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VANADIUM-CONTAINING WASTES RECYCLING FOR ENTERPRISES USING FUEL OIL: HIGH EXPECTATIONS

Demand for vanadium and its compounds grows: vanadium compounds are extensively used in various industries. Vanadium compounds extraction from industrial wastes is more cost-effective than from natural raw materials. In Belarus, sludge from thermal power plants and wastes of sulfuric acid manufacturers are the sources of secondary vanadium-containing raw materials. Vanadium-containing wastes generation and accumulation in the territory of the Republic of Belarus for recent years are analyzed. The article demonstrates that the development and implementation of recycling procedures for these wastes will resolve environmental problems and save valuable substances not common in nature but applicable in industrial production in the Republic of Belarus.

Introduction. In highly developed countries, such as Japan and Germany, the recycled-to-total waste ratio is as high as 98 and 95% respectively. In accordance with unofficial information sources, this ratio in the Republic of Belarus is 35%. In different industries, substances are used varying in amounts of their use and abundance in nature. Ideally, all industrial wastes shall be recycled; however, as a rule, this is not the case. On the one hand, transportation of wastes to the storages results in environmental problems; on the other hand, if the wastes contain any compounds of elements rarely occurring in nature, these valuable substances are lost irretrievably.

Vanadium, a transition metal, is an element rarely occurring in nature in the form of compounds. Its concentration in nature is 0.02 wt %. Industrial vanadium-containing wastes are important sources of vanadium compounds that are widely applied in various industries and in medicine. Many researches are in progress related to the development of technologies for vanadium-containing wastes recycling [1].

In the territory of the Republic of Belarus, these wastes include ash residues from thermal power plants (TPP) produced when fuel oil is fired, containing, in accordance with published sources, about 15–20% of vanadium (V) oxide; and spent vanadium catalysts with vanadium (V) oxide concentration about 5–10 wt %. In accordance with the data available from Ecologiya Belarusian Scientific Research Center ("BelSRC "Ecologiya"), the total amount of accumulated vanadium-containing wastes from thermal power plants in the Republic of Belarus, as of the beginning of 2010, was 10,366.98 t; in 2009, 53.27 t of these wastes were produced. It should be noted that these results include only the data from enterprises that use oil fuel and demonstrate vanadium-containing wastes in their reports. Indeed, the amounts of generation of these wastes are higher because not all enterprises specify in their reports that these wastes exist. Fuel oil is applied widely. However, some enterprises use it as an alternate fuel, i.e. only when the fuels primary for the enterprise are unavailable; this mode sometime results in impossibility to collect ashes separately.

Main part. See Fig. 1 for diagrams demonstrating annual amounts of generation and accumulation of vanadium-containing wastes. These diagrams are based on the reports submitted by enterprises to "BelSRC "Ecologiya"; the number of these reports was 9–10.

It was already mentioned that the real number of enterprises using fuel oil is much greater.

Vanadium-containing wastes from TPS are not used in the Republic of Belarus; in most instances, they are not transported to the waste disposal facilities but stored at the enterprises. The amount of generated wastes varies randomly from year to year.

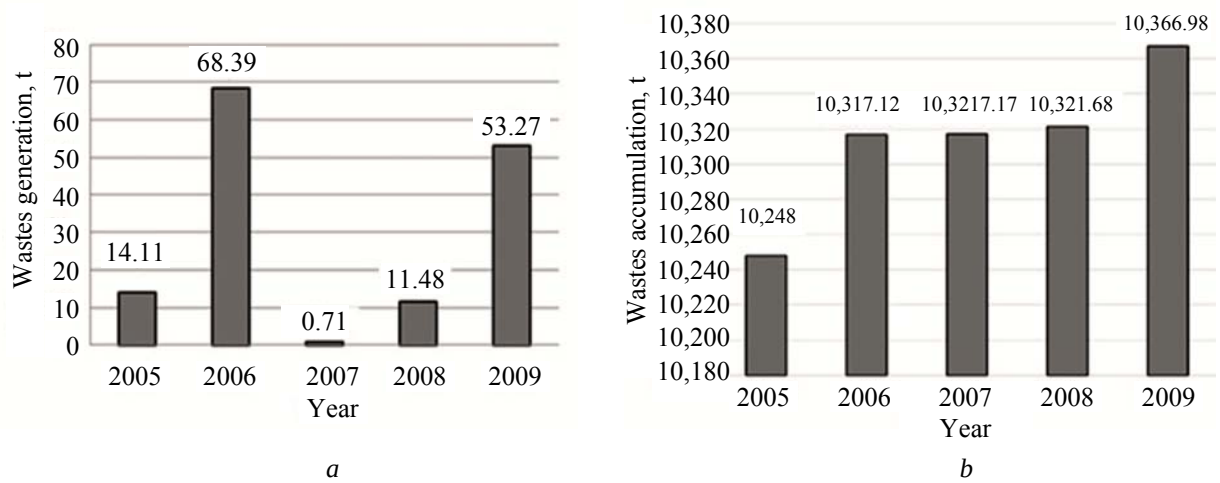

Fig. 1. Annual vanadium-containing wastes generation (*a*) and accumulation (*b*)

Therefore, in terms of provision with raw material resources, it is more reasonable to estimate maximum waste generation amounts for business entities separately.

