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A Low Temperature Chlorination-Volatilization Process for the Treatment of Chalcopyrite Concentrates

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The chlorination of two chalcopyrite concentrates with Cl_2+N_2 was investigated under isothermal conditions in the temperatures range from 20 °C to 750 °C using boat experiments. The effects of gas flow rate, chlorine content of the gas mixture and reaction time on the reaction rate were also investigated. The reaction products were analyzed by SEM, XRD, and chemical analysis.

The chlorination of chalcopyrite concentrates started from 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 more valuable metals' chlorides were concentrated in the chlorination residues, while those of iron and sulfur were volatilized. Chlorination at higher temperatures allowed the volatilization of valuable metal chlorides. A process for the selective chlorination of chalcopyrite concentrates at low temperatures was suggested. It could be considered as an attractive route for the sulfides' treatment without SO_x emissions. In addition, low operating temperatures offer another advantage for the chlorination process with regard to higher energy consumption of the common pyrometallurgical routes.

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I. INTRODUCTION

In a previous paper from this laboratory^[1], the kinetics of the chlorination of the chalcopryrite concentrates at temperature up to 300 °C, using thermogravimetric analysis (TGA), were discussed in details. It was observed that the chlorination of chalcopryrite concentrates was generally little dependent on the temperature and the reaction times of few minutes were sufficient at 300 °C to achieve full chlorination of sulfides and volatilization of the sulfur and iron chlorinated-compounds. However, the kinetics study was performed with several milligrams of samples in order to minimize the effect of mass and heat transfer phenomena on the chlorination process.

Even using TGA experiments, the chlorination rate as well as the volatilization rate of the chlorides is affected by the amount of sample used. Figures 1 (a) to (c) gather some data concerning the chlorination of a chalcopryrite concentrate at 300 °C using 12, 25, and 50 mg of sample for various chlorine contents in the gas mixture. About 60 minutes were necessary to achieve full chlorination of sulfides and volatilization of S_xCl_y and $FeCl_3$ when 50 mg of sample were chlorinated by a Cl_2+N_2 gas mixture containing 10 % Cl_2 . The reaction time became about 6 times shorter when the amount of the sample used was 12 mg. As it could be expected, the reaction time decreased with the increase of the chlorine content in the chlorinating gas mixture. Thus, about 3 minutes are sufficient to reach a complete reaction of the sample by chlorine alone when 12 mg of the sample were used (refer to Figure 1 (c)). Results obtained suggested that the fluidized bed will be the best reactor from the chlorination kinetics point of view. Nevertheless, the partial fusion as well as the softening of materials occurred during the chlorination of sulfides resulting in the choking of the fluidized bed.

The literature review, summarized in Reference 1, revealed that low (≤ 300 °C) and high (≥ 400 °C) temperatures were used for the chlorination of sulfides. However, the use of temperatures higher or equal to 500 °C will lead to the partial decomposition of chalcopryrite and pyrite to cubanite and pyrrhotite, respectively^[2], this prior to the chlorination gas mixture will be introduced. On the other hand, the use of high chlorination temperatures will cause the partial volatilization of valuable metal chlorides such as $CuCl_2$, $CuCl$, $ZnCl_2$, $PbCl_2$, besides S° , $FeCl_3$, and S_xCl_y , decreasing the selectivity of the chlorination process.

For these reasons, the chlorination of several grams of the chalcopryrite 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 chalcopryrite concentrates as well as on the selective volatilization and separation of valuable metals' chlorides from those of iron and sulfur.

II. MATERIALS AND EXPERIMENTAL PROCEDURES

A. Materials

Two chalcopyrite concentrates as well as CuFeS_2 , ZnS , PbS , and FeS_2 were the selected materials used for this investigation. Their physico-chemical characteristics were described in details previously^[1]. The chemical and mineralogical compositions of two concentrates are given in Table I. As shown, these concentrates are characterized by different contents of valuable metals (Cu, Pb, and Zn). The valuable metal (Cu, Zn) content of first sample was about 11.6 pct and was called low grade concentrate (LGC). The total valuable metal (Cu, Zn, Pb) content of second sample was about 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 essentially contained quartz and clinochlore. The HGC was rich in chalcopyrite (81.7 pct). Moreover, it bore some amounts of lead and zinc compounds, whilst its gangue content was low.

