Use of Electrochemical Methods in the Establishment of Low-Waste Production

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Abstract

The possibility of a substantial decrease in the amount of industrial wastes by supplementing the technological process with the stages performed by means of electrolysis was demonstrated for the examples of processes of isolation of elemental arsenic from the aqueous solutions of sodium arsenite, syntheses of the esters of phosphic acid from elemental phosphorus, obtaining arsenic acid by the electrolysis of a suspension of arsenic (III) oxide, synthesis of azodicarbonamide, ketopanlactone and arsine.

INTRODUCTION

As a result of the work of many years aimed at the establishment of low-waste production, we stated that in order to solve the formulated problem it is reasonable to use electrochemical methods, which allows one in some cases to achieve a substantial decrease in hazardous emissions in industrial processes and decrease the amount of industrial waste. Some routes allowing one to solve the indicated problem may be shown.

ESTABLISHMENT OF A CLOSED CYCLE AS A RESULT OF REAGENT RECOVERY

When considering the scheme of extermination of lewisite, a technology of the isolation of elemental arsenic from the reaction mass was proposed; it excludes the disposal of toxic arsenic-containing wastewaters. The essence of the proposed process is as follows [1].

The simplest way to exterminate lewisite is its alkaline hydrolysis proceeding according to equation

$$AsCl_2(CHCHCl) + 6NaOH \rightarrow Na_3AsO_3 + CH{=}CH + 3NaCl + 3H_2O$$

The reaction proceeds violently with the evolution of a large amount of heat. One can see in the equation that hydrolysis results in the formation of acetylene, aqueous solution of sodium arsenite and chloride.

Concentrating hydrolyzate by evaporation one may precipitate the major part of sodium chloride and use it afterwards to make an anolyte.

One of the ways to extract arsenic from thus obtained solution of sodium arsenite is electrolysis [2–4]. Sodium arsenite is reduced at the cathode in weakly alkaline solutions according to equation

$$Na_3AsO_3 + 3H^+ + 3\bar{e} \rightarrow As + 3NaOH$$

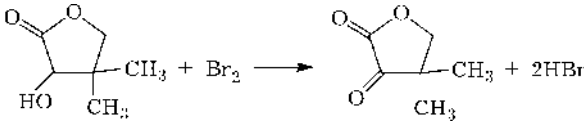
As a side reaction, reduction of sodium arsenite to arsine (AsH_3) occurs. The ratio of elemental arsenic to arsine depends on temperature, concentration of sodium arsenite in solution, current density and cathode material. Under the conditions when the maximal substance yeild of arsenic is achieved (95–96 %), the yield of arsine does not exceed 4 %. Pyrolysis of arsine allows obtaining the high-purity arsenic.

It is reasonable to perform the electrochemical recovery of arsenic in an electrolyzer with a cation-exchange membrane using the sodium

chloride solution formed at the stage of evaporation of the reaction mixture as an anolite. In this case, chlorine will be liberated at the anode, while the equivalent amount of sodium hydroxide will be accumulated in the cathode chamber. The solution containing sodium hydroxide, residual amount of sodium arsenite and chloride is returned to the hydrolysis of a fresh portion of lewisite after the removal of arsenic by filtering.

So, a closed cycle is performed without disposal of arsenic-containing wastes, which is important because the compounds of As(III) are highly toxic. This process was recommended for industrial application.

Another example of the efficiency of electrochemical regeneration may be the synthesis of ketopantolactone [10], a promising preparation for pharmaceutical industry. A known method of its synthesis is oxidative dehydrogenation of pantolactone proceeding under the action of free bromine:



It follows from this equation that an equivalent amount of hydrogen bromide is formed in the process; this is a difficultly disposable waste product.

Technological consideration showed that, unfortunately, the attempt to recover bromine directly during dehydrogenation from the reaction mixture was not successful. So, regeneration of bromine in a separate apparatus was used instead. Dehydrogenation of pantolactone is carried out in chloroform under illumination with an incandescent lamp in the presence of a small amount of water. Hydrogen bromide formed in the reaction is extracted with water. The aqueous layer of the hydrogen bromide solution is distilled to separate the tarring products and admitted into the anode chamber of electrolyzer for electrolysis. At the graphite anode with the current density of ≈ 1 kA/m^2, the yield of bromine as a function of current approaches the quantitative one. The anolyte circulates continuously during electrolysis with the help of a rotary pump through the extractor in which bromine evolved at the anode is extracted with a fresh portion of chloroform. The solution of bromine in chloroform is directed to the subsequent synthesis of ketopantolactone.

A stable yield of ketopantolactone (about 88 % for substance) was obtained with the help of the developed technological scheme; the loss of bromide due to its volatility does not exceed 2 %. The only waste product of the production is tar-like matter formed during dehydrogenation.

USE OF HALOGEN AS MEDIATOR

An extremely simplified version of the recovery of a reagent is its electrochemical recovery directly during synthesis. The most vivid example is the use a halogen that acts in this case as a mediator, or transferring catalyst.

