Enrichment and Separation of Gallium from Leach Liquors by Extraction Methods Consisting Solid Liquid and Liquid Liquid Systems: A Review

Prashant B Thorat[1], Laxman V Gavali[2], Prajakta S More*[1]

[1]Chandibai Himathmal Mansukhani College, Ulhasnagar, Maharashtra, India 421003

[2]Karmaveer Bhaurao Patil College, Vashi, NaviMumbai, Maharashtra, India 400703

Abstract:- Gallium separation had always appeared indeed as an analytical challenge in traditional hydrometallurgical processes because of alike chemical and physical features with the associated impurities. Electrodeposition, Fractional precipitation, ion exchange or solid phase extraction, liquid-liquid extraction are the key separation methods studied and appealed for the recovery of gallium. Electrodeposition method used for gallium separation including problem associated with hydrogen evolution reaction and mercury cathode toxicity have been discussed. Aluminium-Gallium separation by fractional precipitation using CO2 and lime method is appreciable but it generates several tons of spoiled solution containing $3CaO. Al_2O_3.6H_2O$ during conventional hydrometallurgical process. Proper choice of sorbent grafted with functional group can separate gallium from the associated metal ions by ion exchange method. Basic methods used for preparation of columns consisting sorbent with various acidic, basic and neutral extractants had been discussed. Liquid-liquid extraction practice used for recovery of Gallium from variety of aqueous media have been discussed. Optimized parameters like concentration of aqueous phase, metal ion, extractant, temperature, kinetics, composition of the extracted species studied during liquid-liquid extraction of gallium from leach liquors or synthetic mixtures is discussed.

Keywords:- *Gallium separation, electro deposition, fractional precipitation, ion exchange, liquid-liquid extraction*

I. INTRODUCTION

Gallium was found in 1875, by a French chemist Paul-Emile Lecoq de Boisbaudran in Paris. It was noted as violet line in the atomic spectrum of zinc pluck out from zinc blende ore. This new metal was isolated, purified and placed below aluminium in Mendeleev periodic table. Gallium is a soft, silvery-blue metal, atomic number 31, atomic weight 69.723, specific gravity 5.904 (for solid), specific gravity 6.905 g/cm3 (for liquid). It has low Melting Point 302.98K. Therefore, it can show unusually large liquid range and can liquefy even when one holds a solid piece of gallium in hand. It has hardness of 1.5mohs, high boiling point of 2676K. The observed crystal structure of solid gallium is orthorhombic with conchoidal fracture similar to glass. (1).

Gallium has six isotopes but only two isotopes i.e. Ga68 (60.40%) and Ga71 (39.60%) are stable. Gallium can present in +1 and +3 oxidation states. Chemical features of gallium and aluminium are alike. It can form hydride, halide, chalcogen and many organo-metallic compounds. Gallium is stable element, but reacts vigorously with aqua regia as well as with concentrated NaOH in aqueous medium. It vigorously forms halides with halogens even at low temperature. (2) Gallium in liquid state can dissolve many metals. It freely forms eutectic alloys in conjunction with many metals. Lowest melting materials chiefly eutectic Ga-In and eutectic Ga-Sn alloys are some important alloys of Gallium. Galinstan consisting mixture of gallium, indium and tin is one of the important eutectic alloy, whose voltametric properties were compared with mercury electrode. Galinstan can be used as liquid electrode in place of mercury electrode for voltammetric analysis of various metal ions such as lead, cadmium in supporting electrolytes. (3) Some other alloys i.e. specific compositions of gallium with other elements like V_3Ga, Nb_3Ga and Zr_3Ga shows superconducting properties below 14.3°, 14.5° and 10.5° respectively. Compositions of gallium with tin and silver are the substitute dental amalgam used in dental filling (4) Gallium form compounds with elements of nitrogen family (group 15) and possess semiconducting property e.g. GaAs and GaN. (5) Gallium Arsenide and Gallium Phosphide has application in rectifiers and transistors as they are semiconductors. The electronic structure of gallium-arsenide supports the high electrical conductivity. The valence band maxima and conduction band minima of gallium arsenide are aligned at the same frequency consequently the direct recombination of the electrons is permitted in the energy gap resulting into emission of light photon. Due to this property of the gallium arsenide, it has wide applications in making of light emitting diodes (LED's), laser diodes, solar cells and photodetector. This property is again important for making high performance computers and smartphones. (6-7).

