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TITLE : NEW APPROACH FOR VALUABLE ELEMENTS
RECOVERY FROM CONCENTRATES & WASTES
BY SELECTIVE CHLORINATION THROUGH
BINARY CHLORIDES

PROJECT

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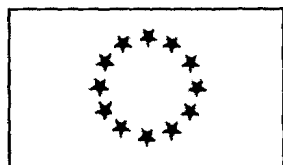
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Abstract

This research project started in 11/1992 in the frame of the EU Contract N° BRE2-CT92-0173. The coordinator of this consortium is the Institut National Polytechnique de Lorraine 'INPL'-L laboratoire Environnement et Minéralurgie 'LEM' (Vandœuvre, France). The partners are Laboratorios de Investigación y ASesoramiento METalurgico 'INASMET' (San Sebastian, Spain) and Instituto Nacional de Engenharia e Tecnologia Industrial 'INETI' (Lisbon, Portugal).

This investigation involves pyrometallurgical chlorination technique for the recovery and/or elimination of a specific element contained in the concentrates and or industrial wastes. The materials to be treated were chalcopyrite and chromite concentrates and metallurgical residues. This project was composed of two phases : laboratory scale research by the INPL-LEM team and the scale-up of successful results by the INASMET and INETI teams.

The use of chlorine in the extractive metallurgy is an advantageous approach to separate selectively a specific element of interest contained in the low grade ores, concentrates and/or industrial wastes and by-products. This is due to the high reactivity of chlorine towards many compounds at moderate temperatures. Chlorine is a by-product of NaOH manufacturing by the electrolysis of NaCl. Although the NaOH demand is important that of chlorine is limited. The cost of the surplus chlorine elimination is a burden for the European Chemical Industry. This project can provide various uses of chlorine in the field of mineral processing, extractive metallurgy and the waste treatments.

The thermodynamic study concludes that the chlorination of sulfides is favorable while complete chlorination of chromite compounds required the presence of a reducing agent. It also suggests that the industrial waste can be decontaminated using chlorinating or oxidizing or again reducing atmospheres.

Selective chlorination of the chalcopyrite concentrates at about 300 °C was performed. This research was successful in eliminating the quasi totality of iron compounds and concentrating the copper ones in the treatment's residue. Scale up of this process by fixed bed and rotary kiln was achieved by INASMET. In the two cases, chlorination of about 100 kg of chalcopyrite concentrate at T about 350 °C leads to the elimination of about 9870 of iron compounds and the recovery of 90 % of copper ones. Generated sulfur chloride was partially recycled as a chlorinating agent or decomposed to S⁰ and HCl. A flow-sheet of the process was suggested. Chlorination of the chalcopyrite concentrate using fluidized bed, performed by the INETI team, allows the extraction of about 98% of the sulfur and iron contained in this concentrate.

Due to the impossibility of upgrading the chromite concentrates by physical methods, selective chlorination of this concentrate was performed. At T ≤ 600 °C, it was possible to double the Cr/Fe ratio of the chromite concentrate thus increasing its market value and short circuiting, for rich chromite ores, the traditional mineral processing. In addition, partial or complete selective extraction of chromium compounds was successful. Scale-up of the process by INASMET using rotary kiln and by INETI employing fluidized bed was successful and confirms results of the laboratory scale experimentation concerning the increase of the Cr/Fe ratio.

Decontaminating/ recycling of industrial by-products or wastes of the European non-ferrous metallurgy was investigated through thermal treatments in controlled atmospheres below 800 °C. It was possible to eliminate 99 % of toxic elements and to concentrate valuable metals, in the treatments' residues by a factor of about 2.5. A part of these solids can be recycled directly in the conventional metallurgical processes. The final residues are considered as environmentally acceptable.

Results of this project suggest new approaches to the mineral processing sector, the metal extraction industry and the emerging new sector of recycling/ decontamination of industrial wastes.

I. INTRODUCTION

Most of the present hydro and/or pyrometallurgical processes lack a flexible input specification. They are optimized for a specific element with a narrow range tolerance of their input. This may be considered as a handicap especially for the recycling of the high metal content of industrial residues. Spent catalysts, which may contain up to 25 % of valuable elements, or hydrometallurgical by-products or wastes, having up to 45 % of Cu, Pb, Zn, . . . contain elements such as As, Hg, Cd, . . . are considered as wastes and are currently stocked in waste disposals. Such materials couldn't be recycled directly in the classical operating hydro and/or pyrometallurgical plants. Yet, the recycling of these materials may avoid the needs of expensive waste disposals. Besides the loss of the economic value of such metals, these materials are generally dangerous for the soil and the water resources.

The increase of waste disposal costs, stricter environment regulations, the low metal market, . . . cause some EU enterprises to lose market shares and competitiveness. On the other hand, the decontamination and recycling of the industrial secondary products and wastes is emerging as a new industry. For this decade, the estimated EU market volume is 10 to 30 billion Ecus per year. The opening of European subsidiaries of foreign companies and the important investment in this field are a confirmation of the importance of this industry to the EU countries.

The objective of this research proposal is to supply the EU industry with a flexible technology that may be applied to the extraction of a specific element or elements from concentrates or ores and/or the decontamination and recycling of industrial scrap, by products and wastes. Such a technology has relatively low capital and operating costs. It is a flexible, energy saving and environmentally friendly.

Very few EU research centers are working in the field of chloride technology because of the considerable engineering effort implied in designing, manufacturing and operating chlorination equipments. Few publications and reports have been published in this field. On the other hand, the European market of NaOH is characterized by a surplus of chlorine with respect to the soda consumption. The cost of chlorine elimination is a burden for the European Chemical Industry. The use of chlorination in the field of mineral processing, metal extraction and the recycling/ decontamination processes can provide useful methods of chlorine consumption. For these reasons and because of the traditionally conservative attitude of the industry, this research proposal is upstream with respect to industrial application.

