

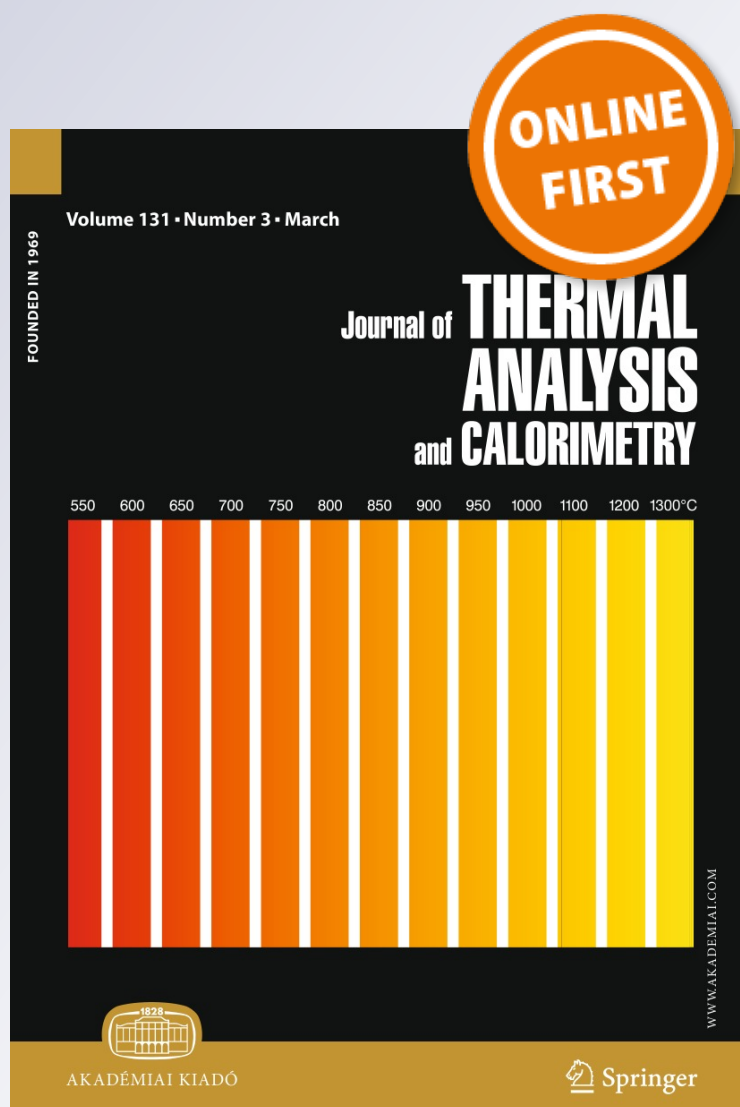
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Journal of Thermal Analysis and Calorimetry
An International Forum for Thermal Studies

ISSN 1388-6150

J Therm Anal Calorim
DOI 10.1007/s10973-018-7104-3



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Application of thermal analysis to the rhenium recovery process from copper and molybdenum sulphides minerals

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Received: 7 August 2017 / Accepted: 23 February 2018
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Abstract

Rhenium production from copper and molybdenum sulphides involves the use of a pyrometallurgical process. In traditional pyrometallurgy processes, gases emissions produce unacceptable air pollution and damage the extractive metallurgy equipment, leading to high production cost. Due to the environmental disadvantages presented by the oxidizing roasting, in this paper the carbothermal reduction process application on molybdenum–copper sulphides with Re, is studied as a possible alternative. The main purpose of the study is to concentrate the element (Re) applying non-traditional process, with low operating costs and good environmental response avoiding polluting gases such as SO₂. The concentrates were previously treated by an alkaline leaching process to remove impurities such as As, Se and Sb. These impurities are penalized and in addition they produce a calcine that is inefficient from an economic and a production point of view. The traditional production of Re involves Re oxide volatilization during the molybdenite processing, which is then condensed at low temperature to generate a dilute solution of a Re compound. The results show that Re was collected as metallic Re and in a form of a carbide compound avoiding Re₂O₇ volatilization and reducing total gases emissions in ≈ 36%.

