Utilization of Vanadium Extraction from Vanadium-bearing Steel Slag

Mantang Ding
School of Vanadium and Titanium, Pan Zhi Hua University, Panzhihua, Sichuan, China
dmtpglgc@126.com

Abstract. Vanadium extraction from vanadium-containing steel slag mainly includes fire method and wet method. The advantages and disadvantages of various ways of vanadium extraction from vanadium-containing steel slag are discussed and analyzed. The prospects and suggestions for future development were put forward. It is proposed that the submerged arc furnace carbothermal reduction method, the sub-molten salt method, the production of vanadium alloys, calcification roasting-acid leaching, and two-part acidification to extract vanadium are the future development directions.

Keywords: vanadium-bearing steel slag; utilization of vanadium extraction; carbothermal reduction method; sub-molten salt method; production of vanadium alloys; vanadium extraction by acidification; single slag return method.

1. Preface
Vanadium-titanium magnetite becomes vanadium-titanium magnetite concentrate by magnetic separation. Vanadium-titanium magnetite concentrate is converted into vanadium-containing molten iron by sintering, pelletizing process, blast furnace smelting or electric furnace reduction and melting. After the vanadium-containing molten iron was passed through the steelmaking process, vanadium enters the steel slag and becomes vanadium-containing steel slag. The main components of vanadium-containing steel slag are shown in Table 1 [1].

Table 1. Main components of vanadium-containing steel slag

| project | CaO | SiO₂ | MgO | Al₂O₃ | MnO | V₂O₅ | FeO | P   | S   |
|---------|-----|------|-----|-------|-----|------|-----|-----|-----|
| composition % | 40.48 | 11.27 | 8.32 | 4.52  | 2.72 | 3.94 | 21.06 | 0.546 | 0.244|

2. Development and utilization of vanadium extraction

2.1. High temperature metallurgy utilization

2.1.1. Single slag return method. Single slag return method is also called vanadium-containing steel slag return method for vanadium extraction. It is that the vanadium-containing steel slag is added as a
flux to the sintering process and then sent to the blast furnace for smelting to enrich vanadium into the vanadium-containing iron water. Finally, the process of extracting vanadium from vanadium-containing iron water is carried out.

The vanadium-containing steel slag contains high free calcium oxide content. Its reducibility was good. It can improve the quality of sinter, and improve the melting characteristics of sinter. Technical and economic indicators such as the qualification rate of sinter and the first-class product rate have been significantly improved. The recovery rate of vanadium was above 80%. This method can simultaneously recover calcium, vanadium, iron and other valuable elements in vanadium-containing steel slag. It could reduce the cost of sintering and ironmaking with obvious effect [2-4]. Currently, it was industrialized application.

But the shortcomings of it are also obvious. When the number of returns is too much, it will cause the enrichment of phosphorus in the molten iron, and increase the converter dephosphorization slagging smelting cost.

2.1.2. Ore-Heat furnace carbothermal reduction method. This method uses a submerged arc furnace for high temperature reduction smelting of vanadium-containing steel slag. By controlling the reducing atmosphere in the furnace, the vanadium in the vanadium-containing steel slag is reduced and enriched into molten iron to obtain high-vanadium pig iron. Then it use the existing converter vanadium extraction and vanadium slag processing technology to extract and produce vanadium products. It could realize the effective extraction and comprehensive recovery of vanadium resources. Panzhihua Iron and Steel uses vanadium-containing steel slag containing 1.6% to 4% V₂O₅ to produce high-vanadium pig iron containing 3% to 10% V through submerged arc furnace smelting. The reduced slag smelted in the submerged arc furnace can be used as white cement or steel slag cement clinker after composition adjustment, etc., and can also be used as a raw material for continuous casting mold slag, which has a wide range of uses. The vanadium content of reduced vanadium-containing molten iron is 20-30 times higher than that of conventional vanadium-containing molten iron. The V₂O₅ grade of vanadium slag produced by reducing high-vanadium-containing molten iron can reach an average of 46%. It is a high-quality raw material for vanadium extraction. The V₂O₅ grade of vanadium slag produced by ordinary vanadium-containing molten iron is only 16-20% [1, 5-6].

