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A low temperature chlorination–volatilization process for the treatment of chalcopyrite concentrates

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Abstract

Chlorination of two chalcopyrite concentrates with $Cl_2 + N_2$ was investigated under isothermal conditions in the temperature range of 20–750°C using boat experiments. The effects of gas flow rate, chlorine content of the gas mixture and residence time on the reaction rate were also investigated. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and chemical analysis are used for the physico-chemical characterization of the reaction products.

The chlorination of chalcopyrite concentrates started at room temperature generating chlorides of Cu, Pb, Zn, Fe, and S. The reaction of chlorine with sulfides is almost complete at about 300°C and the overall reaction is exothermic. At this temperature, the valuable metal chlorides were concentrated in the chlorination residues, while those of iron and sulfur were volatilized.

A flow sheet is proposed for the selective chlorination of chalcopyrite concentrates at low temperatures. Such flow sheet could be considered as an attractive route for the sulfide concentrates' treatment without SO_x emissions. It could be also regarded as energy saving with respect to the classical pyrometallurgical routes.

Keywords: Chalcopyrite; Chlorination–volatilization

1. Introduction

The kinetics of the chlorination of the chalcopyrite concentrates at temperatures up to 300°C, using thermogravimetric analysis (TGA), were studied by Kanari et al. [1]. At 300°C, this study shows that the chlorination of chalcopyrite concentrates was almost independent of temperature and reaction times few minutes were sufficient to achieve full chlorination of metal sulfides and volatilization of the sulfur and iron chlorinated-compounds. However, the kinetics study was performed using ≈50 mg of samples to minimize the effect of mass and heat transfer phenomena on the chlorination reaction.

At 300°C, increasing the mass of the sample or increasing the chlorine content of the gas mixture changes the kinetic data as shown in Fig. 1a–c. About 12 min were necessary to achieve full chlorination of sulfides and volatilization of S_xCl_y and $FeCl_3$ when

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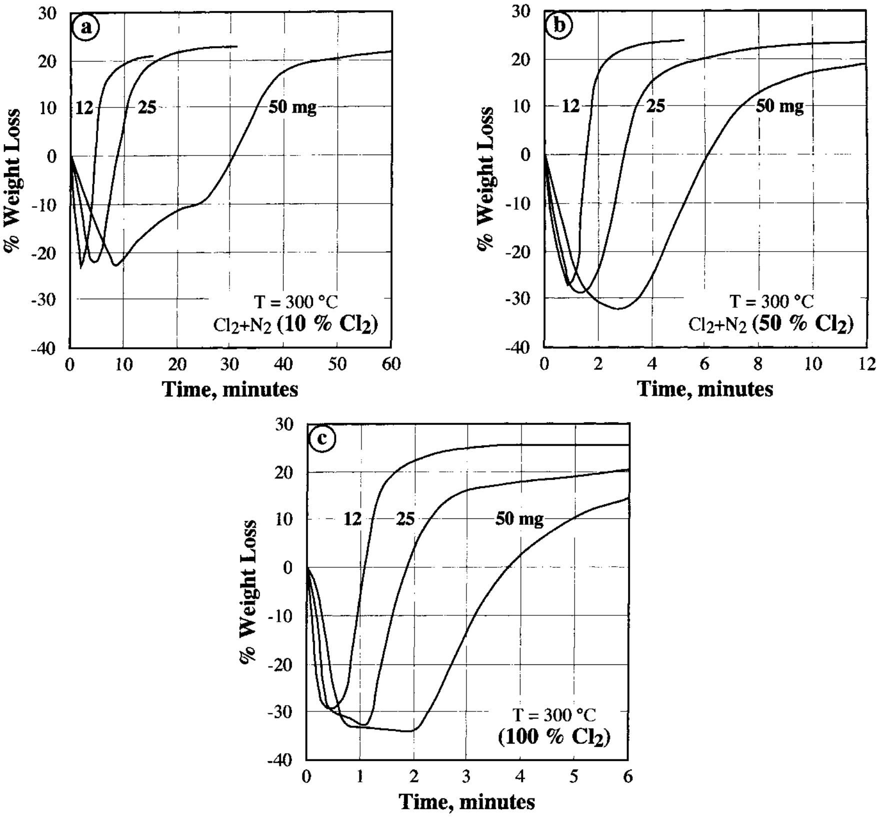


Fig. 1. Effect of the sample weight on the chlorination of a chalcopyrite concentrate at 300°C with (a) (10% Cl_2) + N_2, (b) (50% Cl_2) + N_2, (c) 100% Cl_2.

12 mg of the sample were chlorinated by a $Cl_2 + N_2$ gas mixture containing 10% Cl_2. While using a sample weight of 50 mg necessitates a reaction time of about 60 min to achieve full chlorination and volatilization of the reaction products. As it could be expected, the reaction time decreased with the increase of the chlorine content in the chlorinating gas mixture. Thus, about 3 min are sufficient to reach a complete reaction of the sample by chlorine alone when 12 mg of the sample were used (Fig. 1c). Results obtained suggested that a fluidized bed would be the best reactor from the chlorination kinetics point of view. Nevertheless, the partial fusion and softening of metal sulfides may occur during their chlorination due to the exothermic nature of these reactions. This will probably lead to the clogging of the fluidized bed.

On the other hand, thermal treatment of metal sulfides in inert atmosphere at temperatures higher or equal to 500°C will lead to the partial decomposition of chalcopyrite and pyrite to cubanite and pyrrhotite, respectively [2]. This will allow partial recovery of sulfur as S^0 and can be performed prior to the chlorination reaction. Moreover, use of high chlorination temperatures will lead to partial volatilization of valuable metal chlorides such as $CuCl_2$, CuCl, $ZnCl_2$, $PbCl_2$, beside S^0, $FeCl_3$, and S_xCl_y, thus decreasing the selectivity of the chlorination process.

For these reasons, the chlorination of several grams of the chalcopyrite concentrates was carried out from room temperature to 750°C using boat experiments. The results are discussed in terms of the effects of gas flow rate, temperature, chlorine content and reaction time on the chlorination rate of the chalcopyrite concentrates as well as on the selective volatilization and separation of valuable metals' chlorides from those of iron and sulfur.

2. Materials and experimental procedures

2.1. Materials

Two chalcopyrite concentrates as well as relatively pure $CuFeS_2$, ZnS, PbS, and FeS_2 were used for this investigation. Their physico-chemical characteristics were described in detail in [1]. The chemical and mineralogical compositions of two concentrates are grouped in Table 1. The main difference between these two concentrates are their contents of valuable metals (Cu, Pb, and Zn). The valuable metal content of the first sample was ≈11.6 pct and was called low-grade concentrate (LGC). The total valuable metal content of second sample was ≈36.5 pct and it was designated as high grade concentrate (HGC). The major sulfides of the LGC were $CuFeS_2$ and FeS_2. The LGC gangue is essentially composed of quartz and clinochlore. The HGC was rich in chalcopyrite (81.7 pct) and contained about 12% of lead and zinc compounds. HGC was almost gangue free.

Table 1
Chemical and mineralogical composition of the chalcopyrite concentrates (Wt pct)

Element	LGC	HGC	Phases	LGC	HGC
Cu	10.8	28.3	$CuFeS_2$	31.2	81.7
Fe	29.7	26.3	FeS_2	23.8	3.0
S	24.0	32.1	ZnS	1.2	6.4
Zn	0.8	4.3	$CaCO_3$	3.2	–
Pb	–	3.9	$PbSO_4$	–	5.7
Ca	1.3	–	MgO	1.9	–
Si	6.7	0.3	SiO_2	14.4	0.7
Al	2.1	–	FeO	11.8	–
Mg	1.2	–	Al_2O_3	4.0	–
O	14.5	1.6	Clinochlore[a]	ND	–
Total	91.1	96.8		91.5	97.5

[a] Clinochlore: $(Mg, Fe)_6(Si, Al)_4O_{10}(OH)_8$.