Keywords Pyrometallurgical process · Copper · Carbothermal reduction · Thermal analysis · Rhenium

Introduction

Rhenium (Re) is present in nature in a very low concentration, the average content in the Earth's crust is around 10⁻⁷. It is contained in complex sulphides minerals of chalcopyrite (CuFeS₂) combined with molybdenite MoS₂. Re is one of the most interesting transition element due to its particular properties. It is useful mainly in the petroleum-reforming industry and in the production of special metal alloys such as: nickel base super alloys, refractory alloys, high-performance alloys (applied for example in aerospace application) [1–6]. In medicine, 186Re and 188Re radioisotopes are widely used in a pancreatic cancer

therapies that use the listeria bacteria as a vehicle. Thus, through the bacterium, it is possible to infect the tumour cells and eliminate them through radioisotopes [4]. The world's annual production is currently 5 ton, and rhenium reserves are estimated at 3500 t. It is mainly present in ores in the USA, Russia and Chile [5]. It is also used in electronic equipment and other fields [6]. At present, the rhenium market demands exceeds supply, so the recovery of rhenium from calcination exhaust has become very important.

Molybdenum concentrate, which is the main raw material of the production of molybdenum and molybdenum chemical product, requires to undergo oxidation roasting and desulphurization. During an oxidation roasting process, it emits MoS₂, MoO₃, MoO₂, SO₃, SO₂, dust and other harmful gases. The concentrate roasting process produces gases with certain amount of Re₂O₇ [6]. Also, copper and molybdenum sulphides processing requires pyrometallurgical process [3, 6]. Sulphide roasting is considered one of the main ways to extract copper from copper sulphide concentrates or polymetallic sulphides, obtained through a flotation stage. In traditional

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pyrometallurgical processes, gases emissions produce unacceptable air pollution and damage the extractive metallurgy equipment, leading to high production cost [7, 8]. Due to the environmental disadvantages of the pyrometallurgical processes used such as the oxidizing roasting, in this paper the separation of rhenium from molybdenite roasting dust by carbothermal reduction, an environmentally friendly alternative, is presented. The purpose of carbothermal reduction is to obtain a calcine with a high percentage of rhenium recovery, low operating costs and good environmental response, avoiding polluting gases such as SO_2 [9]. The calcine obtained from the carbothermal reduction is treated by an alkaline leaching process to remove the rhenium from impurities such as arsenic, selenium and antimony. These impurities are penalized, turning the calcine inefficient from an economic and a production point of view. It is relevant to mention that the roasting processing of molybdenite could produce the volatilization of rhenium oxide. This paper proposes the application of carbothermal reduction for the rhenium collection in the calcine, avoiding rhenium oxide emission to the atmosphere and obtaining a product of metallic Re as result. In order to increase the knowledge on the first stage of the process (oxidative roasting), it is relevant to study the reactions that occur in molybdenum–copper sulphides systems, in relation with temperature. The kinetics of reactions and emissions (such as SO_2) are studied by thermal analysis tests (DTA TG), performed at constant heating rate ($\beta = 10 \text{ }^\circ\text{C min}^{-1}$) on concentrates samples with different chemical compositions. The information is correlated with results from the concentrates samples characterization that include: chemical composition determination, phases identification through the application of microscopy techniques such as: optical microscopy, scanning electron microscopy (SEM with EDS analysis) and X-ray diffraction (XRD). The results obtained are correlated with the information acquired through a thermodynamic simulation of the systems considering three specific conditions, applying the equilibrium module of the software FactSage 7.1 [10]. On the base of the information obtained carbothermal reduction tests were carried out. Wang et al. [11] applied a similar methodology including DTA TG and FactSage simulation, to study the carbothermal reduction in titanium oxide. Aydinyan et al. [12] studied the mechanism of copper molybdate carbothermal reduction at non-isothermal conditions by carrying out simultaneous differential thermal (DTA) and thermal-gravimetric (TGA) analyses combined with X-ray diffraction (XRD) analysis of intermediate and final products.

Methodology

In this paper, concentrates samples of copper and molybdenum sulphides (with Re) are studied. They were obtained from different flotation processes, such as: rougher flotation and differential flotation (giving rise to different laws of the elements). The concentrates were subjected to the carbothermic reduction process in which the working parameters were determined. The capture values and the reducing agent were adjusted in order to retain the highest concentrations of sulphur. The temperature and time conditions were established to reach the highest recovery of the elements desired. Samples of molybdenum–copper sulphide concentrates with Re were treated by an alkaline leaching process to remove impurities such as As. The leaching agent is an acidic sodium sulphide in the presence of sodium hydroxide NaSH/NaOH. The sample with the highest content of Re was selected for the study and processed considering three different conditions:

- *Sample S1*: processed without CaO and C.
- *Sample S2*: processed with CaO (0.2) and C (0.5 g).
- *Sample T1*: processed with CaO (0.2) and C (0.5 g) and heated at $400 \text{ }^\circ\text{C}$ during 30 min.

