

A NEW TECHNOLOGY FOR NEUTRALIZATION AND PURIFICATION OF MINE AND INDUSTRIAL WATERS FROM As AND OTHER HEAVY METALS

*MADEN VE ENDÜSTRİYEL ATIK SULARININ AS VE
DİĞER AĞIR METALLERDEN ARINDIRILMASI İÇİN
YENİ BİR TEKNOLOJİ*

Vlodko Panayotov *

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ÖZET

Endüstride, özellikle metalürji tesisleri ile ilgili sorunlardan biri, artık suların As ve diğer ağır metaller ile zararlı elementlerden arındırılmasıdır.

Arseniği ayıran bileşiğin veya çökeltinin geniş bir pH aralığında ikinci kez çözünmemesi gerekmektedir. Bu çalışmada bunun için geliştirilen teknolojik çözüm elde edilen sonuçlarla açıklanmaktadır.

ABSTRACT

The problem of purification of industrial waste waters is one of the most serious problems of modern industrial society. The solution of this problem is complex and ambiguous as it is connected with the development of new technological solutions which should be ecological, economical and efficient. One of the problems attending many industrial processes and especially the metallurgical one is the efficient purification of As and other heavy and harmful elements in waste waters.

One hard requirement is that the obtained residues or compounds separating As should not dissolve secondarily in a quite wide pH interval. The present work concerns these problems pointing out the concrete technological solution, the obtained results as well as the possibility of universalization of the method of purification and other components.

* University of Mining and Geology, Dept. of Mineral Processing,
1156 Sofia, Bulgaria

1. MAIN PRINCIPLES AND METHODS OF INVESTIGATION

The existing methods of waste water purification from As could be systematized in the following groups:

- sedimentation and cosedimentation with hydroxides of heavy metals. Flotation methods. (Laguition, 1976; Fukuzen, 1974)
- sorption and ion exchange on the basis of natural sorbents and synthetic polymers (Ztshiladze, 1969; Dobrovolskii, 1958)
- others (Rosanski, 1971; Sugavara, Tanaka, 1956; Panayotov, 1992)

The high sanitary requirements to toxic As for different water categories (from 0,2 to 0,02 mg/dm³) raise various problems with the waste water purification. The more economical technologies hardly reach the admissible concentration results in diluting the purified waste water or multistage purification scheme. There exist many efficient technologies but they are too expensive. The optimization of the technological parameters (reagents condition, way of their contact with the waste water, pH, duration of the process etc.) is of great significance.

According to the type of chemical production and waste water pH As is present mainly as oxygen containing ions: metaarsenite AsO_2^- , arsenite AsO_3^{3-} . Free ions of arsenic As⁰ and As⁺ are contained in highly acidic waste waters but in practice there are no such cases in mineral processing and metallurgical enterprises.

In same production process when there are free sulphide ions arsenic can exist in the form of thiosalts AsS_2^{2-} , AsS_3^{3-} , AsS_4^{3-} . Most widely used sedimentation methods of As are those with hydroxides of polyvalent metals in the form of hardly dissolved metals arsenites and arsenates. Table 1 gives the value of solubility constant of some arsenites and arsenates. As the table shows one of the most stable compounds of arsenic is feric arsenate. That is why one of the main points of the suggested water purification technology from As is its coherence with dissolved metal ions (in the case Fe³⁺) obtained by electrolytic way. The dissolution of a definite ion type is a selective process depending on the concrete technical and economical assessment as well as on the requirements to the waters to be purified. (Table 1 shows that other metal ions could also settle arsenic satisfactorily).

