

Thermal analysis of chalcopyrite roasting reactions¹

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Abstract

Roasting of chalcopyrite and of the binary copper and iron sulphides covellite, chalcocite, pyrrhotite and pyrite has been the subject of many investigations. The addition of salts to such reactions is of practical interest because it lowers the decomposition temperature and leads to water-leachable sulphates and chlorides.

The salt roasting of copper bearing sulphides is a very complex process involving numerous reaction steps which have not been adequately characterized.

The aim of the present investigations was to study the reaction mechanism of sulphide roasting in more detail. The combination of thermo-analytical methods (Mettler Thermosystem TA 4000) and X-ray diffraction (XRD) proved to be very useful for such studies. Mixtures with different ratios of CuFeS_2 (and also CuS and FeS_{1-x}) and NaCl , KCl or NH_4Cl were heated in an oxidizing atmosphere either continuously (heating rates from $0.2\text{--}10^\circ\text{C min}^{-1}$) or stepwise isothermally. Pure chalcopyrite starts to oxidize at about 400°C .

Addition of alkali chlorides to chalcopyrite lowers the temperature decomposition and oxidation quite drastically, especially in the case of NH_4Cl and KCl . A strongly exothermic reaction with corresponding weight increase had already begun at about 200°C . Slow heating rates throughout the decomposition region (not faster than $0.2^\circ\text{C min}^{-1}$), covered crucibles and addition of excess salt (preferably 4–5 moles of salt to 1 mole of chalcopyrite) are important for the completeness of the reaction in mixtures with NH_4Cl .

INTRODUCTION

Traditionally, the reduction of sulphidic copper ores is accomplished by pyrometallurgical techniques involving melting and oxidation to remove the major impurities. Environmental restrictions on SO_2 emission (2 t of SO_2 are formed in the pyrometallurgical processing of CuFeS_2 to 1 t of Cu) and the need to reduce energy consumption have led to the development of new techniques. These concern especially hydrometallurgical processes such as chlorination, salt and sulphate roasting, segregation roasting and heap leaching [1–3]. Practical application of such processes, however, still

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meets with some difficulties, such as the disposal of waste solutions and mill waste, the lack of experience with large scale plants, the sensitivity of the processes to the mineralogy of the ore and the loss of precious metals during the operation. However, hydrometallurgical processes have some important advantages, such as decreased emission of gases and dust, lower energy consumption, smaller and simpler processing plants and higher quality products [4,5].

This paper concentrates on the chloride roasting of chalcopyrite, CuFeS_2 . In a recent paper by Ngoc et al., the roasting of chalcopyrite with NaCl was discussed in some detail [6]. We performed similar investigations, which generally confirmed the results obtained by these authors. Of main interest to us was an extension of this study to other chlorides such as KCl and NH_4Cl . By means of thermoanalytical methods and X-ray investigations we have tried to find out more about the kinetics of the chloride roasting of chalcopyrite, the onset temperature of the reaction and the transient phases formed. The results obtained should contribute to establishing the optimum conditions for preferential leaching of copper from such roasted chloride-chalcopyrite mixtures.

EXPERIMENTAL

The mineral samples used were well-crystallized chalcopyrite (Hall, Austria), covellite (Bor, Yugoslavia) and pyrrhotite (Trepca, Yugoslavia). The monomineralic composition of each was checked by X-ray diffraction (XRD). For the experiments they were all finely ground in an attrition mill for 1 hour. The size fraction $< 20 \mu\text{m}$ was used mostly; coarser fractions had the effect of raising the reaction temperatures by about 50°C . The mixtures with the various salts (NH_4Cl , NaCl , KCl , all pro analysi) were prepared with addition of acetone for faster homogenization. Sample weights were in the range 30–150 mg for the thermoanalytical measurements. Larger samples (up to 2 g) were prepared for chemical analysis and further X-ray analysis. The salt roasting was performed with various mixture ratios, at various temperatures and for various times. When NH_4Cl is used, it is important to heat up very slowly (preferably $0.2^\circ\text{C min}^{-1}$ from 150°C) and to cover the crucible (or beaker) with a lid in order to avoid volatilization of the NH_4Cl before it has the possibility of reacting with the chalcopyrite. Mixtures of chalcopyrite with KCl or NaCl should be spread out flat to facilitate access of oxygen from the air. Such mixtures can be heated up rather fast to the reaction temperatures (250°C and 360°C respectively), but they should be held at this temperature for a minimum of 3 hours. The salt roasting reactions were performed in a drying oven (up to 270°C) and in an electric furnace (for the higher temperatures). After cooling to room temperature, all the reaction mixtures were leached with boiling water and filtered. The residues were washed thoroughly with hot

water and dried at 120°C. The leach liquors, containing predominantly Cu but also Fe in some cases, were subjected to chemical analysis by automatic titration (Mettler DL 70).

