UDC: 669.624

AN INNOVATIVE METHOD FOR PROCESSING OF USED VANADIUM CATALYSTS FOR OBTAINING VANADIUM PENTOXIDE

Turobov Shahriddin Nasritdinovich,
Assistant of the Department of Metallurgy,
Navoi State Mining Institute

Hasanov Abdirashid Salievich,
Doctor of Technical Sciences, Professor,
Deputy Chief Engineer for Science, AMMC

Abstract. *All in all, there are about 60 million vanadium deposits in the world, 90% of which are localized in the territory of the five countries: Russia, South Africa, Venezuela, the United States and China. Sulfuric acid production is the main consumer of vanadium in the form of vanadium catalysts (V_2O_5 pentoxide). The demand for vanadium and its compounds keeps growing every year, as a result of the increased interest in processing of secondary vanadium-containing raw materials. One of the main sources of vanadium are the spent vanadium catalysts – SVC. About 100 thousand tons of spent vanadium catalysts are formed throughout the country, which are considered to be potentially hazardous for the environment and local population. Disposal of spent vanadium catalysts used for oxidizing of sulfur dioxide represents a serious environmental threat due to the lack of effective technologies for their processing. This work is devoted to a method for processing of spent vanadium catalysts to obtain a stuff that will be suitable for modifying of steels. The pyrometallurgical method of processing of technogenic raw materials by oxidative firing has been investigated and the parameters of firing – optimal firing time and temperature for extracting vanadium from the material – have been identified.*

Keywords: *vanadium, catalyst, roasting, pentoxide.*

VANADIY PENTOKSID OLISH UCHUN FOYDALANILGAN VANADIY KATALIZATORLARINI QAYTA ISHLASHNING INNOVATSION USULI

Turobov Shaxriddin Nasritdinovich,
Navoiy davlat konchilik instituti “Metallurgiya” kafedrasi assistenti

Xasanov Abdirashid Saliyevich,
texnika fanlari doktori, professor,
OKMK bosh muhandisining ilm-fan bo‘yicha o‘rinbosari

Annotatsiya. *Umuman olganda, dunyoda 60 millionga yaqin vanadiy konlari mavjud bo‘lib, ularning 90 foizi beshta davlat hududida joylashgan: Rossiya, Janubiy Afrika, Venesuela, AQSh va Xitoy. Sulfat kislota ishlab chiqarish vanadiy katalizatorlari (V_2O_5 pentoksid) shaklida vanadiyning asosiy iste’molchisi hisoblanadi. Ikkilamchi vanadiy saqlovchi xomashyoni qayta ishlashga qiziqish ortib borayotgani bois vanadiy va uning birikmalariga bo‘lgan talab yil sayin ko‘paymoqda. Vanadiyning asosiy manbalaridan biri sarflangan vanadiy katalizatorlari – IVK hisoblanadi. Ishlatilgan vanadiy katalizatorlari mamlakat bo‘ylab taxminan 100 000 ming tonna shakllanadi. Bu yerda to‘plangan chiqindilar atrof-muhit va mahalliy aholi uchun eng xavfli* *moddalardan biri. Oltingugurt dioksidini oksidlash uchun sarflangan vanadiy katalizatorlarini utilizatsiya qilish ularni qayta ishlashning mavjud texnologiyalari yo‘qligi sababli jiddiy ekologik muammodir. Ushbu ish po‘latlarni legirlash uchun mos mahsulotni olish maqsadida ishlatilgan vanadiy katalizatorlarini qayta ishlash usuliga bag‘ishlangan. Texnogen xomashyoni oksidlovchi kuydirish usuli bilan qayta ishlashning pirometallurgiya usuli ko‘rib chiqiladi, kuydirish parametrlari topiladi, ya’ni materialdan vanadiyni ajratib olish uchun optimal kuydirishning vaqti va harorati aniqlanadi.*

Kalit so‘zlar: *vanadiy, katalizator, kuydirish, pentoksid.*

ИННОВАЦИОННЫЙ СПОСОБ ПЕРЕРАБОТКИ ИСПОЛЬЗОВАННЫХ КАТАЛИЗАТОРОВ ВАНАДИЯ ДЛЯ ПОЛУЧЕНИЯ ПЕНТОКСИДА ВАНАДИЯ

Туробов Шахриддин Насритдинович,
ассистент кафедры “Металлургия”
Навоийского государственного горного института