II. RESOURCES OF GALLIUM

Earth crust contains very low amount of gallium, less than 19ppm, thus it is quite rare. Moreover, gallium does not exist in free elemental form or owes its mineral. However, its very wide spread is found in minute concentrations (≈50ppm) in ore of other metals and coal. The geochemical affinity between Al and Ga is concentrated in bauxites and hosted by diaspora, various alumino silicates such as clays, apatite nepheline and

frequently alunite. Gallium exhibits chalcophile affinity and hence occurred as gallite ($CuGaS_2$) and mostly replacing Zn and Cu in sulphides, frequently in sphalerite (ZnS), germanite ($Cu_{26}Fe_4Ge_4S_{32}$) and chalcopyrite ($CuFeS_2$)(8).

So, it is not recommended to mine any mineral simply to recover gallium. Economically, gallium is recovered as by-product of the processing of Zn and Al from sphalerite and bauxites respectively. Alumina production from bauxite ore generates Bayer liquor, the biggest feedstock resource of gallium. In Bayer process, about 70% of the Gallium is leached from the bauxite into the caustic soda (NaOH) solution. Followed by the crystallization of alumina trihydrate, the liquid phase is enriched with the leached gallium as hydroxide, since Al $(OH)_3$ can precipitate at higher pH (10.6) while the pH required for precipitation of Ga $(OH)_3$ is at lower side (pH 9.4-9.7). Various methods such as ion exchange, solvent extraction and precipitation have been developed for gallium recovery from this leached solution. This is followed by electro wining to produce pure gallium metal. Approximately, 90% of the annual worldwide primary gallium production is based on the Bayer liquor containing 100-300mg/L of gallium, while the zinc residue containing 0.003-0.4 weight % gallium is utilized for 10% of the annual gallium production. (9).

A. Method of separation

Broadly two major types of systems are used for the enrichment and recovery of gallium from environmental matrix, they are as follows: 1) Solid liquid systems comprising electrochemical deposition, fractional precipitation and solid phase extraction 2) Liquid liquid systems comprising liquid-liquid extraction or solvent extraction.

B. Electrochemical deposition

Gallium electrodeposition has been mainly studied for the production of very highly pure gallium metal, gallium-based semiconductors and electro-wining of gallium from Bayer liquor. The standard reduction potential of Gallium (III)/ Gallium (0) redox couple is negative (E0= -0.529 Vs S.H.E.) therefore hydrogen evolution reaction is more prominent while electrodeposition gallium in aqueous solution. Thus, the current efficiency of the process is low mainly in acidic solution. Hong et al found Gallium (I) in the form of Ga_2O during study of the redox reactions of gallium in alkaline solution. (10) R. Dorin et al demonstrated electrodeposition of gallium from synthetic Bayer liquor comprising 4.5M sodium hydroxide, 0.2M sodium carbonate, 0.3M sodium chloride and 1.7M aluminium hydroxide. Hydrogen evolution reaction observed parallel with deposition of gallium and can be controlled by mass transfer and electron transfer step. (11)

Flamini et al studied that in acidic aqueous solution, Reduction of Gallium (III) to Galllium (I) occurs at low current densities, whereas the electrodeposition of metallic Gallium and the hydrogen evolution occurs at higher current densities. (12)

W. Monnens et al studied Gallium electrodeposition from electrolyte bath composed of $GaCl_3$, an inert background salt and 1,2-dimethoxy ethane. The deposition process by electrolytic reduction occurs in two steps: i) from Ga(III) to Ga(I) and ii) Ga(I) to Ga(0) i.e metallic gallium. The electrodposition was observed in the form metallic nano spheres of gallium. Droplet-on-Droplet mechanism was proposed for the elecrodeposition. X-ray photoelectron spectroscopy showed that each gallium sphere was coated with fine gallium oxide shell. Gallium oxide shells prevented agglomeration of every nano gallium sphere. (13)

The hydrogen overvoltage at the mercury electrode is high and deposition potential of gallium at mercury is low, this offered mercury cathode electrolysis for precipitation of gallium during electrolytic process. Gallium ions can discharge and deposit at liquid mercury cathode, although Bayer liquor contains very small concentration of gallium ions. However, large amount of mercury circulation can deposit very few amount of gallium from sodium aluminate along with formation of sodium amalgm. (1).

C. Fractional precipitation

Fractional precipitation method involves addition of precipitating agent to selectively precipitate either gallium or impurity from the solution. Aluminium-Gallium separation is very important step in the recovery of gallium from Bayer liquor. Recovery of gallium by fractional precipitation approach involves Aluminium-Gallium precipitation with carbon dioxide and subsequent precipitation of aluminium and gallium using lime milk or sodium aluminate solutions. Although process is complicated, approach is environmentally friendly. In lime method, the key step for the separation of Al-Ga is, the difference in chemical reaction between $Ca(OH)_2$ and Al or Ga. To produce 1Kg gallium by lime method, 7 tons of 3CaO. $Al_2O_3.6H_2O$ residue is obtained. Thus, the major problem is to treat these large quantities of the residue. (1).

