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ANALYSIS OF PROCESSING SCHEMES OF VANADIUM-CONTAINING WASTE, FORMED WHILE RESIDUAL OIL BURNING, FABRICATION OF ALUMINA AND TITANIUM

The given paper analyzes technological schemes of processing technogenic raw materials, containing vanadium: waste of solid products of residual oil burning at thermal power stations, titanium and alumina production. Chemical composition of waste, namely, content of accompanying detrimental impurities determines the scheme of its processing: for the ash of thermal power stations main impurity is sulphur, for slimes of alumina production – sulphur and phosphorus, for slimes of titanium production – calcium monoxide. Processing of this waste is promising, as it allows to extract from the waste metal or its compounds and, at the same time, decrease the pollution of the environment.

Key words: *vanadium pentaoxide, vanadium slurry, ashes of thermal power stations, alumina, ammonia, limed cake.*

Introduction. Nowadays large volume of technogenic vanadium-containing waste has been accumulated in Ukraine, the waste is stored on the territory of industrial enterprises. The following substances can be referred to vanadium-containing waste of technogenic origin: ashes of thermal power stations (TPS), slimes of titanium and alumina production, waste of vanadium and ferrovanadium production, worked out catalysts of sulphuric acid production, etc. [1]. Processing of this waste provides maximum reduction of its negative impact on man and the environment.

Ashes from thermal power stations are formed as a result of burning of liquid organic fuel (residual oil) at thermal power plants and pollute the environment. Content of toxic vanadium compounds is within 1.5 % to 20 % of V_2O_5, and nickel – 1…5 % [2]. Regarding the content of vanadium pentaoxide in ashes of TPS they are divided into poor (up to 10 %) and rich (more than 10 %). However, the ashes of domestic TPS are not processed in our country, because they are poor and are not prepared for processing: they possess excess moisture content, considerable amount of impurities and they are heterogeneous by chemical content. In CIS countries the share of TPS, burning vanadium-containing residual oil, in total generation of electric energy is about 75 % [3].

Bauxites are used for production of alumina, they contain from 0.001 % to 0.2 % of vanadium and further pass into red mud. Content of V_2O_5 in red mud (RM) is within the limits of 0.5 % to 2 % [4]. As a result of RM processing vanadium slurry is obtained, it contains: from 6 to 18 % of V_2O_5, from 25% to 50 % of Na_2O, from 0.3 to 14 % of P_2O_5. Increased content of P adversely affects the quality of end product and completeness of V_2O_5 precipitation in the process of hydrolysis [5], stability of aluminium solutions decreases at thickening of red muds, in the process of solutions decompositions more fine crystal aluminium hydroxide is formed, that is why, slimes of alumina production are not suitable for processing.

During processing of hydroargillite bauxites with high content of silicon into alumina compounds of vanadium in large quantities change into aluminate solutions and are gradually accumulated in them [6, 7]. While extraction of vanadium from the solution two problems are solved simultaneously: on one hand, quality of alumina and metallic aluminium grade increase, on the other hand — index of bauxite raw material usage complexity is improved, that allows to reduce the cost of alumina.

In the process of producing titanium from the ore vanadium changes into technical $TiCl_4$ in the form of admixture $VOCl_3$ (0,007…0,008 %). Cleaning of titanium tetrachloride from vanadium is carried out by aluminium powder, combining cleaning with rectification. As a result, the slime of titanium production, containing 5…15 % of V_2O_5 and large amount of chlorine compounds are formed. That is why, for processing of the given technogenic raw material, it is necessary to get rid of chlorine or considerably reduce its concentration.

Hence, the necessity to develop the method of industrial usage of the above-mentioned technogenic waste in order to obtain vanadium pentaoxide is urgent economic and ecological problem.

Aim. To analyze technological schemes of technogenic vanadium-containing raw material processing, determine the impact of impurities content in raw material on the extraction of vanadium pentaoxide, maintain the most optimal conditions for maximum possible extraction of vanadium pentaoxide.