Maximum amounts of vanadium-containing sludge are produced at Minsk Combined Heat and Power Plant N 3 (Minsk TPS-3) operated by MinskEnergo Republican Unitary Enterprise (see Table 1).

As demonstrated by the presented data, Minsk TPS-3 produces 75–80% of the annual total wastes amount included in the statistical data. This was not the case in 2006 only, when the larger amount of wastes (54.5 t) was generated at Vitebsk Combined Heat and Power Plant. That's why Minsk TPS-3, as the most promising facility in terms of wastes generation, was chosen for the research of chemical composition of wastes. There are several specific features of wastes generated at Minsk TPS-3: they are placed within the enterprise territory in the special storage, and lime is subsequently added into it. Lime amount is sufficient to neutralize an acidic component in the solution for boiler washing. Thus, sludge is heavily watered from the very beginning; the laboratory water sampler was used to obtain sludge samples. There is no roof above the waste storage, and it cannot be constructed because of technical reasons. Therefore, water from precipitations and, in spring, from thawing snow is added to the sludge water.

Vanadium-containing wastes from TPS are accumulated, together with other industrial wastes, in open sludge storages; wastes remain there for a long time, resulting in their dilution down to vanadium concentration as low as 1 wt %. The scanning electron microscope, JEOL JSM-5610 LV, provided with the elemental analysis system, EDX JED-2201, was used to measure this concentration. The number of analyzed samples was at least 20 for each sample type.

Supernatant fluid and sediments from the Minsk TPS-3 sludge storage were tested. Supernatant fluid was evaporated to extract sediment. Sediment samples were dried at 40°C until they became air-dry.

Also, EDX method was used to determine the averaged compositions of vanadium-containing sludge from Beryozovskaya GRES Thermal Power Plant (Beloozersk), operated by BrestEnergo Republican Unitary Enterprise, and of aqueous extracts obtained from this vanadium-containing sludge. For the results, see Table 2.

Because of reasons listed above, it was difficult to identify large economic entities having vanadium-containing sludge in their wastes; until now, samples of ash produced by fuel oil firing were obtained from one enterprise only, Vitba Vitebsk Confectionary Plant Communal Unitary Enterprise (Polotsk), where fuel oil is used. EDX method was used to determine the elemental composition; for the results, see Table 3.

Table 1

Vanadium-containing wastes generation at Minsk Combined Heat and Power Plant N 3

Characteristic	2005	2006	2007	2008	2009
Generation, t	11.69	12.43	0.39	109.05	41.48
Percentage in total amount	83	18	55	87.5	78

Table 2

Compositions of vanadium-containing industrial wastes from TPS

Waste type	Concentration, wt %													
	C	O	Na	Mg	Al	Si	S	Cl	K	Ca	V	Fe	Cu	Zn
Vanadium-containing sludge, TPS-3 Combined Heat and Power Plant (Minsk)	19.83	23.68	–	1.03	0.54	1.46	–	–	–	48.63	0.17	4.60	–	–
Sludge storage supernatant fluid, TPS-3 (Minsk)	12.46	28.32	23.95	–	–	–	9.03	13.24	2.84	6.38	0.38	–	0.94	–
Vanadium-containing sludge, Beryozovskaya GPS Thermal Power Plant (Beloozersk), operated by Brest-Energo Republican Unitary Enterprise	10.08	37.74	–	4.11	0.49	9.69	0.40	–	–	14.19	1.21	22.10	–	–
Vanadium-containing sludge aqueous extract, Beryozovskaya GPS Thermal Power Plant (Beloozersk), operated by BrestEnergo Republican Unitary Enterprise	4.88	39.22	8.29	3.61	–	11.23	8.27	1.22	1.20	19.12	0.25	0.88	0.78	1.05

Table 3

Compositions of vanadium-containing industrial wastes from Vitba Vitebsk Confectionary Plant Communal Unitary Enterprise (Polotsk)

Waste type	Concentration, wt %														
	C	O	Na	Mg	Al	Si	S	Cl	K	Ca	V	Fe	Cu	Zn	Ni
Ash from oil fuel firing	20.92	34.05	–	0.57	0.99	1.97	12.92	19.02	–	19.02	1.77	7.79	–	–	–
Enriched ash from oil fuel firing	6.46	33.84	0.17	0.54	0.90	2.25	17.22	–	0.63	24.76	2.94	6.96	0.52	1.74	1.08

All these data demonstrate that the amount of vanadium-containing sludge accumulated in the territory of the Republic of Belarus is quite large. Even if we assume that the vanadium-containing compounds concentration in ‘diluted’ sludge is 1% only, the total weight of these compounds is 103 t. All these substances are stored in improper conditions, making them the significant sources of environment pollution.

