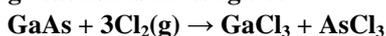


GaAs CHLORINATION STUDY

F.M. TÚNEZ, J. GONZALEZ and M. DEL C. RUIZ

*Instituto de Investigaciones en Tecnología Química (INTEQUI-CONICET) Universidad Nacional de San Luis
fntunez@unsl.edu.ar*

Abstract— The compound GaAs is at the present time an essential part of electronic devices. The recovery of elements from electronic wastes is fundamental for the metallurgic industries. In this work, the following reaction is investigated:



With the aim of recovering constituent elements by chlorination, several variables were studied such as: chlorine partial pressure, in the range between 0.2 and 1 atm, by dilution with N₂; and temperature of reaction, in the -29°C to 200°C range. The reagents used were GaAs of analytical quality, chlorine and nitrogen gas of high purity. The reagents and products were analyzed by X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electronic microscopy (SEM) and atomic absorption spectrophotometry (AAES). The results show that the rate of chlorination did not change significantly with the temperature, but increased with the chlorine partial pressure. It was found that AsCl₃ was partially evaporated at temperatures above 20°C, while the GaCl₃ start to be evaporated at 100°C. These partial results show that chlorination is a selective and economic methodology for the recovery of gallium from electronic wastes.

Keywords— Gallium, Recovery, Chlorination and Arsenic.

I. INTRODUCTION

Gallium is a metallic element of growing use in the modern industry. This element is extensively used as GaAs and GaP in the electronic industry for the manufacturing of semiconductors, solar diodes of light emission, laser, cells, microwaves devices and integrated circuits, among others. Also, it constitutes a strategic element in alloys with plutonium (Habashi, 1997).

Kramer (1988) has elaborated a report that summarizes the uses, properties, worldwide demand and resources and technologies of gallium recovery and purification from different sources, and informs on the manufacture of GaAs. The importance of gallium recovery from different materials containing it can be inferred from this report. It also permits us to infer that the recovery processes of this metal through wet methods include a great amount of stages to obtain high-purity gallium.

Gallium is considered a rare element because its concentration on the Earth's crust is 16 ppm, it is not contained by any specific mineral and it is mainly obtained from by-products of the aluminum and zinc industries. Due to the increasing demand of gallium and

its limited production, knowledge is necessary on the recovery of this element from electronic wastes.

There is an extensive literature on how to recover gallium from different materials. Bautista (1989) has described the stages involved in gallium recovery through acid leaching, and the subsequent metal purification until obtaining gallium 7-N. Bartlett (1988) has investigated the recovery and separation of As and Ga from GaAs electronic wastes, using a Cu alloy in liquid state at temperatures ranging between 1150 and 1200°C. The output obtained was 98% and 96 % for Ga and As, respectively. The leaching with nitric acid of electronic scrap containing GaAs and the later separation and electrolytic purification has been investigated by Charlton and Redden (1981). Another process to obtain and purify gallium is the liquid-liquid extraction with solvents (Nishihama *et al.*, 1999) or by means of resins of ionic interchange (Nakayama and Egawa, 1997).

A number of methods for recovering gallium from electronic scrap are well-known, some of which have been briefly described by Shibasaki *et al.* (1989) who studied the recovery of gallium from GaAs by chlorination. The methods stated by these authors include:

i) The Japanese patent N° 56-386641B (1981) reveals a process based on the dissolution of wastes containing gallium and arsenic in acid medium in the presence of an oxidant reagent. Then, the solution pH is adjusted from 2 to 8 to precipitate the gallium and arsenic hydroxides, and the precipitate is collected by filtration. After that, the precipitate is dissolved in an alkaline solution as sodium gallate, and finally, the gallium is electrolytically recovered.

ii) The Canadian patent N° 1094328 includes: the dissolution of wastes containing arsenic and gallium in an acid medium, wastes elimination by filtration, the increase of the solution pH to 11 or higher with NaOH to precipitate the arsenic as calcium arsenate through the addition of CaO or Ca(OH)₂, the precipitate separation by filtration and then the gallium electrolytic recovery.

