CHEMISTRY AND TECHNOLOGY OF INORGANIC MATERIALS AND SUBSTANCES

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EXTRACTION OF VANADIUM-CONTAINING PRODUCTS FROM THE SLUDGE OF THERMAL POWER STATIONS

In the Republic of Belarus a potential source of vanadium-containing secondary raw materials is vanadium-containing sludge generated by the combustion of fuel oil in the boiler units of power plants. Vanadium concentration there is ten times greater than its content in the traditional ore raw materials. The total number of vanadium-containing sludge on the territory of the Republic of Belarus for the beginning of 2012 wasdetermined. Methods of vanadium-containing compounds extraction from vanadium-containing sludge ThPS were developed with the use of hydrometallurgical method. The methods influence of the vanadium-containing compounds extraction from sludge of ThPS on their composition and amount of extraction was studied.

Introduction. Shortage of vanadic products in the Republic of Belarus as one of the basic elements of steel doping, as raw materials for manufacture of catalytic agents, colorants, coloured enamels, glazes and glasses is evaluated by tens of tons. Vanadium-containing raw materials and finished goods are imported to our country from the Russian Federation and other foreign countries.

In the Republic of Belarus the potential source of vanadium-containing secondary raw materials is combustion products of hydrocarbon raw materials on thermal power stations (ThPS), waste vanadic catalytic agents of the sulfuric acid production. Vanadium concentration there is 10–100 times greater than its content in the traditional ore raw materials – titanium-magnesium ores (approximately 0.14–0.17% in terms of V_2O_5). In the high-temperature zone of the boiler unit while burning black oil the ash residues with high (up to 20%) content of V_2O_5 are formed. The sludge received after neutralization of the solid combustion products formed on the air heater surface contain up to 10% of vanadium oxide (V) [1].

In addition to increased content of vanadium compounds in solid combustion products of carbon-bearing raw materials, their value as the secondary raw materials source consists in that they do not require additional stages of extraction: ore-dressing, sintering, blast-furnace smelting and vanadium extraction from cast iron in converters. The given technological processes are obligatory at production of converter vanadic slags – the raw product for vanadium production with the help of the pyrometallurgical technique.

Now in the Republic of Belarus there are no industrially tested techniques of vanadium extraction from industrial vanadium-containing waste. The urgency of processing of the vanadium-containing industrial wastes is caused by not only profitability of manufacture, but also by the ecological situation in the Republic of Belarus which becomes aggravated. Previously enterprises could take out the vanadium-containing waste for processing to the Russian Federation, but after entry into force in the Republic of Belarus on March, 9th, 2000 of the Basel convention on control over transboundary transportation of dangerous wastes and their disposal, the enterprises are obliged to organize long-term storage of this kind of waste which belongs to the second class of danger, on their territories. Storing of vanadium-containing waste is connected with the withdrawal of the land for sludge-storage and tailing pits, with contamination of the surface runoffs and underground waters, and also ground atmosphere and soils by the toxic components which spread to considerable distances. Therefore development of processing methods of vanadium-containing waste ensures the solution of two main problems: the raw-material base extension on extremely scarce metal and ecological load lowering on environment.

Main part. Together with RUE “Bel SRC “Ecology” the analysis of formation, movement and accumulation of thevanadium-containing sludge waste on various subjects of management of the Republic of Belarus was carried out in 2011 (Table 1).

According to the statistical data, the summarized volume of formation of the vanadium-containing sludge in 2011 was 4.43tons, while in 2010 it was 19.85 tons. The main suppliers of the given kind of waste are ten large subjects of management: thermal power stations, state district power stations, the inter-district enterprises of electric networks. Smaller enterprises using black oilas a fuel, do not take account of the given kind of the waste. The largest producer of the vanadium-containing sludge for the last 10 years, is the Minsk heat and power plant № 3 of the republican unitary enterprises “MinskEnergo” – 4.35 tons (2011).

Recently an essential volumes reduction of the vanadium-containing sludge formation is due, first of all, to the fact that the enterprises generating thermal energy do not use black oil and transfer to other kinds of fuel. However, in spite of the fact that formationvolumes of the given kind of waste during the last years on a national scale are insignificant, accumulation volumes are rather essential, increase every year and at the beginning of 2012 were 10,391.26 tons.

Analysis results of the averaged element compositions of the vanadium-containing waste of ThPS show that the vanadium content in the supernatant fluid from sludge storages and in sediments of sludge storages does not exceed 1 wt%. This is explained by the fact that the vanadium-containing wastes of ThPS are placed together with other industrial wastes in open sludge storages. The greatest content of vanadium is found in ashes from black oil burning (about 2–3 wt%).

Vanadium-containing ash residues formed at black oil burning at RUE “Vitebsk confectionery complex “Vitsba” (Polotsk), containing 4.56 wt% of vanadium in terms of V_2O_5 were chosen for study.

