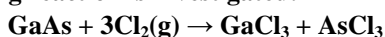


GaAs CHLORINATION STUDY

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