D. Solid Phase Extraction

Solid phase extraction deals with the sorbent which can adsorb matter of interest by ion exchange mechanism. Sorbents are polymeric substances grafted by functional group, that when come in contact with the electrolyte, can do ion exchange. The chemical nature of polymeric matrix may be organic (resins /organic nanomaterials) or inorganic (silica, clays etc.). Extraction of gallium by solid phase extraction or ion exchange method was first reported from chloride system same as solvent extraction system. Some of the active functional groups namely –OH, -SH, -NH₂, =NOH, =NH of chelating resins are able to extract gallium selectively. P. Selvi et al prepared one cross linked poly-hydroxamic acid ion exchange resin in the laboratory by polymerization of acrylonitrile and divinyl benzene through suspension polymerization followed by hydrolysis of copolymer with 50% sulphuric acid and reacting the produced polyamide with hydroxylamine solution. Extraction behavior of gallium from Bayer liquor with the prepared ion exchange resin was studied at room temperature. The prepared chelating ion exchange resin showed good selectivity for gallium, fast kinetics (t1/2 ≈

1minute), good stability towards acids and alkalis, also recycling ability of the resin. (14)

K Srinivasa Rao et al synthesized ion exchange resin by suspension polymerization method by the steps given below: i) Purification of acrylonitrile by washing with dilute NaOH, followed by with dilute H2SO4 , dilute sodium carbonate, then finally with water. ii) The washed acrylonitrile monomer was then purified by vaccum distillation. iii) The vaccum distilled acrylonitrile was then mixed with 5% divinyl benzene and benzoyl peroxide. iv) The mixture was then slowly added to an emulsifier solution containing calcium carbonate, sodium sulphate and gelatin at room temperature. v) The temperature gradually raised to 85ºC vi) Hydrolysis of polymer was carried out with 1:1 sulphuric acid at 85ºC vii) Hydrolysed product was further treated using CH3COONa, NaOH and NH2OH. HCl viii) washing of the product with 0.2M H2SO4 and then with water until it becomes sulphate free. Gallium extraction studies were carried out using the synthesized ion exchange resin containing hydroxamic acid functional group. Gallium extraction was dependent on reaction and concentration of alkali. The prepared resin could not react with aluminium and extraction kinetics of vanadium was different from gallium. (15)

V. N. Sagdeiv et al used D-403 as weakly basic anion exchange resin for extractive separation of gallium in the form of hydroxo complex from alkaline aluminate matrix. Ion exchange equilibrium constant and Gibbs free energy for the sorption of tetrahydroxogallate ions in presence of aluminium from strongly alkaline solution had been determined. The ion exchange resin D-403 is macroporous chelate polystyrene resin consisting copolymer of styrene and benzene divinyl having active functional group in the form of tertiary N atom. (16)

T. H. Cheng et al investigated suitability of commercial weak acid chelating resin, Diaion CR-11, for separation of gallium from Ga-As scrap at low pH. The active functional group characterized in the Diaion CR-11 resin is iminodiacetate acid. The resin was used in the sodium salt form for the study. Nitrogen atom and two oxygen atoms are the sites of interest for binding metal cations with the resin. The conditions for leaching and ion exchange method were optimized for recovery of gallium from gallium arsenide scrap. 98% dissolution of both gallium and arsenic were investigated with 2.0 N of nitric acid for 2g/100mL, temperature 30ºC, leaching time 1hour. At very low pH, highly charged Ga(III) ions have the ability to form complexes with the iminodiacetic acid chelating resin Diaion CR-11 and separates itself from H3AsO4. (17).