2.2. Experimental procedures

Test of the isothermal chlorination of chalcopyrite concentrates was carried out using the experimental set-up schematized in Fig. 2. This apparatus is composed of a gas-metering unit followed by a gas-purification system and a horizontal furnace. Several grams of sample were spread uniformly in a quartz boat (10 cm long, 1 cm wide and 1.5 cm deep). This boat with the metal sulfide sample is placed into the reactor and heated to the desired temperature in nitrogen atmosphere. Once the sample's temperature was attained, the nitrogen flow was turned off and the chosen chlorinating gas mixture was introduced in the reactor. At the end of experiments, the solid condensates were recovered from the reactor wall because of the natural temperature gradient. The composition of the chlorination reaction products was determined by scanning electron microscopy (SEM), X-ray diffraction (XRD), and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Few experiments were also performed using the TGA set-up described earlier [3] so as to record continuously the evolution of the sample weight.

As the boat used for the experimental tests was relatively long, attempts were made to measure the temperature profile of the sample. Thus, the temperature of the furnace was fixed at a desired value, between 200 and 600°C, and the temperature at the

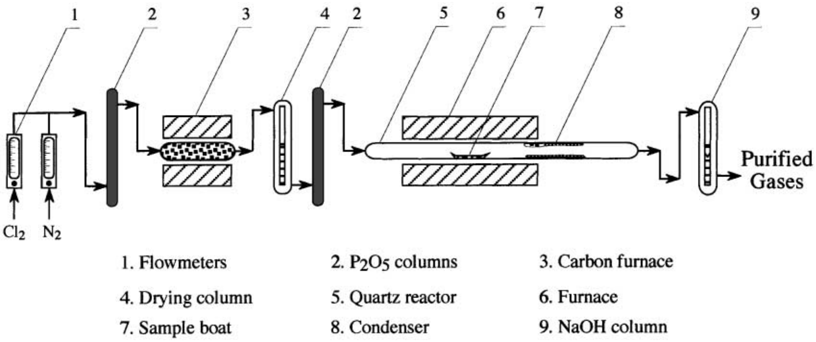


Fig. 2. Experimental set-up used for the chlorination.

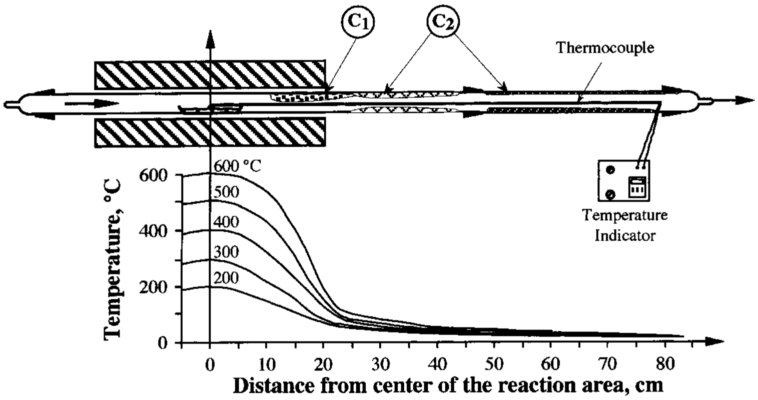


Fig. 3. Temperature profiles of the reaction area and the condensation zone of chlorides.

sample surface was recorded by setting a thermocouple inside the reactor. Similarly, the inner temperatures of the entire reactor and condenser were measured. The tests were carried out under nitrogen atmosphere. Fig. 3 represents the obtained results. It is obvious that the temperature of the sample was almost constant (±5°C) on the explored temperature range. This figure also shows the temperature profile of the condensation zone of chlorides and the location of the condensates (designated C_1 and C_2). At the end of experiments, these condensates were collected and examined by XRD, SEM, etc.

The sample's temperature was also measured during the chlorination at 300°C of LGC and HGC by $Cl_2 + N_2$ having different chlorine content in the gas mixture. These measures were performed to determine the temperature increase due to the exothermic nature of the chlorination reactions of metal sulfides. Results will be detailed in the following sections.

3. Results and discussion

3.1. Effect of the gas flow rate

Experimental tests to check the effect of the gas flow rate on the chlorination of two chalcopyrite concentrates were performed at 300°C using the $Cl_2 + N_2$ gas mixture with a Cl_2/N_2 molar ratio equal to 1. The reaction time was 1 h. Fig. 4 traces the percentage weight loss (PWL) of the used samples versus the gas flow rate. The chlorination extent of the

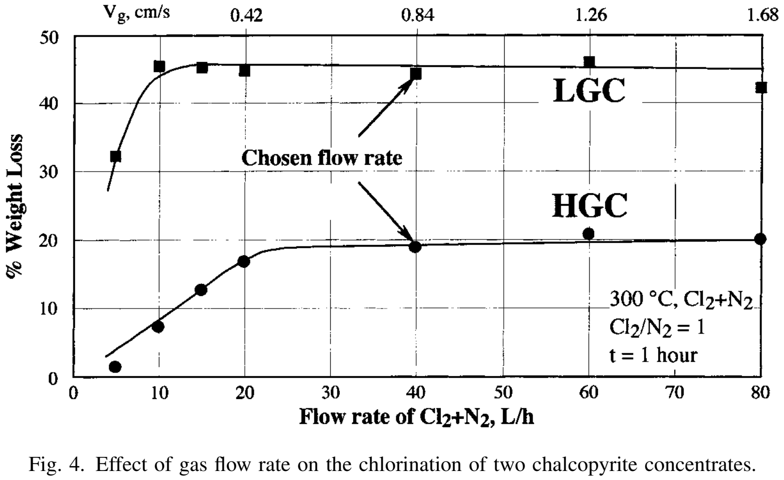


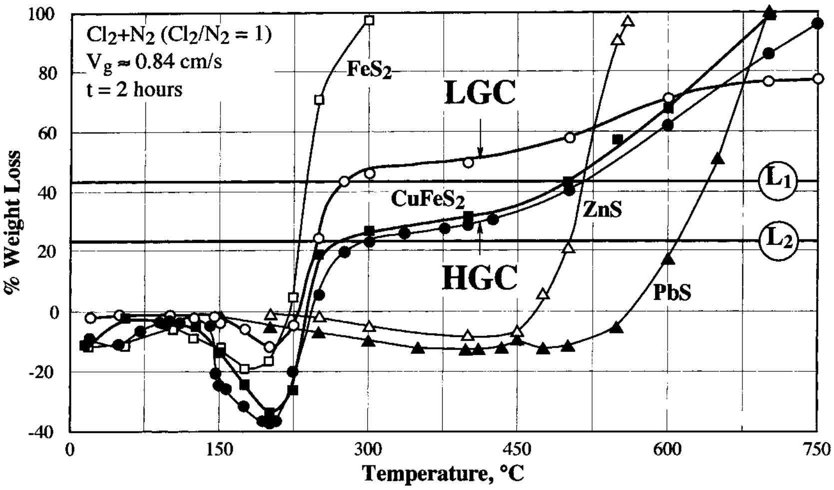
Fig. 4. Effect of gas flow rate on the chlorination of two chalcopyrite concentrates.

HGC seems to be more dependent on the gas flow rate than the LGC one. However, a flow rate higher than 20 l/h (gas velocity: 'V_g' ≈ 0.42 cm/s) will be adequate for the minimization of mass transfer phenomena. For this reason, a chlorinating gas mixture with a $V_g \approx 0.84$ cm/s (40 l/h) was used for the study of the chlorination of both concentrates at different temperatures.

3.2. Chlorination of sulfides at different temperatures during 2 h

An extensive series of isothermal chlorination tests were carried out between 20 and 750°C. The materials subjected to chlorination were LGC, HGC, $CuFeS_2$, FeS_2, ZnS, and PbS. A chlorinating gas mixture of $Cl_2 + N_2$ ($Cl_2/N_2 = 1$) was used and the reaction time was 2 h. Results are grouped in Fig. 5 as PWL versus temperature. Pyrite and chalcopyrite started to react at room temperature and a maximum weight gain was observed around 200°C. Full reaction and volatilization of the reaction products of the pyrite chlorination were achieved at 300°C. A plateau of weight loss was observed at about 350°C for the chalcopyrite chlorination followed by an increase of the PWL with temperature. The sulfides of zinc and lead reacted with chlorine at temperatures ≥150°C leading to their respective chlorides. However, complete reaction of ZnS was achieved at about 560°C while that of PbS exceeds 700°C. These observations related to the chlorination of metal sulfides suggest that full reaction and volatilization of products depend on the vapor pressure of the metal chlorides. As shown in Fig. 6 [4], the vapor pressure of chlorides of sulfur, iron, copper, zinc, and lead are different for a given temperature and the sequence of metal sulfides' chlorination follows that of the chlorides' volatilization. Cupric chloride is expected to decompose into cuprous chloride followed by its volatilization.