Identification of the various phases in the reacted mixtures and in the residues after leaching was made by X-ray powder techniques (Guinier de Wolff camera, Cu $K\alpha$ radiation). This proved to be quite difficult for some samples, because the various reaction products, e.g. CuCl_2 , $\text{Fe}_2(\text{SO}_4)_3$ and the double salts of NH_4 , Na or K, have a wide range of stoichiometries, are hygroscopic and some are unknown. The identification of the phases in the residues after leaching was less problematic. The Mettler thermoanalyzer TA1 was used for simultaneous TG and DTA, and in addition the Mettler TA 4000 especially for TG in a controlled atmosphere. The heating rates were varied from 0.2 to 4°C min⁻¹. Pt crucibles were used, and also thin walled alumina crucibles for the pure sulphides.

RESULTS AND DISCUSSION

Previous investigations of the oxidative decomposition of chalcopyrite during heating in air have been concerned with the effects of experimental conditions such as grinding (wet or dry), grain size, heating rate, isothermal treatment, atmosphere, bed depth, and dilution with inert powders [7,8]. There is general agreement that the final reaction products are CuSO_4 and Fe_2O_3 below 700°C and copper ferrite above 900°C (after the decomposition of CuSO_4 to CuO). Salt roasting of CuFeS_2 (mainly with NaCl) has also been investigated, because it lowers the decomposition temperature of chalcopyrite and leads to water soluble chlorides and sulphates [9]. However, there is still a need to identify and characterize the complex phases formed during such salt roasting reactions, and their stability and solubility. Some of these intermediate phases are not listed in the ASTM-card file and are of unknown composition. It is assumed that in the salt roasting of CuFeS_2 sulphation also takes place, in addition to chlorination. Which one of these reactions dominates depends on the type of salt, on the mixture ratio $\text{CuFeS}_2/\text{salt}$, and of course on the temperature of roasting. This was confirmed by the present investigations. The leach liquors from such salt roasted calcines are therefore rather complex and contain varying amounts of chlorides and sulphates of Cu and Fe, in combination with the cations of the salts (Na, K and NH_4).

The results of chloride roasting of chalcopyrite with KCl and NH_4Cl obtained so far are discussed below. For comparison, some investigations of roasting pure CuFeS_2 and $\text{CuFeS}_2/\text{NaCl}$ mixtures are also included.

Chalcopyrite

According to the literature, CuFeS_2 is decomposed during heating in air at first with liberation of sulphur, and secondly with sulphide oxidation

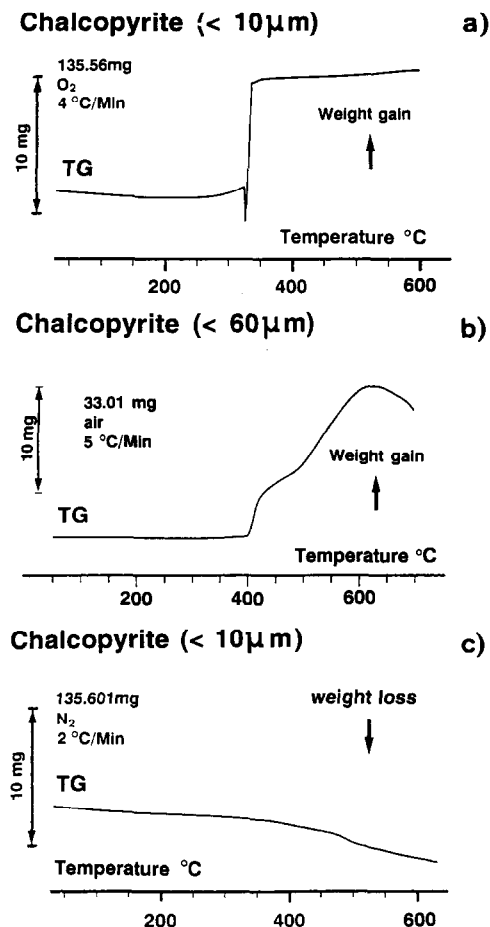


Fig. 1. TG curves of chalcopyrite: (a) heated in O₂; (b) heated in air (coarse fraction); (c) heated in N₂.