Chloride technology is a relatively new one. The most important advantage of the chlorination process is its fast kinetics and the low boiling points of the majority of chlorinated valuable elements' compounds (groups IVB, VB, VIB, VIII, IB, IIB, IIIA, IVA of the periodic table) with respect to those of oxides. Consequently, the valuable elements' chlorides can either be transported by the gaseous phase or accumulated in the treatment's residue. Selective condensation of refractory metal chlorides permits their recovery in a relatively pm-e state. Leaching the treatment's residue with acidified water allows the separation of valuable metal chlorides. One may underline that chlorination or carbochlorination is applied on industrial scale for the extraction of Ti, REE, Ta, Nb, Sn, . . .

During the chlorination process, gaseous complex metal chlorides 'GCMC' could be synthesized in small amounts. These compounds decompose at room temperature and liberate the valuable metal chloride. Their general formula is MN_xCl_y . Where M is an element of the refractory, precious and transition metal groups or a metalloid. N could be Al, Fe, Ga or In. X could vary from 1 to 4 and y from 5 to 15 (i.e., $MNCl_5, MNCl_6, MNCl_8, MN_2Cl_8, MN_2Cl_9, MN_3Cl_{12}, MN_4Cl_{14}, MN_4Cl_{15}, \dots$). These binary chlorides enhance the reactivity of the treated solids and increase the metal concentration in the gaseous phase by a factor varying from 25 to 10^{12} depending on the nature of elements M and N. Applying special experimental conditions favor the formation of these binary chlorides during the chlorination process.

The extraction of valuable elements from concentrates, the recycling of economic metals and the decontamination of industrial residues can be carried out by selective chlorination. The advantages of such a process are:

1. a reduction in the size of the reactor due to the high reactivity of solids and the kinetics of their reaction with respect to the chlorinating gas mixture,
2. energy saving due to a higher partial pressure of binary chloride with respect to that of simple metal chloride for the same reaction temperature,
3. a higher recovery rate of the valuable metal,
4. environmentally safe wastes are generated because of the high reactivity of heavy metals with respect to the chlorinating gas mixture,
5. a simpler flow-sheet for the separation of economic elements from their gang,
6. eventual short-circuiting the mineral processing in case of rich ores or ameliorating the obtained concentrate,
7. flexibility with respect to the concentration of the valuable elements in the process input.

This research was focused on eight samples :

- A. a low grade copper concentrate,
- B. two high grade copper concentrates,
- C. two chromium concentrates,
- D. three hydrometallurgical residues having a high basic metal content (≈ 25 to 45%) and elements such as As, Cd, Pb, Hg, . . .

The conventional pyrometallurgical processes for the extraction of copper from its concentrates lead to sulfur oxides' emissions. Beside the lose of the economic value of sulfur, these emissions increase the acidity of the rain leading to the contamination of water resources and sterilize the soil.

According to OECD, the industrial SO_x emissions of the EU countries decreased from about 2.5 million tons in 1980 to about 1 million tons in 1990. Further decrease requires the modification of the actual flow sheet of processing valuable elements contained in the sulfide concentrates. This research may provide a new process characterized by the recovery of sulfur compounds and low temperature processing of these sulfide concentrates.

A higher added value of the chromite concentrates can be obtained either by increasing the their Cr/Fe ratio or the extraction of the chromium chlorinated compounds. One may mention that the market price of pure Cr_2O_3 is almost one hundred times that of chromium concentrate.

Finally, the extraction of toxic elements from industrial residues and the concentration of valuable elements promotes the recycling of the treated solids avoiding its waste disposal and facilitating the reutilization of valuable elements.

The success of this project will open new possibilities for the mineral processing sector, the industry of non-ferrous metal extraction and the recycling/ decontamination of industrial residues. The ultimate residues of such processes are generally oxides that are environmentally safe.

II. TECHNICAL DESCRIPTION

II.1. Experimental sets

Different types of experimental sets were designed and/or modified for the chlorination of the samples. TGA and horizontal experimental sets were employed for small scale experiments. The fluidized bed reactor and rotary kiln were used for large scale experimentation.

II.2. Methods of physiochemical characterization

The following methods were used to characterize the raw samples and the reactions' products :

- a.** Size distribution analysis (classical and laser measurements),
- b.** Specific surface area 'BET' measurements,
- c.** Optical microscopy,
- d.** Scanning electron microscopy (SEM),
- e.** X-ray diffraction (XRD),
- f.** X-ray fluorescence (XRF),
- g.** Microprobe analysis,
- h.** Volubility measurements and Standard lixiviation test,
- i.** Thermogravimetric analysis (TGA),
- j.** Porosity measurements,
- k.** Humidity and Apparent density measurements,
- l.** Mechanical resistance testing,
- m.** Atomic absorption spectroscopy (AAS),
- n.** Inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

11.3. Raw materials

Samples used for this research were : three concentrates of chalcopyrite, two chromite concentrates and three metallurgical residues. The composition of the chalcopyrite concentrates is given in Table I. The first two concentrates contain about 31 and 82 % of chalcopyrite and designated as low and high grade copper concentrates 'LGCC and HGCC', respectively. The third one 'CFSU' was employed for the scale-up of results by the INASMET and the INETI teams. This concentrate contains about 71 % of chalcopyrite. The HGCC and CFSU have small amounts of sphalerite, pyrite, lead compounds and silica. The LGCC contains, in addition to the above mentioned minerals, silica, clinocllore, . . . The average specific surface area of the CuFeS_2 concentrates is about $0.63 \text{ m}^2/\text{g}$ indicating that the sample's particles are compact.

Table I: Composition of the chalcopyrite concentrates.

Phase	LGCC	HGCC	CFSU
CuFeS ₂	31,2	81.7	70.7
FeS ₂	23.8	3.0	22.1
ZnS	1.2	6.4	3.0
PbSO ₄	ND	5.7	0.3
SiO ₂	14.4	0.7	ND
Total	70.6"	97.5	96.2

* The rest is composed of the oxidized compounds of Fe, Mg, Ca, Al, . . .