Other significant sources of vanadium-containing compounds are spent vanadium catalysts (SVC) stored at the enterprises producing sulfuric acid. For example, the amount of catalysts necessary for Grodno Azot Enterprise is about 100 t a year. Annually, 20% of this amount is subject to replacement. The enterprise does not recycle these wastes; they are accumulated and transported to the Russian Federation for recycling payable by Grodno Azot.

At present, we have developed the hydrometallurgical method for SVC recycling [2, 3]. The method is capable to extract up to 95 wt % of vanadium-containing compounds from SVC (see Fig. 2).

Within the scope of development of the method for SVC recycling, the electrochemical method [4] is found to be applicable for comprehensive SVC recycling. The opportunities provided by methods listed above are as follows:

– stages of primary and reductive leaching can be combined, and cathode leaching provides capability to increase the extraction of vanadium compounds making it as high as 95% (in terms of vanadium extraction); at the same time, the total SVC weight loss, resulting from dissolution, grows by 15–20% as compared with the hydrolytic method;

– the SVC preliminary grinding stage becomes unnecessary, and the cathode leaching process can be applied directly to granulated wastes;

– the pre-hydrolysis waste oxidation process can be made more intensive by V (III–IV) oxidation to V (V); as a result, additional reagent consumption is avoided, as compared with the chemical oxidation process.

In parallel with the development of the method for SVC recycling, efforts were made to reveal potential scope of direct application for industrial wastes and for products resulting from wastes recycling [5]. As a result, both wastes and recycling products were found to be applicable in the industry of the Republic of Belarus.

The series consisting of ten compositions of glaze glass with a wide range of components has been designed; SVC solid residues, resulting from vanadium-containing component extraction by leaching, are applicable to make these products.

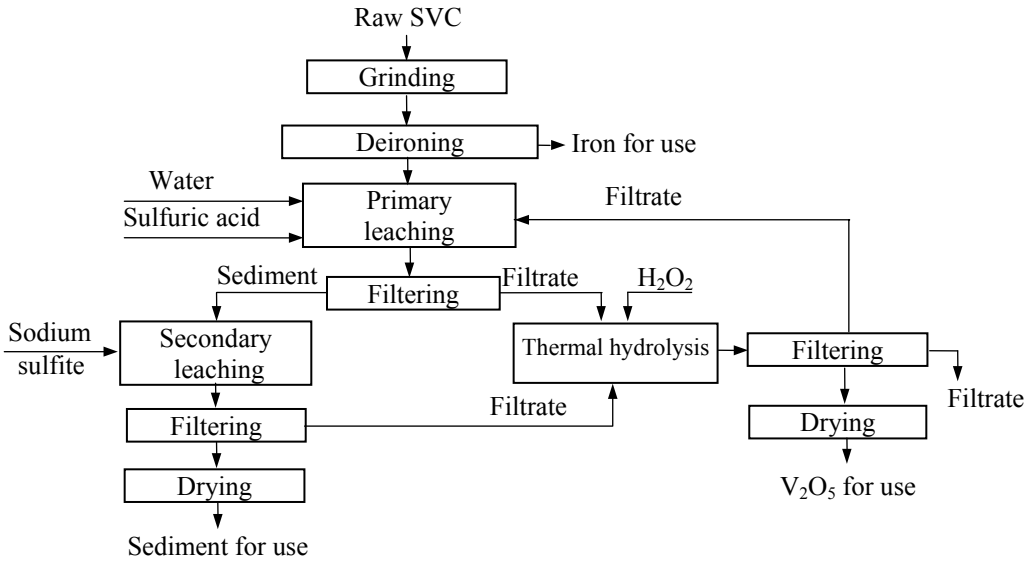

Fig. 2. SVC recycling

The SVC solid residues were found to be applicable for making decorative glass, the characteristics of which include uniform gloss throughout its surface and glaze coating demonstrating good coverage and various shades of grey color. Also, vanadium compounds extracted from industrial wastes were found to be applicable for paint making [6].

These data demonstrate that implementation of the proposed procedure for SVC recycling shall result in comprehensive recycling of industrial wastes and their effective use in the industry of the Republic of Belarus.

Conclusion. The analysis of wastes accumulation from enterprises using fuel oil and description of compositions of industrial ashes containing vanadium demonstrate that the development of technologies for these wastes recycling and for SVC recycling is undoubtedly of great interest. As a result of these wastes recycling, the problem of import replacement will be resolved: the need for import of vanadium-containing compounds for various Belarusian industries (ceramics, glass, paints, metallurgy) will be reduced. At the same time, environment pollution by vanadium-containing compounds, classified as the substances of the second class of hazard, will be prevented. The key problems for the development of recycling methods include identification of waste generation sources and appropriate waste storage. For these purposes, efforts shall be made to draw attention of agencies responsible for appropriate use of industrial wastes and of general public to the problem of vanadium-containing wastes disposal.

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