We developed an ecologically safe method of obtaining arsenic acid [4, 7, 8], which is used in the synthesis of arsenates, organoarsenic compounds, *etc.* A classical method of its synthesis which is based on the oxidation of arsenic (III) oxide with nitric acid does not allow one to obtain sufficiently pure arsenic acid and is accompanied by a substantial amount of nitrogen oxides.

Another method, which involves hydrogen peroxide as an oxidizer, though substantially eliminates the disadvantages of the classical procedure, still causes some difficulties in the apparatus arrangement because the reaction proceeds with the substantial heat evolution and may attain explosion-like character in case of any mistakes in reagent dosing.

The developed electrochemical method of obtaining pure arsenic acid involves electrolysis of a suspension of As_2O_3 in diluted (2–3 %) hydrochloric acid in an electrolyzer with a cation-exchange membrane.

Electrolysis involves discharge of chloride ions at the anode; elemental chlorine is formed. It acts as an oxidizer. The overall process scheme can be represented as follows:

$$2Cl^- - 2\bar{e} \rightarrow Cl_2$$

$$As_2O_3 + 2Cl_2 + 5H_2O \rightarrow 2H_3AsO_4 + 4HCl$$

Chloride ions are not consumed in this process; instead they act as a transferring

catalyst (mediator). As a result of electrolysis, aqueous solution of arsenic acid containing hydrochloric acid is formed. This solution is evaporated under not very high vacuum till dry, then hydrochloric acid is distilled. The residue is pure arsenic acid. Pure arsenic (V) oxide can be obtained by calcination of arsenic acid at 250–300 °C. The yield is 95–98 % (substance) and the yield as a function of current is up to 95 %.

The distilled hydrochloric acid may be returned after some correction into the cycle in order to prepare an electrolyte for electrochemical oxidation of the next portion of arsenic (III) oxide. So, arsenic (III) oxide and water are consumed in the process. Hydrogen chloride is to be added only in the amounts necessary for the compensation of inevitable losses in technological operations. Only hydrogen formed at the cathode can be considered as a waste product.

Together with the Ufa Institute of Herbicides and Plant Growth Regulators, we developed [9] a low-waste method of synthesis of azodicarbonamide, an efficient foaming agent for plastics. Its application is based on its ability to decompose at a temperature above 180 °C forming a large amount of gaseous products.

The first stage of obtaining azodicarbonamide is the interaction of urea with hydrazine hydrate; hydrazodicarbonamide is formed. It is subjected to dehydrogenation by the interaction with chlorine or bromine. As bromine allows one to obtain the product of better quality, its application as a dehydrogenating agent is preferable. Dehydrogenation of hydrazodicarbonamide proceeds according to equation

$$H_2NC(O)NH{-}NHC(O)NH_2 + Br_2 \rightarrow H_2NC(O)N{=}NC(O)NH_2 + 2HBr$$

Electrochemical process allows one to minimize the consumption of bromine in this reaction. The source of bromine in the developed process is potassium bromide; its electrolysis results in the evolution of bromine at the cathode according to reaction

$$2Br^- - 2\bar{e} \rightarrow Br_2$$

Usually it is recommended to use graphite electrodes for the anode evolution of bromine, buts tests showed that graphite, though to a small extent, is destroyed with the formation of graphite dust, which contaminates the product. An alternative route, which is the use of oxide ruthenium-titanium anode (ORTA), turned out to be unsuitable due to the depassivation of titanium basis by bromine. Because of this, the permissible concentration of potassium bromide in the concentrated solution of sodium chloride was determined, so that no destruction of the titanium basis would occur.

It was established in the development of the technological arrangement of the process that organic compounds present in the solution and in suspension form are almost unreduced at graphite and titanium. This allowed us to use a simple diaphragm-free electrolyzer. On an industrial scale, enamelled apparatus with a volume of 100 l was used as electrolyzer. The positions of the electrodes were concentric; cathodes were made of titanium VT-1 and anodes of ruthenium and titanium oxides (ORTA). The interelectrode gap was 3.0–3.5 mm. Tests showed that when the optimal electrolysis conditions are met (pH 1–1.5, temperature 40–50 °C, current density 1 kA/m^2), the yield of azodicarbonamide as to substance reaches 90–92 %. Since azodicarbonamide is almost insoluble in the electrolyte, it is separated by ordinary filtering and the filtrate after the corresponding correction is returned to the next operation. A five-fold recycle of the solution allows one to decrease the consumption of potassium bromide and the amount of waste products almost by a factor of 4 in comparison with the chemical method, and to improve the quality of the resulting product.

ELIMINATION OF INTERMEDIATE STAGES

There are processes in chemical technology in which the intermediate compounds are the halogenated ones. In the subsequent stages a halogen is removed (usually in the form of hydrogen halide) and are not incorporated in the product. These processes lead to the formation of a large amount of difficultly utilizable wastes. In this case, the synthesis may be performed in one stage with the help of electrolysis.

An example may be the synthesis of the esters of phosphoric acid (trialkyl phosphates). These compounds are widely used as solvents,

heat carriers, extragents, plasticizing agents and fireproofing compounds.