The chlorination of chalcopyrite concentrate at laboratory scale was achieved without any physical and/or chemical pretreatment. While the concentrate (CFSU) used for the tests of the scale-up was pelletized before its chlorination.

Table II summarizes the contents of major oxides of two chromite concentrates. The first sample of these concentrates is rich in chromium ($\approx 47\%$) and it is characterized by a Cr/Fe ratio of 3.14 while the second one also contains about 46 % Cr but its Cr/Fe ratio is 1.54. Moreover, these concentrates are distinguished by different contents of Al, Mg and Si oxides.

The industrial wastes were obtained from an important European operator in the field of extractive metallurgy. The chemical compositions of these samples are grouped in Table 111. Theirs content of toxic (As, Hg, Cd, . . .) and valuable (Cu, Pb, Zn) elements vary from about 7 to 23 % and from 14 to 42 %, respectively. One may underline that these solids are composed of different phases that may include toxic elements or valuable metals or both. The arsenic compound seems to be essential y arsenolite (As₂O₃). Angle site (PbSO₄) is the major identified phase bearing lead.

II. 4. Thermodynamic considerations

The selective extraction of an element or group of elements can be based on their economic value and on thermodynamic considerations. Although the chlorine demand is low, its production is almost unavoidable as it is a by-product of the NaOH manufacture. On the other hand, the reactivity of chlorine for many sulfides and oxides is high. All sulfides contained in the investigated chalcopyrite concentrates could be chlorinated by chlorine at relatively low temperature. However, the presence of a reducing agent is necessary to decrease the oxygen partial pressure during the complete chlorination of oxides contained in the chromite samples. The chlorination in the presence of oxygen could be selective as the chromium is transformed into CrO₂Cl₂. The chlorination products could be the chlorides and oxychlorides having melting and boiling points lower than those of sulfides and oxides. Moreover, the melting and boiling points of these products are different. As the boiling point of FeCl₃ is about 305 °C and those of ZnCl₂, PbCl₂ and CuCl₂ are higher than 500 °C, a chlorination of sulfides at about 300 °C allows the volatilization of ferric chloride and the concentration of the valuable metals' chlorides in the chlorinating residues. The high volubility of metals' chlorides in water is also advantageous to use chlorine for the recovery and/or concentration of a specific element contained in the considered samples. These thermodynamic considerations were taking into account to define the chlorinating experimental parameters.

Table H : Chemical analysis of the chromite concentrates (Weight percentage),

Oxide	Sample 1	Sample 2
FeO	13.37	26.27
Cr ₂ O ₃	47.67	45,55
MgO	17.83	10.37
Al ₂ O ₃	8.83	15.72
SiO ₂	7.13	0.92
Total	94.83	98.83
Cr/Fe	3.14	1.54
Cr/Mg	3.79	5.00
Fe/Mg	1.21	3.28

Table III : Chemical composition of the metallurgical residue (Weight percentage),

Element	Sample 1	Sample 2	Sample 3
As	13.90	0.6	21.7
Hg	0.60	3.2	0.6
Cd	0,04	0.1	0.8
Se	ND	3.3	ND
Pb	4.30	33.2	4.8
Zn	3.20	0.16	16.9
Cu	6.30	8.2	2.1
Ag	0.06	0.18	0.03
S	10.60	11.5	22.9
Fe	14.01	0.0	1.0
Sb	0.45	ND	0.1
Si	1.40	ND	ND
O	10.4	15.8	12.2
Σ T. E	14.5	7.2	23.1
Σ V. M	13.8	41.6	23.8
Total	65.23	76,3	83.2

Σ T.E : Sum of toxic elements, Σ V.M : Sum of valuable metals, ND : Non determined.

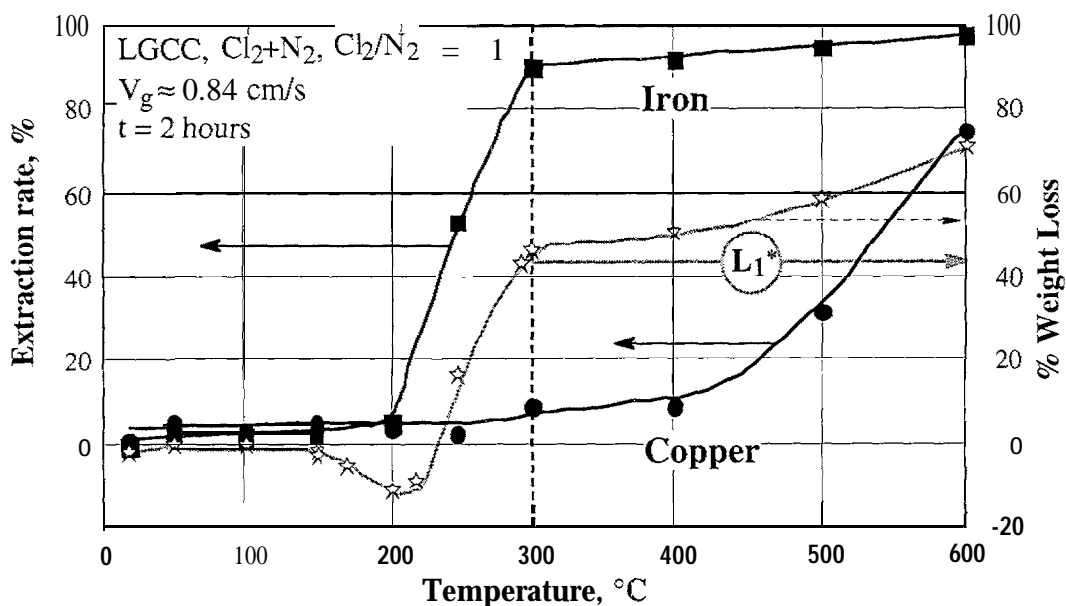
III. RESULTS AND CONCLUSIONS

111.1. Chlorination of chalcopyrite concentrates on laboratory scale

Several parameters such as gas flow rate, temperature, time, chlorine pressure . . . were varied during the chlorination of LGCC and HGCC. Figures 1 and 2 show the evolution of percent weight loss and the extraction rate of iron and copper during the chlorination of LGCC and HGCC, respectively. Almost complete extraction of the iron compounds is possible at 300 °C for a treatment duration of 2 h, a chlorine content in the gas mixture lower than 40 % and a gas velocity of about 0.8 cm/second. More than 95 % of the copper chloride is concentrated in the chlorination residues. Thus allowing the selective chlorination of the two chalcopyrite concentrates at this temperature on laboratory scale experimentation.

