AA30 - Research on the Source and Recovery Methods of Gallium

Siming Lu[1], Qing Yu[2], Chengyu Li[3], Shaojie Kang[4], Gengbiao Xie[5] and Chunhui Zheng[6]
1.Engineer
2.Engineer
3.Engineer
4.Engineer
5.Engineer
6.Senior Engineer
Zhengzhou Non-ferrous Metals Research Institute Co. Ltd., CHALCO, China
Corresponding author: zyy_lsm@rilm.com.cn

Abstract

In recent years, gallium has been widely applied in high-tech industries, such as optoelectronics, microelectronics, high-quality semiconductors, LED lights, mobile devices, television, laptop displays, solar cells, and pharmaceuticals/radiopharmaceuticals. However, no single mineral deposit of gallium is found in nature. This article provides an overview of the sources of gallium and introduces the current recycling status of various sources, which is expected to provide potential routes for recycling and utilization of gallium in the future.

Keywords: Gallium, Source, Extraction

1. Introduction

Gallium is a shining, slightly white, rare metal with a low melting point and high boiling point. It is widely applied in semiconductors, alloys, optoelectronics, and other fields [1-2]. Gallium is particularly scarce because it is found in low-content ores, and it is only produced as a by-product of other metal production [3-4]. Different extraction methods are used to recover gallium from different sources, such as zinc ore, bauxite, fly coal ash, and other minerals. This paper briefly introduces the source and methods of recovering gallium, which is expected to provide new ideas for recovery and utilization of gallium in the future.

2. Sources of Gallium and Current Status of Gallium Recovery

2.1 Recovery from Zinc Ore

Resources of zinc ore with gallium content ranging from 0.01 % to 0.04 % can be obtained after flotation, roasting, leaching, and other processes.

In addition, zinc slag is also considered to be an important source of gallium. Qiu [5] extracted gallium and indium from zinc slag using P204 and TBP as extractants (the process flow is shown in Figure 1). By adjusting the acidity, gallium and indium were extracted, respectively, with the final extraction rates of both elements being above 99 %.

Luo Jinhua [6] showed that Cu, Zn, Fe, Cd, Ga, and other elements in zinc refinery residue were easy to leach through atmospheric pressure leaching experiments, and the leaching rate increased with the increase of sulfuric acid concentration, reaction temperature, liquid-solid ratio, and reaction time. Under optimal leaching conditions of 1.5 M sulfuric acid, a leaching temperature of 80 °C for 3 h, with a liquid-solid ratio of 7.5, the leaching rates of gallium and germanium were 97.74 % and 82.46 %, respectively. The effects of leaching agent (sulfuric acid), leaching temperature, leaching time, liquid-solid ratio, and agitation speed on the leaching rate of Ga and Ge were also examined through a two-stage hot-acid leaching.