Table 1. Solubility constant for some arsenates and arsenates

Arsenic compound	Solubility constant
As ₂ O ₃	9,5.10 ⁻¹⁶
AlAsO ₄	1,6.10 ⁻¹⁶
Ba ₃ (AsO ₄) ₂	1,1.10 ⁻¹³
Ca ₃ (AsO ₄) ₂	6,8.10 ⁻¹⁹
Cd ₃ (AsO ₄) ₂	2,2.10 ⁻³³
Co ₃ (AsO ₄) ₂	7,6.10 ⁻²⁹
Cu ₃ (AsO ₄) ₂	7,6.10 ⁻³⁶
CrAsO ₄	7,8.10 ⁻²¹
FeAsO ₄	5,8.10 ⁻²¹
Mg ₃ (AsO ₄) ₂	2,1.10 ⁻²⁰
Mn ₃ (AsO ₄) ₂	1,9.10 ⁻²⁹
Pb ₃ (AsO ₄) ₂	4,1.10 ⁻³⁶
Sr ₃ (AsO ₄) ₂	1,3.10 ⁻¹⁸
Zn ₃ (AsO ₄) ₂	1,03.10 ⁻²⁸
Ag ₃ AsO ₄	1.10 ⁻¹⁹
As ₂ S ₃	4.10 ⁻²⁹

Table 2. K_s' and S' of FeAsO₄

pH	K _s '	S' (mg/dm ³ As)
1,0	2,29.10 ⁻³	3,59.10 ³
2,0	5,25.10 ⁻⁶	1,72.10 ²
3,0	1,29.10 ⁻⁷	2,66.10
4,0	3,30.10 ⁻⁸	1,36.10
5,0	2,70.10 ⁻⁸	1,24.10
6,0	4,30.10 ⁻⁸	1,53.10
7,0	3,80.10 ⁻⁷	4,62.10
8,0	2,19.10 ⁻⁸	3,50.10 ²
9,0	2,51.10 ⁻³	3,57.10 ³
10,0	0,71	6.37.10 ⁴

Table 3. K_{As}' and S' of Ca₃(AsO₄)₂

pH	K _{As} '	S' (mg/dm ³ As)
4,0	2,82.10 ²	very soluble
5,0	2,82.10 ⁻²	1,54.10 ⁵
6,0	3,72.10 ⁻⁶	3,13.10 ⁴
7,0	2,00.10 ⁻⁹	7,01.10 ³
8,0	2,00.10 ⁻⁹	2,37.10 ³
9,0	8,71.10 ⁻¹²	9,13.10 ²
10,0	8,32.10 ⁻¹⁶	3,76.10 ²
11,0	1,35.10 ⁻¹⁷	1,60.10 ²
12,0	2,00.10 ⁻¹⁶	1,11.10 ²

As one of the most widely used methods in practice for As purification is the so called lime method which is in fact waste water processing with milk of lime - Ca(OH)₂, the properties of the obtained sedimentations from FeAsO₄ and Ca₃(AsO₄)₂ should be compared.

Table 2 and 3 show respectively the sedimentation solubilities of these two compounds and the priority of FeAsO₄ over Ca₃(AsO₄)₂. The main problem is how to generate these ferric ions to reach the most efficient water purification.

2. THEORETICAL ARGUMENTATION OF THE CHOICE OF THE PURIFICATION METHOD

The short literature survey of the waste water purification methods from arsenic proves that the sedimentary methods and especially the "lime" and "ferric" methods find the widest application. A theoretical basis of these heterogeneous equilibria are the respective solubility constants of the sedimentations obtained - arsenates and the calculated from them solubilities.

It has been established that the solubility constant K_s is constant only under given circumstances. With the change of pH the temperature or the solvent composition K and respectively the solubility S change in wide limits. So it is extremely important to examine their change as a function of pH to define the optimal conditions of sedimentation of $\text{Ca}_3(\text{AsO}_4)_2$, respectively FeAsO_4 . The calculated values of K_s and S for given pH are indexed as conventional solubility constant K' and solubility constant S^1 and are presented in Table 2. The table shows that the optimal values of pH for the sedimentation of ferric arsenate are from pH = 4 to pH = 6. The lowest solubility is achieved at pH = 5 - 12,4 mg/dm³ As. When using stoichiometric quantities Fe:As = 1:1 the content of As in the solvent over the sedimentation is significantly higher than the concentration allowed for all water categories. That is the reason why comparatively greater stoichiometric quantities of Fe are necessary to obtain As sedimentation.