The behavior of HGC chlorination is close to that of chalcopyrite, whilst that of LGC is similar to that of pyrite in $Cl_2 + N_2$ up to 275°C, and chalcopyrite in $Cl_2 + N_2$ for higher temperatures. These similarities are consistent with the chemical composition of these concentrates (Table 1). Fig. 5 contains the calculated limits (expressed as PWL) for the selective chlorination of each concentrate and they were designed as L_1 and L_2 for LGC and HGC, respectively. They were defined assuming a full chlorination of sulfides and volatilization of iron and sulfur compounds. The validity of these limits will be discussed after the qualitative and quantitative analyses of the reaction products of the chlorination of LGC and HGC. However, these limits seem to be close to that of the



L_1 : % WL calculated for full chlorination of sulfides and volatilization of Fe and S chlorinated compounds for LGC,
L_2 : Idem for HGC.

Fig. 5. Effect of temperature on the chlorination of two concentrates and their main sulfides.

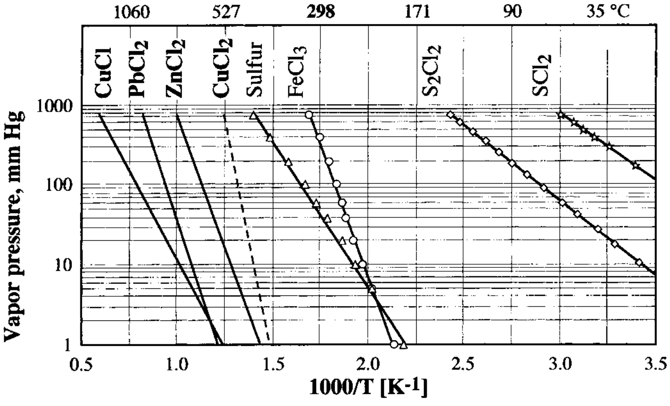


Fig. 6. Evolution of vapor pressure of several chlorides as a function of the temperature [4].

experimental PWL obtained for the two concentrates at 300°C.

The sample percentage weight loss obtained during the chlorination of sulfides using boat experiments is the algebraic sum of those due to the partial thermal decomposition of sulfides, the formation of chlorides and their volatilization. Prior to the chlorination, it was observed that the weight of the sample was decreased during its heating under nitrogen atmosphere at temperatures ≥475°C. This is due to the partial or complete thermal decomposition of chalcopyrite and pyrite [2] as described by Eqs. (1)–(3). Fig. 7 gives an example of the HGC treatment between 335 and 780°C. During the chlorination of the HGC, the initial weight gain of the sample decreases with increase of the chlorination temperature.

$$4CuFeS_2 \rightarrow 2CuFe_2S_3 + Cu_2S + S^0 \quad (1)$$

$$2CuFe_2S_3 + Cu_2S \rightarrow 0.8Cu_5FeS_4 + 3.2FeS + 0.6S^0 \quad (2)$$

$$7FeS_2 \rightarrow Fe_7S_8 + 6S^0 \quad (3)$$

The formation of eutectics of low melting points between different chlorides, such as CuCl–$FeCl_3$ [1], make the sulfides' chlorination a complex process. Another example is the chlorination of PbS. Lower chlorination extent of PbS was achieved at 450°C than at 400°C (Fig. 5). To clarify this phenomenon, two TGA tests of PbS chlorination using $Cl_2 + N_2$ were performed at 400 and 450°C and the results are given in Fig. 8. The initial

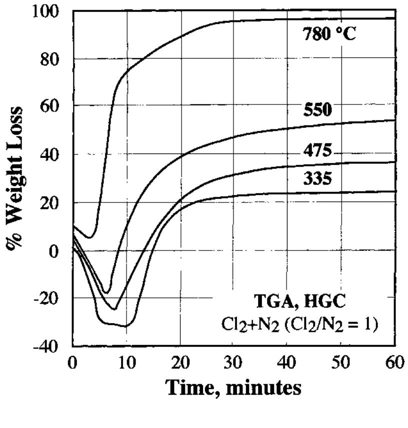


Fig. 7. TGA of HGC in $Cl_2 + N_2$ gas mixture between 335 and 780°C.

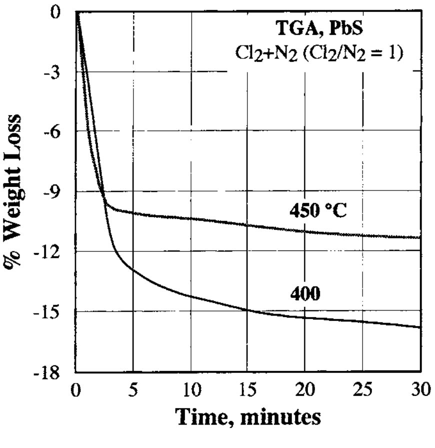


Fig. 8. TGA of PbS in $Cl_2 + N_2$ gas mixture at 400 and 450°C.

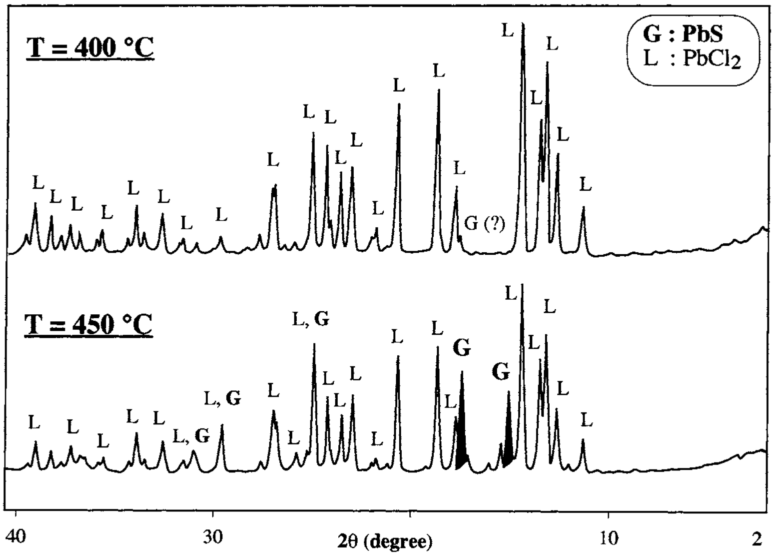


Fig. 9. Results of XRD analysis of the residues obtained during the treatment of PbS in $Cl_2 + N_2$ gas mixture at 400 and 450°C.

reaction rate of the PbS chlorination at 450°C is quite rapid and then the reaction seems to be stopped. While at 400°C, almost full chlorination of PbS was achieved. Results of XRD of the chlorination residues are reported in Fig. 9. Only $PbCl_2$ was identified in the residue of chlorination at 400°C, while PbS and $PbCl_2$ are present in the residue obtained at 450°C. Lower PbS chlorination extent at 450°C compared with that at 400°C could be explained by the presence of an eutectic at 450°C in the $PbCl_2$–PbS system, as shown by Fig. 10 [5]. The formation of this liquid phase leads to the constitution of a liquid layer that decreases the heat and mass transfer rates of the reaction of PbS with Cl_2 at 450°C.

3.3. Analysis of the reaction products of the concentrates' chlorination

Systematic SEM, XRD, and chemical analysis of the reaction products of the chlorination of the two concentrates at different temperatures were performed. Details of these analyses are available in [6]. An overview of the most representative results will be given in the following paragraphs.