Table I. 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*	ND	—
Total	91.1	96.8		91.5	97.5

Clinochlore : $(\text{Mg}, \text{Fe})_6(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_8$.

B. Experimental Procedures

Test of the isothermal chlorination of chalcopyrite concentrates was carried out using the experimental set-up schematized in Figure 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). The boat of sample is placed into the reactor, and heating at the desired temperature was done under nitrogen atmosphere. Since then, the nitrogen flow was turned off and the chosen chlorinating gas mixture was

introduced in the reactor. The solid condensates were recovered after their condensation on the reactor wall because of the natural temperature gradient. The composition of the chlorination 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 by using the TGA set-up described earlier^[3], this in order 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 distribution of the whole sample. Thus, the temperature of the furnace was fixed at a desired value, between 200 °C and 600 °C, and the temperature at the sample surface was recorded by setting a thermocouple inside of the reactor. Similarly, the inner temperatures of the entire reactor and condenser were measured. The tests were carried out under nitrogen atmosphere. Figure 3 represents the results obtained. It is obvious that the temperature at the whole sample was almost constant (± 5 °C) on the temperature interval checked. This figure shows also the temperature profile of the condensation zone of chlorides and the location where from the condensates (named as C₁ and C₂) were dragged away to be analyzed.

The sample temperature was also measured during the chlorination at 300 °C of both chalcopyrite concentrates (LGC and HGC) by Cl₂+N₂ at various contents of chlorine in the gas mixture, this in order to determine the increase of temperature due to the exothermic nature of the chlorination reactions of the sulfides. The results will be reported in Section III of this article.

III. RESULTS AND DISCUSSION

A. *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 by using the Cl₂+N₂ gas mixture with a Cl₂/N₂ molar ratio equal to 1. The reaction time was fixed to be 1 h. Figure 4 traces the percentage weight loss (PWL) of the used samples as a function of the gas flow rate. The chlorination of the HGC seems to be more affected than the LGC one by the gas flow rate. However, a flow rate higher than 20 L/h (gas velocity: $V_g \approx 0.42$ cm/s) will be adequate for the minimization of mass transfer phenomena. Since, a chlorinating gas mixture with a $V_g \approx 0.84$ cm/s was used for the study of the chlorination of both concentrates at different temperatures.

B. *Chlorination of Sulfides at Different Temperatures for 2 Hours*

An extensive series of the isothermal chlorination tests was carried out between 20 °C and 750 °C. The materials subjected to chlorination were LGC, HGC, CuFeS₂, FeS₂, ZnS, and PbS. A

chlorinating gas mixture of $\text{Cl}_2 + \text{N}_2$ ($\text{Cl}_2/\text{N}_2 = 1$) was used and the reaction time was 2 hours. Results are represented in Figure 5 as evolution of PWL *versus* temperature. Pyrite and chalcopyrite started to react from room temperature and a maximum weight gain was observed at 200 °C. Full reaction and volatilization of the reaction products for the pyrite chlorination were achieved at 300 °C. A plateau of weight loss was observed at about 350 °C for the chalcopyrite chlorination, since then the PWL increased continuously with temperature. The sulfides of zinc and lead reacted with chlorine at temperatures equal to or higher than 150 °C leading to their respective chlorides. However, complete reaction of ZnS was achieved at temperature lower than that of PbS . These observations for the chlorination of the sulfides suggest that full reaction and volatilization of products depend on the vapor pressure the chlorides. As shown in Figure 6^[4], the chlorides of sulfur, iron, copper, zinc, and lead are characterized by a wide difference on the vapor pressure at a given temperature and the sequence of the sulfides' chlorination follows that of the chlorides' volatilization. Cupric chloride was expected to be decomposed into cuprous chloride followed by the volatilization of the last.