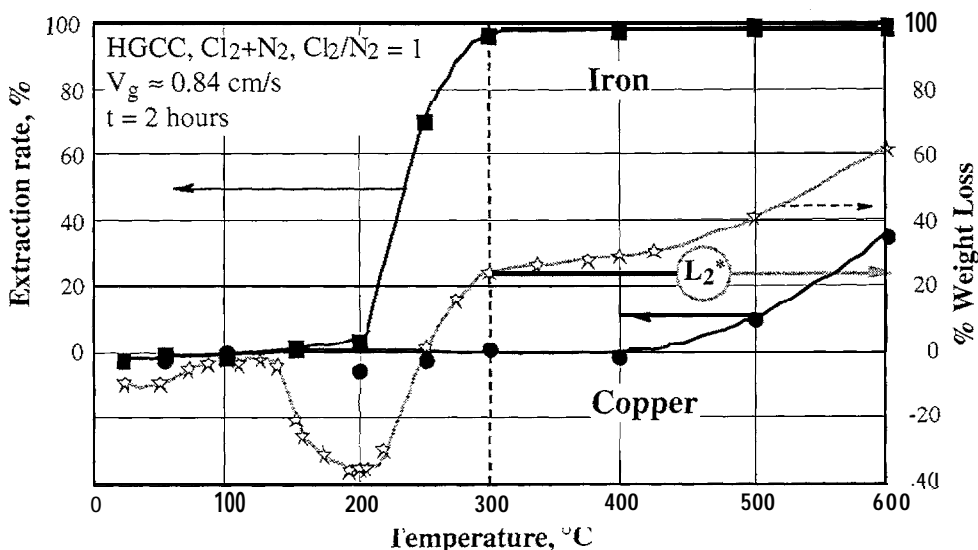
Figure 3 summarizes the proposed flow-sheet for the chlorination of the chalcopyrite concentrate. Chlorination of this concentrate can be made by a gas mixture containing less than 40 % of chlorine between 27.5 °C and 325 °C. The solids' residence time varies from one to two hours and depends on the sulfide content of the concentrate. Ferric chloride is separated from the gaseous phase by cooling to room temperature. It can be oxidized and the generated Cl_2 or HCl could be recycled,

Cooling the gases to about - 10 °C, allows the condensation of sulfur chlorides that can be used as a chlorinating agent or hydrolyzed to recover up to 90 % of sulfur as S^0 and HCl . Another alternative is the reduction of the sulfur chloride gases at about 500 °C generating elementary sulfur and HCl . The residue of the chalcopyrite chlorination can be lixiviated to recover chlorides of copper, zinc and lead. Standard lixiviation test indicates that the gangue is environmentally safe.



* Limit of selective chlorination of LGCC.

Figure 1: Extraction rate of Cu and Fe compounds as a function of temperature during chlorination of LGCC by Cl_2+N_2 .



* Limit of selective chlorination of HGCC.

Figure 2: Extraction rate of Cu and Fe compounds as a function of temperature during chlorination of HGCC by Cl_2+N_2 .

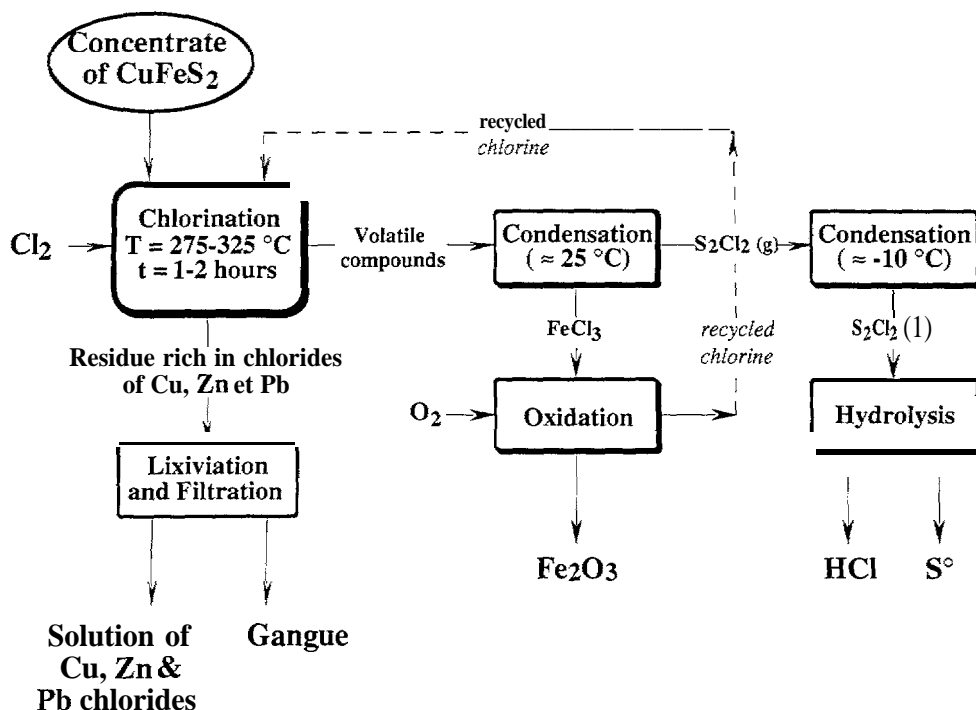


Figure 3: Suggested flow-sheet for the extraction of valuable metals by selective chlorination.

