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METHODS FOR PROCESSING ASH RESIDUES OF TPS VANADIUM CONTAINING SLURRY

Application of vanadium industrial waste complex processing provides the decision of two main tasks: expanding the raw material base for extremely scarce metal and reduction of an environmental impact on nature. Combined and hydrometallurgical methods of vanadium extraction from the ash residues of TPS vanadium sludge have been developed. These methods allow to extract up to 95% of vanadium that contains in waste, and to obtain a vanadium product suitable for using in different areas of industry.

Introduction. In some industrialized countries, the number of vanadium, produced from recycled vanadium raw materials represents a significant proportion of the total produced from traditional raw materials.

Despite the fact that most of the major manufacturers of thermal energy in the Republic of Belarus are now turned to the use of natural gas, the development of methods of processing vanadium slurry (VS) of thermal power stations is relevant, since the volume of the accumulations of this type of waste in the territory of the republic are very important and at the moment, according to RUE "BRC" Ecology", account for more than 10 thousand tons. In addition, the fuel oil is a reserve fuel, the volume of its production in the country is constantly increasing and in the past three years represents about 55,500–60,000 th. tons / year [1]. For all that about 80% of fuel oil is exported and the rest is consumed by domestic enterprises. If we assume that the country consumes annually about 1,000 tons of fuel, which average ash content is 0.1% and the vanadium content in the ash in terms of V_2O_5 is 3%, then every year about 1 thousand tones of vanadium slurry including about 30 tones of V_2O_5 are produced. Relevance of the studies is also due to the fact that in recent years a number of companies in the construction industry widely use as a fuel petroleum coke, which ash content is 0.8–1.5% and the vanadium content in the ash is up to 0.1% [2–5].

In the Republic of Belarus, there are no currently commercially tested technology to extract vanadium from vanadium-containing industrial wastes. Therefore, the development of processing methods of VS provides the decision of two main objectives: expansion of the resource base on extremely scarce metal and decrease of ecological burden on the environment.

Main part. Vanadium containing ash residues formed during the combustion of fuel oil at CUE "Vitebsk confectionery factory "Vitba"(Polotsk) containing 4.56 wt. % of vanadium calculated as V_2O_5 were selected for the study.

Solubility of VS in water at different temperatures and in solutions of hydrochloric acid and sulfuric acid, ammonia, alkali of various concentration [6–8] was gravimetrically studied. It is established that most power plants slurry is soluble in hydrochloric acid, the lowest solubility is observed in the solution of ammonia, sulfuric acid and water at a temperature of 20 °C. To optimize the water consumption and the increase of the degree of separation of vanadium components the leaching process is advantageously carried out in two stages with the ratio of the solid and liquid phase of 1:5 with stirring for 10 min. Ultrasound treatment of ash suspensions in the oxidizing sulphate medium does not lead to a substantial increase in the solubility of the ash residues and the degree of extraction of vanadium compounds from them.

It is established that the optimal conditions of thermal hydrolytic extraction of vanadium compounds from leach solutions are pre-oxidation of prehydrolysis ammonium with persulfate solution at a molar ratio of n (V_2O_5): n ($(NH_4)_2S_2O_8$) = 5: 1 and with hydrogen peroxide – n (V_2O_5): n (H_2O_2) = 1: 2.

The studies allowed to propose two ∞ ways of processing ash residues of vanadium slurry of TPS: combined (Fig. 1) and hydrometallurgical (Fig. 2).

The combined process (Fig. 1) separating the vanadium containing products from TPS slurry comprises the following steps:

1) high-temperature roasting with the addition of sodium carbonate, sodium chloride, or their mixtures as a reactive additive, and mixtures of sodium chloride and ammonium persulfate;

2) leaching of the fired charge with water and solutions of sulfuric acid;

3) precipitation of vanadium compounds from solutions by thermal hydrolytic method or ammonium hydroxide.

To conduct oxidative roasting the ash is sieved beforehand, crushed and dried to constant weight at a temperature of 60 °C. A batch of ash was mixed with the reactive additive and the resulted batch was calcined in a muffle furnace at a temperature of 900 °C for 90 min. After calcination, the crucible was cooled in a desiccator. Based on the results of weighing the reaction mixture before and after the calcination was determined mass loss during sintering. Leaching of vanadium components of the sinter was carried out in aqueous electrolyte solutions in the ratio of solid and liquid phases of 1 : 10. The resulting precipitates were filtered after leaching, dried in an oven at a temperature of 60 °C and weighed.