Then samples S1, S2 and T1 were characterized. The chemical composition was determined by the correlation of the results obtained through different instrumental techniques. The crystalline phases identification was carried out by X-ray diffraction (using a Philips X 'Pert diffractometer and the software Match 3.0 for the post-processing of the obtained data). The structure of the concentrate particles was observed by optical microscopy (OM) using an Olympus GX51 microscope with a Leco IA 32 image analysis system and a Zeiss microscope with polarized light and differential interference contrast microscopy (DIC). The structural study includes the observation and chemical analysis carried out by scanning electron microscopy (SEM) including semi-quantitative analysis (EDS), with a field emission gun, FEI QUANTA 200. The thermal behaviour of the samples including the non-isothermal reduction process is determined by thermal analysis (DTA TG) using a SHIMADZU TA 60 instrument. The tests were performed up to $700 \text{ }^\circ\text{C}$, considering a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in air. The results are correlated with the thermodynamic simulation carried out by FactSage 7.1 [10]. The databases used are: FTmisc 7.1, FTOxCN 7.1, FToxid 7.1, FTsalt 7.1, FactPS 7.1.

Table 1 Chemical composition of the samples in wt %

Sample	Cu	Fe	Na	K	Mo	Mn	Ca	Mg	Re	S	As
S1	2.92	1.07	0.06	0.11	50.67	0.01	0.50	0.18	0.10	23.05	0.05
S2	1.39	1.95	0.06	0.11	51.07	0.01	6.04	0.18	0.10	26.04	0.05
T1	1.37	1.91	0.06	0.11	55.10	0.01	5.92	0.17	0.19	25.53	0.05

Results and discussion

The chemical composition of the samples is observed in Table 1. It is relevant to note that sample T1 treated with CaO (0.2) and C (0.5 g), at 400 °C during 30 min present the highest content of Re (0.19) and Mo (55.10 wt%). The Re content of the samples is consistent with the results reported by Juneja [13]. The crystalline phases present in the three samples were identified by X-ray diffraction, see Fig. 1a–c. The results show that the main crystalline phases determined in all the samples are: molybdenite (MoS_2) and chalcopyrite (CuFeS_2). Rhenium is present in all the

samples as oxide (ReO_3) and metallic Re. In sample T1, treated with CaO (0.2) and C (0.5 g) at 400 °C during 30 min, carbide (CFeORE_2) is also identified. The information obtained is consistent with the chemical composition of the samples.

The structural study, carried out by optical microscopy (OM) and scanning electron microscopy (SEM–EDS analysis), corroborates the presence of molybdenite and chalcopyrite particles in the samples, with irregular morphologies and the presence of different phases. In addition, isolated bright particles are also observed. In sample T1, the presence of carbon particles is identified. Figure 2a, b