Main part. According to [6 – 8], the obstacle for processing of certain kinds of ashes may become the presence of alkaline metals, able to be accumulated in the water of reversible cycle. Hence, the question, regarding the possibility of utilization of certain kinds of ashes in the process of V_2O_5 production is necessary to solve along with the problem of impurities reduction, that prevent their processing [6]. Chemical composition of basic components of secondary vanadium-containing raw material is presented in Table 1.

Table 1

Chemical composition of ash from thermal power stations

Place of sample taking	Mass content of main components, %							
	V_2O_5	NiO	Fe	CaO	SiO_2	MnO	S	C
Ash of Zaporizhia TPS	27.2	5.6	9.3	5.4	17.7	0.1	6.8	2.8
Ash of Uglegirska TPS	27.0	6.6	10.5	12.0	6.8	0.05	10.2	2.6
Slime of Kyiv TPS-5	4.7	2.4	19.6	20.9	1.1	0.33	2.71	5.9
Slime of Zaporizhia TPS	7.31	0.66	31.5	17.5	5.2	0.3	5.2	2.7
Ash-slag of Uglegirska TPS	31.3	5.2	7.5	7.8	35.0	0.2	5.8	0.6

The authors of the work [2] suggest to process the waste according to technological scheme, shown in Fig. 1.

The technology of processing includes the following operations: oxidation and ash leaching, gypsum precipitation, filtration, drying and thermohydrolysis of slurry. Ash residue, grinded by roll crusher with addition of calcium hydroxide and sulphuric acid are oxidized and then are leached in autoclaves at high temperatures. Filtration and washing of slurry is carried out in cooled state with obtaining of gypsum precipitation, which is directed for recurrent filtration, adding sulphuric acid and calcium sulphate.

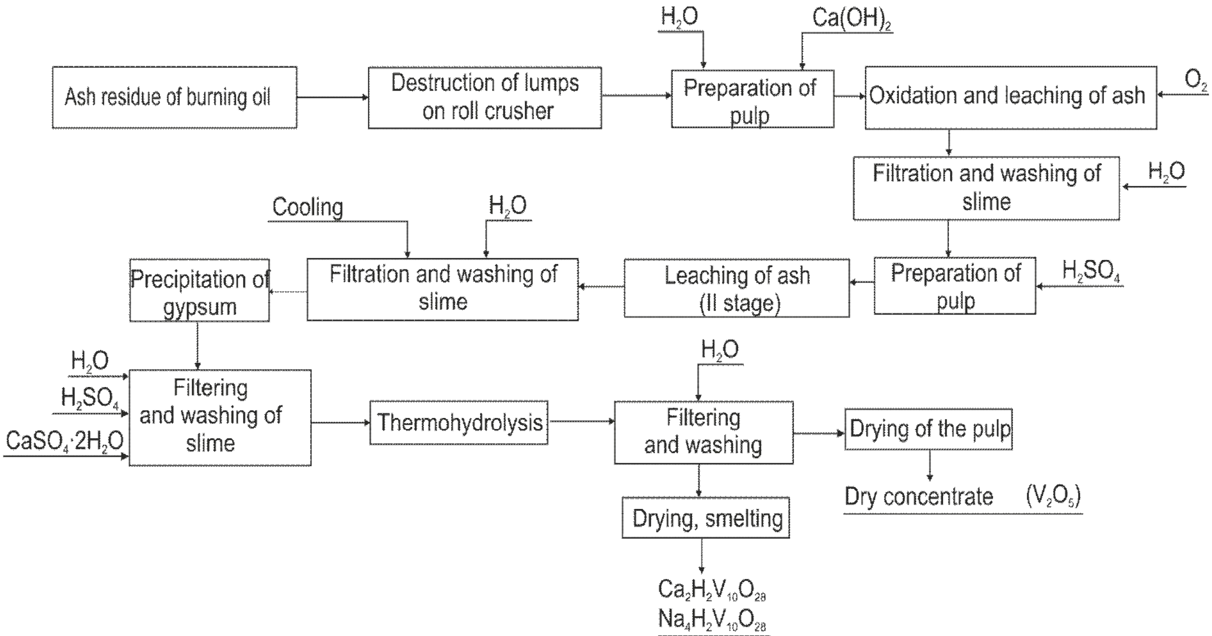

Fig. 1. Schematic technological diagram of vanadium extraction from ashes of TPS [2]

