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► **To cite this version:**

Ndue Kanari, I. Gaballah, Eric Allain, Nouredine Menad. Kinetics of Chlorination of chalcopyrite concentrates. Metallurgical and Materials Transactions B, Springer Verlag, 1999, 30 (4), pp. 567-576. <10.1007/s11663-999-0017-6>. <hal-01508039>

**HAL Id: hal-01508039**

**<https://hal.univ-lorraine.fr/hal-01508039>**

Submitted on 13 Jun 2017

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## **Kinetics of Chlorination of Chalcopyrite Concentrates**

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Chlorination behaviors of two chalcopyrite concentrates and their pure constituents in  $\text{Cl}_2+\text{N}_2$  were investigated by thermogravimetric analysis in non isothermal conditions up to 1000 °C. The effect of temperature on the reaction of chlorine with both concentrates was studied between 170 °C and 300 °C under isothermal conditions. 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 and X-ray diffraction.

Results showed that the chlorination of the chalcopyrite concentrates generating chlorides of Cu, Pb, Zn, Fe and S was rapid at temperatures approaching 300 °C. The iron and sulfur chlorides were volatilized leading to a residue containing valuable metal chlorides. A process for the selective chlorination of sulfides' concentrates at low temperatures was suggested.

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## I. INTRODUCTION AND LITERATURE REVIEW

Sulfide ores and concentrates are still the major source of the primary production of metals such as Cu, Pb, Zn, etc. The extractive metallurgy of these metals from sulfides based on dry method is one of the responsible for the environmental pollution due to the  $\text{SO}_x$  generation. Although the technological progress, the  $\text{SO}_x$  emissions remain a serious problem from the ecological point of view. The conversion of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  is marginal because of the transportation cost and the state of the sulfuric acid market. Different methods had been proposed to avoid sulfur dioxide formation during the extraction of valuable metals from sulfides. Gaballah *et al.*<sup>[1]</sup> suggested the thermal treatment of complex sulfides' ores under controlled atmosphere ( $\text{N}_2$ ,  $\text{H}_2$ ) at temperatures lower or equal to 1000 °C. The proposed flow-sheet permits the recovery of sulfur, galena, trace element's compounds, zinc and a residue rich in copper. Habashi<sup>[2]</sup> suggested that the hydrometallurgical route offers the possibility of obtaining sulfur at moderate temperature and pressure thus solving the sulfur problem of sulfides' treatment.

Several researches were devoted to the chlorination process as an efficient alternative to recover the copper from its sulfides at relatively low temperatures. Donaldson and Kershner<sup>[3]</sup> studied the chlorination of  $\text{CuFeS}_2$  by chlorine between 25 °C and 300 °C in a horizontal experimental set. They observed that the intensive chlorination of  $\text{CuFeS}_2$ , generating the copper and iron chlorides, started at 150 °C and almost full chlorination was achieved near to 250 °C. Landsberg *et al.*<sup>[4]</sup> employed thermogravimetric analysis 'TGA' to investigate the chlorination of  $\text{CuFeS}_2$  by  $\text{Cl}_2+\text{Ar}$  from 25 °C to 300 °C. A value of apparent activation energy ' $E_a$ ' of about 35.6 kJ/mol was pointed out by these authors between 25 °C and 100 °C. They mentioned the formation of a product layer at about 200 °C and that the slowest step is the diffusion towards this layer. Finally, they concluded that the chlorination reaction became exothermic at 300 °C and the sulfur, the iron and the copper were easily chlorinated, but the chlorination rate depended on the rate of volatilization of the reaction products.

Olsen *et al.*<sup>[5]</sup> developed a process for the chlorination of a pelletized chalcopyrite concentrate in a vertical reactor in the temperature range from 550 °C to 650 °C. They suggested, that in the absence of excess chlorine, the main products of  $\text{CuFeS}_2$  chlorination were  $\text{CuCl}_2$ ,  $\text{FeCl}_2$  and  $\text{S}^\circ$ . About 99 pct of sulfur was distilled from the top of reactor. Iron and copper chlorides were treated with  $\text{O}_2$  between 800 °C and 900 °C. Over 80 pct of the iron chlorides were converted to oxides while the copper chlorides remained unaffected. The authors recovered the copper in powder form by electrowining of chloride solution using a diaphragm cell.

Habashi<sup>[6]</sup> carried out the chlorination of  $\text{CuFeS}_2$  concentrate by chlorine in a horizontal reactor between 100 °C and 500 °C. He recovered three main products that they were identified as

$S_2Cl_2$ ,  $FeCl_3$  and  $CuCl_2$ . The author concluded that at 300 °C, practically all the sulfur was collected in the sulfur chloride liquid fraction, all the iron in the ferric chloride solid fraction, and all the copper remained in the reactor in a water-soluble form. The author mentioned also the exothermic character of the chlorination reactions.

Yee *et al.*<sup>[7]</sup> investigated the chlorination of a pelletized  $CuFeS_2$  concentrate by  $Cl_2+N_2$  between 550 °C and 750 °C in a vertical reactor. They indicated that more than 96 pct of  $CuFeS_2$  were converted to copper-iron chlorides and elemental sulfur. After filtration, elemental sulfur of greater than 99 pct purity was obtained. According to these authors, the valence state of copper and iron in the metal chlorides' product depended on the reaction temperature and chlorine flow rate used.

Kumar *et al.*<sup>[8]</sup> performed the chlorination by  $Cl_2$  of a  $CuFeS_2$  concentrate in powder and pellet form between 400 °C and 550 °C using TGA. According to these authors, the reaction products were condensed cuprous and ferrous chlorides as well as gaseous elemental sulfur. The ferrous chloride was transformed into gaseous ferric chloride. The last could interact with chalcopyrite giving the same reaction products as in the case of  $CuFeS_2$  with  $Cl_2$ . The authors suggested a flow-sheet for extraction of copper, iron and other by-products from chalcopyrite. The proposed process was estimated to have an energy requirement of approximately 1780 kWh/tonne of cathode copper, about half the energy consumption for conventional hydrometallurgical processes.

In another article, Kumar *et al.*<sup>[9]</sup> studied the kinetics of chlorination of  $CuFeS_2$  powder in the same temperature range mentioned above. They developed a mathematical model to gain some insight into the reaction mechanism. The value of  $E_a$  for the chlorination of  $CuFeS_2$  by  $Cl_2$  was about 2.1 kJ/mol while that of the reaction of  $FeCl_2$  with  $Cl_2$  to give  $FeCl_3$  was about 10.5 kJ/mol. The authors concluded that the low values of  $E_a$  could be due to highly exothermic nature of the reaction. Consequently, the increase of the reaction temperature affected not only the rate of the reaction, but also the physical structure of products. Finally, it has been mentioned by these investigators that the adsorption of chlorine on chalcopyrite could be the most possible reaction mechanism. Some aspects of the chlorination kinetics of chalcopyrite by chlorine were also given by Jena and Brocchi<sup>[10]</sup>. They carried out the chlorination experiments between 350 °C and 450 °C. The calculated value of  $E_a$  was about 25.5 kJ/mol, while the chlorination rate of copper at 400 °C was almost independent of chlorine partial pressure ' $P_{Cl_2}$ ' for the value of ' $P_{Cl_2}$ ' higher than 0.4 atm. It has been suggested that the chlorination of  $CuFeS_2$  was controlled by an adsorption mechanism.

This paper is a part of a research program concerning the use of chlorine for the extraction of valuable metals from wastes such as spent catalysts<sup>[11]</sup>, tin slag<sup>[12]</sup> and from raw materials such as chromite.<sup>[13]</sup> It deals with the kinetics study of the chlorination of two chalcopyrite concentrates in order to achieve a selective separation of the valuable metal (Cu, Pb, Zn) compounds.

## II. MATERIALS AND EXPERIMENTAL PROCEDURES

### A. Materials

Two chalcopyrite concentrates were used for this study. The physico-chemical characterization of the samples was realized by different analysis such as : scanning electron microscopy 'SEM', X-ray diffraction 'XRD', inductively coupled plasma-atomic emission spectrometry 'ICP-AES', size and specific surface measurements, etc.

Figure 1 gives the SEM spectrum of two concentrates used in this study. The major elements detected in the first sample 'S<sub>1</sub>' (Figure 1 a) were Fe, S, Si, Cu, O, Al, Mg, Zn, etc. While the second sample 'S<sub>2</sub>' (Figure 1 b) is essentially composed of S, Fe, Cu, Pb and Zn. The results of X-ray diffraction of both samples were represented by Figure 2. The first concentrate contains CuFeS<sub>2</sub>, FeS<sub>2</sub>, SiO<sub>2</sub> and (Mg, Fe)<sub>6</sub>(Si, Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub> (clinochlore) as the main phases identified by XRD. The principal identified phase in the second concentrate was CuFeS<sub>2</sub>. However, other phases such as : PbS, PbSO<sub>4</sub>, Pb(Cu, ...)<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> and ZnS were also detected in this concentrate.

Table I summarizes the results of chemical analysis of these concentrates. The first sample 'S<sub>1</sub>' contained about 10.8 pct Cu. The copper content of the second sample 'S<sub>2</sub>' was 28.3 pct. The valuable metal (Cu, Zn) content of S<sub>1</sub> was about 11.6 pct and was called low grade concentrate (LGC). The total valuable metal (Cu, Zn, Pb) content of S<sub>2</sub> was about 36.5 pct and it was designated as high grade concentrate (HGC). Based on the results of SEM, XRD and chemical analysis, a calculation of phases' content of two concentrates is given in Table I. Clearly, the major sulfides of the LGC were CuFeS<sub>2</sub> and FeS<sub>2</sub>. The presence of pyrite in this concentrate was probably due to the ineffectiveness of the physical processing. The LGC gangue was essentially constituted of the quartz and clinochlore. The HGC was rich in chalcopyrite (81.7 pct). Moreover, it contained some amounts of lead and zinc compounds, while its gangue content was feeble.

The concentrates were obtained by the enrichment of their ores using the flotation technique. The size measurements indicated that d<sub>50</sub> is about 85 and 35 μm for the LGC and HGC, respectively. The average specific surface of two samples was 0.63 ± 0.01 m<sup>2</sup>/g.

The chlorination behaviors of two concentrates were compared with that of their simple constituents such as CuFeS<sub>2</sub>, ZnS, PbS, FeS<sub>2</sub> as well as S°. The used minerals were of natural origin. The SEM and XRD analyses were used to check theirs composition.

### B. Experimental Procedures

Thermogravimetric analysis chlorination tests were realized with 50 mg of sample, using an experimental set schematized previously<sup>[13]</sup>. Its main unit is a CAHN 1000 microbalance having a sensitivity of 10 μg. The chlorination gas mixture composed of Cl<sub>2</sub>+N<sub>2</sub> was purified through H<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> columns before reaching the reactor. The sample was uniformly distributed in a

quartz crucible. This crucible was hooked to the balance using quartz rods. For a TGA test under non isothermal conditions, the sample was directly heated in the chlorinating atmosphere. For TGA isothermal runs, the sample was first heated in nitrogen atmosphere to a given temperature before the chlorination atmosphere is introduced. The exhaust gases were purified by a NaOH solution before their release to the atmosphere.

Table I : Chemical and Mineralogical Composition of the Chalcopyrite Concentrates (Wt pct).