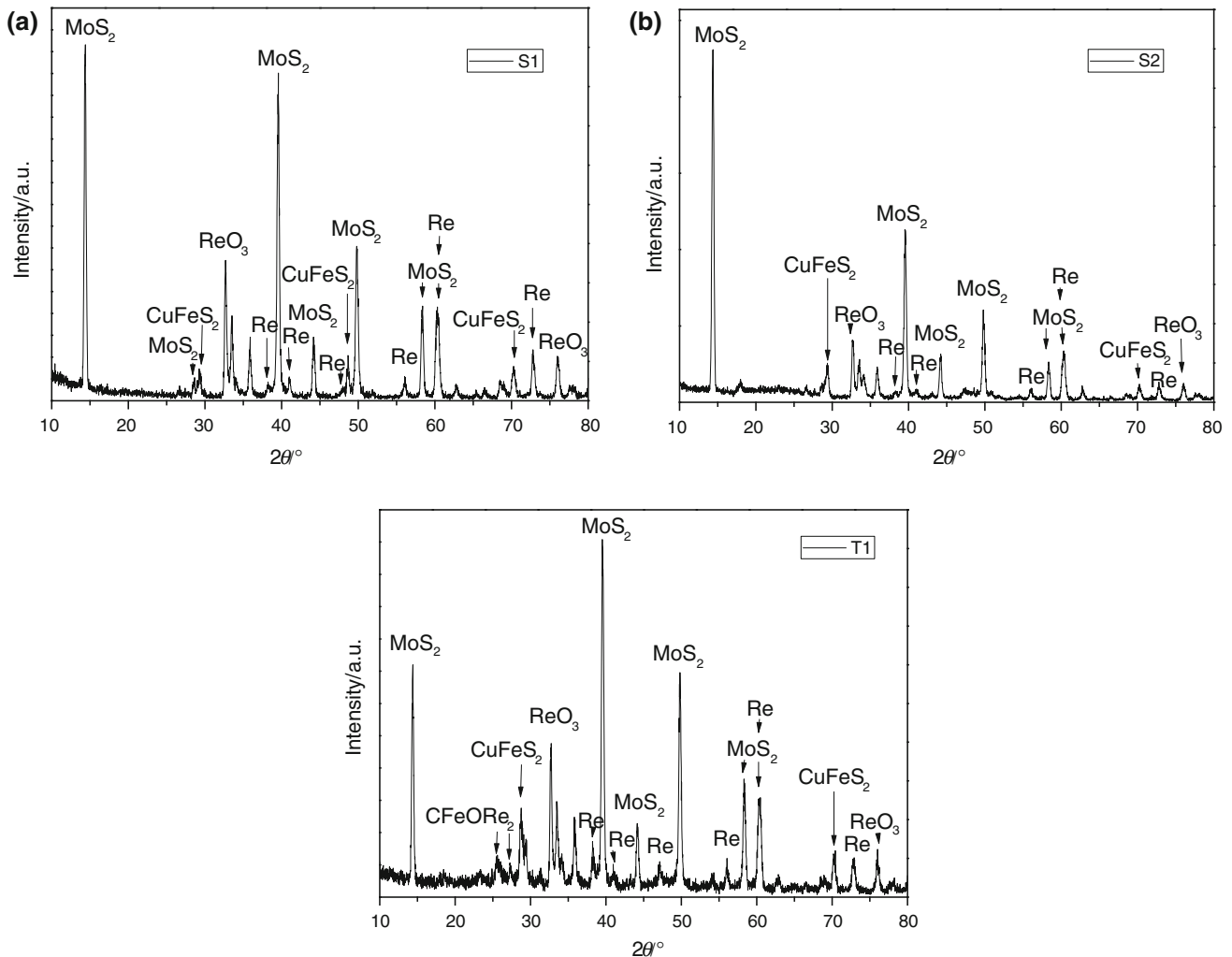


Fig. 1 Crystalline phases identified in samples. **a** S1, **b** S2, **c** T1

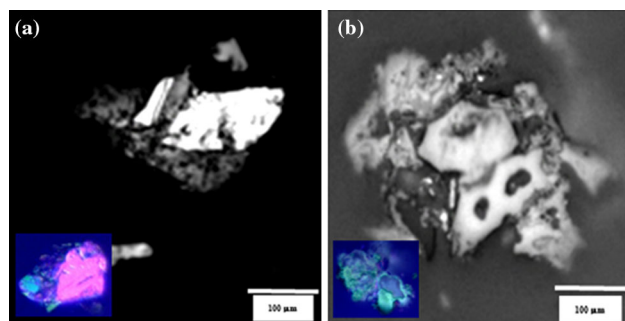
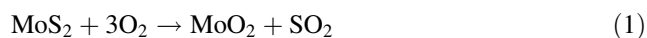


Fig. 2 Particles observed in the samples by optical microscopy (OM) and details of them observed using polarized light and differential interference contrast microscopy (DIC). **a** Irregular molybdenite (MoS_2) particle with different phases present. **b** Irregular particle of chalcopyrite (CuFeS_2) with different phases

shows the characteristics of the main particles and the colour obtained through polarized light and DIC observation.

The molybdenite (MoS_2) is visualized in magenta, and chalcopyrite (CuFeS_2) is visualized in green. Both phases are commonly associated with the presence of other minerals and element traces. By SEM and EDS analysis, the chemical composition of all the phases was determined. Also Re content was detected inside the particles combined with molybdenite (MoS_2) and chalcopyrite (CuFeS_2). The result of this paper related to the presence of Re in MoS_2 is in agreement with Drábek et al. [14]. Figure 3a–e shows the maps of the main elements: Mo, Cu, Fe and Re. Re is associated with the CuFeS_2 phase of the particle.