III. 2. Scale-up of the chlorination of chalcopyrite concentrate

The chalcopyrite pellets were chlorinated by the INASMET team by operating either in a batch or continuous modes using fixed bed reactor or rotary, respectively. Best results were obtained by chlorinating the pellets in the rotary kiln at temperature of 370 °C using a total flow rate of 250 L/h ($V_g = 1.1$ cm/sec) composed of $Cl_2 + Ar$ having a ratio equal to 1 and a rotation speed of furnace less than 25 rpm. In these conditions about 98 % of $FeCl_3$ was eliminated and 95 % of the copper was chlorinated. Copper losses were less than 10 %. In these conditions, the mass balance was calculated (Table IV) and the suggested flow-sheet of the process is summarized by Figure 4.

The INETI team achieved the chlorination of chalcopyrite pellets in fluidized bed. In the optimum conditions [$T \approx 350$ °C) more than 95 % of the iron and sulfur compounds were eliminated. However, technical problems were observed due to the clogging of the fluid bed.

Table IV : Mass balance for continuous chlorination of the chalcopyrite concentrate in rotary kiln.

	1 *	2	3	4	5	6	7	8
Temperature (°C)	25	25	25	300-350	90	90	-25	-25
Total gas flow ($N m^3/h$)	-	≈ 235	-	≈ 220	-	≈ 215	-	≈ 210
Total solid/ liquid	100	-	≈ 75	-	≈ 40	-	≈ 35	-
Cl_2 ($N m^3/h$)		33	-	8	-	8	-	8
Ar ($N m^3/h$)	1	200	-	200	-	100	-	200
Copper conc. pellets (kg/ batch)	50	-	1,4	-	-	-	-	-
$FeCl_3$ (kg/ h)			0,2	41,7	41,7	-	-	-
$CuCl_2$ (kg/ h)			22,3	2,7	2,7	-	J	-
$S_2Cl_2 + SCl_2$ ** (kg/ h)	-	-	-	36,3	1	-	36,3	36,3
Sand	50	-	50	-	-	-	-	-

* Numbers correspond to that of flow-sheet of Figure 4

** expressed as S_2Cl_2 .

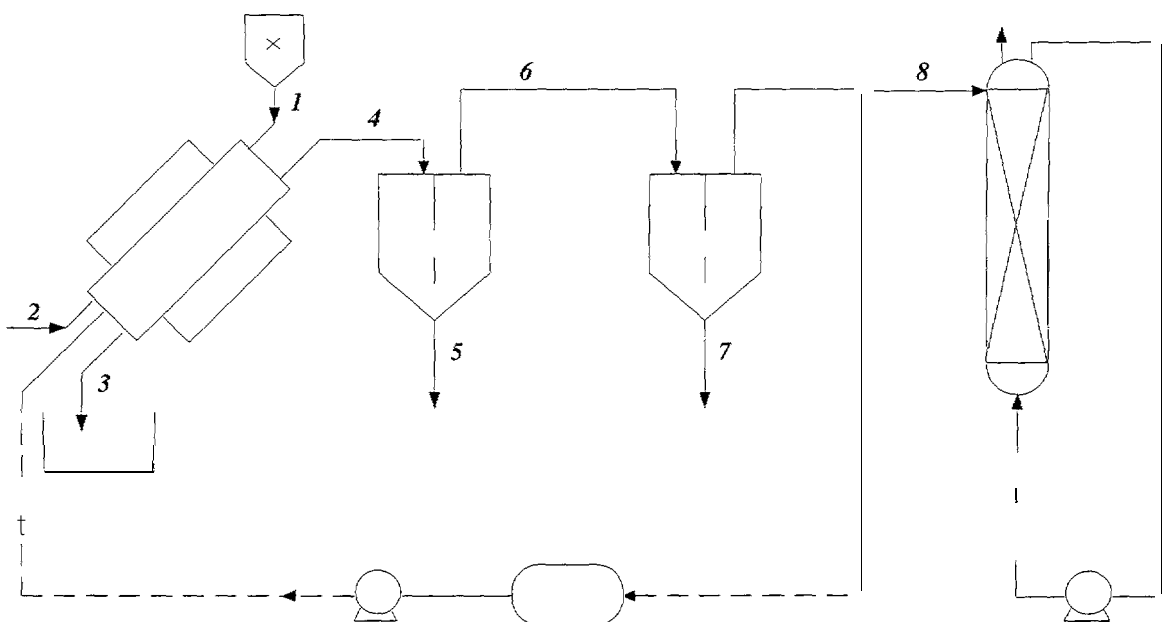


Figure 4: Flow-sheet of continuous chlorination of the chalcopyrite concentrate in rotary kiln.

This can be attributed to the formation of eutectics of metal chlorides having low melting point. The proposed flow-sheet for the chlorination of chalcopyrite concentrate could be achieved using two fluidized beds successively. The first allows the partial chlorination by sulfur chlorides generated in the second step. In the second step, the chalcopyrite concentrate partially chlorinated in the first step is treated by Cl_2 added to gases produced generated by the decomposition of ferric chlorides. Cooling the reaction gases leads to the condensation of solid FeCl_3 . It could be oxidized to produce Fe_2O_3 and Cl_2 that could be recycled for the total chlorination of chalcopyrite concentrate in the second step of the flow-sheet.

III. 3. Chlorination of chromite concentrates on laboratory scale

The chromite concentrate was chlorinated by different chlorinating gas mixture (Cl_2+CO , Cl_2+N_2 , Cl_2+air , $\text{Cl}_2+\text{AlCl}_3$ and $\text{AlCl}_3+\text{CO}+\text{N}_2$) in the temperature range of 400 °C to 1000 °C. The results show that selective chlorination of iron compounds is possible leading to a residue rich in chromium having a Cr/Fe ratio higher than initial concentrate. Based on the best results, the following flow-sheets were suggested for the treatment of chromite concentrates.

