Technical science and innovation

Volume 2020 | Issue 3 Article 2

9-30-2020

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Z. Sh. Nazirov
Tashkent State Technical University named after Islam Karimov, raximshokirov3@gmail.com

Recommended Citation
Nazirov, Z. Sh. (2020) "PURIFICATION OF POLLUTED WATER AT THE MUBAREK GAS PROCESSING PLANT LTD USING BY ION EXCHANGERS," *Technical science and innovation*: Vol. 2020: Iss. 3, Article 2.
DOI: https://doi.org/10.51346/tstu-01.20.3-77-0066
Available at: https://btstu.researchcommons.org/journal/vol2020/iss3/2

UDC 661.182.547.721

PURIFICATION OF POLLUTED WATER AT THE MUBAREK GAS PROCESSING PLANT LTD USING BY ION EXCHANGERS

Z. Sh.Nazirov[1*], J.A. Ibragimov[2], S.M.Turabdzhanov[1], M.A. Khashimova[1], L.S. Rakhimova[1]

[1]Tashkent State Technical University named after Islam Karimov

[2]Specialist of the Technical Department of Mubarek gas processing plant Ltd.

Abstact: *The full chemical composition of the circulating and make-up water of the Mubarek Gas Processing Plant JSC "Uzbekneftigaz" has been investigated. Raw water sources are the Kui-Mazorsk reservoir and groundwater (artesian water).The amount of released impurities after their softening by passing through the layers of the KU-2-8 cation exchanger is determined. This method is simple, effective and energy-saving in water treatment, LLC "Mubarek" GPP.*

Key words: *ion exchanger, purification, circulating water, heavy metal ions*

Introduction. The Mubarek Gas Processing Plant (GPP)is one of the largest gas treatment plants in Uzbekistan. The demand for natural gas is growing year by year due to the growth in the population. In addition, in the technological processes of this enterprise, in order to obtain purified water from sources, measures are required to reduce the content of metal ions in them. Today, the construction of water treatment facilities and their operation is a rapidly developing area. Any advances in this area can improve the quality indicators of treated water, while reducing operating costs and the cost of treatment services to certain water standards.

There were many investigations regarding water purification with various methods in this plant demonstrated works. The acidic waters of the Mubarek gas fields in Uzbekistan contain significant amounts of hydrogen sulfide. In view of the corrosiveness in relation to the metal equipment of wells operating at elevated temperature and pressure, it is advisable to take measures to reduce the content of hydrogen sulfide in them before returning the associated water underground [1]. Technological methods have been developed for neutralizing and extracting it from these waters. They have been successfully tested under production conditions, and a method of electrochemical neutralization of hydrogen sulfide is being implemented [2]. Furthemore to study the quality of water at these enterprises and scientifically substantiate the stages of water softening by the method of ion exchange played an important value [3,4].

Methods. In the study, we used two types of cation exchanger - industrial sulfonic cation exchanger grade KU-2-8 strongly acidic cation exchanger, copolymer of divinylbenzene and styrene, Anta Ltd, Russia For the determine of the copper ions in the solution used photometric method.The method is based on measuring the optical density (A) of a blue solution of copper (II) ammonia, obtained as a result of the reaction:

$$Cu^{2+} + 4NH_4OH \leftrightarrow [(Cu(NH_3)_4]^{2+} + 4H_2O$$

and using the functional dependence of optical density on the concentration of Cu (II) ions according to the Bouguer-Lambert-Beer law

$$I = I_o exp\cdot(-\varepsilon\cdot c\cdot \ell),$$

where I_o is the intensity of the incident light, c - is the concentration of the absorbing substance (mol / l), ε - is the molar absorption coefficient (l / mol · cm).

A sample weighing 3.927 g of chemically pure copper sulfate $CuSO_4{\cdot}5H_2O$ was transferred into a volumetric flask with a capacity of 1000 ml, dissolved, added 5 ml of concentrated sulfuric acid (density 1.84 g/cm^3) and brought up to the mark with water. 1 ml of this solution contains 1 mg of Cu^{2+} ion. 5 standard solutions were prepared from standard solution 1. For this purpose, 20, 15, 10, 5, and 2.5 ml of a standard copper salt solution were measured with a burette in five volumetric flasks with a capacity of 100 ml. To each of the flasks, 10 ml of diluted (1: 3) ammonia solution was added and the volume was brought to the mark with distilled water. To plot a calibration graph, 10 ml of diluted (1: 3) ammonia was transferred into a 100 ml volumetric flask, one drop of concentrated sulfuric acid was added and distilled water was brought to the mark (zero solution). A solution with an average concentration was photometrically measured in the wavelength range of 400–750 nm. We chose a light filter at which the absorption maximum of the solution is observed - 670 nm. This light filter was used for further work [5].