The thermo-gravimetric behaviour and the exothermicity of samples S1, S2 and T1 were determined through DTA TG tests up to 750 °C, see Fig. 4a–c. In the DTA TG curves of sample S1 (processed without CaO and C), it is possible to observe that at temperatures between 20 and 200 °C the sample is preheated and dried. At higher temperatures, the DTA curve shows an exothermic reaction (at $T_{p1} = 555$ °C) accompanied with a mass loss (in the TG curve) of $\Delta m = -11.6\%$, see Fig. 4a. The reaction was reported in [2] at a similar temperature and it is justified by a mechanism of molecular oxygen diffusion of the air, into the molybdenite (MoS_2) particles. The oxygen reacts with MoS_2 to form gradually the products: MoO_2 at ≈ 400 °C (Eq. 1), MoO_3 at ≈ 555 °C (Eq. 2) and also some sulphates. The information is consistent with results reported in [12]. Wang et al. [15] describe the reaction (1) as the most violent exothermic reaction that produce more than the 85% of the total heat released



The DTA curve of sample S2 [processed with CaO (0.2) and C (0.5 g)] presents three exothermic peaks:

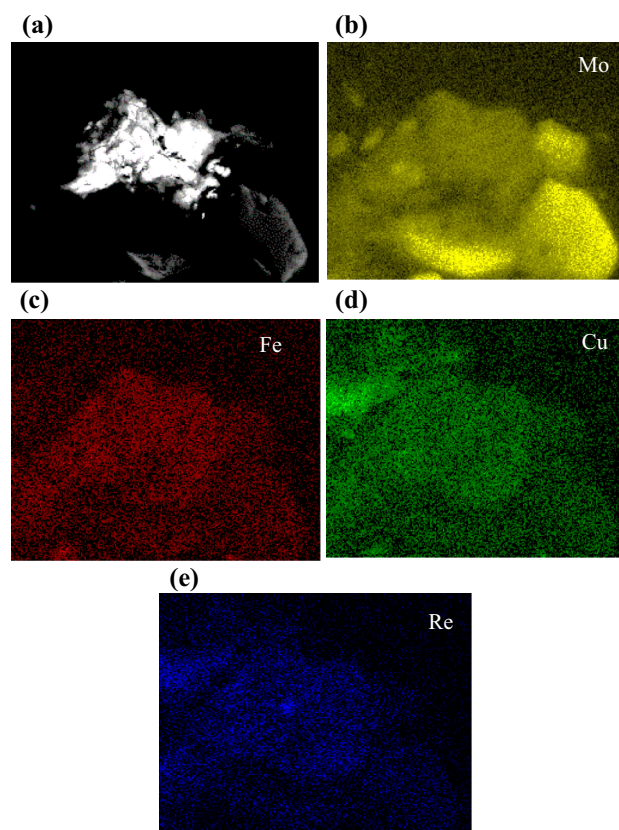


Fig. 3 Particle with molybdenite (MoS_2) and chalcopyrite CuFeS_2 that contains Re. The information is corroborated by the maps of the elements, **b** Mo, **c** Fe, **d** Cu, **e** Re, obtained by EDS

$T_{p1} = 484$ °C, $T_{p2} = 508$ °C and $T_{p3} = 609$ °C (Fig. 4b). The TG curve of the same sample shows in coincidence with the exothermic reactions associated with T_{p1} and T_{p2} , a mass loss $\Delta m = -13$ and $\Delta m = -17.5\%$, respectively. On the contrary, the exothermic reaction that occurs at T_{p3} present a gain of mass $\Delta m = +2.7\%$. It is noted that sample S2 presents a total mass loss up to $T = 508$ °C of $\Delta m_{\text{tot}} = -30.5\%$ resulting in higher emissions in comparison with sample S1, processed without CaO and C. According to [9], molybdenite oxidation reactions (Eqs. 1) and (2) are affected by oxygen concentration in the atmosphere and the action of surface atomic force of the particles. The DTA curve of sample S2 demonstrated that the contents of CaO and C also affect the reactions kinetics (corroborated by the displacement of the peaks to temperatures lower than the obtained for sample S1). The same behaviour was observed in the curves obtained for sample T1, also processed with CaO (0.2) and C (0.5 g). Nevertheless, the DTA curve of sample T1 (see, Fig. 4c) allows to note that the exothermicity of molybdenite oxidation reactions (Eqs. 1) and (2) is affected by heat treatment conditions at 400 °C, during 30 min. The thermogram indicates that the total mass loss up to 505 °C is

