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ENVIRONMENTALLY SAFE TECHNOLOGY FOR PREPARING METAL OXIDE ANODE

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Abstract The article is devoted to the development of low - waste environmentally safe technology for the production of combined metal oxide anodes. Low waste is realized due to recycling of nitrogen oxides and heavy metal compounds. It is established that the depth of purification of air from nitrogen oxides with water with neutralization of nitric acid with manganese carbonate exceeds 95 %. It was determined that the residual concentrations of heavy metals of lead and copper in treated wastewater do not exceed, respectively, 0.002 and 0.06 mg/m^3. The resulting manganese nitrate and lead and copper hydroxides are returned to anode production.

Keywords: metal oxide anodes, manganese and lead oxides, waste recycling, purification from nitrogen oxides and heavy metal ions.

1. Introduction

Electrochemical processes are used in many technologies. They have many advantages over chemicals – low waste, easy control, minimization of the amount and increase in the efficiency of reagents, etc. In some cases, electrochemical treatment is generally unalterable. Thus, purifying highly mineralized waters and brines from iron and sulfide compounds is otherwise ineffective (Mykhaylenko et al., 2021).

Therefore, there is a need for relatively cheap and at the same time relatively stable metal oxide anodes that do not contain precious metals and their compounds.

2. Experimental part

There is a method of manufacturing low-wear metal oxide anodes (UA Pat., №124996, 2021). The method consists of the deposition on a titanium base of a layer of manganese dioxide by thermal decomposition of manganese nitrate at a temperature of 400^{0}C according to the reaction:

$$Mn(NO_3)_2 \rightarrow MnO_2 + 2\ NO_2\uparrow.$$

After that, the resulting blank is covered with a thin (0.3–0.5 mm) layer of lead dioxide from an alkaline complex electrolyte. The composition of the solution – NaOH – 2 mol/dm^3; 2Na – salt of ethylenediaminetetraacetic acid – 0.6 mol/dm^3; ethylene glycol – 0.1 mol/dm^3; PbO - to saturation. The electrolyte temperature is 600°C, the anode current density is 100 A/m^2, and the deposition time is 7–11 hours. The electrolyte is fed with lead oxide monoxide. To suppress the formation of bottom deposits of mixed oxides, lead metal lead with a surface that is not less than 6 times larger than the surface of the anodes is immersed in the electrolyte. After thorough rinsing with water, the workpiece is covered with a thick (4 - 5 mm) layer of lead dioxide

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from the acid nitrate electrolyte. The composition of the electrolyte - Pb $(NO_3)_2$ – 1 mol/dm^3; $Cu(NO_3)_2$ – 0.4 mol/dm^3; $Al(NO_3)_3$ – 0.2 mol/dm^3; HNO_3 – 0.1 mol/dm^3; gelatin – 0.5 g/dm^3. Electrolysis temperature – 60 ^{0}C, Anode current density – 500–1000 A/dm^2. Coating build-up speed – 0.2–0.29 mm/h. The schematic diagram of obtaining metal oxide anodes is shown in Fig. 1.