The behavior of HGC chlorination is close to that of chalcopyrite, whilst that of LGC is similar in sequence to : pyrite in $\text{Cl}_2 + \text{N}_2$ up to 275 °C, and chalcopyrite in $\text{Cl}_2 + \text{N}_2$ for higher temperatures. These similarities are consistent with the chemical composition of these concentrates (refer to Table I). Figure 5 contains the calculated limits (expressed as PWL) for the selective chlorination of each concentrates 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 both concentrates. However, these limits seem to be close to the 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 an algebraic sum of those due to the partial thermal decomposition of sulfides, chlorides' formation, and chlorides' volatilization. Figure 7 gives an example of the HGC treatment between 335 °C and 780 °C. It was observed that fractions of the sample were lost during the sample heating under nitrogen atmosphere at temperatures higher or equal to 475 °C, prior to the chlorination. This is due to the fact that chalcopyrite and pyrite undergo thermal transformation^[2] as described by Eqs. [1] through [3]. On the other hand, the initial weight gain of HGC sample, during its chlorination, decreases with the increase of the chlorination temperature.

The formation of eutectics of low melting points between different chlorides, such as CuCl-FeCl_3 ^[1], led to complexity of the sulfides' chlorination. Another example is the chlorination of PbS. Lower chlorination extent of PbS was achieved at 450 °C than at 400 °C (refer to Figure 5). To clarify this phenomenon, two TGA tests of PbS chlorination using Cl_2+N_2 were performed at 400 °C and 450 °C and the results are given in Figure 8. The initial reaction rate of the PbS chlorination at 450 °C is quite rapid, then the reaction seems to be stopped. While at 400 °C, about full chlorination of PbS was achieved. The XRD results of the chlorination residues are reported in Figure 9. Only PbCl_2 was revealed in the residue of chlorination at 400 °C, while PbS remained as a main phase, besides PbCl_2 , 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 $\text{PbCl}_2\text{-PbS}$ system, as shown by Figure 10^[5]. The formation of this liquid phase could probably decrease the reaction rate of PbS with chlorine at 450 °C.

C. Analysis of the Reaction Products of the Concentrates' Chlorination

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

1. SEM analysis

Several SEM spectra of the chlorination residues of LGC and HGC between 20 °C and 300 °C are given in Figure 11. The presence of chlorine in the LGC and HGC residues obtained at room temperature 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 showed that the residues obtained from both concentrates were sulfur-free indicating that full 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 removed as ferric chloride. However, iron was detected in the LGC residue at 300 °C. This is probably due to the unreacted iron found in clinocllore : $(\text{Mg, Fe})_6(\text{Si, Al})_4\text{O}_{10}(\text{OH})_8$.

Condensates of chlorination of both concentrates were significantly observed at temperatures higher than 200 °C. Figure 12 shows some spectra from the condensates obtained during the chlorination of the LGC at temperatures of : 250 °C, 400 °C, and 600 °C. Similar spectra were obtained by the chlorination of HGC. Condensates were recovered at different condensation zone along the reactor (see Figure 3 for C_1 and C_2). These condensates were essentially composed of Fe and Cl for a chlorination temperature lower than 300 °C showing that iron was removed as FeCl_3 which is characterized by a vapor pressure of about 1 atm 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 (C₁ and C₂) was probably due to the natural temperature gradient of the condensation zone. Sulfur was not detected in the solid condensates regardless the chlorination temperature, indicating that sulfur was essentially removed as S_xCl_y (S₂Cl₂+SCl₂) which have sufficiently high vapor pressures (see Figure 6) to be transported out by the exhaust gases. The formation of sulfur dichloride is probably due to high partial pressure of chlorine in the chlorination process.

