

The Lime Method, the Optimal Method for the Treatment of Arsenical Solutions in the Chemical Fertilizers Plant – Fier

Valbona Hoxha

Department of General and Inorganic Chemistry

Polytechnic University of Tirana

E-mail: bonahoxha@gmail.com

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Abstract: In the Plant of Nitrogen Fertilizers in Fier there were about 900 m³ arsenical solutions inherited from 25-30 years ago as a result of the change of use of the raw material, country's diesel with methane gas. The country's diesel has a high content of sulfur and for the production of hydrogen, is needed it's purifying from the sulfhidric gas. In order to realize this was applied the Jamaica-Ventrocok process that used arsenate solution and sodium arsenate. Also for further purifying of hydrogen from the carbonic gas was used solution of potassium arsenate. According to the state of depositing resulted deposited large amounts of arsenic with an calculated average content of As totally about 25gr/liter as As₂O₃. The arsenic was mainly in the pattern of As +5. This constituted a very concerning problem from the standpoint of environmental and the safety of human life and required a fast and safe solution. In this context was required finding and studying the ways for the treatment of arsenical solutions in order the risk to be minimized. To treat arsenical solutions were used physical and chemical methods and special methods. Chemical methods that are used for the determination of total arsenic As +5, As +3, based on the colorimetric determination with dietilditiokarbamat argjendi. These methods are: a. methods with pyrites, b. methods with lime, and c. methods with iron salts. During the work were treated initial arsenical solutions, mother waters and the washing waters of feculence. There were made some poll proofs to determine the optimal parameters of arsenic feculence. In the study have been seen and evaluated some variants, was determined the influence of different factors of treatment and optimal conditions. Based on the obtained results is built a more appropriate variant. According to this variant are made enlarged technological proofs from which are obtained the necessary data and respective balances. From the works of the poll made with the arsenical solutions of Nitrogen Fertilizers Plants in Fier was evidenced the possibility of the lime treatment for the segregation of arsenic. This chemical method is the most optimal and the most economical method for the arsenical feculence. This method gave a high degree of the perception of arsenic to the extent 99%. The content of arsenic in mother waters after the perception fluctuated in 50 - 200mg/liter from about 25gr/liter that is in the initial solution.

Keywords: arsenic, lime method, optimal parameters of feculence, colorimetric determination.

Introduction

As a consequence of the several-year activity of the facilities of the purification of synthesis gas of ammonia, which have used arsenical solutions, the territory in this plant is contaminated with arsenic. The surface of this contaminated territory is located between the facilities of the purification of gas 160 – 169 PS and after them in the western direction to the surrounding wall of ammonium nitrate plant. Also in the large pool are deposited waters with high content of arsenic. The contaminated surface, according to the terms of reference, is 3000 m². From the surveys made with some proofs of land within the territory of the line of ammonia ammonium nitrate plant results that there is a significant contamination of the terrain with arsenic with values from 0.0014g/kg land to 0.26g/kg land (extraction with NaOH). It is certain that the arsenic is not only in columns where is deposited but also in the equipment from which is emptied, in the diluted waters and in the land. The state of deposit, the amount and the

content of arsenical solutions in the Plant of Nitrogen Fertilizers in Fier presented in Table 1:

	Components gr/l	The place of deposition and the amount of solution in m ³							
		Co1.C3a/ 160PS	Co1.C3b/ 160PS	Co1.C3c/ 160PS	Co1.C3d/ 160PS	Rez.SR2/ 160PS	Gazgolder of combustion gas	Res. SR2/169PS	Pool of arsenica lwaters
		255	255	255	13	34	35	53	15
1	As tot(siAs ₂ O ₃)	32.00	20.6	20.6	34.00	26.86	-	8.41	1.87
2	As ⁺³ “	6.3	3.1	3.1	6.21	3.66	-		
3	As ⁺⁵ “	25.7	17.5	17.5	27.79	23.2	-	-	
4	S (as sulfur of tioarseniat) CdS	4.83	5.6	5.6	5.12	1.2	-	1.57	
5	Total alkalinity as Na ₂ CO ₃	13.02	9	9	16.74	9.55	-	-	
6	Total alkalinity as K ₂ CO ₃	-	-	-	-	-	-	54.52	
7	SO ₄ ²⁻	4.11	-	-	-	-	-	0.06	
8	Cl	0.9	-	-	-	-	-	1	
9	pH	8.3	8.3	8.3	8.1	7.7	-	9.5	

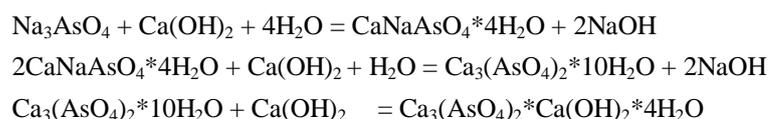
As shown by the data presented in this table in Plant there are deposited large amounts of arsenic with an average content (calculated) of total As in these waters with about 25 gr/liter as As₂O₃ and the arsenic is usually in the form of As⁺⁵ (in the extent over 80 %).