Various derivatives of 8-hydroxyquinoline commonly known as kelex-100 had gained special importance as liquid chelate ion exchange resin in hydrometallurgy for selective extraction of gallium from matrix. Organic adsorbents like macroporous styrene and divinyl benzene copolymer beads prepared by suspension polymerization process were not always suitable for the separation of trace amount of metal ions in their aqueous solution due to their

hydrophobicity. M. Nakayama et al investigated Kelex-100 chemically, 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline loaded ion exchange resin (prepared by suspension polymerization) for the Ga+3 sorption from Bayer liquor i.e. sodium aluminate solution formed in Bayer process. The physical pore structure and the ion exchange group mainly affects the adsorption of Ga+3 from strongly alkaline media. In general, the Kelex-100 loaded carboxylic acid type resin with macroporous structures has the capability to separate Ga(III) from Al (III) in concentrated NaOH. (18) N. Hatori et al studied solid phase extraction of Ga(III) with six kinds of Hydrophobic 8- quinolinol (HQs) impregnated resins from aqueous acidic and alkaline solutions. Solid phase extraction was affected by various factors mainly substituents of HQs, concentration of HCl and NaOH in aqueous phase, concentration of HQ in the resin and equilibrium time. (19)

M. Carvalho et al recovered gallium from flue dust Al residues generated in plants by using commercial polyether type polyurethane foams in solid phase extraction system. Gallium was separated from the bulk containing high concentrations of Al, Fe, Ni, Ti, V, Cu, Zn, SO4-2, Cl-, F- by extraction with polyurethane foam from the medium containing 3.0 M sulphuric acid and 3.0 M sodium chloride with 92% efficiency. (20)

U. Divrikli et al investigated rapid, sensitive method for preconcentration and recovery of trace of gallium by using mini columns filled with Amberlite XAD-4 resin (polystyrene divinyl benzene copolymer). The sample solution of Ga(III) as 4-(2-thiazolylazo) resorcinaol (TAR) complex was allowed to passed though the column under gravity and then elution was done with 2-10mL of 1M HNO3 in acetone at flow rate 5 mL per minute. The method was then applied to drinking water, sediment samples and geological samples. (21)

Resin used in the ion exchange method must be able to bear highly alkaline conditions of Bayer liquor and highly acidic conditions of stripping agent. R. Joris et al prepared hybrid chitosan-silica (CS) adsorbent which permits immobilization of organic ligands such as 8-Hydroxyquinoline (8-HQO) and 8-Hydroxyquinaldine (8-HQA). Adsorption study of Ga(III) and Aluminium(III) by the stationary phase made of Chitosan-silica (CS) functionalized 8-HQO and 8-HQA were carried out w.r.t. equilibrium concentration, kinetics, aqueous pH and temperature for selective recovery of Ga(III). Better separation of Ga(III) from Bayer solution was reported with CS functionalized with 8-HQA. (22)

H. R. Aher et al developed extraction chromatographic separation for Ga(III), In(III) and Tl(III) using liquid anion exchanger n-octylaniline on silica gel as stationary phase. Reverse phase extraction behavior towards n-octylaniline as a function of hydrochloric acid was studied for separation of Ga(III), In(III) and Tl(III). Optimized HCl concentrations found for quantitative extraction of Ga(III), In(III), and Tl(III) were 6.0M, 0.7M and 0.7M respectively using 0.3% i.e. 0.135M n-octylaniline. Distilled water was recommended for elution

of extracted metal ions. The method was extended to generate flow chart for separation Gallium and Indium or Gallium and Thallium. (23)

Thus, solid phase extractions require extractants along with supporting solid materials. Very few novel extractant reagents as well as supporting solid materials have been reported in the past decade for recovery of Gallium especially.

E. Liquid-Liquid Extraction

Compared to other extraction systems, solvent extraction or liquid-liquid extraction is very promising separation technique due to its simplicity. Extractant is dissolved in organic solvent resulting one phase which then shaked with the aqueous phase containing desired metal ion. The metal ion component distribute itself between organic phase and aqueous phase by Nernst's distribution law to achieve separation. On the same ground, selective solvent extraction of gallium from hydroxide, chloride, sulphate and nitrate aqueous media had been reported by using different organic extractants including carboxylic acids, organophosphorous compounds, alkyl amines, quaternary ammonium salts, 8-Hydroxyquinoline derivatives, ethers, ketones etc. The extracted gallium species may be in the form of cation, anion or neutral, decided by the acidity and type of ligand. The various extractants such as acidic, basic, neutral were studied in the solvent extraction systems of gallium preconcentration.