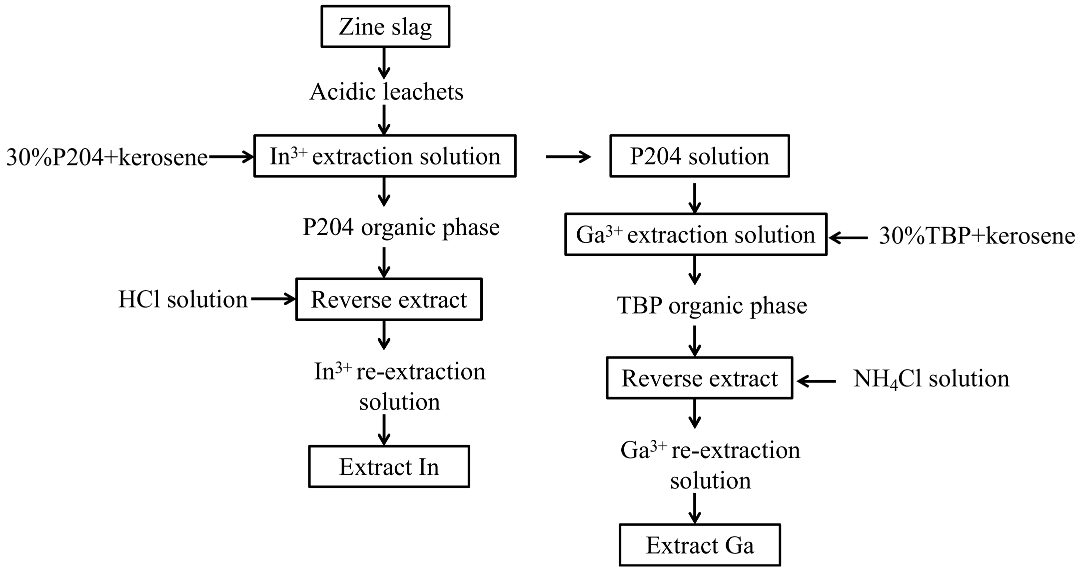

Figure 1. Flow sheet for extraction method from zinc slag [5].

Ma's [7] results showed that the optimal leaching conditions were as follows: an initial mass concentration of sulfuric acid of 188 g/L, a leaching temperature of 95 °C, a leaching time of 3 hours, an L/S ratio of 5:1, and a stirring speed of 300 r/min. Under these conditions, the leaching rates of Ga and Ge in the acid leaching solution from the multi-group comprehensive tests were improved from 72 % to 86 %.

Rao's [8] study of zinc, gallium, and germanium showed that they could be selectively leached from zinc refinery residue by controlling a suitable pH condition.

Wu Xuelan [9] extracted gallium with 10 % G315, 5 % P204 and 2.5 % isooctanol. After four stages of extraction, three stages of washing and three stages of reverse extraction, the extraction rate was higher than 96 % and the reverse extraction rate was higher than 97 %. In industrial production, the process of extracting gallium from zinc residue is widely adopted by combining hydrometallurgy and pyrometallurgy.

However, the gallium content in the leaching solution is extremely low compared with other metal ions such as zinc, copper, and iron, resulting in poor extraction efficiency of gallium. Moreover, high energy consumption, a long process and secondary pollution hinder the industrial expansion of production.

2.2 Recovery from Bauxite

Bauxite, a major raw material for alumina production, is estimated to contain more than one million tons of Ga, with an average concentration of approximately 50 ppm. Gallium is usually extracted from bauxite using the Bayer process. After leaching, adsorption, desorption, purification and electrolysis, 4N high-purity gallium can be produced. The process flowsheet is shown in Figure 2.

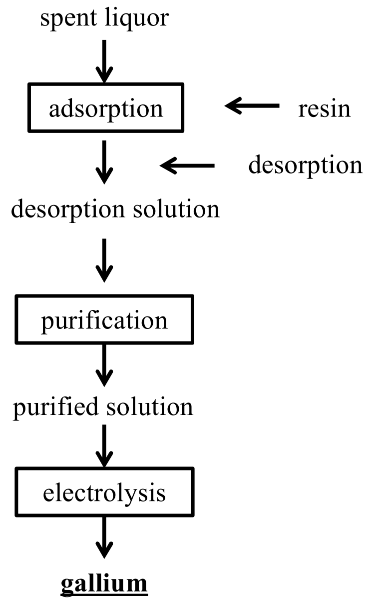

Figure 2. Flow sheet for ion exchange method from spent liquid.

From 1953 to 1958, the content of gallium in bauxite was first tested, and laboratory extraction methods were studied in Hungary.

The famous amidoxime impregnated amide resins DHG586 and Duolite ES-346 [10], which have a good selective effect on recovering gallium from sodium aluminate solution, were synthesized by Kataoka, Sumitomo Corporation of Japan. The adsorption rate of gallium was 96 %, while the adsorption rate of aluminum was only 0.1 %. The resin was desorbed by HCl to obtain a gallium-bearing solution, which was then extracted with Kelex-100, and a gallium electrolyte was obtained after alkalization [11].

