Fe}_x\mathrm{S}_z$ was identified by X-ray diffraction (XRD) as pyrrhotite. Lukesh also mentioned that pyrite (FeS_2) and iron diarsenide ($FeAs_2$) may also form, depending on the initial composition of arsenopyrite. Strathdee and Pidgeon [2] studied the decomposition in an inert atmosphere and found that, in the temperature range 500–700°C, the reaction proceeds with the formation of pyrrhotite in the solid phase and arsenic and arsenic disulphide (As_2S_2) in the gas phase. Isabaev et al. [3] studied the kinetics of decomposition in an inert atmosphere in the temperature range 625–670°C and suggested that the reaction occurs with the formation of pyrrhotite, iron diarsenide and gaseous arsenic. On extended heating at the same temperature or heating to higher temperatures (800–900°C), the two solid products react to form troilite (FeS) and gaseous arsenic. Kopp and Kerr [4], Asensio and Sabatier [5] and Maurel [6] found that the oxidation of arsenopyrite also takes place in the temperature range 500–600°C. The last author concluded that the oxidation reaction occurs with the formation of Fe_2O_3, As_2O_3 and SO_2.

In the present study, the influence of the addition of calcium oxide on the thermal decomposition of arsenopyrite in inert and oxidizing atmospheres was examined. Calcium oxide may prove to be effective in the removal of sulphur and arsenic oxide gases during the roasting process of arsenical gold ores.

MATERIALS AND EXPERIMENTAL PROCEDURE

A fairly pure arsenopyrite mineral from Madoc, Ontario and an industrial arsenopyrite concentrate were used in the present study. The XRD of the arsenopyrite mineral identified the major constituent as arsenopyrite, FeAsS. The concentrate was analysed spectrochemically and was found to contain 28.4% SiO_2, 24.9% Fe, 9.4% As and 17.9% S, with iron and sulphur contents in excess of their stoichiometric amounts in FeAsS. Scanning electron microscopy (SEM) analyses indicated that, in addition to arsenopyrite, the concentrate contains pyrite, quartz and a minor amount of silicates.

A Du Pont 9900TA thermal analysis system with a 951TGA thermobalance module was used in the study. For the identification of the gaseous species evolved during the analysis, the thermobalance was interfaced with a BOMEN-MB100 Fourier transform infrared (FTIR) spectrometer with a Compaq 386/20e computer capable of simultaneous control of the balance and the spectrometer. A gas cell, 10 cm long, with standard KBr windows was used in the spectrometer. In some cases a multipath (approx. 3 m) gas cell was used. The evolved-gas transfer line between the thermobalance and the spectrometer was made of a small-diameter glass tubing connected to a glass filter for the removal of particulates from the gas stream. The TG and FTIR measurements were made simultaneously.

In the experiments, 20–40 mg samples of arsenopyrite or mixtures of arsenopyrite and calcium oxide were subjected to programmed heating at 20°C $\min^{-1}$ in a stream of oxygen-free helium or dry air. A gas flow rate of 50 ml $\min^{-1}$ was used. The time lag between the gas evolution in the thermobalance and the gas detection in the spectrometer was less than 10 s. The ratio of CaO to FeAsS in the mixtures was based on selected Ca/S molar ratios of 1, 3 and, in some cases, 6. The sulphur content of the mineral was based on the stoichiometric formula of arsenopyrite, and that of the concentrate was based on the chemical analysis determination.

RESULTS AND DISCUSSION

Figure 1 shows TG diagrams for the arsenopyrite mineral in inert (He) and oxidizing (air) atmospheres. In helium, a weight loss of 43% occurred in the temperature range 450–700°C. Metallic arsenic and traces of ele-

