Gallium Extraction from Extracting Vanadium Tailing Slag

Mantang Ding *

School of Vanadium and Titanium, Pan Zhi Hua University, Panzhihua, Sichuan, China

* Corresponding author e-mail: dmtpglgc@126.com

Abstract. The gallium contained in extracting vanadium tailing slag was 0.014%. It is typical of the rich gallium raw materials. The various methods that it extracted gallium from extracting vanadium tailing slag were compared and discussed. The effective dissociation of gallium from the complex structure of aluminosilicate of gallium is the key of extracting gallium from extracting vanadium tailing slag. And the future development was prospected. The future development direction was high-temperature alkaline roasting- high temperature pressurized alkaline leaching- alkaline extraction (or resin adsorption)-electrolytic extracting gallium.

Key words: extracting vanadium tailing slag, gallium extraction, vanadium-titanium magnetite ore, high-temperature alkaline roasting, high temperature pressurized alkaline leaching, alkaline extraction.

1. Introduction
Gallium is widely used in communications, fiber optics, computers, satellites, high-speed signal and image processing, vehicle positioning, automotive driverless, energy-efficient lighting, solar cells and other modern high-tech fields and biomedical fields, and so on. Semiconductor materials that it was compounded by high-purity gallium and some metal and non-metal have become the new technology support materials required by the departments of modern telecommunications, electronic computers, aerospace, energy and health. It have the reputation of "the pillar of the electronics industry." In recent years, the use of gallium has been continuously expanded, and the demand for gallium has also increased also with the rapid development of science and technology and the improvement of people's living and health. Gallium is a rare metal. There is no independent mineralization in nature. It is often found in bauxite, sphalerite, coal and other minerals in the form of isomorphism. The gallium required for industry is extracted from various industrial by-products containing gallium.

A large amount of gallium is present in the vanadium-titanium magnetite in Panxi. The gallium contained in vanadium-titanium magnetite Panzhihua was 0.0014%-0.0028%. An average of it was 0.0019%. The total reserves are 92,400 tons. It was 41%-42% of the world's reserves. It was 54%-55% of domestic metal gallium reserves. Extracting vanadium tailing slag was produced from vanadium-titanium magnetite was smelted and extracted vanadium. It contain of valuable metal elements of iron, chromium, vanadium, titanium, gallium, etc. The content of gallium is 0.014%, which is much higher than the requirement of 30g/t of the gallium industrial grade[1]. The composition of extracting vanadium tailing slag from Panzhihua was shown in Table 1.
Table 1. Extracting vanadium tailing slag composition (%)

| composition          | Ga    | SiO₂ | CaO  | MgO  | Al₂O₃ | TiO₂ | TFe  | V₂O₅ | MnO  | Cr   | Na₂O |
|----------------------|-------|------|------|------|-------|------|------|------|------|------|------|
| extracting vanadium  | 0.014 | 12.5 | 1    | 2    | 2.6   | 4.2  | 40   | 2.4  | 5    | 1    | 2.8  |
| tailing slag         |       |      |      |      |       |      |      |      |      |      |      |

2. Present situation
So far, industrial applications for extracting gallium from extracting vanadium tailing slag have not yet been realized. The ways that gallium was extracted from extracting vanadium tailing slag in laboratory has more. It have mainly chlorination volatilization method, acid leaching method, pressing-leaching method, reduction electrolytic acid hydrolysis and roasting method, etc.

2.1. Chlorination volatilization method
The chlorination volatilization method is based on the principle that the boiling point of gallium chloride is low. It used chlorination metallurgy. Ga is converted into GaCl₃ by NaCl doping and calcined into soot for enrichment recovery. The chlorination method is calcined at 900 °C. NaCl and carbon powder are 20% and 5% respectively. The chlorinating agent causes Ga₂O₃ to form low-boiling GaCl₃ into the soot and most of the iron remains in the slag. The slag iron separation is realized, and the gallium extraction rate is 46% [2]. The HCl corroded equipment produced in the production of chlorination reduction volatilization is severe, so the chlorinating agent added should not be excessive. Gallium is entrapped by other impurities in the tailing slag. Too little chlorinating agent is difficult to effectively destroy the crystal structure, so that gallium is exposed to participate in the chlorination reaction to obtain enrichment and purification is difficult. Increasing the chlorination temperature will increase the chlorination effect, but it will increase energy consumption and equipment corrosion. Therefore, it is necessary to solve the problem of equipment corrosion and energy consumption.

2.2. Press-dip method
Gallium oxide is an amphoteric oxide that could reacts with a base and is enriched in solution. At present, gallium resources was recovered from alumina red mud is widely used. The extracting vanadium residue was added to the alkali solution by a boil-leach method, and the leaching rate of gallium was only 13.5% at 270 °C for 2 h. The problem that gallium was separated from iron is not ideal, and the cost of it is high[3].

The reason why the gallium recovery rate is not high in the process of recovering gallium from the extracting vanadium residue by the boiling-leaching method may be that the gallium in the immersion liquid reacts with other elemental substances to form a precipitate which is lost along with the filter residue. For example, gallium is very close to aluminum, and the SiO₂ in the vanadium residue is high, so that the Na₂O₃·Ga₂O₃·xSiO₂·nH₂O precipitate that could be formed was lost together with the filter residue.