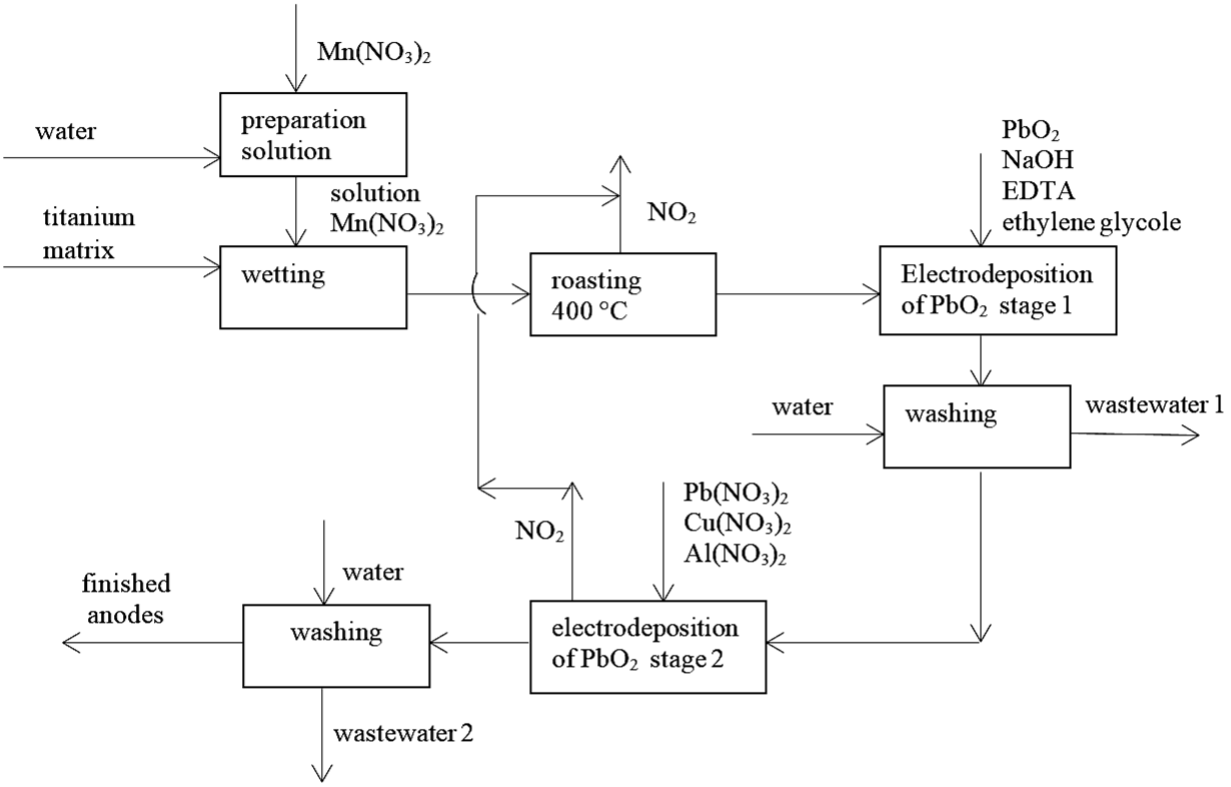

Fig. 1. Schematic technological scheme of manufacturing metal oxide anodes

This complex technology of double electrodeposition of PbO_2, first from alkaline complex and then from acidic nitrate electrolytes, is due to the following factors.

In the electrolysis of nitrate and other acid-containing electrolytes, the PbO_2 release potential is reached after the oxygen release potential. Therefore, lead dioxide and oxygen are simultaneously released at the anode from such electrolyte, and the predominant release of PbO_2 is due to significant oxygen overload. But when using a titanium base pre-coated with manganese dioxide, the anode process takes place on the MnO_2 layer, which is one of the few materials on which the anodic release of oxygen is facilitated. Therefore, it is necessary to give too high current densities (more than 10000 A/m^2) to start the separation of lead dioxide from acidic electrolytes in the MnO_2 sublayer.

In contrast to acidic solutions, the release of lead dioxide from the alkaline complex electrolyte begins before the oxygen release potential is reached. Therefore, at low current densities (100–200 A/m^2) deposition at the PbO_2 anode occurs without the release of oxygen. And after the MnO_2 layer is completely covered by PbO_2, you can proceed to the electrodeposition of the main coating layer of nitrate electrolyte. At the same time, such double coating of the base with two layers of PbO_2 minimizes the use of alkaline complex electrolyte. Alkaline complex electrolyte for PbO_2 precipitation has many technological advantages over nitrate. PbO_2 precipitate is dense with a metallic lustre, it has virtually no internal stresses. In addition, the electrolyte is easy to work with, and most structural materials in it are stable. However, this electrolyte has one drawback - it is kinetically unstable. During electrolysis, a small proportion of tetravalent lead in the form of hydroplubate anion $HPbO_3$ remains in the solution, and after accumulating over several hours in interaction with plumbite ions, it forms mixed oxides of lead of variable composition. These oxides are deposited on all surfaces immersed in the electrolyte and, above all, on the anodes. They are included in the coating and destroy it. Immersion of metal lead in the electrolyte

significantly slows down the accumulation of seals but does not completely suppress it. Therefore, the use of an alkaline complex electrolyte only for the deposition of a thin layer of PbO_2 can significantly extend the period of its use until the periodic chemical neutralization of the accumulated seals.

This technology allows the manufacture of anodes that are stable at any pH of the environment and can be used in the processes of electrochemical treatment of solutions. Their production is associated with the formation of emissions of nitrogen oxides during the coating of manganese dioxide and lead. Also, during the washing of blanks and finished anodes, wastewater containing heavy metal compounds is formed.

Fig. 2 shows a photo of a bench installation for coating titanium plates with lead dioxide and its electrode unit and Fig. 3 – a photo of a titanium plate and finished anode.