3.3.1. SEM analysis

Several SEM spectra of the chlorination residues of LGC and HGC between 20 and 300°C are given in Fig. 11. The presence of chlorine in the LGC and HGC residues obtained at 20°C indicate that chlorine had reacted with the sulfides' concentrates. The peak intensity of sulfur decreased with temperature rise, while that of chlorine increased. At 300°C, SEM analysis shows that the residues obtained from both concentrates were sulfur-free indicating that full

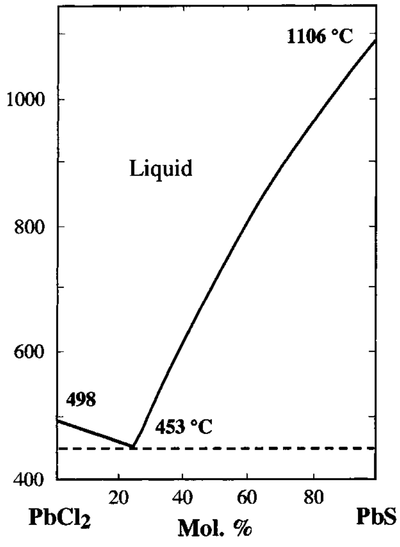


Fig. 10. Phase diagram of $PbCl_2$–PbS system [5].

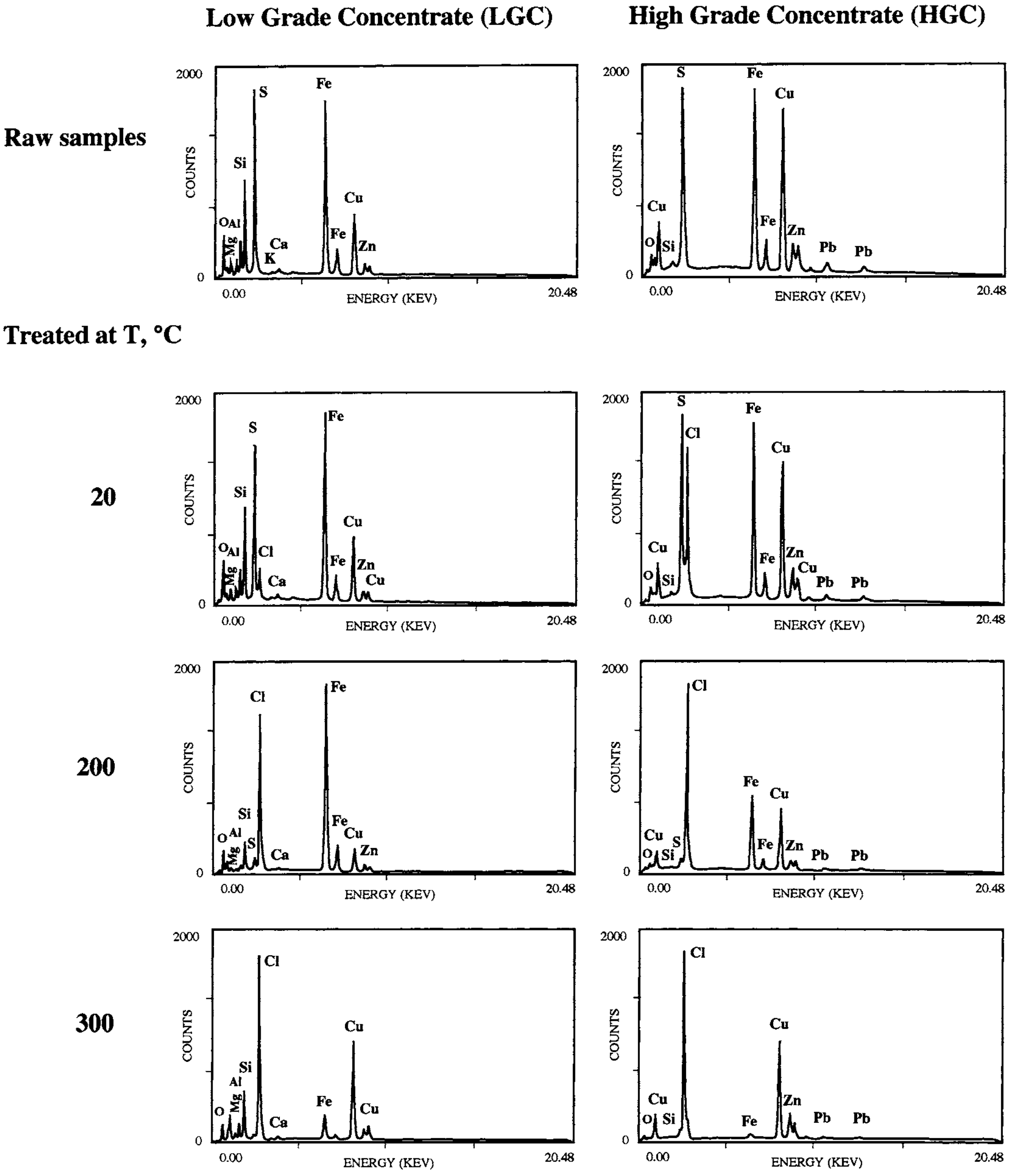


Fig. 11. Results of SEM analysis of the residues obtained during the chlorination of LGC and HGC between 20 and 300°C.

chlorination of the sulfides was achieved. On the other hand, the HGC residue obtained at 300°C was almost iron-free indicating that iron was volatilized as ferric chloride. However, iron was detected in the LGC residue at 300°C. This is probably due to the unreacted iron found in clinochlore: $(Mg, Fe)_6(Si, Al)_4O_{10}(OH)_8$.

Condensates of chlorination of both concentrates were observed at temperatures higher than 200°C. Fig. 12 shows spectra of some condensates obtained during the chlorination of LGC at temperatures of 250, 400, and 600°C. Similar spectra were obtained by the chlorination of HGC. Condensates were recovered at

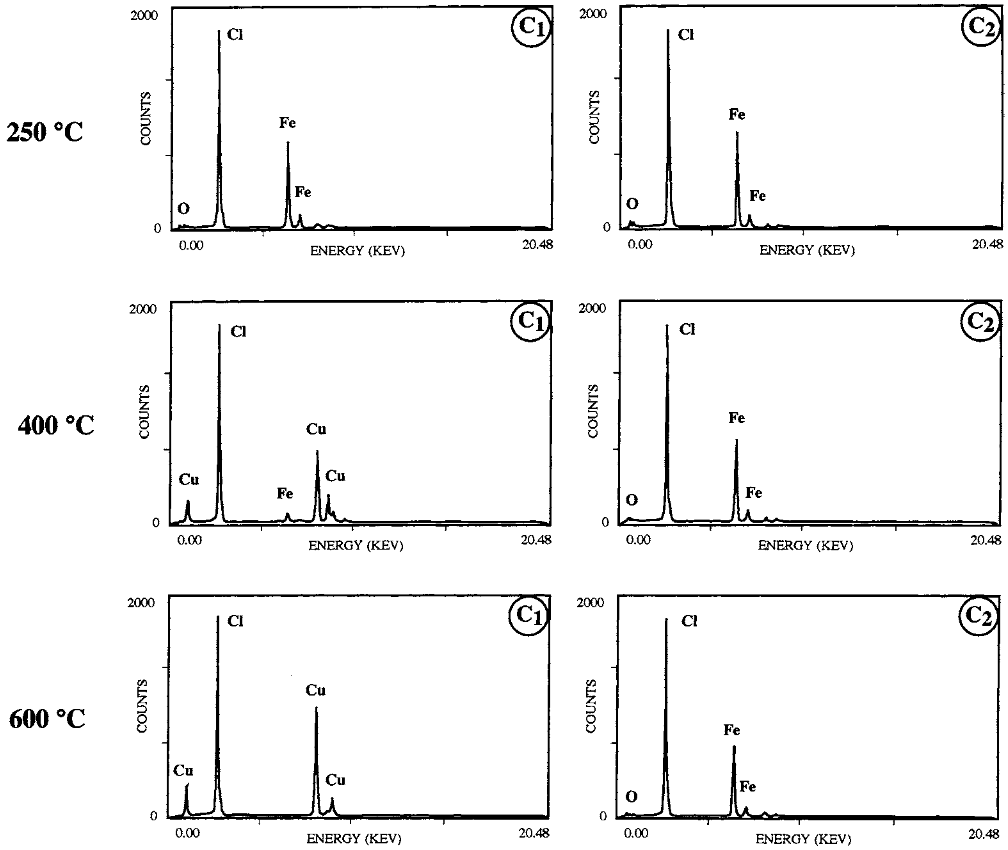


Fig. 12. Results of SEM analysis of the condensates obtained during the chlorination of LGC at different temperatures.

different condensation zone along the reactor (Fig. 3). These condensates were essentially composed of Fe and Cl for a chlorination temperature lower than 300°C confirming that iron was removed as $FeCl_3$ that is characterized by a vapor pressure of about 760 mmHg at temperatures close to 300°C. At temperatures equal and higher than 400°C, copper was also detected in the condensate (C_1), and it was almost iron-free. Best separation of copper chlorides from ferric chloride was achieved during the chlorination at 600°C. This selective separation of condensates (C_1 and C_2) was probably due to the natural temperature gradient of the condensation zone. Sulfur was not detected in the solid condensates regardless the chlorination temperature. This is probably due to the formation of as S_2Cl_2 and/or SCl_2 that have important vapor pressures at room temperature (Fig. 6). These gases are probably transported out by the outlet gases. The formation of sulfur chlorides is probably due to the high partial pressure of chlorine in the chlorination process. One may underline that the melting and boiling points of S_2Cl_2 and SCl_2 are −80 and 137°C and −78 and 59°C, respectively.