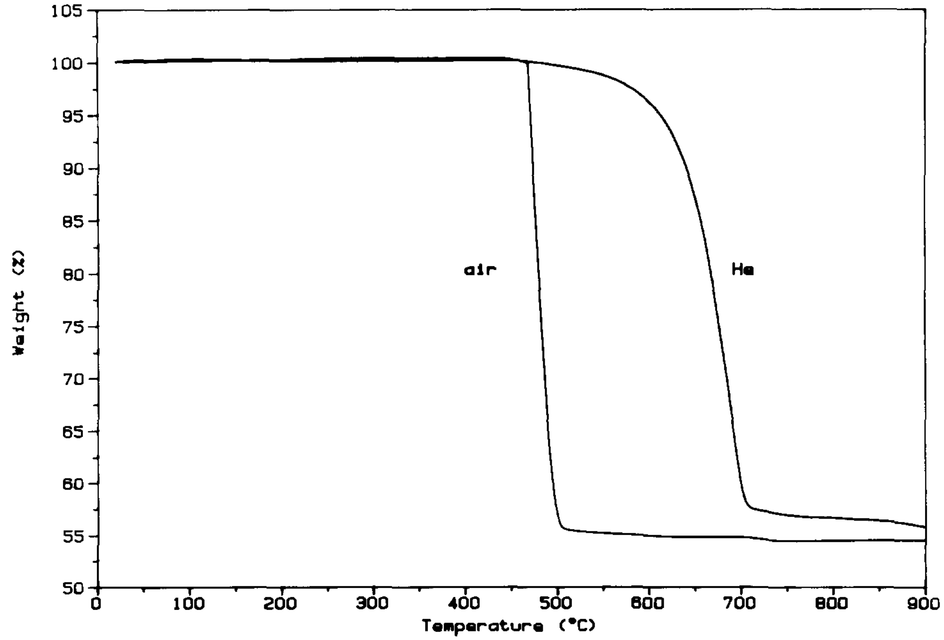

Fig. 1. TG diagrams for an arsenopyrite mineral in inert (He) and oxidizing (air) atmospheres.

mental sulphur deposited on the colder part of the reaction tube, and a trace amount of CO_2 in the exit gas was detected by FTIR. The CO_2 may have originated from minor amounts of carbonates in the starting material. The final product was identified by XRD as mainly pyrrhotite. A minor amount of Fe_3O_4 was also identified, indicating the presence of surface oxidation in the starting material. A complete decomposition of arsenopyrite to pyrrhotite and gaseous arsenic would result in a weight loss of about 46%, depending on the stoichiometries of both arsenopyrite and pyrrhotite.

In air, a weight loss of 45% started at the same temperature as that in helium (450°C) but was complete at 500°C. During the weight loss, SO_2 was detected by FTIR in the exit gas and a white precipitate of arseneous oxide deposited on the reaction tube. The final product was determined by XRD as mainly Fe_2O_3, together with a minor unidentified component. The oxidation reaction may, therefore, be represented as

$$2FeAsS + 5O_2 = Fe_2O_3 + 2SO_2 + 0.5As_4O_6 \qquad (2)$$

in agreement with Maurel [6]. The weight loss, as determined by TG, was somewhat lower than the theoretical weight loss of 51% for reaction (2). This also may be explained by the presence of surface oxides (and probably minor amounts of quartz) in the starting material, and hence less arsenopyrite available for oxidation.

Figure 2 shows TG/FTIR diagrams for a mixture of arsenopyrite mineral and calcium oxide with a Ca/S ratio of 1, in helium. Four stages of weight loss appeared at 350–400, 600–650, 650–700 and above 800°C. The first and third stages seem to be due to the decomposition of minor amounts of $Ca(OH)_2$ and $CaCO_3$ in the starting CaO, as verified by the simultaneous evolution of H_2O and CO_2 respectively. During the experiments, arsenic and sulphur deposited on the colder parts of the reaction tube above 600°C. In separate experiments, heating was interrupted at preselected temperatures and the sample was examined by XRD. At 500°C, it was found to contain only the starting materials while, at 800°C, it contained CaS, FeAs, unreacted CaO and a trace amount of unidentified material. These results indicate that the second weight loss is mainly due to a reaction leading to the formation of CaS and FeAs, and to the volatilization of some arsenic and sulphur. The final weight loss above 800°C may be due to the decomposition of iron arsenide.