Figure 5 illustrates the possible steps of carbochlorination for upgrading the chromite concentrates. According to this figure and to the initial physiochemical characteristics of the chromite ore and/or concentrate, it is possible to double the Cr/Fe ratio by treating these materials between 500 °C and 600 °C for a reaction time of 1 to 2 h using a gas mixture of Cl_2+CO ($\text{Cl}_2/\text{CO} = 1$). Decomposition of ferric chloride to iron oxide allows the recycling of chlorine and the production of environmentally safe residue.

Results of the carbochlorination of the chromite concentrate suggest the possibility of obtaining pure chlorinated compounds, Thus, complete chlorination of the chromite concentrate will generate pure CrCl_3 , MgCl_2 and a mixture of iron and aluminum chlorides. The chromium and magnesium chlorides can be used as a raw material for the production of ultra pure Cr_2O_3 and Mg° . Figure 6 schematizes a flow-sheet for complete carbochlorination

of chromite concentrate. Its carbochlorination at 900 °C during 2 h using a gas mixture of Cl_2+CO ($\text{Cl}_2/\text{CO} = 1$) allows the separation of major elements of this concentrate. Cooling the gaseous phase to about 300 °C, allow the condensation of almost pure chromium chloride with a recovery rate higher than 90%. The gaseous phase is subjected to an oxidizing atmosphere allowing the formation of Fe and Al oxides. The generated chlorine can be recycled. Finally, leaching the carbochlorination residue by water permits the extraction of magnesium chloride. The ultimate residue is mainly composed of silica that is environmentally safe.

Oxychlorination of chromite concentrate either by chlorine+air or chlorine+oxygen allows almost complete extraction of iron and partial recovery of chromium contained in the chromite concentrate at relatively low temperatures. This again can increase the Cr/Fe ratio and thus upgrading the chromite concentrate and allow the formation of high added value chromium oxide. Moreover, the treatment residue has a higher Mg/Fe ratio leading to better thermal, mechanical and chemical characteristics than that of the initial concentrate. This material can be used for the production of refractory material of high quality or used for special applications in foundry. Figure 7 schematizes the suggested flow-sheet. Between 900 °C and 950 °C, partial oxychlorination of the chromite concentrate and/or ore during 2 h leads to the extraction of less than 20 % and 75 % of Cr and Fe, respectively. The decomposition of chromium oxychloride allows the formation of Cr_2O_3 . One may underline that the price of this oxide is some 100 to 150 times more than that of the chromite concentrate, Iron chlorinated compounds were completely recovered in the condensates giving a residue that is rich in chromium and magnesium compounds. Such material is appreciated by the manufacturers of chromite refractory and the moulders due to their higher thermal, mechanical and chemical stability.

III. 4. Scale-up of chlorination of chromite concentrate

The INASMET had chlorinated the chromite concentrate in the rotary kiln using Cl_2+air and Cl_2+CO in the temperature range of 500 °C to 600 °C. Results are summarized by

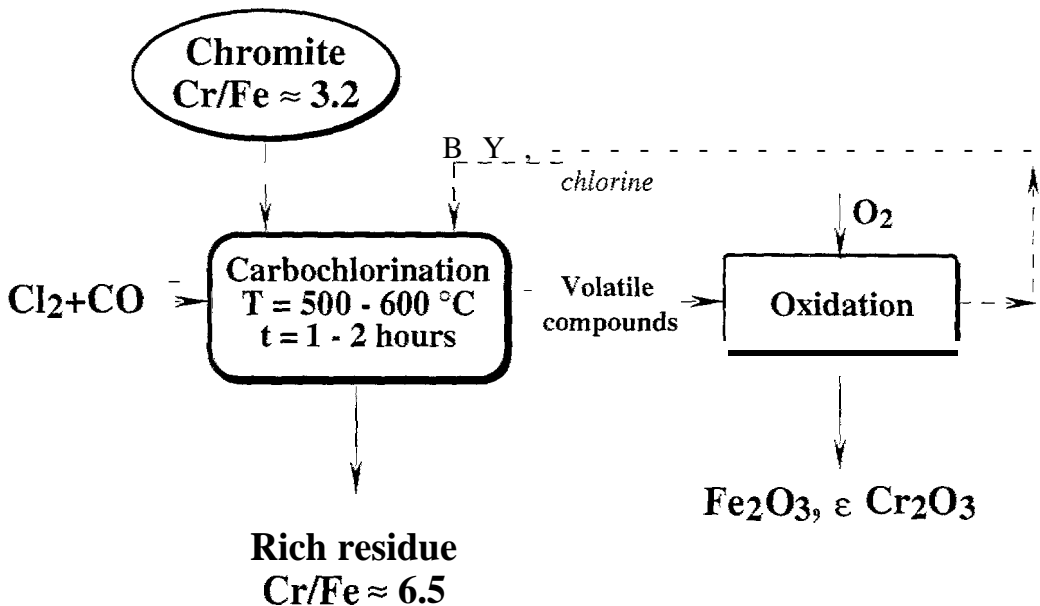


Figure 5: Flow-sheet proposed for increasing Cr/Fe ratio of poor chromite concentrates.

the flow-sheet of Figure 8 and Table V. These results confirm the partial elimination of iron compounds leading to a residue of higher Cr/Fe ratio than the initial concentrate. This ratio was increased from 1.6 to 1.93 during the carbochlorination of chromite concentrate at 600 °C. The chlorination of chromite concentrate with Cl_2+N_2 and Cl_2+air in fluid bed was successfully achieved by the INETI team. Chlorination or oxychlorination of the chromite concentrate in a fluidized bed at about 700 °C and 9.50 ‘C, respectively, allows the increase of the Cr/Fe ratio to about 2.