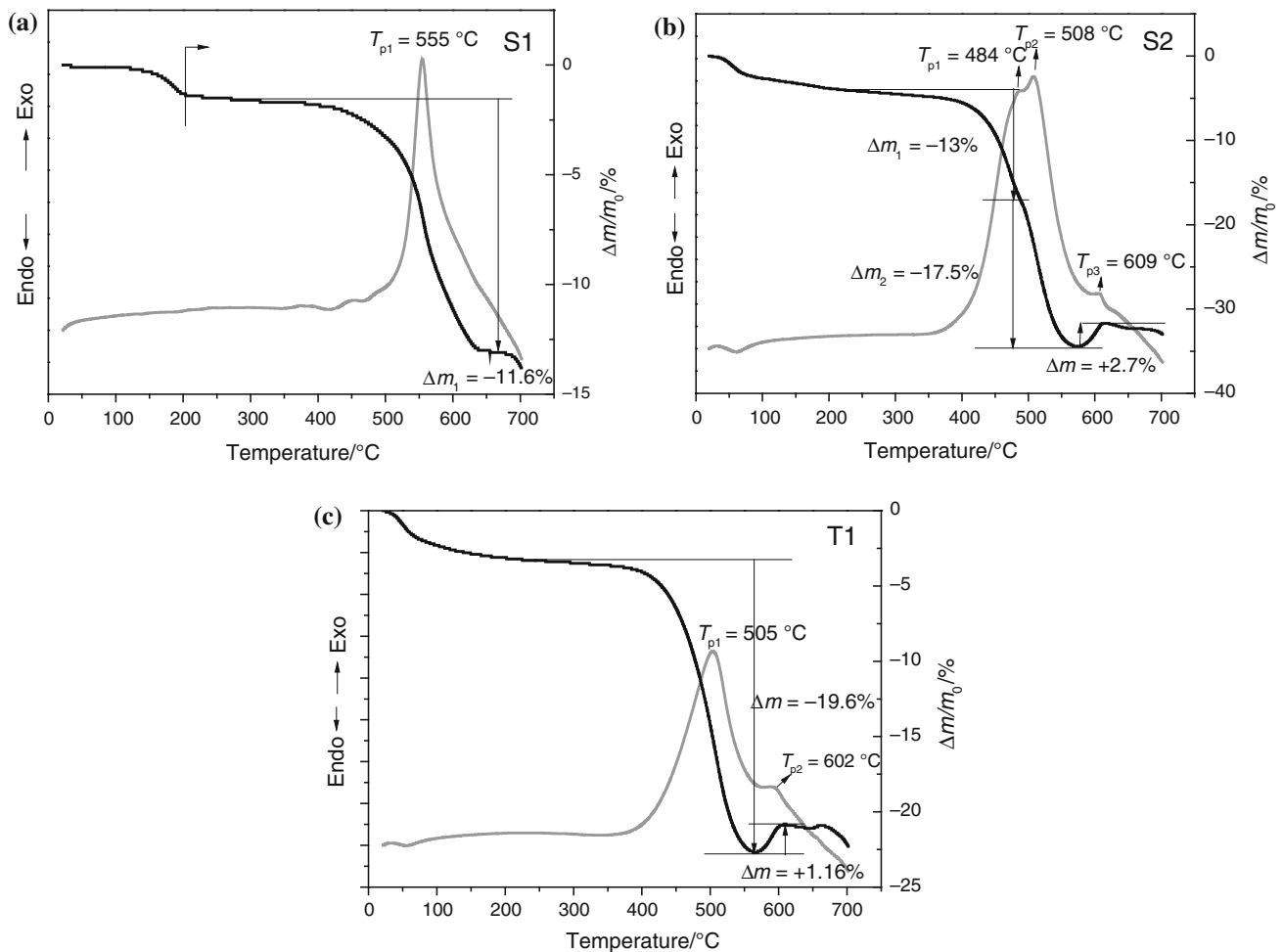


Fig. 4 DTA TG curves of samples, **a** S1, **b** S2, **c** T1

$\Delta m_{\text{tot}} = -19.6\%$ and it is noticeably reduced $\approx 36\%$, in comparison with sample S2. The data obtained from comparing TG curves of samples S1, S2 and T1 confirms that assertion, see Fig. 5.