Riveros [12] studied the extraction of gallium from Bayer solution using amidoxime resin Duolite ES-346 with the structure of R-C (=NOH) NH2, where R stands for resin matrix. The results showed [13] that Duolite ES-346 had good adsorption properties for gallium in Bayer solution in terms of load capacity, kinetics, and selectivity. The maximum loading capacity of the wet resin was about 5 g/L Ga, which was 8 times higher than the 600 mg/L Ga obtained by extraction method (in 10 % Kelex 100, 5 % Versatic 911 and 10 % isodecyl alcohol Varsol™ solvent) [14].

Comparing with solvent extraction, the extraction of gallium from bauxite is preferred by ion exchange method. This is likely due to the drawbacks of solvent extraction, such as the expense and large consumption of extractants, low extraction kinetics, and the possibility of contamination of the circulating liquor by dissolved extractant, which would affect the normal production process.

Jiang Changju [15] reported that the leaching rate of gallium could be reached to more than 73 % through increasing the temperature, prolonging the reaction time, and increasing the concentration of sodium hydroxide.

Zhu Zhongping [16] conducted basic research on the new comprehensive utilization technology of iron, aluminum, silicon, vanadium, gallium, etc., taking a high iron-bearing gibbsite in Guangxi as the object. The results showed that almost all gallium ions can be recovered in the process of reduction roasting-magnetic separation-leaching. The Iwataki Company in Japan [18] used CQ10/20, Dowex-1, and UR10/20 chelating resins containing oxime groups (=NOH) to adsorb gallium in acidic solutions, achieving good results. When the pH was adjusted to 2–3, gallium could be selectively adsorbed by chelating resins containing capric acid groups, with an adsorption capacity of 105 mg/g, and only minimal interference from coexisting ions such as Zn^{2+} and Al^{3+}. However, the resins have poor selectivity and low adsorption capacity from sodium aluminate alkaline solutions.

At present, 90 % of primary gallium comes from alumina production processes. After 20 years of development, China has developed a series of technologies to recover gallium from bauxite, taking advantage of domestic bauxite to account for 90 % of the world's production of primary gallium.

Apart from Bayer liquor, other by-products in the aluminum industry also contain accumulated gallium.

Qu [18] has been exploring a novel technique to extract Ga from the red mud of Guizhou Province, China. The sample containing 33 ppm Ga had a mean fine particle size of 0.9 μm, which was beneficial to improving the leaching efficiency. The preliminary results demonstrated that the Ga leaching rate reached 95 % at 55 °C for 4 h in a 4.3M hydrochloric acid solution at a L/S ratio of 8 under atmospheric pressure. The treatment of red mud by autoclave leaching for its conversion into ferrous hydrogarnet product and extraction of valuable components (i.e. Na_2O, Al_2O_3, Ga and V_2O_5) was investigated by R.A. Abdulvaliyev [19]. Leaching of red mud using high modulus alkaline solution (Na_2O 240 g/L; $\alpha_к$=30) in the presence of lime at 240–260 °C was found to allow the recovery of the contained values (98.5% Na_2O, 65.3% Al_2O_3, 55.5% Ga and 65.8% V_2O_5).

Eva Ujaczki [20] evaluated the effect of inorganic acids (H_2SO_4, HCl and HNO_3) and organic acid (oxalic acid) on leaching gallium from red mud. The highest gallium leaching efficiency was obtained using $H_2C_2O_4$ compared to other acids, achieving a leaching rate of gallium in red mud is 94 % under the optimum condition. Electrostatic precipitator dust generated during aluminum hydroxide calcination contains a concentrated amount of Ga (occurring as Ga_2O_3). Currently, a Ga recovery trial from electrofilter dust was reported by Gladyshev, the target dust contained 38 ppm Ga_2O_3 and 89.5 wt% Al_2O_3. A process route based on sintering and two-stage carbonization was also developed for the treatment of electrofilter dust from calcinations plant for Ga recovery. It was shown that a Ga-rich precipitate could be produced after a series of alkaline digestion and then two-stage carbonate precipitation procedure. This precipitate was found to be suitable for the preparation of Ga_2O_3 electrolyte (0.6 g/L) for electrolysis [21].