Essential difference of water solubility of the main components of the ash residues of ThPS stipulates a possibility of usage of hydrometallurgical and combined methods of their processing. The main stages of the hydrometallurgical processing method of vanadium-containing industrial wastes are leaching of the main sludge components and extraction of vanadium-containing compounds from the received solutions.

Table 1

Formation, usage and disposal of the vanadium-containing sludge in 2011

Enterprise name	Waste presence at the beginning of year, tons	Volume of waste formation, tons	Waste used, disposed, realized, tons	Volume of the waste taken away, tons	Waste presence at the end of year, tons
Berezovskaya SDPS	35.04	0.00	0.00	0.00	35.04
Vitebsk ThPS branch of the republican unitary enterprise of electric power industry “VitebskEnergo”	1,510.50	0.00	0.00	0.00	1,510.50
Novopolotsk ThPS branch of the republican unitary enterprise of electric power industry “VitebskEnergo”	265.96	0.00	0.00	0.00	265.96
Lukomlsky SDPS of republican unitary enterprise “VitebskEnergo”	2,782.23	0.06	0.00	0.06	2,782.23
Minsk heat and power plant No 3 of RUE “MinskEnergo”	5,773.23	4.35	0.00	4.35	5,777.57
Mozyr heat and power plant	5.87	0.02	0.00	0.02	5.89
Grodno heat and power plant No 2 of RUE “GrodnoEnergo”	0.089	0.01	0.00	0.01	0.90
Molodechno electric networks of republican unitary enterprise “MinskEnergo”	0.80	0.00	0.00	0.00	0.80
Zhodino heat and power plant of RUE “MinskEnergo”	4.35	0.00	0.00	0.00	4.35
Branch of the Mogilev republican unitary enterprise of electric power industry “MogilevEnergo” of concern “BelEnergo” – the Bobruisk ThPS–2	7.97	0.00	0.00	0.00	7.97
Total	10,386.83	4.43	0.00	4.43	10,391.26

For the leaching stage optimization of vanadium-containing components from vanadium-containing ash residues the process peculiarities of their solution in water and in water solutions H_2SO_4, HCl, $NH_3 \cdot H_2O$, KOH, and also in solutions of hydrochloric or sulfuric acids containing an oxidizing agent (H_2O_2 or $(NH_4)_2S_2O_8$) [2] are determined.

It is found out that the ratio of liquid (L) and solid (S) phases has an essential influence on the quantity of the total mass loss of the ash residues only to the values, equal to five, and their peak solubility is reached already during the first 10 minutes (Fig. 1).

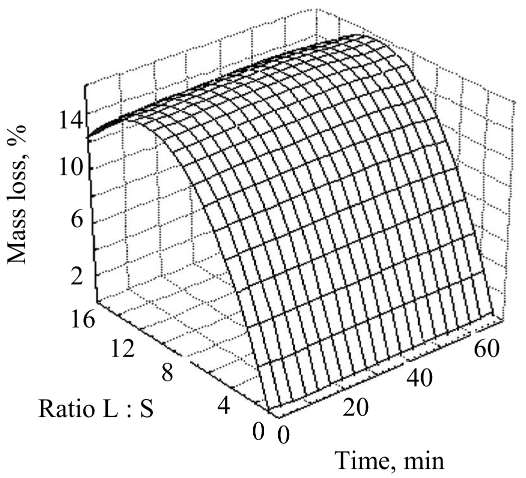

Fig. 1. Solution dynamics of the ash residues in water at different ratio S : L. Temperature 20°C

Increase of the leaching time on more than 60 minutes and ratios L : S on more than 12 leads to some reduction of the ashes mass loss and the leaching degree of the vanadium-containing components from them, and it may be caused by intensification of the hydrolysis processes.

Rise in temperature does not influence essentially the solution speed of the ash residues and the leaching degree of the vanadium-containing components from them.

Research results show that the most preferable solvents are solutions of hydrochloric acid. With concentration increase of the hydrochloric acid from 0.1 to 6.0 mole/dm^3 the total ashes mass loss increases by 41%, and the extraction degree of vanadium-containing components from them – by 47%, and it is related to a good solubility of metals chlorides being formed (Fig.2).

When introducing hydrogen peroxide into the solutions of hydrochloric acid the vanadium extraction degree increases 1.5 times (Table 2). To stimulate the extraction process of the vanadium-containing components from ThPS sludge the ash residues solubility was studied while doing acoustochemical processing. There to the ultrasonic (US) device with the piezoelectric radiator manufactured by the company "IN-LAB" (Russia) IL 100-6/1 with the following characteristics was used: power – 630 W, working frequency – 22 kHz, oscillation amplitude - not less than 40 micron, volume of suspension being processed – 50 ml, processing time – 3 minutes.