Table 1: Structures of neutral extractants used in solvent extraction system of Gallium

Trade name	Chemical name	Structural formula
TBP	Tri-n-butyl phosphate	$R_3P=O$ Where, $R = O\text{-}n\text{-}C_4H_9$
TOPO or Cyanex 921	Tri-n-octylphosphine oxide (93%)	$R_3P=O$ where, $R = CH_3(CH_2)_7\text{-}$
Cyanex 923	mixture of four trialkyl phosphine oxides	$R_3P=O$ (14%), $R_2R'P=O$ (42%), $RR'_2P=O$ (31%), $R_3'P=O$ (8%) Where, $R = $ n-octyl, $R' = $ n-hexyl
Cyanex 925	bis-2,4,4-trimethyl pentyl-n-octyl phosphine oxide	$R_1R_2R_3P=O$ Where, $R_1 = R_2 =$ $t\text{-}C_4H_9CH_2(CH_3)CHCH_2\text{-}$ $R_3 = $ n-C_8H_{17}

B. Y. Mishra et al reported cyanex-921 in toluene as neutral extractant for the recovery of Ga(III) from solution of pH range 4.5 to 6.0 and stripping was done with 2.0M nitric acid. Cyanex 921 being neutral extractant often extract neutral uncharged complexes of metal ions. $GaCl_4\text{-}$ formed stable solvation complex with cyanex-921 and get extracted in the organic phase. (24) B. Gupta et al investigated wide range of high HCl concentration for the Gallium(III) recovery compared to sulphuric acid and nitric acid using Cyanex-923 in toluene. It was followed by stripping with low concentration of HCl i.e. 0.1M Solvation mechanism comprising extraction of $GaCl_3$. 3Cyanex-23 species was identified. The optimized conditions were applied for the recovery of Gallium (III) from LED waste and bottom ash. (25) S. D. Pawar et al investigated pH range for sequential separation of Ga(III), In(III) and Tl(III) using Cyanex-923 (26) I. M. Ahmed et al suggested Cyanex-925 as powerful extractant than Cyanex-923 under the given conditions of aqueous solution but preferred Cyanex-923 due to its commercial availability. Production of Gallium in the cyclotron may be associated with Zn(II) and Cu(II) in 5M HCl, hence, the flow chart for the efficient recovery of Ga(III) was proposed using Cyanex-923 0r Cyanex-925. (27) A. K. De et al studied systematic separation of Ga(III), In(III) and Tl(III) in solvent extraction system, consisting Tributyl phosphate as neutral extractant. Organic phase comprising 100% TBP showed quantitative extraction of all three metals in specific concentration range of HCl as follows: Gallium (2.0 to 6.0 M HCl), Indium (6.1 to 8.0 M HCl) and Thallium (1.0 to 6.0 M HCl) (28)

Optimum extraction conditions for liquid-liquid extraction of Ga(III) using various extraction systems have been summarized w.r.t aqueous phase, organic phase and strippants along with special comment for its applicability to the environmental matrix are given in TABLE 2.

Table 2: Optimum extraction conditions for liquid-liquid extraction of Gallium (III)

Extractant	Aqueous phase	Organic phase	Strippant	Ref.
	Special comment:			
Kelex100				
	Bayer liquor	ethanol + Kerosene	1.5M HCl	29
	93.39% Ga recovery from Bayer liquor supplied by Jajarm Alumina			
Kelex100				
	Bayer process liquor	Kerosene + iso-decanol	1.5M HCl	30
	The kinetics of the extraction system was improved by decreasing the volume percentage of isodecanol and addition of petroleum surfactant.			
Kelex100				
	Bayer process liquor	Kerosene + iso-decanol	1.5M HCl	31
	The rate of Ga extraction decreased due to addition ocylamine as surfactant however addition of petroleum sulphonate and versatic 10 increased it.			
8-Quinolinol derivatives (synergism study)				
	Weak acid	Chloroform	---	32
5 –substituted 8-hydroxyquinolines (YEN 10 and YAN 5)				
	3.5M NaOH	Kerosene	----	33
Oximes of alkyl salicyladehydes				
	Bayer process liquor	Kerosene	2.0M HCl	34
	Bayer liquor of Alumina Tanrai (Vietnam) was used for extraction study.			
LIX 26 (alkyl-substituted 8-hydroxyquinoline)				
	pH about 8	Kerosene and n-decanol	2M HCl	35
	The process was extended for the separation of Ga from Bayer process liquor containing 180 ± 30mg/L Ga, 420-450g/L Na_2O, 70g/L Al_2O_3			
D2EHPA				
	pH 3	Kerosene	2M HCl	36
	Recovery of Gallium, Indium and zinc was studied from leached spent Gallium Zinc Oxide (GZO) and (Indium Gallium Zinc Oxide (IGZO) targets from thin film solar industry and display panel manufacturing.			
D2EHPA	NaCl	Kerosene	6M HCl	37
	Recovery of Ga and In from zinc refinery residue was studied.			
OPAP				
	pH as low as zero	Kerosene + Isodecanol	1.5M H_2SO_4	38
	Gallium was extracted from the H_2SO_4 leached filtrates produced from hydrometallurgical zinc residues.			
OPAP (octyl phenyl acid phosphate)				
	HNO_3, $NaNO_3$	Kerosene and n-decanol	H_2SO_4	39
1-phenyl-3-methyl-4-tri flouroacetylpyrazolone-5				
	pH 4	Chloroform	0.2M KCN	40
Polyoxyethylene nonyl phenyl ethers				
	HCl	Chloroform, Dichloromethane, 1,2-Dichloroethane	water	41
	Extraction method was applied to the acid leaching solution from zinc refinery residues.			
Amberlite LA-2				
	Cl⁻	Kerosene	water	42
Tris(2-hydroxy-3,5-dimethylbenzyl)amine				
	Aqueous solution	Chloroform	----	43
Adogen-464 (methyl trialkyl ammonium chloride)				
	pH 2.75	Toluene	0.5M HCl	44
	The optimized extraction conditions were applied for the extraction of Gallium(III) from some leach liquor samples of silicates collected from Wadi Sikait, South Eastern Desert, Egypt.			
Aliquat 336S				
	Ascorbate PH 4.0-6.0	Xylene	1M HNO_3	45
	The proposed method was used for separation of gallium from multi component mixtures and high purity aluminium.			
2-octylaminopyridine				
	HCl (6.0-9.0M)	Chloroform	1M HCl	46
	The method was applied for the determination Gallium in Bauxite ore by standard addition method.			