2.1.3. Production of vanadium alloys. The shaft furnace is mainly used of vanadium-containing steel slag and the pellets with some vanadium-titania magnetite. Its were solidified and dried, and then supplied to the submerged arc furnace to produce high-vanadium pig iron. Then, a one-step process of top oxygen blowing and bottom argon blowing in the AOD refining furnace is used to oxidize and extract vanadium and obtain a low vanadium alloy containing 0.3 to 0.8% V. The vanadium slag produced was then smelted with a tilting electric furnace to obtain FeV25Si7 with V content of 20-25%, 25-30%, and 30-35%, and other silicon-vanadium alloys [7-8].

2.2. Extraction of vanadium by water method

2.2.1. Sodium extraction vanadium. Using table salt or soda as additives, first it was sodiumization roasted, and then water leached or carbonated to extract vanadium. The process has large sodium salt consumption, high roasting temperature, low vanadium leaching rate, difficult equipment forwarding, and the roasting process pollutes the environment. It was failed to be industrialized [6, 9]. The leaching residue has high sodium content and can not be used comprehensively.

2.2.2. Vanadium extraction by calcification. It uses lime as additives for high-temperature roasting, and uses carbonation or sulfation to extract vanadium [9]. The leaching residue does not contain sodium salt, which is conducive to comprehensive utilization. Hydrolyzed vanadium precipitation products contain 88～94% V₂O₅. Due to the difficulty of phosphorus removal, calcification roasting to extract vanadium is not suitable for high phosphorus vanadium steel slag. Therefore, there is a certain degree of selectivity
for materials. For general steel slag, there are problems such as low conversion rate, large acid consumption, and high cost. It is currently in the laboratory research stage.

2.2.3. Vanadium extraction by acidification. Directly leaching vanadium-containing steel slag with sulfuric acid, the vanadium leaching rate can reach 94% [10]. Extraction or ion exchange is used to separate vanadium from most of the impurities in the leachate to partially replace the purification process. Follow the extracting liquid or the ion exchange liquid was vanadium precipitated and roasted to extract vanadium. The acidic extractants commonly used in this method include N235 and TBP sulfonated kerosene system, P507, P204, etc. This method uses a large amount of acid, and the waste liquid cannot be processed. It was failed to carry out large-scale use, just stay in the experimental stage.

2.2.4. Phosphate decreased calcium and sodium roasting. In order to solve the problem that the high CaO in the vanadium-containing steel slag causes the difficulty of leaching vanadium. Decreasing Calcium roasting is to mix steel slag with Na3PO4 and Na2CO3 to roast at high temperature. Na3PO4 combines with CaO to form Ca3(PO4)2. Vanadium and sodium produce water-soluble Na3VO4. Then the vanadium can be dissolved out by leaching in water. The method only stays in the laboratory research stage, and the proportion of phosphate is large, and the cost is high [13].

2.2.5. Extraction of vanadium by two-step acidification. The two-step acidification method is used to extract vanadium. The raw materials are pretreated first, and then the calcium is removed and reduced by acidification to reduce the ratio of calcium to vanadium. Finally, vanadium is leached by acid. The leaching rate of vanadium is about 85% [14, 15].

2.2.6. Sub-molten salt method. Extraction of vanadium from vanadium-containing steel slag by sub-molten salt method is to use KOH or NaOH sub-molten salt to treat vanadium-containing steel slag, so that vanadium is directly leached into the solution. When the temperature is 240 °C and the ratio of alkali to slag is 4:1, the dissolution rate of vanadium can reach more than 90%, which opens up a new way for the vanadium extraction process from vanadium-containing steel slag. However, in view of the difficulty of separating low-concentration vanadium-containing solutions under high alkalinity, the residue after treatment contains higher Ca(OH)2, higher potassium and sodium content, the processing is more difficult. And because vanadium-containing steel slag contains lower vanadium content, which make the raw material cost higher [16, 17].