The degree of leaching of vanadium components from VS of TPS and their degree of isolation from the resulting leach solutions was determined by gravimetric analysis and energy dispersive X-ray spectroscopy of the original ash and ash residues obtained after oxidative roasting and leaching.

It was established that sinters obtained at high calcination mixture containing sodium chloride also possess the highest solubility, which is apparently due to the good solubility of the metal chlorides comprising the vanadium-containing slurries.

The maximum solubility (more than 40% of the original batch weight) was observed for the sinters obtained for the batches of the following compositions: ash and NaCl (mass ratio of 1 : 1); ash, NaCl and $(NH_4)_2S_2O_8$ (mass ratio of the components 5 : 4 : 1). It should be noted that the solubility in water of the sinters obtained from a batch containing ammonium persulfate exceeds the solubility of a 1 M solution of sulfuric acid, which is due to the formation of sparingly soluble sulfates of metals present in the ash.

The degree of leaching of vanadium components according to the studied schemes of vanadium containing processing slurry of power stations based on V_2O_5 varies from 40 to 95%. The minimum degree of leaching is observed when processing with water sinters obtained by firing batch containing ash, NaCl and $(NH_4)_2S_2O_8$ in a weight ratio of components 5: 4: 1. The maximum degree of leaching is observed when processing 1 M H_2SO_4 sinters obtained by firing batch containing ash, Na_2CO_3 and NaCl in a weight ratio of components 2 : 1 : 1.

The vanadium content in the isolated from the leaching solution product depends upon its method of extraction and ranges from 1.3 to 10.0 %. Reuse of leach solutions allows to obtain a more concentrated solution on a vanadium component and increase vanadium content in the isolated product to 25–30%. (The radiophase analysis) RPA data indicate that the isolated product is a sodium magnesium vanadate ($NaMg_4(VO_4)_3$).

