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An overview study of chlorination reactions applied to the primary extraction and recycling of metals and to the synthesis of new reagents

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ABSTRACT

Energy intensive classical metallurgical processes, the depletion of high-grade ores and primary sources push the scientific and technical communities to treat lean and complex ores as well as secondary metal resources for the recovery of valuable metals. Chlorination technique could be a suitable technology for this purpose. This paper summarizes laboratory experimentation of chlorination processes developed for the extraction of tantalum and niobium from their bearing materials, the upgrading of chromite, the treatment of sulfide concentrates, and the decontamination of jarosite, as well as for the synthesis of potassium ferrate.

Each investigation started by a thermodynamic study of different systems (M–O–Cl, M–S–Cl, M = metal) including the calculations of the standard free energy of chlorination reactions and phase stability diagrams of these systems. The kinetics of these chlorination reactions was studied by thermogravimetric analysis. The effects of total gas flow rate, temperature, individual reactant partial pressures, etc., on the chlorination reaction rate were investigated. Besides, experiments were also conducted in tubular furnaces. Several different qualitative and quantitative analyses methods were used to evaluate the selectivity and performance of the chlorination processes.

The results reported in this paper show the advantages of the chlorination technology in terms of energy saving, selectivity of the processes, and recovery rate of valuable metals. They also demonstrate the possibility to treat lean raw materials, to improve the decontamination of wastes, to generate environmentally safer residues, to engineer new compounds, etc.

1. Introduction

Chlorine is one of the major inorganic chemicals. Its production and consumption level is a reliable index of the importance of the chemical industry of a country. As mentioned in Ref. [1], there are more than 500 chlor-alkali producers at over 650 sites around the globe, with a total annual production capacity of over 55 million tonnes of chlorine.

It is well known that chlorine possesses a high reactivity towards many compounds at relatively low temperature. This property drove the metallurgists to use chlorine for the extraction of valuable elements from their bearing materials. Besides, the depletion of high-grade ores and primary sources necessitated the treatment of leaner and more complex ores as well as the recycling of secondary materials.

With this in perspective, during the last two decades the authors have been focusing their efforts on developing several chlorination techniques for the treatment of numerous raw materials and solid industrial wastes [2–30]. The literature pertaining to specific processes is described here. This paper scope is to highlight some of the most important findings concerning the chlorination processes published earlier as listed below.

- Recovery of Ta and Nb compounds from their bearing materials [2,3,9,14,15],
- recycling of spent hydrorefining catalyst and recovery of Co, Ni, Mo and V [4,10,11–13],
- upgrading of chromite concentrates and/or extraction of valuable elements [6,8,17–21,23–28],
- low temperature treatment of copper concentrate [6,22,29],
- decontamination of various non-ferrous residues [5,7,16],
- recycling of ferrous sulfate *via* synthesis of potassium ferrate [8,30].

The thermodynamic aspects such as free energy calculations 'ΔG°' and phase stability diagrams of specific cases were studied in detail. The outputs were used for both undertaking the choice of a suitable chlorinating agent ($Cl_2 + CO$, Cl_2, $Cl_2 + O_2$, etc.) and

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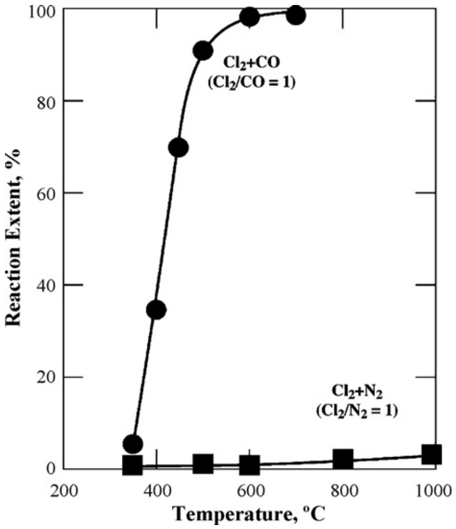

Fig. 1. Chlorination of Al_2O_3 by $Cl_2 + N_2$ and $Cl_2 + CO$.

interpreting the kinetic results. Attempts were also made to resolve any discrepancies between thermodynamic and kinetic data.

2. Experimental

The kinetics of the chlorination reactions was studied by thermogravimetric analysis 'TGA' using a CAHN 1000 microbalance with a sensitivity of 10 μg. The effects of total gas flow rate, temperature, reactants partial pressures, etc., on the chlorination reaction rate were investigated. Laboratory scale experimentations were carried out using horizontal set-ups described previously [2–8]. These apparatuses are generally composed of a gas-metering unit followed by a gas purification one and a horizontal furnace equipped with a temperature controller. The explored temperature range varied from 20 °C to 1050 °C depending on the sample type and chlorination mixture used. The gaseous reaction products were recovered in condensers. Oxychlorides and/or chlorides volatile at room temperature were condensed in a second step vessel at a temperature of about −35 °C. The output gases were purified before their release to the atmosphere. Several qualitative and quantitative analyses methods were used to evaluate the selectivity and performance of the different chlorination processes.