Materials and Methods

During the experimentation our goal was:

- Maximum separation of arsenic from arsenical solutions
- Perk of a product or a mixture in the form of precipitate with minimum water solubility
- The maximum content of arsenic in the separated precipitated
- The formation of secondary waters (mother waters and bathing waters) in minimum volumes.

In this study, is worked by using as raw material mixture of solutions that are deposited in the Nitrogen Fertilizers Plant in Fier. The total content of arsenic in the solution of the labor is 29, 4 gr/liter (as As₂O₃) and As⁺³ 5, 9 gr/liter As₂O₃. Arsenic in them is mainly in the form of thioarsenates. The lime method is based in the treatment of sodium arsenate with lime milk gaining calcium arsenate. This process runs in several stages according to the following reactions:



There were made some poll proofs for determining the parametres of arsenate fertilizer, which are:

Determination of the amount of fertilization reagent

Determination of the time of fertilization

Determination of the temperature of fertilization

1. The treatment of arsenical solutions with lime

From the sample of arsenical solutions, (after is mixed), are taken 200 ml and pass to a glass 400 ml. The glass is placed in a water bath provided with thermoregulator and over the glass is mounted the mechanical mixer. The temperature of treatment (in the solution) is kept 95-98 °C, whereas by the mixer is provided an intensive

movement of the content of the glass. After the solution in the glass reaches the specified temperature in it gradually is added the calculated amount of the lime milk. The mixing continues for 60 minutes. After the treatment is measured pH and the content of the glass is filtered (in vacuum). Is measured the volume of mother waters (which will be analyzed later) and is weighed the precipitate separated on filter.

2. Preliminary elaboration proofs of arsenical solutions with hydrogen peroxide (H₂O₂) and treatment with lime

In a glass 400 ml are settled 200 ml arsenical solution, the glass is placed over the cooker, in it is mounted the mixer and for 5 minutes gradually is added the calculated amount of perhidrol. The treatment continues up to the boiling of solution, the solution is left to boil for 5 minutes. After it is removed from boiling is measured the pH of the solution. In another glass is added 50 ml lime milk, in the glass is mounted the mixer and in the lime milk for 15 minutes is added the heated arsenical solution. Upon completion of this addition the proof is left to the mix for another 60 minutes. In the end is measured the pH of attrition and is made the separation of the phases with filtration. Is weighed the wet precipitate and is measured the volume of mother waters (which will be analyzed later).

3. Proof treatments in different perhidrol quantities

In a glass 400 ml are settled 200 ml arsenical solution, gradually for 5 minutes is added 1 ml sulfuric acid decreasing the pH up to 6. Then the glass is placen over the cooker, in it is mounted the mixer and gradually for 5 minutes is added the calculated quantity of perhidrol. The treatment continues up to the boiling of the solution, the solution is left to boil for 5 minutes. After it is removed from boiling is measured the pH of the solution. . In another glass is added 50 ml lime milk, in the glass is mounted the mixer and in the lime milk for 15 minutes is added the heated arsenical solution. Upon completion of this addition the proof is left to the mix for another 60 minutes. In the end is measured the pH of attrition and is made the separation of the phases with filtration. Is weighed the wet precipitate and is measured the volume of mother waters (which will be analyzed later). In these proofs the amount of perhidrol varies from 2 deri 10 ml /200 ml arsenical solution.

4. Preliminary treatment proofs with sulfuric acid and further precipitation with lime

We saw the possibility of substitution of the perhidrol with a less costly preparation. For this purpose were made proofs of arsenical solution treatment with sulfuric acid and precipitation with lime. In the beginning were conducted proofs by varying the acid amount from 1 up to 5 ml/200 ml arsenical solution. In a glass 400 ml, are added 200 ml arsenical solution, the glass is placed on a cooker, and the solution is heated up to 80 °C, and in it is mounted the mixer. We remove the cooker and in the solution gradually for 5 minutes is added the certain quantity of acid, the mixing continues up to 15 minutes. Then is put in the cooker and the solution is heated up to boiling and boils for 5 minutes. Further the cooker is removed, the glass is removed from the mixer and is measured the pH of the solution. In another glass (400 ml) is added 70 ml lime milk with concentration 231 g/liter Ca(OH)₂, the glass is placed in the mixture and in it gradually is added arsenical solution (heated) preliminarily treated. The addition of arsenical solution in the lime milk is made gradually (for 15 minutes) and is associated with continuous mixing. Further continues the treatment for 1 hour. The pH of the solution is measured and is made the separation of the phases with filtration. Is weighed the wet precipitate and is measured the volume of mother waters (which will be analyzed later).