Measurement of absorbance A was started with the solution having the highest copper concentration. To do this, the solution from the flask was poured into a cuvette with a working width of 1 cm, the cuvette was closed with a lid, and the absorption of the solution was measured with a yellow filter. Having measured the absorption A of all solutions, a calibration graph was built. Experiments carried out at a temperature of 298 K.

To determine the total hardness, the complexometric method is used [6], based on the formation of strong intracomplex compounds with Trilon B and the indicator Eriochrome black by Ca^{2+} and Mg^{2+} ions.

Results and its discussion. Investigated the full chemical composition of circulating and impregnating water used at the plant. The results of the chemical analysis given at the table 1,2.

Table 1

Full chemical analysis of circulating water

Cations	**Containing components in:**			**Hardness**	
	ml/l	**mg-eqv/l**	**%-eqv/l**	**mg-eqv/l**	
Na^+	137	5.99	40	Total	9.00
K^+	5	0.13	1	Carbonate	2.40
NH_4^+	---	---	---	Non-carbonate	6.60
Ca^{2+}	112	5.60	37	pH	7.80
Mg^{2+}	41	3.40	22	CO_2 free.mg/l	11
Fe^{3+}	0.3	0.02	---	CO_2 agr. mg/l	4
Fe^{2+}	0.2	0.01	---	Oxidizability, mg O_2/l	1.45
Total		15.15	100%	SiO_2 mg/l	14
Anions	**Containing components in:**			K_2SiO_3,mg/l	18
	mg-eqv/l	**mg-eqv/l**	**mg-eqv/l**	H_2S, mg/l	---
Cl^-	177	5.00	33	Dry residue	
SO_4^{2-}	368	7.66	50	by experimentation mg/l	980
NO_2^-	0.3	0.01	---	by calculation mg/l	933
NO_3^-	5	0.08	1	Physical properties:	
CO_3^-	---	---	---	Transparency	Transpary
HCO_3^-	146	2.40	16	Taste	Fresh
Total		15.15	100%	Color	colorless
Formula of salt composition of water				Smell	No smell
$0.9\,\frac{SO_4^{50}Cl^{33}HCO_3^{16}}{(Na+K)^{41}Ca^{37}Mg^{22}}$				Sediment	Slight sediment
				Na^+ on the flame photometer mg/l	132

Raw water comes from two sources.The first is surface water from the Kui-Mazorsk reservoir in the Bukhara region. The daily water volume is 7-8 thousand m^3/day, the length of the water supply system is 130 km, the pipe diameter is 820 mm. The second is groundwater (artesian water) from the Shakhrisabz-Yakkabag water pipeline with a length of 170 km, a pipe diameter of 820 mm for drinking purposes. The daily demand for artesian water is 2.5-3 thousand m^3/day.

Table 2

Full chemical analyses of impregnating water

Cations				**Other determines**	
	ml/l	**mg-eqv/l**	**%-eqv/l**	**Hardness, mg-eqv/l**	
Na^+	189	8.22	39	Total	12.50
K^+	2	0.05	---	Carbonate	0.30
NH_4^+	6,0	0.33	2	Non-carbonate	12.20
Ca^{2+}	40	2.00	9	pH	3.80
Mg^{2+}	128	10.50	50	CO_2 free.mg/l	440
Fe^{3+}	---	---	---	CO_2 agr. mg/l	-
Fe^{2+}	0.3	0.01	---	Oxidizability, mg O_2/l	28,66
Total		21.11	100	SiO_2 mg/l	8
Anions				K_2SiO_3 mg/l	10
	mg-eqv/l	**mg-eqv/l**	**mg-eqv/l**	H_2S, mg/l	---
Cl^-	44	1,25	6	Dry residue	
SO_4^{2-}	26	0.53	3	by experimentation, mg/l	1680
NO_2^-	0,2	---	---	by calculation, mg/l	1624
NO_3^-	1180	19.03	90	Physical properties:	
CO_3^-	---	---	---	Transparency	Transpary
HCO_3^-	18	0.30	1	Taste	Fresh
Total		21.11	100	Color	Colorless
Formula of salt composition of water				Smell	No smell
$1{,}7\,\frac{NO_3^{90}}{Mg^{50}Na^{39}}$				Sediment	Slight sediment
				Na^+ on the flame photometer mg/l	200

According to experimental data, the total hardness of water at the enterprise ranges from 9-13 mg-eq /l with a range of pH = 3.80-7.80. To reduce the hardness of water, the method of ion exchange is used on ion-exchange filters of H- and Na-cation. The cation exchanger KU-2-8, based on styrene and divinylbenzene, is used as a crosslinker agent [7]. In connection with the use of water not only for technical purposes, but also for drinking water by enterprises, studied the organoleptic properties of the impregnating water. Organoleptic studies make it possible to indirectly determine the amount of emitted impurities on the basis of the taste and odor sensations they cause, make it possible to assess the quality of drinking water after softening raw water with passing through the layers of the cation exchanger KU-2-8. Determination of the intensity of sensations was also carried out on a standard 5-point scale and results obtained presented on table 3. The 0-5 organoleptic scale range is used widely in research and in trials to measure the efficacy of odor agents [8].