With the decline of ore grade, the production of gallium is also gradually decreasing. The bottleneck of high-quality gallium resources must be urgently solved. At the same time, gallium, as an important strategic resource, has broad application prospects in electronic communications, chips, national defense and security, military industry, and new energy. Therefore, the research on the recovery of gallium from the by-products of alumina production is of great strategic significance. Although the recovery of gallium from red mud and electrostatic precipitator is still in the laboratory research stage, with technological means and research updates, and the constant improvement of recovery technology, it will provide a new source to produce gallium, reducing the loss of gallium and improving the comprehensive recovery rate of gallium.

2.3 Recovery from Coal Fly Aash

The main sources of gallium ore are bauxite and lead-zinc ore. However, in 2010, due to the discovery of 857 000 tonnes of coal bearing-gallium deposits in Zhungeer City, Nei Menggu, China, with prospective reserves reaching 3.1 million tonnes, the global distribution of gallium reserves has undergone significant changes [22]. The proportion of global gallium resource distribution is shown in Figure 3.

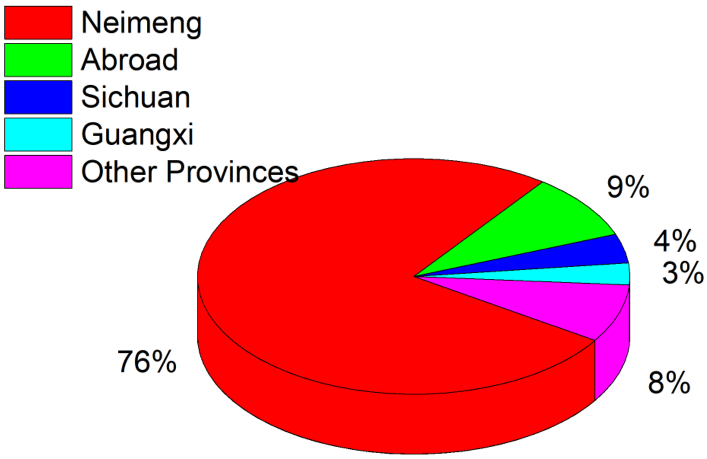

Figure 3. Global distribution ratio of gallium resources.

In recent years, the extraction of gallium from coal fly ash produced has received attention. Zheng and Gesser [23] developed a technique for recovering Ga from coal fly ash, in which a sample containing 107 ppm gallium was first calcined at 500 °C for 10 hours. Subsequently, it was leached in 2M hydrochloric acid with a L/S ratio of 6 at room temperature for 2 hours. The experimental results showed that more than 95% of Ga in ash could be leached into the solution. In addition to the acid leaching process, Oriol [24] also evaluated the recovery of Ga from coal fly ash by sodium hydroxide extraction. Eight coal fly ash samples were collected for gallium extraction, and the content of gallium ranged from 149 to 320 ppm. The optimal leaching rate of gallium (60–86 %) was obtained at a L/S ratio of 5 under room temperature in 0.7–1 M sodium hydroxide solution leaching for 6 h. Re-circulation of the leaching liquor increased the initial Ga concentration from 25–38 mg/L to 188–215 mg/L. The concentrated liquor (containing Ga in the form of $[Ga(OH)_4]^-$) was further treated by a two-stage carbonation process to recover Ga, and the recovery rate of gallium was about 98.8 %.

Fang [25] proposed an effective recovery process for gallium in coal fly ash without secondary environmental pollution by optimizing conditions such as acid strength, temperature and time, and by using relatively mild leaching conditions, including two-stage leaching, removal of silica and calcium, reduction of Fe^{3+}, extraction of gallium, purification and recovery of aluminum and iron.