Results and discussion

1. The treatment of arsenical solutions with lime

Denomination of the proof	The added amount of lime milk in ml	Molar ratio CaO/ /As ₂ O ₃	pH after the treatment	"Mother" solution		Precipitation in gr.	The amount of separated arsenic in %
				Volume in ml	As ₂ O ₃ tot. gr/lit		
p9	40	4	9	225	-	16	-
p10	50	5	9.5	240	19.8	20	19.2
p12	50	5	9.5	240	-	16	-
p2	100	10	13	260	17.8	33.6	21.3
p3	200	30	13	325	3.55	126.4	80.4
p13	100	10	13	240	8.87	36	63.8
p15	50	5	11	210	13.17	67	51

Discussion

From the results of tests carried out (first five proofs) according to the described methodic turns out that the direct treatment with lime of arsenical solutions does not give eligible results. Proofs for the usage of lime in ratio with As₂O₃ over 30 weren't made because we are dealing with unwanted increase of the quantity of precipitate. In the proofs P13 and P15 is worked according to the described method, with the single difference, that the arsenical solution is added in the lime. In this case although the desired results are not provided is noticed a significant improvement of the results. This ascertainment was also considered in the other proofs. Then we can say: The treatment of arsenical solutions only with lime does not provide the desired results of the separation of arsenic.

2. Preliminary elaboration proofs of arsenical solutions with hydrogen peroxide (H₂O₂) and the lime treatment

Denomination of the proof	Treatment with H ₂ SO ₄		Treatment with H ₂ O ₂		pH after the lime treatment	"Mother" waters		The weight of precipitate (in gr.)	The separated amount of As ₂ O ₃ in total (in %)
	The amount of H ₂ SO ₄ in ml	pH after the treatment.	The amount of H ₂ O ₂ in ml	pH after the treatment.		Volume in ml	As ₂ O ₃ in gr/l		
PoP1	-	-	6	8	10-10.5	175	14.05	83	58.2
P6	-	-	4	8	10-10.5	160	14.08	30	45.4
P18	1	6	-	-	10-10.5	225	11.9	39	54.5
P29	1	6	6	5	13	230	0.85	60	96.6
P22	1	6	6	5	13	210	0.43	50	98.5

Discussion

As it is shown in the table we have negative results again. By focusing on this anomaly, was reevaluated the nature of the two arsenical solutions. In this aspect was concluded in the shown proofs the pH value stands almost unchangeable. The arsenical solution with which is worked (formed by mixtures of samples C3a + C3d), is characterized with approximate pH values, but with different values of total alkalinity. In the above circumstances was thought and were made reduction treatment proofs of pH by using H₂SO₄. The addition of 1 ml sulfuric acid /200 ml arsenical solution decreases the pH of the attrition in 6. In these proofs the applied methodic is the same with the one we described above, with the single difference that before the treatment with perhidrol, is made acidification with gradual addition (for 5 minutes) of the sulfuric acid and mixture for 15 minutes. As it is shown

from the table 4 in these proofs (P29 and P22) is achieved the separation of arsenic in the extent 98 %. The treatment with only 1 ml sulfuric acid without the usage of perhidrol (proof 18) does not provide satisfied results.

3. Treatment proofs in different quantities of perhidrol

The results of these proofs are shown in the table 4.

Denomination of the proof	pH after the treatment with H ₂ SO ₄	Treatment with perhidrol		pH after the treatment with lime	"Mother" waters		Weight of precipitate (in gr.)	The separated amount of As ₂ O ₃ in total (in %)
		The added amount of H ₂ O ₂ (ml)	pH after the treatment		Volume in ml	As ₂ O ₃ in gr/l		
P27	6	2	7	13	230	4.03	47	84.2
P26	6	3	7	13	240	2.78	50	88.6
P28	6	4	6-7	13	220	2.18	56	91.2
P29	6	6	5	13	230	0.85	60	96.6
P30	6	8	5	13	230	0.55	58	97.8
P19	6	6	5	13	215	0.24	51.5	99.1
P55	6	6	5	13	275	3.1	43	85.5
P56	6	6	5	13	250	0.66	41	97.1
P57	6	6	5	13	260	0.24	44	99.0
P58	6	6	5	13	230	0.24	40	99.0
P59	6	6	5	13	250	0.19	41	99.2
P60	6	6	5	13	215	0.24	60	99.1

