

GALLIUM RECOVERY — TECHNOLOGICAL ALTERNATIVES

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Bayer liquor is the principal source for gallium production. India is a large aluminium producing country and thus has a vast potential to produce gallium to the tune of 10 to 12 TPA from its five alumina plants. Various options are available for obtaining gallium metal from Bayer liquor depending on the history and quality of the liquors which vary from plant to plant through one of the following technologies viz., amalgam metallurgy, cementation of gallium with aluminium or aluminium-gallium alloys, solvent extraction and ion exchange resins. The merits and otherwise of the various technologies will be discussed with reference to their feasibility of commercial scale adoption in Indian Alumina plants, and their impact on the economy of alumina production. The world scenario of gallium production and consumption will also be dealt with.

Keywords: Bayer liquor, gallium and amalgam metallurgy.

INTRODUCTION

The advent of the electronic age and the use of semiconductors on an ever increasing scale has made gallium a hi-tech metal in the past two decades. Due to its broad liquid range from 303K to 2170K it has attracted the attention of physicists and scientists. Its intermetallic compounds with arsenic, phosphorous and antimony are sought after for higher memory capacity and greater computational rates in electronic devices. Gallium based materials have an edge over silicon and germanium for applications involving higher processing speed, more radiation and temperature tolerance, lesser power need and compatibility with optical devices. Gallium has promising uses in light emitting diodes, laser diodes, digital integrated circuit chips and solar cells.

The ever increasing uses for gallium have resulted in a renewed interest in the recovery of gallium. The metal is reactive and hence primary sources are scarce. It occurs in Germanite $\text{Cu}_3(\text{FeGa})\text{S}_4$ to the extent of 0.5-0.8% and upto 0.001% in coal ash as a byproduct in the coke dust. It also occurs in the leach residue obtained after treatment of zinc ore. Although the reserves of gallium can be considered virtually unlimited, gallium is mainly recovered from sodium aluminate liquor (Bayer liquor) of aluminium industry.

Gallium is invariably associated with bauxite ore to the extent of 0.002-0.1%, and dissolves along with aluminium during the digestion of bauxite with alkali. Because of successive leaching, it attains concentrations of 100- 250 mg dm^{-3} depending upon the origin and nature of the Bayer liquor. About 95% of the world's commercial production comes from this liquor.

Recovery of gallium from Bayer liquors

Various options are available for obtaining gallium metal from Bayer liquor depending on the history and quality of the liquors which vary from plant to plant. Some of the methods used are electrochemical reduction using mercury/sodium amalgam, cementation with Al or Al-Ga alloy, solvent extraction and use of chelating ion exchange resins.

Conventional methods for the recovery of gallium from Bayer process liquors always include a preconcentration step. The Breteque process [1] involves the electroreduction of gallium into a mercury cathode, or by a slight modification of sodium amalgam cathode [2]. The Beja process [3] uses carbonation of the liquor for gallium concentration which is not suitable if the liquor has to be recycled as it results in a loss of sodium.

Amalgamation process

In this process, Bayer liquor is subjected to electrolysis using mercury pool/amalgam as cathode and M.S or Ni as anode. During electrolysis, sodium ions are first discharged at the cathode yielding sodium amalgam and, later, the gallium present in solution passes into the mercury through displacement yielding Na-Ga-Hg amalgam. The resultant amalgam is subjected to deoxidation to obtain sodium gallate solution. After concentration, the solution on electrolysis yields gallium metal.

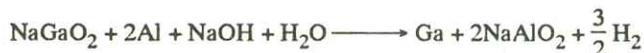


The basic aspects of gallium deposition onto the mercury surface occurs through a process of secondary phase exchange by sodium amalgam primarily formed during electrolysis or polarization. The influence of organic and inorganic impurities present in the Bayer liquor were investigated using electrochemical techniques [4-7].

A process based on amalgam metallurgy was initiated at CECRI and successfully demonstrated at MALCO, Mettur Dam, Tamil Nadu. Approaching a purity of 4N gallium is a noteworthy feature of this process. But in the present day context, it is not an environment friendly process and hence the need for alternative methods of gallium recovery.

Cementation with Al-Ga alloy

Extraction of gallium metal by cementation with aluminium or aluminium-gallium alloy is a non-toxic method [8]. A difference in potential of about 300 mV between aluminium and gallium in concentrated alkali solution makes the process feasible, since hydrogen overvoltage on the aluminium-gallium is higher than with solid aluminium, the rate of gallium extraction from the liquor is enhanced.