The obtained solution is sent to thermohydrolysis, after that the formed pulp is dried and dry concentrate of V_2O_5 is obtained. The given technology provides the extraction of 83…85 % of vanadium from waste.

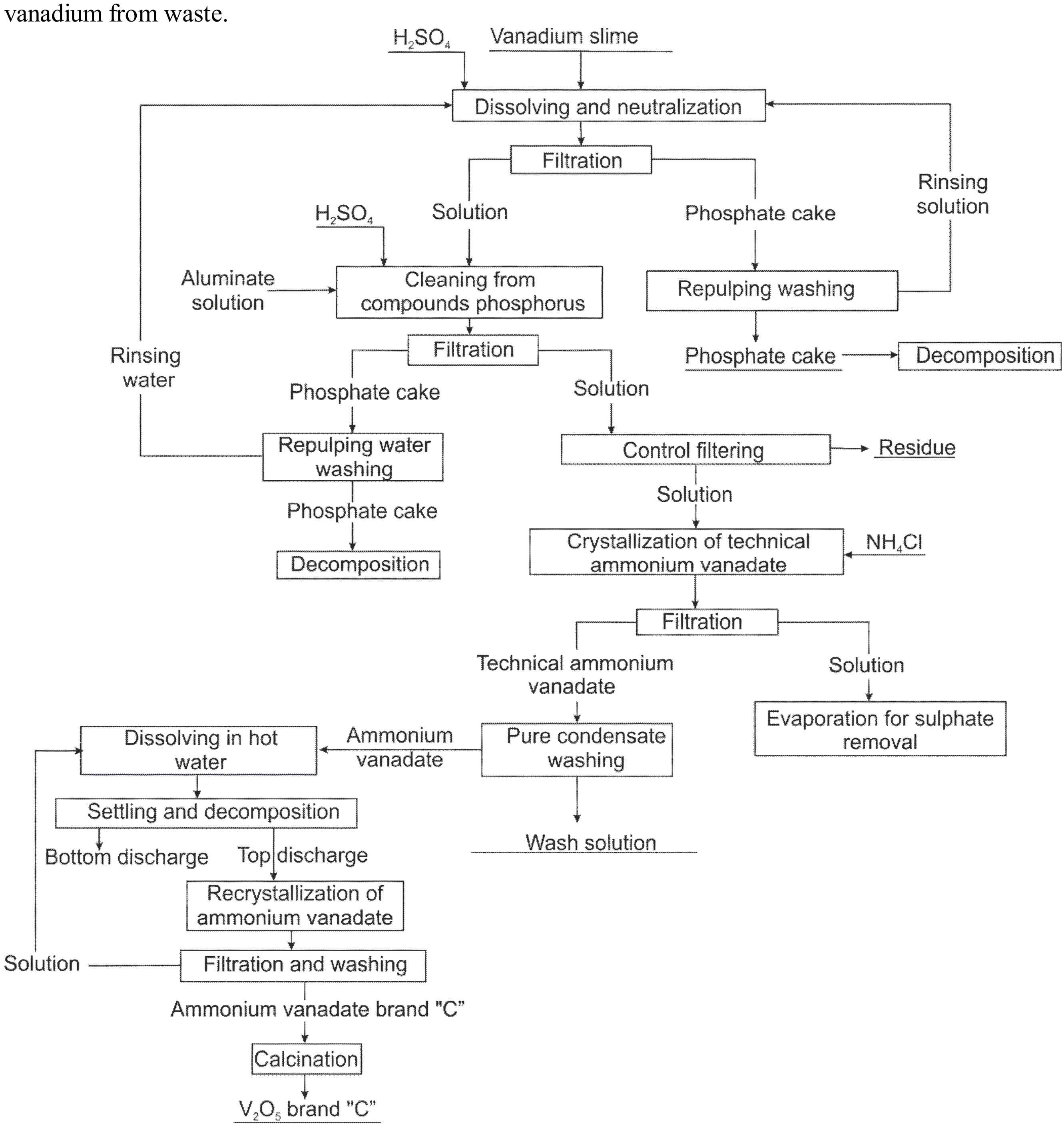

Fig. 2. Diagram of obtaining vanadium pentaoxide from slime , containing vanadium [11]

While alumina production slimes, containing V_2O_5 are formed, they can be obtained applying the method, suggest in [10] (Fig. 2). As initial product for precipitation of ammonium vanadate vanadium-containing solutions, cleared from phosphorus and aluminium compounds and other impurities are mainly used. Chemical composition of vanadium slime , obtained from the mixture of mother liquor and reversing solutions contains, in %: 13…18 of V_2O_5; 6…8 of P_2O_5; 10…13 of Al_2O_3; 30…40 of $Na_2O_{com.}$; 0.4 of SiO_2; 0.6…1.2 of As; 2.5…3 of F; 0.of 5 Pb; 0.of 8 Zn; 0.04 of Cr_2O_3; 0.5 of Fe; 0.of 2 $S_{com.}$ and others [6, 7]. Slime was subjected to water leaching and cleaning from certain impurities by means of neutralization by sulphuric acid up to pH 7…8. After pulp neutralization if the content of phosphorus pentaoxide in the solution is higher than 0.1 g/l, corresponding amount of sodium aluminate was added in the form of aluminate solution for cleaning from phosphorus [9]. Vanadium-containing solution is initial product for precipitation of technical ammonium vanadate.