Both wet processes generally include the dissolution of gallium-containing wastes in an acid or alkaline aqueous medium and the separation of the required metals from the non-required ones by precipitation and filtration in order to finally recover gallium electrolytically from the filtrate. However, the gallium recovered by these techniques does not have the satisfactory purity for being used as a semiconductor material, and requires greater purification. Besides, the wet processes, in general, consume much time and energy.

iii) Another gallium recovery process is presented in the Japanese patent N° 57-101625A (1982), in which the

gallium-containing wastes are subjected to a vacuum distillation at high temperatures (1100-1150°C), the sublimated arsenic is recovered by condensation and the melted gallium is cooled and then dissolved in an acid, recovering it by crystallization in purified state. This methodology requires high temperature and consumes much energy. Besides, it is not appropriate when chromium is present in the wastes due to the fact that separation between chromium and gallium is difficult to achieve through this process.

iv) The chlorination process proposed by the authors of the U.S. patent N ° 4.666.575 (Shibasaki *et al.*, 1989) involves the separation of the arsenic and gallium chlorides by distillation. This chlorination process is beneficial since the gallium obtained is of higher purity and can be recovered more easily.

Other authors have also investigated gallium recovery through chlorination. For example, the chlorination of GaAs with the initial addition of AsCl₃, followed by the separation by distillation or treatment with NaOH has been studied by Kubo *et al.* (1990), and Túnez (2003) has studied the chlorination of Ga₂O₃ at temperatures higher than 600°C.

According to Kubo *et al.* (1990), the main advantages of the chlorination process in relation to other refinement methods for gallium recovery from GaAs can be summarized as follows: operation temperatures are low, most of the impurities can be effectively eliminated, high-purity metallic gallium can be obtained and the productivity increase is significant.

Shibasaki *et al.* (1989) have also pointed out some advantages of the dry chlorination processes over the wet ones for the recovery of gallium from wastes. According to these authors, dry processes are faster than wet treatments since gallium can be obtained in fewer stages, and the stages are simpler than those used in the wet processes. Besides, the chlorides refinement process is a useful method to produce high-purity metals at commercial scale, and it is used for the refinement of gallium and other metals by Sumitono Metal Mining Co., Ltd. (SMM) in the Isaura plant, where metals are obtained with a purity normally ranging between 99,9999% and 99,99999% (Ohwa *et al.*, 1989).

A wide use of the chlorine chemistry is expected in the future due to the selectivity in the treatment and separation processes, as well as the development of some materials resistant to corrosion for the manufacturing of reactors (Jena and Brocchi, 1991). However, although the refinement process can be easily carried out at laboratory scale, the main disadvantage of the chlorination process lies in the corrosive nature of the metallic chlorides. Therefore, the selection of the equipment building material is fundamental for the application at commercial scale. Special attention should be paid to the materials handling, and leaks should be controlled to avoid risky situations (Ohwa *et al.*, 1989).

In this work, the study of pure GaAs chlorination with Cl₂ gas was made with the purpose of knowing the effect of the main reaction variables of this material

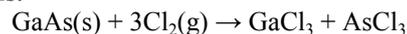
chlorination in order to contribute to an improvement in the chlorination process and a greater reliability for industrial use. The operation conditions investigated were temperature, from -29°C to 200°C and partial chlorine pressure between 0.2 and 1 atm.

II. THERMODYNAMIC CONSIDERATIONS

The thermodynamic analysis of the GaAs-Cl₂(g) system was carried out using HSC Chemistry for Windows, version 5.1. This software has a thermodynamic data base updated to 2003 (HSC, 2003).

Figure 1 shows the equilibrium diagram for the studied system, in the -30 and 250°C temperature range. For the calculation, based on the energy minimization method of the system, a mol of GaAs and 4 mols of Cl₂(g) were taken as initial conditions. Thus, due to the fact that the chlorine gas is above the stoichiometrically needed, so that all the GaAs reacts, the experimental conditions are adequately represented. In relation to the reaction products, all the compounds that contain the three elements and are present in the software database were included for the calculation, but only those whose formation is more thermodynamically feasible were graphed.

The results in Fig. 1 show that the most probable reaction is:



where the product aggregation state varies according to the reaction temperature.

It can be observed that between -30°C and 30°C, the reaction products are in their solid and liquid phases whereas the formation of AsCl₃ in gas phase starts at a higher temperature. After around 80°C, the (GaCl₃)₂(g) species appears, whose formation increases with the temperature increase, and it starts to be decomposed above 150°C resulting in GaCl₃(g).

The calculation of the standard Gibbs free-energy change and of the enthalpy change for chlorine gas mol as a function of temperature was done for the species in equilibrium shown in Fig. 1. The results can be seen in Figs. 2 and 3, respectively.

Figure 2 shows that the thermodynamically feasible reactions are all exothermic within the studied temperature range.

