AA33 - Effect of Vanadium Ion Impurity on the Adsorption of Gallium on Resin

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Abstract

Gallium is widely applied in solar energy, semiconductor, biology and chemical industry; it accounts for 80–85 % of the world's semiconductor applications. 95 % of the primary gallium originates from bauxite. Therefore, extracting and recovering gallium from bauxite has become a significant research topic. At present, gallium extraction is mainly carried out by resin adsorption method in industry. However, there are a large number of co-existing ions in the gallium-enriched solution, which can have an adverse effect on the process of gallium adsorption on the resin; such is especially the case of vanadium, which competes with gallium on the functional groups of the resin. Therefore, it is necessary to study the influence of vanadium on the gallium adsorption process.

Keywords: Bauxite, resin adsorption , gallium, vanadium

1. Introduction

Gallium has an important application in the semiconductor industry. With the development of new technologies and the demand for metal gallium in various applications, processes to efficiently and quickly produce gallium are in high demand. In recent years, China's compound wafer industry, mainly composed of gallium arsenide, has rapidly expanded and grown rapidly, resulting in a sharp increase in demand for gallium. At present, about 90 % of the world's gallium is recovered from the production process of alumina, while the remaining small amount of gallium is extracted from leaching zinc slag, iron slag, and fly ash. China is a major global alumina and aluminum producer; the weight percentage of gallium in the ore used for alumina production is about 0.007 %. Gallium exists in the spent Bayer liquor in the form of sodium galliate and continuously enriches, with an equilibrium concentration of up to 100–300 ppm [2–4]. Scholars have conducted in-depth research on how to enrich and purify gallium from the sodium aluminate liquor to obtain metallic gallium.

Ion exchange technology is an effective method for extracting gallium [5–7]. There are many known selective ion exchange resins, namely chelating resins, which have high capacity and selectivity compared to certain metals. Such resins have atoms such as O, N, S, P, As with lone pair electrons. The lone pair electrons of these atoms form coordinate covalent bonds with metal ions [8], forming a stable structure similar to a small molecule chelation. This has the advantages of large adsorption capacity, strong selectivity and stable properties. Therefore, the application of ion-exchange resins may enable the selective extraction of gallium ions from process liquors and the subsequent production of metallic gallium.

2. Mechanism of Resin Adsorption of Gallium

The extraction of gallium from the sodium aluminate liquor using a resin mainly relies on the active functional groups present in the resin structure, such as=NOH, NH, - OH, - SH,=NH, and so on. Because the atoms in these active functional groups have unbound lone pairs of electrons, they can form coordinate covalent bonds with gallium ions, generating stable structures similar to small molecular complexes, and realize the adsorption of gallium by resins. Currently, there are is a mainstream mechanism for the binding of gallium ions on the resin: Gallium ion generally exists in the form of Ga $(OH)^{4-}$ in an alkaline solution. When Ga $(OH)^{4-}$ is adsorbed by the resin, H^+ on the hydroxyl group of=N-OH is released, and then the remaining oxygen atom forms a coordinate covalent bond with gallium. However, there may be no coordination reaction between Ga and N. At the same time, the released H^+ will combine with an OH^- from Ga $(OH)^{4-}$ to generate H_2O. Therefore, it can be considered that the oxygen binding mode may be the main mode of binding between resin and gallium ions in solution [9–12]. The possible reaction between =N-OH and Ga $(OH)^{4-}$ in amidoxime is shown in the following equation:

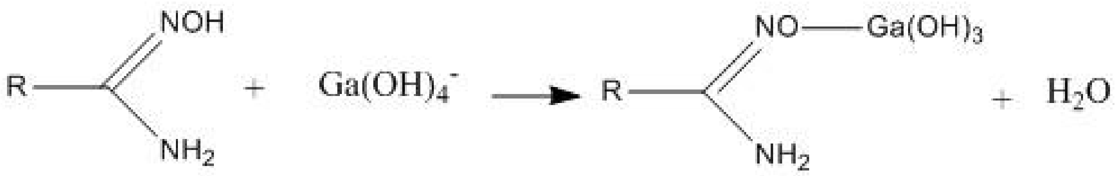

Figure 1. Resin adsorption of gallium

3. Effect of Vanadium on Resin Adsorption of Gallium

3.1 Mechanism of Resin Adsorption of Vanadium

Due to the presence of a large amount of impurities in sodium aluminate solution, this will inevitably have a negative impact on the process of gallium adsorption by resin, especially with the case of vanadium ion. Zheng Qi [3] conducted FT-IR and XPS analysis on the resin and found that there was a cross adsorption of gallium and vanadium on the resin. Gallium ion in alkaline solutions only interact with the oxime group in the resin, while vanadium ion react with the oxygen atoms of the oxime group (C=NOH) in the resin and the nitrogen atoms of the amino group ($C-NH_2$), which leads to a stronger interaction force between vanadium ion and the resin, which in turn makes it difficult for vanadium ion to desorb from the resin. Therefore, gallium and vanadium form competitive adsorption, and the adsorption of vanadium by the resin will reduce the adsorption capacity of the resin for gallium. Vanadium ion mainly exist in the form of VO_4^{3-} in strong alkaline solutions [13–14], so the possible reaction formula between vanadium ions and effective groups in the resin is as follows:

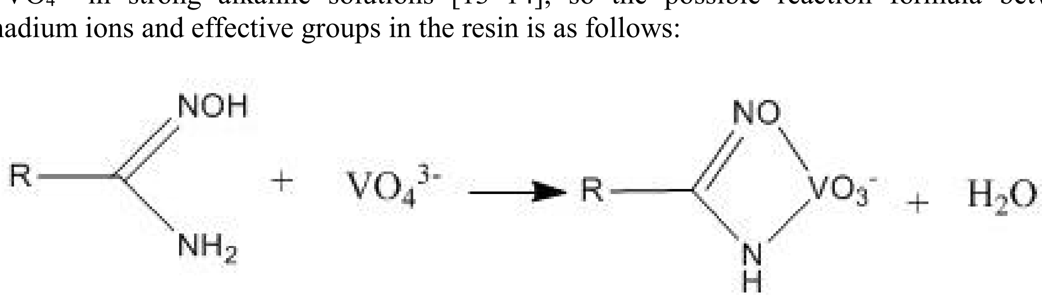

Figure 2. Resin adsorption of vanadium

In addition, as the concentration of vanadium increases, the resin changes from light yellow to dark brown. Due to the resin adsorbing gallium, a considerable amount of vanadium is also adsorbed and difficult to desorb. As a result, vanadium gradually accumulates in the resin during cycling and occupies the corresponding functional positions in the resin, reducing the resin's cyclic adsorption capacity for gallium and shortening its service life. In conclusion, the accumulation of vanadium can lead to serious operational problems such as frequent resin replacement.

3.2 Resin Adsorption Data

Experiment process: 2 g resin was weighed into a conical flask with a stopper, measured 50 mL of sodium aluminate liquor prepared in advance containing a certain amount of gallium ion and vanadium (NaOH=160 g/L), which was oscillated and adsorbed at 40 °C for 2 hours, and then wash the resin with ice water until it is weakly alkaline; During desorption, 50 mL of prepared dilute sulfuric acid with a certain concentration needs to be added to the weakly alkaline resin. After shaking for desorption at room temperature for half an hour, the solution was analyzed using ICP.

Table 1. Adsorption and desorption of Ga and V by resin (NaOH=160 g/L).

ion	Starting solution concentration (g/L)	Final solution concentration (g/L)	Eluent solution Concentration (g/L)	Adsorption rate (%)	Desorption rate (%)
Ga	0.17	0.022	0.15	87.06	100
	0.17	0.018	0.15	89.41	98.68
	0.17	0.025	0.22	85.29	100
V	0.67	0.48	<0.0005	28.36	0
	0.32	0.24	0.0005	25.00	0.63
	0.21	0.17	<0.0005	19.05	0

Table 1 shows that when the concentration of Ga ion is constant, the adsorption rate of Ga has almost no effect, and the adsorption rate of V ion gradually decreases with the increase of V ion concentration; Secondly, When desorbing in a dilute acid solution, Ga is almost completely desorbed, while V is not desorbed, meaning that V ion continue to occupy the effective functional groups of the resin. It can be speculated that as the number of cycles increases, V will accumulate more on the resin, which has a significant impact on the resin until it will need replacement.

Under the same conditions, sodium aluminate liquor with higher alkali concentration (NaOH = 220 g/L) was prepared, and the above adsorption and desorption processes were carried out. The results are shown in Table 2:

Table 2. Adsorption and desorption of Ga and V by resin (NaOH = 220 g/L).

ion	Starting solution concentration (g/L)	Final solution concentration (g/L)	Eluent solution Concentration (g/L)	Adsorption rate (%)	Desorption rate (%)
Ga	0.19	0.025	0.17	86.84	100
	0.23	0.030	0.20	86.96	100
	0.31	0.038	0.27	87.77	99.26
V	0.24	0.21	<0.0005	12.5	0
	0.30	0.26	<0.0005	13.3	0
	0.40	0.35	<0.0005	12.5	0

From Tables 1 and 2, it can be seen that when the alkali concentration increases, the adsorption and desorption rates of Ga remain almost unchanged, while V ions adsorption decreases.

Therefore, it can be inferred that high concentration of alkalis has an inhibitory effect on the adsorption behavior of vanadium ions on the resin.

4. Discussion on Reducing the Adsorption of Gallium on Resin by Vanadium

4.1 The Effect of Vanadium on the Adsorption of Gallium by Resin

The type of effective functional groups in the resin is an important factor determining the adsorption performance of the resin for gallium. Due to the presence of unbonded lone pair electrons in the =NOH and - NH_2 groups, they can form coordination bonds with gallium ions that lose their outermost electrons and have empty orbitals, forming a stable structure similar to a complex, achieving the adsorption of gallium by the resin. Therefore, strong alkaline resins containing =NOH and - NH_2 groups are ideal resins for gallium adsorption.