The technology of vanadium-containing slime processing includes: filtration and slime precipitation, rinsing by repulping phosphate cake, crystallization and calcinations of technical ammonium vanadate. Vanadium slime is dissolved and neutralized, adding concentrated sulphuric acid and is sent for filtration, obtaining the solution, containing compounds of phosphorus and phosphate cake. The solution is cleaned from the compounds of phosphorus by filtration, obtaining technical ammonium vanadate and phosphate cake is sent for rinsing by repulping. The obtained technical ammonium vanadate is sent for crystallization with addition of NH_4Cl and filtrated until ammonium vanadate of «ч» quality is obtained, after that it is calcinated at temperature 500…550 °C, at the output the end product V_2O_5 is obtained and the solution, received after filtration, is directed for evaporation to extract sulphates. This technology provides the obtaining of pure vanadium pentaoxide at the level of 90…93 %.

Zaporizhia titanium Institute suggested the following methods of secondary technogenic raw materials processing: neutralization of aluminovanadium cake (AVC) by lime and further processing of limed cake (Fig. 3), concentration of vanadium in dry carbon cake by bituminous scheme, extraction of vanadium from technical titanium tetrachloride by stage-rectification technology [11, 12].

Chemical composition of limed cake, that arrives for processing (Fig. 3) is the following %: 24.47 of V_2O_4; 18.43 of TiO_2; 0.8 of Fe_2O_3; 56.73 of Al_2O_3; 2.57 of CaO. However, limed cake has drawbacks: it is very hydroscopic and is not a commercial product of wide application [12]. To eliminate this drawback the scheme was developed, it included the operations of washing of valuable limed cake component from chlorides, oxidizing calcinations of residues and conversion of vanadium into the form suitable for extraction.