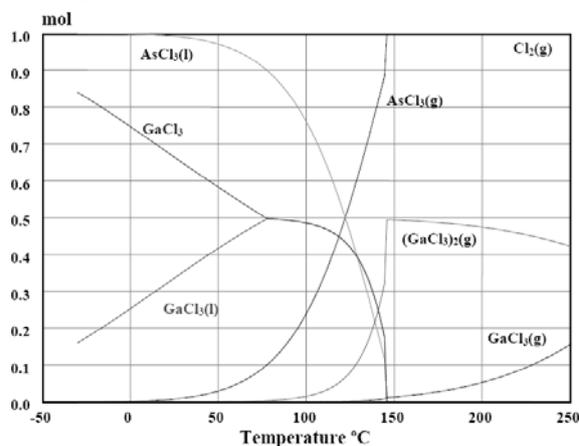


Figure 1. Equilibrium composition for the GaAs-Cl₂ system.

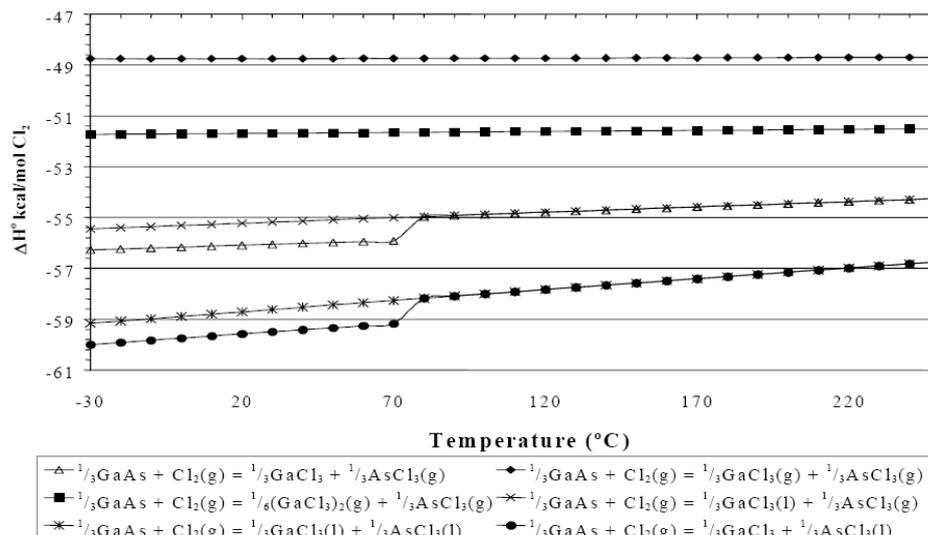


Figure 2. Enthalpy change, as a function of temperature.

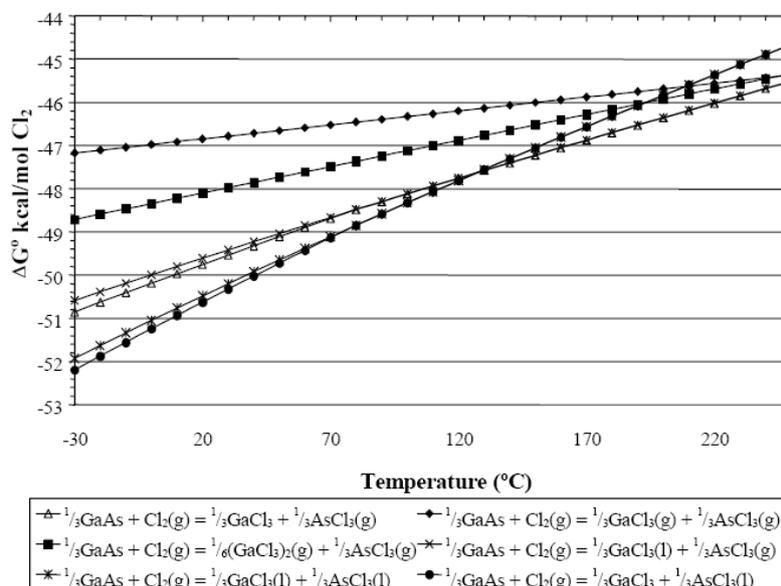


Figure 3. Standard Gibbs free-energy change, as a function of temperature.

Figure 3 indicates that as temperature increases, GaAs chlorination is less feasible due to a decrease in the enthalpy change in the studied reactions.

III. EXPERIMENTAL

A. Materials

The materials used in all the experiments were GaAs of analytical quality (Sigma-Aldrich, 99.999%), Cl₂ (INDUPA ARGENTINA, 99.9%) and N₂ as gas for dilution and purge (AGA ARGENTINA, 99.9%).

B. Equipment and Procedure

The chlorination reaction was studied by means of a thermogravimetric system developed in our laboratory and capable of working in corrosive atmospheres (González *et al.*, 2006).