Table 3 systematizes the calculated values for K' and S^1 as a function of pH for calcium arsenate. The table data that the lowest values for K as a function of pH are obtained in the interval for pH from 10 to 12. The content of As in the solvent is 9 higher than its content in the sedimentation as FeAsO_4 , and many times exceeds the admissible content for purified water. It is important to stress that providing pH in the interval 11 - 10 in open basins is impossible because of the presence of CO_2 in the air. When pH is in the interval 4 - 6 calcium arsenate practically does not form sedimentation.

The following conclusions may be drawn from the comparison of the results in table 2 and table 3 about the solubility of FeAsO_4 and $\text{Ca}_3(\text{AsO}_4)_2$.

1. The purification of waste water from arsenic by its sedimentation as FeAsO_4 is preferable to $\text{Ca}_3(\text{AsO}_4)_2$ as under optimal sedimentary con-

ditions for both compounds the quantity of As which has not been sedimented is 20 - 25 smaller than that remaining in $\text{Ca}_3(\text{AsO}_4)_2$.

2. In the interval for pH from 4 to 6 sediment of arsenates of other heavy metals accompanying arsenic in waste waters such as Cu, Ni, Pb, Zn, Cd etc. is observed. In this way purification of waters from the ions of heavy metals is achieved on one side and the consumption of Fe is decreased on the other.

3. The FeAsO_4 sediment in open settling pits is stable as pH is naturally supported in the interval from 4 to 6 by the presence of CO_2 in the air. In this pH interval the greater part of the sediment $\text{Ca}_3(\text{AsO}_4)_2$ passes into the water solvent and the content of arsenic sharply increases.

4. When using the "lime" method the pH of water should be increased 11-12 times. It is connected with the consumption of CaO the main part of which is used inefficiently because it is sedimented as CaSO_4 . The CaSO_4 sediment is the main mass in the common sediment accumulating in the settling pits for waste waters.

These conclusions prove that the "ferro" technology has significant advantages compared with the "lime" technology for waste water purification from As. The chemical analysis of representative probe from unpurified and two stage purified waste water by "ferro-electrolytic" technology developed by a working group of the Institute of Mining and Geology confirms in broad lines the theoretical calculations and conclusions obtained. The results from the analysis of the waste water sediments and the influence of pH on the solubility and the content of arsenic are shown in table 4, 5, 6 consecutively.

Table 4. Analysis of waste waters (content in mg/dm^3)

	Pb	Zn	Cu	Ni	Fe	Co	Cd	Se	As
Sample 1									
Input, pH=1	5,79	117,1	422,7	1,031	111,5	0,613	18,91	1,908	113,8
Sample 2									
Output, pH=6	0,002	0,928	0,478	0,038	$9 \cdot 10^{-3}$		0,484	0,0463	0,14

In table 4 results show that after a two stage purification the arsenic content in the waste waters decrease to $0,14 \text{ mg}/\text{dm}^3$ which corresponds to the requirements for waters III category. The content of Pb, Zn, Ni and Co is also under the admissible limits for waters II and III categories. The content of Cd and Se exceeds the admissible limits. It is curious to

mention that the analysis of the same probe a weak later shows significantly smaller content of arsenic. It is may be due to the slow sedimentation and cosedimentation of some arsenates. The use of coagulants could improve the results of the arsenic purification from waste water.

Table 5 represents the results from the chemical analysis of the sediments containing in the waste waters at the input and the output of the purification installation. The sediments are isolated by water filtering, dried up to a constant mass and dissolved nitric acid /1:1/.