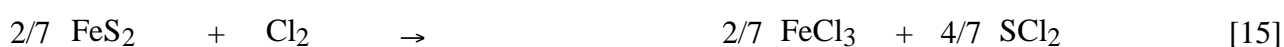
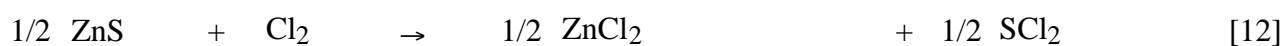
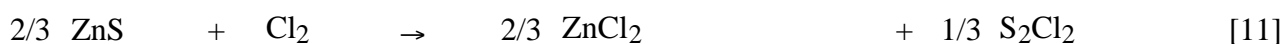
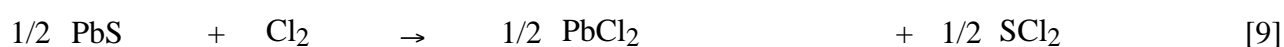
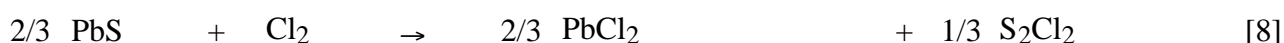
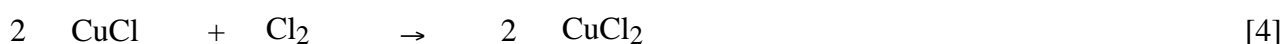
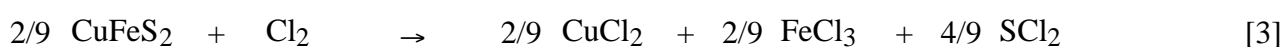
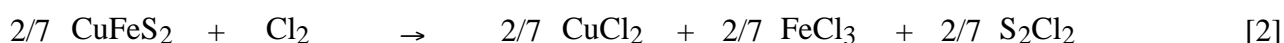
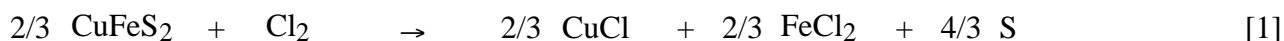
Element	S <sub>1</sub> (LGC)	S <sub>2</sub> (HGC)	Phases	S <sub>1</sub> (LGC)	S <sub>2</sub> (HGC)
Cu	10.8	28.3	CuFeS <sub>2</sub>	31.2	81.7
Fe	29.7	26.3	FeS <sub>2</sub>	23.8	3.0
S	24.0	32.1	ZnS	1.2	6.4
Zn	0.8	4.3	CaCO <sub>3</sub>	3.2	—
Pb	—	3.9	PbSO <sub>4</sub>	—	5.7
Ca	1.3	—	MgO	1.9	—
Si	6.7	0.3	SiO <sub>2</sub>	14.4	0.7
Al	2.1	—	FeO	11.8	—
Mg	1.2	—	Al <sub>2</sub> O <sub>3</sub>	4.0	—
O	14.5	1.6	Clinochlore*	ND	—
<b>Total</b>	<b>91.1</b>	<b>96.8</b>		<b>91.5</b>	<b>97.5</b>

Clinochlore : (Mg, Fe)<sub>6</sub>(Si, Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub>.

### III. THERMODYNAMIC CONSIDERATIONS

The thermodynamic calculations were used to forecast the possible reactions of CuFeS<sub>2</sub>, ZnS, PbS and FeS<sub>2</sub> with chlorine. These calculations were performed using the data listed in References 14 and 15 and the results were given in Figure 3 as evolution of the standard free energy changes ( $\Delta G^\circ$ ) between 25 °C and 1000 °C for the envisaged reactions. Equations [1] through [3] and [7] through [15] were suggested to describe the chlorination of these sulfides. The results indicated that the chlorination of all sulfides is thermodynamically favorable for the considered reactions. The reaction of CuCl with Cl<sub>2</sub> (Eq. 4) was also favorable up to 400 °C. The formation of ferric chloride and sulfur dichloride from ferrous chloride and sulfur monochloride (Eqs. 5 and 6, respectively) were also possible from the thermodynamic point of view. The phase stability diagrams of (Cu, Pb, Zn, Fe)-S-Cl systems at 300 °C showed that CuCl<sub>2</sub>, PbCl<sub>2</sub>, ZnCl<sub>2</sub> and FeCl<sub>3</sub> were the predominant phases of metal-S-Cl system at high partial pressure of chlorine.<sup>[13]</sup>

The chlorides generated from the chlorination of sulfides are characterized by a widely difference in their vapor pressure at a given temperature. Figure 4 shows the evolution of vapor pressure of several chlorides as a function of the temperature.<sup>[16]</sup> The ferric and sulfur chlorides possess a high vapor pressure at temperature lower or equal to 300 °C. Thus, if the chlorination of sulfides could be achieved at this temperature, these chlorides can volatilize leading to a residue containing the valuable metals. It seems that this is the important factor to separate selectively the valuable metals. For this reason, the effects of some parameters on the concentrate's chlorination were studied at 300 °C.



## IV. RESULTS AND DISCUSSION

### A. TGA of non isothermal treatment

The thermogravimetric analysis of the two concentrates (LGC and HGC) under  $\text{Cl}_2+\text{N}_2$  ( $\text{Cl}_2/\text{N}_2 = 1$ ) were carried out between 25 °C and 1000 °C. The heating rate of furnace was about 25 °C/minute. The major constituent of these concentrates ( $\text{CuFeS}_2$ ,  $\text{ZnS}$ ,  $\text{PbS}$ ,  $\text{FeS}_2$ ) as well as  $\text{S}^\circ$  were also treated in the same conditions. Figure 5 traces the percent weight loss (pct WL) of the used samples as a function of temperature.

The chlorination of chalcopyrite started from room temperature. A weight loss observed at about 150 °C could be attributed to the volatilization of the sulfur chlorides. The weight gains observed up to 300 °C is due to the intensive chlorination of the chalcopyrite sample according to Eqs. [1] through [3]. Then, the volatilization of ferric chloride could be the responsible of the pct WL observed up to about 475 °C. The slow down of the weight loss between 550 °C and 700 °C may explain by the partial volatilization of  $\text{CuCl}_2$  and its decomposition into  $\text{CuCl}$  (Eq. 4) followed by the volatilization of cuprous chloride at higher temperatures (Figure 4).

Galena and sphalerite started to react with chlorine at temperature higher than 200 °C and the weight gains recorded at low temperatures were due to the formation of lead and zinc chlorides (Eqs. 7 to 12). The pct WL at temperatures higher than 600 °C and 700 °C for the  $\text{ZnS}$  and  $\text{PbS}$ , respectively were due to the volatilization of zinc and lead chloride (Figure 4).

The substitute of sulfur by chlorine (Eqs. 13 to 15) justified the weight gain detected when the pyrite sample was contacted with chlorine. While the losses of sample at temperatures higher than 250 °C were attributed to the volatilization of the gaseous ferric chloride. About 80 pct of sulfur were volatilized at temperature lower than 400 °C. It is probably that the curve of pct WL of sulfur could be the overlapping of the volatilization curves of sulfur and its chlorides.<sup>[13]</sup>

The curve of the LGC chlorination gathered the characteristics of the  $\text{CuFeS}_2$  and  $\text{FeS}_2$  chlorination curves (Figure 5). This is in good agreement with the composition of this concentrate containing 31.2 pct  $\text{CuFeS}_2$  and 23.8 pct  $\text{FeS}_2$ . About 75 pct of the sample was chlorinated and volatilized at 1000 °C. The final residue was essentially composed of Si, Al and Mg oxides.

The chlorination behavior of the HGC was close to that of the chalcopyrite. The high contents of chalcopyrite (81.7 pct) in this concentrate explain this similarity. More than 95 pct of this concentrate were chlorinated and volatilized at about 850 °C. This was due to low content of the inert compounds in HGC.

## B. Kinetics of chlorination of concentrates

### 1. Effect of gas flow rate

To minimize the impact of external mass transfer on the chlorination kinetics of the copper concentrates, the effect of the flow rate of a gas mixture of  $\text{Cl}_2+\text{N}_2$  ( $\text{Cl}_2/\text{N}_2 = 1$ ) was studied at 300 °C between 8 and 80 L/h. Several of the isothermal chlorination tests of LGC using different flow rates are represented in Figure 6 as the pct WL *versus* chlorination time. The reaction started by a weight increase due to the chlorides' formation. This step was followed by a weight loss of the sample caused by the volatilization of sulfur and iron chlorides. Figure 7 gives the data obtained during the chlorination of HGC in the same conditions as LGC.



Figures 8 (a) and (b) trace, respectively, the evolution of the initial reaction rate of the LGC and HGC as function the gas flow rate. It has been observed that the chlorination of LGC was almost independent of gas flow rates higher than 30 L/h. While the flow rates higher than 50 L/h were required for the chlorination of HGC. To be assured that the mass transfer phenomena will not affect the kinetics of chlorination of the chalcopyrite concentrates, the gas flow rate used for the kinetic study of the chlorination of LGC and HGC were chosen 60 L/h (gas velocity ' $V_g$ ' = 0.83 cm/s) and 72 L/h ( $V_g$  = 0.99 cm/s), respectively.

## 2. Effect of partial pressure of chlorine

It has been studied during the isothermal treatment at 300 °C for both concentrates using a gas mixture of  $Cl_2+N_2$  varying the molar chlorine content in the gas mixture from 10 to 100 pct. Figures 9 and 10 group the evolution of the pct WL as a function of the reaction time for the different chlorine content in the  $Cl_2+N_2$  in the case of LGC and HGC, respectively. These figures contain the calculated limits (expressed as pct WL) 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 supposing a full chlorination of sulfides and volatilization of iron and sulfur compounds.

The effects of chlorine content and reaction time on the selective chlorination of copper concentrates are illustrated in Figures 11 (a) and (b) for LGC and HGC, respectively. As could be expected, the time required to reach the limits of the selective chlorination of both concentrates decreased with the increase of the chlorine content in the gas mixture. A reaction time of 10 minutes seems to be adequate for the selective chlorination of LGC using a gas mixture of  $Cl_2+N_2$  containing 40 pct  $Cl_2$ . Whilst, the selective chlorination of HGC is somewhat more affected by the chlorine content.

In order to define the apparent reaction orders with respect to chlorine for the chlorination of LGC and HGC, the data were represented in Figure 12 as evolution of the initial reaction rate *versus* partial pressure of chlorine on natural logarithm scale. The apparent reaction orders deduced from this figure were about 1.19 and 1.28 for LGC and HGC, respectively. Such values indicate a complex chlorination mechanism consisting probably of intermediate steps.

## 3. Effect of temperature

This effect on the chlorination of LGC was studied by isothermal treatments in a temperature range from 180 °C to 300 °C. Figure 13 shows the evolution of the pct WL during the LGC chlorination with a  $Cl_2+N_2$  gas mixture, having a  $Cl_2/N_2$  molar ratio of 1. The selective chlorination limit ( $L_1$ ) was reached at temperatures higher than 250 °C and for a reaction time of 30

minutes. It seems that the volatilization rate of  $\text{FeCl}_3$  is feeble at temperatures lower than  $250\text{ }^\circ\text{C}$ . Ferric chloride remained in the chlorination residue and can stop the progress of the reaction.

The effect of the temperature on the chlorination of HGC was studied between  $170\text{ }^\circ\text{C}$  and  $300\text{ }^\circ\text{C}$ . Typical isotherms were traced in Figure 14 as the pct WL *versus* time. The chlorination curves for the temperatures lower or equal to  $200\text{ }^\circ\text{C}$  were characterized by a weight increase of the sample for the first three minutes of the treatment. Since then, the weight increase was very slowly. This could be attributed to the presence of chlorides which prevent further chlorination. At temperatures higher than  $220\text{ }^\circ\text{C}$ , the weight increases of the sample was followed by the loss of the sample due to the volatilization of sulfur and iron chlorides. The final weight losses obtained at temperatures higher than  $250\text{ }^\circ\text{C}$  were closed to the calculation limit for the selective chlorination of HGC.

