Conference Paper

Physico-Chemical Foundation of Sludge Processing Hydrometallurgical Production of Vanadium Pentoxide. Investigation of Forms of Vanadium Compounds

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Abstract

To develop the physico-chemical basis of a complex technology for processing slurries hydrometallurgical production of vanadium pentoxide it is necessary to know in what form vanadium compounds are in the dump sludge and at what stage of processing they were formed, which is why vanadium is not completely extracted into the solution. This paper investigates the behavior of vanadium in the existing process chain (with the study of intermediate products of technological conversion) using a set of modern analytical methods (X-ray diffraction, SEM, X-ray diffraction, thermogravimetry).

Keywords: vanadium, slag, sludge, vanadium pentoxide, oxidation state, phase composition, processing technology

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Vanadium is considered one of the promising alloying metals for steel with high mechanical and operational properties. The main vanadium raw materials are titanium magnetite ores. The current technology of production of ferrovanadium includes four redistribution: obtaining vanadium cast iron, the redistribution of iron in semifinished steel and BOF slag, preparation of technical vanadium pentoxide chemical redistribution of vanadium slag, electric furnace or ladle smelting ferrovanadium [1–3].

The main wastes of vanadium pentoxide production are dump slurries formed after vanadium leaching from the burnt charge [4]. The yield of dump sludge is approximately 80 % of the amount of charge processed in the case of sodium-containing additives and about 95% in the case of slag processing with limestone. EVRAZ vanadium Tula JSC annually produces about 80 thousand tons of slurries of hydrometallurgical production of vanadium pentoxide, and the total number of slurries accumulated in the slime silos is more than 2 million tons [5]. JSC "Chusovskoy metallurgical plant" annually produces more than 20 thousand tons of solid vanadium-containing waste products of vanadium pentoxide [6], which are currently not processed and sent to the sludge storage.

The resulting waste contains valuable metals, but occupies large areas, and can cause environmental problems. Soluble compounds of vanadium and chromium, if the latter is contained in the oxidation state +6, pose a serious environmental threat. Previously, we studied the mobile forms of elements in samples of annealed vanadium slag and sludge using chromatography and selective dissolution methods [8]. According to X-ray phase analysis, vanadium and manganese in the sludge are in the form of oxides of trivalent elements – karelianite and bixbyite. However, the high degree of vanadium extraction by hydroxylamine hydrochloride solution suggests that soluble compounds V (IV) and V (V) are present in the sludge. Using different solvents at room temperature, the degree of transition of vanadium from sludge in the solution amounted to 3-17 %. Thus, there may be a potential environmental problem of long-term storage of vanadium sludge.

A review of the scientific literature shows that, despite the importance of the problem of processing waste vanadium sludge, it is not given enough attention. Known methods of processing of vanadium sludge can be divided into two types – hydrometallurgical [4, 6] obtaining vanadium concentrate and pyrometallurgical [7, 10–12] with the production of cast-iron, alloys, steel billets. Evraz vanadium-Tula uses dump slurries to charge the vanadium-rich ashes of thermal power plants during their processing, and also adds to Converter slags containing 17-20% V_2O_5 and Cao less than 3 %. This additive makes it possible to utilize the vanadium of dump slurries and has a positive effect primarily on the technological process of oxidative firing, preventing the formation of sinters [4, 9].

The disadvantage of the described pyrometallurgical technologies of sludge processing is the production of a semi-product with a high content of sulfur, phosphorus, titanium, chromium and other impurities due to the high contents of these elements in the feedstock, as well as emissions of sulfur compounds during processing. This circumstance limits the scope of the obtained intermediates. In concentrates obtained by hydrometallurgical methods, there is a high content of phosphorus.

Extraction of vanadium from slag depends, ceteris paribus, on the mineral composition and structure of the slag. The composition of raw materials, melting conditions, slag cooling rate affect the composition of the individual phases and the degree of transition of vanadium during firing into a water-soluble form. The microstructure of vanadium slag (phase composition, size, location of spinel grains, etc.) significantly affects the recovery rates of vanadium. Due to the high electrochemical activity and lability of vanadium compounds, pairs V (III) – V (IV), V (IV) – V (V) can exist simultaneously in the solution, and three or more forms can exist in solid samples. Therefore, it is preferable to use methods that do not require dissolution of the sample. In early works, chemical methods (redox titration, conversion to complex compounds, electrochemical methods) were mainly used for these purposes, and modern physical methods (EPR, IR spectrometry) are referred to detection methods. Since then, there has been a qualitative leap in the development of physical research methods. In [13] we investigated the samples of initial and annealed vanadium slag using x-ray spectroscopy and x-ray photoelectron spectrometry. In slag vanadium content in terms of oxides amounted to 12 % V_2O_5, 7 % VO_2 and 4 % V_2O_3, in the annealed slag (or cinder) 17 % VO_2 and 2 % V_2O_3. The phase composition of vanadium sludge is given in [8], a more detailed study of the forms of compounds of elements in this material is not found in the literature.