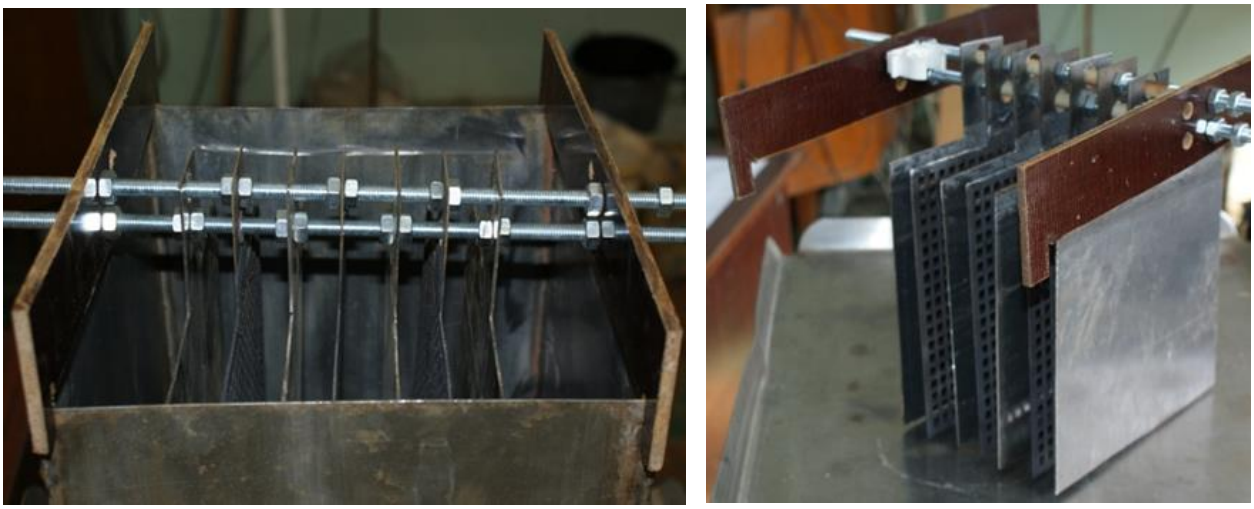

Fig. 2. Bath for electrodeposition of PbO_2 coating and electrode unit (right)

Fig. 3. Basis for the manufacture of bench anodes and the finished anode

3. Results and Discussion

Further research aimed to increase the environmental safety of the method of obtaining low-wear metal oxide anodes. This goal is achieved by cleaning emissions and effluents and reusing the products. There is a method of purification of gaseous emissions from nitrogen oxides by catalytic oxidation and reduction in the gas phase (Ru. Pat. № 2676642, 2019). It consists of passing a stream of polluted gas through an adsorbent that includes manganese dioxide as a catalyst for redox processes. In this case, nitrogen oxides are reduced to molecular nitrogen and thus neutralized. The disadvantage of this method is the inactivation of nitrogen oxides.

The technology of absorption of nitrogen oxides from the gas phase with water with the formation of nitric acid is known (Ru. Pat. №2470856, 2012). The disadvantage of this technology is the low degree of the capture of nitrogen oxides from the gas phase, which does not exceed 72 % (Zabelin, 2003).

To increase the degree of the capture of nitrogen oxides to the gas mixture to be cleaned, ozone is added for better oxidation of nitrogen oxides (Ru. Pat. № 2100058, 1997, Ru. Pat. № 2686037). However, this does not sufficiently increase the degree of absorption of nitrogen oxides as they are poorly soluble in the solutions of nitric acid which is formed during the purification process.

To transform the technology of obtaining stable metal oxide anodes into environmentally friendly ones, nitrogen oxide emissions are sucked out together with air and passed through water. At the same time, there is an absorption of nitrogen oxides with the formation of nitric and nitric acids, which in case of their accumulation inhibit their further absorption. To reduce the concentration of free nitric acid, it is neutralized with manganese carbonate powder, and this significantly deepens the degree of purification of the air from nitrogen oxides. At the same time, nitric acid is oxidized by air oxygen and converted into nitric acid. The manganese nitrate solution formed during the neutralization of nitric acid is then used to wet the new titanium bases to obtain new anodes.

The residual concentration of nitrogen oxides in the inlet air was experimentally established – 55 mg/m^3; in purified air – less than 2 mg/dm^3, i.e., the degree of purification is 95–98 %.

The addition of hexavalent chromium compounds (Torosyan, 2014) or 8-oxyquinoline (Ru. Pat. № 2019523, 1994) is sometimes used to treat lead-containing wastewater. However, such methods involve the formation of lead-containing sediments that are difficult to dispose of.

