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PRODUCTION OF GALLIUM — PRELIMINARY EXPERIENCES OF A PILOT PLANT OPERATION

A N RAO, O N MATHUR, C M A JEROME, K RAMACHANDRAN and R VENKATARAMAN
Madras Aluminium Company Limited, Mettur Dam-636 402
R SRINIVASAN, J A M ABDUL KADER and A VARADHARAJ
Central Electrochemical Research Institute, Karaikudi-623 006
G N SRINIVASAN
Regional Research Laboratory, Bhubaneswar-751 013

The Madras Aluminium Company, Mettur Dam has put up a pilot plant for the extraction of gallium from sodium aluminate liquors based on amalgam metallurgy, the process and the engineering design being supplied by Central Electrochemical Research Institute, Karaikudi. The performance of the pilot plant and the results obtained in the first few months of operation are described in this paper.

Key Words: Gallium, amalgam metallurgy, sodium aluminate liquor

INTRODUCTION

Gallium has an edge over conventional electronic materials owing to the speed obtainable and the low energy consumption of the integrated circuit chips based on its intermetallic compounds. The higher energy conversion and resistance to radiation damage make it a unique material for space application and for special computer devices. The metal remains scarce due to the inherent nature of being highly dispersed in the earth's crust. The presence of gallium in bauxite and its similar chemical properties to aluminium, enable the enrichment of gallium in the aluminate liquors of alumina plants to a concentration of 200-250 $mgdm^{-3}$. Though the concentration met with is low viewed from hydrometallurgical standards, it forms one of the attractive sources for this interesting metal, as no separate processing is involved to dissolve gallium.

The Madras Aluminium Co. (MALCO) has an installed capacity of 25,000 t of aluminium per annum. It derives bauxite mainly from Yercaud and Kolli hills. The gallium content in bauxite from these sources varies from 60-80 ppm. There are two concentrated streams of aluminate liquor viz. concentrated soda and superconcentrated soda in the process. The superconcentration step wherein alkali concentration is raised to about 400gdm^{-3} is intended for the removal of vanadate, phosphate and sodium carbonate from the liquor. The supersoda solution has a gallium content of around 200 $mdgm^{-3}$. This becomes the starting material from which gallium is extracted. The potentiality for gallium extraction from the alumina plant can be worked out on the basis of bauxite milling rate and assuming a value of 20% for overall effective recovery. The MALCO plant has a potentiality of 400 kg/annum gallium production.

A pilot plant with one prototype cell assembly based on the amalgam route has been installed in MALCO with the technical know-how and engineering design of Central Electrochemical Research Institute (CECRI), Karaikudi and financial participation of National Research and Development Corporation of India (NRDC). The pilot plant which has a capacity of 25-30 kg/annum started functioning from April, 1986.

PROCESS

The process comprises of deposition of gallium from the sodium aluminate liquor as an amalgam, denudation of the amalgam to give sodium gallate and finally electrolysis of the sodium gallate solution (Fig 1.).

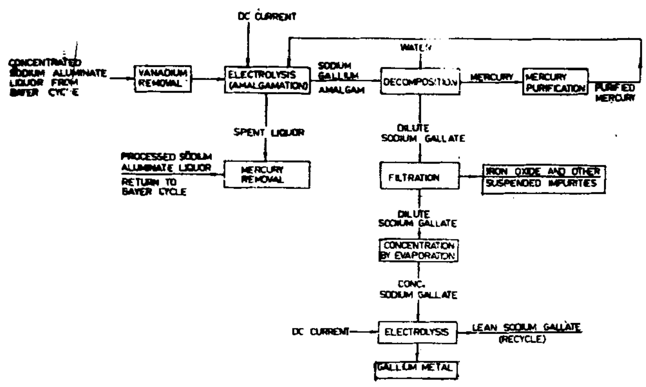

Fig.1 General process flow sheet for recovery of gallium

The amalgamation step is critically affected by the presence of vanadium which acts by lowering the hydrogen overvoltage on mercury and thereby hindering the exchange reaction between sodium in amalgam formed insitu and gallium in the liquor. The elimination of vanadium from the liquor is achieved by a process of cooling and settling for 24-48 hrs. The concentration of vanadium gets lowered to around 100 $mgdm^{-3}$ at which level the deleterious effect is not serious.

AMALGAMATION ELECTROLYSIS

The amalgamation is done by electrolysis of the liquor with an agitated pool of mercury as the cathode in a plastic vessel provided with special agitators. Mild steel semicircular plates suspended in the solution serve as the anode. The cathode current density (c.d) is in the range of 100 -400 Am^{-2}. A batchwise recirculation technique is used for treating sufficiently large volume of aluminate liquor. The current density, temperature and rate of agitation are optimised to give a high rate of extraction. The results of a few batches at the pilot plant are presented in Table I.

Table I: Result of amalgamation electrolysis batches
Volume of liquor per batch : 3 M^3; Temperature : 50°C

S.No.	Current (Amp.)	Gallium concentration Initial ($mgdm^{-3}$)	Final ($mgdm^{-3}$)	Gallium recovery per day (g)	Yield (%)
1.	100-200	205	75	78	63
2.	125-250	208	85	74	59
3.	150-300	212	85	77	60
4.	150-250	230	83	89	64
5.	150-275	223	88	82	61
6.	150-250	195	88	64	55
7.	100-200	185	93	55	50
8.	150-250	156	94	39	40

The capacity of the whole plant primarily depends on the efficiency of extraction of gallium into mercury which is a slow process. It could be seen that the concentration of gallium in the feed liquor has to be around 250 $mgdm^{-3}$ to get the rated output from the plant. In addition to vanadium, the extraction is known to be affected by the presence of organic carbon and iron in the liquor.

AMALGAM DENUDATION

The gallium amalgam formed in the amalgamation step is denuded adopting an electrolytic technique. This approach is beneficial in that iron amalgam formed along with gallium during the first step is also decomposed and the regenerated mercury becomes fit enough to be recycled. The denudation is incorporated with a built-in control measure so that the mercury is not affected during the process. The rate of denudation is about 50 times greater than that of amalgamation.

FINAL RECOVERY OF GALLIUM

The sodium gallate solution obtained from the denudation is first concentrated. The resulting gallate solution is subjected to electrolysis whereby gallium metal is produced. The concentration of gallium in the final gallate solution is kept above 10 gdm^{-3} to get a satisfactory deposit with reasonable current efficiency. A typical assay of gallium metal obtained is presented in Table II.

Table II: Impurities in ppm in gallium obtained in the pilot plant

Ag < 1	Hg = 8	Sn < 2
Al < 4	In < 2	Ti < 2
Bi < 1	Mg < 1	V < 2
Co < 2	Mn < 1	Zn = 9
Cr < 2	Mo < 2	Pb = 19
Cu = 113	Ni < 2	
Fe < 5	Sb < 2	

Purity of gallium : 99.98%

CONCLUSION

A pilot plant for the extraction of gallium from sodium aluminate liquor has been installed and commissioned at MALCO. The unit has a capacity of 25-30 kg of gallium production per annum. The amalgam metallurgy process developed at CECRI and adopted in this plant has the advantage of a high rate of extraction. In addition, this process incorporates a more efficient method of decomposition of the amalgam so that the regeneration of mercury is rendered easy.

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