



Resources and extraction of gallium: A review



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ABSTRACT

Gallium (Ga) is extensively employed in integrated circuits and advanced electronic devices as it provides the benefits of low energy consumption and high computation speeds. However, the Ga-bearing host minerals are scarce in nature. Ga occurs in combination with several minerals, mainly including aluminum, zinc, iron ores and coals, of which bauxite, zinc ores and coals are the primary original sources of Ga currently. Mining minerals for the sole extraction of Ga is not economical due to the low concentration of Ga. Accordingly, Ga is mainly recovered as a by-product from the processing of minerals. The current main commercial resources of Ga are Bayer liquor and zinc residue, which contribute to nearly all of the worldwide Ga production. The production of low-grade (99.99% pure) Ga has been increasing at an average rate of 7.4% p.a. for the past four decades and amounted to 375 tons in 2016. It is estimated to increase by 20-fold by the year 2030 compared to the yield of 275 tons in 2012. The mounting worldwide demand for Ga necessitates the search for additional resources and recovery technologies for this particular element. Apart from the Bayer liquor and the zinc residue, there are several other Ga-resources, which include red mud, coal fly ash, Ga-bearing electronics industrial waste, and flue dust from electric furnaces at phosphorus factories. Based on the chemical properties of Ga, it is evident that both strong acidic/basic conditions and high temperatures favor the efficient extraction of Ga from its corresponding minerals. Several hydrometallurgical processes based mainly on acid/alkaline leaching along with solution purification and recovery (e.g. ion exchange, solvent extraction and precipitation) have been proposed for Ga extraction from these resources. In this paper, the current status of Ga recovery was reviewed and specific examples were utilized for each resource to discuss the extraction methods, the recoveries and the optimum Ga-recovery conditions for each resource. Additional research appears to be necessary to establish a highly efficient and environmentally friendly process to recover Ga from these resources.

1. Introduction

Gallium (Ga), a soft and silvery-blue metal, was discovered in 1875 by the French chemist Paul-Émile Lecoq de Boisbaudran (Moskalyk, 2003). With an average crustal abundance of 17 ppm, Ga is considered a trace metal (Redlinger et al., 2015). This element exhibits an extraordinarily wide temperature range in the liquid state due to its low melting point (302.98 K) and high boiling point (2676 K). Moreover, the metal also displays a low vapor pressure even at high temperatures. Solid Ga crystallizes in an orthorhombic unit cell and displays a conchoidal fracture similar to that observed in glass. The main physical properties of Ga include its atomic weight (69.723 g/mol), characteristic expansion upon solidification (3.1%), hardness (1.5 mohs), and density (5.904 and 6.905 g/cm³ for the solid and liquid phases,

respectively) (Moskalyk, 2003; Zhao et al., 2012).

In addition, six Ga isotopes have been identified, of which only ⁶⁹Ga (60.4%) and ⁷¹Ga (39.6%) are stable. Ga often takes on the oxidation states of Ga⁺ and Ga³⁺ (Chemical Elements, 2003). The element can form many substances, such as bromides, chlorides, hydrides, iodides, nitrides, oxides, selenides, sulfides and tellurides. Also, the material is insoluble in water, while it can dissolve in acids with pH values of < 2 and with an Eh value higher than 600 mV, according to the Eh-pH diagram of the gallium-water system (Pourbaix, 1974). It can also dissolve in concentrated alkali in an aqueous medium due to its amphoteric property (Ullmann's Encyclopaedia of Industrial Chemistry, 2002). It tends to form low-melting alloys with many metals, such as mercury.

The industrial utilization of Ga began in the US in the 1940s;

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however, it significantly increased in the 1970s when the semi-conducting properties of Ga compounds with elements of group 15 were discovered (Chou et al., 2008). Gallium arsenide (GaAs) and gallium nitride (GaN), for instance, are valuable compounds used in advanced semiconductors and LED chips. These materials are utilized in many electronic devices, such as cell phones, photovoltaic generation panels, optical communication devices and computers (Han et al., 2008; Kida et al., 2009; Okabe, 2010). Due to its unique properties, Ga is irreplaceable by other materials/metals for current technological applications.

It is worth mentioning that Ga-bearing host minerals are rare. The majority of Ga is currently produced as a by-product of bauxite processing and the remainder produced from zinc-processing residues (Alonso et al., 2012; Frenzel et al., 2016; U.S. Geological Survey, 2017). The Ga production has been increasing at an average annual rate of 7.4% over the past four decades (Alonso et al., 2012) and it amounted to 375 tons in 2016 (U.S. Geological Survey, 2017). The limited natural resources and the ever-growing market demand might trigger the global competition for Ga resources (Frenzel et al., 2016).

Efficient recovery techniques for Ga extraction from its sources have attracted intensive interest; however, few of these techniques have been developed into practical industrial methods. While there are a few previous literature reviews on Ga processing exist (Moskalyk, 2003; Zhao et al., 2012; Frenzel et al., 2016), there is limited information available on the resources and recovery methods of Ga considering the rapid development of Ga industry in recent years. This paper provides an overview of the main resources for Ga acquisition and the corresponding extraction technologies. The processing routes, recoveries and optimum extraction conditions for individual Ga-rich resources are described. This manuscript concludes with an outlook of the Ga-derived resources and extraction technologies applications of the future.

2. Resources of Ga

The worldwide demand for Ga is increasing and is expected to expand by 20-fold in 2030 compared to the yield of 275 tons in 2012 (Gladyshev et al., 2015). In 2016, the global production of low-grade (99.99% pure) and high-purity (99.9999% and 99.999999% pure) Ga production was estimated to be 375 and 180 tons, respectively. Approximately 93% of low-grade Ga is refined in China. The principal producers of the high-purity metal were China, Japan, the United Kingdom and the United States (U.S. Geological Survey, 2017). In contrast, Ga-bearing host minerals are considered quite rare due to the inability of Ga to form the corresponding minerals in natural conditions (Poledniok, 2008). Ga is never found in its pure state, and it is usually present in various amounts in aluminum ores, zinc ores, iron ores, coals and other rocks, among which bauxite, zinc ores and coals are the main sources of Ga currently (Torma and Jiang, 1991; Font et al., 2007). The potential reserves of Ga in these three raw materials are estimated according to the available reserves and Ga concentrations, and are presented in Table 1 (BP, 2015; Thakur, 2017; Frenzel et al., 2016; U.S.

Table 1
Estimates of Ga potential reserve.
(BP, 2015; Thakur, 2017; Frenzel et al., 2016; U.S. Geological Survey, 2017).

Raw material	Estimated reserve (10 ⁹ tons)	Ga average content (ppm)	Ga potential resources (10 ⁶ tons)
Bauxite	55–75	50	> 1
Zinc ore	1.9	50 ^b	0.095 ^c
Coal ^a	> 1000	10	10 ^c

^a Coal reserve to a depth of approximately 1000 m was estimated.

^b This present study referred to the Ga content of U.S domestic zinc ore owing to no available information on Ga average content in world zinc resources.

^c The Ga potential resources of zinc ore and coal were calculated according to the corresponding Ga average contents, respectively.

Geological Survey, 2017). Bauxite, which is a major raw material for alumina production, is estimated to contain > 1 million tons of Ga, with an average concentration of approximately 50 ppm (Frenzel et al., 2016). The identified zinc resources of the worldwide are approximately 1.9 billion tons, indicating that zinc ore is a significant Ga resource in world (U.S. Geological Survey, 2017). It is noteworthy that approximately 10 million tons of Ga are contained in coal resources (BP, 2015; Thakur, 2017). Thus, more attention should be paid to these resources as a significant source of Ga in the future. The current worldwide reserves of Ga are considerable, and can likely supply adequate amounts of Ga for several hundred years at the present rate of consumption. Unfortunately, only a portion of Ga in the resources is potentially recoverable (U.S. Geological Survey, 2017).