3.3.2. XRD analysis

All residues of the LGC and HGC chlorination at temperatures ranging from 20 to 700°C were subjected to XRD analysis. Fig. 13 represents the diffractograms of some residues of LGC chlorination between 50 and 500°C. They confirm the decrease of $CuFeS_2$ and FeS_2 peaks' intensity and increase of those of $CuCl_2$. Cupric chloride was identified as a mixture of $CuCl_2$ and $CuCl_2{\cdot}2H_2O$ due to the hygroscopic nature of $CuCl_2$. Ferric chloride was not revealed by XRD analysis, but its presence in the chlorination residues at lower temperatures was confirmed earlier by TG

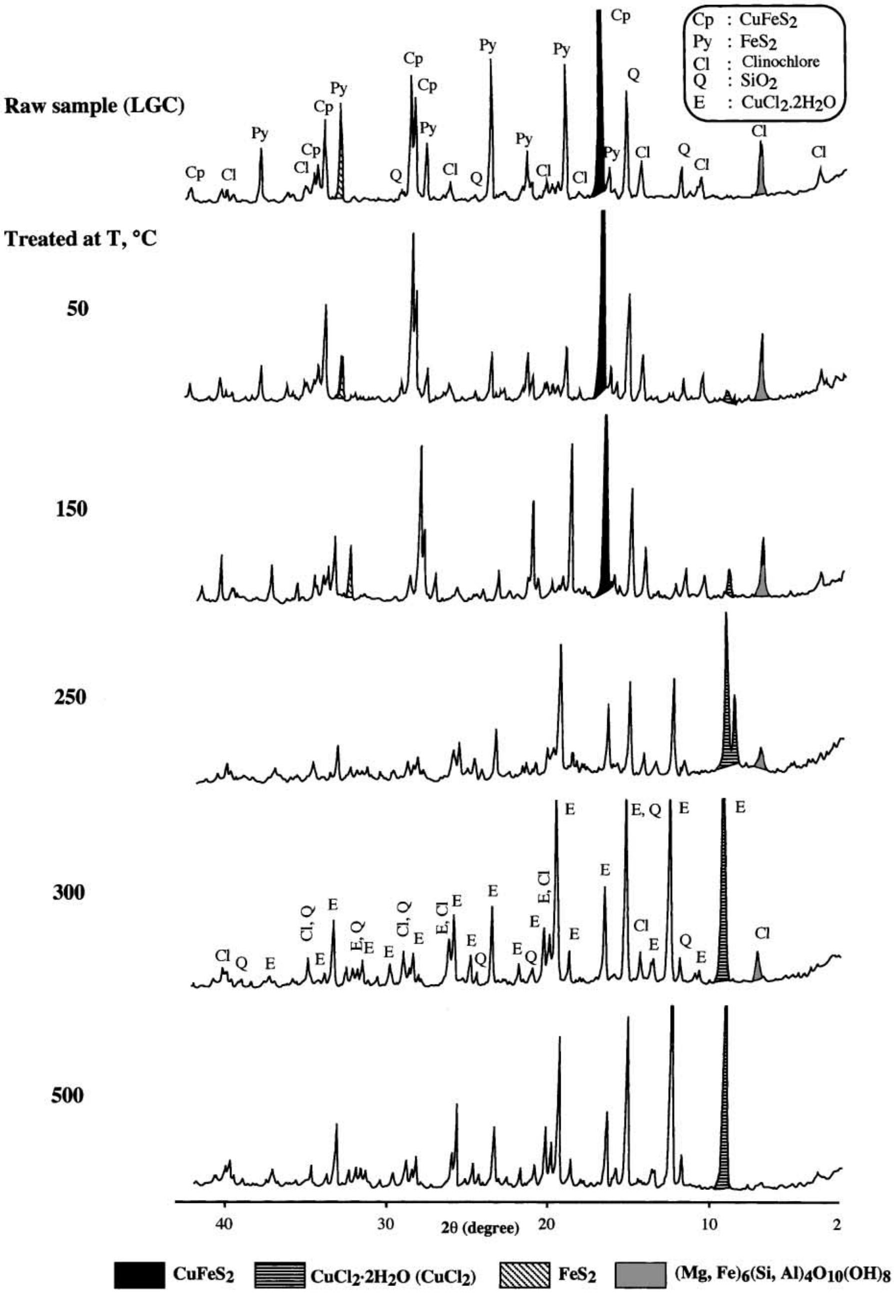


Fig. 13. Results of XRD analysis of the LGC chlorination residues obtained at different temperatures.

analysis [1]. No sulfides were detected in the chlorination residue obtained at 300°C. Clinochlore was decomposed at temperatures closer to 500°C. However, the decomposition products were not identified.

Fig. 14 gives similar results concerning the HGC residues' chlorination. Chlorination residue at 300°C was essentially composed of copper, lead, and zinc chlorides. However, $ZnCl_2$ was not detected by XRD