3. Prospects and recommendations
The following important principles must be considered in the extraction and comprehensive utilization of vanadium-containing steel slag: (1) The separation efficiency of vanadium is high; (2) It does not produce cyclic enrichment of harmful elements; (3) The equipment has high production capacity and large processing capacity; (4) It has minimizes secondary pollution and meets the requirements of environmental protection and sustainable development; (4) It has economic and overall cost-effective.

From the above analysis, we can see: (1) The single slag return method can comprehensively recycle resources such as vanadium and calcium oxide in vanadium-containing steel slag to achieve the goal of comprehensive recycling. However, too many returns will cause phosphorus enrichment and increase the difficulty and cost of steelmaking operations; therefore, the number of returns should not be too many. (2) The carbothermic reduction method has a high efficiency in the recovery of vanadium. And the residue can also be used to produce cement. Which is beneficial to the comprehensive recovery and utilization of vanadium-containing steel slag. But the problem of excessive energy consumption needs to be solved. (3) The method of combining submerged arc furnace and AOD furnace to produce alloy is beneficial to the recovery of vanadium, but the economics need to be verified. The process of recycling vanadium-containing steel slag by fire method is generally feasible, but the problem of excessive energy consumption needs to be solved. (4) The wet process includes roasting, leaching, purification and vanadium precipitation to obtain vanadium salt. The key link is roasting and leaching. Basically,
environmental pollution and ammonia nitrogen wastewater treatment problems exist in the treatment of residual liquid, and the cost is relatively high. (5) Sodium salt roasting will cause environmental pollution, and the one-way recovery rate is not high, so it has been eliminated. (6) The process of lime roasting and acid leaching to extract vanadium has the advantages of high vanadium yield and low cost. (7) The clean vanadium extraction technology by sub-molten salt method can achieve high-efficiency dissolution of vanadium and chromium at low temperatures, with high vanadium recovery rate and clean process. It is a new process for processing vanadium and chromium-containing resources. Large-scale production still needs further study. (8) Direct leaching in two-step sulfuric acid method would remove calcium first, and then extract vanadium. Which can achieve high-efficiency leaching of vanadium and chromium at low temperature. Sulfuric acid method could make use of hydrolyze waste acid of titanium dioxide for leaching. Which can turn waste into treasure and treat waste acid ,also obtained vanadium chromium products.

Based on the above analysis, the future development prospects and suggestions are as follows: (1) In the use of vanadium-containing steel slag by fire method, the development of single slag return method, carbothermic reduction method, and alloy production method should be emphasized, but the reduction temperature and reduction energy consumption should be applied to improve economy. (2) In the wet utilization of vanadium-containing steel slag, the lime roasting-acid leaching method, the sulfuric acid two-step leaching method, and the sub-molten salt method should be developed first, but the vanadium recovery rate should be increased, the waste liquid treatment cost should be reduced, and the environmental pollution should be reduced.

4. Conclusion
The return method of vanadium-containing steel slag can achieve the purpose of comprehensive utilization of vanadium-containing steel slag, but the number of returns should be limited to prevent phosphorus enrichment.

In the utilization process of vanadium-containing steel slag carbothermic reduction method and production alloy method, the purpose of comprehensive utilization can be achieved, but energy consumption should be reduced and economic efficiency should be improved.

In the wet utilization of vanadium-containing steel slag, lime roasting-acid leaching method, sulfuric acid two-step leaching method, and sub-molten salt method can achieve the purpose of recovering vanadium; however, all resources in vanadium-containing steel slag cannot be fully recovered, and vanadium recovery rate should be improved. Moreover all should reduce waste liquid treatment costs and reduce environmental pollution.

