ОПТИМИЗАЦИЯ ЭКОЛОГИЧЕСКИХ И ЭКОНОМИЧЕСКИХ ЗАДАЧ ПРИ ПЕРЕРАБОТКЕ СЫРЬЯ, ПОЛУЧЕННОГО ИЗ РЕАКЦИОННЫХ МАСС ЛЮИЗИТА, В ОКСИД МЫШЬЯКА МАРКИ «ТЕХНИЧЕСКИЙ»

В статье представлены результаты по техническим решениям процесса переработки сырья, полученного из продуктов детоксикации люизита в оксид мышьяка (III). Оптимизация операций вывода из состава системы соединений мышьяка (V) и очистка хлорида натрия от примесей соединений мышьяка позволяют улучшить экономические и экологические показатели всего процесса переработки арсенита натрия гидролизного (АНГ) в оксид мышьяка (III). Совершенствование ряда технологических операций позволило оптимизировать общую схему процесса.

Ключевые слова: технологии переработки, арсенит натрия гидролизный, оксид мышьяка (III), хлорид натрия
OPTIMIZATION OF ECOLOGICAL AND ECONOMICAL TASKS AT PROCESSING RAW MATERIALS OBTAINED FROM LEWISITE REACTION MASSES INTO COMMERCIAL ARSENIC OXIDE

The paper presents original technical solutions for processing the raw materials obtained from the lewisite detoxication products into arsenic (III) oxide. Our optimization of arsenic (V) compounds removal from the system and sodium chloride purification from impurities of arsenic compounds allow improving the economical and ecological parameters of the whole process of hydrolyzed sodium arsenite (HSA) conversion into arsenic (III) oxide. Our improvement of certain technological operations has made possible to optimize the general process scheme.

Key words: processing technologies, hydrolyzed sodium arsenite, arsenic (III) oxide, sodium chloride

In Russia, lewisite is neutralized by means of high-temperature alkaline hydrolysis to form liquid reaction masses. The main lewisite stock was at the storage facility in the Kambarka town (Udmurt Republic). In the process of lewisite detoxication, 42,500 tons of such liquid reaction masses have been obtained. Prior to transporting that amount to the Gorny settlement (Saratov Region), the masses were evaporated to obtain 12,500 tons of dry salts with a trivial name of hydrolyzed sodium arsenite (HSA). This evaporated product was manufactured according to Russian Technical Specification 2622-159-0487202-2005. This is a complex multi-component system containing a number of major components, namely: sodium arsenites and arsenates, sodium chloride, water-insoluble substances (mainly bentonite clay), and other compounds in substantially smaller amounts (organic arsenic compounds, heavy metal oxides and hydroxides, etc.). The product’s technical specification does not fully reflect such a complex composition. Moreover, the actual content of the major components is frequently beyond the technical specification (see Table 1). The most complete examination of the HSA properties is presented in [1].

The above factors and the wide variation range of the major component contents in various HSA batches make hydrolyzed sodium arsenite a variable-composition raw material. Thus, HSA processing requires universal technical solutions capable of considering all the above factors.

The idea of using the lewisite reaction masses (both liquid and HSA) as a new type of arsenic-containing raw material to get commercial products seems to be evident. Nevertheless, hitherto all main developments (except for those by Federal Institute of General Chemical Technology, Moscow [2]) were principally aimed at utilization and subsequent burial. However, the electrolysis method of producing elemental arsenic, proposed by the said institute, does not fully solve the problem of processing relatively
small volumes of the liquid reaction masses (LRM). The developers have failed to puzzle out the complex LRM composition, which has hindered their electrolysis facility to reach its designed capacity with obtaining a product of intended quality.

The complex HSA composition required the development of physical-chemical grounds for the separation processes of the major components, simple methods of their isolation from HAS, and subsequent transformation into arsenic (III) oxide and arsenic [3]. Besides, the problem of transforming large amounts of sodium chloride contained in HSA into a commercial product should be solved. This would eliminate the need of burying it in disposal areas.

The technical solutions developed by the authors have made it possible to design diverse process schemes to produce arsenic oxide and elemental arsenic [4-5]. They allow processing both HSA and the initial substance (LRM).

We propose a more efficient, practically zero-cost method for LRM processing, namely: LRM are used at the first stage of HAS processing (dissolution) as a solvent, instead of water. As the LRM possess the same salt composition as HSA (except unwanted bentonite clay), their usage increases the content of arsenic compounds, thus improving the performance of the process.

It should be noted that attempts were made to implement the electrolysis method only due to the enormous expenditures already spent for its design, hardware support, and starting attempts during six years.

After six years of attempting to run an electrolysis line, the plant was suspended and the LRM were transported to Kambarka and transformed into HSA. This confirms that the complex composition of these reaction masses makes the problem of their processing non-trivial.