The evolution of weight loss as function of temperature and reaction time were compared in Figures 15 (a) and (b) for the LGC and HGC, respectively. These figures clearly show that for the temperatures higher than  $280\text{ }^\circ\text{C}$  and the reaction time higher than 20 minutes are necessary for the selective chlorination of both concentrates. It has been observed that the residues of HGC chlorination were systematically agglomerated while that of LGC did not undergo this phenomenon. This is probably due to the presence in LGC of inert materials towards chlorine such as quartz and clinocllore that prevent the sample particles' agglomeration.

Attempts were made to evaluate the effect of temperature on the initial reaction rate of chlorination of two concentrates. Figures 16 (a) traces the Arrhenius plots for the chlorination of LGC between  $200\text{ }^\circ\text{C}$  and  $300\text{ }^\circ\text{C}$ . The Arrhenius diagram for the chlorination of HGC from  $170\text{ }^\circ\text{C}$  to  $300\text{ }^\circ\text{C}$  is illustrated in Figure 16 (b). This figure contains also the effect of temperature on the chlorination of sulfur between  $170$  and  $240\text{ }^\circ\text{C}$ .

The chlorination of LGC was characterized by a value of  $E_a$  of about  $21\text{ kJ/mol}$  between  $200\text{ }^\circ\text{C}$  and  $240\text{ }^\circ\text{C}$ . Then, an anomaly was observed in the temperature range from  $240\text{ }^\circ\text{C}$  to  $255\text{ }^\circ\text{C}$  where the chlorination rate decreased with the rise of temperature. To explain this phenomenon, a chalcopyrite sample was chlorinated at  $260\text{ }^\circ\text{C}$  for a reaction time lower than 20 seconds. The chlorination residue was analyzed by XRD and the obtained result is given in Figure 17. As shown by this figure,  $\text{CuCl}$  and  $\text{FeCl}_2$  were detected in the chlorination residue. The ferric chloride was not identified because of its hygroscopic and amorphous character. In presence of cuprous and ferric chlorides, it is possible to form eutectics having a melting point lower than individual chlorides as indicated by Figure 18.<sup>[17]</sup> One of these eutectics formed at about  $260\text{ }^\circ\text{C}$  containing more than 80 pct  $\text{FeCl}_3$ . It is probable that this eutectic was responsible for the anomaly observed between  $240$  and  $255\text{ }^\circ\text{C}$ . The apparent activation energy for the chlorination of LGC between  $255\text{ }^\circ\text{C}$  and  $300$

°C was about 94 kJ/mol indicating that the chemical reaction could be the lowest step of the overall chlorination process.

The chlorination of HGC processed with the value of  $E_a$  (Figure 16 b) of about 1, 50 and 2 kJ/mol in the temperature ranges of 170 °C to 210 °C, 210 °C to 240 °C and 240 °C to 280 °C, respectively.

The low value of the apparent activation energy between 170 °C and 210 °C for the chlorination of HGC suggests that the overall reaction rate could be controlled by the diffusion through the liquid layers. To confirm that, a series of TGA tests was performed as follow :

1. the HGC was chlorinated for 100 minutes by  $\text{Cl}_2+\text{N}_2$  at 200 °C in order to evaluate the evolution of its pct WL during the chlorination,
2. the same sample was chlorinated by  $\text{Cl}_2+\text{N}_2$  at 200 °C for 10 minutes. Then, the chlorination residue was heated at 200 °C in  $\text{N}_2$  to obtain information about the presence of volatile products in the chlorination residue at this temperature. Another HGC sample chlorinated in  $\text{Cl}_2+\text{N}_2$  at 200 °C for 10 minutes was analyzed by XRD,
3. samples of ferric chloride and sulfur were also heated separately in  $\text{N}_2$  at 200 °C for 90 minutes to estimate their volatilization rate.

The curves of these TGA tests are traced in Figure 19. The pct weight loss of the HGC chlorination residue and heated in nitrogen were situated between those of ferric chloride and sulfur heated in the same conditions. This suggests that the sulfur and probably its chlorides as well as ferric chloride were present in the chlorination residue of HGC.

The XRD result of the HGC chlorination residue at 200 °C for 10 minutes and leached at  $\text{pH} \approx 2$  is given in Figure 20. The sulfur was detected in the residue besides the  $\text{CuFeS}_2$  non reacted. These results suggest that the sulfur and/or its chlorides as well as iron chlorides remained in the chlorination residue. Consequently, these compounds can act as a barrier for the diffusion of chlorine towards the sulfides.

The value of the  $E_a$  of about 50 kJ/mol between 210 °C and 240 °C indicates that the chlorination of HGC is still little affected by the temperature. An apparent activation energy of about 54 kJ/mol (Figure 16 b) was obtained for the sulfur chlorination by  $\text{Cl}_2+\text{N}_2$  in the same temperature range. These values suggest that the liquid sulfur and/or its chlorides generated during the chlorination could remain in the residues thus preventing the progress of the reaction. Although the sulfur chlorides were in gaseous state at this temperature range (Figure 4), in presence of sulfur they can coexist in liquid state. Ingraham and Parsons<sup>[18]</sup> mentioned that the sulfur monochloride is a good solvent for sulfur. The presence of dissolved sulfur decreased the activity of sulfur

monochloride very noticeable. Substantial amounts of both materials may be present in a liquid phase even at 250 °C, according to these authors.

The apparent activation energy of the HGC chlorination between 240 °C and 280 °C was found to be about 2 kJ/mol. As mentioned before, Kumar *et al.*<sup>[9]</sup> revealed a value of  $E_a$  2.1 kJ/mol for the chlorination of  $\text{CuFeS}_2$  by  $\text{Cl}_2$  between 400 °C and 550 °C and they mentioned that this low value could be due to highly exothermic nature of the reaction.

The chlorination reactions of sulfides by chlorine are exothermic.<sup>[13, 14]</sup> For instance, the standard enthalpy ( $\Delta H^\circ$ ) of the chlorination of chalcopyrite at 300 °C according to Eq. 3 is equal to -453.7 kJ/mol of  $\text{CuFeS}_2$ . In order to estimate the increase of sample temperature provoked by the heat evolved from the exothermic reactions a series of experiments was performed at 300 °C in a horizontal experimental set described previously.<sup>[13, 19]</sup> About two grams of LGC and HGC samples were chlorinated by  $\text{Cl}_2+\text{N}_2$  containing 15 to 100 pct  $\text{Cl}_2$ . Figure 21 traces the increases of the sample temperature as function of the reaction time for the HGC chlorination. As could be expected, the increase of temperature was higher in case of higher chlorine content in the gas mixture. On the other hand, the temperature increase was observed at the beginning of the treatment. Although, the temperature was measured at the sample surface, an increase of about 30 °C was observed when the chlorination of HGC was carried out using chlorine alone. The same observations were available for the LGC chlorination, but the temperature increase was somewhat lower. This agrees with the lower sulfides content of this concentrate.

The boat experiments using several grams of samples were performed to follow the chlorination rates of copper and iron contained in both concentrates. The chlorination tests using  $\text{Cl}_2+\text{N}_2$  ( $\text{Cl}_2/\text{N}_2 = 1$ ) were conducted from room temperature to 750 °C and the chlorination residues were subjected to the chemical analysis.<sup>[13, 19]</sup> It has been observed that almost full extraction of iron and sulfur chlorinated compounds were achieved at about 300 °C for a reaction time of one to two hours. The calculated limits for the selective chlorination of two concentrates ( $L_1$  and  $L_2$ , respectively) agreed well with the pct weight loss obtained at 300 °C. More than 95 pct of copper was concentrated in treatment residue as  $\text{CuCl}_2$  at this temperature. In the case of HGC, the majority of lead and zinc was found in chlorination residues as metal chlorides. However, small amounts of valuable metal chlorides (Cu, Pb, Zn) were detected in the condensates. As the vapor pressures of these chlorides were negligible at this temperature (Figure 4), their presence in the condensates was probably caused by the formation of gaseous complex metal chlorides between these chlorides and ferric chloride. It is well known that  $\text{FeCl}_3$  ( $\text{Fe}_2\text{Cl}_6$ ) enhances the apparent vapor pressure of the metal chlorides thanks to the synthesis of these binary chlorides.<sup>[20]</sup>

Results reported early<sup>[13, 19]</sup> concerning the use of chlorine technique for the selective extraction of valuable metals from copper concentrate and those described above suggested a simplify flow-sheet represented in Figure 22. 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 presence of the liquid phase in the sulfide-chlorine system suggested that the fluidized bed will not be suitable for the chlorination of sulfides. The reaction time depends on the concentrate composition. The gas-phase of the 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<sup>[21, 22]</sup> to give hematite and chlorine. The last will be used in the chalcopyrite chlorination unit. In addition, ferric chloride can be used as chlorinating agent.<sup>[23]</sup> The sulfur chloride, after its condensation, will be subjected to hydrolysis in order to obtain elementary sulfur.<sup>[24]</sup> However, as mentioned in the literature<sup>[4, 25, 26]</sup>, sulfur monochloride reacted with several sulfides producing metal chlorides and elementary sulfur.

The chlorination residue will leach with acidified water at a needed temperature in order to dissolve the chloride of Cu, Zn, Pb. Others hydrometallurgical treatments will required to recover selectively these metals.

Although the chlorination process was conduced at lower temperature compared with conventional pyrometallurgical ones, the problems related to the equipments' corrosion, the difficulties to proceed in a continuous system, etc. have to be taken into account.

## V. CONCLUSIONS

The chlorination of copper, lead, zinc and iron sulfides is thermodynamically favorable up to 1000 °C. The selective separation of valuable metal chlorides from iron and sulfur chlorides at temperatures approaching 300 °C was possible thanks to difference in the vapor pressure of these two groups of chlorides.

During non isothermal treatment, the complete chlorination of the selected sulfides and volatilization of the reaction products can be classified by following descending order :  $S > FeS_2 > CuFeS_2 > ZnS > PbS$ . The overall chlorination behavior of low grade concentrate up to at least 500 °C was intermediate between that of  $FeS_2$  and  $CuFeS_2$  agreeing with the chemical composition of this concentrate. The behavior of HGC appeared to be closed to that of  $CuFeS_2$ .

The initial chlorination rate of two concentrates was affected by the partial pressure of chlorine. The apparent reaction orders with respect to chlorine at 300 °C were 1.19 and 1.28 for

LGC and HGC, respectively. However, the chlorine content of about 40 pct during the chlorination for time higher than 10 minutes was sufficient to achieve almost selective chlorination of both concentrates.

Excepted for the chlorination of LGC between 255 °C et 300 °C for which the apparent activation energy was about 94 kJ/mol, the effect of temperature on the initial rate of chlorination of both concentrates was feeble. The presence of liquid and solid products' layer as well as the exothermic nature of the chlorination reactions seem to be responsible of low value of the apparent activation energy.

The selective separation of iron and sulfur chlorides from those of valuable metals was possible during the chlorination of the chalcopyrite concentrates at 300 °C for a reaction time less two hours. More than 95 pct of copper was concentrated in treatment residue free from iron and sulfur.

The obtained results confirmed that chlorination will be seen as an attractive technique for the treatment of sulfides at low temperatures without SO<sub>x</sub> emissions.

## **ACKNOWLEDGMENTS**

This work was performed in the frame of contract N° BRE2-CT92-0173 thanks to the financial support of the European Union (DG-XII). The authors thank Dr. H. L. Schmidt for discussion, suggestion and help. They also would like to thank Dr. J. C. Mugica (INASMET, San Sebastian, Spain) and Dr. M. Coelho (INETI, Lisbon, Portugal) for providing samples and technical discussions. Authors are indebted to A. Bonazébi, M. Djona, S. Ivanaj and N. Mirghaffari for discussions and help on different subjects and to Mrs. C. Tanchel for technical and administrative support.