3. Brief thermodynamic and kinetics aspects

The first investigation step of each study was the calculation of standard free energy changes of the considered reactions. The software 'HSC' thermochemical database [31] was mostly used for this purpose. Results showed that the chlorination of several oxides becomes favorable only in the presence of a reducing agent such as carbon monoxide (CO). As an example, the chlorination of Al_2O_3 with Cl_2 and its carbochlorination by $Cl_2 + CO$ could be described by Eq. (1) and (2), respectively. From thermodynamic point of view, the chlorination of Al_2O_3 at 700 °C is not feasible with a value of ΔG° of about 99 kJ/mol, while its reaction with $Cl_2 + CO$ is largely favorable. The experimental results of chlorination and carbochlorination of Al_2O_3 (Fig. 1) confirmed the thermodynamic prediction. Full carbochlorination of alumina was achieved at about 600 °C, while it seems to be inert in pure chlorine up to 1000 °C. This indicates that alumina can be used as construction material for chlorination reactors operating in absence of reducing medium.

$$\tfrac{1}{3}Al_2O_3 + Cl_2 \rightarrow \tfrac{2}{3}AlCl_3 + \tfrac{1}{2}CO_2 \quad \Delta G^\circ(700\,^\circ C)(kJ/mol\,Cl_2) = 99.4 \qquad (1)$$

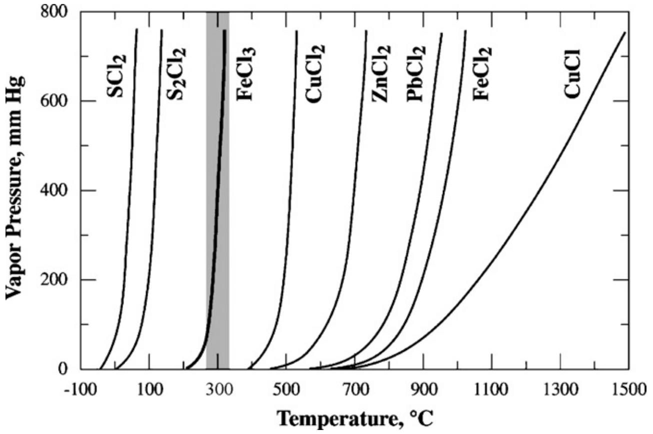

Fig. 2. Evolution of vapor pressure of several chlorides [32].

$$\tfrac{1}{3}Al_2O_3 + Cl_2 + CO \rightarrow \tfrac{2}{3}AlCl_3 + CO_2$$
$$\Delta G^\circ(700\,^\circ C)(kJ/mol\,Cl_2) = -45.5 \qquad (2)$$

An advantage of the chlorination process is the low melting and boiling points of the generated chlorides as well as the difference between their vapor pressures in the explored chlorination temperature range. As an example, the chlorination of sulfides ($CuFeS_2$, FeS_2, PbS and ZnS) is thermodynamically favorable at about 300 °C [6,22,29]. However, the selective separation of valuable metal chlorides ($CuCl_2$, $PbCl_2$ and $ZnCl_2$) from those of ferric and sulfur chlorides was feasible due to the difference in vapor pressure between the two groups of chlorides at 300 °C (Fig. 2).

The chlorination in the presence of oxygen (oxychlorination) was sometimes used to separate selectively a group of elements. This is supported by the fact that the presence of oxygen in the system could lead to different thermodynamic feasibility of the specific oxychlorination reactions. As shown in Fig. 3, the chlorination of ZnO at 750 °C by a mixture $Cl_2 + O_2$ ($Cl_2/O_2 = 1$) will generate $ZnCl_{2(g)}$ as predominant phase while hematite seems to be a stable phase under this conditions. This property of oxychlorination was used to remove selectively zinc from jarosite [7]. Similarly, oxychlorination can successfully be applied for Zn recovery from electric arc furnace dust. The feasibility of this procedure is now under investigation.

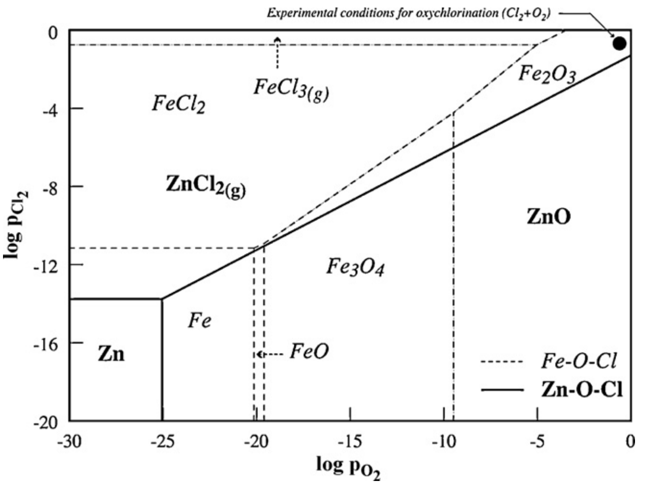

Fig. 3. Phase stability diagrams of (Fe, Zn)–O–Cl systems at 750 °C [31].

Table 1
Chemical composition of the tin slag and leaching concentrate (wt%).

Sample	Nb_2O_5	Ta_2O_5	SiO_2	CaO	FeO	Al_2O_3	SnO_2	MnO	K_2O	TiO_2	H_2O
Slag	5.2	7.5	41.9	11.6	3.3	11.2	0.7	3.7	1.4	1.3	≈0
Concentrate	28.0	31.1	10.0	0.6	0.2	0.6	0.2	0.0	0.4	1.4	≈20

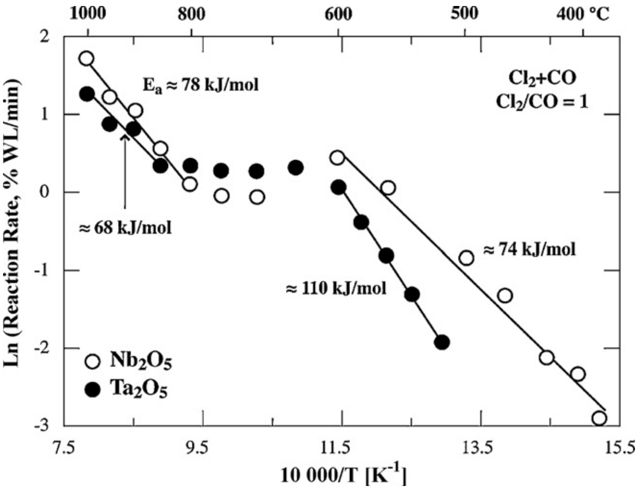

Fig. 4. Arrhenius plots for the carbochlorination of Nb_2O_5 and Ta_2O_5.