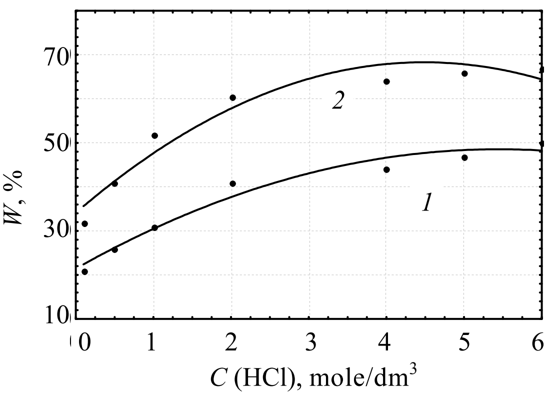

Fig. 2. Mass loss of the ash residues (*1*) and extraction degree of the vanadium-containing components (*2*) in hydrochloric acid solutions. S : L = 10. Temperature is 20°C

The conducted examinations show that the acoustochemical processing of the ash suspensions in the acidic mediums does not lead to solubility growth of the ash residues. The extraction degree of the vanadium-containing components at US-processing varies very slightly: with oxidizing agent absence in the leaching solution – it decreases, and in the solutions containing hydrogen peroxide or ammonium persulfate – it increases by 2–5% (Table 2). The obtained data testifies that the extraction degree of vanadium from ThPS sludge is determined mainly by the presence of an oxidizing agent as a part of leaching solutions. Acoustochemical processing intensifies a little the oxidation reaction of thevanadium-containing ashes components. However activation of the hydrodynamic regime, the cavity phenomena by which US-influence is accompanied, do not influence the leaching process of the vanadium-containing components. Therefore US usage at this stage of ThPS sludge processing is not justified economically.

To intensify the leaching stage, to increase the extraction degree of the vanadium-containing components from the waste being processed, to reduce the reagents usage, to optimize water consumption the possibility of usage of electrochemical methods in the course of processing of the vanadium-containing sludge of ThPS was studied.

Table 2

Leaching of the vanadium-containing component from the ash residues of ThPS without and with usage of an ultrasonic field

Compositions of leaching solutions	Ash mass loss, %	Vanadium extraction degree, %	
		without usage of an ultrasonic field	with usage of an ultrasonic field
Water	14.5	19.8	19.7
H_2SO_4 (pH = 1.25)	13.5	13.9	13.7
H_2SO_4 (pH = 1.25) + 0.2 mole/dm^3 H_2O_2	13.6	20.3	20.8
H_2SO_4 (pH = 1.29) + 0.03 mole/dm^3 $(NH_4)_2S_2O_8$	16.0	22.8	24.0
HCl 0.1 mole/dm^3	20.4	31.21	30.8
HCl 0.1 mole/l + 0.07 mole/dm^3 H_2O_2	20.9	42.77	43.2

So far as the most preferable solvent of ThPS sludge are the hydrochloric acid solutions containing oxidizing agents, the solutions of HCl were used as a background electrolyte of electrochemical leaching. Electrolysis was carried out in a single-camera electrolyzer during 30 minutes at temperature of 20°C. A hollow graphite cylinder adherent to the electrolyzer walls was used as anode. An iron plate placed in a chlorine fabric cover and anchored to the cathode rod at the electrolyzer center served as cathode. Area ratio of anode and cathode was 5 : 1. Ash was placed in the electrolyzer with ratio of solid and liquid phases as 1 : 10. Mixing was done with the help of a magnetic stirrer. The conducted research results are shown in Fig.3.

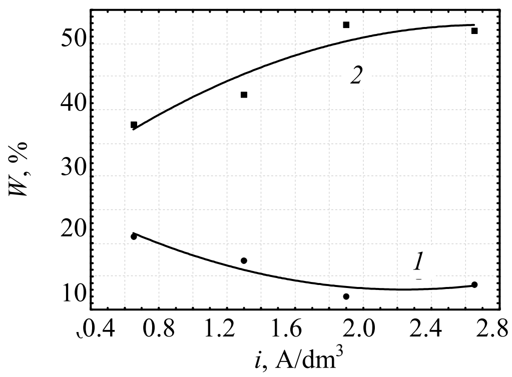

Fig. 3. Mass loss of the ash residues (*1*) and extraction degree of the vanadium-containing components (*2*) with increase of the anode current density

As it is clear from the given data, with increase of the anode current density the total mass loss of the vanadium-containing sludge of ThPS decreases. It is possible to explain it by the fact that with current density increase the hydrogen current efficiency increases. Alkalization in the cathode region leads to intensification of hydrolysis processes and formation on the cathode of the dendrite – like sediments of hydroxides and of the basic salts of metals which are present in the electrolyte. The extraction degree of the vanadium-containing components in the course of electrochemical leaching reaches 40−50% and with growth of the anode current density from 0.7 to 2.7 A/dm^2 it increases by more than 30%. When heating up the leaching solutions received the vanadium compounds are exposed to hydrolysis. Thus, thermo-hydrolytic precipitation process of V_2O_5 is observed. To intensify the process of extraction and concentration of vanadium from leaching solutions the influence of temperature and preliminary oxidation of prehydrolytic solutions on vanadium (V) hydrolytic precipitation speed was studied.