Lv [26] obtained Bif-ILEs ([A336][D2EHPA], [A336][PC88A], [A336][Cyanex 272]) by an acid-base neutralization method, and used Bif-ILEs to study the recovery and separation of gallium from coal fly ash leaching solution. Studies have shown that Bif-ILEs not only has a high extraction rate of gallium, but also can extract gallium and aluminum in the water phase, when the initial water phase pH = 2. The separation effect of P507 and Cyanex 272 on gallium in coal fly ash leaching solution were investigated by Zhao [27]. The results showed that Ga(III) could be effectively separated by controlling the equilibrium pH values and by employing appropriate extractant based on the different ionic potential and electronic configurations of metal ions. At an equilibrium pH ≤ 0.8, the impurities Ti(IV) and Fe(III) in the liquor could be preferably removed by a two-stage cross current extraction with 1 mol/L P507. Then Ga(III) could be selectively separated against Al(III) using 0.5 mol/L Cyanex 272 at an equilibrium pH of 2.4–2.6. The separation factors of Fe/Ga, Fe/Al and Ga/Al can reach 145, 133 and 40, respectively.

However, there are still obvious drawbacks in the current research methods for gallium. For example, most of the processes for extracting gallium from coal fly ash are too complex, resulting in poor product purity and low recovery rates. The trace components in coal fly ash are difficult to separate alone without the influence of impurities. During leaching treatment, gases or a large amount of waste residue are produced, making it difficult to achieve recycling and utilization, which can pollute the environment.

In addition to the issues mentioned above regarding the separation and extraction of gallium from coal fly ash, different leaching methods should be selected according to the content of gallium in coal fly ash. For high-content fly ash, suitable conditions should be selected to leach gallium while minimizing the leaching of other impurities; for low-content fly ash, optimal conditions should be selected, and a simpler method should be studied to deal with impurities through process optimization.

2.4 Recovery from Other Ores

Not only zinc ore, bauxite, and coal fly ash, but some other ores also contain trace amounts of gallium, such as iron ore, copper ore, lead ore, cassite, tungsten and molybdenum ore. Generally, the gallium content in these minerals is too low to be exploited alone, but can be recycled as a by-product in other metal extraction processes, which is currently a potential source of gallium, accounting for less than 10 % of the world's gallium metal production. The boehmite co-exists in the aluminite claystone and coal seam was found in the No. 6 low-sulfur bituminous coal in Ordos, Neimeng province, which contains abnormally large amounts of gallium and rare earth elements. The average amount of Ga in Section 7 coal seam is 44.8 μg/g. The clay layer and bauxite layer of upper carboniferous Benxi, Liaoning province produced from the weathering denudation surface at the top of Middle Ordovician are also important sources of gallium. In addition, significant volcanic crystals and volcanic ash are found in clayey conglomerates, which can partially become sources of gallium [28].

3. Conclusion

In summary, the source of gallium mainly depends on the mining and utilization of zinc ore, bauxite and coal fly ash, while other minerals can only be used as potential sources. With the increasing demand for gallium and the change of resource conditions, new extraction methods and sources may develop in the future.

4. References

1. Alfaify S, Alam K, Haq B U, et al. Structural, Electronic, and optical properties of the pressure-driven novel polymorphs of gallium nitride: first-principles investigations[J]. International Journal of Energy Research, 2022, 46(3): 2361-2372.
2. Rao F, Zheng X, Zhang X, et al. Research on recovery process and kinetics of gallium and indium from MOCVD production waste[J]. The Chinese Journal of Process Engineering, 2022, 22(05): 689-698.
3. Mangababu A, Goud R, Byram C, et al. Multi-functional gallium arsenide nanoparticles and nanostructures fabricated using picosecond laser ablation[J]. Applied Surface Science, 2022, 589: 152802.
4. Okada A, Nakatani M, Chen L, et al. Effect of annealing conditions on the optical properties and surface morphologies of (201)-oriented β-Ga2O3 crystals[J]. Applied Surface Science, 2022, 574: 151651.
5. Qiu W M, Xi C S, Qiu X Z, et al. Extraction of Gallium and Indium from Zinc Smelting Industrial Waste [J]. Non ferrous Metals (Smelting Part), 2017 (05): 28-32.
6. Luo J H. Recovery of gallium and germanium from zinc replacement slag by combined wet-fire process[D]. Jiangsu University of Science and Technology, 2022.
7. Ma X H, Qin W Q, Wu X L, et al. Study on hot acid leaching of gallium and germanium from zinc leaching slag[J]. Mining and Metallurgy Engineering, 2012, 32(02): 71-75, 79.