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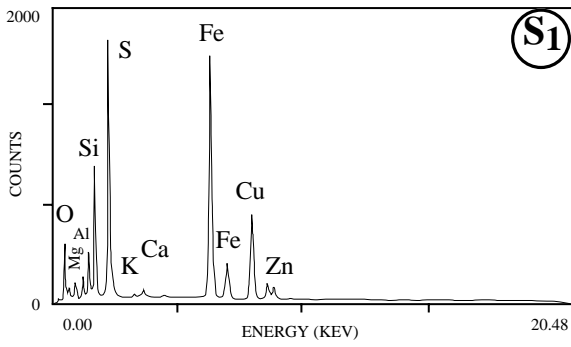


# Kinetics of Chlorination of Chalcopyrite Concentrates

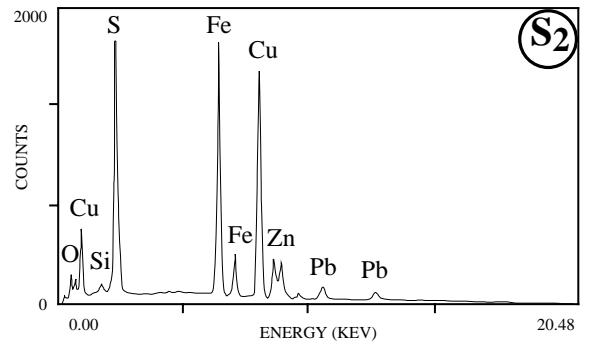
N. KANARI, E. ALLAIN\*, N. MENAD\*\* and I. GABALLAH

## Figure Captions

- Figure 1 : Results of SEM of two chalcopyrite concentrates.
- Figure 2 : Results of X-ray diffraction of two chalcopyrite concentrates.
- Figure 3 : Evolution of the standard free energy changes ( $\Delta G^\circ$ ) as a function of temperature for the chlorination of the compounds contained in the chalcopyrite concentrates.<sup>[14,15]</sup>
- Figure 4 : Evolution of vapor pressure of several chlorides.<sup>[16]</sup>
- Figure 5 : TG analysis of sulfides and two concentrates in  $\text{Cl}_2+\text{N}_2$ .
- Figure 6 : Isotherms of chlorination of LGC with  $\text{Cl}_2+\text{N}_2$  using various gas flow rates.
- Figure 7 : Isotherms of chlorination of HGC with  $\text{Cl}_2+\text{N}_2$  using various gas flow rates.
- Figure 8 : Chlorination of (a) LGC and (b) HGC as a function of flow rate of  $\text{Cl}_2+\text{N}_2$ .
- Figure 9 : Isotherms of chlorination of LGC using different chlorine contents in the  $\text{Cl}_2+\text{N}_2$  gas mixture.
- Figure 10 : Isotherms of chlorination of HGC using different chlorine contents in the  $\text{Cl}_2+\text{N}_2$  gas mixture.
- Figure 11 : Effects of the chlorine content in the gas mixture and reaction time on the chlorination of (a) LGC and (b) HGC.
- Figure 12 : Apparent reaction orders with respect to chlorine for the chlorination of LGC and HGC.
- Figure 13 : Isotherms of chlorination with  $\text{Cl}_2+\text{N}_2$  of LGC between 200 °C and 300 °C.
- Figure 14 : Isotherms of chlorination with  $\text{Cl}_2+\text{N}_2$  of HGC between 170 °C and 300 °C.
- Figure 15 : Effects of temperature and reaction time on the chlorination with  $\text{Cl}_2+\text{N}_2$  of (a) LGC and (b) HGC.
- Figure 16 : Arrhenius plots for the chlorination of (a) LGC and (b) HGC with  $\text{Cl}_2+\text{N}_2$ .
- Figure 17 : XRD result of the chlorination residue of chalcopyrite at 260 °C,  $t \leq 20$  seconds.
- Figure 18 : Phases' diagram of  $\text{CuCl}-\text{FeCl}_3$  system<sup>[17]</sup>.
- Figure 19 : Behavior of chlorination residue of HGC, of sulfur and  $\text{FeCl}_3$  at 200 °C in  $\text{N}_2$ .
- Figure 20 : XRD result of the residue obtained during the HGC chlorination at 200 °C for 10 minutes (leached at  $\text{pH} \approx 2$ ).
- Figure 21 : Increase of temperature during the chlorination of HGC in a horizontal experimental set using different chlorine contents in  $\text{Cl}_2+\text{N}_2$  gas mixture.
- Figure 22 : Suggested flow-sheet for the extraction of valuable metal chlorides by chlorination.



(a)



(b)

Fig. 1 : Results of SEM of two chalcopyrite concentrates.

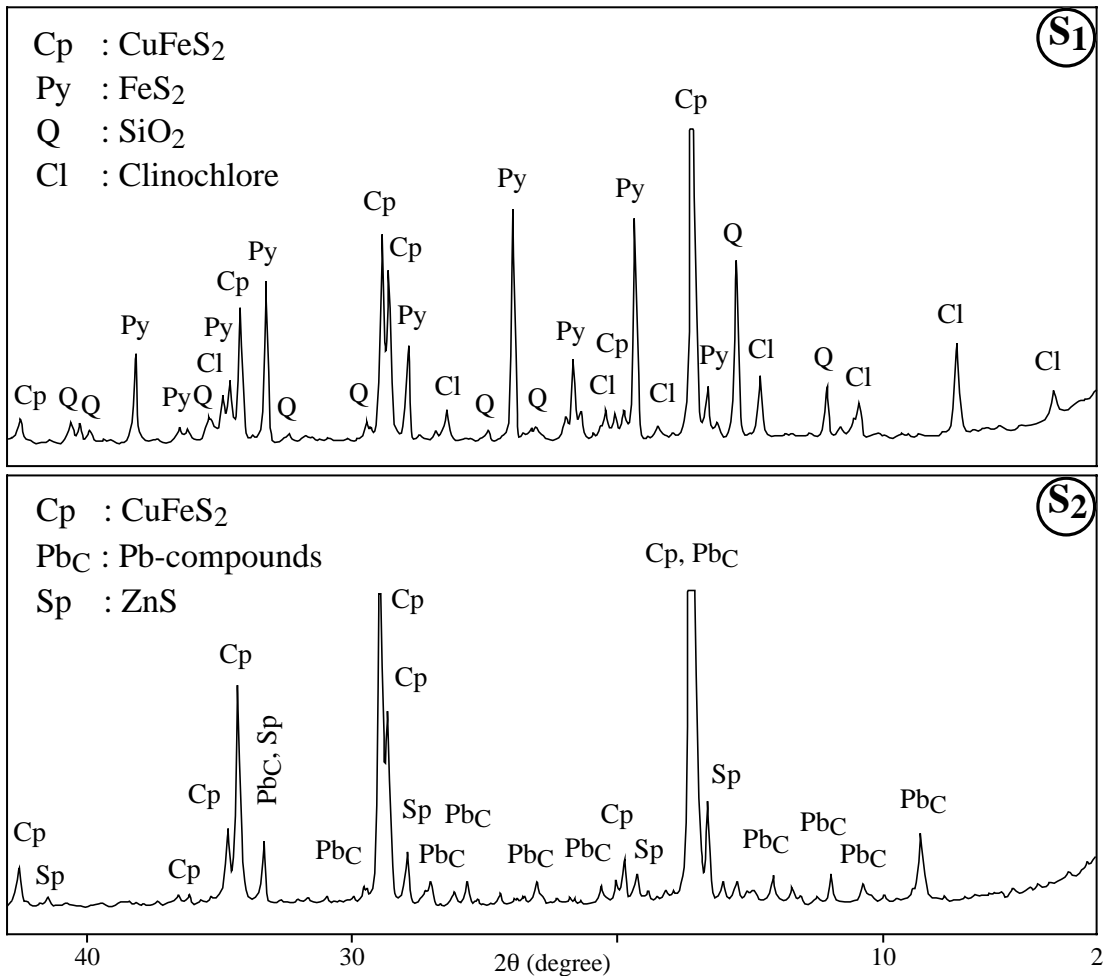


Fig. 2 : Results of X-ray diffraction of two chalcopyrite concentrates.

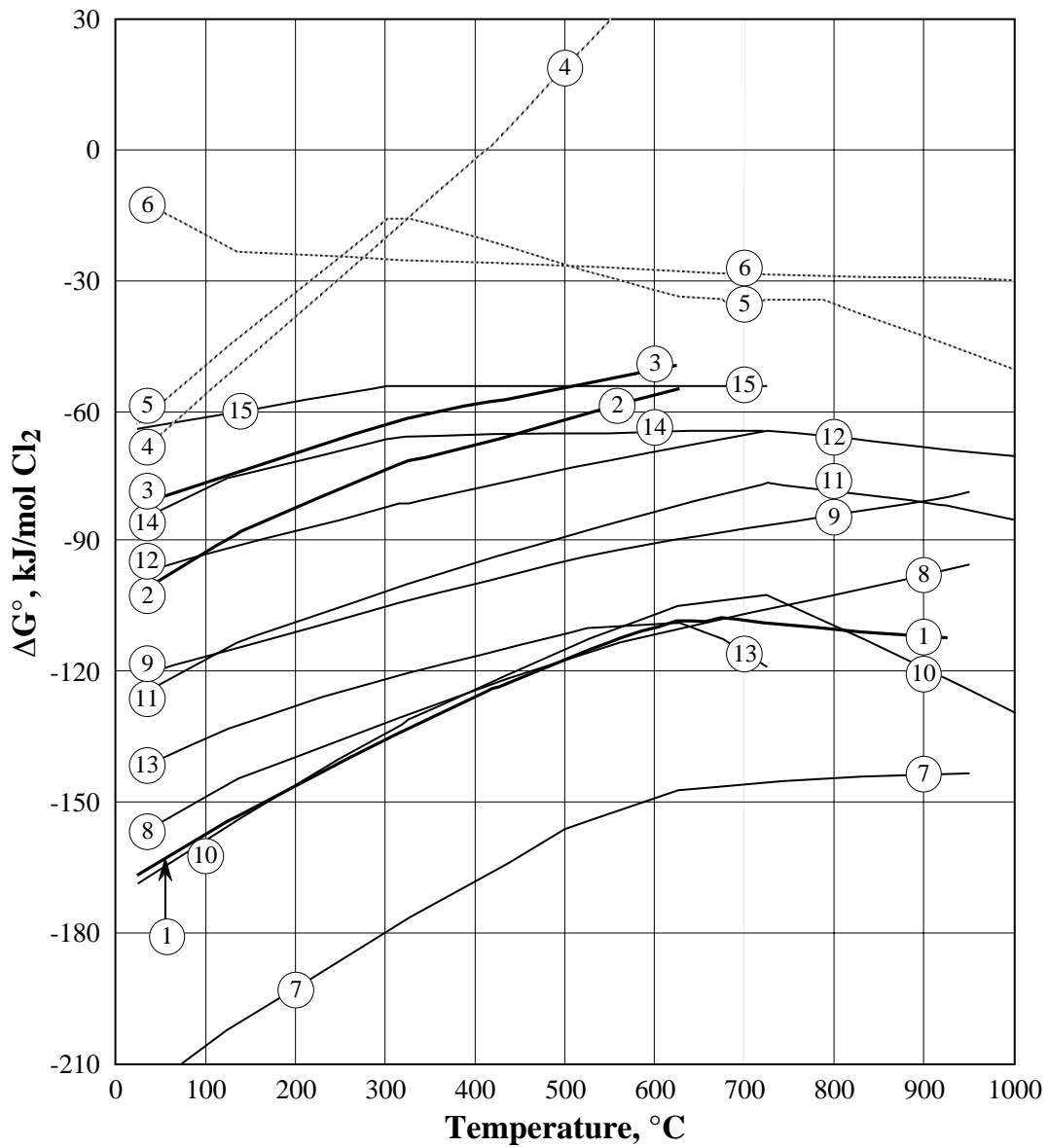


Fig. 3 : Evolution of the standard free energy changes ( $\Delta G^\circ$ ) as a function of temperature for the chlorination of the compounds contained in the chalcopyrite concentrates<sup>[14,15]</sup>.