Thermodynamic aspects were also used to explain the experimental phenomena observed during chlorination of different solids. Fig. 4 gives the Arrhenius diagram for the carbochlorination of Nb_2O_5 and Ta_2O_5. Although a mixture of $CO + Cl_2$ was used in this study, it is possible that the chlorination of oxides at temperature lower than 600 °C was actually achieved by $COCl_2$ formed in the reaction zone. The anomalies observed in the Arrhenius plots between 600 °C and 800 °C could be explained by the absence of $COCl_2$ in the carbochlorinating gas mixture in this temperature range. Thermodynamic calculation [14] showed that $COCl_2$ is dissociated as temperature increases, reaching less than 5% $COCl_2$ at 600 °C.

Anomalies in the reaction rate were also observed when liquid phases are present in the chlorination process. Fig. 5 shows a typical example during the carbochlorination of MgO [6,20]. About 67% of MgO are chlorinated at 500 °C and increases with the temperature reaching 82% at 675 °C. Then, the reaction rate decreased rapidly and only 35% of the sample is chlorinated at 700 °C. This is probably due to the fusion of $MgCl_2$ that inhibits the mass transfer. Although the melting point of $MgCl_2$ is 714 °C [32] the exothermic nature of the carbochlorination reaction of MgO could locally increase the temperature to reach the melting point of magnesium chloride. A temperature higher than 900 °C is required to achieve the same rate obtained at 675 °C.

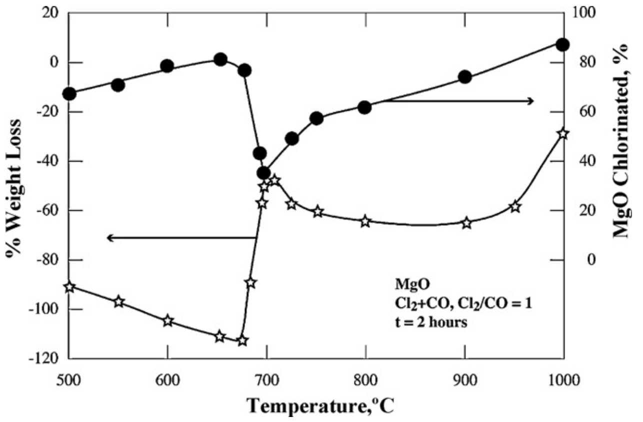

Fig. 5. Effect of liquid phase formation on the carbochlorination rate of MgO.

The decrease of the reaction rate due to the liquid phase formation, as well as the exothermic nature of the chlorination reactions were also observed during the sulfide treatment in chlorine at low temperatures [6,22,29].

The following sections will be devoted to a brief summary of the experimental results obtained by our laboratory in the field of chlorine technology used for metal recovery, mineral processing, waste decontamination and/or recycling.

4. Results and discussion

4.1. Extraction of Ta and Nb from tin slags

Niobium and tantalum are important elements used in many high technology applications such as electronic, energy, superconductors and aerospace. The industrialized countries consume the majority of the world production (≥95%) of these refractory metals and produce less than 5% [3]. Their main bearing minerals are pyrochlore, microlite, tantalite, columbite and columbo-tantalite. These minerals are often geologically associated to cassiterite. The mineral processing of these ores leads to a cassiterite (SnO_2) concentrate containing up to 2% of Nb and Ta oxides as mixed grains or inclusions. During the pyrometallurgical extraction of tin from cassiterite, oxides of Ta, Nb, Ti, Zr, Rare Earth Elements, Si, Fe, Al and Ca are concentrated in the slag. Conventional methods used for the extraction of niobium and tantalum compounds from tin slag consist of full dissolution with HF, $HF + H_2SO_4$ or smelting in electric furnaces [3]. Currently, these processes are limited either by economic or by environmental considerations. Due to the current low metal market and new environmental regulations, more efficient, flexible and environmentally friendly processes are required for the extraction of these metals from ores, industrial by-products or wastes. The recovery of tantalum and niobium from tin slag was carried out in our laboratory using a two-step process of leaching [9] followed by the chlorination or the carbochlorination of the resulting concentrates.

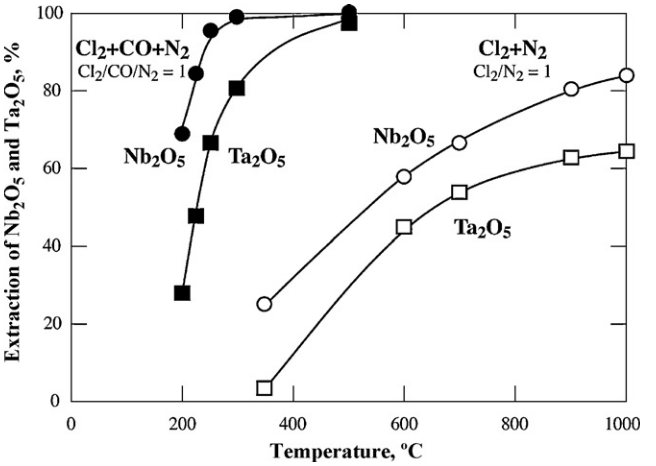

Fig. 6. Evolution of the % Nb_2O_5 and Ta_2O_5 extracted as a function of temperature during chlorination of Ta–Nb concentrate.

Table 2
Results of chlorination of Ta–Nb concentrate (wt%).