Gallium is obtained with a purity of 98-99%. This method does not result in the introduction of foreign ion or metal into the aluminate liquor. However, this method calls for an initial gallium concentration of about 300 mg dm⁻³ (as Ga) and aluminate solutions relatively free from impurities such as vanadium and organics.

Solvent extraction

Gallium solvent extraction is frequently used in analytical procedures and in secondary recovery of gallium from scraps in acidic media. Kelex 100 and Lix 26 with alkylated derivatives of 8-hydroxy quinoline as the active component are the only commercially available extractants suited to

gallium recovery from highly alkaline solution [9]. But prolonged use gradually degrades the solvent due to the high basicity of the medium [10].

Chelating ion-exchange resins

The use of ion exchange chelating resin for metal recovery process has gained importance in recent times. These chelating resins are those in which ligands capable of forming complex metal ions are introduced onto a basic polymer matrix. The relatively low concentration of gallium in the Bayer liquor suggests that an ion exchange process for its extraction is feasible [11]. It has been reported that chelating resins having a combination of one =NOH group and another active group such as -NH₂, -OH, -SH or =NH exhibit extracting properties for gallium. However no industrial application has been reported and information about gallium extraction with chelating resins is very scarce.

Commercially available chelating resins such as Dowex Al and Duolite ES-346 have been tried for gallium recovery from Bayer liquor but their main drawback is the eventual degradation of the resin due to the hostile highly alkaline nature of the liquor. Towards avoiding this drawback, it was found that copolymers having pendant acrylic or methacrylic ester groups when incorporated with hydroxamic acid ligand are expected to have excellent properties of gallium extraction from Bayer liquor [12]. Work has been initiated at CECRI to synthesize such chelating ion exchange resins and evaluate their efficacy for the efficient recovery of gallium.

Table I gives a comparison of the different routes used for gallium recovery; and is based on projected figures. From the Table it is evident that the ion-exchange process is the most feasible method of recovery.

Purification of Bayer liquor

A typical Bayer liquor is a strongly basic, viscous and dense solution containing large amounts of aluminium, sodium hydroxide, sodium carbonates, humic acids and traces of

TABLE I: Comparison of different routes for gallium recovery

| | Amal-gam | Cemen-tation | Ion exchange |
|---|----------|--------------|--------------|
| Initial concn (mg/l) | 220 | 250-300 | 200 |
| Final concn. (mg/l) | 120 | 175-210 | 80 |
| Percentage extraction | 40 | 30 | 60 |
| Vol. of lye taken for 1 kg production (m ³) | 10-11 | 10-11 | 8-9 |
| Total Ga (kg) | 2.42 | 2.75-3.30 | 1.6-1.8 |

other elements such as vanadium, zinc, iron etc. Different methods of gallium recovery are effected by the presence of impurities in Bayer liquor. With the help of voltammetry [7], it is shown that the heavy metals viz., vanadium, iron, copper etc. as well as organics, normally found as impurities inhibited gallium deposition into mercury/sodium amalgam due to the formation of thin films on the cathode surface. However, by using a 0.5% sodium amalgam cathode [2] vanadium, a major impurity was reduced to the insoluble vanadium(III) form. The vanadium should be brought to a tolerable level before the amalgamation step, otherwise it gets reduced during the electrolysis and forms a finely suspended vanadium hydroxide precipitate. For removal of vanadium, the liquor is gradually cooled and allowed to settle down by which the vanadium concentration is brought down to below 100 ppm or by reacting the aluminate liquor with calcium hydroaluminate at 353-363 K. Removal of vanadium and organics is also a prerequisite for recovery of gallium by concentration route because their presence facilitates wasteful hydrogen evolution thus lowering the displacement efficiency.

In case of chelating ion-exchange resins, the presence of humic acids is reported to be harmless [11] as they are not adsorbed on the resin surface. It has been found that removal of humic acid by a strong base resin like Amberlite IRA-400 does not effect the extraction of gallium but there is an increase in the extraction of vanadium probably because humic acids are likely to form complex compounds with vanadium.

World scenario of gallium production

The potential reserve of gallium which can be extracted depends on the exploitation of bauxite or zinc ores. Current world extraction capacity increased from 62 to 145 tonnes per annum according to latest reports [13,14]. Most of the production comes as a byproduct of the conversion from bauxite into alumina. Sixtyfive per cent of primary active world capacity is concentrated in Western Europe and Japan. Eastern Europe and China provide an additional 20% of world gallium production capacity.