Хасанов Абдирашид Салиевич,
доктор технических наук, профессор,
заместитель главного инженера по науке АГМК

Аннотация. *Всего в мире ванадиевых залежей насчитывается порядка 60 млн тонн, из которых 90% локализируются на территории пяти государств: России, ЮАР, Венесуэлы, США и Китая. Производство серной кислоты является главным потребителем ванадия в виде ванадиевых катализаторов (пентаоксид V_2O_5). Спрос на ванадий и его соединения растет по миру ежегодно, как следствие, повышается интерес к переработке вторичного ванадийсодержащего сырья. Одним из основных источников ванадия являются отработанные ванадиевые катализаторы – ОВК. По всей стране образуются около 100000 тыс. тонн отработанных ванадиевых катализаторов, являющихся потенциально опасными веществами как для окружающей среды, так и для местного населения, там, где скапливаются отходы. Утилизация отработанных ванадиевых катализаторов окисления диоксида серы представляет серьезную экологическую проблему в связи с отсутствием действующих технологий по их переработке. Данная работа посвящена способу переработки отработанных ванадиевых катализаторов с получением продукта, приемлемого для модификации сталей. Рассмотрен пирометаллургический способ переработки техногенного сырья методом окислительного обжига, выявлены параметры обжига, т.е. оптимальное время и температура для извлечения ванадия из материала.*

Ключевые слова: *ванадий, катализатор, обжиг, пятиокись.*

Introduction

Sulfuric acid known as the “bread” of chemical industry is mostly produced by a contact method. To speed up the process, catalysts based on vanadium-containing compounds are used. Vanadium is used for making of extra-ductile and strong steels, and is regarded as an essential component in the alloy with manganese steel 110G13L.

In turn, copper pipes and high quality cement are in great demand, both in the domestic market and abroad.

The average content of vanadium in the earth’s crust is quite high: 0.017%, which is 16 times higher than that of lead, and 2000 times higher than that of silver. The most important minerals of vanadium ores are: decasite (23%), cuprodekluisite (16-23%), vanadinite with 18% V_2O_5, carnotite (22%), patronite (16-30%), roskoelite (20-30%). Although the content of vanadium in the earth’s crust is high and contains its own minerals, vanadium is one of the rare elements and is mainly found in complex polymetallic minerals of the lithosphere. Internal vanadium minerals do not form significant accumulations or are already depleted.

About 90% of the vanadium produced is used in ferrous metallurgy for alloying steels, the rest is used in production of titanium and other metal alloys, as well as in the chemical industry. New applications for vanadium, such as batteries, hydrogen storage systems, etc., are predicted to lead to declines in metallurgy. Vanadium batteries could account for 17% of the battery market by 2025, up from 2% today, according to Lux Research Inc. This will lead to a significant increase in the consumption of vanadium trioxide and pentoxide.

From 2000 to 2015, global steel production - the main consumer of vanadium – has increased from 850 to 1600 million tons / year, and most likely, the trend will continue. Individual consumption of vanadium is also forecasted in connection with the development of thermonuclear energy. An increase in electricity production associated with construction of new nuclear power plants using alloys containing vanadium in their ligatures, which can last 50-80 years, will benefit the industry from 400 to 800 tons / year.

The work was carried out on the industrial sites of the copper-smelting shop at JSC ‘Almalyk Mining and Metallurgical Plant’.

The sulfuric acid plant produces about 30 tons of spent vanadium catalysts every year. If we count with that, more than 50 years have passed since the sulfuric acid production was started; then today in the dumps of JSC ‘AGMK’, 1500 tons of those catalysts have accumulated.

Vanadium catalysts used in the production of sulfuric acid are periodically removed from contact and are stored when the catalytic activity decreases. Various technologies have been proposed for extracting metal from them, but industrial processing has never been put in practice. The main reasons are the low tonnage of raw materials and the complexity of the proposed technological processes. Collecting of spent catalysts – toxic vanadium oxides – affects the environmental situation [1].