$Cl_2 + N_2$	Initial	350 °C	600	900	1000
Weight loss (WL)		13.0	43.2	70.7	73.7
Ta_2O_5	31.1	38.9	34.1	44.8	47.4
Ta_2O_5 extracted		3.1	44.5	62.5	64.5
Nb_2O_5	28.0	24.5	21.2	19.2	17.3
Nb_2O_5 extracted		24.7	57.4	80.2	83.9
Ta_2O_5/Nb_2O_5 ratio	1.1	1.6	1.6	2.3	2.7
$Cl_2 + CO + N_2$	Initial	200 °C	250	300	500
WL		40.4	68.5	79.9	92.0
Ta_2O_5	31.1	33.9	35.1	22.8	5.7
Ta_2O_5 extracted		27.9	60.5	83.7	98.4
Nb_2O_5	28.0	16.5	4.6	2.0	1.1
Nb_2O_5 extracted		69.1	95.5	98.7	99.7
Ta_2O_5/Nb_2O_5 ratio	1.1	2.1	7.7	11.4	5.1

Table 3
Chromite specifications by use (wt%).

	Met.[a]	Chem.[a]	Ref.[a]	Foundry
Cr_2O_3	>46	>44	30-40	>44
Cr/Fe	>2	>1.5	2-2.5	2
SiO_2	<10	<3.5	6	<4
Al_2O_3			25-30	
CaO				<0.5

[a] Metallurgical, chemical and refractory.

Table 4
Composition of chromite concentrate (wt%).

	Chemical analyses	Microprobe	
Oxide	(Average)	Chromite	Gangue
Cr_2O_3	47.7	59.4	0.7
FeO	13.4	13.9	3.7
MgO	17.8	14.2	42.0
Al_2O_3	8.8	9.5	1.4
SiO_2	7.1	0.1	39.7

This section focuses on the chlorination and carbochlorination of a tantalum and niobium bearing concentrate with $Cl_2 + N_2$ and $Cl_2 + CO + N_2$ gas mixtures. A concentrate high in tantalum and niobium oxides was used in this study. The chemical composition of the tin slag and that of concentrate obtained by the hydrometallurgical treatment of this slag are grouped in Table 1. After this treatment, the slag's initial content of the tantalum and niobium oxides was increased by a factor of 6.7 in the concentrate. This concentrate was chlorinated to separate the tantalum and niobium bearing compounds from the gangue. Results are reported in Fig. 6 and Table 2.

Chlorination by $Cl_2 + N_2$ seems to be inefficient even at 1000 °C. Only 65% and 85% of Ta_2O_5 and Nb_2O_5 were respectively chlorinated. The extraction rate of niobium is systematically higher than that of tantalum.

Extraction of Ta and Nb using carbochlorination is significant from 200 °C. The carbochlorination of Nb_2O_5 was complete at about 300 °C and that of Ta_2O_5 at 500 °C. The condensates were essentially composed of tantalum and niobium chlorides and/or oxychlorides. Residue obtained at 500 °C is essentially composed of SiO_2.

4.2. *Chromite upgrading*

Although the chromium is found in a variety of minerals (crocoïte $PbCrO_4$, lopezite $K_2Cr_2O_7$, vauquelinite $Pb_2Cu[CrO_4][PO_4]$, uvarovite $Ca_3Cr_2[SiO_4]_3$, merumite 4 $(Cr, Al)_2O_3{\cdot}3H_2O$, etc.), the main ore of chromium is the chromite mineral that is a spinel with the simple formula $FeCr_2O_4$. However, naturally occurring chromite ore is characterized by the substitution of Fe^{2+} by Mg^{2+} and that of Cr^{3+} by Al^{3+} and Fe^{3+} with the following general formula $(Mg, Fe^{2+})(Cr, Al, Fe)_2{}^{3+}O_4$. The gangue is essentially composed of orthopyroxene, olivine and plagioclase, as well as hydrous alteration products such as serpentine, chlorite and talc.

About 75% of chromite is used for the ferro-chromium production. In addition, chromite is used for chemical, refractory and foundry applications. Natural characteristics such as the chromium to iron ratio, the chromite grain size and the SiO_2, Al_2O_3, MgO, and P contents can be as important as the Cr_2O_3 content in determining the suitability of a chromite product for various end uses as well as its market price. Some chromite specifications for different uses are given in Table 3 [33]. Thus, the metallurgical chromite is characterized by its high chromium content and a Cr/Fe ratio higher than 2. Conventional mineral processing cannot modify the composition of chromite. This composition can be modified only by using chemical or thermal methods. This section is devoted to the thermal treatment of the chromite concentrate to increase its Cr/Fe ratio through selective chlorination and oxychlorination of iron compounds.

A European chromite concentrate was used in this investigation. Its chemical characteristics are summarized in Table 4. Combining the results of chemical and microprobe analysis, chromite

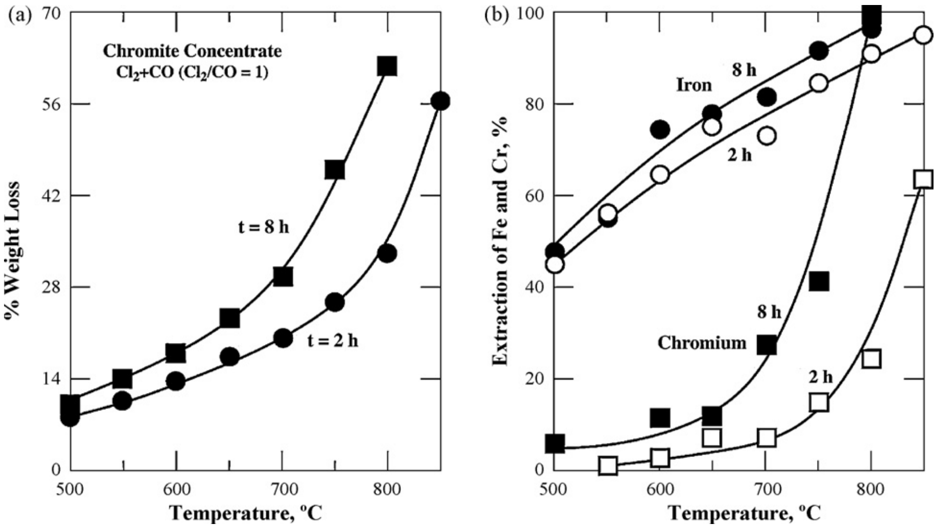

Fig. 7. Effects of temperature and reaction time on the carbochlorination of chromite concentrate.