Table 5. Element content in sediments (mg/dm³)

	Pb	Zn	Cu	Ni	Fe	Co	Cd	Se	As
Input	570	2	25	3.10 ⁻³	62	5,6.10 ⁻³	1,95	1,95	22,3
Output	187	26	122	0,6	211	4,3.10 ⁻²	3,69	?,46	35,7

The results from the analysis of dissolved sediments show that at "input" there is a significant arsenic quantity possibly in the form of As₂S₃, as arsenates are not sedimented in the acidic waste waters at the input of the installation (pH = 1). The As and Fe contents in the sediment obtained at the installation output show that approximately 6 multiple shortage of Fe for the better sedimentation of arsenic as FeAsO₄ is provided. The sedimentary solubility has also been investigated obtained after processing waste water with pH = 1 by the "Ferro-electrolytic" technology. Probes from this sediment were put into contact with a definite pH control by a pH-meter, shaken for 24 hours in a shaking machine at room temperature, filtered with a definite concentration of As passed from the sediment to the solvent.

The results from table 6 show that at pH = 5 arsenic content in the purified waters is the smallest. With the increase of pH arsenic content in the solvent over the sediment increases but remains under the admissible limit of limit-admissible concentration. The increase corresponds to the increase of the conventional solubility constant K' of FeAsO₄. Detailed explanation cannot be made as the sediment contains a great number of metal ions with very complex content.

Table 6. Influence of pH on the sediment solubility (output)

pH	C_{AS} (mg/dm ³)
4,0	0,0164
5,3	0,0037
7,0	0,0450
11,55	0,0355

As a conclusion the "ferro-electrolytic" method is a very fool-proof technology for waste water purification from arsenic. The mixed sediment of ferroarsenate and arsenates of other heavy metals is stable in a wide pH interval from 4 to 11,5. The pouring of this water (pH=6) into settling pits for sediments obtained by purification "lime" method will not increase arsenic content in them. One of its main advantages is that no reagents are added and it is ecologically pure.

3. OBTAINED RESULTS

One of the least soluble arsenic compounds is $FeAsO_4$ ($K = 5,8 \cdot 10^{-21}$). The sedimentation with ferrisalts brings to best results. In solvents containing sulphates of Fe, Zn, Cu, Cd arsenates with changing composition (from acidic to alkalic) depending on the environmental pH are formed. $FeAsO_4$ is sedimented at lower values for pH than $Zn_3(AsO_4)_2$, $Cu_3(AsO_4)_2$ and $Cd_3(AsO_4)_2$, are sedimented. It is important to determine the minimum Fe concentration in the solution necessary for the entire arsenic sedimentation. It is determined by the formula:

$$E = K \cdot A^p$$

where: E - quantity of Fe in mg/100 cm³ solution; H - constant depending on the temperature; A - arsenic concentration in mg/cm³; p - constant 0,57 for all temperature.

It is most difficult to achieve sedimentation of small quantities of arsenic 1C - 20 mg/dm³. In such cases a two stage purification is applied. The smaller the arsenic concentration the greater correlation Fe:As is used for arsenic sedimentation. With $C_{As} = 10$ mg/dm³, 1 mg/dm³, 0,1 mg/dm³ the correlation Fe:As in the sediment is respectively 4, 13, 42. If the Fe contained in the solution is not sufficient some more $FeSO_4$ is added up to an admissible limit as the formation

of large quantities of $\text{Fe}(\text{OH})$ makes the separation of the sediment with As more difficult.

In one of the copper processing enterprises in Bulgaria the waste waters contain $2 - 200 \text{ mg/dm}^3$ As. These waters enter a sedimentary lake (fig. 1), where there remain for final sedimentation of arsenic purified with $\text{Ca}(\text{OH})_2$. All results given in the present paper are obtained after minimum lime processing of waters.

Fig. 1. shows the general type of the electrochemical module containing isolating cradle (1), electrodes (2) for the purification of waters, space for collecting the sediment (3) and space for sediment separation (4). The power supply of the electrochemical module which is the main part of the purifying installation is made by current supplying bars (5).