To increase the environmental safety of the technology of obtaining anodes, wash water, after the deposition of the coating of alkaline and acid electrolytes are mixed and mutually neutralized. After subsequent adjustment of the pH of the mixed water to pH = 5.8–6.2, the precipitate of hydroxides of lead, copper and aluminum is separated and used to feed the nitrate electrolyte.

These pH limits are due to the fact that at a pH of below 5.8, complete precipitation of hydroxides of these metals is not achieved. At a pH of more than 6.2, the solubility of lead and copper increases due to the formation in the alkaline environment of a complex compound of the corresponding metals with EDTA. If the pH of water is within these limits, experimentally established residual concentrations of soluble forms of copper and lead in wastewater do not exceed respectively 0.06 and 0.002 mg/dm^3.

The scheme of realization of the offered ecologically safe technology of reception of metal oxide anodes is given in Fig. 4.

The titanium base is wetted with a solution of manganese nitrate and sent for calcination at a temperature of 4000 ^{0} C. Next, the base covered with a layer of manganese dioxide is fed to the coating with a thin layer of lead dioxide by electrodeposition from an alkaline complex electrolyte. The base covered with a thin layer of PbO_2 is thoroughly washed with water and fed to the coating with a thick layer of PbO_2 by electrodeposition of nitrate electrolyte. After thorough rinsing with water, we obtain a metal oxide anode.

Gas emissions of nitric oxide NO_2, formed during the calcination of the base after wetting with manganese nitrate, and formed at the cathode during electrodeposition of the main layer of PbO_2 due to the cathodic reaction

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2\uparrow + 2H_2O,$$

are sucked together with air and fed to the scrubber for absorption by water to prepare a solution of manganese nitrate $Mn(NO_3)_2$. Due to the reaction

$$4NO_2\uparrow + 2H_2O + O_2 \rightarrow 4HNO_3$$

free nitric acid is formed in the water, which inhibits the further absorption of nitric oxide. To improve the purification of the air from nitrogen dioxide, the

formed nitric acid is neutralized with manganese carbonate powder according to the reaction

$MnCO_3 + 2\ HNO_3 \rightarrow Mn(NO_3)_2 + CO_2\uparrow + H_2O$.

The resulting manganese nitrate solution is used to wet new titanium bases before calcination.

The wash water after electrodeposition of lead dioxide from both alkaline complex and acid nitrate electrolytes is mixed, and their mutual neutralization occurs. After that, the wastewater is further neutralized with hydrochloric acid or sodium carbonate to reach pH = 5.8–6.2. Hydroxides of lead and copper are separated, washed with water and added to the acid nitrate electrolyte to feed it during the electrodeposition of new metal oxide anodes.