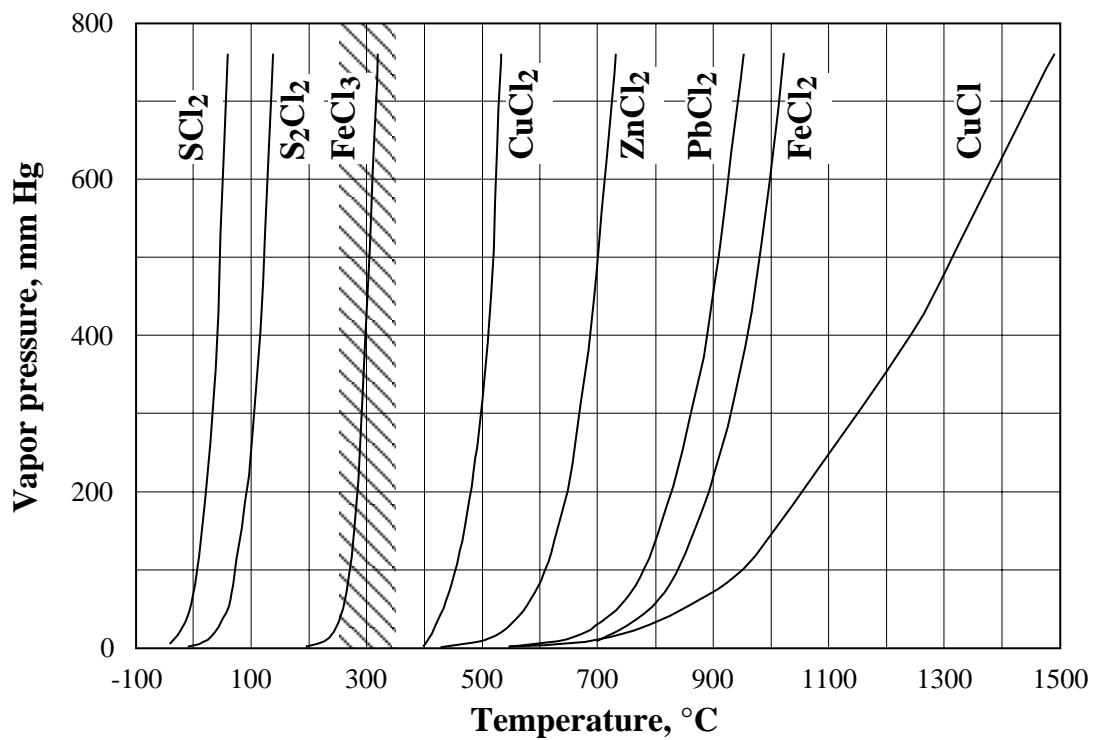


Fig. 4 : Evolution of vapor pressure of several chlorides<sup>[16]</sup>.

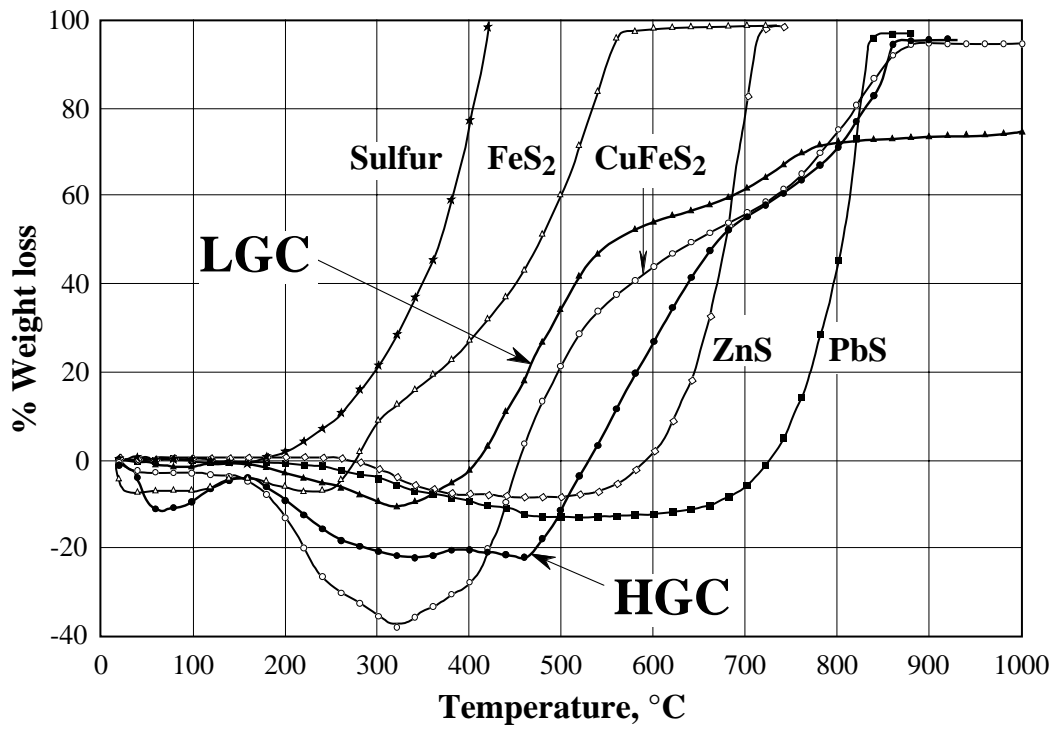


Fig. 5 : TG analysis of sulfides and two concentrates in  $\text{Cl}_2 + \text{N}_2$ .

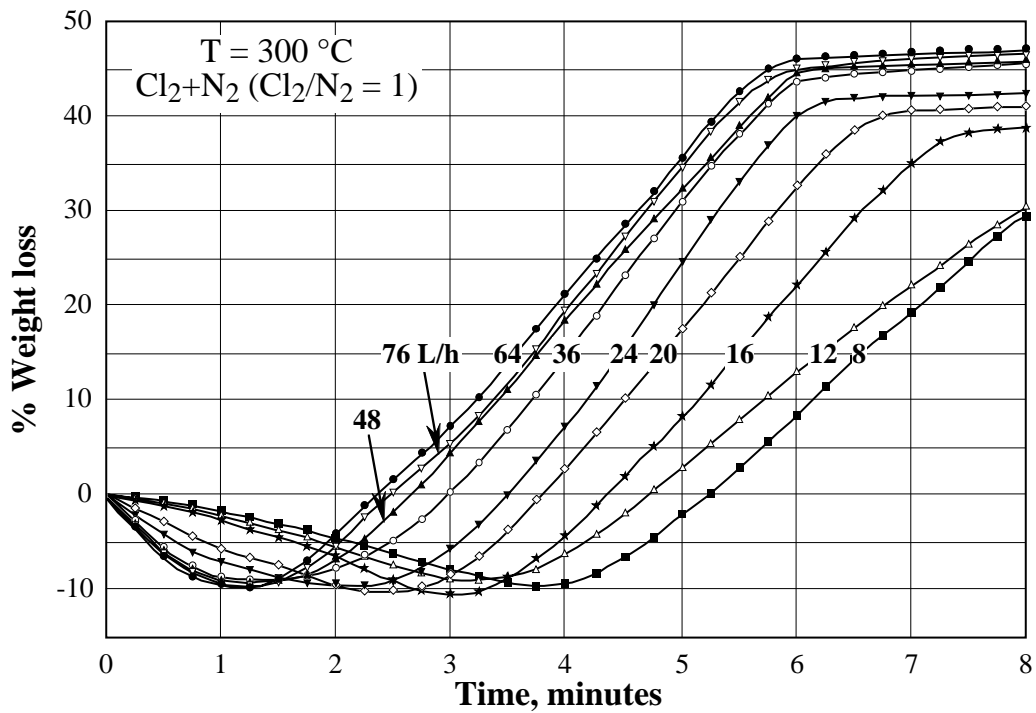


Fig. 6 : Isotherms of chlorination of LGC with  $\text{Cl}_2 + \text{N}_2$  using various gas flow rates.

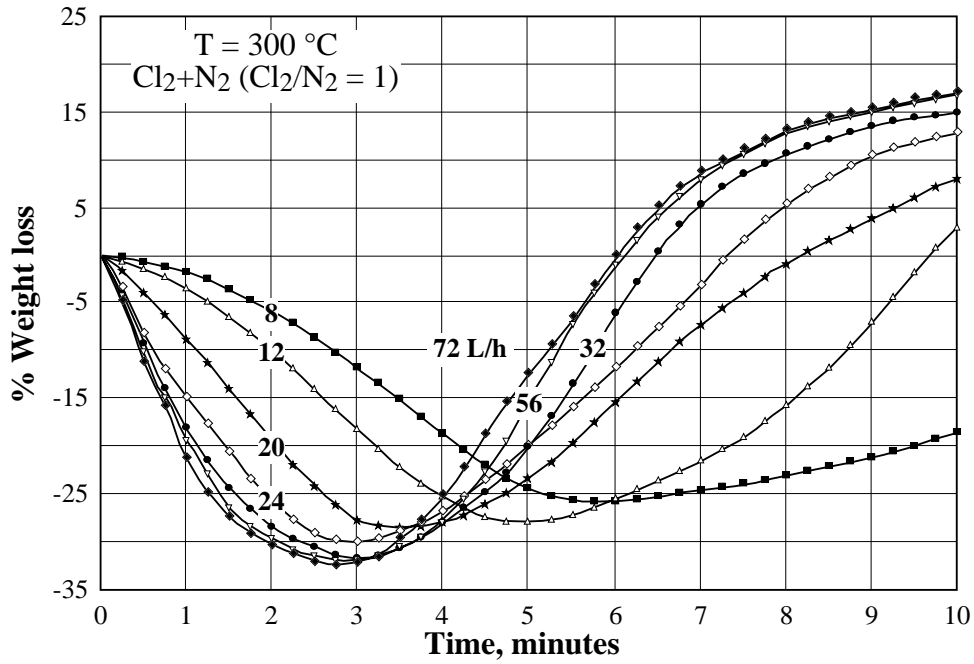
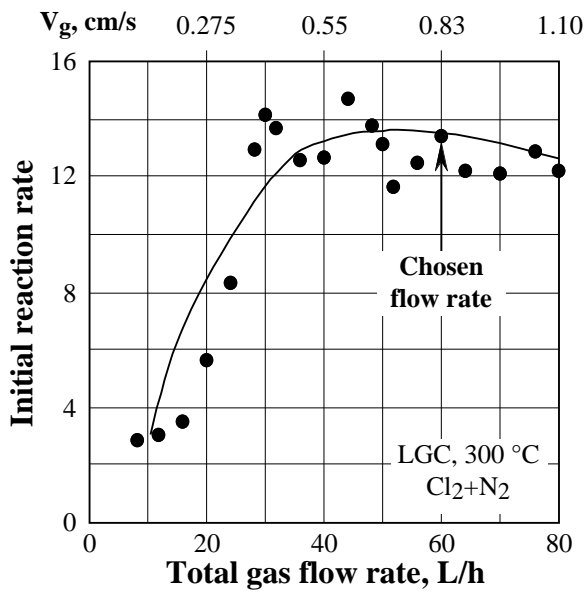
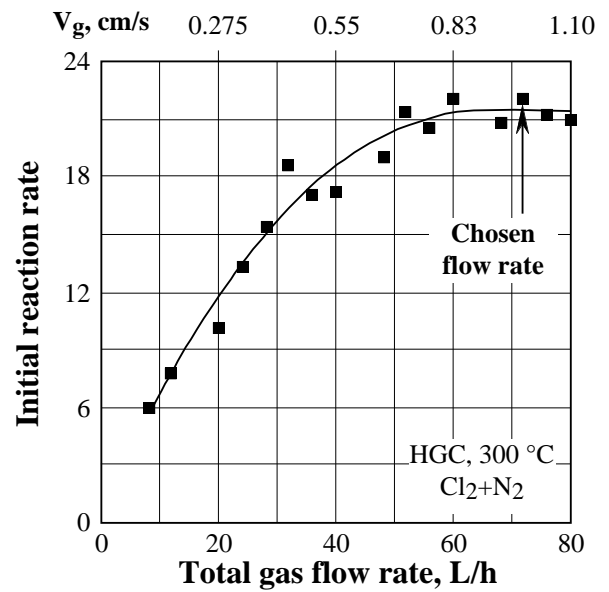


Fig. 7 : Isotherms of chlorination of HGC with Cl<sub>2</sub>+N<sub>2</sub> using various gas flow rates.