Table 5
Evolution of Cr/Fe ratio in the carbochlorination residues of chromite concentrate as a function of the treatment conditions.

T, °C	Time, h	% WL	Cr (wt%)	Fe (wt%)	Cr/Fe
Raw Sample			34.2	10.8	3.2
500	2	7.81	40.9	6.3	6.5
	8	9.45	35.7	6.6	5.4
600	2	13.33	38.5	4.4	8.8
	8	17.81	36.7	3.4	10.8
700	2	19.90	39.9	3.7	10.8
	8	29.51	35.2	2.9	12.1
800	2	32.81	38.7	1.5	25.8

constitutes about 80% of the concentrate. Data processing of the microprobe analyses suggests that the general formula of chromite mineral is $(Fe_{0.30}{}^{2+}, Mg_{0.70})(Cr_{1.56}, Al_{0.37}, Fe^{3+}{}_{0.07})O_4$. Its Cr/Fe ratio is 3.2. On the other hand, this solid could be represented as the simple spinels of weight composition: 30.9% $FeCr_2O_4$, 51.0% $MgCr_2O_4$, 13.7% $MgAl_2O_4$ and 4.4%Fe_3O_4. The gangue totals about 20% and essentially composed of Mg_2SiO_4 and $Mg_3Si_2O_5(OH)_4$.

Fig. 7a shows the evolution of % WL during the carbochlorination of the chromite concentrate as function of temperature for different reaction times. Increasing the reaction time and/or temperature augments the reaction extent. The extraction rate of iron and chromium as function of the reaction temperature and reaction duration is shown in Fig. 7b. At 700 °C and a reaction time of 2 h, about 80% of iron compounds were extracted while that of chromium was limited to less than 10%.

Table 5 summarizes the results obtained during the carbochlorination of chromite concentrate between 500 °C and 800 °C. The Cr/Fe ratio increases as the carbochlorination temperature and time augments. It was doubled during the carbochlorination of the chromite concentrate at 500 °C with limited loss of chromium. This suggests that around 500 °C, the carbochlorination of a chromite ore and/or a concentrate having a low Cr/Fe ratio will lead to the increase of this ratio to a level satisfactory for the ferro-chromium production specifications. The selective chlorination of iron could be also advantageous for chromite concentrates used for other applications.

According to these results, upgrading of the chromite concentrate can be performed between 500 °C and 600 °C using a gas mixture of $Cl_2 + CO$ for reaction duration of 1–2 h. Cooling of the exhausted gases at 25 °C allows the condensation of the iron and chromium chlorides. These chlorides could be oxidized to recover chlorine which mixed with the rest of exhausted gases can be recycled after the adjustment of their composition.

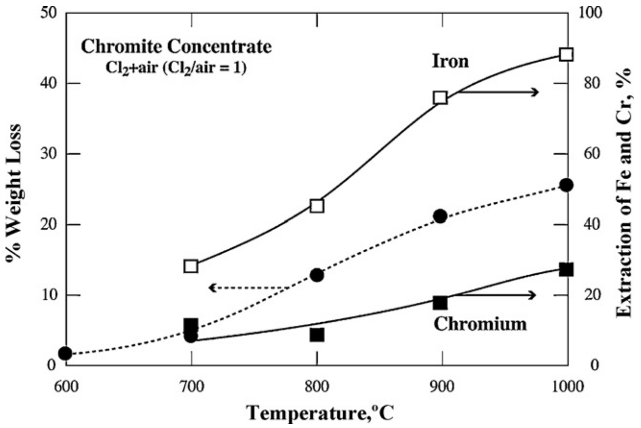

Fig. 8. Evolution of % WL and extraction of Fe and Cr as a function of temperature during the oxychlorination of chromite concentrate for 2 h.

Another possibility of upgrading the chromite concentrate is its oxychlorination using a gas mixture of chlorine and air. Such gas mixture is cheaper than that of $Cl_2 + CO$ and less toxic. For these reasons, a series of boat experimentation was performed and results are grouped in Fig. 8. This figure shows the evolution of % WL and that of extraction extent *versus* temperature. About 80% of iron compounds was extracted at 900 °C for 2 h of treatment, while that of chromium compounds was less than 20%. The initial Cr/Fe ratio was more than tripled thus confirming the possibility of upgrading the chromite concentrate by oxychlorination.

TGA results of oxychlorination of chromite between 925 °C and 1050 °C are given in Fig. 9a. They indicate that (Fe_3O_4 and $FeCr_2O_4$) are easily chlorinated at 925 °C, while oxychlorination of $MgCr_2O_4$ was achieved at higher temperature with low kinetics. The evolution of apparent activation energy 'E_a' values *versus* reaction extent 'X' is shown in Fig. 9b. It clearly confirms two-steps oxychlorination of chromite characterized by mean values of E_a of about 60 kJ/mol ($X \leq 0.25$, $FeCr_2O_4$) and 265 kJ/mol ($X \geq 0.4$, $MgCr_2O_4$).