111.5. Thermal treatment of the metallurgical residues on laboratory scale

The thermal treatments of three metallurgical wastes, between 200 °C and 800 °C using different oxidizing, reducing and chlorinating gas mixtures were performed. It was possible to eliminate about 99 % of toxic elements and to concentrate valuable metals, in the treatments’ residues by a factor of about 2.5. A part of these solids can be recycled directly in the conventional metallurgical processes. The rest can be considered as environmental acceptable as

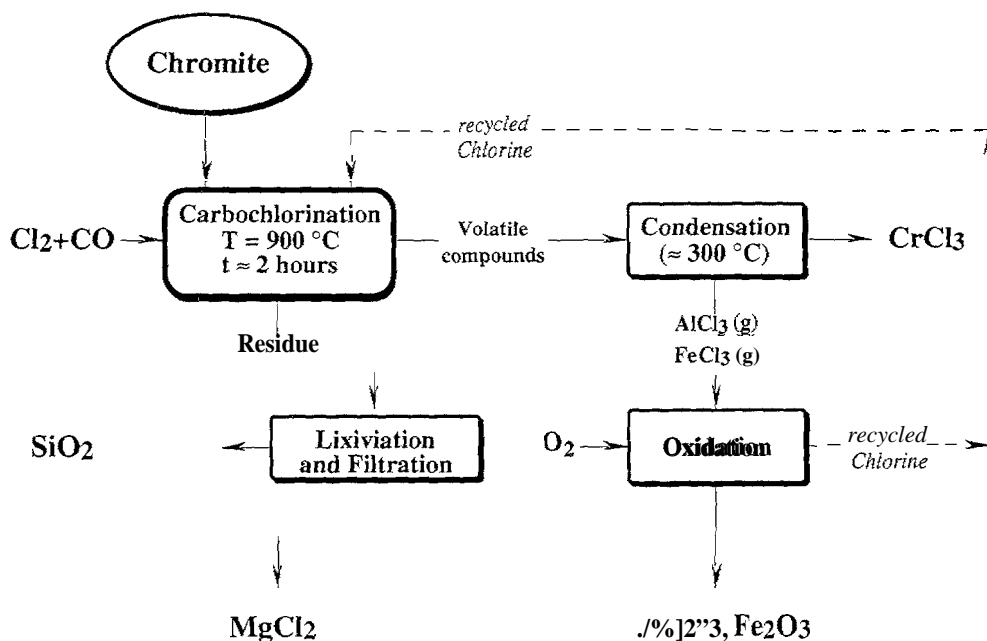


Figure 6: Flow-sheet proposed for complete carbochlorination of chromite concentrates.

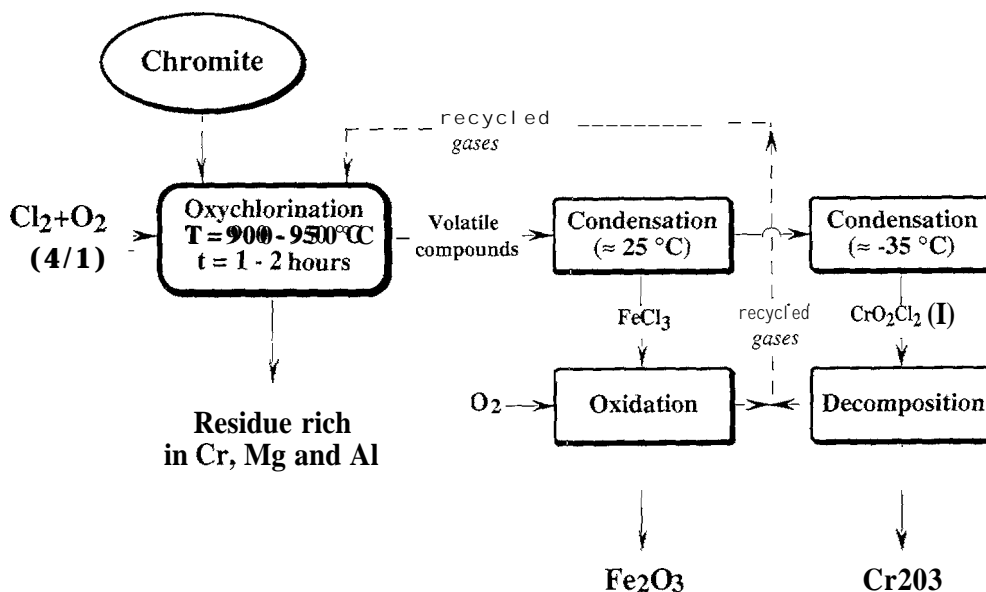


Figure 7: Flow-sheet proposed for partial oxychlorination of chromite concentrates.

heavy metal compounds are separated. Results indicate that the best treatment of these wastes could be achieved either in reducing or oxidizing atmospheres or again a combination of these two treatments. Figure 9 schematizes the flow-sheet proposed for the treatment of the industrial wastes.

111.6. Conclusions

The selective chlorination of chalcopyrite concentrate is successful. Results indicate that the elimination of more than 95 % of iron compounds is possible. This leads to the concentration of the about 95 % of the produced copper chlorides in the treatments' residue. Leaching of this residue with acidified water allows the complete recovery of the contained valuable metal chlorides. The generated sulfur chlorides can either be directly recycled for the chlorination of the copper concentrate or used by the chemical industry (the price is about 1000 Ecus/ ton). However, the annual EU consumption is less than 10 000 tons. The sulfur chlorides had been decomposed or reduced and about 90 % of their sulfur content was recovered as elementary sulfur. Rotary kiln or fixed bed reactors are the most adequate equipments for this process.

Table V: Mass balance for the carbochlorination of the chromite concentrate.