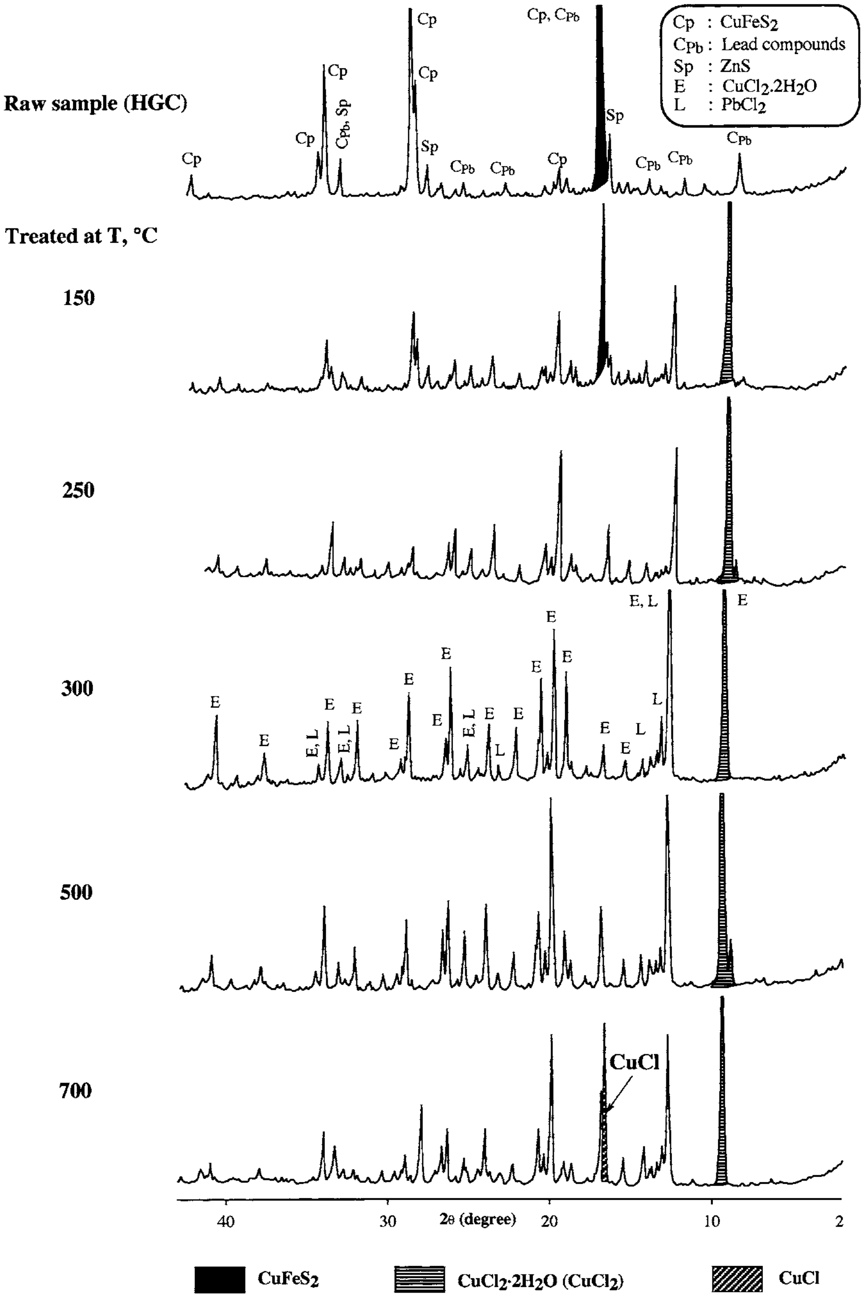


Fig. 14. Results of XRD analysis of the HGC chlorination residues obtained at different temperatures.

analysis because of its amorphous nature. The presence of CuCl besides $CuCl_2$ at high temperatures was confirmed by XRD. Although the decomposition of $CuCl_2$ into CuCl occurs at about 537°C [7], its partial decomposition is due to the high partial pressure of chlorine in the chlorinating gas mixture.

A summary of the phases identified by XRD analysis in the residues obtained at different chlorination temperatures for LGC and HGC is given in Tables 2 and 3, respectively. As shown by Table 2, the chlorination residue of LGC at 300°C is composed of $CuCl_2$, clinochlore and quartz. High temperature chlorination of LGC allows the decomposition of clinochlore and $CuCl_2$. Similarly, the HGC residue obtained at 300°C is sulfide-free (Table 3) and contains mainly the chlorides of valuable metals.

Although the condensates were subjected to XRD analysis, the identification of the different phases was impossible due to their amorphous character. However, the presence of iron in the condensates at lower temperatures suggests that it was volatilized as $FeCl_3$ since the boiling point of $FeCl_2$ is 1026°C [4]. Copper is probably removed partially as $CuCl_2$ at lower temperatures and as $CuCl_2 + Cu_3Cl_3$ [7] at higher temperatures.

3.3.3. Chemical analysis

In our experimental conditions, results of SEM and XRD indicate that full chlorination of sulfides contained in both concentrates and volatilization of sulfur and iron chlorinated-compounds was achieved at about 300°C. To check this hypothesis, iron and copper contents of the chlorination residues were determined by chemical analysis.

Fig. 15 is a data compilation of the chlorination of LGC between 20 and 600°C. Iron extraction was started at 200°C and was incomplete at 300°C. This is probably due to the presence of iron in the clinochlore. Full extraction of iron could be achieved with the decomposition of clinochlore at temperatures higher than 500°C. Copper extraction became significant at temperatures higher than 400°C and about 75 pct of copper were extracted at 600°C. The PWL curve traced in Fig. 15 for the LGC chlorination is in good agreement with the extraction extents of iron starting from 200°C and of copper from about 350°C. On the other hand, the calculated limit (L_1) for selective chlorination of LGC is fairly consistent with the PWL of the LGC sample and with the results of chemical analysis of the residue obtained at 300°C.

Results of chemical analysis concerning the extraction of iron and copper during the chlorination of HGC up to 600°C are illustrated in Fig. 16. Almost complete iron extraction was achieved at 300°C. This is because the iron of HGC is present as sulfides. The selective chlorination limit (L_2) is consistent with the value of the obtained PWL and the extraction extent of iron obtained at 300°C. The copper extraction started at higher temperatures than in the case of LGC and about 40 pct of copper were extracted at 600°C. This is probably due to the fact that the HGC residues were systematically agglomerated whilst those of LGC are less affected by this phenomenon. The presence of inert compounds in LGC, such as SiO_2, prevented the agglomeration of the residues.

The agglomeration of the chlorination residues of HGC was probably caused by the increase of temperature thanks to the exothermic nature of the sulfides' chlorination reactions. To confirm this hypothesis, a series of isothermal chlorination tests at 300°C using 2 g of LGC and HGC samples was performed. A gas mixture of $Cl_2 + N_2$ with different chlorine contents and with a $V_g \approx 0.84$ cm/s was used. Fig. 17a and b plot the temperature increases of LGC and HGC, respectively, during their chlorination under the above-mentioned conditions. As could be expected, the sample temperature augmented with the increase of chlorine content in the gas mixture. In addition, the increase of temperature for HGC is higher than that of the LGC. This is supported by the fact that the HGC sulfides' content is higher than that of LGC one.

As shown by Fig. 17, the increase of temperature was observed at the beginning of the chlorination reactions. This may be explained by a rapid exothermic reaction of chlorine with sulfides followed by an endothermic volatilization of species such as S_xCl_y and $FeCl_3$. On the other hand, the chlorides formed at the surface of the sample covered the unreacted part of the sample thus forming a diffusion barrier. This will lead to a lower reaction rate due to difficulties of chlorine to diffuse through the chlorides' layer.

3.4. Effect of reaction time and gas composition on the chlorination of LGC and HGC

As mentioned in the preceding sections, the chlorination of both concentrates was achieved for a reaction time of 2 h at 300°C using an equimolar $Cl_2 + N_2$ gas mixtures with a total gas flow rate of 40 l/h. It is interesting to check the effect of the reaction time and that of chlorine content, gas flow rate on the complete

Table 2
Phases identified by XRD in the LGC chlorination residues between 20 and 700°C[a]

Phases	Raw	20°C	50	100	150	200	250	300	400	500	600	700°C
$CuFeS_2$	■	■	■	■	■	■	▒					
$CuCl_2$		■	■	■	■	■	■	■	■	■	■	▒
CuCl											▒	■
FeS_2	■	■	■	■	■	■	▒					
$FeCl_3$[b]		▒	▒	▒	▒	▒	▒					
Clinochlore	■	■	■	■	■	■	■	■	■			
SiO_2	■	■	■	■	■	■	■	■	■	■	■	■

[a] ■: identified phase; ▒: probable phase.

[b] Confirmed by TGA and SEM.

Table 3
Phases identified by XRD in the HGC chlorination residues between 20 and 700°C

Phases	Raw	20°C	50	100	150	200	250	300	400	500	600	700°C
$CuFeS_2$	■	■	■	■	■	■	▨					
$CuCl_2$		■	■	■	■	■	■	■	■	■	■	■
CuCl											■	■
FeS_2[a]	■	■	■	■	■	■						
$FeCl_3$[b]		▨	▨	▨	▨	▨	▨					
Pb compounds[c]	■	■	■	■	■							
$PbCl_2$					■	■	■	■	■	■	■	■
ZnS	■	■	■	■	■	■						
$ZnCl_2$							▨	▨	▨	▨	▨	▨

[a] HGC pyrite content is low.

[b] Confirmed by TGA.

[c] $PbSO_4$, $Pb(Cu)_3(SO_4)_2(OH)_6$, and PbS.

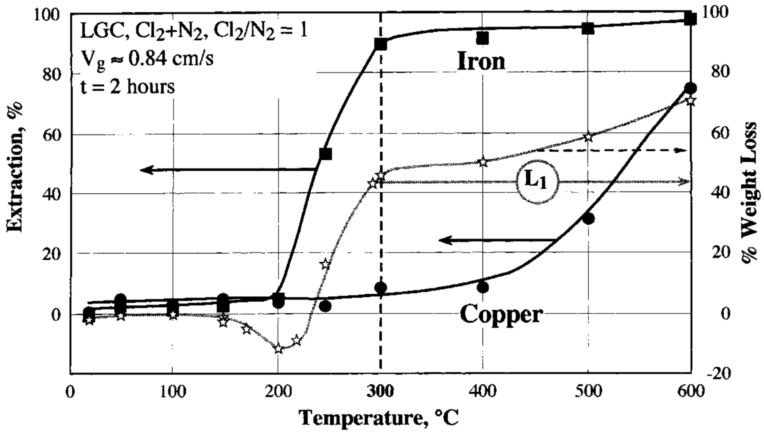


Fig. 15. Extraction of copper and iron from LGC during its chlorination at different temperatures.