Currently, mining any mineral solely for Ga extraction is not economical due to its low concentration; thus, Ga is mainly recovered as a by-product from the processing of minerals. The commercial Ga is the by-product from Bayer liquor obtained from the bauxite leaching process and zinc residue generated by hydrometallurgical treatment of zinc concentrates (Zhao et al., 2012; Frenzel et al., 2016; U.S. Geological Survey, 2017). In the Bayer process, approximately 70% of the Ga is leached from the bauxite into the caustic soda solution, while the remaining 30% is disposed of with the red mud waste. Following the alumina trihydrate crystallization, the leached Ga is enriched in the liquid phase as hydroxide because Ga(OH)₃ precipitates at a lower pH value (9.4–9.7) than that of Al(OH)₃ (pH 10.6) in a strong basic solution (Xu and Xu, 2002). The resulting concentration is roughly 100–300 mg/L after several successive circulations (Figueiredo et al., 2002). Ga production from Bayer liquor accounts for approximately 90% of the annual global Ga supply (Lu et al., 2008; Zhao et al., 2012). The other important commercial resource of Ga is zinc residue produced by roast-leach-electrowinning process for the smelting of zinc ores (Temple, 1986; Fugleberg, 1999). Where > 98% of Ga remains in the leaching residues containing Ga of 0.03–0.4 wt% (Kinoshita et al., 2011; Gu et al., 2014; Liu et al., 2016). Currently, the zinc residue accounts for nearly 10% of the annual Ga production worldwide (Wu et al., 2012; Frenzel et al., 2016).

It is critical to reserve Ga resources and develop efficient extraction technologies to guarantee the current and future demands for the material. In addition to the Bayer liquor and zinc residues, Ga is also found in small amounts in industrial waste products, such as red mud (Liu and Li, 2015), electrostatic precipitation dust produced during alumina calcination (Gladyshev et al., 2015), scrubber dust from fume extraction in aluminum plants (Abisheva et al., 2012; Carvalho et al., 2000), coal fly ash (Conzemius et al., 1984; Zheng and Gesser, 1996; Yao et al., 2015), Ga-rich electronics industry waste (Sturgill et al., 2000; Swain et al., 2015a,b; Lu et al., 2015) and flue dust from the electric furnaces of phosphorus factories (Xu et al., 2004, 2007). Particularly, red mud, the coal fly ash and the electronics industry waste are of much interest, and are being considered as significant potential Ga resources due to their high output volume and recoverable concentration.

The waste produced from the Bayer process for alumina extraction from bauxite ores is called ‘red mud’ and it contains high amounts of trace metals (Qu et al., 2013, 2015; Liu and Naidu, 2014). Generally, Ga content in this waste is in the 20–80 ppm range (Liu and Li, 2015), and occurs as α-GaOOH and Ga(OH)₃ species. Annually, approximately 120 million tons of red mud are generated with an estimated global inventory of over 3 billion tons (Power et al., 2011). Coal fly ash, produced from coal-fired power plants, is another abundant waste materials (Yao et al., 2015). Combustion of every 4 tons of raw coal generally produces 1 ton of coal ash fly and this amount is anticipated to reach 580 million tons by 2015 in China alone (Ren et al., 2012; Zhu et al., 2016). Generally, the Ga concentration in fly ash is 6–10 times higher than that in raw coal, varying from 30 ppm to over 100 ppm (Conzemius et al., 1984; Zheng and Gesser, 1996; Dai et al., 2006; Wang et al., 2015). Ga occurs in coal mainly as an inorganic phase and replaces Al in aluminiferous minerals (mainly boehmite) in the form of

isomorph (Dai et al., 2006), and remains in the same form in fly ash after coal combustion (Wang et al., 2015). Ga is an essential element for advanced semiconductors and light emitting diode (LED) chips, due to its unique properties (Okabe, 2010; Swain et al., 2015a,b). The metal is usually present in electronic devices as gallium arsenide (GaAs), gallium nitride (GaN) or indium gallium nitride (InGaN) (Sturgill et al., 2000; Lu et al., 2015; Swain et al., 2015a,b). With the expansion of electronic industries, the large amount of generated electronic waste is also considered as a Ga-rich resources.

3. Chemical properties of Ga

The investigation of Ga extraction methods from Ga-bearing minerals requires knowledge of the chemical properties of Ga, especially for regarding its aqueous species and the solubilities of related compounds. The chemical properties of Ga are reviewed in this section to provide a better understanding of the processes of Ga recovery.

3.1. Chemical speciation of Ga in aqueous solution

It is known that Ga forms anionic complexes and exists in ionic form in solutions (Luong and Liu, 2014). Wood and Samson (2006) reviewed the geochemistry of Ga and reported that Ga(III) is its stable oxidation state in aqueous solution. Fig. 1 presents the species of Ga(III) as a function of pH based on the hydrolysis constants of Ga(III) at 25 °C. The $[\text{Ga}(\text{OH})_2]^+$ and $[\text{Ga}(\text{OH})_3]^0$ species are not predominant at any pH, while soluble Ga^{3+} is predominant at $\text{pH} < 2.0$. The $[\text{Ga}(\text{OH})_2]^{2+}$ species peaks at about pH 3, which is responsible for approximately 75% of soluble Ga(III). When pH is about 4, $[\text{Ga}(\text{OH})_2]^+$ reaches its highest amount of approximately 25%. At pH 4.5, the neutral species, $[\text{Ga}(\text{OH})_3]^0$, has a narrow range of predominance. The negative species, $[\text{Ga}(\text{OH})_4]^-$, is the dominant species in the pH range of 4–14, especially at alkaline pH (Luong and Liu, 2014). Furthermore, $[\text{Ga}(\text{OH})_4]^-$ has a substantial field of predominance at any temperature (Wood and Samson, 2006).

In addition to Ga-hydroxide complexes, Ga is also prone to form complexes with chloride, sulfate, fluoride, and phosphate due to its high charge. Ga(III)-chloride complexes in aqueous solution are present as $[\text{GaCl}_2]^{2+}$, $[\text{GaCl}_2]^+$, $[\text{GaCl}_3]^0$ and tetrahedral $[\text{GaCl}_4]^-$. Generally, the hydrated Ga^{3+} ion is octahedrally coordinated by water molecules, but the tetrahedral coordination of water may be replaced by a sufficient number of other ligands (Wood and Samson, 2006). Thus $[\text{GaCl}_4]^-$, in our opinion, is the dominant species in strong hydrochloric acid media. Izatt et al. (1969) studied the interaction of sulfate ion with several metal ions. The results suggest that the primary Ga(III)-sulfate complexes are $[\text{GaSO}_4]^+$ and $[\text{Ga}(\text{SO}_4)_2]^-$ in aqueous solution. There is relatively little data available on Ga(III)-phosphate complexes,

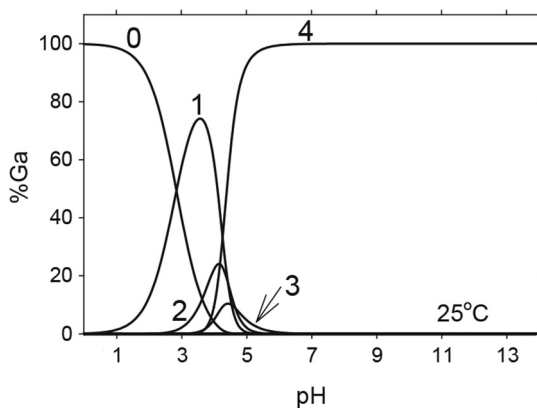
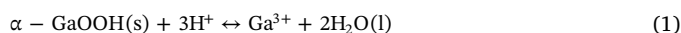