At present, almost all the trialkyl phosphates are manufactured by the traditional method involving alcoholysis of phosphorus oxytrichloride, which is prepared by oxidizing trichloride synthesized by the interaction of white phosphorus with chlorine. The multistage character of the process and the large amount of wastes are remarkable, because the whole amount of chlorine consumed to obtain phosphorus trichloride at the stage of alcoholysis turns into hydrogen chloride or chlorides.

Much attention is attracted, both in the technological and in the ecological aspects, to the direct methods of synthesis of trialkyl phosphates from elemental phosphorus and the corresponding alcohol. Since white phosphorus is manufactured from the mineral raw material, it is the cheapest material for the production of organophosphorus compounds.

For several years, we studied the possibility to synthesize trialkyl phosphates by the electrochemical method using white phosphorus. As a result, we have developed essentials of the electrochemical synthesis of triethyl phosphate at the scale of a laboratory set-up according to the reaction

$$P_4 + 12ROH + 4H_2O \xrightarrow{\pm 12\bar{e}} 4(RO)_3PO + 10H_2$$

Using this version we obtain an insignificant amount of wastes. Electrosynthesis is carried out in alcohol with the addition of a small amount of water in a flow diaphragm-free electrolyzer equipped with the graphite anode and cathode. Hydrogen chloride is used as an electrolyte.

In this case chloride ion formally acts as a mediator, too, though the mechanism of the process is much more complicated than that in the above-described examples. Some amount of hydrogen chloride is consumed for the formation of the side product – ethyl chloride, which is also formed in the traditional method of obtaining triethyl phosphate.

As a result of experiments, the apparatus is proposed which provides minimal fire risk of the process and allows one to perform electrolysis in the continuous mode. The apparatus and technological scheme of electrosynthesis and isolation of triethyl phosphate in the continuous mode is presented. The yield of triethyl phosphate is more than 95 % as to substance and more than 80 % as to current.

Preliminary economic estimation of the production of triethyl phosphate using the electrochemical method showed that the net cost of the product is 1.5–2 times lower than that in the case of the traditional method. The consumption of direct current energy is 3.5–3.8 thousand kW · h per one ton of triethylphosphate.

The process was patented in Russia [5] and claimed for patenting in Germany [6].

The developed method of electrosynthesis of triethyl phosphate was tested for the synthesis of esters of phosphoric acid with the general formula $(RO)_3PO$ where $R = C_nH_{2n+1}$ ($n = 1–5$). The process is based on the electrolysis of a solution of white phosphorus in the corresponding alcohol.

The results of investigations allow us to develop electrochemical methods for obtaining phosphorous acid, dialkyl phosphites, phosphonates and other organic compounds of phosphorus from white phosphorus.

PERFORMANCE OF THE PROCESSES UNPERFORMED BY THE CHEMICAL METHOD

The use of electrolysis allows one to perform the processes that cannot be carried out by means of the chemical interaction of reagents. The products synthesized using this method are obtained in industry in several stages with the formation of a large amount of wastes.

For instance, to manufacture highly pure arsine, magnesium arsenide is synthesized and its acidic hydrolysis and low-temperature rectification are carried out in order to remove impurities. Since arsenic-containing compounds are toxic, it is necessary to establish low-waste technologies with the minimal amount of wastewater. In order to solve the formulated problem, electrochemical methods realized at room temperature and atmospheric pressure are promising; they simplify the development of ecologically safe processes.

We developed an original method of obtaining pure arsine. As we have already mentioned, electrolysis of the salts of arsenous

acid and acidified solution of arsenic (III) oxide is always accompanied by the formation of elemental arsenic which should be periodically removed from the electrolyzer. Our investigations showed [4, 11, 12] that electrochemical reduction of the free arsenic acid proceeds with the high selectivity almost without side products:

$$H_3AsO_4 + 8H^+ + 8\bar{e} \rightarrow AsH_3 + 4H_2O$$

The process allows one to make a small-size generator of arsine and to obtain pure arsine directly at a site of its consumption for the synthesis of gallium or indium arsenides for electronic industry. This method is attractive because only two components are required for the synthesis of arsine: H_3AsO_4 and H_2O, as only arsenic acid itself serves as electrolyte. In addition, the compounds of arsenic (V) possess much lower toxicity.

A solution of arsenic acid is charged into the anode and cathode spaces of the membrane electrolysis tank. During electrolysis, the catholyte is depleted in the acid, which is compensated by the addition of a concentrated solution of the acid. The level of anolyte is maintained by adding distilled water. Arsine is formed at the copper cathode at the current density of 2 kA/m^2 with the yield as a function of current 94–96 %. Arsine contains a minimal amount of impurities, which simplifies its subsequent purification.

CONCLUSION

So, the application of electrochemical methods allows one to decrease substantially or even exclude almost completely the formation of toxic wastewater and wastes. It is especially efficient to use electrolysis in the processes in which halogen ions act as mediators. At present, the high cost of electricity prevents a wide use of electrolysis in chemical industry. It may be expected that with the development of new methods of energy production decreasing its cost the role of electrochemical processes will increase.

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