(above 350°C) [10]. Our investigations have shown that the initial decomposition, with volatilization of SO₂, is followed immediately by a strong weight increase in the temperature region 330–350°C for CuFeS₂ powders of < 10 μm and heating rates of 2 or 4°C min⁻¹ (Fig. 1a). Coarser grained chalcopyrite (< 60 μm) started to oxidize only above 400°C (Fig. 1b). In all cases, the reaction products were identical: only α -Fe₂O₃ and CuSO₄ were present in CuFeS₂ samples after heating in air above 450°C; above 600°C CuSO₄ decomposed to CuO, which reacted with Fe₂O₃ at still higher temperature to form CuFe₂O₄. When chalcopyrite was heated in nitrogen, practically no decomposition was observed up to 500°C. The TG curve (Fig. 1c) showed a very small weight loss (about 1% above 500°C), which may be assigned to the beginning of the decomposition of chalcopyrite. Pure CuS started to oxidize, mainly to CuSO₄ and to Cu₂(SO₄)O above 390°C, but also with partial oxidation of S²⁻ to SO₂.

TABLE 1
NH₄Cl roasting

Starting mixture	Conditions	Reaction products	Hot-water leach	
			Residue	Leach
1CuS/2NH ₄ Cl	air, 190°C, 2h	(NH ₄) ₂ CuCl ₄ ·4H ₂ O (NH ₄) ₂ Cu(SO ₄) ₂ ·6H ₂ O		
1FeS/2NH ₄ Cl	air, 190°C, 2h	No reaction		
1CuFeS ₂ /1NH ₄ Cl	air, 225°C, 2h	(NH ₄) ₂ CuCl ₄ ·2H ₂ O CuFeS ₂ Fe ₂ O ₃	CuFeS ₂ Fe ₂ O ₃	46% Cu
1CuFeS ₂ /2NH ₄ Cl	air, 225°C, 2h	(NH ₄) ₂ CuCl ₄ ·2H ₂ O (NH ₄)Fe(SO ₄) ₂ ·12H ₂ O	NH ₄ -jarosite	85% Cu
1CuFeS ₂ /3NH ₄ Cl	air, 225°C, 2h	(NH ₄) ₂ CuCl ₄ ·2H ₂ O (NH ₄)Fe(SO ₄) ₂ ·12H ₂ O	NH ₄ -jarosite	89% Cu
1CuFeS ₂ /3NH ₄ Cl	air, 210°C, 1h	CuFeS ₂ , CuS (NH ₄) ₂ CuCl ₄ ·2H ₂ O	CuFeS ₂ , CuS	
1CuFeS ₂ /3NH ₄ Cl	air, 210°C, 4h	(NH ₄) ₂ CuCl ₄ ·2H ₂ O (NH ₄)Fe(SO ₄) ₂ ·12H ₂ O	NH ₄ -jarosite	
1CuFeS ₂ /3NH ₄ Cl	air, 210°C, 8h	(NH ₄) ₂ CuCl ₄ ·2H ₂ O (NH ₄)Fe(SO ₄) ₂ ·12H ₂ O	NH ₄ -jarosite	

exothermic DTA peak corresponds to the oxidation sulphide → sulphate in the case of CuS. The reaction product is a mixture of (NH₄)₂Cu(SO₄)·6H₂O and (NH₄)₂CuCl₄·H₂O (owing to the hydration at room temperature). This reaction between CuS and NH₄Cl takes place at about 165°C, approximately 200°C lower than the oxidation of pure covellite.