To obtain prehydrolytic solutions containing mainly vanadium (V) compounds, the leaching solutions of ash residues were treated with hydrogen peroxide and ammonium persulfate. The main benefits of the oxidizing agents used are providing fast rate and oxidation completeness, and also absence of additional components which pollute the used leaching solutions and complicate its subsequent regeneration.

As determination of vanadium compounds in different degrees of oxidation at their combined presence in a solution is rather difficult, so the primary formation of some form of vanadium was estimated by comparing the leaching solutions color to the known analogues.

While treating the leaching solutions by peroxide compounds in a strong-acid medium (pH up to 2), solutions are formed containing peroxide-salts of radical $[V(O_2)]^{3+}$, having a brown-red color.

With pH value more than 2, yellow solutions containing mono- and di-peroxide-vanadate-ions $[VO_3(O_2)]^{3-}$, $[VO_2(O_2)_2]^{3-}$ are formed.

At storage in water the vanadium peroxide-compounds are exposed to hydrolysis with formation of hydrogen peroxide which in turn decays with oxygen release [3, 4].

It was found out that introduction of H_2O_2 and $(NH_4)_2S_2O_8$ into leaching solutions leads to the solution color change from green, characteristic for leaching solutions, to brown and that testifies formation of radical $[V(O_2)]^{3+}$ in the peroxide-salt solution.

It is determined that residual vanadium concentration in sulfuric solutions after thermo-hydrolysis in terms of V_2O_5 does not depend on their initial concentration and oxidizing agent amount in the solution does not exceed 0.0033 mole/dm^3.

As follows from the given data (Fig.4), the preliminary oxidation of leaching solutions by hydrogen peroxide leads to generation rate growth of sediment up to 60%.

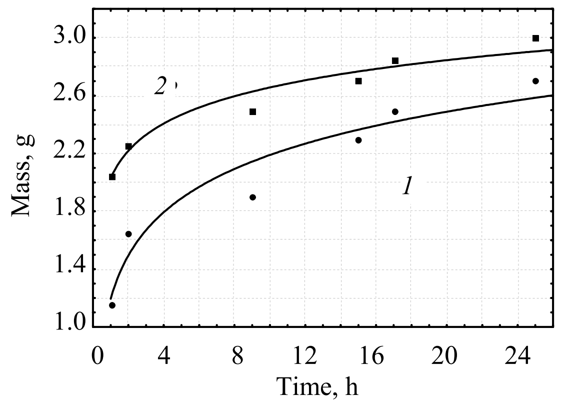

Fig. 4. Dynamics of hydrolytic precipitation of V_2O_5 at 45°C:
1 – without oxidizing agents treatment;
2 – leaching solution treated by an oxidizing agent

It is found out that for V_2O_5 extraction from the leaching solutions the following relation $n\,V_2O_5 : n\,H_2O_2 = 1:2$ and $n\,V_2O_5 : n\,(NH_4)_2S_2O_8 = 5:1$ is optimal. It is determined experimentally that at boiling of the obtained solutions during 5 minutes practically all vanadium contained in the leaching solutions moves in to sediment. Besides, further increase of the oxidizing agent content in the solution does not lead to the amount growth of the extracted vanadium (V) oxide, on the contrary, it complicates extraction of oxidation products from solutions.

Usage of ammonium persulfate as an oxidizing agent allows reducing of the extraction temperature of the vanadium compounds from leaching solutions of the vanadium-containing sludge of ThPS.

Analysis of elemental compositions found with the help of EDX method shows that the vanadium content in the extracted product from the pre-oxidized leaching solutions exceeded 40% in terms of V_2O_5.

Conclusion. Thus, the conducted research showed a possibility of usage of the hydrometallurgical processing method of the vanadium-containing sludge of ThPS, including stages of oxidation leaching in muriatic solutions and thermo-hydrolytic extraction of V_2O_5 from the received solutions.

The leaching degree of the vanadium compounds from the ash exceeds 40% from the total vanadium amount present in the initial sample. Conducting the oxidation leaching process at the anode current density of 0.6–2.5 A/dm^2 permits to increase the vanadium extraction degree by 10–20% as compared to chemical leaching in solutions without an oxidizing agent.

The vanadium content in the extracted product from the leaching solutions in the process of thermo-hydrolysis exceeded 40% in terms of V_2O_5.

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