The overall increase in gallium production capacity that has occurred in the late eighties is substantial. The Sumitomo Chemical of Japan, Ingal International Gallium of West Germany, Tingzhan Aluminium of China and Ote Metal of Japan are the producers who have expanded or put up new plants giving an added total capacity of 20-25 TPA. In addition, several other projects are planned to increase capacity or replace an obsolete capacity. The most significant among these is the Rhone-Poulenc primary gallium

extraction plant at Pinjana, Western Australia using plant liquors from Alcoa, Australia.

Scrap is a significant source of supply for gallium, principally because the process required to make wafers for a range of gallium products yields a significant amount of scrap. This secondary gallium is produced by a variety of chemical dissolution processes suitable for treatment of scraps obtained from specific sources. The operating costs are computed from the sum of unit consumption times the unit costs. The current price for 3N-4N gallium is around \$ 400 but secondary gallium prices range from \$ 120-240 per kg above the cost of gallium contained in the scrap.

Gallium production potentiality in India

There is ample scope for gallium extraction from all the alumina plants in the country. If a steady recovery is not made, the gallium that is dissolved from bauxite will only be wasted along with the aluminium hydroxide. The conditions adopted for digestion and the other steps involved in the Bayer's process of alumina manufacture decide the equilibrium level of gallium in the Bayer liquor apart from the gallium content of bauxite. In order to have efficient recovery, gallium in the feed liquor is to be not less than 200 ppm. Also, complete extraction is not normally essential, as the practise is to recycle the solution to the alumina plant and expect the depleted gallium content to be replenished.

A typical analysis of the Bayer liquor obtained from different alumina smelters and the estimated gallium production potentiality is shown in Table II. For a production of one tonne of aluminium, five tonnes of bauxite is consumed. Taking an average gallium content of 0.002% in bauxite and an overall 20% recovery of gallium, the estimated 10-12 TPA expected gallium recovery is arrived at from the aluminium plants in India.

TABLE II: Bayer liquor obtained from different alumina smelters and the estimated gallium production potentiality

| Name of the alumina plant | Aluminium production capacity TPA | Estimated gallium recovery TPA |
|---------------------------|-----------------------------------|--------------------------------|
| HINDALCO | 150,000 | 2.4 |
| BALCO | 100,000 | 2.0 |
| INDALCO | 120,000 | 2.4 |
| MALCO | 25,000 | 0.5 |
| NALCO | 218,000 | 5.0 |
| Total | 613,000 | 12.3 |

The know-how for amalgamation process is developed in India by CECRI, Karaikudi and demonstrated at a pilot plant level with a capacity of 25-30 Kg PA to M/s. MALCO, Mettur Dam, Tamil Nadu. A feasibility report for a 0.5 TPA commercial plant has been drawn up jointly with M/s. NRDC and M/s. EIL, New Delhi. Subsequently a DPR has been prepared by M/s. NRDC and NALCO through M/s. EIL for putting a commercial plant of 1.0 TPA capacity at NALCO. A noteworthy feature of this process is the availability of 4N purity gallium and less than 1 kg mercury loss per kg of gallium produced. A pilot plant for gallium recovery based on amalgam metallurgy developed by Bhabha Atomic Research Centre (BARC), Bombay has been established at M/s. Hindustan Aluminium Company (HINDALCO), Renukoot with a capacity of 30 kg PA. M/s. BALCO have prepared a feasibility report for gallium production using cementation technology by the VAMI Institute, Leningrad, USSR.

Hence there is a need to tap the available 10-12 TPA of gallium which India can produce from its alumina plants due to a steadily increasing overseas demand of high purity as well as crude gallium.

Though the adaptability of amalgamation technique is feasible for all the Indian plants the main drawback, apart from environmental constraints, is the involvement of a number of unit operations which in turn reflects on the cost of production. Thus, the cost of gallium per kg is much higher than the other alternate routes.

As regards the cementation process, although it is non-toxic, it is not suitable for Indian plant liquors because of their low gallium concentration. Methods like evaporation, lime treatment, impurities removal etc., which are normally adopted for improving the liquor concentration should take care to avoid altering the liquor composition because it has to be recycled into the alumina cycle.

Recovery of gallium using chelating ion exchange resins may eventually become a cost effective and environment friendly technology. Except for a pilot plant reported in Japan, literature survey shows no serious attempt in this direction. Due to the non-availability of a commercial resin which could be used specifically for gallium recovery, the work becomes complex.

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