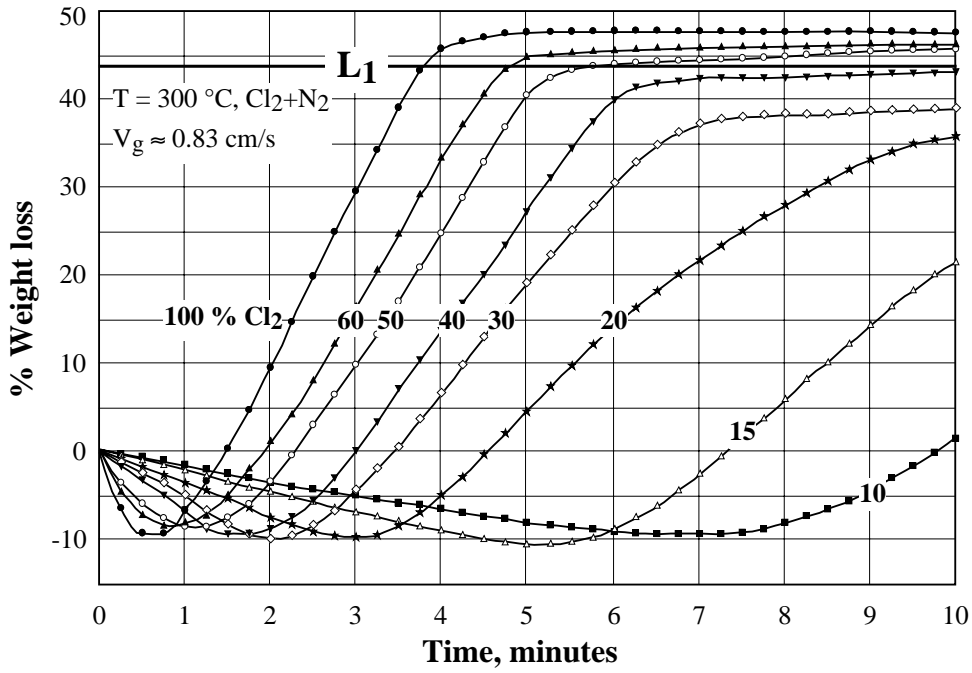


(a)



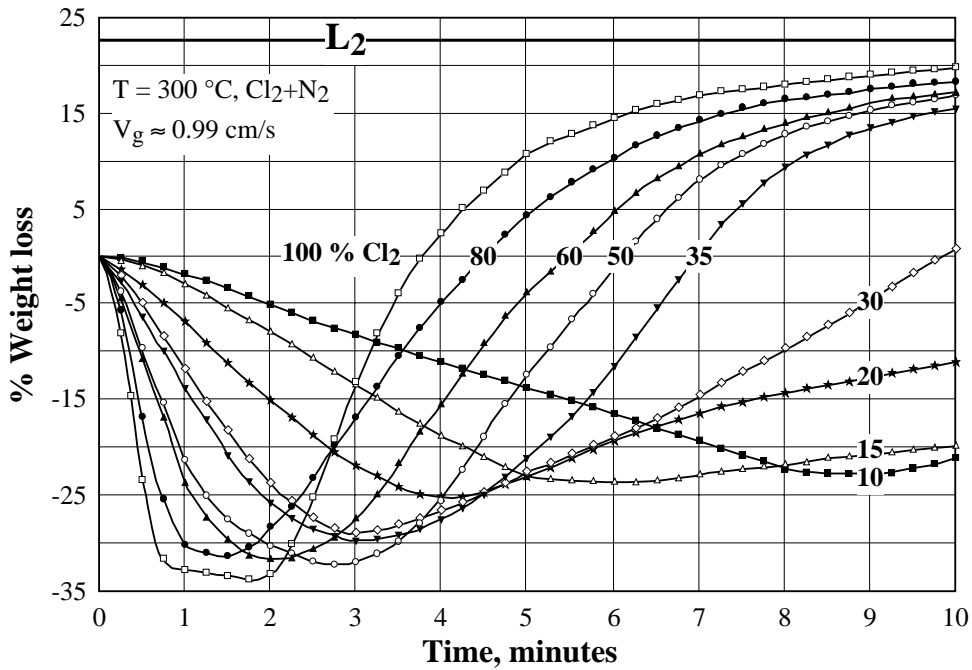
(b)

Fig. 8 : Chlorination of (a) LGC and (b) HGC as a function of flow rate of Cl<sub>2</sub>+N<sub>2</sub>.



L1 : full chlorination of sulfides and volatilization of iron and sulfur chlorinated compounds for LGC.

Fig. 9 : Isotherms of chlorination of LGC using different chlorine contents in the  $\text{Cl}_2+\text{N}_2$  gas mixture.



L2 : full chlorination of sulfides and volatilization of iron and sulfur chlorinated compounds for HGC.

Fig. 10 : Isotherms of chlorination of HGC using different chlorine contents in the  $\text{Cl}_2+\text{N}_2$  gas mixture.

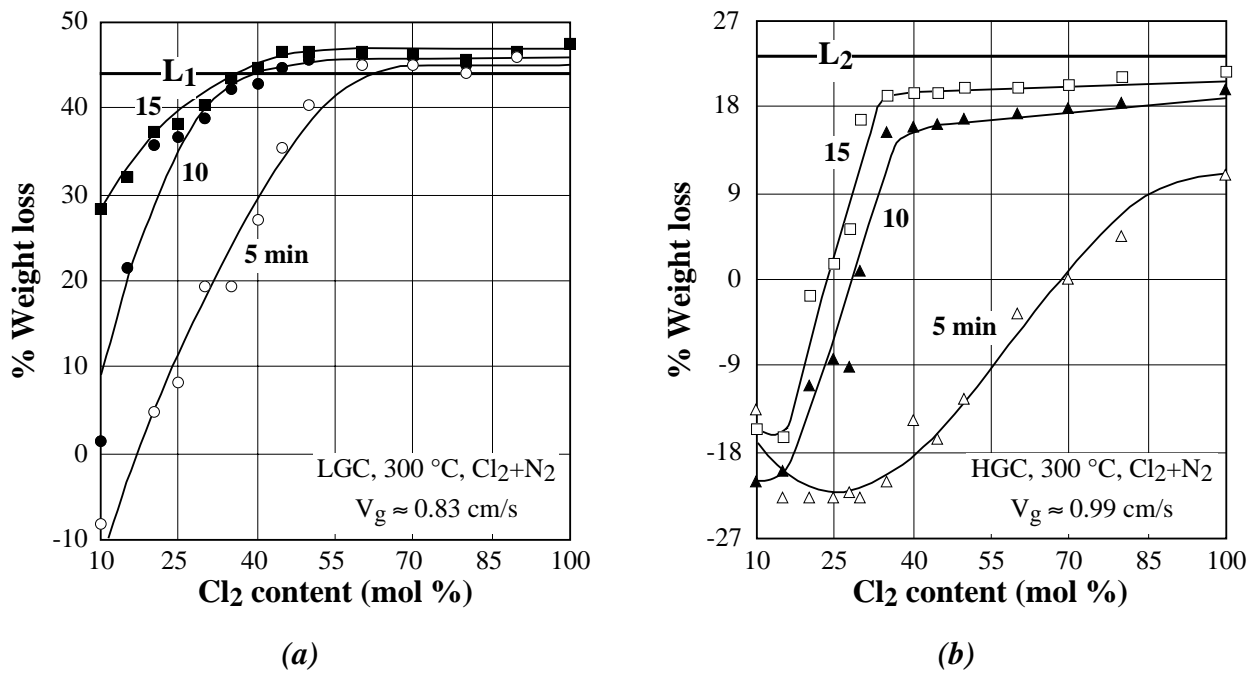


Fig. 11 : Effects of the chlorine content in the gas mixture and reaction time on the chlorination of (a) LGC and (b) HGC.