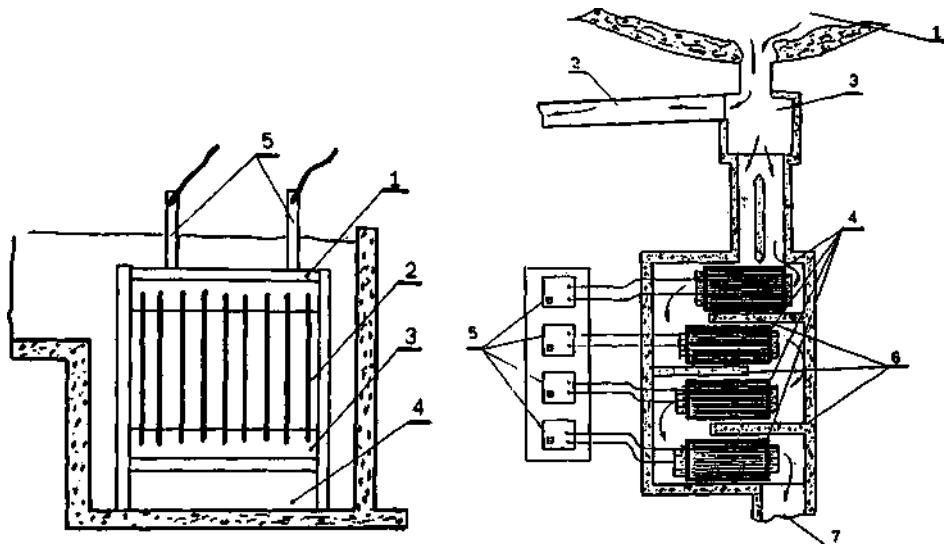


Fig. 1. Electrochemical module

fig. 2, A purifying installation

An installation shown in fig. 2 is realized in case the purification is made at the exit of the water basin containing arsenic ions. Waters come from lake (1), pass through separators forming flows (2) and (3), flow (3) going for purification. The entire flow can also pass through the purifying station or in case when the composition of arsenic is under the limited norm to form a flow (2). The electrochemical modules (4) are supplied by current sources (5) the maximum contact time of arsenic containing waters is guaranteed by barrier (6). At exit (7) water with less than $0,2 \text{ mg/l}$ arsenic content comes out.

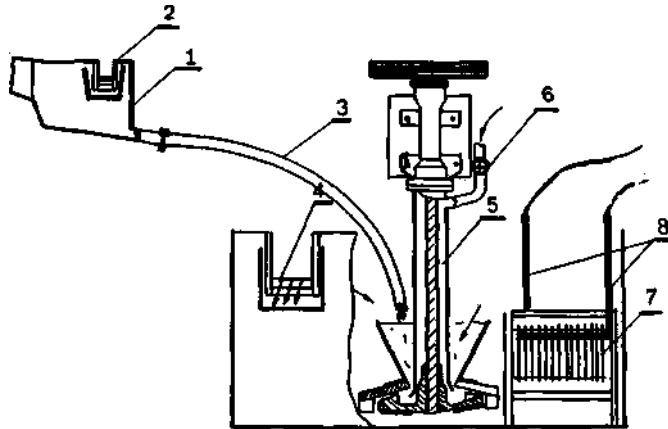


Fig. 3. Flotation machine

When arsenic concentration is less than 200 mg/l at the entrance of the water basin the equipment shown in fig. 3 is used. It is realized on the basis of a traditional flotation machine type "Dunver - 300".

Arsenic containing waters are regulated by a valve (1) their main flow being (2). The entire quantity or a part of it can be purified the water to be purified passes through pipe (3) of the machine in which by a device (4) constant level is sustained and the water running out of the machine is purified. Aerating is periodically done by an aerating mechanism (5) the air going in through valve (6). The purifying electrochemical modul (7) is supplied by electrical station (8). The speed of sedimentation increases five times in comparison with the usual one when the electrochemical modules work. Results obtained are given in table 7.

Table 7. Industrial testing of water purification from As

No of test	pH input	pH output	As input(mg/l)	As output(mg/l)
	3,17	6,85	0,24	0,04
	1,79	6,25	113,81	0,14
	2,17	4,48	16,10	0,08
	12,2	12,2	0,24	0,15
	4,3	6,5	91,40	0,12
	2,18	6,55	24,57	0,08
	3,12	6,65	10,76	0,03

4. APPRECIATIONS

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