These results suggest that upgrading of the chromite concentrate could be performed between 900 °C and 1000 °C for a reaction time of 2–4 h using a gas mixture of Cl_2 + air. The formed ferric chloride is separated from the gas stream by cooling to 25 °C while chromium oxychloride (CrO_2Cl_2) is recovered at −35 °C. The iron and chromium chlorinated compounds could be oxidized to

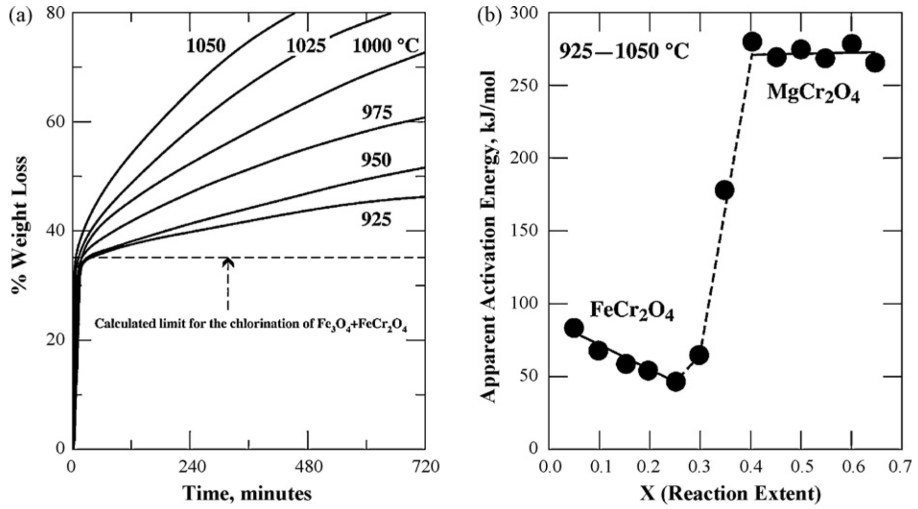

Fig. 9. Isotherms of oxychlorination of chromite from 925 °C to 1050 °C (a) and (b) evolution of E_a as a function of the reaction extent.

Table 6
Chemical and mineralogical composition of copper concentrates (wt%).

Element	LGCC	HGCC	Phases	LGCC	HGCC
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: $(Mg, Fe)_6(Si, Al)_4O_{10}(OH)_8$.

recover the chlorine, Fe_2O_3 and Cr_2O_3. Chromium oxychloride can be decomposed generating Cr_2O_3. The exhausted gases and chlorine could be recycled after the adjustment of their composition.

4.3. Low temperature chlorination of copper concentrates

Sulfide ores and concentrates are still the major source of the primary production of metals such as Cu, Pb, Zn, etc. The conventional direct pyrometallurgical routes are limited due to generation of dangerous SO_x gases. Even with the modern SO_x processing techniques, certain ecological problem persists. This section deals with the possibility of using low chlorination temperature for a selective separation of valuable metal (Cu, Pb, Zn) compounds. Details of this investigation were given previously [6,22,29].

The chemical and mineralogical compositions of two copper concentrates, used for this study, are given in Table 6. 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% and was called low grade copper concentrate (LGCC). The total valuable metal (Cu, Zn, Pb) content of second sample was about 36.5% and it was designated as high-grade copper concentrate (HGCC). The major sulfides of the LGCC were $CuFeS_2$ and FeS_2. The LGCC gangue essentially contained quartz and clinochlore. The HGGC was high in chalcopyrite (81.7%). Moreover, it contains some amounts of lead and zinc compounds, while its gangue content was low.

Thermodynamic calculations [6,22] showed that all chlorination reactions of sulfide concentrates are favorable up to 1000 °C. However, as shown in Fig. 2, the ferric and sulfur chlorides possess a high vapor pressure at temperature of about 300 °C. It seems that this is the important factor to separate selectively the valuable metals.

Fig. 10 is a data compilation of the chlorination of LGCC 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 pertaining to 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% of copper was extracted at 600 °C. The % WL curve described in Fig. 10 for the LGCC 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 % WL of the LGCC sample and with the results of chemical analysis of the residue obtained at 300 °C.

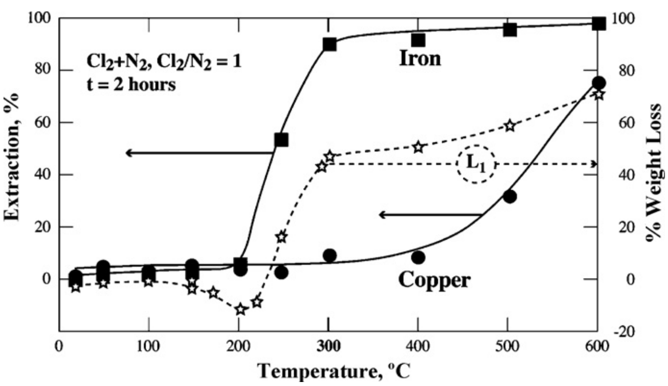

Fig. 10. Results of LGCC chlorination at different temperatures.

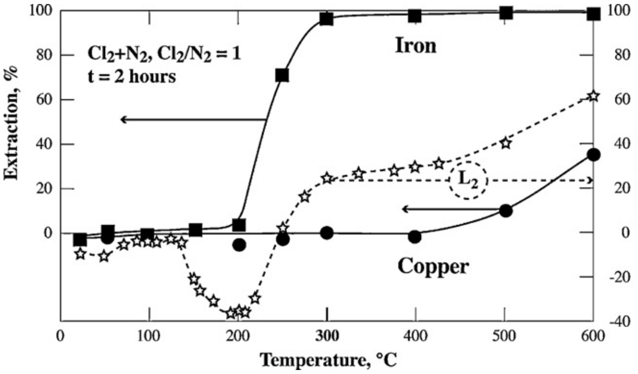

Fig. 11. Results of HGCC chlorination at different temperatures.