Another mixture with a Ca/S ratio of 3 was also examined and the results were similar to that of the mixture with a Ca/S ratio of 1, except that the second weight loss was much smaller and the volatilization of As and S was much less, indicating the capture of more As and S by the CaO additive.

Following the same procedure, another series of experiments was carried out on mixtures of the mineral and CaO in air. Figure 3 shows the TG/FTIR results of mixtures with Ca/S ratios of 1, 3 and 6. For the sake

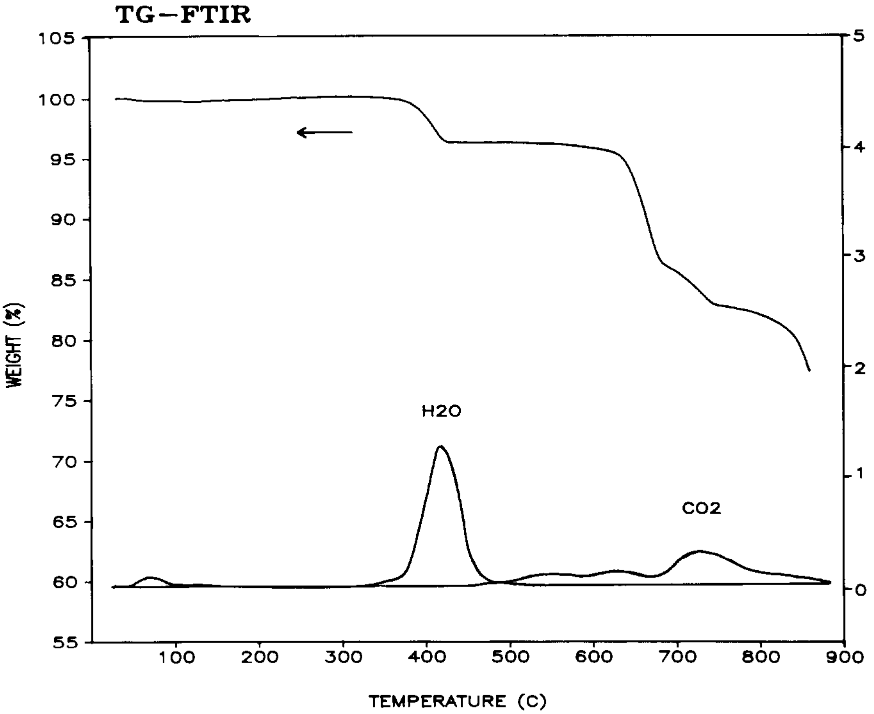

Fig. 2. A TG diagram for a mixture of arsenopyrite mineral and CaO (Ca/S ratio of 1), in helium, with corresponding FTIR gas evolution curves.

of clarity, gas evolution curves for H_2O and SO_2 only are shown, although trace amounts of CO_2 were also detected in the exit gas. As previously discussed, the weight loss at 350–400°C, accompanied by H_2O evolution, signifies the decomposition of $Ca(OH)_2$ originating from the starting CaO. As expected, the magnitude of this particular weight loss and the corresponding H_2O evolution increased with the increase in the CaO ratio in the mixture. In Fig. 3(a) (Ca/S ratio of 1), a gradual weight gain and an overlapping weight loss followed the initial weight loss. The weight gain is thought to be due to the reaction

$$2FeAsS + 5CaO + 7O_2 = Fe_2O_3 + Ca_3(AsO_4)_2 + 2CaSO_4 \tag{3}$$

Indeed, an XRD analysis of the solid product (from about 550°C) confirmed the presence of the three products of reaction (3). The major weight loss, accompanied by the evolution of SO_2 and the deposition of As_2O_3 on the colder parts of the reaction tube, is related to the oxidation of arsenopyrite according to reaction (2).