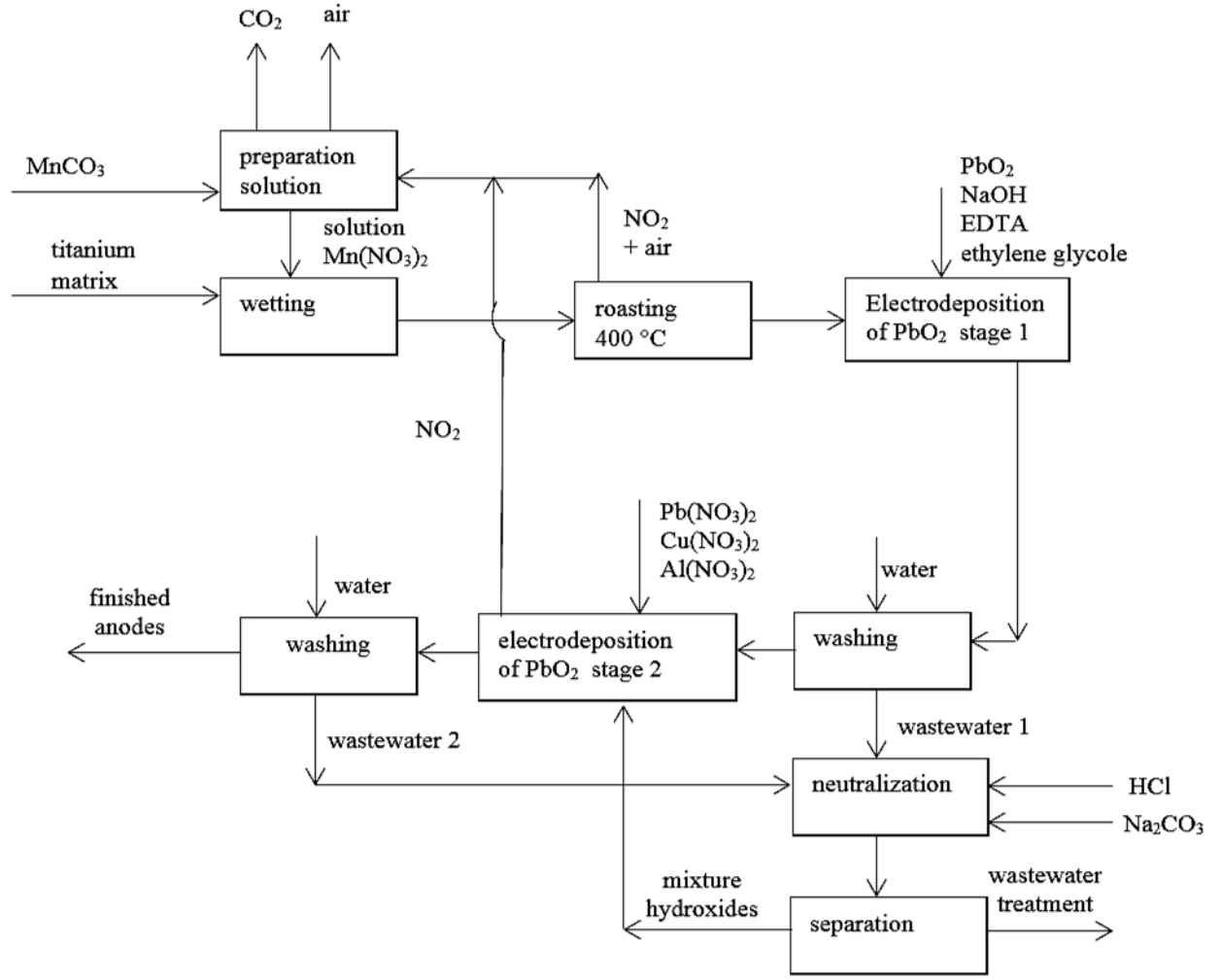

Fig. 4. Cyclic environmentally friendly technology for the manufacture of metal oxide anodes

4. Conclusion

1. Low-waste environmentally friendly technology for the production of combined metal oxide anodes has been developed. Low waste is realized due to the recycling of nitrogen oxides and heavy metal compounds.

2. It is established that the depth of purification of air from nitrogen oxides with water with neutralization of nitric acid with manganese carbonate exceeds 95 %.

3. It is determined that the residual concentrations of heavy metals of lead and copper in treated wastewater do not exceed, respectively, 0.002 and 0.06 mg/m^3.

5. Acknowledgements

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References

Barabash, I. G., Kustanovich, G. M., Onishchenko, G. D., & Kretova,O. N (2012). *Ru. Patent No 2470856*.

Djangiryan, V. G., Krivenko, I. V., & Namestnikov, V. V. (2019). *Ru. Patent No 2686037*.

Lukanin A. V., Solomaha G. P., & Tarasova, T. A. (1997). *Ru. Patent No 2100058*.

Mahnin, A. A., Belorossov, E. L., & Frolova, E. A. (1994). *Ru. Patent No 2019523*.

Mykhaylenko, V. G., Hil, Z. P., Lukyanov, Ye. F., Lukyanova, O. I. & Khinnyevich, O. Ye. (2021). *UA Patent No 124996*. Ukrainskyi instytut intelektualnoi vlasnosti (Ukrpatent).

Mykhaylenko, V., Yurchenko, V., Antonov, O., Lukianova, O., & Gil, Z. (2021). Advanced Technologies For Processing Liquid Waste Of Galurgical Productions. *Environmental Problems*, *6*(1), 1–6. doi: https://doi.org/10.23939/ep2021.01.001

Tkachenko, I. G., & Shablya, S. V. (2019). *Ru. Patent No 2676642*.

Torosyan, V. F., Torosyan, E. S., & Belskih, T. B. (2014). Treatment of wastewater from lead compounds metered addition of solutions with compounds of hexavalent chromium. Technology of technosphere safety, 4(56). Retrieved from htpp://ipb.mos.ru/ttb

Zabelin, L. V. (2003). Air purification from acid emissions in the production of cellulose nitrates. *Izvestiya Tomskogo Politehnicheskogo Universiteta*, *306*(1), 83–88.