Fig. 1. Speciation of Ga(III) as affected by pH at 25 °C at saturated water vapor pressure and infinite dilution. The species shown are: 0- Ga^{3+} ; 1- $[\text{Ga}(\text{OH})_2]^{2+}$; 2- $[\text{Ga}(\text{OH})_2]^+$; 3- $[\text{Ga}(\text{OH})_3]^0$; and 4- $[\text{Ga}(\text{OH})_4]^-$ (Wood and Samson, 2006).

but it is known that Ga(III)-phosphate complexes occur as $[\text{Ga}(\text{HPO}_4)]^+$, $[\text{Ga}(\text{HPO}_4)_2]^-$, $[\text{Ga}(\text{H}_2\text{PO}_4)]^{2+}$, and $[\text{Ga}_2(\text{HPO}_4)]^{4+}$ in aqueous phase. To the best of our knowledge, there are no reports on the composition and stability of complexes of Ga(III) with nitrate. The NO_3^- ion, similar to Cl^- , is a weakly complexing ligand (Izatt et al., 1969). Thus, it can be deduced that the Ga(III)-nitrate complexes may mainly exist as $[\text{Ga}(\text{NO}_3)_4]^-$ in strong nitrate solution. It should be noted that other complexes besides Ga(III)-hydroxide and Ga(III)-fluoride (occurring as $[\text{GaF}]^{2+}$, $[\text{GaF}_2]^+$, $[\text{GaF}_3]^0$ and $[\text{GaF}_4]^-$) are comparatively weak (Wood and Samson, 2006).

3.2. Solubilities of α -GaOOH solid phase

As mentioned earlier, bauxite is the major source of Ga currently. Ga frequently substitutes for Al in the mineral due to their similar ionic radii ($\text{Ga}^{3+} = 0.62 \text{ \AA}$, $\text{Al}^{3+} = 0.57 \text{ \AA}$) (Torma and Jiang, 1991; Liu and Li, 2015). Thus, α -GaOOH phase represents an end-member for Ga substitution in oxyhydroxide phases of bauxite (Wood and Samson, 2006). Solubilities of α -GaOOH(s) at saturated water vapor pressure were calculated from relevant thermodynamic data based on reaction (1) and discussed in detail by Diakonov et al. (1997) and Wood and Samson (2006).



The solubility results of α -GaOOH(s) are depicted in Fig. 2. At 25 °C, the minimum solubility occurs at about $10^{-9.3} \text{ m}$ ($\sim 0.03 \text{ ppb}$) and at pH of about 4.3. Moreover, the solubility increases with change in pH ($\text{pH} > 4.3$ or < 4.3) and increasing temperature. It is noteworthy that a higher temperature leads to a significant improvement in solubility. For instance, at 300 °C, the minimum solubility reaches approximately 220 ppb at about $10^{-5.5} \text{ m}$. Also, $[\text{Ga}(\text{OH})_4]^-$ is the predominant species at any pH value at 300 °C (Wood and Samson, 2006).

From the above discussion of Ga chemical properties, it is evident that strong acidic/basic conditions and high temperatures are favorable for highly efficient extraction of Ga from its minerals. The extraction methods of Ga from Ga-bearing resources are discussed in the following section.

4. Extraction methods of Ga

4.1. Bayer process liquor

Ga recovery techniques in the Bayer process are well studied and include fractional precipitation, electrochemical deposition, solvent extraction, and ion-exchange processes (Zhao et al., 2012; Hoang et al., 2015). The fractional precipitation approach is based on Al–Ga precipitation with CO_2 to form $\text{Al}(\text{OH})_3/\text{Ga}(\text{OH})_3$. This is followed by the subsequent separation of Al and Ga with lime milk or NaOH solutions,

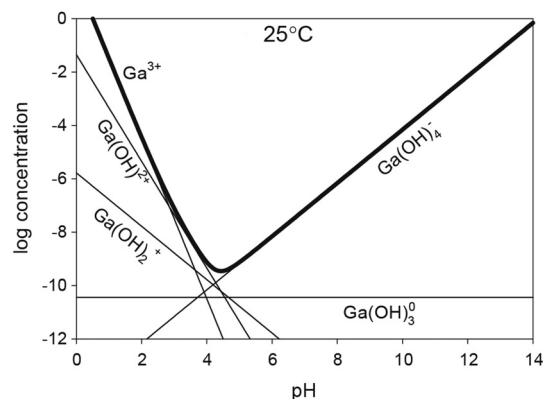


Fig. 2. Solubility of α -GaOOH as a function of pH without ionic strength at saturated water vapor pressure (Wood and Samson, 2006).

after which the Ga is finally recovered from the $\text{NaGa}(\text{OH})_4/\text{NaAl}(\text{OH})_4$ solution by a two-stage carbonation process. The electrochemical method includes both mercury cathode electrolysis and cementation; however, mercury cathode electrolysis is prohibited in many countries due to its high toxicity. Cementation is an electrochemical process that involves a displacement reaction between Ga and a reductant, such as sodium amalgam, aluminum or an aluminum-gallium alloy. The solvent extraction method is based on gallium or aluminum extraction through a cation-exchange mechanism into the organic phase. This method has limited industrial application due to the slow extraction kinetics and high cost of degradation as well as dissolution of the extracted species. Only the ion-exchange technology has been proven as one of the most effective methods for Ga recovery from Bayer liquor. This method offers several advantages, such as the simplified process, high recovery rate, easy operation, and negligible effect on alumina processing.

The first ion-exchange process for direct Ga extraction from Bayer liquor was patented by Kataoka et al. (1984). In this study, it was discovered that certain chelating resins contain active groups, such as $=\text{NOH}$, $-\text{NH}_2$, $-\text{OH}$, $-\text{SH}$ or $=\text{NH}$, exhibit excellent selective extraction ability for Ga. The process has been employed by many alumina plants to recover Ga with the rapid development of the resin industry in China in recent years. Fig. 3 presents a schematic of the ion-exchange technology used in the Guizhou branch of Chalco, and the physico-chemical characteristics of the commercial amidoxime resin (LSC-600) employed in the process are summarized in Table 2.

The Bayer liquor in the plant contained 73 g/L of Al_2O_3 , 174 g/L of Na_2O and 163 mg/L of Ga_2O_3 . The maximum loading of 9.4 g Ga/L in the resins was obtained through an industrial experiment at a resin dosage of 8 g/L at room temperature for 16 h. The process mainly

Table 2
Resin main performance parameter.

Particle size	Water content	Surface area	Adsorption capacity ^a
0.25–0.65 mm	35–45%	300–600 m ² /g	9.4 g/L

^a Adsorption capacity of LSC-600 toward Ga was calculated according to the industrial experiment data.

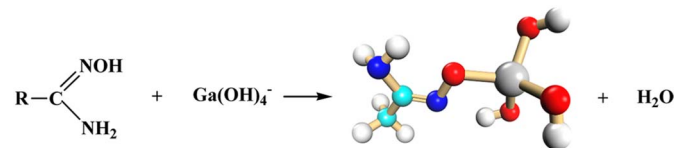


Fig. 4. Adsorption mechanism of Ga(III) onto LSC600 (Zhao et al., 2015).

consisted of the following steps: **resin adsorption** (duration time of 16 h, temperature of 45–50 °C, concentration of $\text{Ga} \geq 160$ mg/L, content of suspended solids < 1.0 g/L) → **acid desorption** (6 M sulfuric acid) → **precipitation** (≥ 10 M sodium hydroxide) → **purification for three times** (content of impurity < 0.01 wt%, purified liquid containing 40–50 g/L of Ga) → **Electrolysis** (duration time 20 h, Ga raffinate < 1000 mg/L). The adsorption mechanism of Ga(III) onto LSC600 resin is depicted in Fig. 4 (Zhao et al., 2015).

The resin, which has an amidoxime group $[-\text{C}(=\text{NOH})\text{NH}_2]$, can absorb Ga, and Ga is present as $[\text{Ga}(\text{OH})_4]^-$ in the strong basic Bayer liquor. When the O bonds with Ga, the released H^+ will combine with one OH^- from $[\text{Ga}(\text{OH})_4]^-$ to form H_2O .