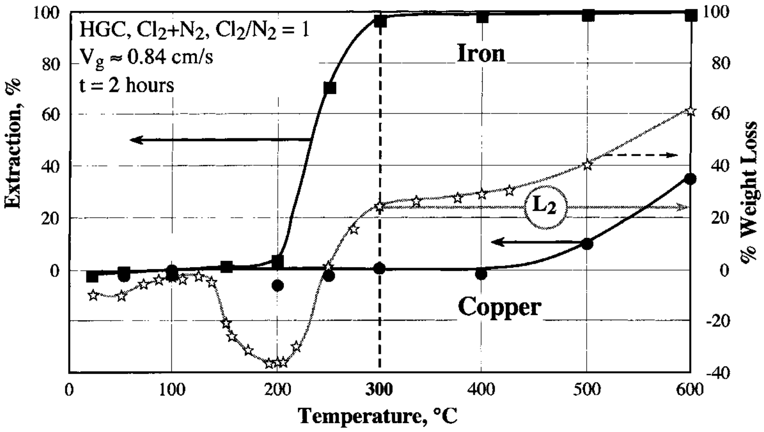


Fig. 16. Extraction of copper and iron from HGC during its chlorination at different temperatures.

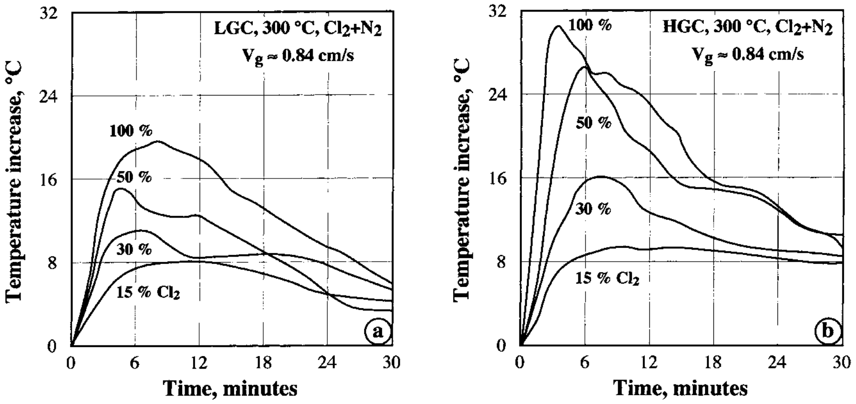


Fig. 17. Increase of temperature during the chlorination of (a) LGC and (b) HGC at 300°C using different chlorine contents in the $Cl_2 + N_2$ gas mixture.

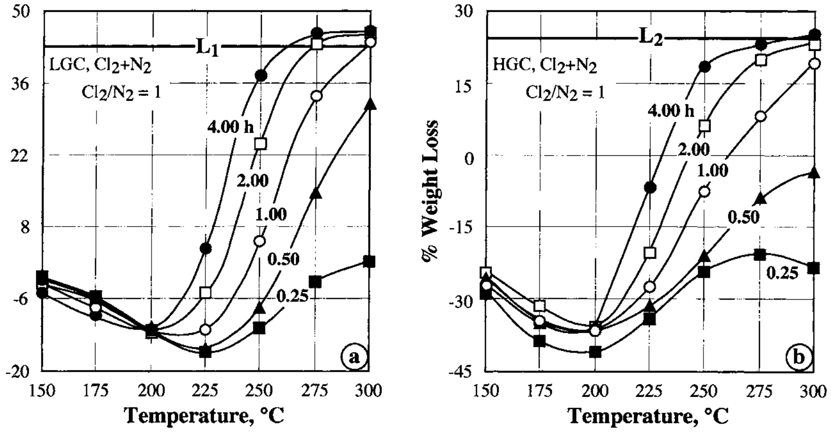


Fig. 18. Chlorination of (a) LGC and (b) HGC between 150 and 300°C for different reaction times.

chlorination of concentrates. The results are discussed in terms of how these parameters affect the chlorination reaction of these concentrates within the defined limits of selective chlorination.

3.4.1. Effect of reaction time

This was studied between 175 and 300°C during the chlorination of LGC and HGC with $Cl_2 + N_2$ ($Cl_2/N_2 = 1$). The reaction time was varied from 0.25 to 4 h. Fig. 18a and b summarized the obtained results given as PWL versus temperatures at different reaction times. Only weight gains were observed for the chlorination of LGC for temperatures lower than 225°C regardless the explored reaction times. The samples' weight increase is due to the formation of metal chlorides. Temperatures of about 275°C and a reaction time of 2 h are necessary to reach the selective chlorination limit of LGC. While, a reaction time of about 1 h is sufficient to attain the selective chlorination limit of LGC at 300°C. It was observed that the LGC chlorination residues were slightly agglomerated. The evolution of PWL of HGC versus temperature was similar to that of LGC (Fig. 18b). However, residues of HGC chlorination were significantly agglomerated. PWL lower than the selective chlorination limit of HGC reflects incomplete chlorination reaction. This is due to the formation of metal chloride layer that covers the unreacted agglomerated metal sulfide. This layer acts as diffusion barrier and probably responsible of the incomplete chlorination of HGC.

3.4.2. Effect of chlorine content

As temperatures closer to 300°C were necessary to achieve selective chlorination of both concentrates, tests to check the effects of chlorine contents of the $Cl_2 + N_2$ gas mixtures at different gas flow rates and reaction times were performed at this temperature. Fig. 19 groups the experimental results for the LGC chlorination. The effect of chlorine was significant for chlorine contents up to 40 pct in the $Cl_2 + N_2$ gas mixture. Higher chlorine content did not improve the chlorination process at the selected reaction time and gas flow rate ranges. Consequently, a $Cl_2 + N_2$ gas mixture containing about 50 pct Cl_2 will be adequate for a selective chlorination of LGC at 300°C during 1 h.

Results concerning HGC chlorination for the same conditions mentioned above are given in Fig. 20. Chlorination of HGC is more dependent on the chlorine content of the gas mixture especially for short reaction time. However, a gas mixture of $Cl_2 + N_2$ containing about 50 pct Cl_2 would be considered appropriate for the selective chlorination of HGC during a reaction time >1 h.

3.5. Flow sheet of the proposed process

Results of the chlorination of two chalcopyrite concentrates in different conditions using boat experiments indicate that it was possible to achieve low temperature chlorination-volatilization of concentrates at about 300°C. This allows selective separation

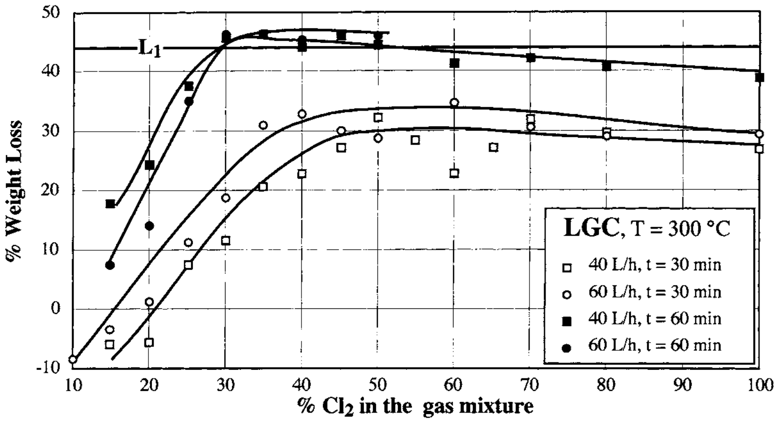


Fig. 19. Chlorination of LGC at 300°C using various chlorine contents in the gas mixture.

of valuable metal chlorides from the gangue. According to these results a proposed flow sheet is schematized in Fig. 21. In this flow sheet, the chalcopyrite concentrate is chlorinated at about 300°C for a reaction time of 1 to 2 h. The residence time depends on the concentrate's composition.