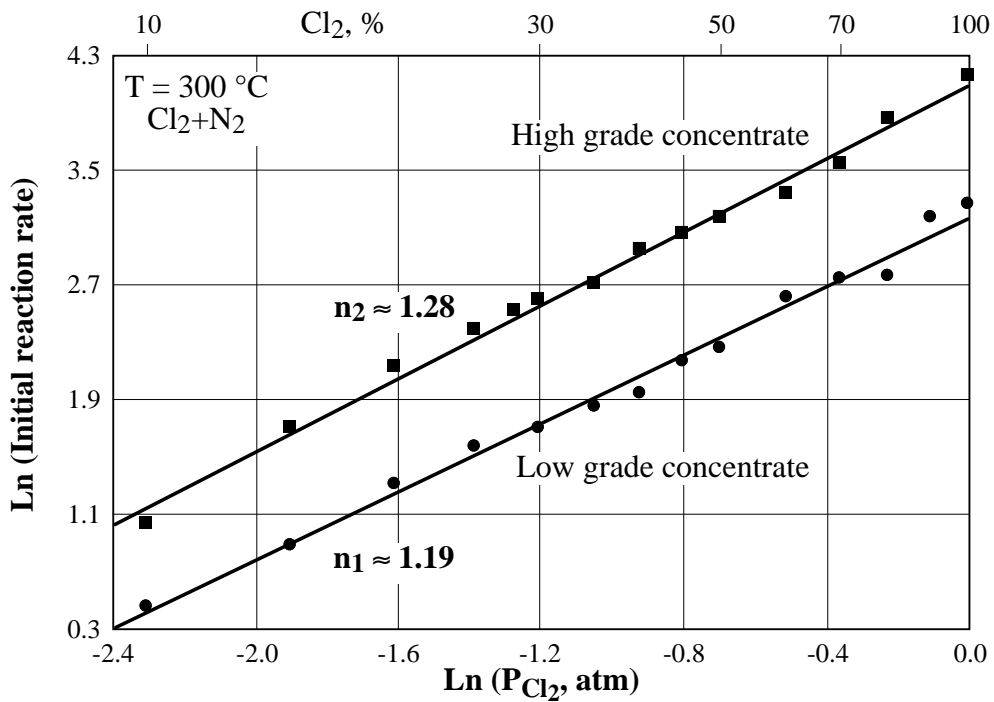
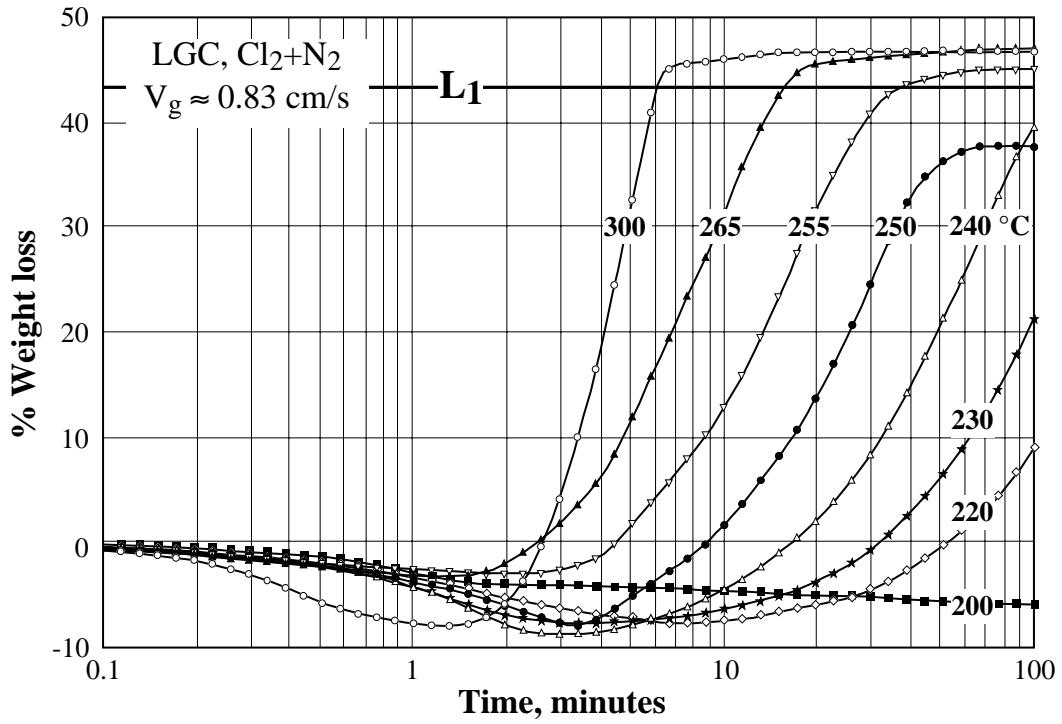
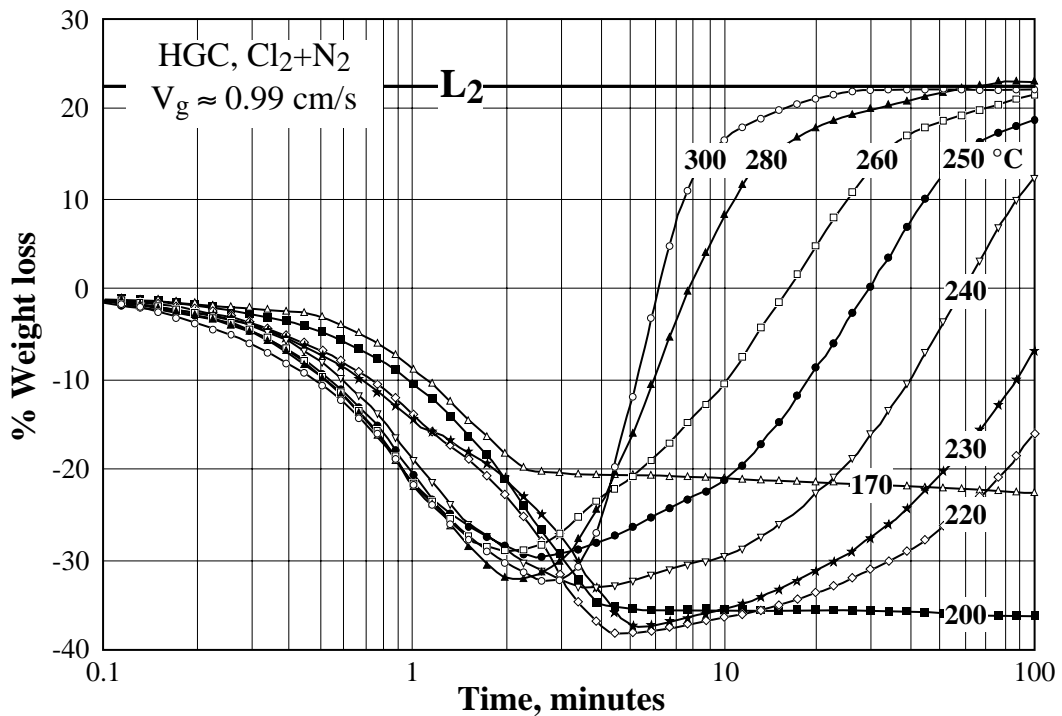


Fig. 12 : Apparent reaction orders with respect to chlorine for the chlorination of LGC and HGC.



L<sub>1</sub> : full chlorination of sulfides and volatilization of iron and sulfur chlorinated compounds for LGC.

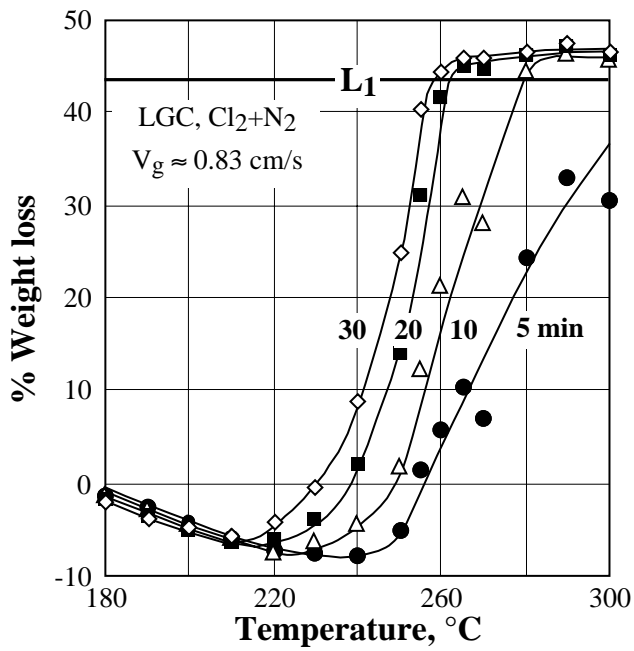
Fig. 13 : Isotherms of chlorination with Cl<sub>2</sub>+N<sub>2</sub> of LGC between 200 °C and 300 °C.



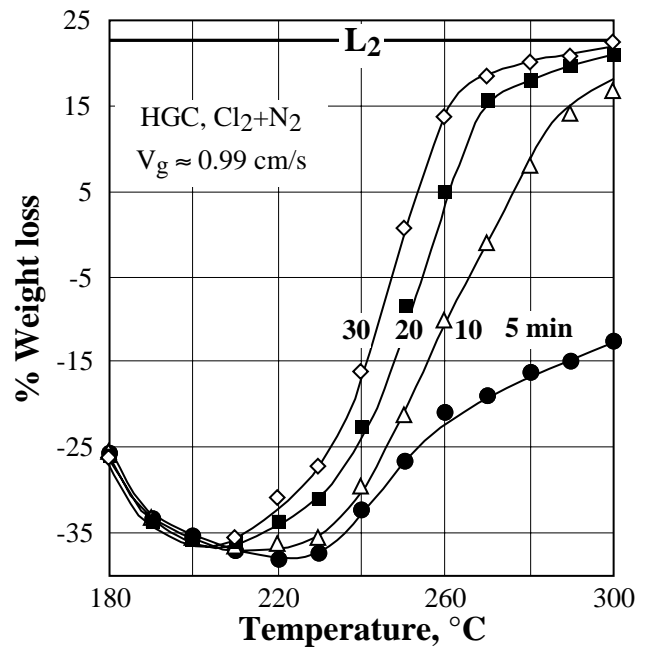
L<sub>2</sub> : full chlorination of sulfides and volatilization of iron and sulfur chlorinated compounds for HGC.

Fig. 14 : Isotherms of chlorination with Cl<sub>2</sub>+N<sub>2</sub> of HGC between 170 °C and 300 °C.



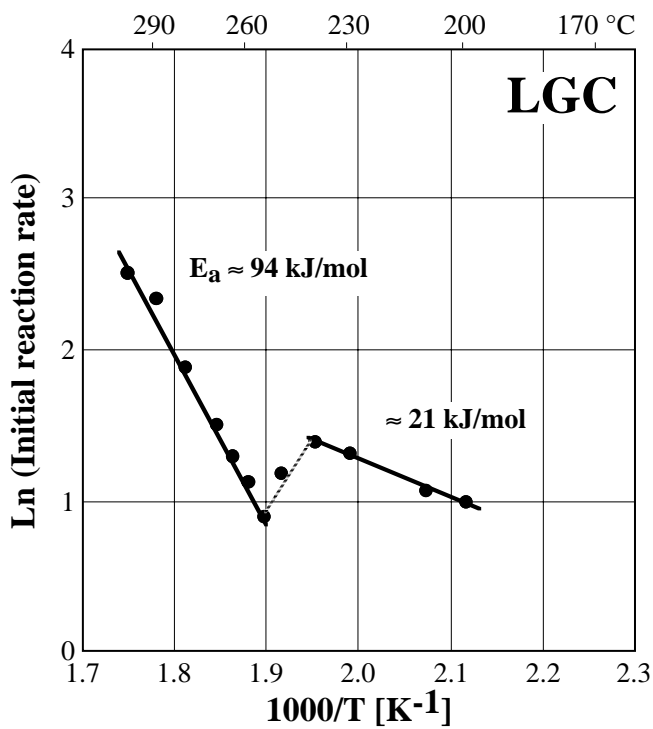


(a)

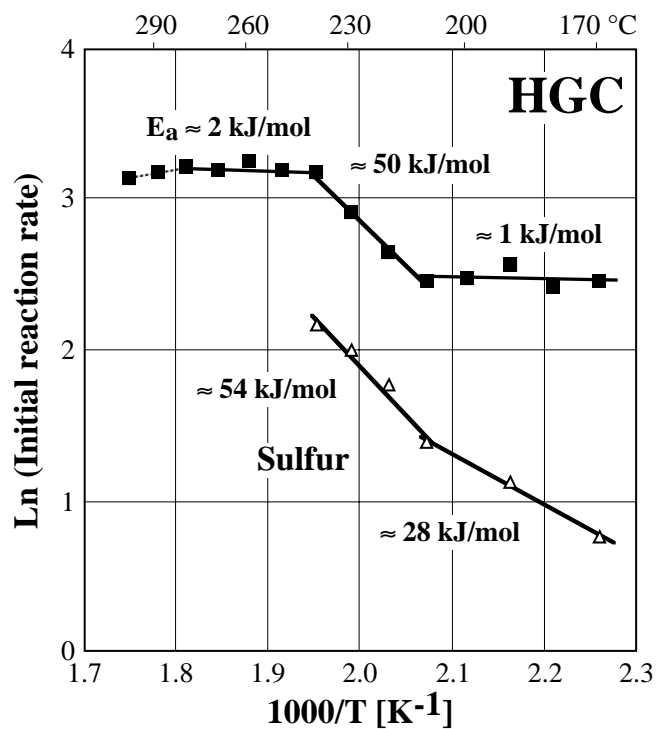


(b)

Fig. 15 : Effects of temperature and reaction time on the chlorination with  $\text{Cl}_2+\text{N}_2$  of (a) LGC and (b) HGC.



(a)



(b)

Fig. 16 : Arrhenius plots for the chlorination of (a) LGC and (b) HGC with  $\text{Cl}_2+\text{N}_2$ .

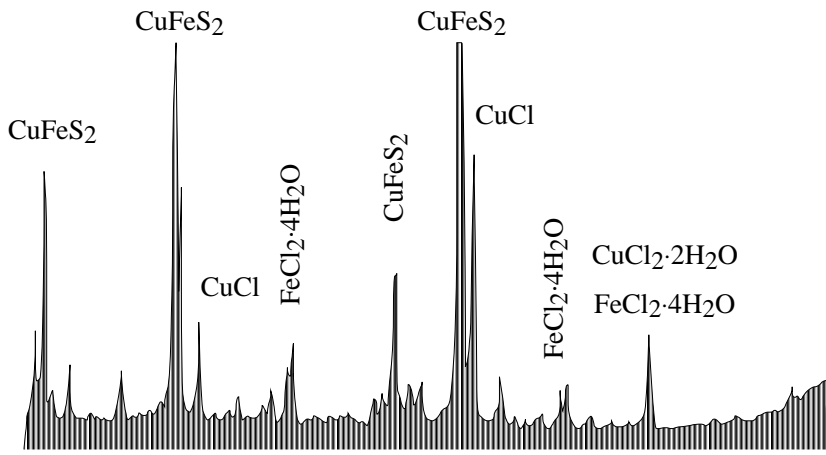


Fig. 17 : XRD result of the chlorination residue of chalcopyrite at 260 °C,  $t \leq 20$  seconds.