The overall recovery of Ga was 46.47% in the above system. The obsolete carbonation method produced only 10 tons/year, while this novel process could recover 40 tons/year from the same system of alumina refinery. Additionally, the purity of Ga product was improved from 99.9% to 99.99%.

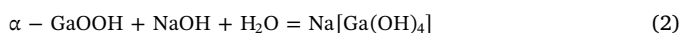
4.2. By-products of aluminum industry

In addition to Bayer liquor, several other by-products in the aluminum industry such as red mud produced from alumina extraction in Bayer process, electrostatic precipitation dust generated from aluminum hydroxide calcination and scrubber dust obtained from fume extraction aluminum electrolysis also contain accumulated Ga. Ga recovery from these by-products has attracted significant interest.

4.2.1. Red mud

Recovery techniques of base metals, including alumina, soda, ferric oxide and titanium oxide, from red mud are of much interest (Balomenos et al., 2011; Lindsay, 2011; Samouhos et al., 2013; Gladyshev et al., 2015; Liu and Li, 2015; Okudan et al., 2015; Qu et al., 2015). However, few systematic investigations have been conducted regarding the Ga extraction from the residue.

One approach to recover Ga and V from red mud is using the Bayer-hydrogarnet process, as is illustrated in Fig. 5 (Abdulvaliyev et al., 2015). The sample contained 23.95 wt% Al_2O_3 , 25 ppm Ga, and 200 ppm V_2O_5 , and it was leached through a high-modulus solution (i.e., $\alpha_x = 30$; 240 g/L Na_2O) in the presence of lime for 90 min at 240 °C under 20 atm with a liquid to solid ratio (abbreviated as L/S hereafter) of 6. The related chemical reactions are as follows.



The Ga leaching solution (Ga as $[\text{Ga}(\text{OH})_4]^-$) was treated by precipitation, followed by a two-stage carbonation process to generate a concentrate containing 0.32 wt% Ga and 3.7 wt% V_2O_5 . The concentrate could be further treated for the selective recovery of Ga and

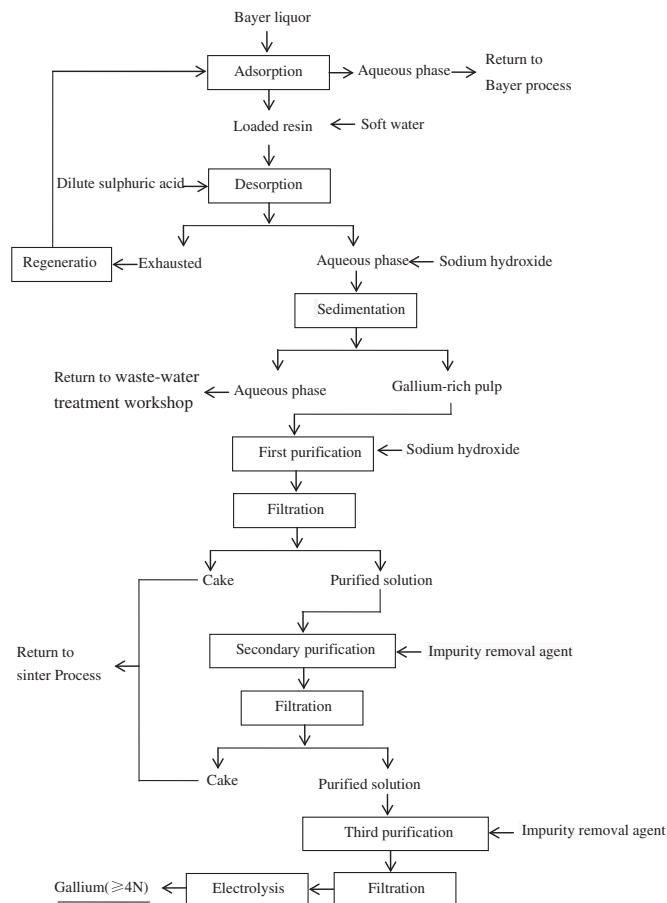


Fig. 3. Schematic diagram of ion-exchange method applied in Guizhou branch of Chalco for gallium production.

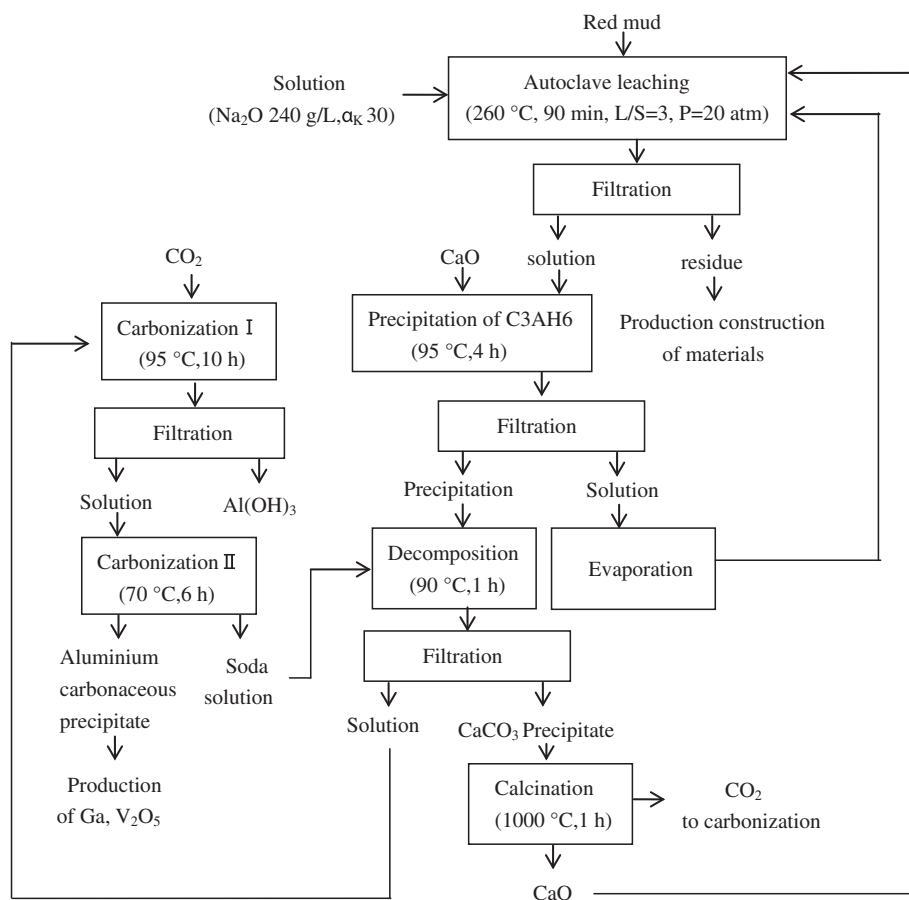


Fig. 5. Schematic diagram of Bayer–hydrogarnet process of red mud (Abdulvaliyev et al., 2015).

V_2O_5 , respectively.

Apart from the Bayer-hydrogarnet process, a bioleaching process has also been investigated for Ga recovery from red mud with the fungus *Aspergillus niger*, which produces a high volume organic acids (Qu et al., 2015). The best leaching ratio was approximately 54% for Ga from the sample containing 570 ppm of Ga under the conditions of 30 °C, agitation rate of 300 r/min, air flow rate of 180 L/h, duration time of 40 h, pH 1.9, 200 mL of red mud pulp (2% pulp density) and 23.1 g/L biomass in continuous leaching tests. The result indicated that the performance of bioleaching for Ga from red mud was poor.