On increasing the Ca/S ratio of the mixture (Fig. 3(b) and (c)) a decline in the amount of SO_2 in the gas was observed and, at the same time, little or no As_2O_3 deposited on the reaction tube. Moreover, more unreacted

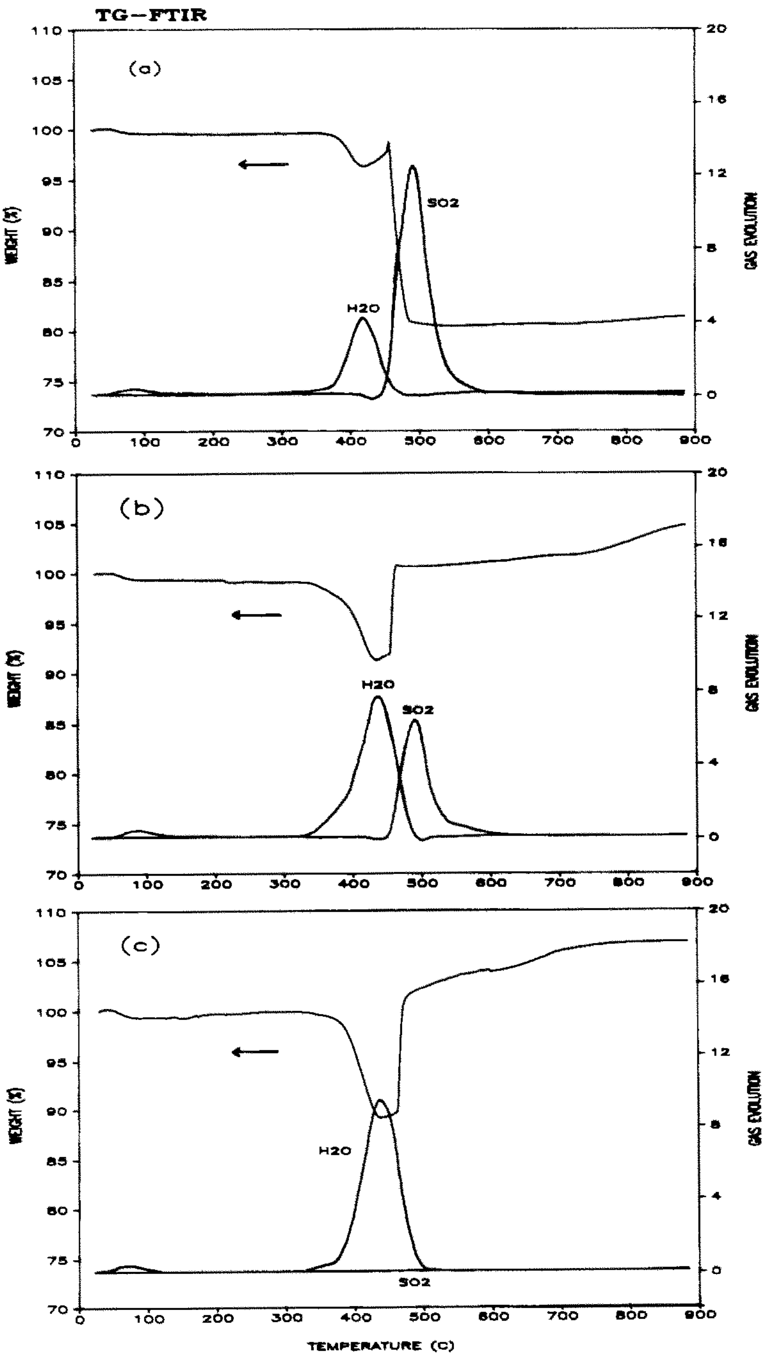

Fig. 3. TG diagrams for mixtures of arsenopyrite mineral/CaO, in air, with Ca/S ratios of (a) 1, (b) 3 and (c) 6, and corresponding FTIR gas evolution curves.