The roasting reactions between chalcopyrite and NH₄Cl were studied in relation to the heating rate, temperature, holding time and mixture ratio. The results are summarized in Table 1. The reaction products were identified by X-ray methods. Chemical analysis for Cu and Fe was performed on the leached roasted mixtures. Whereas the cold water leach liquors contained high amounts of Fe in addition to Cu, the hot water leach contained very little Fe. This is due to the formation of NH₄-jarosite (NH₄Fe₃(OH)₆(SO₄)₂) at the higher temperatures, which takes up almost all the Fe and forms an insoluble precipitate.

Chalcopyrite-KCl

The chemistry of roasting in this system is also very complex and involves numerous reactions. The main reaction, the oxidation of sulphide to sulphate (and SO₂) with simultaneous formation of complex sulphates and chlorides, occurs at slightly higher temperatures than in the NH₄Cl roasting. The onset temperature of the reaction is about 220–240°C, still much lower than for CuFeS₂–NaCl mixtures (Fig. 4). The advantage of KCl over

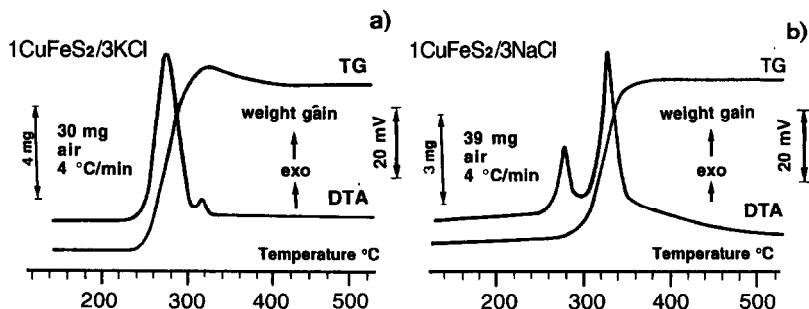


Fig. 4. TG/DTA curves of the reaction between chalcopyrite and (a) KCl and (b) NaCl.

NH_4Cl is that the former does not volatilize during heating up. Therefore, much faster heating rates can be used (typically $2\text{--}5^\circ\text{C min}^{-1}$) up to the reaction temperature. Holding time at this temperature is about 4 hours. The bed depth should be shallow to facilitate oxidation. At higher temperatures ($> 280^\circ\text{C}$), the complex Fe-sulphates and Cu-chlorides are decomposed with corresponding weight losses. The final reaction products were Fe_2O_3 , K_2SO_4 and $\text{K}_2\text{CuSO}_4\text{Cl}_2$. For unambiguous identification of chlorothionite, this compound was synthesized by a solid state reaction between $2\text{KCl} + 1\text{CuSO}_4$ at 650°C . Figure 5 compares the reaction behaviour of $1\text{CuFeS}_2 + 3\text{KCl}$ mixtures in oxygen and nitrogen atmospheres. Whereas no reaction occurred in nitrogen, a strong weight increase was found in oxygen above 230°C , with formation of $\text{KFe}(\text{SO}_4)_2$, $\text{K}_2\text{CuSO}_4\text{Cl}_2$ and K_2CuCl_4 . Results of KCl-chalcopyrite roasting in relation to the mixture ratio are summarized in Table 2.

The reactions of CuS and FeS with KCl have also been investigated. After heating up to 600°C in air, the reaction products were $\text{K}_2\text{CuSO}_4\text{Cl}_2$ and some K_2SO_4 , K-Fe sulphate and K_2SO_4 , respectively (Fig. 6). Leaching of the roasted $\text{CuFeS}_2\text{--KCl}$ mixtures showed similar results as for the NH_4Cl roasting. Here, Cu could also be leached preferentially with boiling water, owing to the precipitation of most of the Fe as insoluble potassium jarosite ($\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$). Cold water leaching showed high concentra-

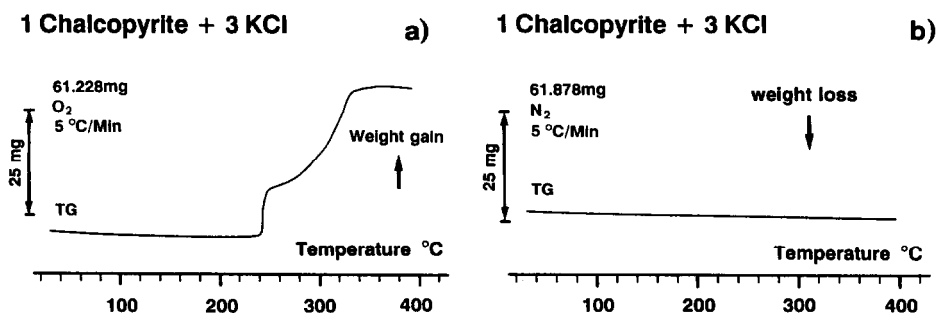


Fig. 5. TG curves of roasting chalcopyrite with KCl in (a) O_2 and (b) N_2 .