The authors' research group 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% in a 4.3 M hydrochloric acid, with L/S ratio of 8, and leaching temperature of 55 °C for 4 h, at 300 r/min under atmospheric pressure. The adsorption efficiency and recovery rate for Ga from the leaching liquor by ion-exchange technology are currently being investigated.

4.2.2. Electrostatic precipitator dust

Electrostatic precipitator dust generated during aluminum hydroxide calcination contains concentrated Ga (occurring as Ga_2O_3). Several previous studies have mainly focused on the recovery of aluminum from the dust, rather than Ga extraction (Sancho et al., 2009; Ayala et al., 2010). Recently, a Ga recovery trial from electrofilter dust was reported (Gladyshev et al., 2015). The target dust contained 38 ppm Ga_2O_3 and 89.5 wt% Al_2O_3 . The detailed process is illustrated in Fig. 6. The dust sample was sintered with soda ash (Na_2CO_3) for 90 min at 1000 °C, and then digested in an alkaline solution (50 g/L Na_2O , 90 °C). Then, the solution (containing Ga as $[\text{Ga}(\text{OH})_4]^-$) was subjected to a

two-stages of carbonation process to precipitate Al as hydroxide. The precipitate containing concentrated Ga was further leached in an alkaline solution (240 g/L Na_2O) at 90 °C for 1 h at a L/S ratio of 2. Following this, the pregnant leachate was filtered and neutralized via carbonation to obtain a Ga concentrate. This resulted in a pregnant solution containing 0.6 g/L Ga_2O_3 , which is suitable for Ga electrolysis process.

4.2.3. Dust of aluminum electrolysis plants

Ga recovery from the dust of aluminum electrolysis plants has received some interest. The dust tends to accumulate Ga (as Ga_2O_3) during the sublimation process (Carvalho et al., 2000), and contains roughly 0.1 to 1.0 wt% Ga_2O_3 . Abisheva et al. (2012) characterized several dust products from the electrolysis of aluminum, which contained 0.071–0.125 wt% Ga and 26.6–29.9 wt% Al_2O_3 . In this study, approximately 64–83% of Ga was extracted from the dust products in 1.0 M H_2SO_4 with a L/S ratio of 4 at 90 °C. Another study involving the extraction of Ga from Ga-bearing dust (0.22 wt% Ga) was conducted by Carvalho et al. (2000). The flue dust was first sintered at 200 °C for 2 h and subsequently leached with the treated samples in a 1:1 hydrochloric acid solution (v/v) at 110 °C for 5 h with a L/S ratio of 5. The Ga leaching rate reached a value as high as 99.01%. The leaching liquor (containing Ga as $[\text{GaCl}_4]^-$) was firstly treated using a polyether-type polyurethane foam (PUF) to extract Ga and then, the loaded PUF was quickly re-extracted using an 80% ethanol solution. The recovered Ga was precipitated with a sodium hydroxide solution, followed by purification by reprecipitation and calcination. The final oxide product contained 98.6% Ga_2O_3 .

Among the aforementioned Ga resources, Bayer liquor is the primary Ga resource in the aluminum extraction industry, from which approximately 90% of the worldwide Ga metal is produced. Ga

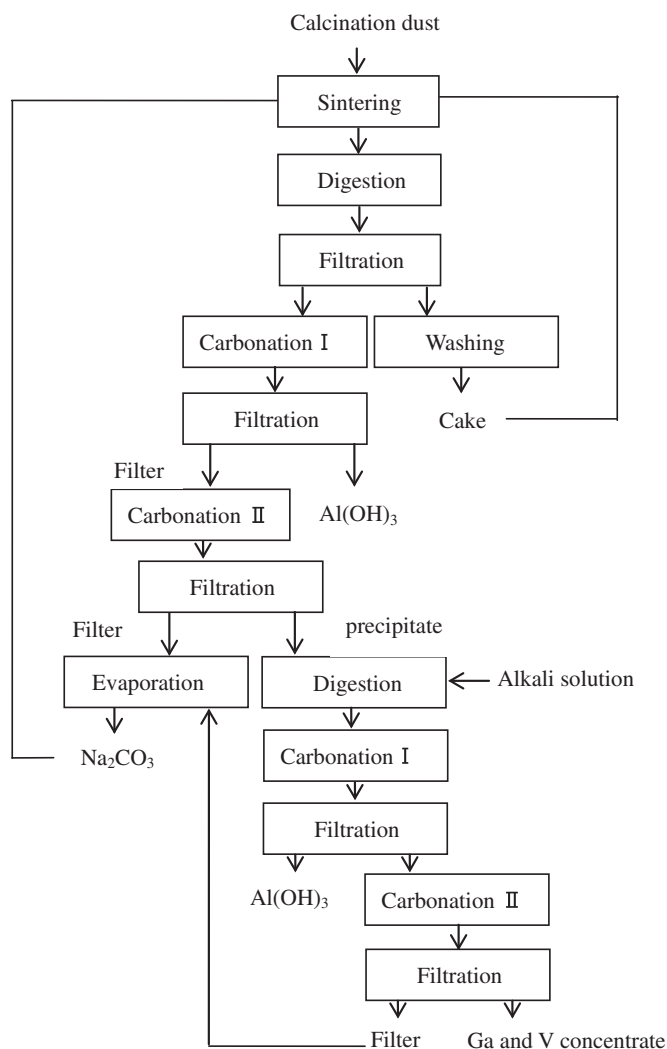


Fig. 6. Schematic diagram of gallium recovery from electrofilter dust (Gladyshev et al., 2015) (Note: $C_3AH_6 \cdot 3CaO \cdot Al_2O_3 \cdot 6H_2O$).

extraction from the other by-products of the aluminum industry is difficult, and most methods are not suitable on an industrial scale due to high costs and complex processes. However, with the depletion of bauxite resources and the development of novel technologies, the red mud, which is one of the most important by-products of the aluminum industry with sizable production quantities, is expected to become a vital source of Ga.

4.3. Zinc industry wastes

Apart from Bayer liquor, the zinc residues are also considered an important commercial resource of Ga. The Ga element mainly exists in zinc ferrite ($ZnO \cdot Fe_2O_3$) through an isomorphous substitution with Fe (Wu et al., 2012). A combined pyro- and hydrometallurgical technique is widely employed for Ga extraction from zinc residues in industrial production. In a zinc plant at Porto-Marghera in Italy, Ga was successfully extracted from zinc residues for the first time in 1969, and the related process is presented in Fig. 7 (Cottill et al., 1970). Moreover, the same feat was achieved by a zinc smelting plant in Zhuzhou, China in 1975 (Wu, 2013). However, low-level recovery, high energy consumption, long processes, and secondary pollution are the main drawbacks of the technology. Therefore, exploring “greener” methods to extract Ga from zinc residues is of great importance.