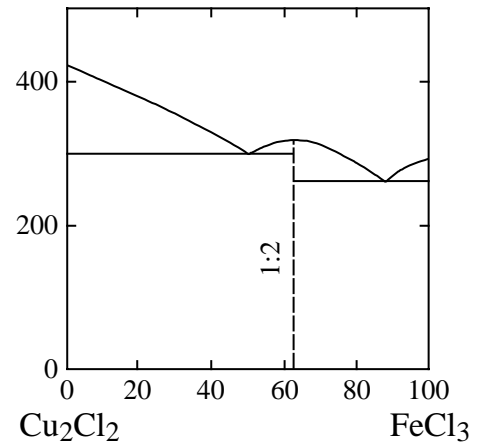


Fig. 18 : Phases' diagram of CuCl-FeCl<sub>3</sub> system.[17]

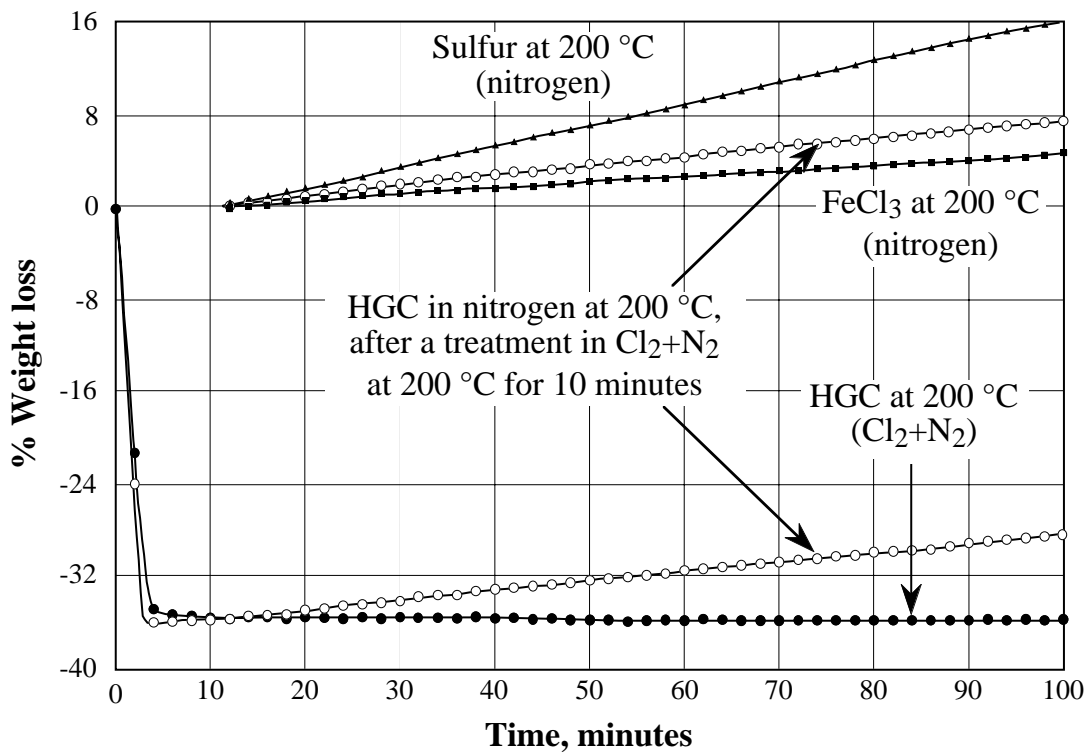


Fig. 19 : Behavior of chlorination residue of HGC, of sulfur and FeCl<sub>3</sub> at 200 °C in N<sub>2</sub>.

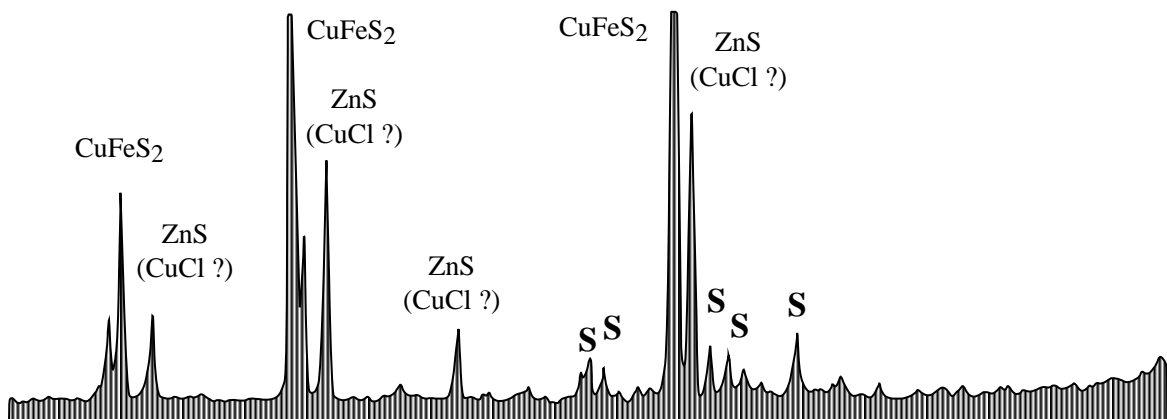


Fig. 20 : XRD result of the residue obtained during the HGC chlorination at 200 °C for 10 minutes (leached at  $\text{pH} \approx 2$ ).

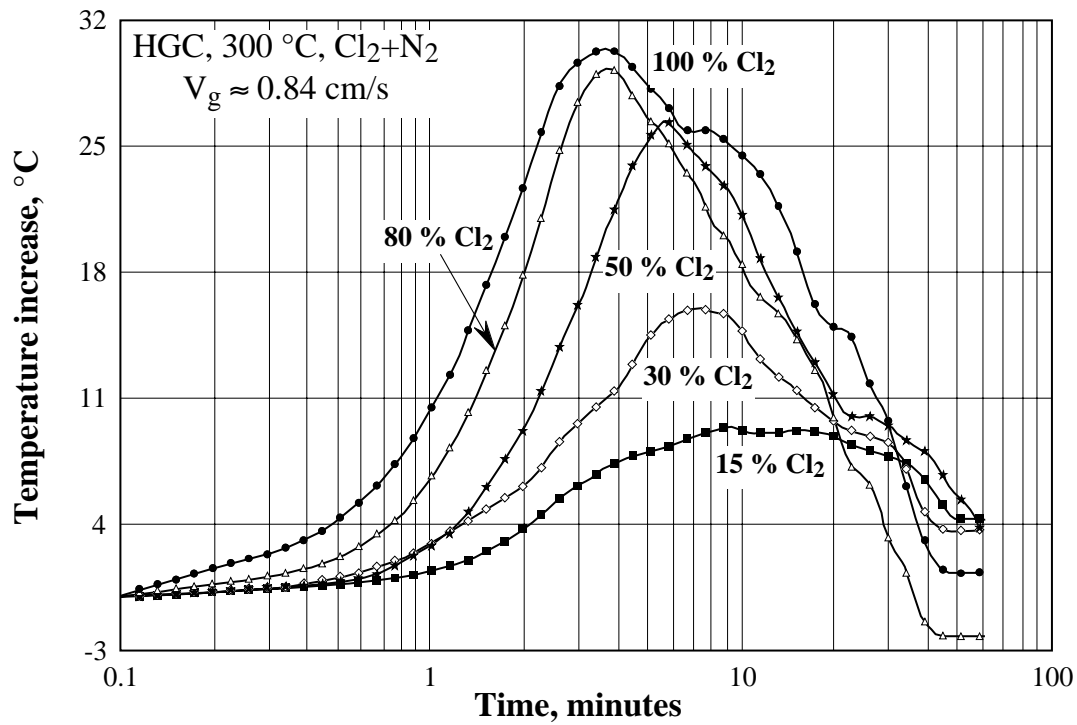


Fig. 21 : Increase of temperature during the chlorination of HGC in a horizontal experimental set using different chlorine contents in Cl<sub>2</sub>+N<sub>2</sub> gas mixture.

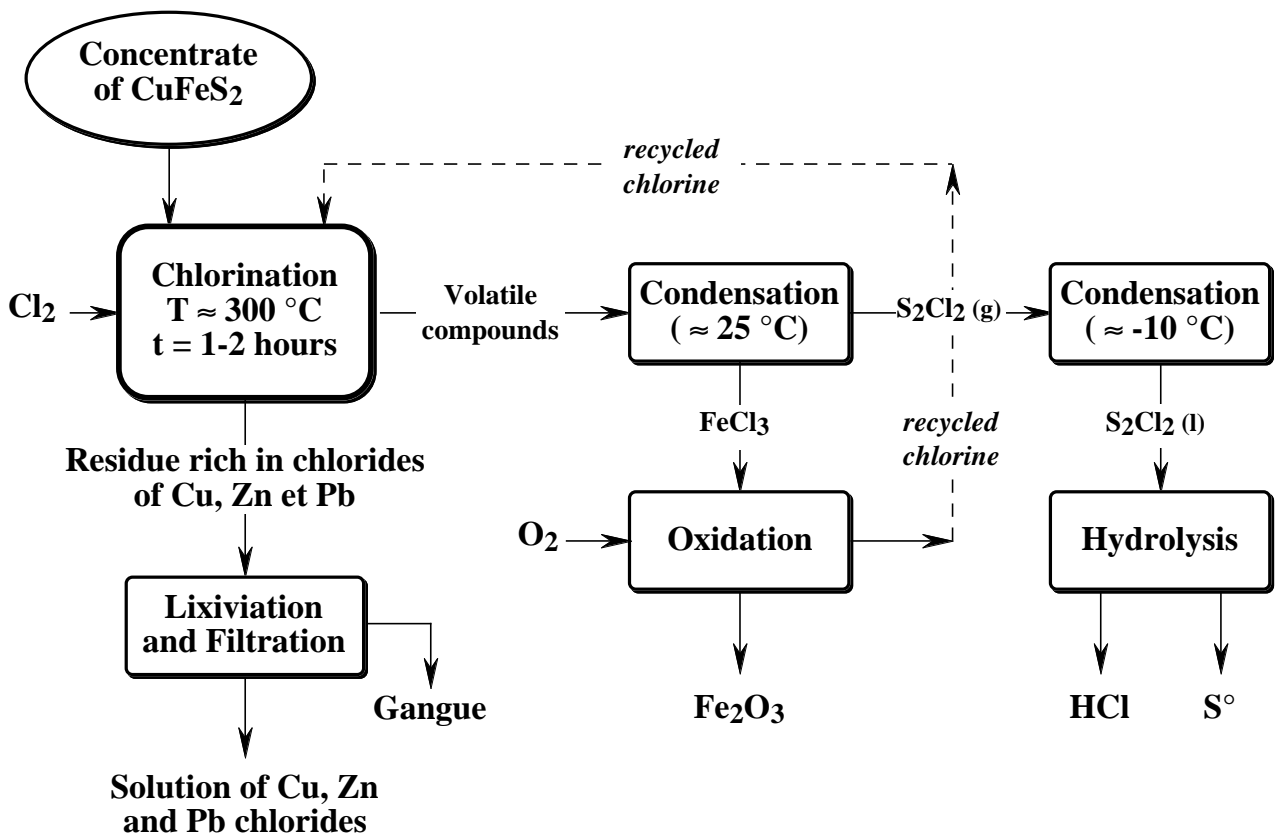


Fig. 22 : Suggested flow-sheet for the extraction of valuable metal chlorides by chlorination.