References
[1] S.B.Yang, Z.Z. Luo, Y.C.Wen. et al. Vanadium Recovery from BOF Slag Containing Vanadium Oxide [J] Iron and Steel, 2005, 40(5): 72-75.
[2] D.J.Shi. Practice of Vanadium Concentration in Blast Furnace [J] Iron and Steel, 1989, 24(10): 6-10.
[3] B.Z.Ni. Vanadium-Bearing Steel Slag Returned to 28M3 Blast Furnace for Smelting High-Vanadium Pig Iron [J] Iron Steel Vanadium Titanium, 1983, (2): 45-49.
[4] Z.L.Luo. Return of vanadium-containing steel slag to sintering to produce high-vanadium sinter [J] Iron Steel Vanadium Titanium, 1983, (1): 43-47.
[5] Y.H.Cai, B.Y. Li, C.M.Zhao, et al. Study on Separation of Vanadium Slag , Phosphorus and Vanadium by Carbon Thermal Reduction [J]. Multipurpose Utilization of Mineral Resources, 2018, (6): 106-110.
[6] Z.B.Fu. Development Process and Trends of Vanadium Extraction from Vanadium-Titanium Magnetite Ore [J] China Metallurgical, 2011, (6): 29-33.
[7] T.Yu, Z.Y.Jiang, Q.C.Li, et al. Process Exploration on Producing Vanadium Alloys from BOF Slags [J] Industrial Furnace, 2019, 41(5): 62-64.
[8] T.Yu, Q.C.Li, X.Y.Ning. New Process of Smelting Vanadium Alloys from Vanadium -Bearing
Bof Slags [J] Ferro-Alloys, 2019. (5):8-10

[9] F.Z.Chang, B.B.Zhao, L.J.Li, et al. Research Status and Prospect of Vanadium Extraction from Vanadium Titanium magnetite [J] Iron Steel Vanadium Titanium, 2018. 39(5): 71-78.

[10] G.H.Ye, W.He, L,Lu, et al. Direct Leaching of Vanadium from V-Bearing Steel Slag with Sulfuric Acid under Normal Temperature and Pressure [J]. Chinese Journal of Rare Metals, 2013.37(5): 807-813.

[11] L.H. Xue. Experimental research on extracting vanadium from acid leaching solution of vanadium-containing steel slag [D] Kunming: Kunming University of Science and Technology, 2008.

[12] M.L.Gao, X. Zhou, H.X.Wang, et al. Selective pretreatment and vanadium extraction of vanadium-bearing steel slag [J] The Chinese Journal of Nonferrous Metals, 2019. 29(11): 2635-2644.

[13] M. C. Amiri. Recovery of vanadium as sodium vanadate from converter slag generated at Isfahan steel plant, Iran Transinsten [J] Mineral Processing & Extractive Metallurgy Imm Transactions, 1999, 108: 113-114.

[14] H.Zhang, G.H.Ye, L.Lu, et al. Thermodynamic Study on Sulfuric Acid Leaching for Vanadium Extraction from V-bearing Steel Slag [J] Iron Steel Vanadium Titanium, 2020, 41(1): 1-6.

[15] Y.Xie, G.H.Ye, Q.Zuo, et al. New Technology of Vanadium Extraction from Vanadium-bearing Steel Slag [J] Iron Steel Vanadium Titanium, 2019, 40(1): 69-77.

[16] M.L. Gao, D.H.Chen, L.J.Li, et al. Dissolution Behavior of Vanadium from Vanadium-bearing Steel Slag in KOH Sub-molten Salt [J]. The Chinese Journal of Process Engineering, 2011, 11(5): 761-766.

[17] M.L.Gao, D.H.Cheng, L.J.Li, et al. Process and Mechanism of Leaching Vanadium from Vanadium-bearing Steel Slag with Sub-molten Salt [J]. The Chinese Journal of Process Engineering, 2013, 13(6):984-986.