Continuous counter-current foam separation method was proposed

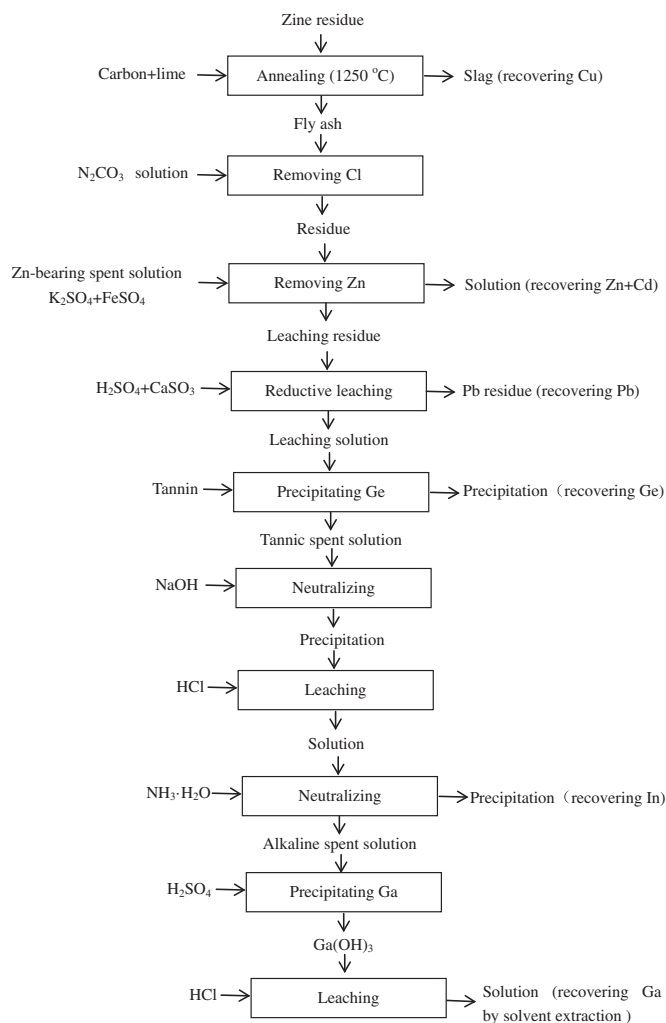
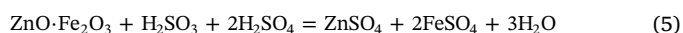


Fig. 7. Schematic diagram of gallium recovery from zinc residue in zinc plant of Porto-Marghera in Italy (Cotterill, C., 1970).

by Kinoshita et al. (2011) to extract Ga from a leaching solution of zinc refinery residues. The sample, which contained 0.03 wt% Ga, was processed using a 6 M hydrochloric acid. The filtrate (Ga present as $[GaCl_4]^-$) was then diluted to provide a metal solution. Poly(oxyethylene) nonylphenyl ether was employed as both foam-producer and metal collector in the experiment. A complete recovery of Ga was obtained under the conditions of 6 M hydrochloric acid, surfactant concentration of 0.10 wt%, an air flow rate of $50 \text{ cm}^3/\text{min}$, metal solution injection rate of $0.35 \text{ cm}^3/\text{min}$ and surfactant solution of $0.25 \text{ cm}^3/\text{min}$. Wu et al. (2012) investigated the recovery of Ga from zinc residues containing 0.043 wt% Ga using a reductive leaching process. Through this method, 91% Ga, 90% Zn and 96% Fe were extracted under the following optimal conditions: 80 g of zinc residues, 56 g/L sulfuric acid concentration, sulfur dioxide partial pressure of 200 kPa, L/S ratio of 7, and 120 min leaching at 100 °C. The main reactions involved are listed below:

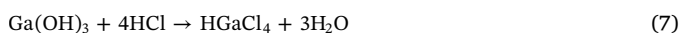


Recently, Liu et al. (2016) used a pressure acid leaching process to extract Ga from zinc refinery residues containing 0.266 wt% Ga. The result demonstrated that over 98% of Ga was leached under the optimal conditions of 150 °C, 156 g/L sulfuric acid concentration, a L/S ratio of 8, 0.40 MPa, calcium nitrate addition of 20 g/L, 300 r/min stirring rate, and 3 h leaching duration.

Although the recovery rates are high for the aforementioned routes, they are highly limited to the laboratory scale due to high costs and technical problems. Therefore, the high-efficiency methods for Ga recovery from zinc residues require further study.

4.4. Coal fly ash

Considerable effort has recently been devoted to the extraction of Ga from the fly ash generated by coal-fired power plants. For example, Zheng and Gesser, 1996 developed a technique for Ga recovery from coal fly ash, in which the sample containing 107 ppm of Ga was first roasted at 500 °C for 10 h. Subsequently, it was leached at room temperature for 2 h using 2 M hydrochloric acid with L/S ratio of 6. The equilibrium reactions in the acidic system of gallium-chloride-water are:



The result demonstrated that over 95% of Ga in the ash could be leached into solution.

Gutiérrez et al. (1997) also studied Ga recovery from fly ash by an acid leaching and dual solvent extraction process. The ash, which contained 110 ppm of Ga, was treated with 6 M hydrochloric acid. The leaching liquor (containing Ga as $[\text{GaCl}_4]^-$) was then mixed with Amberlite LA-2 (5 vol%) dissolved in kerosene to extract both Ga and Fe. Then, the loaded organic phase was washed with distilled water to strip Ga and Fe, and then Fe was precipitated from the washing solution with sodium hydroxide. The Ga remaining in solution was subsequently extracted selectively with a 10 vol% LIX 54 solution in kerosene. The Ga-loaded organic phase was stripped with a 0.5 M hydrochloric acid solution. Using this method, approximately 114 ppm of Ga was obtained from the stripped solution with 83% recovery. In addition to the acid leaching process, the sodium hydroxide extraction method was also evaluated for Ga recovery from fly ash by Oriol et al. (2007). Eight fly ash samples were collected for Ga extraction tests, in which the Ga content ranged from 149 to 320 ppm. The optimal Ga extraction conditions were as follows: 25 °C, 0.7–1 M of NaOH, L/S ratio of 5 L/kg and 6 h. A Ga leaching rate of approximately 60–86% was obtained. Recirculation of the leachates increased the initial Ga concentrations from 25 to 38 mg/L to 188–215 mg/L. The concentrated solution (containing Ga as $[\text{Ga}(\text{OH})_4]^-$) was further treated by a two-stage carbonation process to recover Ga. Approximately 98.8% of the Ga was recovered.

A pilot plant producing 4000 tons of alumina with a Ga recovery system was built in 2012 in Ordos, west China by the Shenhua Energy Company Limited (Vladimir, 2012; Ding et al., 2016). The pilot plant was based on a previously developed laboratory-scale process for Ga recovery from a circulating fluidized-bed fly ash, as presented in Fig. 8 (Gu et al., 2014). Firstly, the raw fly ash was crushed (≤ 100 mesh) and the iron was removed through magnetic separation (iron level ≤ 1 wt %). Subsequently, the pretreated sample was dissolved in hydrochloric acid (20–37 wt%) to obtain leachate (pH = 1–3, Ga present as $[\text{GaCl}_4]^-$). Ga in the leachate was then adsorbed with a macro-porous cationic resin. Subsequently, the eluent produced from washing the loaded resin was treated with a masking agent to mask ferric ions, and Ga was re-adsorbed on the resin from the purified solution. Then, the secondary eluent, generated from eluting the resin, was subjected to an alkalinity-adjustment with a sodium hydroxide solution (180–245 g/L). Finally, the filtered Ga-rich solution was electrolyzed at 35–45 °C under a current of 180–200 mA/L and a voltage of 4 V to produce Ga metal (99.9% purity). Through this process, the Ga adsorption efficiency and the iron removal rate were > 96% and 80% in hydrochloric acid leachate, respectively.