TABLE 2

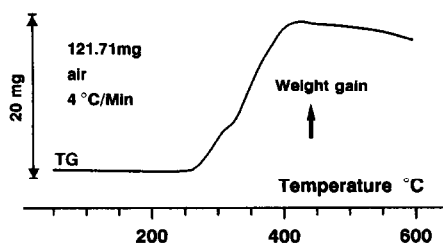
KCl roasting

Starting mixture	Conditions	Reaction products	Hot-water leach	
			Residue	Leach
1CuS/2KCl	air, 280°C	$K_2CuSO_4Cl_2$, K_2SO_4		
1FeS/2KCl	air, 330°C	KFe-sulphate (-chloride?) K_2SO_4		
1CuFeS ₂ /0.5KCl	320/370°C ^a	Fe ₂ O ₃ CuCl (?) $K_2Cu_2(SO_4)_3$ (?)	Fe ₂ O ₃	
1CuFeS ₂ /1KCl	290/360°C ^a	$K_2Cu(SO_4)_2$ (?) KFe(SO ₄) ₂ · xH ₂ O (x = 0–12)	K-jarosite Fe ₂ O ₃	
1CuFeS ₂ /2KCl	280/380°C ^a	$K_2CuSO_4Cl_2$ KFe(SO ₄) ₂ · xH ₂ O	K-jarosite	
1CuFeS ₂ /3KCl	270/390°C ^a	$K_2CuSO_4Cl_2$ KFe(SO ₄) ₂ · xH ₂ O K_2CuCl_4	K-jarosite	
1CuFeS ₂ /3KCl	1 h/310°C ^b	CuFeS ₂ , CuS $K_2Cu(SO_4)_2$ (?)	CuFeS ₂ , CuS	22.5% Cu
1CuFeS ₂ /3KCl	4 h/310°C ^b	KFe(SO ₄) ₂ · xH ₂ O $K_2CuSO_4Cl_2$	K-jarosite (Fe ₂ O ₃)	73.7% Cu
1CuFeS ₂ /3KCl	20 h/310°C ^b	KFe(SO ₄) ₂ · xH ₂ O $K_2CuSO_4Cl_2$ K_2CuCl_4	K-jarosite	86.8% Cu
1CuFeS ₂ /3KCl	O ₂ , 400°C	$K_2CuSO_4Cl_2$ K_2CuCl_4 , K_2SO_4 KFe(SO ₄) ₂ · xH ₂ O		
1CuFeS ₂ /3KCl	N ₂ , 400°C	No reaction		

^a Onset/final temperatures of reaction.^b Time/temperature.

tions of Fe in the leach liquor and no formation of K-jarosite. The thermal stability of K-jarosite was studied by TG/DTG. The final reaction products were identified as α -Fe₂O₃ and K₂SO₄ (Fig. 7.)

Covellite + 2 KCl



Pyrrhotite + 2 KCl

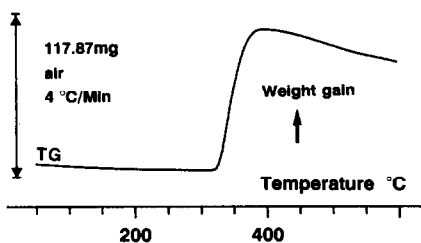


Fig. 6. TG curves of roasting covellite + 2KCl and pyrrhotite + 2KCl in air.