The analysis of the solid reagent was carried out by X-ray diffraction in a Rigaku equipment model D-Max

IIC, scanning electronic microscopy (SEM) in a LEO 1450 VP equipment and by means of X-ray fluorescence with a Philips equipment model PW 1400. The chlorination reaction products were analyzed by atomic absorption, with a Shimadzu 6800 AA equipment.

The experimental procedure for the study of GaAs chlorination by thermogravimetry was as follows. The sample, previously ground and classified by particle size, was supported on a quartz previously weighed crucible. Approximately 50 mg of the solid was used in each experiment. The sample was covered with a thin quartz wool in order to avoid projections. The crucible with the sample was supported on the thermogravimetric system. The temperature and other work conditions were fixed and the sample was subjected to a nitrogen flow rate of 50 ml/min for 30 min. After stabilizing the work conditions, a previously regulated flow of chlorine

was introduced to the system by operating of valves. At that moment, the chronometer was switched on and the mass changes vs. the time were recorded. Finally, the gas chlorine flow was interrupted and the thermogravimetric system was purged with N₂. The chlorination residue was dissolved in NaOH 1M and analyzed by atomic absorption. All the effluent gases of the chlorination system were purified using H₂SO₄ and NaOH traps.

IV. RESULTS AND DISCUSSION

A. GaAs Characterization

The results of the solid reagent characterization by XRD are shown in Fig. 4. It can be observed that the reagent is a pure and crystalline solid, exhibiting a good correspondence with the JCPDS 32-389 card of GaAs (Powder Diffraction Files, 2003).

The analysis by XRF presented in Fig. 5 shows that the solid is highly pure. Its characteristic lines are detailed in Table 1.

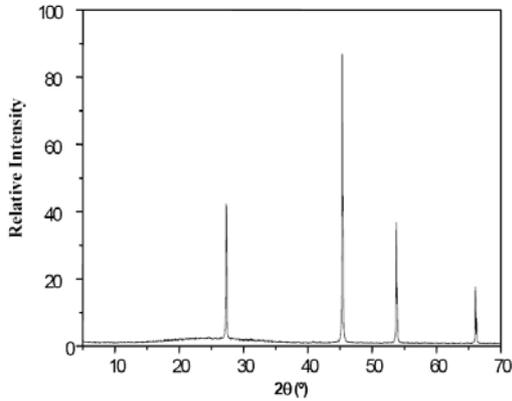


Figure 4. XRD of solid reagent.

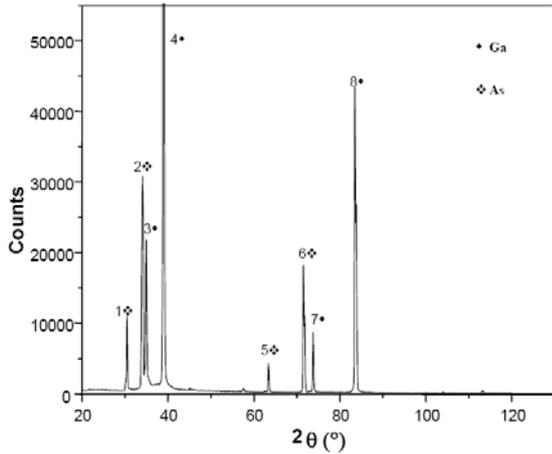


Figure 5. XRF of solid reagent.

Table 1. Characteristic lines of the GaAs.

Number	2θ (°)	Line	Order
1	30.5	K _{β1}	1
2	34.1	K _α	1
3	35.0	K _β	1
4	39.1	K _α	1
5	63.4	K _{β1}	2
6	71.6	K _α	2
7	73.6	K _β	2
8	83.6	K _α	2

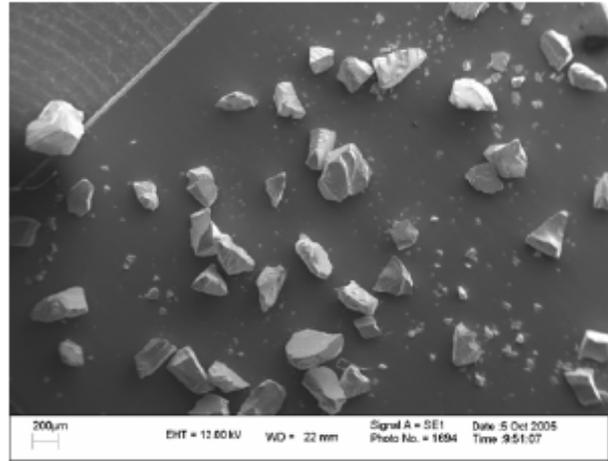


Figure 6. SEM micrograph of GaAs. General view.