The adsorption of Ga is only related to the oxygen atoms of the amidoxime group (C=NOH), while the adsorption of V is related to both nitrogen and oxygen atoms of the amidoxime group, including C=NOH and C-NH_2. Due to the adsorption mechanism of Ga and V both are related to the C=NOH, there is a competitive adsorption onto C=NOH between Ga and V. The existence of V on resin would decrease the adsorption capacity of Ga. Furthermore, because of the strong chemical bond binding force between V and the resin, it is also difficult for vanadium to be desorbed from the resin.

In addition, with the development of research, we have found that: the adsorption capacity of V increased quickly in the low vanadium concentration and was kept unchanged at higher initial concentrations. At lower concentrations of metal ions, the sensitivity of this adsorption indicates that adsorption is mainly influenced by the electrostatic attraction (physical adsorption) [15]. Therefore, in addition to the role of two chemical bonds, electrostatic attraction should play an important role. Furthermore, due to the small impact of initial concentration changes on the adsorption of Ga, it is considered that adsorption mainly relies on chemical adsorption.
The positive values of enthalpy changes（ΔH）indicated that the adsorption process was an endothermic process. The adsorption heat of physical adsorption generally does not exceed a maximum of 40 kJ/mol, while the adsorption heat of chemical adsorption process is greater than that of physical adsorption process. The ΔH values of Ga and V are 47.74 and 16.69 kJ/mol, respectively, which confirms that the adsorption process of Ga may be chemical adsorption, while V may be mainly affected by physical adsorption [10].

In summary, it can be seen that the presence of vanadium does have an impact on the adsorption of gallium. The reason for this phenomenon is due to the competitive adsorption of two ions on the resin. In addition, vanadium have both physical and chemical binding forces, resulting in vanadium occupying the effective groups of the resin and making it difficult to dissociate. As the number of cycles increases, the effective groups of the resin gradually decrease, causing adverse effects on the resin [13].

4.2 Reducing the Impact of Vanadium

In the process of optimizing resin extraction of gallium, in order to achieve the optimal adsorption capacity of gallium, it is necessary to control the process conditions in favor of gallium adsorption while minimizing the adsorption of vanadium. One is source control, which directly adds a remover to the solution to remove vanadium metal; The second is to reduce the resin's adsorption of vanadium by controlling the conditions during the process of resin adsorption of gallium; The third is that during the cyclic production process, due to the gradual accumulation of vanadium ions on the resin, the resin is regularly "purified" to remove vanadium, restoring the effective group positions on the resin.

When discussing the mechanism, it was found that the adsorption capacity of V rapidly increases at low concentrations, while the change of Ga is not significant; At higher concentrations, the adsorption rate of Ga is much faster than that of V. Therefore, within a short period of contact between the solution and the resin, most of Ga ions are adsorbed on the resin, while the adsorption amount of V is much smaller. As time goes on, the adsorption capacity of V ions will gradually increase, which will greatly hinder the resin's adsorption of gallium. It can be inferred that the shorter the contact time, the more favorable it is for the resin to adsorb gallium. Therefore, during the dynamic adsorption process of the resin, a certain range of high spent Bayer liquor flow rate and short contact time are beneficial for the adsorption of Ga.
In the previous chapters, it is known that the adsorption of gallium and vanadium by resin is an endothermic process, and an increase in temperature is beneficial for the adsorption of gallium and vanadium. The adsorption rate of Ga ion varies slightly with temperature changes, while V ions are sensitive to temperature changes, and the adsorption rate of V ion increases with temperature, which may be related to their chemical properties [3]. Therefore, by adjusting the temperature within a lower range, the adsorption of vanadium by the resin can be reduced.

In addition, during the desorption process, Ga ions are almost completely desorbed in acidic solutions, while V ions are hardly desorbed. Therefore, acidic desorption solution is used to reduce the desorption of vanadium and achieve the separation of the two metals; Secondly, it can be seen from the test data that V ions are more sensitive to the change of alkali concentration, showing the opposite trend when the concentration of sodium hydroxide changes, and the adsorption capacity decreases with the increase of alkali concentration, but the change of alkali concentration has little effect on Ga ion, which indicates that the resin can be washed regularly with concentrated alkali solution to reduce the accumulation of vanadium, however the strongly alkaline desorption solution cannot make V ion completely desorbed, and it may only achieve the purpose of extending the service life of the resin.

5. Conclusions

The strong alkaline conditions in the alumina production process and the complexity of solution composition make the resin adsorption of gallium susceptible to impurities. This article discusses why the resin adsorbs vanadium ions and how to reduce the impact of vanadium ions. Resin adsorption is a complex physical and chemical process, which requires comprehensive consideration of various influencing factors to guide the actual production process. Further in-depth research is needed in the future.

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