2.3. Smelting reduction method
The smelting reduction method is abbreviated as the SR method. The mixture that extracting vanadium tailing slag is mixed with carbon was heated to 1600 °C to obtain an iron gallium alloy, and then gallium is recovered from the anode mud by electrolysis. The process also has the problems of long process flow, high cost, low gallium recovery rate, and gallium recovery rate of only 64.9%[4].

2.4. Reduction smelting-iron electrolysis-acid hydrolysis–extraction
The extracting vanadium tailing slag are used as raw materials, and carbon powder is added for reduction smelting and iron electrolysis. The iron in the tail slag is first extracted into electrolytic iron; then the anode mud is subjected to acid hydrolysis, extraction and electrolysis of gallium to produce metal gallium and electrolytic iron products. The acid solution was 6 mol/l hydrochloric acid, and the liquid-
solid ratio was 3:1, and the leach was at 95 °C for 2 h. Extraction was with TBP. Gallium recovery rate after electrolysis is 64.9% [5-6]. The problem is that the process route is long, the cost is high, and the gallium recovery rate is not high.

2.5. Acid leaching
Gallium oxide is an amphoteric oxide, it can react with an acid to allow it to enter the solution for enrichment. The acid leaching method is to mix the vanadium residue with 2 mol/L sulfuric acid with a liquid-solid ratio of 6:1, and leaching at 80 °C for 2 h, and the leaching rate of the gallium gets to 80% [7]. H₂SO₄ can react with the main phases such as iron oxide and silicate in the vanadium residue, destroy the crystal structure of the gallium-containing phase, and effectively transfer the gallium into the solution to obtain enrichment. However, the content of SiO₂ in the extracting vanadium residue is too high. In the process of sulfuric acid leaching and filtration, silicate condensed into a gel make filtering and separating difficult. Moreover, a large amount of ferrous ions in the filtrate causes subsequent gallium extraction difficulties. The process also has environmental problems that make it difficult to discharge acid leaching waste liquid.

2.6. Alkali leaching
Alkali leaching method uses vanadium slag as raw material, and the leaching rate of gallium is high, which can avoid the problem of difficult separation of iron and gallium, but it will cause difficulties in subsequent vanadium extraction [1-3]. The method is divided into two processes, one is direct alkali leaching of vanadium slag, and the other is leaching of vanadium slag after calcification and sodium roasting. The vanadium slag is directly alkali leached, and V, Cr and Ga can be leached, and Fe is not leached, which omits the difficulty of Fe separation. However, there is a problem that the V and Cr leaching rates are high and the Ga leaching rate is low. If the vanadium slag: CaO:Na₂O₂ is 100:120:40, the calcium-alkali combined roasting and dilute alkali leaching process can make the leaching rate of V and Cr>90%, and the Ga leaching rate>85%. Ga is then extracted from the leachate by electrolysis or sodium humate flocculation. The method is technically feasible, but the amount of alkali used is large and uneconomical. This method is not applicable to the traditional vanadium slag sodiumation extraction process, and can be considered in the vanadium slag calcification extraction process.

2.7. Roasting method
In the roasting method, the vanadium residue is mixed with lime and soda ash at a ratio of 1:0.4:0.4, it was roasted at 700-1100 °C for 2 h, and then it was leached with 100 g/L of alkali solution for 1 h. Extracting gallium rate was up to 55% [7].

3. Discussion and analysis
At present, the main reason that the effect of gallium extraction of from vanadium tailing slag is not high have: (1) The gallium in the vanadium tailing slag is present in the crystal where aluminosilicate, iron oxide and gallium formed a complex crystal structure. The entire crystal structure must be completely destroyed, and the gallium can be dissociated from it. (2) The content of SiO₂ in the extracting vanadium tailing slag is high. It will produce a large amount of silicate gel during the leaching and filtering process of the acid leaching process; so that it is difficult to be filtered, the leaching rate of gallium is low. (3) There is a large amount of iron in the extracting vanadium tailing slag, which causes the presence of a large amount of iron ions in the leachate, affecting the extraction process, and the extraction rate of Ga is not high.

4. Solution ideas and prospects
The future development direction must be the process of economy, low consumption, and green extraction gallium. It must to be been avoided that the waste of gallium resources in the extracting vanadium residue, and at the same time green environmental protection and comprehensive utilization will achieve. The specific development direction is: extracting vanadium residue - high temperature
alkaline roasting - high temperature pressure leaching - alkaline extraction (or resin adsorption) - electrolysis - metal gallium.

First, the vanadium residue is added with an alkali metal salt for high-temperature roasting to destroy the complex structure of the gallium aluminosilicate, so that the gallium is sufficiently dissociated. Secondly, the calcined product is subjected to pressurized alkali leaching to remove iron, and V, Cr and Ga simultaneously enter the alkali solution. Then, the extract is subjected to alkaline extraction or ion exchange to extract gallium. Finally, vanadium and chromium are separately recovered from the leaching residue.

5. Conclusion
The key that gallium was extracted from vanadium residues is to destroy the complex structure of gallium aluminosilicate, so that gallium is fully dissociated from it.

At present, the main methods for extracting gallium from vanadium tailing slag have: chlorination volatilization method, smelting reduction method, acid leaching method, pressurized hot leaching method, reduction electrolytic acid hydrolysis method, alkali leaching method and roasting method, etc.

The future development direction of gallium extraction from vanadium residue is: vanadium residue - high temperature alkaline roasting - high temperature pressurized alkaline leaching - alkaline extraction (or resin adsorption) - electrolysis - metal gallium.

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