N-n-octylaniline				
	HCl (6.0M)	Benzene	water	47
n-octylaniline				
	Aqueous succinate pH 4	Toluene	water	48
	The method was used for the separation of Ga(III) from variety of binary mixtures containing by use of suitable masking agents.			
Tri-n-octylamine				
	Oxalate pH 1.12-2.76	Xylene	---	49
Adogen 364				
	HCl, HBr, HI	Toluene	---	50
	Separation of Ga, In and Al was studied			
4-Methyl-N-n-octylaniline				
	HCl (5.0M to 10.0M HCl)	Xylene	water	51
	Leach liquor prepared from LED waste used for the recovery of Gallium			
Tri(octyl-decyl) amine (N235) and TBP				
	Oxalate leach pH 0.5	Sulphonated kerosene	2.5M H_2SO_4	52
	Separation of Ga(III) and Ge(IV) studied from zinc refinery residues			
Sec-octylphenoxyacetic acid and primary amine N1923				
	Cl^-	n-heptane		53
2-ethylhexyl thioglycolate				
	Aqueous NH_4NO_3	Toluene		54
Cyphos IL 101 (trihexyl tetradecyl phosphonium chloride)				
	2M HCl	Kerosene	0.1M HCl	55
	Gallium was recovered from photodiodes.			
Cyphos IL 104				
	3M HCl	Toluene	1M H_2SO_4	56
	Recovery of Ga was achieved from leach liquors of photodiodes and co-extraction of vanadium observed while extraction from red mud			
LIX63 and Versatic10acid				
	Sulphate leach solution pH 3.0	Shell Sol D70	0.05M H_2SO_4	57
	Ga(III) and In(III) recovery from synthetic leach solutions of zinc cementation were studied.			
Hexaacetato Calix(6)Arene				
	pH 3.5	Xylene	0.1N HCl	58
Sec-Nonylphenoxy acetic acid				
	Cl^- (pH 2.5-3.5) SO_4^{-2} (pH 3.5-6.5)	Kerosene	---	59
CA-12 (sec-octylphenoxyacetic acid)				
	Cl^- (pH 4.2)	Kerosene	3M HCl	60
	Analysis of alloy sample			

III. CONCLUSION

Gallium is becoming critical metal due to its rapidly growing consumption in the electronic market and being produced only as a byproduct during production of alumina. Demand of gallium is continuously increasing in the global market but the global system for manufacturing and recycling has yet not described in literature. Technological progress and change in consumer pattern are reducing the useful life of electrical and electronic gadgets. There is a big problem of handling E-waste, however, E-waste can become potential resource for rare gallium. Fundamental investigations related to extraction and separation of Gallium are reviewed w. r. t. solid -liquid and liquid-liquid system. Electrodeposition, fractional precipitation, solid phase extraction, liquid-liquid extraction techniques are some promising basic methods to be studied for the enrichment and separation of gallium. Amongst various methods, solid phase extraction and liquid-liquid extraction are the most studied methods for the recovery of gallium due to their simplicity, but in the past decade very few papers have been published. Finally, in view of current demand of Gallium upgradation of the existing simple methods is required.