Chlorination results of HGCC up to 600 °C are illustrated in Fig. 11. Almost complete iron extraction was achieved at 300 °C. This was possible because the iron of HGC is contained in the sulfides, essentially in the chalcopyrite. The selective chlorination limit (L_2) is fully consistent with the % WL and extraction extent of iron obtained at 300 °C. The copper extraction started at higher temperatures than in the case of LGCC and about 40% of Cu was extracted at 600 °C. This is probably due to the fact that the HGCC residues were systematically agglomerated while those of LGCC did not undergo such phenomenon. The presence of inert compounds in LGCC, such as SiO_2, prevented the agglomeration of the residues.

Data collected from the chlorination of two chalcopyrite concentrates at different conditions suggested the flow-sheet represented in Fig. 12. According to this flow-sheet, the chalcopyrite concentrate is chlorinated at about 300 °C in a fixed bed for a reaction time of 1–2 h. The reaction time depends on the concentrate composition. 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 to give hematite and chlorine.

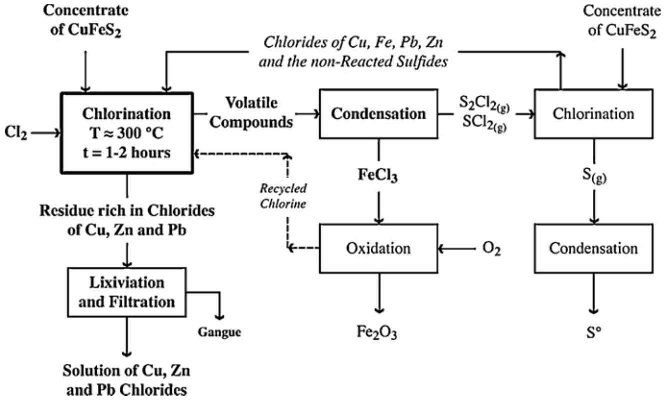

Fig. 12. Suggested flow-sheet for chlorination of copper concentrate.

Table 7
Chemical composition of treated jarosite samples (wt%).

Sample	Fe	Zn	Pb	Cd	Cu	ΣHM^a	C_{tot}
S_1	32.2	5.3	4.2	0.0558	NA[b]	9.60	3.00
S_2	35.4	5.9	4.4	0.0400	0.22	10.47	6.03
S_3	35.1	7.7	5.3	0.0900	0.67	13.66	2.50

[a] Sum of heavy metals.
[b] Non available.

The last will be recycled to the chalcopyrite chlorination unit after a composition adjustment. 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.

4.4. Decontamination of jarosite

More than 80% of world zinc is produced by hydrometallurgical routes. After roasting the concentrates, sulfuric acid is used to dissolve zinc oxide and ferrite from the calcine. In the pH range of 1–1.5 at about 95 °C, iron is precipitated using K^+, Na^+, NH_4^+, . . . as jarosite $X[Fe_3(SO_4)_2(OH)_6]$ where X is H_3O^+, Na^+, K^+, NH_4^+ or 1/2 of heavy metal cations such as Pb^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, etc. Most of the produced jarosite is disposed in legal or illegal waste disposal sites that are considered as an environmental threat to water resources and to the soil. Due to the jarosite's high content in heavy metals and their partial solubility in acid solution, jarosite is classified as dangerous waste that requires treatment. Raw jarosite was used to oxidize the liquid manure of farming [34]. During this process, the iron, lead, zinc, . . . compounds contained in the raw jarosite were converted to the equivalent metal oxide or sulfide. The solid fraction of the reaction products containing heavy metals is subjected to chlorination.

The average chemical composition of the samples (S_1, S_2, S_3) used in this study is grouped in Table 7. The heavy metal content exceeds 9% in all cases while the iron content is about 35%. These samples were chlorinated by a gas mixture of Cl_2 + air during 3 h between 700 °C and 800 °C. This gas composition was chosen in order to chlorinate heavy metal compounds and to prevent chlorination of iron oxide (see Fig. 3). The chemical composition of these solids was determined before and after their treatment. To measure the efficiency of these treatments, the concept of decontamination extent is used. It is based on the percentage of heavy metals eliminated after the chlorination treatment (ΣHM_f) with respect to the initial content of these heavy metal compounds (ΣHM_i) in the jarosite.

Table 8 groups the experimental conditions and the initial and final contents of HM as well as the decontamination factor of different samples. The final content of HM oscillates between 0.4wt% and 1.2 wt% depending on the initial content of HM and the experimental conditions. The decontamination factor varies from about 91% to 96%. In addition, the leaching test of the final residues was performed according to the protocol defined by the French test AFNOR X31-210. Results indicate that the final residue could be considered as non hazardous waste.

Table 8
Decontamination of different samples of treated jarosite.

Sample	Gas mixture	T °C	ΣHM_i (wt%)	ΣHM_f (wt%)	DE[a]
S_1	(3.8% Cl_2) + air	700	9.6	0.59	93.9
S_1	(3.8% Cl_2) + air	800	9.6	0.42	95.6
S_2	(6.7% Cl_2) + air	700	10.5	0.99	90.6
S_3	(6.7% Cl_2) + air	700	13.7	1.23	91.0

[a] Decontamination extent.

4.5. Synthesis of potassium ferrate (K_2FeO_4)

Potassium ferrate ($K_2Fe^{VI}O_4$) is a compound containing iron at rare hexavalent state. The importance of ferrate synthesis is related to the oxidant and coagulant properties of FeO_4^{2-} ion. It is a useful compound in drinking water purification and wastewater treatment. Furthermore, it was used for effluent decontamination, soil remediation, cyanide destruction, etc. Although potassium ferrate is known since 1841 by Fremy [35], this compound was not studied extensively and was not produced at industrial scale due to its high oxidizing capacity, its instability and preparation difficulties.