8. Rao S, Wang D, Liu Z, et al. Selective extraction of zinc, gallium, and germanium from zinc refinery residue using two stage acid and alkaline leaching[J]. Hydrometallurgy, 2018, 183:38-44.
9. Wu X L. Study on recovery of Gallium and Germanium from zinc leaching slag[D]. Central South University, 2013.
10. Feng F, Li Y. Effect of Bayer process solution composite on adsorbing gallium by resin[J]. Hydrometallurgy of China, 2006, 25(1): 30.
11. Su Y, Li G B, Luo K B. Research progress on extraction of gallium from metal [J]. Journal of Hydrometallurgy, 2003, 22(1): 9-13.
12. Riveros P A. Recovery of gallium from Bayer liquors with an amidoxime resin[J]. Hydrometallurgy, 1990, 25(1): 1-18.
13. Sahni S K, Reedijk J. Coordination chemistry of chelating resins and ion exchangers[J]. Coordination chemistry reviews, 1984, 59: 1-139.
14. Xu C P. Adsorption and separation of Ga (III) from sulfuric acid impregnated resin [D]. Ludong University, 2017.
15. Jiang C J, Zheng H. Study on extraction and utilization of Gallium from Hungarian bauxite[J]. Light Metals, 1976(01): 49-53.
16. Zhu Z P. Basic research on new comprehensive utilization technology of high iron tribauxite type bauxite[D]. Central South University, 2011.
17. Tera F, Korkisch J, Hecht F. Ion exchange in mixed solvents-IV: The distribution of thorium between alcohol-nitric acid solutions and the strongly-basic anion exchanger dowex-1. Separation of thorium from uranium[J]. Journal of Inorganic and Nuclear Chemistry, 1961, 16(3-4): 345-349.
18. Qu Y, Li H, Tian W, et al. Leaching of valuable metals from red mud via batch and continuous processes by using fungi[J]. Minerals Engineering, 2015,81:1-4.
19. Abdulvaliyev R A, Akcil A, Gladyshev S V, et al. Gallium and vanadium extraction from red mud of Turkish alumina refinery plant: Hydrogarnet process[J]. Hydrometallurgy, 2015, 157: 72-77.
20. Éva Ujaczki, Courtney R, Cusack P B, et al. Recovery of gallium from bauxite residue using combined oxalic acid leaching with adsorption onto zeolite HY[J]. Journal of Sustainable Metallurgy, 2019, 5(2):262-274.
21. Gladyshev S. V, Akcil A, Abdulvaliyev R. A, et al. Recovery of vanadium and gallium from solid waste by-products of Bayer process[J]. Minerals Engineering, 2015,74(4): 91-98.
22. Zhou C Y. Research on the Export Strategy of Gallium Metal [D] Dalian University of Technology, 2002
23. Zheng F, Gesser H. Recovery of gallium from coal coal fly ash[J]. Hydrometallurgy, 1996, 41: 187-200.
24. Oriol F, Xavier Q, Roberto J, et al. Recovery of gallium and vanadium from coal coal fly ash[J]. Journal of Hazardous Materials, 2007,139(3):413-423.
25. Fang Z, Gesser H D. Recovery of gallium from coal coal fly ash[J]. Hydrometallurgy, 1996, 41(2-3): 187-200.
26. Lu T Z. Research on separation and recovery of Gallium from coal fly ash by solvent extraction and its mechanism[D]. Qingdao University of Science and Technology, 2019.
27. Zhao Z, Cui L, Guo Y, et al. Recovery of gallium from sulfuric acid leach liquor of coal coal fly ash by stepwise separation using P507 and cyanex 272[J]. Chemical Engineering Journal, 20201, 381: 122699.
28. Zhang F X, Wang L S. Formation and material origin of the super-large coal-type gallium deposit in Hedaigou, Junge, Inner Mongolia[J]. Geology in China, 2009, 36(02): 417-423.