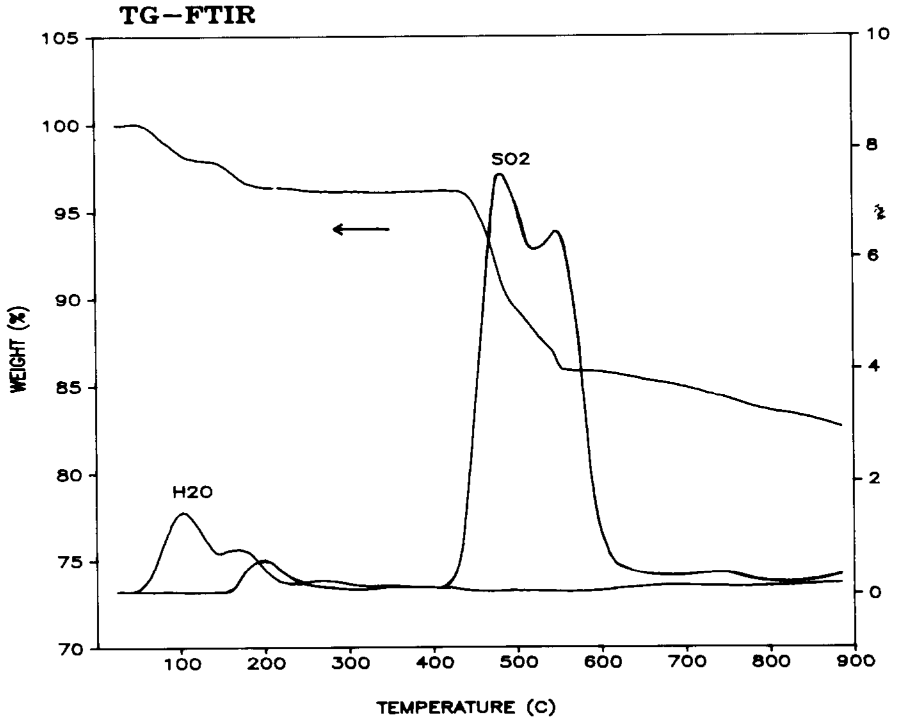

Fig. 4. A TG diagram for arsenopyrite concentrate in air with corresponding FTIR gas evolution curves.

CaO was detected by XRD. Significantly, no iron arsenates were detected by XRD. These observations verified the containment of arsenic and sulphur by the CaO additive, in the form of calcium arsenate and calcium sulphate respectively.

In the second part of this study, the arsenopyrite concentrate was examined using the same sequence of experiments used for the mineral. In addition to arsenopyrite, the concentrate contained significant amounts of pyrite and quartz as well as minor amounts of iron silicates and probably oxides. Figure 4 shows TG/FTIR diagrams for the concentrate in air. The low temperature weight loss is due to the release of moisture as verified by the corresponding H_2O evolution. The main weight loss in the temperature range 400–500°C, accompanied by SO_2 evolution and As_2O_3 deposition on the reaction tube, is due to the oxidation of arsenopyrite (reaction (2)) and pyrite in the sample. In air, pyrite is known to decompose according to the reaction [6]

$$2FeS_2 + 5.5O_2 = Fe_2O_3 + 4SO_2 \tag{4}$$

Some CO_2, probably originating from carbonates in the original concentrate, also appeared in the exit gas (not included in the gas evolution