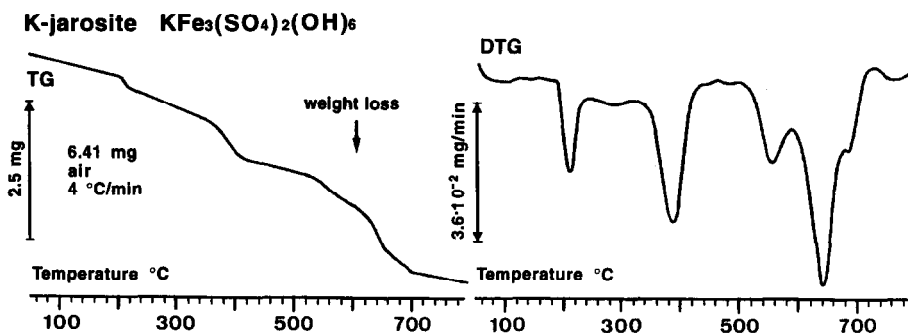


Fig. 7. TG/DTG curves of the decomposition of K-jarosite.

The different roasting behaviours of chalcopyrite with NH_4Cl , KCl and NaCl are compared in Fig. 8. For identical heating rates and mixture ratios, the thermal analysis (TG, DTA and DTG) proved that the reactions take place at temperatures increasing in the order $\text{NH}_4\text{Cl} < \text{KCl} < \text{NaCl}$. The reaction is almost spontaneous for KCl , slower for NH_4Cl and of variable rate for NaCl .

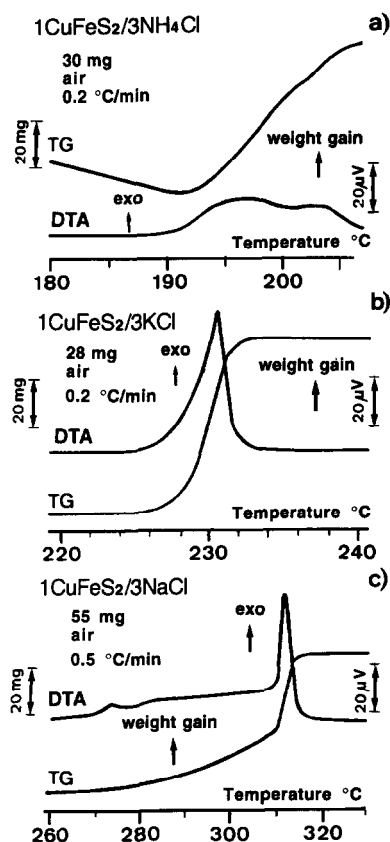


Fig. 8. TG/DTA curves of roasting chalcopyrite with (a) NH_4Cl , (b) KCl and (c) NaCl .

CONCLUSIONS

TG/DTA combined with XRD is useful for determining and optimizing the essential parameters in salt roasting reactions between alkali chlorides and chalcopyrite: mixture ratio, particle size, heating rate, maximum temperature, holding time, bed depth.

The roasting (reaction) temperature of CuFeS_2 is lowest with NH_4Cl (190–210°C), followed by KCl (220–240°C) and NaCl (290–320°C).

Volatilization of NH_4Cl during roasting can be minimized by high bed depth, covered crucibles, slow heating rate ($0.1^\circ\text{C min}^{-1}$) above 140°C, and a maximum temperature $< 210^\circ\text{C}$.

Mixtures of KCl-CuFeS_2 can be heated quickly (5°C min^{-1}) to the reaction temperature. Shallow bed depth is favourable for complete oxidation, with a holding time of 4 h at 240°C.

Reaction products from salt roasted CuFeS_2 are a mixture of partly unknown alkali-iron sulphates and alkali-copper sulphate-chlorides. The product depends on the type of chloride, on the mixture ratio and on the temperature.

Copper obviously has a stronger tendency to form chloride-containing phases, whereas Fe predominantly combines with SO_4^{2-} in the roasted mixtures.

Extraction of the roasted salt-chalcopyrite mixtures brings almost all of the Cu and Fe into solution. Boiling and leaching of the roasted mixtures with hot H_2O leads to the formation of insoluble NH_4^- or K-jarositcs, which take up most of the iron. The leach solutions contain all the Cu and very little Fe.

X-ray identification of some of the phases in the salt-roasted products is not possible because of their unknown compositions.

The salt-roasting reactions cannot be described by simple chemical equations, because a number of reactions take place simultaneously and/or sequentially.

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