	1 *	2	3	4	5	6
Temperature (°C)	25	25	25	600	25	25
Mode operation	Cont.**	Cont.	cont.	Cont.	Cont.	Cont.
Total gas flow (N m ³ /h)	-	= 150	-	≈ 150	-	≈ 150
Total solid flow (kg/h)	100		91.9	-	15.3	-
Cl ₂ (N m ³ /h)		75		72.2		72.2
CO (N m ³ /h)		75		72.9		72.9
Chromite cone. (k#batch)	100		91.9			
FeCl ₃ (kg/h)				15.3	15.3	-
CO ₂ (N m ³ /h)				2.1		2.1

* Numbers correspond to that of flow-sheet of Figure 8

** Cont. : Continuous

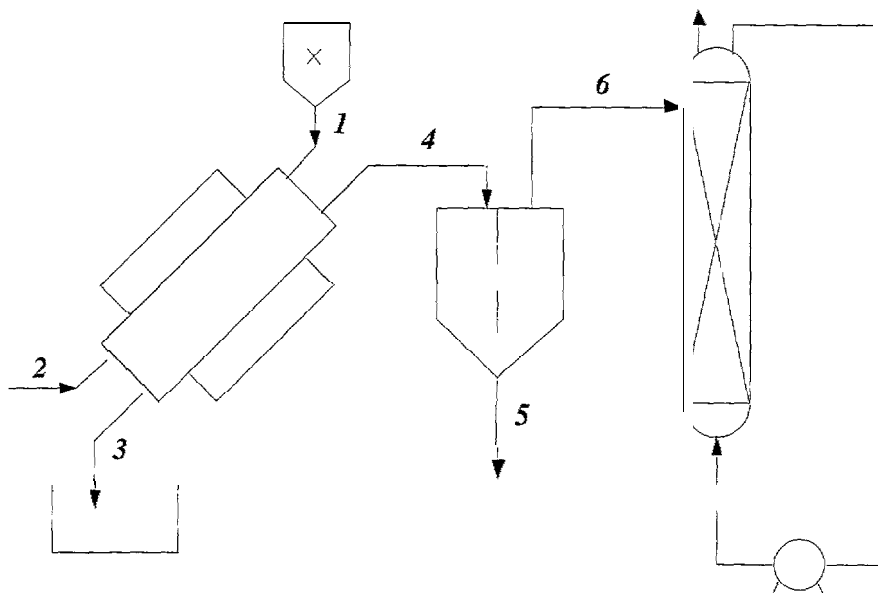


Figure 8 : Flow-sheet of chromite concentrate carbochlorination in rotary kiln.

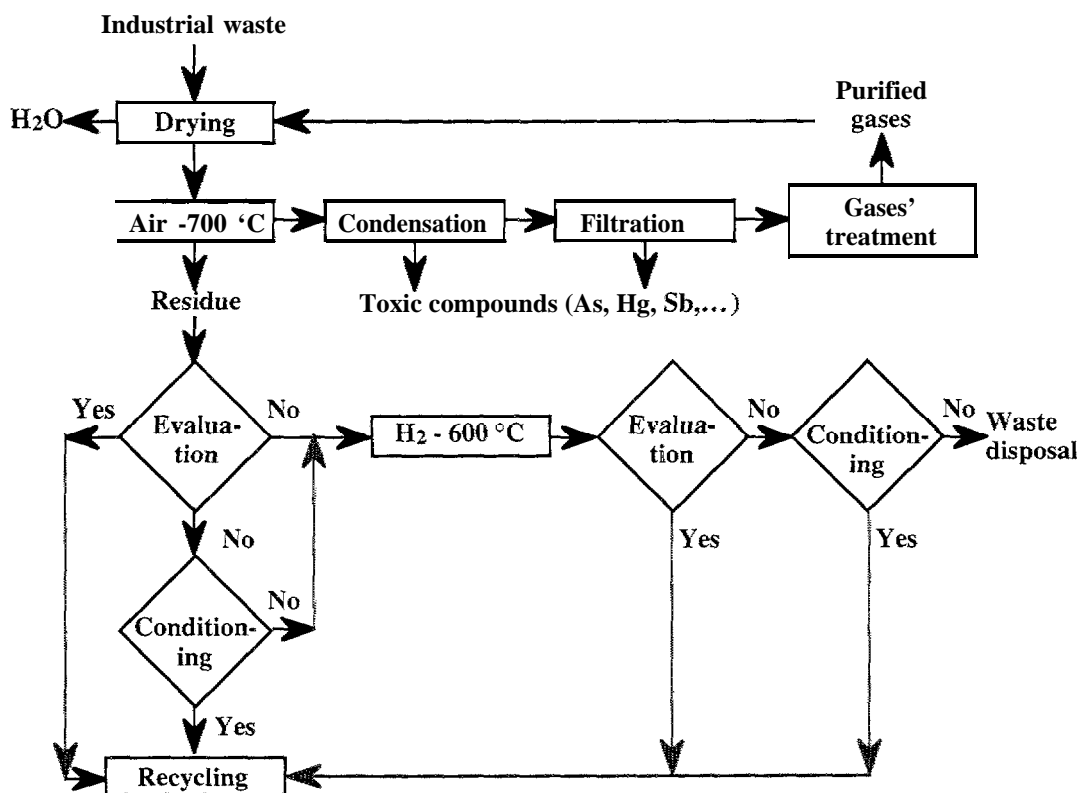


Figure 9: Suggested flow - sheet for the treatment of industrial by-products and/or waste.

Upgrading the chromite concentrate through the augmentation of its Cr/Fe ratio by selective chlorination at moderate temperatures using a chlorine+ air or chlorine+CO gas mixtures is possible. The treatment residue had high Mg/Fe ratio that allows better thermal, mechanical and chemical characteristics. Such material allows the fabrication of high quality refractory material and could be used as high quality sand for foundries. The rotary kiln and fluidized bed are the most adequate for this process. Complete carbochlorination of the chromite concentrate at 900 °C allows the recovery of pure chromium and magnesium chlorides. These compounds could be used for the production of pure high added value products such as chromium oxides or compounds and elementary magnesium.

The treatment of industrial residues for their recycling decontamination is possible through their treatment in oxidizing and/ or reducing atmospheres. Such treatment applied to three samples obtained from an important European non-ferrous operator allows the elimination of 99 % of toxic elements and the concentration of the valuable metals, in the treatment's residue, by a factor of 2.5. The composition of two treated solids matches the input specifications of conventional non-ferrous metal production. The fixed bed reactor as well as the rotary kiln can be used to operate such a process.

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