2. XRD analysis

All residues of the LGC and HGC chlorination at temperatures ranging from 20 °C to 700 °C were subjected to XRD analysis. Figure 13 represents the diffractograms of some residues of LGC chlorination between 50 °C and 500 °C. They confirm the decrease of CuFeS₂ and FeS₂ peaks' intensity and increase of ray intensities of CuCl₂. Cupric chloride was identified as a mixture of CuCl₂ and CuCl₂·2H₂O due to the hygroscopic nature of CuCl₂. Ferric chloride was not revealed by XRD analysis, but its presence in the chlorination residues at lower temperatures was confirmed earlier by TG analysis^[1]. No sulfides were detected in the chlorination residue obtained at 300 °C. Clinocllore was decomposed at temperatures closer to 500 °C. However, the decomposition products were not identified.

Figure 14 gives similar results concerning the HGC residues' chlorination. Chlorination residue at 300 °C was essentially composed of copper, lead, and zinc chlorides. However, ZnCl₂ was not detected by XRD analysis because of its amorphous nature. The presence of CuCl besides CuCl₂ at higher temperatures was confirmed by XRD. Although the decomposition of CuCl₂ into CuCl occurs at about 537 °C^[7], its only partial decomposition is due to the high partial pressure of chlorine in the chlorination process.

A summary of the phases identified by XRD analysis in the residues obtained at different chlorination temperatures for LGC and HGC is given in Table II and III, respectively. As shown by Table II, the chlorination residue of LGC at 300 °C is composed of CuCl₂, clinocllore and quartz. Higher temperatures of the chlorination allow the decomposition of clinocllore, volatilization and/or decomposition of CuCl₂. Similarly, the HGC residue obtained at 300 °C is sulfide-free (Table III) and contains the valuable metals as chlorides.

Although the condensates were subjected to XRD analysis, it was observed that they are generally amorphous, consequently no observation is available on the phases present in the condensates. However, the presence of iron in the condensates at lower temperatures suggests that it was volatilized as FeCl₃ since the boiling point of FeCl₂ is 1026 °C^[4]. Copper is probably removed partially as CuCl₂ at lower temperatures and as CuCl₂+Cu₃Cl₃^[7] at higher temperatures.

Table II. Phases Identified by XRD in the LGC Chlorination Residues between 20 °C and 700 °C.

Phases	Raw	20 °C	50	100	150	200	250	300	400	500	600	700 °C
CuFeS ₂	[Bar chart showing phase stability for CuFeS ₂ across temperatures]											
CuCl ₂	[Bar chart showing phase stability for CuCl ₂ across temperatures]											
CuCl	[Bar chart showing phase stability for CuCl across temperatures]											
FeS ₂	[Bar chart showing phase stability for FeS ₂ across temperatures]											
FeCl ₃ *	[Bar chart showing phase stability for FeCl ₃ across temperatures]											
Clinocllore	[Bar chart showing phase stability for Clinocllore across temperatures]											
SiO ₂	[Bar chart showing phase stability for SiO ₂ across temperatures]											

Identified phase
 Probable phase

* Confirmed by TGA.

Table III. Phases Identified by XRD in the HGC Chlorination Residues between 20 °C 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 *												
FeCl ₃ **												
Pb-comp.***												
PbCl ₂												
ZnS												
ZnCl ₂												

Identified phase
 Probable phase

* HGC pyrite content is low, ** Confirmed by TGA, *** PbSO₄, Pb(Cu, ...)₃(SO₄)₂(OH)₆, and PbS.

3. Chemical analysis

The qualitative analyses such as SEM and XRD indicated that, in our conditions, the temperatures close to 300 °C were adequate for the full chlorination of sulfides contained in both concentrates and for the volatilization of sulfur and iron chlorinated-compounds. In order to check on this hypothesis, iron and copper contents of the chlorination residues were determined by chemical analysis.