REFERENCES

[1]. Z. Zhao, Y. Yang, Y. Xiao, Y. Fan, *Hydrometallurgy,* 125-126, (2012) 115-124.

[2]. Holleman Wiberg, "Inorganic Chemistry" 34thedn(Academic Press, San Diego, London Boston, New York, Sidney, Tokyo, Toronto) 1995, 1028, 1031.

[3]. Surmann, H. Zeyat, *Anal Bioanal Chem* 383 (2005) 1009-1013.

[4]. H. J. Haydar, J. A. Deen, S. A. Shahee, *International Journal of Scientific and Engineering Research,* 6,12 (2015) 619-631.

[5]. K. R. Murali, M. Jayachandran, N. Rangarajan, *Electrochem,* 3,3 (1987) 261-265.

[6]. E. Torma, H. Jiang, Mineral Processing and Extractive Metallurgy Review, 7 (1991) 235-258.

[7]. The Columbia Electronic Encyclopedia, 6th edition, Columbia University Press.

[8]. O. Font, X. Querol, R. Juan, R. Casado, C. R. Ruiz, A. L. Soler, P. Coca, F. G. Pena, *Journal of Hazardous Materials* A139 (2007) 413-423.

[9]. F. Lu, T. Xiao, J. Lin, Z. Ning, Q. Long, L. Xiao, F. Huang, W. Wang, Q. Xiao, X. Lan, H. Chen, *Hydrometallurgy,* 174 (2017) 105-115.

[10]. B. Hong , Y. Wang , X. Wei , Q. Huang , X. Wang , T. Fujita and Y. Wei , *Hydrometallurgy,* 2020, 105344

[11]. R. Dorin, E. J. Frazer, *Journal of applied electrochemistry,* Volume 18, pates 134-141, 1988.

[12]. D. O. Flamini , S. B. Saidman and J. B. Bessone , *J. Appl. Electrochem.,* 2007, 37 , 467 —471

[13]. W. Monnens, P. Lin, C. Deferm, K. Binnemans, J. Fransaer, *Physcial Chemistry Chemical Physics* Issue 29, 2021

[14]. P. Selvi, M. Ramasami, M. H. P. Samuel, P. Adaikkalam, G. N. Srinivasan, *Ind. Eng. Chem. Res.* 43 (2004) 2216-2221.

[15]. K. Srinivasa Rao, D. Sarangi, PK Dash, G Roy Chaudhury, *Journal of Chemical Technology and Biotechnology,* 78, (2003) 555-561,

[16]. V. N. Sagdeiv, O. V. Cheremisina, M. A. Ponomareva, E. S. Zatula, *Metallurgist,* 63, 1-2 (2019).

[17]. T. H. Cheng, C. J. Liu, T. Y. Tsai, Y. H. Shen, *Processes,* 7 (2019) 921.

[18]. M. Nakayama, H. Egava, *Ind. Eng. Chem. Res.,* 36 (1997) 4365-4368.

[19]. N. Hatori, H. Imura, A. Ohashi, K. Ohashi, *Analytical Sciences,* 24 (2008) 1637-1641.

[20]. M. Carvalho, K. C. M. Neto, A. W. Nobrega, J. A. Medeoros, *Separation Science and Technology,* 35,1 (2000) .

[21]. U. Divrikli, M. Soylak, L. Elci, *Analytical letters,* volume 36, No. 4, pp 839-852, 2003.

[22]. R. Joris, M. Steven, B. Koen, *Hydrometallurgy,* 2017, volume 171, pp 275-284

[23]. H. R. Aher and S. R. Kuchekar, *Indian J. Chem. Technol.,* 15 (2008) 403-408.

[24]. B. Y. Mishra, M. D. Rokade, P. M. Dhadake, *Indian J. Chem,* 39A (2000) 1114-1116

[25]. B. Gupta, N. Mudhar, Z. Begum, I. Singh, *Hydrometallurgy,* 87 (2007) 18

[26]. S. D. Pawar, P. M. Dhadake, *J. Serb. Chem Soc.* 68 (2003) 581

[27]. M. Ahmed, EI-Nadi Y. A., EI-Hefny N. E., *Hydrometallurgy,* 131-132 (2013) 24-28

[28]. K. De and A. K. Sen, *Talanta,* 14 (1967) 629-635.

[29]. Mahmood and N. Hojat, *Iran J. Chem. Chem. Eng.* 26, 4 (2007) 109-113.

[30]. G. V. K. Puvvada, K. Chandrasekhar and P. Ramachandrarao, *Minerals Engineering,* 9, 10 (1996) 1049-1058.