Table 3

Intensity of tastory and olfactory sensations during organoleptic studies of the cation exchanger KU-2-8

Ion exchanger	Intensity of olfactory sensations		Color and transparency	Temperature, ^oC	Dry residue, %	
KU-2-8	Taste range	Smell range	Colorless, transparent	t = 25^oC	by exp., %	by calc., %
	2	2			0,150	0,146

From the data obtained, it can be seen that the intensity of the sensations of smell is weak and does not cause disapproval of the water, which indicates the positive characteristics of organoleptic properties of the cation exchanger and the amount of impurities migrating from it. In addition, the determination of the organoleptic parameters of purified water showed a significant improvement in color, taste and odor, while the content of the mass fraction of metals decreased by 94.2%, which corresponds to the permissible level in drinking water [9].

Therefore, taking into account this technological process of water treatment at the Mubarek GPP, it was necessary to study the chemistry of catinization.

During H-cationization, hardness cations from water are absorbed by the cation exchanger, and instead of hydrogen cations enter the water, causing the acidic reaction of the filtrate:

$$Ca^{2+} + 2HR = CaR_2 + 2H^+ , Mg^{2+} + 2HR = MgR_2 + 2H^+ .$$

As a result, at the beginning of the process, the hardness of the filtrate is close to or equal to zero, and the acidity is maximum, and at the end of the process they will be equal to the hardness and acidity of the source water.

During Na-cationization of water, the exchange of cations in the source water for a sodium ion occurs, therefore, at the beginning of the Na-cationization process, the hardness of the filtrate will be close or equal to zero, and at the end of the process it will be equal to the hardness of the source water, the alkalinity of the treated water does not change:

$$2NaR + Ca^{2+} = CaR_2 + 2Na^+, \quad 2NaR + Mg^{2+} = MgR_2 + 2Na^+$$

The widespread use of ion exchange is also facilitated by the undeniable advantages of this method: high productivity, provision of deep water purification from almost any ionic compounds, simple instrumentation of the process, high purification reliability under variable loads, etc.

It is known that cation exchangers are used not only for softening waters, but also for trapping heavy metal ions contained in waters. If in microscopic doses many substances are necessary for biochemical processes in the human body, then exceeding their maximum permissible concentration (MPC) causes pathological phenomena, such as: weakening of the immune system; allergic reactions [10-12]. Based on this, we analyzed the waters of these sources. Heavy-metal concentration values in snow cover in comparison with maximum allowable concentration in water of water objects used for circulating and impregnating purposes is shown in Table 4.

Table 4 shows that ions of heavy metals dissolved in water do not exceed the MPC values and are not fatal to living organisms. And even at low concentrations, heavy metal ions are sorbed by the cation exchanger. Research has shown that ions such as copper, nickel, cobalt, iron are simultaneously absorbed on the surface phase of the cation exchanger [13,14]. Ions of d-elements form complexes of various structures connected with the sulfo group by curved hydrogen bonds, which is the result of the influence of oxygen atoms of sulfo groups. The chemistry of the process is described by the ion exchange reaction:

$$2R\text{-}SO_3H + Me^{2+} =(R\text{-}SO_3)_2Me + 2H^+.$$

Table 4

Analysis of water for heavy metal ions

Elements, mg/l	Type of control water		MPC, mg/l
	Impregnating water	Circulating water	
Hg	0.00026	0.00021	0.2
Al	0.0025	0.0083	0.05
As	0.0016	0.00035	0.0005
Be	0.000002	0.00001	0.0002
Mo	0.0028	0.0015	0.25
Mn	0.00077	0.0028	0.1
Pb	0.00005	0,000042	0.03
Ni	0.001	0.0003	0.1
Se	0.0021	0.00025	0.01
Cu	0.00024	0.00088	1.0
Zn	0.0009	0.00041	3.0
Cd	0.000003	0.000007	0.001
Sr	1.0	0.27	7.0

In these complexes, the tetraaqua cation $[Me(OH_2)_4]^{2+}$, is formed, coordinating with two anions $-SO_3^-$[15,16]. The studies carried out in the field of water purification by the ion exchange method allow us to assert that this method is simple, effective and energy-saving in water treatment at the Mubarek Gas Processing Plant Ltd.

From an environmental point of view, this, in turn, is important, since the ion exchange method is environmentally friendly and safe.

Acknowledgments. This work was carried out within the framework of the project of the Republic of Uzbekistan PZ-20170927346 Development of technology of ion-exchange polymers of polycondensation type for wastewater treatment.

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