As mentioned previously, coal is a significant source of Ga. Therefore, coal fly ash as a by-product of coal combustion should attract significant attention for Ga recovery, due to its large volume and

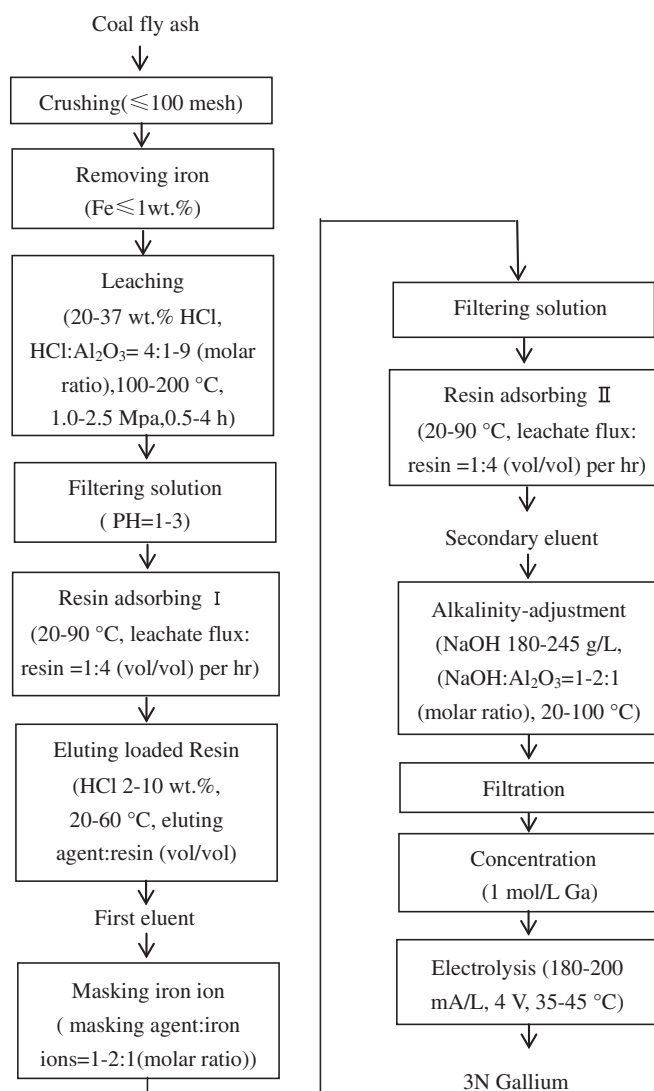


Fig. 8. Schematic diagram of gallium recovery from fly ash (Gu et al., 2014).

rich grade. Fortunately, the above mentioned pilot plant was able to successfully extract Ga from fly ash, which is a big step forward in the process industrialization.

4.5. Electronics industry waste

4.5.1. GaAs new scrap

Compared to silicon, GaAs has about five times faster signal transmittance speed, better optical properties and higher radiation hardness due to its energy band structure. > 85 wt% of GaAs scraps containing 50 wt% Ga is discharged during GaAs wafer production without treatment. Lee and Nam (1998) performed an investigation involving Ga recovery from GaAs scrap. The sample contained 48.6 wt% Ga and 51.2 wt% As. Over 99% of the Ga was leached in 2 h with 2 M HNO_3 at 60 °C, L/S ratio of 5.0, and stirring speed of 500 r/min. The extraction of Ga was believed to be a self-catalytic reaction due to NO gas generated during the process. Recently, Ga was recovered from the new scrap generated during the manufacturing of GaAs-based devices in Canada, China, Germany, Japan, the United Kingdom, and the United States, while old scraps are not utilized on an industrial scale (U.S. Geological Survey, 2017). Unfortunately, sufficient details of the relevant Ga recovery processes from the new scrap could not be found by a recent thorough literature search.

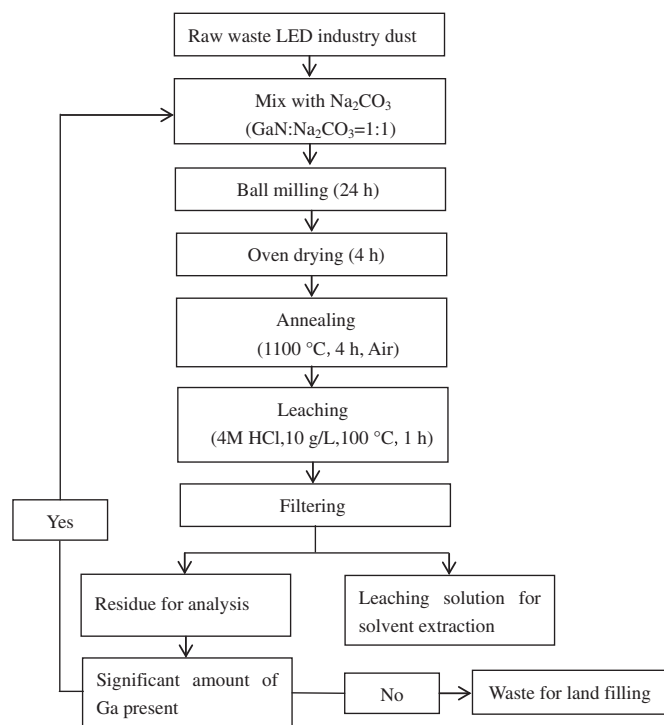
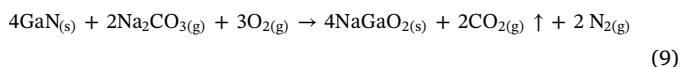
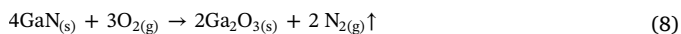


Fig. 9. Schematic diagram of gallium extraction from waste LED industry dust (Swain et al., 2015a,b).

4.5.2. LED waste

LED waste is mainly of two types: the waste dust generated during the manufacturing of LEDs and the end-of-life LEDs. The waste contains significant amounts of gallium and indium, where Ga exists as GaN. Swain et al. (2015a,b) investigated the recovery of Ga from LED waste, and detected 97.76 wt% Ga and 2.24 wt% indium in the LED waste through energy dispersive spectroscopy (EDS) analysis. The leaching-annealing technology used in this study to extract Ga from the waste is depicted in Fig. 9. The sample was firstly mixed with Na₂CO₃, ball milled and subsequently annealed. Finally, it was leached with HCl. The chemical equations below (8, 9 and 10) represent the possible reactions involved in the process:



The results showed that 73.68 wt% of Ga leaching was obtained in 1 h under the conditions of 4 M HCl, at 100 °C and a pulp density of 10 g/L.

The end-of-life LEDs are more complex than GaAs scraps. In contrast, the chips containing GaN in LEDs are combined more closely with quartz substrates. Lu et al., 2015 applied a vacuum metallurgy separation (VMS) technique to recycle Ga from the LEDs waste. The sample was treated with a combination of pyrolysis and physical disaggregation methods to produce rare-metal-rich particles (RMRPs) containing 92.8 wt% Ga. The Ga was subsequently separated from the RMRPs through evaporation and condensation. A Ga recovery efficiency of 93.48% was obtained in 1 h at 1100 °C and at 0.01–0.1 Pa. The decomposition reaction of GaN is as follows:

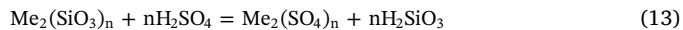


The Ga-bearing electronics industry waste is an extremely important source of Ga. However, most of the waste has not been utilized on an industrial scale except the new GaAs bearing scraps. Further

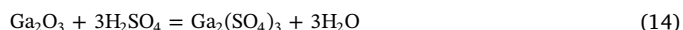
investigations should be made for Ga recovery from old GaAs bearing scraps and the end-of-life LEDs on the basis of economic feasibility and practicability.

4.6. Phosphorus flue dust

Ga is also found in flue dust generated during the electric furnace smelting of phosphate to produce elemental phosphorus. Therefore, the phosphorus flue dust is another potential source of Ga. Xu et al. (2004, 2007) utilized sulfuric acid as a leachant to recover Ga from the flue dust containing 0.053 wt% Ga (Ga likely present as Ga₂O₃). The dissolution process of Ga can be expressed by the following reactions:



$n = 1, 2, 3$ Me represents metal in the flue dust.



The results suggested that the Ga recovery rate increased with increase in temperature, sulfuric acid concentration, and L/S ratio. The acid-soluble Ga could be completely extracted with 20% sulfuric acid at 80 °C and a L/S ratio of 10.

The pyrometallurgical smelting of phosphorus, however, has been almost entirely replaced by a hydrometallurgical process, due to high contamination and energy consumption (Gleason, 2007). Moreover, the new process does not have comparable Ga-enrichment. Consequently, a commercial extraction of Ga is not viable (Frenzel et al., 2016).