Nr of the proof	As tot. as As ₂ O ₃	SO ₄ ⁻	Free alkalinity (si CaO)	Total alkalinity (as CaO)	Free S	Ca total	Loss in 105°C
Precipitat 60/a	18,8%	4,5%	15,12%	28,28%	2,3%	29,2%	2,86%

Discussion

By noticing that the presented results above turns out that with the increase of dose of the perhidrol we have improvement of the results. By considering that perhidrol is a costly product also the effectiveness of the capture of arsenic, we can say that perhidrol should not be used over 6 ml/200 ml arsenical solution. During the poll proofs was seen that the process of the treatment with perhidrol should be performed in heat. Starting from the possibility of simplification of the scheme also was performed the treatment in the environment temperature (without preliminary heat) and without boiling of the solution. The treatment with perhidrol without preliminary heat and without boiling, (proof P55) gives weak results, also the treatment in heat (with preliminary heat) but without boiling (proof P56) does not provide maximum results. The proofs P57, P58 and P59 are similar proofs (parallel) and are made to be seen the continuity of performance of the process. From the indicated results turns out that by working according to the described methodic (in heat) and with perhidrol addition 6 ml/200 ml arsenical solution is provided a normal performance of the process and maximum results possible. The proof P60, performed in the same conditions, but only with the substitution of the lime milk, with quicklime (kernel) speaks about substitution possibility, with the aim of simplifying the technological scheme. In this proof the quicklime was used in the quantity 14 gr for 200 ml solution.

In conclusion of these proofs we can say that:

When the total alkalinity of the solution that is treated is over 9 gr/liter K_2CO_3 should be made preliminary treatment with acid for the decrease of pH up to 6. For the solutions with arsenic content about 30 gr/liter As_2O_3 , the optimal dose of perhidrol results 30 gr/liter solution with concentration 33 %. After the treatment with perhidrol the solution should be boiled for 5 minutes. The treatment with lime should be performed up to pH 13. In these conditions is reached the separation of arsenic in the extent 99 % and the content of arsenic in “mother” waters moves within the limits 0, 24 gr/liter As_2O_3 . The obtained product turns out with the below data:

4. Preliminary treatment proofs with sulfuric acid and further precipitation with lime

Table 5

Denomination of the proof	pH after the treatment with H_2SO_4		pH after the lime treatment	“Mother” waters		Weight of precipitate (in gr.)	The amount As_2O_3 separated (in %)
	H_2SO_4 ml	pH after the treatment		Volume ml	(As_2O_3) in gr/l		
P32	1	6	≥ 13	225	6.2	47.0	76.3
P33	2	6	≥ 13	240	4.0	52.5	83.7
P34	3	6	≥ 13	245	1.8	61	92.5
P35	4	5	≥ 13	250	0.84	69	96.4
P36	5	4-5	≥ 13	245	0.84	68.5	96.5
P41	5	4-5	≥ 13	230	1.16	61	95.5
P24	5	4-5	≥ 13	250	0.39	72	98.3

Discussion

From the proofs conducted above turns out that by preliminary treatment with sulfuric acid and precipitation with lime, the arsenic can be separated in a considerable extent from the treated solutions. Also from these proofs turns out that up to 4 ml addition of acid we have continuous improvement of the results, the usage of the acid over 4 ml does not provide further considerable increase of the results.

Conclusions and Recommendations

1. Arsenical solutions of the Plant of Nitrogen Fertilizers in Fier have a very complex nature, a high content of arsenic and in the existing state are very fairly dangerous, as for the health of the human as well as for the environment.
2. The treatment of the solution should be made in heat, in 80 °C.
3. The treatment of these solutions only with lime (and with a large amount of lime) does not give satisfied results.
4. Preliminary treatment with perhidrol and further precipitation with lime provides satisfied results.
5. The treatment with sulfuric acid by substituting perhidrol provides approximate and eligible results. The amount of used sulfuric acid (H_2SO_4 , 96%) is 20 ml for 1 liter solution.
6. Before the treatment with lime the pH of the solution should be 4-5.
7. The treatment is conducted by adding gradually and continuous mixture of arsenical solution in the lime milk. The dose of the used lime is 0,4 liter for 1 liter solution with concentration 231 gr/l $Ca(OH)_2$.
8. pH in the end of the treatment should not be less than 13.

9. Reproducibility proofs give reliable results.

10. In all cases is needed the further treatment of mother waters and bathing waters.

This because the treatment of mother and bathing waters provides satisfied results, by decreasing the content of arsenic in approximate limits to the allowed norms.

11. After the treatment of arsenical solutions, the arsenic separates in the form of precipitates with different nature and content. These remnants have high toxicity, a factor that should be taken into account in their further treatment.

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