Evrard et al. [36] developed the dry synthesis at room temperature of potassium sulfatoferrate $K_2(Fe_{0.5}, S_{0.5})O_4$ using ferrous sulfate as iron salt. The use of ferrous sulfate hydrate for the synthesis of $K_2(Fe_{0.5}, S_{0.5})O_4$ had two advantages. The synthesis was performed with $FeSO_4{\cdot}7H_2O$ which is considered as a waste for the industries of TiO_2 production and surface treatment of steel. Moreover, the substitution of K_2FeO_4 by K_2SO_4 improves significantly the stability of hexavalent iron. One may underline that potassium sulfate and potassium ferrate possess the same structure.

Although this method has a relatively high Fe^{VI} efficiency, it may be considered as non economic due to the high price of $Ca(ClO)_2$. For this reason, an investigation was undertaken to replace $Ca(ClO)_2$ by chlorine that is cheaper reagent compared with $Ca(ClO)_2$ price. Details of this study were described earlier [8,30]. Fig. 13 summarizes the main steps for the production of potassium ferrate. The following paragraphs describe these steps.

According to this flow-sheet, the $FeSO_4{\cdot}H_2O$ has to be dehydrated at temperatures of about 125 °C. Dehydration of ferrous sulfate heptahydrate is necessary because it allows:

- control of the water quantity during the alkali ferrate synthesis,
- increase of the reactivity of ferrous sulfate by decreasing their particle size through thermal embrittlement.

The most important step of the proposed process is that of ferrate synthesis. The success of these steps is dependent on the reactor design and experimental parameters to insure the following functions:

- good contact of three substances ($FeSO_4{\cdot}xH_2O$, KOH and Cl_2),
- preferential diffusion of KOH towards reaction zone,
- rapid evacuation of the water released from the synthesis reaction,
- high and uniform heat transfer as the overall synthesis reaction is exothermic.

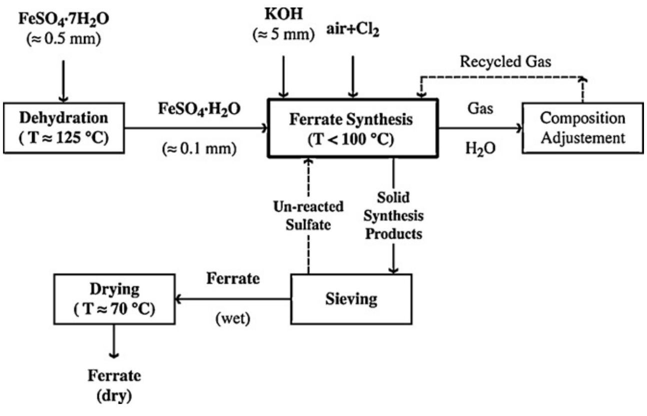

Fig. 13. Suggested flow-sheet for potassium ferrate synthesis.

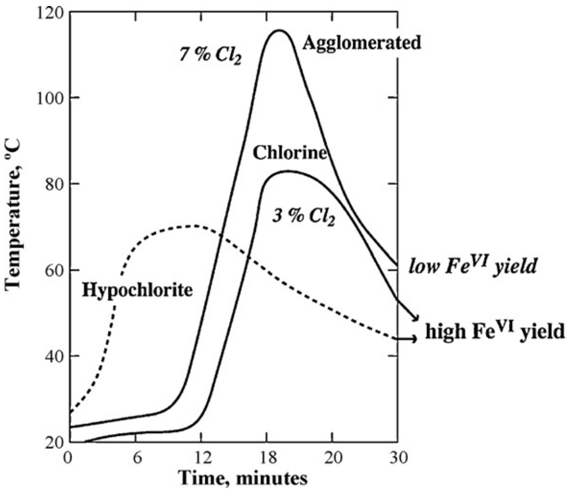

Fig. 14. Thermal conditions for ferrate synthesis.

Although the potassium ferrate synthesis is achieved without external heat supply, the reactor temperature increases due to the exothermic nature of the reactions. An increase of the reactor temperature between about 45 °C and 175 °C is observed [8]. Fig. 14 gives a typical example of the temperature evolution in the reaction zone during synthesis of potassium ferrate using $Ca(ClO)_2$ and/or Cl_2 as oxidant. As could be expected, in the case of using the chlorine as oxidant, the maximum temperature increased with chlorine content. However, as shown in Fig. 14, good results of potassium ferrate synthesis are obtained for temperatures lower than 100 °C which ever is the oxidant. The agglomeration of the solid products and the decrease of the Fe^{VI} efficiency for temperatures higher than 100 °C are supported by the presence of liquid phases in $KOH–H_2O$ system [37].

The last step of the proposed process consists in the separation of the synthesis products from non reacted ferrous sulfate and drying of the obtained alkali ferrates.

- Separation of synthesis products from the non reacted ferrous sulfate is facilitated by the important difference of particle size between the ferrate (≈5 mm) and that of the ferrous sulfate (<0.5 mm). Thus, a simple sieving of the products will allow their separation,
- drying of ferrate could be done at temperatures lower than 70 °C. However, the drying temperature has to be the lowest possible and should never exceed 100 °C.

5. Conclusions

The examples and flow-sheets given in this paper show the possibility of using chlorine technology for mineral processing, metal extraction, waste decontamination and synthesis of a novel reagent. The advantages of the chlorination technology are related to low temperature operation, flexibility to raw material composition, selectivity of the process, etc.

However, large pilot scale experimentation and a rigorous technico-economical evaluation will be necessary for the validation of the proposed chlorination processes at industrial level.

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