Figure 15 is a data compilation of the chlorination of LGC between 20 °C and 600 °C. Iron extraction was remarkable from 200 °C but it was not complete at 300 °C. Iron not removed at 300 °C corresponds to the iron present as an oxide in the clinochlore. Full extraction of iron could be achieved at temperatures higher than 500 °C when the clinochlore was decomposed. Copper extraction became significant at temperature higher than 400 °C and about 75 pct of copper were extracted at 600 °C. The PWL curve described in Figure 15 for the LGC chlorination are in good agreement with the extraction extents of iron 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 Figure 16. Almost complete iron extraction was achieved at 300 °C. This was possible because the iron of HGC is bore by the sulfides, essentially in the chalcopyrite. The selective chlorination limit (L_2) is fully consistent with the PWL and 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 did not undergo such phenomenon. The presence of inert compounds in LGC, such as SiO_2 , prevented the agglomeration of the residues.

The agglomeration of the chlorination residues, essentially for HGC, was probably caused by the increase of temperature thanks to the exothermic nature of the sulfides' chlorination reactions. To confirm that, a series of the isothermal chlorination tests at 300 °C using 2 grams 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. Figures 17 (a) and (b) plot the increases of temperature of LGC and HGC, respectively, during their chlorination under the above-mentioned conditions. As could be expected, the sample temperature increased 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 Figure 17, the increase of temperature was observed at the beginning of the chlorination. 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 non reacted sample, and consequently, the remainder of the sample reacted then slower due to difficulties of chlorine to diffuse throughout the chlorides' layer.

D. *Effect of Other Parameters on the Chlorination of LGC and HGC*

As mentioned in the preceding sections, the chlorination of both concentrates was achieved for 2 hours at 300 °C by using an equimolar Cl_2+N_2 gas mixtures with a total gas flow rate of 40 L/h. It was worthwhile to check the effect of the reaction time, and simultaneously, the effect of chlorine content, gas flow rate, and reaction time on the complete chlorination of concentrates. The results are discussed in terms of how these parameters affect the percentage weight loss in order to reach the defined limits of the selective chlorination of each concentrate.

1. *Effect of reaction time*

This effect was studied between 175 °C and 300 °C during the chlorination of LGC and HGC with Cl_2+N_2 ($\text{Cl}_2/\text{N}_2 = 1$). The reaction time was varied from 0.25 to 4 hours. Figures 18 (a)

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 the temperatures lower than 225 °C regardless the explored reaction times. As mentioned before, low vapor pressure of ferric chloride at this temperature was responsible for this weight gain. Temperatures of about 275 °C are necessary to reach the selective chlorination limit of LGC at reaction time of about 2 h. While, a reaction time of about 1 hour is sufficient to allow the selective chlorination of LGC at 300 °C. It was observed that the LGC chlorination residues were slightly agglomerated. Similarly observations, concerning the evolution of PWL *versus* temperature, were valid for the HGC chlorination (see Figure 18 (b)). However, the residues of HGC chlorination were significantly agglomerated. For the experimental tests resulting to the PWL lower than selective chlorination of HGC, it was observed that the sample surface was essentially composed of the chlorides, while the remainder of sample was the coated-non reacted and agglomerated sulfides' particles.

2. Effect of chlorine content

As temperatures closer to 300 °C were necessary to achieve the 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 300 °C. Figure 19 represents the experimental results for the LGC chlorination. The effect of chlorine was significant for the chlorine content up to 40 pct in the Cl_2+N_2 gas mixture. Higher chlorine content did not improve the chlorination process at two reaction times and at the gas flow rate selected. Consequently, a Cl_2+N_2 gas mixture containing about 50 pct Cl_2 could allow a selective chlorination of LGC at 300 °C during a reaction time of 1 hour.