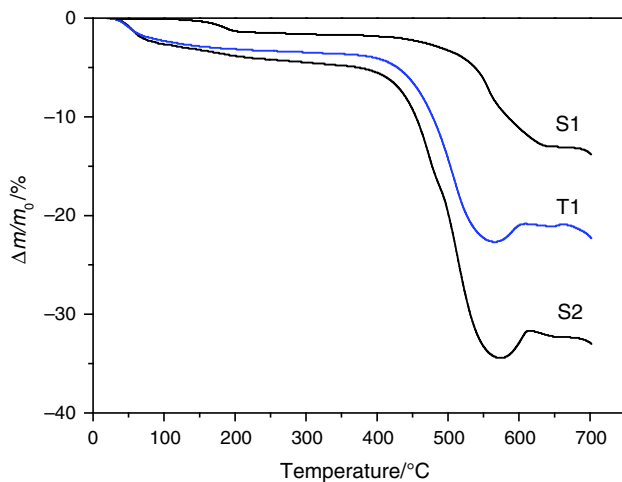


Fig. 5 Comparison between the TG curves of samples S1, S2 and T1

In coincidence with Wang et al. [11], in the systems involved in this study the carbothermal reduction is considered as a solid–solid reaction.

The thermodynamic behaviour of the three samples (S1, S2 and T1) was also determined applying the software FactSage 7.1, at temperatures up to 750 °C.

The simulation of S1 system carried out applying FactSage (Equilib module) predicts that the possible gas emissions (at $T > 400$ °C) could be: S, SO₂, different molybdenum oxides and Re₂O₇. It is relevant to mention that the FactSage (Equilib module) predicts a multicomponent gas phase for the systems considered. However, the diagrams obtained (by Diagram module) show the solid phases + gas, without details of the gas components. The solid reaction products include: Cu and Fe compounds. The analysis of diagrams CuFeS₂–O₂ (Fig. 6) and MoS₂–O₂ (Fig. 7) also brings information of the gas, liquid and solid phases present up to 750 °C [10, 16, 17]. It is important to comment that the group of modules that is the heart of FactSage can interact with databases in a variety of ways

Fig. 6 CuFeS₂–O₂ system with the Cu and Fe sulphides present at temperatures up to 750 °C

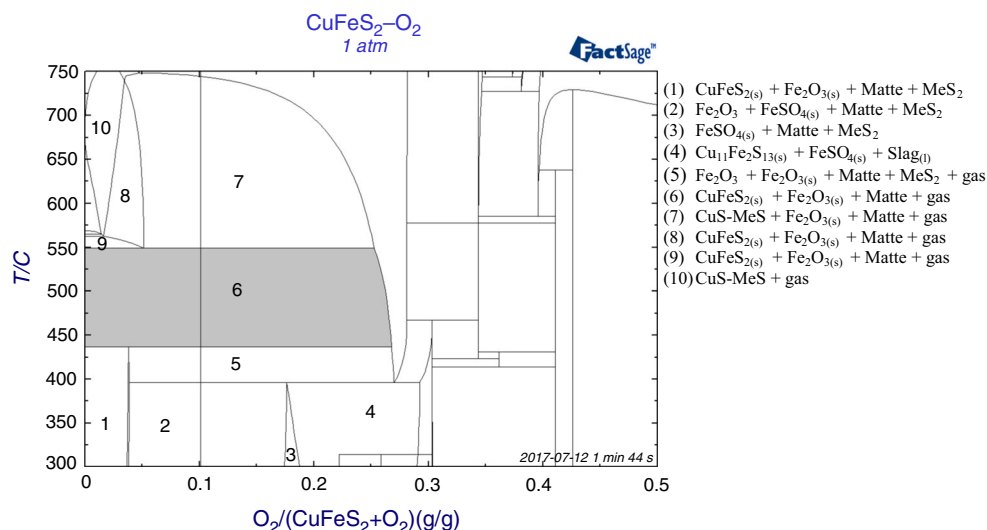
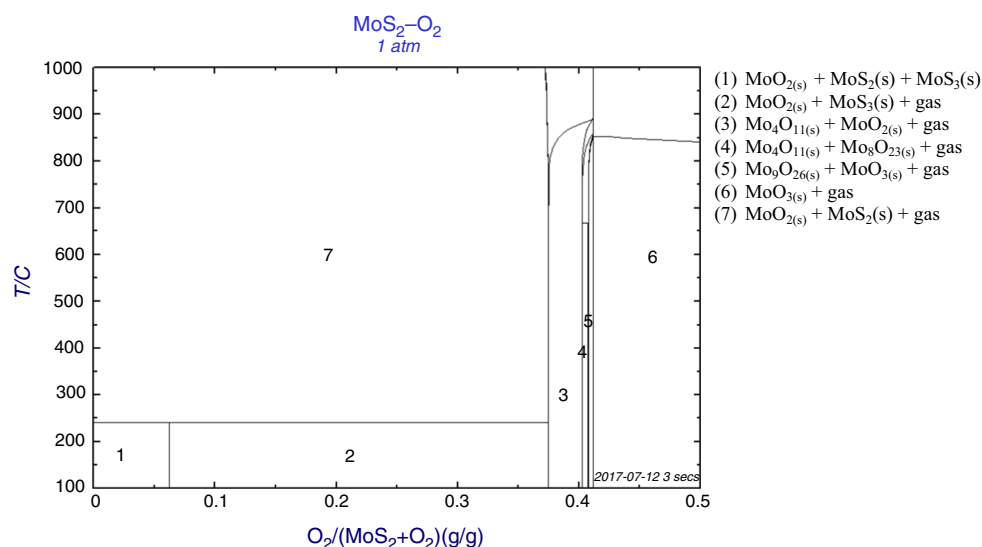