Depending on the nature of raw materials and the stuff they contain, pyrometallurgical, hydrometallurgical or combined vanadium processes are applied to extract the raw material. Pyrometallurgical and combined processes are commonly used for extracting vanadium.

Materials and methods

A known method of processing of a spent vanadium catalyst (extracting vanadium from spent catalysts) is by chlorinating roasting of ground catalysts with sodium chloride at 780 °C for 3 hours, followed by leaching of vanadium with a solution of sulfuric acid and water washing.

The disadvantage of this method is that the process is multistage, since the operation of preliminary grinding of the catalyst is required; the introduction of sodium chloride in the firing stage, which decomposes with the release of chlorides, creating an aggressive ambience in the furnace; loss of vanadium and sulfur during leaching of calcined granules (in the mother liquor, up to 5% with respect to V_2O_5 and 100% sulfur in the form of sulfates remain in the mother liquor, which are not utilized); the length of the process.

The closest to the one described in terms of its technical essence and achieved result, is another known method of processing of a spent vanadium catalyst, which involves roasting of the catalyst at 600-750 °C with a supply of oxygen at the roasting stage, leaching the roasted product with a mineral acid solution, precipitating vanadium in the form of $FeVO_4$ and separating the sediment containing vanadium, and a mother liquor containing sulfates.

The disadvantage of this method is insufficient degree of extraction of vanadium from the raw material (85-92%) and the complete loss of sulfur in the raw material, since the sulfur-containing mother liquor is not used. In addition, the method causes difficulties in technological design due to the presence of a stage of leaching with mineral acid, requires significant volumes and special acid-resistant equipment.

A method of processing of the spent vanadium contact mass by firing from a material containing vanadium is being proposed. The essence of the method: burn the catalyst at a temperature of 850-1050 °C and purge it with flue gas until the ratio of vanadium and sulfur is (1: from 0.11 to 0.40), and the ratio of V pentoxide and Me_2O is (1: 1.3-2), where Me_2O is the total amount of metal oxides, and the separated sulfur-containing gases are sent to the sulfuric acid production.

There is a method for treating the spent vanadium contact mass by chlorination, firing crushed catalysts with sodium chloride for 3 hours at a temperature of 800 °C [2].

The multistage operation was a disadvantage of this method, because the catalyst must be pre-crushed; chloride salt is introduced into the kiln and decomposes with the subsequent release of chlorides, thereby forming an aggressive environment in the kiln unit; in the leaching stage, vanadium and sulfur are lost (in the mother liquor up to 6% V_2O_5 and 100% sulfur in the form of sulfide salts, and they are not used); the duration of the process.

The closest in technical essence and achievement is another method of processing of the spent contact mass, which includes roasting of the catalyst at 550-750 °C, supplying oxygen to the roasting stage using a mineral acid solution, and precipitating it in the form of $FeVO_4$, the precipitate is separated, containing the vanadium salt, and a mother liquor containing sulfate.

The main disadvantage of this method is the following:

- metal recovery from raw materials is incomplete (82-90%);

- the sulfur in the raw material is almost completely lost, since the mother liquor containing sulfur is not used.

Moreover, difficulties arise in the technological design of the acid leaching process, as well as it requires large volumes and special acid-resistant material for equipment.

The main task was processing of the spent contact mass containing vanadium, as a result of which almost all of the vanadium passes into the finished product, as well as the sulfur in the feedstock must be disposed of.

The proposed method for processing waste catalyst solved the problems posed by the authors, including roasting the spent catalyst at 900-1100 °C and, as a result, obtaining a product rich in vanadium content. In accordance with this process, a certain amount of vanadium-containing material is fired and the following ratio is obtained: vanadium: sulfur = 1: (0.1–0.3) and pentoxide V: Me_2O = 1: (1.4–2.0), where Me_2O – the total amount of metal oxides, separation of the final product and gases containing sulfur, which are sent to sulfuric acid production.

The essence of this method is as follows, in order to almost completely eliminate all points of vanadium loss in the spent vanadium contact mass and to obtain a middling product, which can subsequently be used for production of vanadium master alloys and alloy steels, using sulfur in the spent contact mass in order to send it to sulfuric production. acid, it is important to carry out the firing process in some way.