Analysis of the arsenic-compound market shows arsenic (III) oxide and elemental arsenic to be the most demandable products. That is why most of the methods developed for processing the lewisite reaction masses were directed to obtaining these products.

The above facts and the wide area of arsenic (III) oxide application highlight those technologies of HSA processing which are aimed at obtaining this product [6-8]. No technical arsenic oxide is currently produced in the Russian Federation, not to speak of any refined products which were manufactured in the USSR in amounts of up to 2,000 tons per year.

The manufacturing capabilities of the Gorny enterprise can satisfy the entire country’s need in raw materials for its glass industry, particularly, for making special optical glasses and fiber-glass products.

We have developed various schemes for HSA processing to obtain commercial arsenic oxide [4, 8, 9], as well as methods and equipment for its purification [10-11].

Among those, let us highlight the process from Ref. 4, which allows:
- performing principal operations in solution under mild conditions;
- providing the block principle of constructing lines of the technical process, with operations in batch mode;
- providing independent operation of each block of the technical process;
- providing the closed-cycle principle for toxic reagents; and
- minimizing the amounts of solid waste and sewage by designing efficient purification systems.

The present paper deals with more rational operations of arsenic (V) compound removal when arsenic (III) compounds are presented in the system, and those of cleaning sodium chloride solutions from arsenic impurities; this will improve the economic performance and increase the environmental safety of the process developed.

Fig. 1 presents the block scheme of the developed process of HSA processing into arsenic (III) oxide.

It should be noted that our technology is based on the block-module approach. It is obvious from the scheme that the process of separating the complex initial mixture (HSA) into its major components is based on simple, industrially well-proven processes, namely: dissolution, filtration, evaporation, pumping, etc. It is even most important
that the process is based on the closed-cycle principle by arsenic compounds, which almost excludes liquid waste. The implementation of our technical proposals for purification of sodium chloride solutions from arsenic compounds makes it possible to manufacture arsenic oxide of commercial grade, as well as sodium chloride of industrial grade—highly requested in the petroleum and chlorine industries.

Now consider more thoroughly the operations in each module presented in Fig. 1.

**Dissolution and filtration module**

Because of its hygroscopicity and tendency to caking, the starting material (HSA) is grinded to achieve more thorough extraction of arsenic compounds. Further on, specified amounts of HSA and water in a 1:1 ratio are introduced into the dissolution reactor; at the ambient temperature and under continuous stirring for about three hours, a heterogeneous system is formed, containing a mixture of the dissolved arsenic compounds (sodium arsenite and arsenate), sodium chloride, and alkali. The component ratios are chosen on the basis of our preliminary experiments to estimate the sodium chloride solubility in solutions with arsenic compounds (Fig. 2).
The solid phase consists of bentonite clay with the specified absorbed components of the liquid phase. When equilibrium is attained, the system is transported into a subjacent settler tank for preliminary separation. The liquid phase is filtered sequentially through two Nutch filters with filtering panels of different ratings, which provides a slightly colored but transparent filtrate to be directed to the next module.

After consolidation, the solid phase is transferred from the settler to a separate Nutch filter, squeezed out, rinsed with 20% sodium chloride solution (to remove residual amounts of arsenic compounds), rinsed once again, and transferred to a burial area. The rinsing waters are directed to the HSA dissolution reactor and, starting from the second cycle, are used to dissolve a new HSA portion instead of water.

**Module for manufacturing technical arsenic oxide**

The highly alkaline filtrate is transferred to a reactor for sodium chloride separation. Under constant stirring, concentrated hydrochloric acid (36 wt.%) is added in single portions. Sequential neutralization of sodium arsenites and arsenates thus occurs to form dihydro compounds. The course of the processes is controlled by the pH of the liquid phase being formed down to 8.0).

\[
\text{Na}_3\text{AsO}_3 + 2\text{HCl} \rightarrow \text{NaH}_2\text{AsO}_3 + 2\text{NaCl}
\]

\[
\text{Na}_3\text{AsO}_4 + 2\text{HCl} \rightarrow \text{NaH}_2\text{AsO}_4 + 2\text{NaCl}
\]

This provides universality of the approach irrespective of the filtrate salt concentrations, their proportions and composition variations in HSA batches.

The generated heterogeneous system is transported from the reactor to a subjacent filter to separate precipitated sodium chloride and a new filtrate.

The sodium chloride on the filter is rinsed with 20% NaCl solution and transported to a reactant purification reactor to prepare a 20-23% solution. The rinsing water is directed to the HSA dissolution reactor to dissolve new amounts of the raw material. The filtrate with mixed sodium dihydroarsenites and dihydroarsenates, sodium chloride and hydroxide is transported to an evaporating apparatus and evaporated to obtain a solution with a sodium dihydroarsenite concentration above 25 wt.% and a solid phase of sodium chloride. The resulting heterogeneous system is transported to the very filter already used to separate NaCl during the previous operation; operations similar to those performed in block 3 are carried out there.