Results concerning HGC chlorination for the conditions mentioned previously are given in Figure 20. Chlorination of HGC is more dependent on the chlorine content in the gas mixture especially at low reaction time. However, a gas mixture of Cl_2+N_2 containing about 50 pct Cl_2 would be considered as appropriate for the chlorination of HGC, whilst the reaction time can be higher than 1 hour.

E. Flow sheet of the Proposed Process

Data collected from the chlorination of two chalcopyrite concentrates at different conditions using boat experiments indicated that it was possible to use a low temperature chlorination-volatilization process, at about 300 °C, in order to separate selectively the valuable metals from the others. The flow-sheet of the proposed process is represented in Figure 21. Although the results obtained in this study focused only on the chlorination process, other steps are added in the flow-sheet based on the data found in the literature. According to this flow-sheet, the chalcopyrite concentrate is chlorinated at about 300 °C in a fixed bed for a reaction time 1 to 2 hours. The reaction time depends on the concentrate composition.

Based on the experimental results and on the analysis of the reaction products, the main reaction of the sulfides contained in both concentrates with the chlorine at about 300 °C will be those described by Eqs. [4] to [11]. As mentioned previously, the gangue (quartz and clinocllore) was expected to be refractory in chlorine at 300 °C.

The gas-phase of the concentrates' chlorination is composed essentially of iron and sulfur chlorides. Ferric chloride is recovered by cooling the gas phase at room temperature. The obtained ferric chloride can be treated in oxygen^[8, 9] to give hematite and chlorine. The last will be recycled to the chalcopryrite chlorination unit after a composition adjustment. In addition, ferric chloride can be used as chlorinating agent^[10]. As mentioned in the literature^[7, 11, 12], sulfur monochloride reacted with several sulfides producing metal chlorides and elementary sulfur. Thus, a second chlorination unit can be added in the proposed flow-sheet using sulfur chlorides as chlorinating agent. However, the sulfur chlorides obtained after their condensation, could also be subjected to hydrolysis and/or to reduction by hydrogen in order to recover elementary sulfur^[13].

The chlorination residue will be leached with slightly acidified water at an adequate temperature in order to dissolve the chlorides of Cu, Zn, and Pb. The insoluble solids (quartz and clinocllore) are expected to be not dangerous for the environment and could be landfilled. Other hydrometallurgical treatments will be required to recover selectively these metals.

Although the chlorination process was conducted at lower temperature compared with conventional pyrometallurgical ones, the problems related to the equipment's corrosion, the difficulties to proceed in a continuous system, etc. have to be taken into account once calculating the global cost of using the suggested process at industrial scale.

IV. CONCLUSIONS

The chlorination of LGC and HGC concentrates started from room temperature and full chlorination of sulfides was achieved at about 300 °C for a reaction time less or equal to 2 hours. 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 on the vapor pressure between the chlorides of valuable metals and those of sulfur and iron.

Chlorination of both concentrates is exothermic leading to the possibility of developing of the 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 will 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, accurate cooling of the gas phase will be probably necessary for the selective separation of these chlorides. Cupric chloride is decomposed into cuprous one at temperatures higher than 500 °C. At this temperature, clinocllore could be also decomposed. Therefore, the best temperature for the chlorination of both concentrates was chosen to be at about 300 °C.

As the study was performed with several grams of the sample, more investigations at large experimentation will be necessary to validate the use of the low temperature chlorination-volatilization process for the treatment of chalcopyrite concentrates.

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Low Temperature Chlorination-Volatilization Process for the Treatment of Chalcopyrite Concentrates

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Figure Captions

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 .

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

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

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

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].

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

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

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 °C and 300 °C.

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

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

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

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 °C and 300 °C for different reaction times.

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

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.

Fig. 1 : Effect of the sample weight on the chlorination of a chalcopirite concentrate at $300\text{ }^{\circ}\text{C}$ with :

(a) : (10 % Cl_2) + N_2 ,

(b) : (50 % Cl_2) + N_2 ,

(c) : 100 % Cl_2 .

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

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

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

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.

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

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