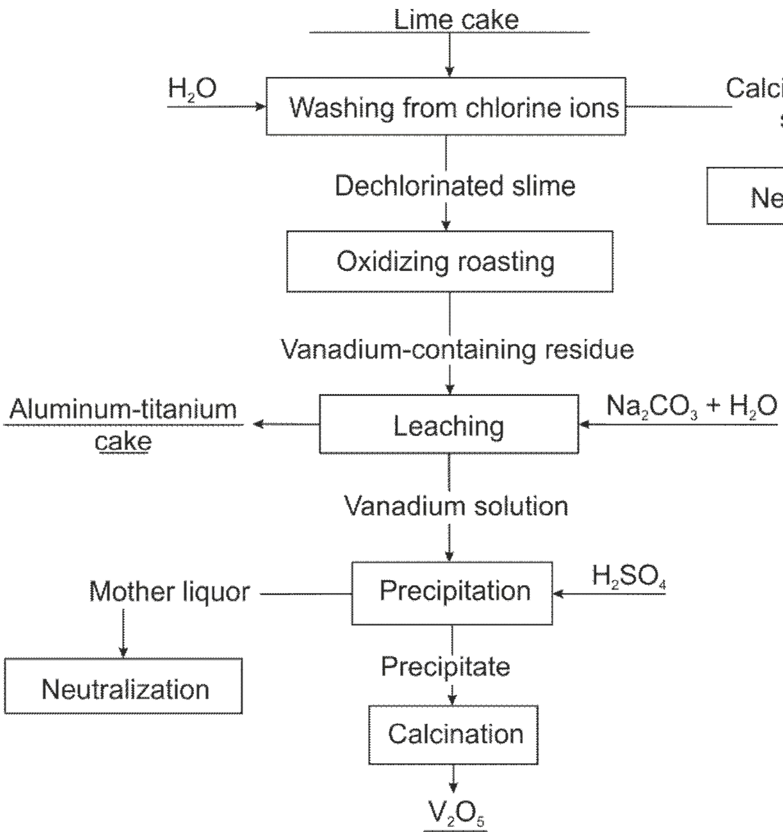

Fig. 3. Technological scheme of lime cake processing into vanadium production [12]

At the first stage water washing is performed compounds of vanadium, aluminium and titanium pass into dechlorinated slime and chlorine-ions and greater part of calcium – into solution. Dechlorinated slime is lighter material for opening (as compared with vanadium-containing slags), that allows to perform oxidizing roasting without introduction of special admixtures. Vanadium concentrate after roasting in muffle electric furnace at temperatures 700…850 °C contains, %: 21,6 of V_2O_5, 46.6 of Al_2O_3, 9.7 of TiO_2, 17. 5 of CaO, 4. 2 of SiO_2 [12]. The obtained vanadium concentrate is subjected to leaching in soda solution. At the next stage V_2O_5 precipitation from the solution, adding sulphuric acid, is performed. Precipitate is subjected to dehydration and vanadium-containing products are obtained.

The suggested technology is suitable for obtaining valuable vanadium production without formation of large amount of waste after fabrication. Laboratory research showed, that the extraction of vanadium from limed concentrate according to the given scheme is 93…95 %. In case of industrial realization of the suggested technology the accumulation of vanadium-containing waste on the polygon will be terminated, and serious obstacle on the way to the increase of the volume of titanium production on titanium-magnesium plant will be eliminated.

Conclusion. The considered schemes allow to process waste, containing 8 to 25 % of vanadium. It is established that availability of impurities in the waste of the production influences the extraction of vanadium: ashes of thermal power stations contain 5.4…20.9 % of CaO and extraction of pentaoxide from this waste is 83…93 %; slimes of alumina production contain 6…8 % of P_2O_5, and extraction of pentaoxide is 90…93 %; waste of titanium production contain 2.5…5 % of CaO and extraction of pentaoxide is 93…95 %. Thus, to increase the level of extraction of useful component from technologenic waste it is necessary, first of all, to get rid of impurities.

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