The separated filtrate is transported to the reactor in block 5. Under stirring, hydrochloric acid is added thereto to achieve a pH of 6.0 ± 0.2 (irrespective of the liquid phase variable composition). The formation (by means of evaporation) of a concentrated solution of sodium dihydroarsenite allows arsenic (III) oxide to be isolated almost instantly:

\[
\text{NaH}_2\text{AsO}_3 + \text{HCl} \rightarrow \text{As}_2\text{O}_3\downarrow + \text{NaCl} + \text{H}_2\text{O}
\]

Contrary to the traditional operations of its synthesis from more diluted salt solutions, when this oxide precipitates in 5-40 h after acid addition.

The heterogeneous system formed in block 5 comprises a mixed precipitate of arsenic (III) oxide and sodium chloride; its liquid phase contains sodium dihydroarsenate, dissolved arsenic (III) oxide, and sodium chloride.

The precipitate is separated on a filter, dried after repulping (to wash out sodium chloride), analyzed for the basic matter content, and directed for further cleaning or packaging. Quality characteristics of the manufactured technical arsenic (III) oxide are presented in Table 2.

### Table 2

**Quality characteristics of arsenic (III) oxide obtained from several commercial product batches**

<table>
<thead>
<tr>
<th>Batch No</th>
<th>As$_2$O$_3$ content wt.%</th>
<th>Content of residue dissolved in aqueous ammonia, wt.%</th>
<th>As$_3$S$_3$ content wt.%</th>
<th>Water content wt.%</th>
<th>Content of chlorides, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>93.5</td>
<td>2.5</td>
<td>0.15</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>22</td>
<td>94.7</td>
<td>1.5</td>
<td>0.1</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>32</td>
<td>95.1</td>
<td>2.0</td>
<td>0.18</td>
<td>0.7</td>
<td>1.6</td>
</tr>
<tr>
<td>38</td>
<td>93.0</td>
<td>3.0</td>
<td>0.15</td>
<td>0.6</td>
<td>1.8</td>
</tr>
<tr>
<td>1</td>
<td>94.5</td>
<td>2.0</td>
<td>0.13</td>
<td>0.5</td>
<td>0.8</td>
</tr>
<tr>
<td>228</td>
<td>96.0</td>
<td>0.9</td>
<td>0.09</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>548</td>
<td>95.7</td>
<td>1.2</td>
<td>0.12</td>
<td>0.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Our mass-spectral analysis of the products has revealed minor metal impurities: V – 79.6; Cr – 4.7; Mn – 2.1; Fe – 227.3; Co – 4.1; Ni – 15.4; Cu – 9.1; and Zn – 17.9 μg/kg. This confirms the value of HSA as a new arsenic-containing raw material and the efficiency of the operations underlying the process of arsenic (III) oxide production.

The filtrate contains a mixture of arsenic (III and V) compounds to be separated by means of an economically expedient way. Because of the presence of various forms of arsenic compounds (arsenic (III) in the molecular and anionic forms, and arsenic (V) in the anionic one), this operation is carried out with a lanthanum chloride solution to precipitate the anionic form; this results in the formation of poorly soluble lanthanum arsenite and arsenate.

The precipitate is separated on a filter and transported to block 12 for recycling.


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The filtrate contains arsenic (III) oxide, sodium chloride, and water. To design a closed cycle by the toxicant (to eliminate any waste-water problems), the filtrate is transported to the block 4 evaporating unity and, upon removal of a desired water amount, joins the filtrate proceeding from block 3 for final reduction by evaporation.

**Purification module for sodium chloride solution**

The sodium-chloride purification reactor is filled with precipitated sodium chloride and a required water amount. Specified amounts of lanthanum chloride and sodium hydroxide solutions are added to the solution under stirring; sodium hydroxide is added to maintain the pH within 7.0-7.5. The precipitating agent removes arsenic compounds as insoluble salts:

\[ \text{NaH}_2\text{AsO}_3 + \text{LaCl}_3 \rightarrow \text{LaAsO}_4\downarrow + \text{NaCl} + 2\text{HCl} \]

\[ \text{NaH}_2\text{AsO}_4 + \text{LaCl}_3 \rightarrow \text{LaAsO}_4\downarrow + \text{NaCl} + 2\text{HCl} \]

(hydrogen chloride is bound with ammonium hydroxide to produce ammonium chloride).

The purified solution of sodium chloride is subsequently passed through a column with a specially prepared sorbent (iron oxyhydroxide) to be finally cleaned from arsenic compounds. Due to toxicant minimum amounts in the sodium chloride solution, one portion of the sorbent is enough to clean substantial amounts of the HSA to be processed.