To develop the physico-chemical basis of a complex technology for processing slurries hydrometallurgical production of vanadium pentoxide it is necessary to know in what form vanadium compounds are in the dump sludge and at what stage of processing they were formed, which is why vanadium is not completely extracted into the solution. The paper investigates the behavior of vanadium in the existing process chain (with the study of intermediate products of technological conversion) using a set of modern analytical methods (X-ray diffraction, SEM, X-ray diffraction, thermogravimetry).

Fourteen samples of vanadium slag produced by “EVRAZ NTMK” were studied. It was found that in the samples of vanadium slag the main phase is spinel (Ti, V,Fe,Cr,Mn)$_3$O$_4$,the content of which is from 28.8 to 52.4 %. In addition, vanadium compounds are presented in the form of Vanadate chromium $CrVO_4$ (0,50-2.50 %) and vanadium dioxide VO_2 (0,13-2.70 %). Thus, vanadium in the samples is in the form of compounds V^{3+}, V^{4+}, V^{5+}. The silicate portion of the slag is represented by fayalite Fe_2SiO_4 (4,8-15,9 %) and cristobalite SiO_2 (0,10-1.30 %), in one of the samples contains 5% of mullite $Al_{4.59}Si_{1.41}O_{9.70}$. In all samples there is a metal iron (0,30- 2.01%). In addition, some samples identified as mixed oxide $FeMnO_3$ (1.5% structure of bixbyite), manganese oxide MnO (0,40-1.19 %), hematite Fe_2O_3 (1,90 %), pseudobrookite Fe_2TiO_5 (0,59 %). The content of the amorphous phase is 28.0-56.3 %.

Analysis of samples by XPS confirmed the presence of vanadium in three degrees of oxidation, and the content of vanadium in a certain degree of oxidation varies for different samples by almost 2 times. In addition, the results of the RFES assessed the content of elements in the oxidation state 2+ and 3+.

Ten samples of vanadium sludge produced by “EVRAZ Vanadium Tula” and obtained in laboratory conditions from vanadium slag were investigated. The major phases in the vanadium slime are hematite Fe_2O_3 (30,6-41,9 %), bassanite $CaSO_4$·0. 5H_2O (16,0-25,4 %), solid solution type pseudobrookite of armalcolite Fe_2TiO_5, $(Fe_{0.5}Mg_{0.5})Ti_2O_5$, $(Fe,Mg)_2(Ti,V)O_5$ (13,5-23.5 %, the structure is changing for different samples). The silicate part consists of a grossular $Ca_3Al_2Si_3O_{12}$ (0,7-2.6 %, in some samples missing) and quartz SiO_2 (2,8-6.0 %). Manganese, in addition to spinel, represented by two minerals: ramsdellite MnO_2 (0,8-3.5%) and pyrohroite $Mn(OH)_2$ (1,5-2.0 %). The sludge also contains rutile TiO_2 (1,0-2.5%) and spinel $(Ti,V,Fe,Cr,Mn)_3O_4$ (1,0-4.4 %). The content of the amorphous phase in different samples of the slurry was 1-29 %.

As a result of comparison of the results of the analysis performed by different methods, it is shown that with increasing content of fayalite in the slag increases the content of Me^{3+}, and in the sludge increases the total content of SiO_2, which is not correlated with the content of quartz. At the same time, there is a noticeable reduction in the values of unit cell parameters of the spinel α (with 0,8492 nm to 0,8471 nm) in the slag and (with 0,8457 nm to 0,8428 nm) in the sludge, indicating a change in its chemical composition. The decrease in V^{3+} is accompanied by an increase in vanadium dioxide VO_2. The increase in the ratio of Me^{3+}/Me^{2+} in slag is also accompanied by a decrease in the residual content of vanadium and spinel in the sludge. By increasing the content of V^{3+} in the slag, the content of total vanadium and spinel in the dump sludge decreases, while the content of total titanium in the sludge also decreases. Based on the observations, it is assumed that the formation of insoluble vanadium compounds increases with an increase in the content of titanium in the slag and sludge, this is accompanied by an increase in the content of V^{4+} and V^{5+} in the slag, but at the same time the ratio of Me^{3+}/Me^{2+} in the slag decreases.

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