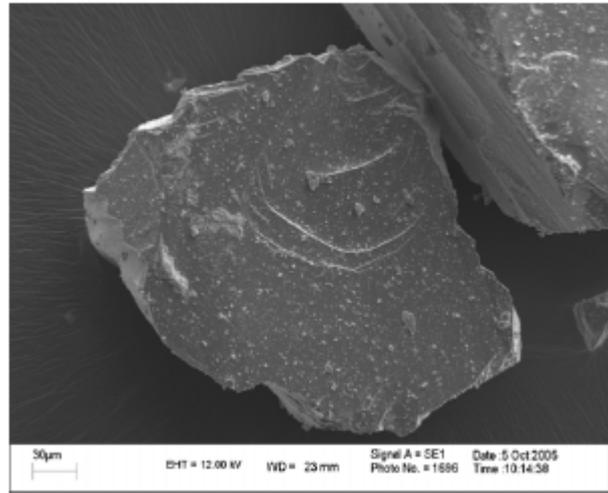


Figure 7. SEM micrograph of a particle of GaAs.

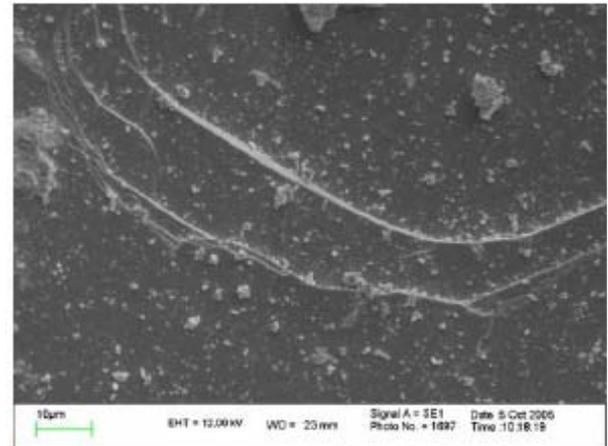


Figure 8. SEM micrograph of a particle surface.

The analysis by SEM is presented in Figs. 6, 7 and 8. The results show that the particles are nonporous and have irregular edges.

B. Temperature effect

Figures 9 and 10 show the results of GaAs chlorination at different temperatures. All the isotherms were obtained working with pure Cl₂, at the atmospheric pressure and flow of 50 mL/min. An induction period can be

observed in both figures, which decreases as the working temperature increases. The complete conversion of GaAs was observed in all the isotherms shown in this work. This fact was determined through the observation of the reaction residues which were oily liquids or small quantities of white solid. GaAs, a crystalline and bright black solid, was not observed.

Range between -30 and 10 °C

Figure 9 shows that the mass increase observed in the isotherms obtained at -29, -10 and 10°C presents, in general, good correspondence with the mass gain of 147% that stoichiometrically would correspond to that produced by the formation of GaCl₃(s) and/or GaCl₃(l) and of AsCl₃(l).

The mass balance calculated from the experimental data for the -29°C isotherm is higher than 147 %, due to the fact that chlorine is absorbed by the sample since the working temperature is close to the chlorine condensation temperature, -34,6°C (CRC, 1980).

The mass gain observed in the chlorination isotherm at -10°C has a very good correspondence with the stoichiometric balance previously mentioned.

The isotherm obtained at 10°C shows a little lower mass gain, which corresponds stoichiometrically to the formation of the Ga and As trichlorides in the liquid or solid phases. At this working temperature, this fact can be attributed to the formation of a small quantity of AsCl₃(g) by the effect of the exothermicity of the GaAs chlorination reaction, as indicated by the thermodynamic analysis shown in Fig. 2. These results coincide with the data of the quantitative analysis carried out with the residues through AA (Fig. 11).

Range between 30 and 50°C

The data analysis of the isotherm obtained at 30°C (Fig. 9) and the analysis of the quantity of Ga and As found in the residue (Fig. 11) indicates that the formation of AsCl₃(g) has been increased by the action of the heat produced by the GaAs chlorination and generated in the reaction zone (Fig. 2). Besides, no evaporation of GaCl₃ has been observed.

The previously mentioned exothermic effect is more notable at 50°C, with a mass gain lower than in the previous cases due to the formation of AsCl₃(g). The evaporation of AsCl₃ can also be observed, which starts to have a considerable vapor pressure, as can be seen in the equilibrium diagram in Fig. 1.