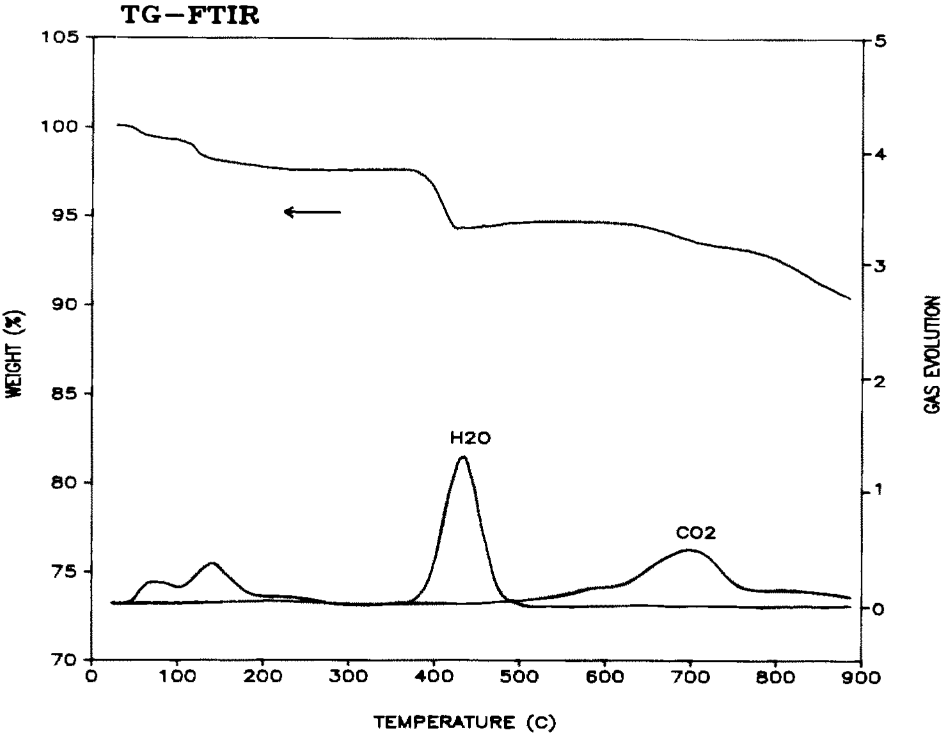

Fig. 5. A TG diagram for a mixture of arsenopyrite concentrate and CaO (Ca/S ratio of 1), in helium, with corresponding FTIR gas evolution curves.

curves). An XRD analysis of the reaction product identified mainly Fe_2O_3 and quartz. A similar TG diagram was obtained when the concentrate was heated in helium. However, metallic arsenic and elemental sulphur deposited on the colder parts of the reaction tube and almost no SO_2 appeared in the exit gas. An XRD analysis of the reaction product identified pyrrhotite ($Fe_{1-x}S$), quartz and a minor amount of Fe_3O_4 as the main constituents.

Figure 5 shows TG/FTIR diagrams for a mixture of arsenopyrite concentrate and CaO with a Ca/S ratio of 1, in helium. The diagrams are quite similar to those obtained for the mineral/CaO mixture but the magnitude of the weight loss due to the interaction of the two starting materials is notably less. This is due to the dilution effect of quartz and other impurities in the concentrate. The appearance of H_2O and CO_2 at different temperatures has been discussed earlier. Traces of SO_2 appeared in the exit gas above 700°C, perhaps due to the decomposition of minor amounts of sulphate in the concentrate. An XRD analysis of the reaction product (from about 800°C) indicated the presence of CaS, Fe_3O_4, $Ca_3(AsO_4)_2$ and pyrrhotite, in addition to quartz. Another mixture with a Ca/S ratio of 3 was also examined and the results were similar to those of