When combustible gases are supplied to the firing stage, it leads to decomposition of the sulfate contained in the catalyst, vanadium is reduced from pentavalent to tetravalent, and vanadium bronze is formed. Combustion temperature also plays an important role, since the sulphate must fully decompose and the extracted sulfur enters the exhaust gases.

The process of metallurgical smelting should not involve large amounts of sulfur and alkali metals in the product containing vanadium, therefore they are fired at a certain ratio of V: S and V_2O_5: Me_2O. This ratio varies depending on the quality of the catalyst, firing time and temperature, but in the final ratio, the ratio should be V: S = 1: 0.10-0.40 and V_2O_5: Me_2O = 1: 1.4-2.0.

It was found out that when using vanadium-containing material in metallurgical melting with $V : S = 1 : 0.10–0.40$ and $V_2O_5 : Me_2O = 1 : 1.4–2.0$ is the best and it does not affect the process.

It was revealed that the use of the ratio V: S = 1: 0.10-0.40 and V_2O_5: Me_2O = 1: 1.4-2.0 when using vanadium-containing materials in metallurgy and smelting does not affect the process.

Findings

It was revealed that when using in metallurgical smelting vanadium-containing material with the ratio of V: S = 1: 0.10-0.40 and V_2O_5: Me_2O = 1: 1.4-2.0 is optimal and it does not affect the process. With an increase in the content of S and Me_2O in these ratios higher (for S> 0.4 and for Me_2O> 2.0), the product does not meet the requirements for materials used in metallurgical smelting. On the other hand, carrying out the process to a lower ratio than V: S = 1: 0.1 and V_2O_5: Me_2O = 1: 1.4 will require a change in the firing conditions, an increase in temperature and time, due to which, easily evaporated compounds will begin to form, which in turn will lead to volatilization and loss of vanadium.

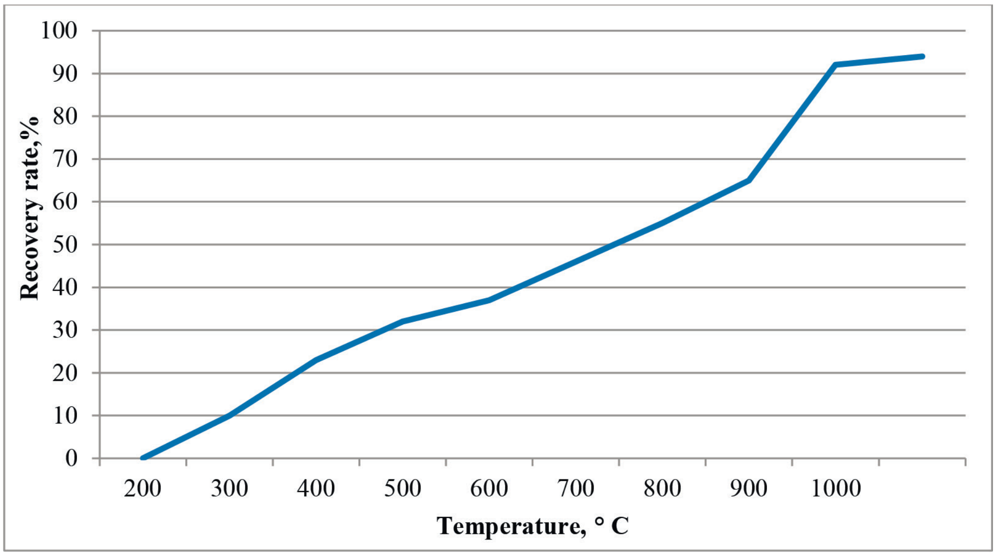

Fig. 1. Dependence of the degree of recovery on the firing temperature of the HVAC

Experiments have shown that if firing is carried out at temperatures below 900 °C, this can lead to a loss of sulfur, and at temperatures above 1100 °C, vanadium can be lost.

Therefore, when the process is performed at a temperature of 900 °C, the recovery rate of the material is 65%, and when performed at the specified temperature (900-1100 °C), the recovery rate of the process is 80-97%.

If the firing temperature exceeds 1100 °C, then more than 20% vanadium is lost to the process with volatilized gases.