[31]. G. V. K. Puvvada, Hydrometallurgy, 52, 1999, 9-19.

[32]. H. Hoshino, A. Ohashi and K. Ohashi, *Bunseki Kagaku,* 52, 9 (2003) 775-780.

[33]. D. Bauer and Y. P. Cluzeau, *Hydrometallurgy,* 18 (1987) 243-253.

[34]. S. Hoang, H. N. Nguyen, N. Q. Bui, H. S. Vu, T. P. Vo, T. V. Nguyen and C. M. Phan, *Minerals Engineering,* 79 (2015) 88-93.

[35]. Bhattacharya, D. K. Mandal and S. Mukherjee, *Sep. Sci. Technol.,* 38, 6 (2003) 1417-1427.

[36]. W. S. Chen, Y. C. Wang and K. L. Chiu, *J. Environ. Chem. Eng.* 5 (2017) 381-390.

[37]. S. Nishishama, T. Hirai and I. Komasawa, *Ind. Eng. Chem. Res.,* 38 (1999) 1032-1039.

[38]. Judd and D. D. Harbuck, *Sep. Sci. Technol.,* 25, 13-15 (1990) 1641-1653.

[39]. Mihaylov and P. A. Distin, *Hydrometallurgy,* 37 (1995) 221-234.

[40]. S. M. Hasany and I. Hanif, *Radiochmica Acta,* 25 (1978) 99-102.

[41]. T. Kinoshita, S. Akita, S. Nii, F. Kawaizumi and K. Takahashi, *Sep. Purif. Technol.,* 37 (2004) 127-133.

[42]. Gutierrez, C. Pazos and J. Coca, *J. Chem. Technol. Biotechnol,* 61 (1994) 241-245.

[43]. N. Hirayama, Y. Horita, S. Oshima, k. Kubono, H. Kokusen and T. Honjo, *Anal. Sci.,* 17 (2001) i1257-i1260.

[44]. T. A. Lasheen, A. T. Kandil, E. A. Manaa, EI. A. Nouh and W. S. Hafez, *Arab Journal of Nuclear Science and Applications,* 48, 4 (2015) 13-21.

[45]. M. A. Karve and S. M. Khopkar, Chem. Anal. *Warsaw,* 38 (1993) 469-476.

[46]. S. V. Mahamuni, P. P. Wadgaonkar and M. A. Anuse, *J. Serb. Chem. Soc.,* 75, 8 (2010) 1099-1113.

[47]. G. N. Mulik, S. R. Kuchekar and M. B. Chavan, *J. Indian Chem. Soc.,* LXIV (1987) 68.

[48]. T. N. Shilmkar, S. S. Kolekar and M. A. Anuse, *J. Serb. Chem. Soc.,* 70, 6 (2005) 853-867.

[49]. Yakabe, H. Kato and S. Minami, *J. Inorg. Nucl. Chem.* 39 (1977) 871-875.

[50]. S. A. Sherif, A. S. Abdel Gawad and A. M. EL-Wakil, *Talanta,* 17 (1970) 137-142.

[51]. L. V. Gavali, V. S. Shivankar, P. S. More, IJCPS, 7,2 (2018) 52-61.

[52]. F. Liu, Z. Liu, Y. Li, B. Wilson, Z. Liu, L. Zeng and M. Lundstrom, *Hydrometallurgy,* 171 (2017) 149-156.

[53]. H. Ma, Y. Lei, Q. Jia, W. Liao and L. Lin, *Sep. Purif. Technol.,* 80 (2011) 351-355.

[54]. R. Miura, M. Tokumaru, T. Oshima and Y. Baba, *Solvent Extraction Research and Development, Japan*, 24, 2 (2017) 123-130.

[55]. S. Nayak and N. Devi, *Turk. J. Chem.,* 41 (2017) 892-903.

[56]. S. Nayak and N. Devi, *Hydrometallurgy*, 171 (2017) 191-197.

[57]. S.Nusen, T. Chairuangsri, Z. Zhu and C. Y. Cheng, *Hydrometallurgy*, 160 (2016) 137-146.

[58]. Y. S. Thakare and D. D. Malkhede, *Sep. Sci. Technol.*, 49 (2014) 1198-1207.

[59]. X. Vang, F. Liu, H. Ye and X. Zhang, *Iran. J. Chem. Chem. Eng.,* 29, 2 (2010) 19-25.

[60]. X. Zhang, G. Yin and Z. Hu, *Talanta*, 59 (2003) 905-912.