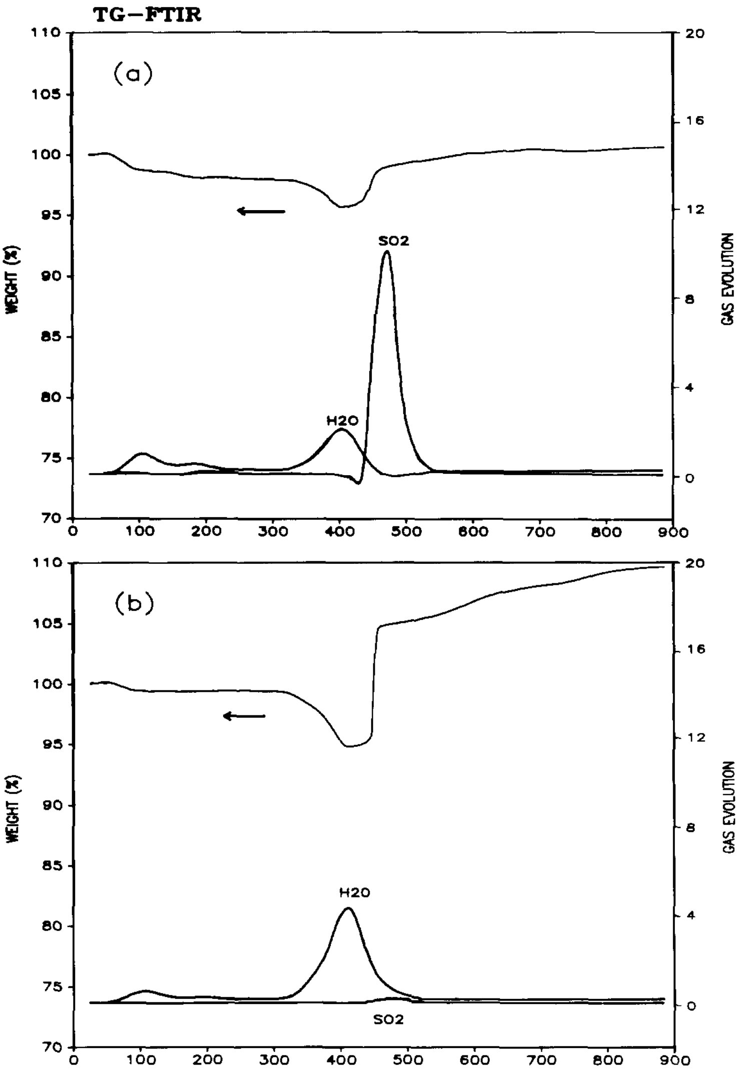

Fig. 6. TG diagrams for mixtures of arsenopyrite concentrate/CaO, in air, with Ca/S ratios of (a) 1, (b) 3, and corresponding FTIR gas evolution curves.

the previous mixture, except for the presence of excess unreacted CaO in the reaction product, and the absence of SO_2 in the exit gas.

The experiments were repeated in air for mixtures of arsenopyrite concentrate and CaO with Ca/S ratios of 1 and 3 (Fig. 6). Figure 6(a) (Ca/S ratio of 1) indicates that, under the same experimental conditions, the behaviour of the concentrate is similar to that of the mineral. The gradual weight gain starting at 400–450°C is due to the interaction between arsenopyrite and CaO according to reaction (3), and the simultaneous appearance of SO_2 in the exit gas suggests that the oxidation of arsenopyrite and pyrite (reactions (2) and (4)) also occurs at the same time. The XRD analysis of the product showed the presence of Fe_2O_3, $CaSO_4$ and $Ca_3(AsO_4)_2$ in addition to quartz and a minor amount of CaO. In the case of a mixture with a Ca/S ratio of 3 (Fig. 6(b)) an increase in the weight gain at 400–450°C is observed while almost no SO_2 appears in the exit gas. The reaction product contained the same components detected in the previous experiment, in addition to an excess of unreacted CaO. These latter results imply that nearly complete containment of arsenic and sulphur occurred when CaO additive was used at a Ca/S ratio of 3. The results also indicate that, in the presence of CaO, the formation of $Ca_3(AsO_4)_2$ by reaction (3) occurs in preference to the oxidation of arsenopyrite or pyrite.

CONCLUSIONS

The results of this study indicated that, in inert atmosphere, the decomposition of arsenopyrite in the presence of CaO occurs below 800°C (probably at 600–650°C) with the formation of CaS and FeAs in the solid phase and the release of arsenic and some sulphur, depending on the amount of CaO added. In an oxidizing atmosphere, arsenopyrite decomposes in the presence of CaO at the same temperature range with the formation of Fe_2O_3, $Ca_3(AsO_4)_2$ and $CaSO_4$. No iron arsenate was detected. With the appropriate amount of CaO additive, a nearly complete containment of arsenic and sulphur during the decomposition of arsenopyrite may be achieved. These findings could be valuable in the search for more environmentally sound processes for the roasting of arsenical gold ores, particularly in the light of the present study which indicated that it is the calcium additive, and not the iron, that complexes with arsenic and sulphur, leaving the roasted iron oxide amenable to the subsequent cyanidation process and the recovery of gold.

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