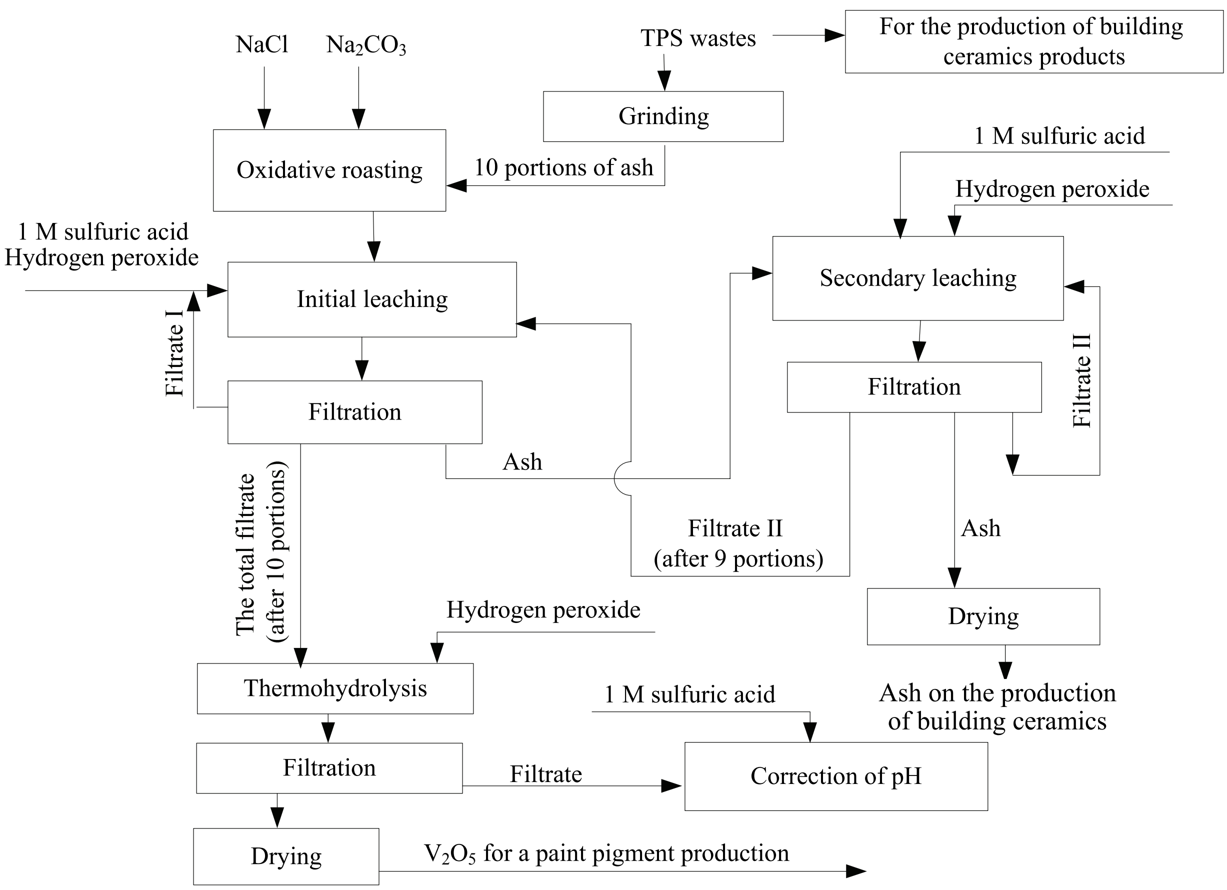

Fig. 1. Scheme of processing ash residues generated during the combustion of fuel oil by the combined method

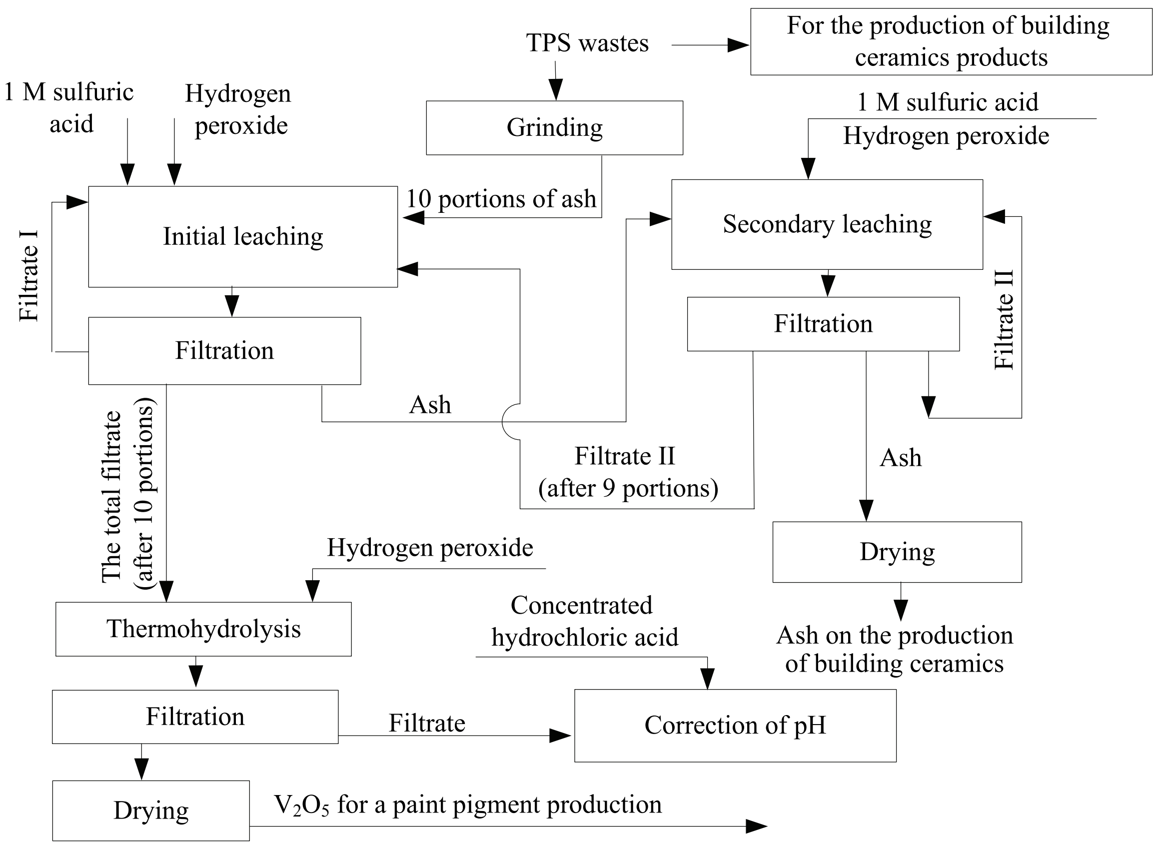

Fig. 2. Scheme of processing ash residues from the combustion of fuel oil by the hydrometallurgical method

Hydrometallurgical method for processing vanadium slurry comprises the following steps (Fig. 2):

1) grinding the raw material;

2) a two stage leaching of vanadium components from ash residues by hydrochloric acid solution with added hydrogen peroxide (pH 1–2);

3) filtering;

4) the allocation of vanadium compounds from leaching solutions by thermal hydrolytic method;

5) separation of V_2O_5 from solution;

6) drying of the precipitate and dedicated V_2O.