Range between 85 and 200°C

Figure 10 shows the GaAs chlorination isotherms obtained at 85, 110, 160 and 200°C.

The data analysis of the chlorination obtained at 85 and 110°C, together with the results of the As and Ga measurements in the residues by AA and the thermodynamic predictions, indicates the following: a) at 85°C the mass gain of 80% observed corresponds to the formation of GaCl₃(l) and AsCl₃(l), which occurs with the simultaneous formation and evaporation of a considerable quantity of AsCl₃(g), and a lower quantity of GaCl₃(g), b) at 110°C almost all the AsCl₃(g) formed is

evaporated and the evaporation of GaCl₃(g) is more notable.

The isotherm obtained at 160°C indicates that the mass loss observed by the thermodynamic analysis is due to the fact that all the AsCl₃ is in the gaseous phase and is carried away from the reaction zone by the chlorination flow. Besides, the evaporation of GaCl₃(g) is higher since the mass loss observed is higher than the loss stoichiometrically corresponding to As elimination as AsCl₃(g).

At 200°C the results indicate that, at the studied reaction time, only a small quantity of GaCl₃(l) remains, since the working temperature is close to the boiling point of this compound (201.3°C) (CRC, 1980).

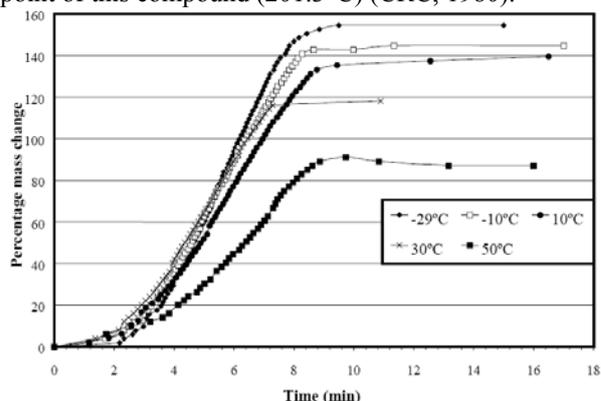


Figure. 9. GaAs chlorination isotherms at -29, -10, 10, 30 and 50°C.

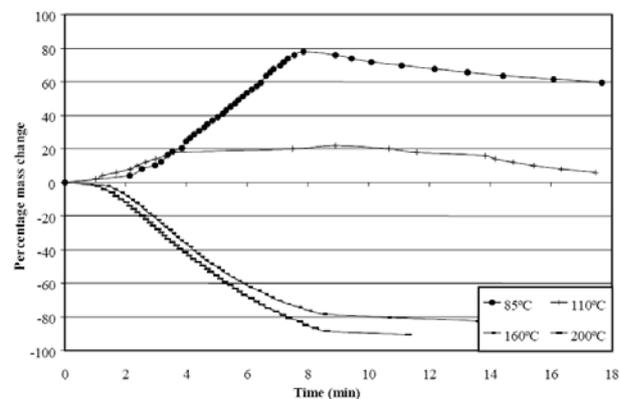


Figure. 10. GaAs chlorination isotherms at 85, 110, 160 and 200°C.

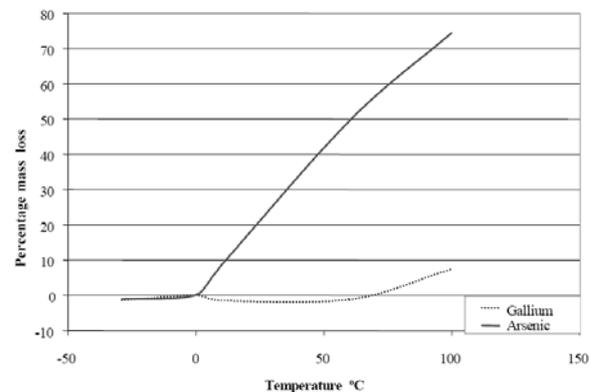


Figure. 11. Ga and As loss in residues, measured by Atomic Absorption.

C. Effect of the chlorine partial pressure.

The study of the influence of the chlorine partial pressure on the GaAs chlorination was carried out in the range between 1 and 0.2 atm, and in three temperature levels: -20, 20 and 85°C. The results are shown in Figs. 12, 13 and 14, respectively, in which it can be observed that the reaction rate of GaAs chlorination decreases as the chlorine partial pressure diminishes, and that the effect is stressed at the lowest working pressures.

Figure 12 shows that at -20°C, and for all the studied chlorine pressures, the mass increase coincides with that corresponding to the formation of GaCl₃(s), GaCl₃(l) and AsCl₃(l), as indicated in section B.