The aforementioned Ga-bearing resources and the corresponding extraction processes, optimum recovery efficiencies, end products and applied scales are summarized in Table 3 (Figueiredo et al., 2002; Zhao et al., 2012; Gladyshev et al., 2015; Carvalho et al., 2000; Abisheva et al., 2012; Carvalho et al., 2000; Liu and Li, 2015; Abdulvaliyev et al., 2015; Klein et al., 1975; Zheng and Gesser, 1996; Gutiérrez et al., 1997; Oriol et al., 2007; Liu et al., 2016; Kinoshita et al., 2011; Gu et al., 2014; Swain et al., 2015a,b; Lee and Nam, 1998; Lu et al., 2015; Xu et al., 2004, 2007).

5. Conclusions and outlook

The economic importance of Ga has increased significantly in recent years due to its extensive applications in high-tech industries. Ga-bearing host minerals are quite scarce (Poledniok, 2008), and the metal occurs in nature in widely dispersed forms and is associated principally with bauxite, zinc ores and coals. Ga resource is relatively abundant in world; however, only a small percentage of these sources can be used as a commercial resource (U.S. Geological Survey, 2017). The increasing demand for Ga has prompted a search for new resources and the development of efficient extraction processes for the metal.

Bayer liquor is the major commercial resource for Ga extraction. Many methods have been developed for Ga recovery from this solution, among which the ion-exchange technology has been proven as one of the most efficient methods. This is due to its simplified process, high recovery rate, fast reaction kinetics, easy operation, excellent Ga selectivity and no negative effect on alumina processing. The second most important commercial resource for Ga extraction is zinc industry waste in the form of zinc residues. Currently, the main disadvantages of recovering Ga from the residue on a commercial scale are low recovery efficiency, high energy consumption, and secondary pollution. Accordingly, a higher efficiency process is still under investigation.

Coal ash fly should be the most promising Ga resource due to its tremendous volume and rich grade. This is supported by the successful operation of the pilot-plant-scale extraction of Ga from coal fly ash in Ordos, China. Therefore, it is believed that coal ash fly would increase the Ga supply. Red mud is expected to become another important resource of Ga, due to its increasing production and recoverable

Table 3
 Summary of gallium-bearing resources and extracting processes.
 Figueredo et al., 2002; Zhao et al., 2012; Gladyshev et al., 2015; Carvalho et al., 2012; Carvalho et al., 2000; Liu and Li, 2015; Abdulvaliyev et al., 2015; Klein et al., 1975; Zheng et al., 1996; Gutiérrez et al., 1997; Oriol et al., 2007; Liu et al., 2016; Kimoshita et al., 2011; Gu et al., 2014; Swain et al., 2015a,b; Lee and Nam, 1998; Lu et al., 2015; Xu et al., 2007, 2004).

Source	Resource	Sample/Ga content	Process/parameter	Results	Product/results	Applied scale
Al industry	Bayer liquor	163 ppm	As shown in Fig. 3		Gallium (99.99% purity)/recovery efficiency:46.47%	Commerce
	Red mud	25 ppm 570 ppm 33 ppm	As shown in Fig. 5 Bioleaching: PH = 1.9, 30 °C, 48 h, 150 r/min, 2% pulp density, 23.1 g/L biomass Acid leaching: 8 M HCl, L/S = 8, 95 °C, 5 h, 150 r/min As shown in Fig. 6		Concentrate/Containing 0.32% of Ga Solution/leaching efficiency: 54% Solution/leaching efficiency: 97.73% Solution/0.6 g/L Ga ₂ O ₃	Laboratory Laboratory Laboratory
Zn industry	Calcination dust	38 ppm	As shown in Fig. 6		Solution/leaching efficiency: 64–83%	Laboratory
	Electrolysis dust	0.071–0.125 wt% 0.22 wt%	Acid leaching:1 M H ₂ SO ₄ , L/S = 4, 90 °C Sintering: 200 °C, 2 h; acid leaching: HCl:1, solution, 110 °C, 5 h, L/S = 5; solvent extraction with PUF; purification; precipitation; calcination		Concentrate/containing 98.6% of Ga ₂ O ₃	Laboratory
Coal-fired power plant	Zinc residue	0.266 wt% 0.043 wt% 0.03 wt%	Pressure acid leaching: 150 °C,156 g/L H ₂ SO ₄ , L/S = 8.0.40 MPa, 20 g/L Ca(NO ₃) ₂ , 300 r/min,3 h Reductive leaching: sulfuric acid 56 g/L, P _{sox} 200 kPa, L/S = 7100 °C,2 h Acid leaching: 8 M HCl; absorbing: surfactant (PONPE) 0.10 wt%		Solution/leaching efficiency ≥ 98% Solution/leaching efficiency: 91% Solution/recovery efficiency ~ 100%, Enrichment ratio 3.2	Laboratory Laboratory Laboratory
	Coal fly ash	104 ppm	Roasting:500 °C, 10 h; Two-stage leaching: 2 M HCl, L/S = 6, 2 h, room temperature, particle size < 150 mesh Acid leaching: 6 M HCl, L/S = 5, 1 h, boiling temperature, dual solvent-extraction: Amberlite LA-2(5 vol%), LIX 54(10 vol%) Alkaline leaching: 25 °C, NaOH 0.7–1 M, L/S = 5, 6 h As shown in Fig. 8		Solution/leaching efficiency ≥ 95% Stripped solution/extracting efficiency:83%	Laboratory Laboratory
LED industry	LED industry dust	198 ppm (average) 12–230 ppm	As shown in Fig. 9		Solution/leaching efficiency: 60–86% Gallium (99.9%purity)/absorption efficiency ≥ 96%	Laboratory pilot
	GaAs new scraps	97.76 wt% 48.6 wt%	Acid leaching:2 M HNO ₃ , 60 °C, 2 h, L/S = 5, 500 r/min Vacuum metallurgy separation (VMS): 1100 °C,0.01–0.1 Pa,1 h		Solution/leaching efficiency: 73.68% Solution/leaching efficiency ≥ 99%	Laboratory Laboratory
P industry	Waste LEDs	2.077 ppm	Vacuum metallurgy separation (VMS): 1100 °C,0.01–0.1 Pa,1 h		Concentrate/recovery efficiency: 93.48%	Laboratory
	Phosphorus flue dust	0.053 wt%	Acid leaching: 20% H ₂ SO ₄ , 80 °C, L/S = 10		Solution/leaching efficiency:~100%	Laboratory

concentration. Simultaneous recoveries of other valuable metals from coal ash fly and red mud should also be considered during the Ga recycling process, which would make the technology even more economically feasible. Ga-rich electronic waste is an additional attractive Ga resource with a high content of Ga. New scrap containing GaAs is being successfully utilized, whereas substantial quantities of the old scrap and LED waste are still not utilized for Ga extraction. Efficient processing of the electronic waste requires further study. Other resources from the aforementioned industrial by-products for possible Ga recovery currently have little commercial significance due to uneconomical technology and insufficient quantity.

Finally, Ga-extraction processes from Ga-bearing resources can be mainly classified into two different types: hydrometallurgy and pyrometallurgy. The former is predominantly employed in most recovery cases. The review of chemical properties of Ga presented in Section 3 indicates that strong acid, concentrated alkali as well as high temperature are conducive for efficient extraction of Ga from Ga-bearing minerals. Thus, acid and alkali have been extensively employed as extractants to recover Ga from Ga-bearing resources in hydrometallurgical process by most of studies. The pyrometallurgy method, in most cases, was only employed as a means to pretreat a sample to obtain high extraction efficiency in the hydrometallurgical process. The primary disadvantage of the two processes is environmental pollution, which results from the treatment of hazardous materials during the extraction. Compared to these two processes, biohydrometallurgy is considered as an environmentally-friendly and cost effective method, and it should be further developed to extract Ga from the resources in future. Both time and effort are required for the microbial leaching of Ga from its relevant resource, to screen the appropriate microorganisms and improve the corresponding extraction efficiency.

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