To optimize the water consumption and increase the degree of separation of the vanadium component of ash residues leaching process is carried out in two stages with the ratio of the solid and liquid phase of 1:5 with stirring for 10 minutes. After the initial leaching ash was filtered and sent to the secondary leach. After the second leaching the ash was filtered and dried in an oven. For higher concentration of vanadium compounds in solution and to optimize the flow of reagents at each step after separation of the precipitate the filtrate was reused for dissolving new ash portions.

After processing, 5–10 portions of ash (one processing cycle) collected filtrates of primary and secondary leaching are mixed and oxidized by hydrogen peroxide and are processed by thermohydrolysis. Thermohydrolysis is carried out at a temperature of 80–90 °C for 5–10 min. Pre-oxidation of leaching solutions with hydrogen peroxide leads to an increase in the rate of precipitation up to 60%.

The resulting precipitate was filtered and dried at a temperature of 60 °C to constant weight. The content of vanadium (calculated as V_2O_5) in the isolated product depends on the composition of vanadium-containing slurry and can reach 85 wt. %, which corresponds to the specifications of active agent.

For subsequent processing cycles the secondary leaching is carried out by recycled filtrate obtained after thermal hydrolysis, and the primary one by the filtrate obtained after the secondary leaching. The required amount of hydrogen peroxide is previously introduced in the solutions and the pH-value is correctied.

Hydrometallurgical method designed for processing TPS slurry allows you to extract up to 95% of vanadium compounds. The calculation of basic ecological and economic performance of environmental measure showed that its implementation is economically and environmentally efficient.

Conclusion. Thus, studies have shown the application possibility of combined and hydrometallurgical processes for recycling vanadium ash residues of slurry waste generated from the combustion of fuel oil at the thermal power stations. Unlike combined, hydrometallurgical process has several advantages: it is simple to implement, requires no special equipment, its use helps prevent the formation of toxic gases, to apply the available solutions of electrolytes, reuse working solutions, develop closed recycle "leaching-regeneration of working solutions". The proposed methods are environmentally safe, they allow to allocate up to 95% of vanadium contained in industrial waste, and to receive commercial vanadium containing product – suitable for further use in different areas of industry.

References

1. Производство важнейших видов промышленной продукции в 2013 году. Оперативные данные // Национальный статистический комитет Республики Беларусь: сайт. Минск, 2013. URL: http://belstat.gov.by/homep/ru/indicators/industrial_output.php (дата обращения: 11.11.2013).

2. Сюняев З. И. Производство, облагораживание и применение нефтяного кокса. М.: Химия, 1973. 295 с.

3. Гунько И. М. Анализ техногенных источников и технологических схем производства пентаоксида ванадия / Запорожская государственная инженерная академия. Запорожье, 2011. 8 с.

4. Тенденции и перспективы вовлечения в промышленный оборот ванадийсодержащих отходов топливно-энергетического комплекса / А. А. Фофанов [и др.] // Химия, технология и промышленная экология неорганических соединений: сб. науч. тр. / Пермский гос. нац. исслед. ун-т. Пермь, 2001. Вып. 4.

5. Уфимцев В. М., Капустин Ф. Л., Пьячев В. А. Применение нефтекокса в производстве вяжущих материалов / Международное аналитическое обозрение: Цемент. Бетон. Сухие строительные смеси. 2008. № 2. С. 39–43.

6. Возможность использования гидрометаллургических методов для переработки ванадийсодержащих шламов ТЭС / С. Е. Орехова [и др.] // Свиридовские чтения: сб. ст. 2012. Вып. 8. С. 50–57.

7. Выделение ванадийсодержащих продуктов из шламов теплоэлектростанций / И. М. Жарский [и др.] // Труды БГТУ. 2013. № 3: Химия и технология неорганических веществ. С. 3–8.

8. Vanadium-containing wastes recycling for enterprises using fuel oil: high expectations / I. M. Zharski [at al.] // Proceedings of BSTU. 2012. No. 3: Chemistry and Technology of Inorganic Substances. P. 3–6.

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