The different isotherms obtained at 20°C (Fig. 13) show, together with the decrease of the reaction rate, that, as the chlorine partial pressure decreases, when working with pure chlorine, there is a change in the gradient curve of the mass variation in relation to time after the reaction finishes. This mass decrease is attributed to the exothermic effect of the GaAs chlorination reaction which causes the temperature in the reaction zone to be higher than that indicated by the measurement instrument due to a deficient dissipation of the generated heat. This temperature increase produces the partial volatilization of the AsCl₃(l) formed. The decrease in the mass loss is not observed at lower chlorine partial pressures, which indicates that the evaporation of AsCl₃(l) is lower due to a better dissipation of the heat generated in the reaction zone. This fact is more notable in the isotherm obtained at 0.2 atm, in which the mass gain is higher than that observed at higher chlorine partial pressures.

Figure 14 shows that in all cases, after the reaction is finished, a decrease in the mass change is produced partly due to the formation of AsCl₃(g), which at 85°C already has a considerable vapor pressure. It can also be observed in this figure that the isotherms obtained at chlorine partial pressures of 0.8 and 0.6 atm present a mass increase higher than that obtained at a pressure of 1 atm. This is attributed to the fact that when working under more energetic conditions and, consequently, with higher reaction rates, the dissipation of the heat generated by the reaction exothermicity is more difficult, which causes a higher volatilization of the As and Ga chlorides. Though apparently contradictory with the previous paragraph, it is worth noting that at the lowest chlorine partial pressures, 0.4 and 0.2 atm, the decrease of the mass gain is higher. This effect can be explained by considering that although heat generation is lower, the reaction rate is also lower, longer times are required to obtain the chlorination of all the GaAs, and consequently, these times are enough to produce the evaporation and carrying away of practically all the AsCl₃(g y l) and of part of the GaCl₃(l) formed.

The results obtained when studying the effect of the chlorine partial pressure, together with the analysis of the temperature influence, permits to suggest that the reaction is controlled by the adsorption of Cl₂ on the GaAs surface, and that as the Cl₂ partial pressure increases, an equilibrium between the adsorbed chlorine

and the chlorine in gaseous phase is established. This might explain why at high chlorine partial pressures the reaction rate is slightly influenced by the variation of the partial pressure.

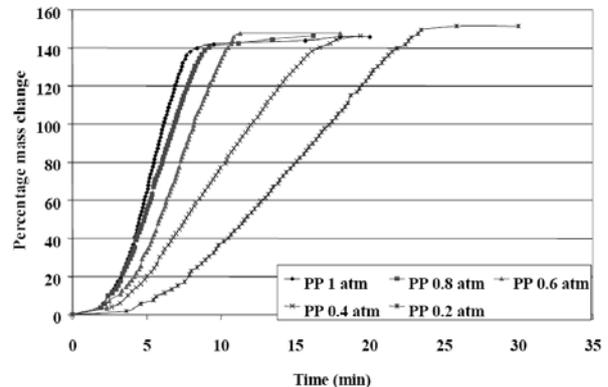


Figure 12. Isotherms of GaAs chlorination at -20°C and different partial pressure of chlorine.

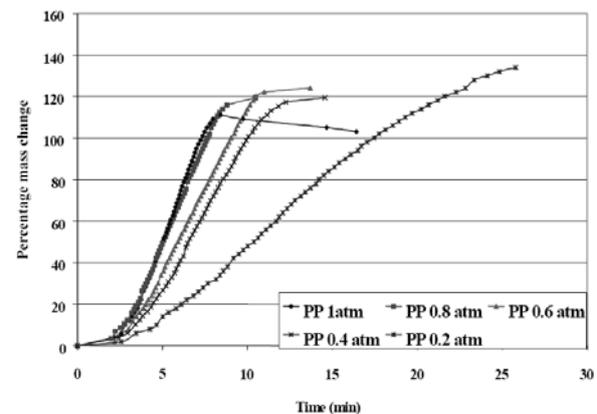


Figure 13. Isotherms of GaAs chlorination at 20°C and different partial pressure of chlorine.

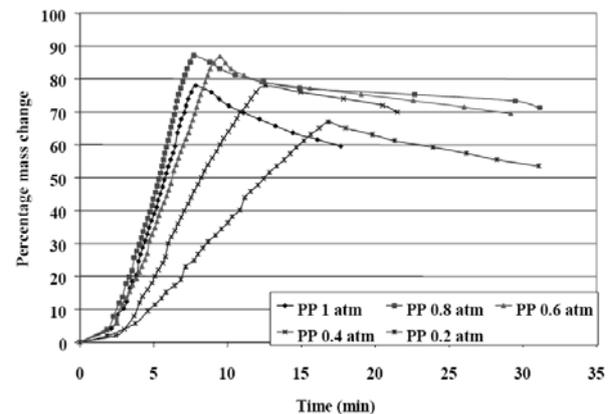


Figure 14. Isotherms of GaAs chlorination at 85°C and different partial pressure of chlorine.