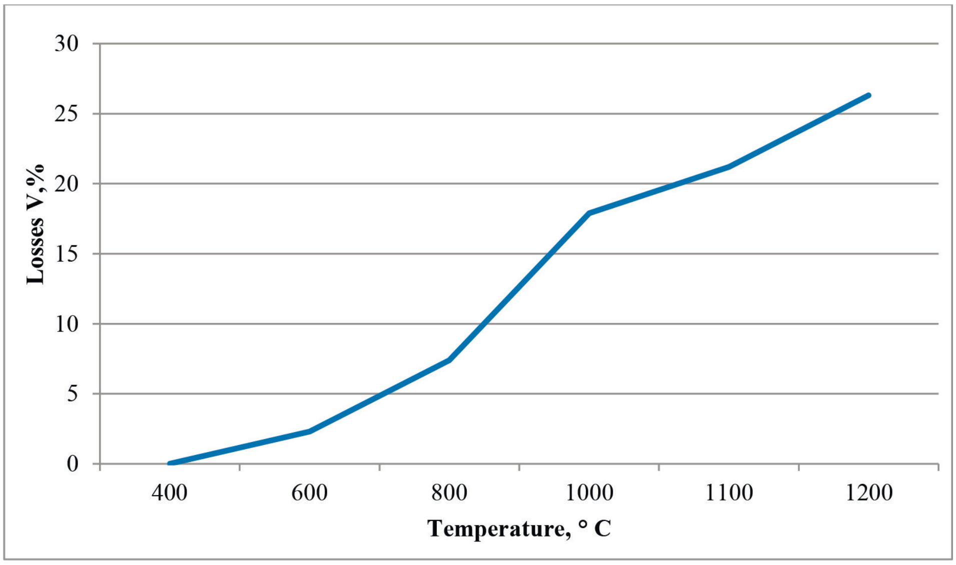

Fig. 2. Temperature dependence of vanadium loss

Example 1 160 kg of a vanadium contact mass containing 5.1% V_2O_5, 25.0% SO_3 and 10.0% K_2O was burned in a natural gas oven at 1000 ° C for 1 hour. After sintering the final product, the ratio V : S = 1 : 0.1, V_2O_5 : Me_2O = 1 : 2.0, the sulfur recovery is 97%, and the product contains vanadium (% of the V_2O_5 content in the final product, the starting catalyst. The V_2O_5 content is 121,5% The product is cooled and bagged, and the waste gas is sent to a cyclone separator for dust removal, then enters the H_2SO_4 rinsing section, and then enters the contact device.

Example 2.110 kg of a vanadium contact mass containing 6.5% V_2O_5, 30% SO_3 and 15% Me_2O is fired in a natural gas oven at 1100 °C for 0.5 hours. After firing in the final product, the ratio is: V : S = 1 : 0.158, V_2O_5 : Me_2O = 1 : 1.68, sulfur is recovered by 95%, the product is enriched by 123% in vanadium. The product is cooled and packaged, and the waste gas is sent to a cyclone separator for dust removal, then enters the H_2SO_4 rinsing section, and then enters the contact device.

Example 3 100 kg of a spent vanadium contact mass containing 7.5% V_2O_5, 30% SO_3, 13% Me_2O was fired in a furnace equipped with natural gas at 900 °C for 1 hour. After firing in the final product, the ratio V : S = 1 : 0.4; V_2O_5 : Me_2O = 1 : 1.4; sulfur is recovered by – 90.0%; the product is enriched with – 123% vanadium. The product is cooled and packaged, and the waste gas is sent to a cyclone separator for dust removal, then enters the H_2SO_4 rinsing section, and then enters the contact device.

Discussion

This method makes it possible to practically prevent the loss of vanadium in the spent vanadium contact mass. Sulfur is used in the form of SO_2 and SO_3 (sulfur recovery is 85-95%) and is sent to sulfur production. Moreover, the scope of application of vanadium-containing products obtained from spent catalysts, which can be used for the production of ferroalloys and can be used for the production of alloyed steels, is expanding. The technology of the method does not require leaching processes and the use of inorganic acids.