Then, the purified NaCl solution is either delivered to the customers as 20-23% solution or subjected to vacuum evaporation to obtain a commercial product (Table 3).

**Table 3. Quality characteristics of our manufactured sodium chloride**

<table>
<thead>
<tr>
<th>Batch No</th>
<th>Index</th>
<th>NaCl content, wt.%</th>
<th>Water content, wt.%</th>
<th>Water-insoluble residue content, wt.%</th>
<th>Content of sulphates, wt.%</th>
<th>Iron content, wt.%</th>
<th>Arsenic content, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td></td>
<td>98.1±1.2</td>
<td>0.6±0.1</td>
<td>0.3±0.05</td>
<td>0.040±0.006</td>
<td>0.10±0.01</td>
<td>0.0030±0.0003</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>98.4±1.1</td>
<td>0.4±0.1</td>
<td>0.1±0.02</td>
<td>0.030±0.005</td>
<td>0.06±0.02</td>
<td>0.0020±0.0002</td>
</tr>
<tr>
<td>32</td>
<td></td>
<td>96.8±1.3</td>
<td>0.8±0.1</td>
<td>0.2±0.03</td>
<td>0.040±0.006</td>
<td>0.05±0.01</td>
<td>0.0040±0.0004</td>
</tr>
<tr>
<td>38</td>
<td></td>
<td>97.3±1.2</td>
<td>0.7±0.1</td>
<td>0.2±0.03</td>
<td>0.020±0.003</td>
<td>0.07±0.01</td>
<td>0.0040±0.0004</td>
</tr>
</tbody>
</table>

The data presented here confirms that the resulting product corresponds to the grade “Sodium chloride (cooking salt) for industrial consumption” (Russian Technical Standard 18-11-3-85). It can be efficiently used in the chlorine industry (due to the low content of sulfates) or in the petroleum industry for making drilling muds. But what is even more important is that technical solutions have been devised to eliminate the problem of burying contaminated sodium chloride by means of transforming it into a commercial product.

The precipitator regeneration block is a separate block in the module.

The lanthanum arsenate from block 8 and the mixture of lanthanum arsenites and arsenates from block 9 enter the regeneration reactor (hermetically-sealed, acid-resistant); and an estimated amount of concentrated (36 wt.%) hydrochloric acid is added to the precipitate. The precipitate dissolves:

\[ \text{LaAsO}_4 + 6\text{HCl} \rightarrow \text{LaCl}_3 + [\text{H}_2\text{AsO}_4 + \text{AsCl}_3] + 3\text{H}_2\text{O} \]

Hydrogen sulfide is then bubbled through the solution (or an estimated amount of ammonium sulfate, (NH₄)₂S, can be added):

\[ 2\text{H}_2\text{AsO}_4 + 3\text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_3\downarrow + 2\text{S} + 8\text{H}_2\text{O} \]

\[ 2\text{AsCl}_3 + 3\text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_3\downarrow + 6\text{HCl} \]

The precipitates of arsenic sulfide and sulfur are filtered out on a Nutch filter, and the remaining LaCl₃ solution is directed to blocks 8 and 9 to be used in new precipitation cycles.

The excessive amount of hydrogen sulfide is absorbed by any absorbents available. In our case, this is the sulfurous acid solution obtained during subsequent annealing of arsenic sulfide.

\[ \text{As}_2\text{S}_3 + 2\text{S} + \text{O}_2 \rightarrow \text{As}_2\text{O}_3 + \text{SO}_2 \]

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3 \]

\[ 2\text{H}_2\text{SO}_3 + \text{H}_2\text{S} \rightarrow 3\text{S} + 3\text{H}_2\text{O} \]

Sulfur is separated on a filter as it accumulates in the hydrogen-sulfide absorbing reactor.

**The technology developed by us has the following advantages:**

- the technological process can be realized with any plant capacity and, due to the simplicity and efficiency of our technical solutions, allows one to obtain materials at a low prime cost;
- it is important that the technology is highly universal, which provides the possibility of processing almost any industrial HSA batches, however wide the range of composition variations could be;
- the technology developed has almost no analogues in terms of environmentally friendly and technically secure processes;
- in the long view, in the case of conversion of the chemical stockpile disposal facilities, the process can be used (with the same equipment) for treat-
ing the dust-like waste (tailings) from metallurgical plants. This circumstance can be used for solving a global problem, namely, toxic arsenic-containing waste utilization, with the current accumulated amount at a level of hundreds million tons. It is important that, beside environmental problems, major economic problems can be solved, extraction of ferrous and non-ferrous metal concentrates (alloys) from tailings.

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Поступила в редакцию 07.07.2016
Принята к опубликованию 12.09.2016

Received 07.07.2016
Accepted 12.09.2016