Based on the experimental results and the analysis of the reaction products, the main reactions of sulfides contained in both concentrates with chlorine are those described by Eqs. (4)–(11). As mentioned previously, the gangue is expected to be refractory to chlorine at 300°C.

$$\tfrac{2}{7}\mathrm{CuFeS_2(s)} + \mathrm{Cl_2(g)} \rightarrow \tfrac{2}{7}\mathrm{CuCl_2(s)} + \tfrac{2}{7}\mathrm{FeCl_3(g)} + \tfrac{2}{7}\mathrm{S_2Cl_2(g)} \quad (4)$$

$$\tfrac{2}{9}\mathrm{CuFeS_2(s)} + \mathrm{Cl_2(g)} \rightarrow \tfrac{2}{9}\mathrm{CuCl_2(s)} + \tfrac{2}{9}\mathrm{FeCl_3(g)} + \tfrac{4}{9}\mathrm{SCl_2(g)} \quad (5)$$

$$\tfrac{2}{3}\mathrm{PbS(s)} + \mathrm{Cl_2(g)} \rightarrow \tfrac{2}{3}\mathrm{PbCl_2(s)} + \tfrac{1}{3}\mathrm{S_2Cl_2(g)} \quad (6)$$

$$\tfrac{1}{2}\mathrm{PbS(s)} + \mathrm{Cl_2(g)} \rightarrow \tfrac{1}{2}\mathrm{PbCl_2(s)} + \tfrac{1}{2}\mathrm{SCl_2(g)} \quad (7)$$

$$\tfrac{2}{3}\mathrm{ZnS(s)} + \mathrm{Cl_2(g)} \rightarrow \tfrac{2}{3}\mathrm{ZnCl_2(s)} + \tfrac{1}{3}\mathrm{S_2Cl_2(g)} \quad (8)$$

$$\tfrac{1}{2}\mathrm{ZnS(s)} + \mathrm{Cl_2(g)} \rightarrow \tfrac{1}{2}\mathrm{ZnCl_2(s)} + \tfrac{1}{2}\mathrm{SCl_2(g)} \quad (9)$$

$$\tfrac{2}{5}\mathrm{FeS_2(s)} + \mathrm{Cl_2(g)} \rightarrow \tfrac{2}{5}\mathrm{FeCl_3(g)} + \tfrac{2}{5}\mathrm{S_2Cl_2(g)} \quad (10)$$

$$\tfrac{2}{7}\mathrm{FeS_2(s)} + \mathrm{Cl_2(g)} \rightarrow \tfrac{2}{7}\mathrm{FeCl_3(g)} + \tfrac{4}{7}\mathrm{SCl_2(g)} \quad (11)$$

The gas-phase of the concentrates' chlorination is composed essentially of iron and sulfur chlorides. Ferric chloride is recovered by cooling the gas phase

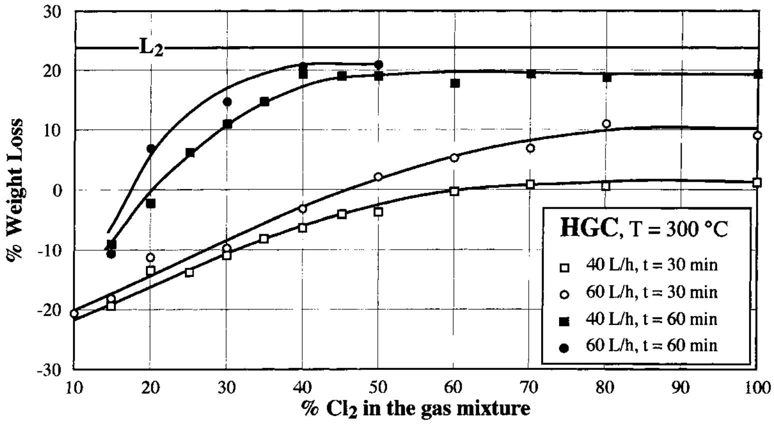


Fig. 20. Chlorination of HGC at 300°C using various chlorine contents in the gas mixture.

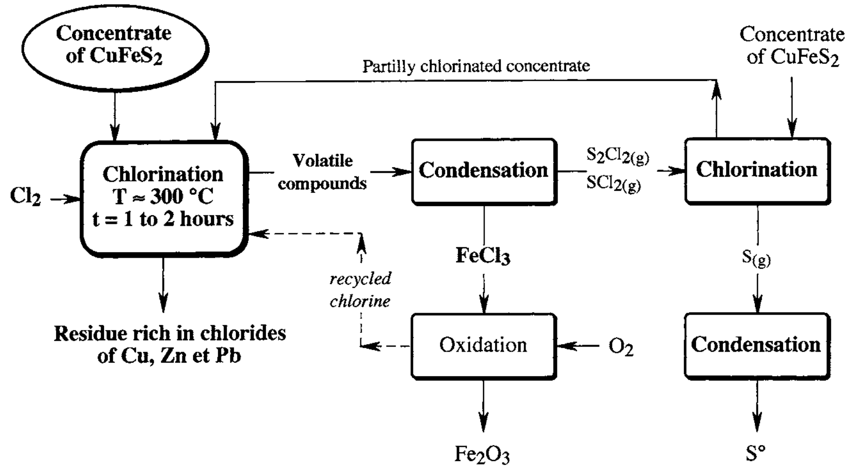


Fig. 21. Suggested flow-sheet for the extraction of valuable metal chlorides by chlorination of chalcopyrite concentrates at low temperature.

at room temperature. The interaction of ferric chloride with oxygen generates hematite and chlorine [8,9]. The generated chlorine could be recycled to the chalcopyrite's chlorination reactor after a composition adjustment. Moreover, ferric chloride can be used as chlorinating agent of sulfide concentrates [10]. On the other hand, the generated sulfur chlorides can be also employed for the chlorination of sulfide concentrates producing metal chlorides and elementary sulfur [7,11–13]. Thus, a second chlorination reactor can be added in the proposed flow-sheet using sulfur chlorides. However, the sulfur chlorides obtained after their condensation, could be also subjected to hydrolysis and/or to reduction by hydrogen in order to recover elementary sulfur [13].

The residue of chlorination is composed of copper, lead and zinc chlorides and the gangue. Separation of metal chlorides from the gangue as well as the individual metal chlorides can be performed by classical hydrometallurgical methods. The generated final solid residue is mainly composed of quartz and clinochlore. Such residue is environmentally safe and can be used for civil work or land filling.

The proposed process takes advantage of the exothermic nature of the chlorine reaction with the sulfide concentrate. Moreover, the generated sulfur chlorides can be used as chlorinating agents thus eliminating all sulfur compounds' emissions. Finally, part of the sulfur is recovered in the elementary form and the final solid residue is environmentally safe.

Although the chlorination process was conducted at low temperature compared with conventional pyrometallurgical ones, problems related to the equipment's corrosion have to be considered in calculating the capital and operating costs using the suggested process on the industrial scale.

4. Conclusions

The chlorination of LGC and HGC concentrates started from 20°C and full chlorination of sulfides was achieved at about 300°C for a reaction time ≥ 2 h. At this temperature, the valuable metals are concentrated in the chlorination residues as $CuCl_2$, $PbCl_2$ and $ZnCl_2$. Iron and sulfur chlorinated-compounds were fully volatilized. The selectivity of the chlorination process was assured by the wide difference of the vapor pressure between the chlorides of valuable metals and those of sulfur and iron.

Chlorination of both concentrates is exothermic that may allows the development of a process with a reduced external energy supply. However, the exothermic nature of the chlorination reaction as well as the presence of low temperature eutectics in different chloride–chloride and/or sulfide–chloride systems may lead to some technical difficulties during the chlorination process.

The chlorination of both concentrates at temperatures higher than 350°C leads to a partial volatilization of valuable metals' chlorides. Consequently, careful temperature control will probably be necessary to achieve selective separation of valuable metal chlorides from ferric chloride.

One may underline that cupric chloride is decomposed into cuprous one at temperatures higher than 500°C. At this temperature, clinochlore could be also decomposed. To avoid such reactions the chlorination temperature of both concentrates was limited to about 300°C.

As this study was performed on the laboratory scale. The industrial application of the proposed flow-sheet will necessitate experimentation on the pilot scale. This will allow a better definition of the mass and energy balances of the proposed flow sheet.

Acknowledgements

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