Conclusion

The method of processing of a spent vanadium catalyst includes firing of a contact mass at a high temperature to separate products with a high vanadium content and sulfur-containing products, and differs in that the firing temperature is 900-1100 °C until a product containing vanadium is obtained with the ratio V : S = 1 : 0, 10-0.40 and V_2O_5 : Me_2 = 1 : 1.4-2.0, Me_2O is the sum of alkali metal oxides, and the separated sulfur-containing gas is sent to the production of sulfuric acid.

The resulting fired product of spent vanadium catalysts may be effective in producing of alloying elements of carbon steels and cast irons used in domestic engineering, mining, etc.

REFERENCES

1. Mukhlenov I.P., Dobkina Ye.I., Deryujkina V.I. et al. Technology of catalysts. Leningrad, Chemistry, 1979, 325 p.

2. Vinarov I.V. et al. Complex use of raw materials, 1988, no. 2, pp. 17-19.

3. Turobov Sh. N., Hasanov A.S., Shodiev A.N. Research into technology of extraction of vanadium using sulfuric acid production waste. Universum: Technical science. 2020, no. 11(80), pp. 82-85.

4. Masidiqov E.M., Karshiboev S. Possibilities of increasing the efficiency of the technology of hydrometallurgical processing of lead concentrates. Academic research in educational sciences, 2021, no. 2 (3).

5. Xasanov A.S., Karshiboev Sh.B. Perspektivy razvitiya texnologii polucheniya germaniya iz texnogennyx otxodov. [Prospects for development of technology for producing germanium from industrial waste]. Universum: Technical science, 2021, no. 8(89).

6. Mirzanova Z. A., Munosibov Sh. M., Raximjonov Z. B., Karimova Sh. K., Tashaliev F. U., Karshiboev Sh. B., Texnologiya pererabotki texnogennix otxodov soderjashie svetnie metalli. [Technology for processing industrial waste containing non-ferrous metals]. Universum: Technical science, no. 6-1 (87), 2021, pp. 59-65.

7. Alikulov Sh.Sh., Karshiboev Sh.B., Jalilov G.B. Izuchenie osnovy sorbsionnoy texnologii pererabotki uranovyx rastvorov. [Study of the basics of sorption technology for processing uranium solutions]. Universum: Technical science, 2021, no. 3(84).

8. Voxidov B.R. Issledovaniye vozmojnosti izvlecheniya oksida vanadiya iz texnogennix otxodov. [Investigation of the possibility of extracting vanadium oxide from industrial waste]. Eurasia Scievce, 2017, pp. 93-95.

9. Lozano L.J. Recovery by solvent extraction of vanadium from spent catalysts leaching solutions using. Primene 81 R. Rev.Met. CENIM, 2001, 37, no. 5, pp. 582-590.

10. Kravchenko K.N. Metod regenerasii otrabotannogo vanadiyevogo katalizatora. [Waste vanadium catalyst regeneration method]. Kemerovo, 2018, p. 10.

11. Juang R.S., Lo R.H. Stoichimetery of vanadium (IV) extraction from sulphate solutions with bis(2-ethylhexyl)phosphoric acid dissolved in kerosene. J. Chem. Eng. Jpn. 1993, 26:219.

12. Marafi M, Stanislaus A. Spent hydrprocessing catalyst management: A review Part II Advances in metal recovery and safe disposal methods. Resour Conserv Recycl, 2008, 53:1–26.

14. Noori M., Rashchi F., Babakhani A., Vahidi E. (2014) Selective recovery and separation of nickel and vanadium in sulfate media using mixtures of D2EHPA and Cyanex, 272. Sep Purif Technol, 2014, 136:265-273.

15. Park K.H., Mohapatra D., Reddy B.R. Selective recovery of molybdenum from spent HDS catalyst using oxidative soda ash leach/carbon adsorption method. J Hazard Mater, 2006, 138:311–316.

16. Rapaport D. Are spent hydrocracking catalysts listed hazardous wastes? Hydrocarb Process, 2000, 79:49-53.

17. Sahu K.K., Agrawal A., Mishra D. Hazardous waste to materials: recovery of molybdenum and vanadium from acidic leach liquor of spent hydroprocessing catalyst using alamine. J Environ Manage, 2013, 125:68-73.

18. Saily A. Studies on liquid-liquid extraction of molybdenum, tugsten and vanadium using alkylphosphine extractants. Indian Institute of Technology, 1997, Roorkee.