Fig. 7 MoS₂–O₂ system with the molybdenum compounds present at temperatures up to 750 °C



and calculate and display thermochemical equilibria and phase diagrams in a multitude of formats [10, 18].

As it is observed in the CuFeS₂–O₂ system, gas emissions are predicted by the reactions (5–10) between 400 and 750 °C. At the same conditions, the possible solid phases are: CuFeS_{2(s)}, MeS₂, Matte and Fe₂O_{3(s)}.

Considering the MoS₂–O₂ diagram (see Fig. 7), it is possible to observe that the molybdenum oxides gas emissions could be possible through the reactions (3)–(7) at the considered tests conditions.

The thermodynamic simulation of samples S2 and T1 (processed with CaO and C) at the same temperature conditions predicts solid phases consistent with the results obtained in the samples characterization. The phases for sample S1 are: (Ca, Mg)S, CuS–MeS, complex compounds of [Ca]/CO₃, SO₄, matte and Re in low percentage. At $T_{p3} = 609$ °C, the mass gain is probably associated with

the formation of matte or CuS–MeS, see reaction (6, 7) in Fig. 6.

On the base of the results obtained for sample T1, it is possible to design new process conditions for the copper and molybdenum sulphides concentrates applying the carbothermal reduction, in order to collect Re and to minimize environmental damage. Processing copper and molybdenum sulphides concentrates with CaO (0.2) and C (0.5 g), heated at 400 °C during 30 min, eliminates Re₂O₇ emission and allows to collect metallic Re and probably a carbide compound, identified by X-ray diffraction as CFeORE₂.

Conclusions

The study and characterization of copper and molybdenum sulphides require the integration of different instrumental techniques (DTA TG, X-ray diffraction and microscopy techniques) with thermodynamic simulation in order to determine chemical and mineralogical composition of the concentrate, the type and percentage of gases emissions and the solid phases generated at the carbothermal reduction conditions.

The carbothermal reduction applied to sample T1 (processed with CaO (0.2) and C (0.5 g) and heated at 400 °C during 30 min) eliminates the Re_2O_7 emission and allows to collect metallic Re and probably a Re and Fe carbide compound. In addition, the results show that the molybdenite oxidation reactions (Eqs. 1) (2) occur at lower temperatures in comparison with sample S1, with a decrease in the exothermicity of the reaction.

The thermodynamic simulation is today an important tool to enrich the understanding of the carbothermal reduction process and contributes to environmental studies through the multicomponent diagrams.

The information obtained is applicable to the extractive metallurgy processes of copper and molybdenum sulphides concentrates in order to achieve relevant economic benefits and decrease environmental damage.

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