IV CONCLUSION

The main conclusions of this work can be summarized as follows:

- 1 GaAs chlorination is feasible and it is produced at very low temperatures and with a very high reaction rate.
- 2 The reaction products are GaCl₃ and AsCl₃ whose aggregation state depends on the working tempera-

ture.

- 3 The reaction rate is influenced by the chlorine partial pressure and such influence is stressed at the lowest partial pressures. This permits to determine that the reaction is controlled by the chlorine adsorption on the GaAs surface, and that as partial pressure increases, an equilibrium between the gaseous and adsorbed phases is established.
- 4 The methodology used for the GaAs chlorination confirms that this technique permits to recover Ga and separate it from As.

ACKNOWLEDGMENTS

The financial support from Universidad Nacional de San Luis, Agencia Nacional de Promoción Científica y Tecnológica and Consejo Nacional de Investigaciones Científicas y Técnicas is gratefully acknowledged.

REFERENCES

- Bartlett, R., "Separation of As and Ga from mixed GaAs electronic scrap", *Arsenic Metallurgy Fundamentals and Applications*, edited by R. G. Reddy, J. L. Hendrix and P. B. Queneau, The Minerals, Metals & Materials Society, 385-400 (1988).
- Bautista, R.G., "Gallium metal recovery", *Journal of Metals*, **41**, 30-31 (1989).
- Charlton, T. and R. Redden, "Recovery of Gallium compounds", *Canadian Patent CA 1094328* (1981).
- CRC, *Handbook of Chemistry and Physics*, 60th ed.; Ed. Robert C. Weast, CRC. Press, Inc. Boca Raton, Florida 33431 (1980).
- González, J., M. Ruiz and F. Túnez, "Aparato de laboratorio para realizar termogravimetrías en atmósferas corrosivas y no corrosivas", *Patente Internacional PO 06 04 00450* (2006).
- Habashi, F., *Handbook of Extractive Metallurgy*, **3**, Editorial Willey-VCH (1997).
- HSC, *Chemistry for Windows Software*, Version 5.1, Outokumu Research, Pori, Finland, (2003).
- Jena, P.K. and E.A. Brocchi, "Metal Extraction Through Chlorine Metallurgy", *Mineral Processing Extractive Metallurgy Review*, **16**, 211-216 (1991).
- Kramer, D., "Gallium, gallium arsenide: supply, technology, and uses", *Bureau of Mines, Inform 9208*, 1-25 (1988).
- Kubo, S., M. Yukinobu, O. Yamamoto, G. Nabeshima and J. Okajima, J., "Recovery of high purity Gallium metal from Gallium-Arsenide scrap", *Second International Symposium-Recycling of Metals and Engineered Materials*, Ed. J. H. L. Van Linden, D. L. Stward, Jr. and Y. Sahai, The Minerals, Metals & Materials Society, 505-513 (1990).
- Nakayama, M. and H. Egawa, "Recovery of Gallium (III) from strongly alkaline media using a Kelex-100 loaded Ion-Exchange resin", *Engineering Chemistry Research*, **36**, 4365-4368 (1997).
- Nishihama, S., T. Hirai and I. Komasaawa, "Separation and recovery of Gallium and Indium from simulated Zinc refinery residue by liquid-liquid extraction", *Industrial & Engineering Chemistry Research*, **38**, 1032-1039 (1999).
- Ohwa, H., M. Yukinobu, J. Nabeshima and M. Yasukawa, "High-purity metals production of Sumitono Metal Mining Co., Ltd. (SMM)", *Extraction Metallurgy*, **89**, 885-898 (1989).
- Powder Diffraction Files, *Cards of JCPDS* (1993).
- Shibasaki, T., E. Kimura and Y. Nishiyama, "Process for recovering gallium from gallium-containing waste", *United States Patent US 4,956,159* (1989).
- Túnez, F., "Estudios preliminares de la cloración de óxidos de Galio e Indio, con miras a la recuperación de dichos metales de desechos electrónicos", *Trabajo Final de Tesis de grado. Universidad Nacional de San Luis* (2003).

Received: December 20, 2005.

Accepted: February 2, 2008.

Recommended by Subject Editor: Alberto Bandoni.

