Demineralization of water by gas hydrate technology

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Abstract: The most ecological and economical gas hydrate method was selected on the base of retrospective analysis of the existing technology in demineralization of water. The perfect variant was elaborated by the capacity of demineralization of water. Its advantages are scientifically based over the famous methods.
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Introduction

Intensive growth of industries must be supplied in maximal level not by increasing the water dikes of fresh water, but by the result of intensive development of the reversible and consistent water supply. The problem of the growing lack of fresh water is recognized as the international actual problem. This deficit can be covered by utilizing salty water by demineralization. Artificial desalination of salty water is prospective. The most successful progress in this sphere was achieved by the State Committee on using salty water, the USA. According to N.P.Karpenko (2004), one of the main directions in solving the problems of increasing the hope for functioning meliorative system is demineralization of the polluted and collector-drainage water, utilizing drainage and polluted water. Over 40 percent of water taken from springs in Central Asian regions, contribute to forming the drainage and polluted water. [8].

The necessity of demineralization of salty water in the south of Uzbekistan is dictated that the presence of fresh underground water in this region is insignificant (In Surkhandarya – 29.14, and in Kashkadarya – 15.6 m^3/c), comparing with Fergana (111,4m^3/c), Pre-Tashkent (90,8m^3/c) and Zarafshan (46,4m^3/c) hydro geological districts. [1]. As V.A.Borisov and others mentioned that the amount of fresh drinking underground water in Uzbekistan within 30 years (1965 -1995)diminished from 471 to 293m^3 and comprised 34 percent of the whole resources of underground water with mineralization of 5 and more gm/l instead of 56 percent. The amount also increased 844 to 853m^3/c.

This problem can be evidently solved by several methods, including:

a) by creating technological methods and technical means, permitting to regulate the quality of water with irrigation system;

b) by regulating the quality of collector-drainage water in the process of forming them directly in irrigation zones, regarding geological, geomorphologic and hydrogeologic conditions, and also climatic and meliorative parameters.

The second problem is solved in every concrete situation and the reuse of drainage water will depend on meliorative conditions of irrigation zones, cultural practice, the soil, mineralization of water and others. [5].

The first method was selected by our principles. All the existing technologies of cleaning and demineralization of sewage, including collector-drainage, underground and lake water can be divided into two large groups. The first group of technology is based on removing the polluted components from water, the second one is based on the contrast principle: the polluted components aren't removed from the sewage water, but the molecules of fresh water.

The first group of technology include many methods of technological, biological, chemical, and also physical-chemical purification of sewage water.

The second group consist of the methods, based on evaporating the sewage water, crystallization of dry residues and condensation of distillate.

Using the first group of technology is more preferable in those conditions when the portion of the polluted components in the mass of sewage water is insignificant. If the concentration of the polluted components reach to more than ten grams for liter, the second group of technology is expediently used.

Exactly the second group of technology is the most perspective in demineralizing the underground, collector-drainage, lake and the polluted water, containing the increased concentration of chloride, sulphate, carbonate, and other inorganic salts. However, the second group of technology is inherent to the existing deficiency: these technologies are characterized by the very high power-consuming.

The modern technical level is characterized by the hydrating technology of demineralization of sewage water, which deprived the above-mentioned deficit –

high power-consuming processes. The human practice sets more and more quantitative and difficult questions to the science. Their successful solution is strong stimulus of the progress of the humanity. However, some phenomena and regularities originally are underestimated.

1. Methods and the object of the research

1.1 Retrospective analysis of gaseous hydrates

According to F.A.Kuznetsov and others (2003), the first researcher who observed the form of gaseous hydrates, in all probabilities was Joseph Priestley, an English chemist (1777-1778). He obtained an extraordinary ice-hydrate of gaseous sulphide, existing in positive temperatures, differing from the ordinary hexagonal ice, it was lost in water solution SO_2. creating the chemistry of gaseous hydrate dated to 1811, when Hemfri Davie, an English chemist and physicist, informed about obtaining hydrate chlorine (chlorine was conducted through the cooled water till 0^0). Michael Faraday, a great English physicist, approximately carried on analysis of the hydrate chlorine ingredients, and added it tachometric formula $Cl^2.\cdot 10H^2O$. In 1829 Lewich discovered bromine hydrate, and in 1840 Fredrick Wyoler, a German chemist, obtained hydrate of hydrogen sulphide, with high exactness he established its content ($H_2S\cdot 6H_2O$). Later Zigmunt Wroblevski, a Polish physicist (1882) synthesized the hydrate of carbon dioxide. In 1884 Hendrick Rosebom, a Netherlands chemist and physicist, suggested the formula of the contain of hydrate-chlorine $8H_2O\cdot Cl_2$. Hydrates of methane, ethane, propane, ethylene, argon, krypton, xenon, and a number of other gases were discovered by P.U.Willar, a French physicist from 1888. At present, methods are being elaborated for distinguishing the contain of gaseous hydrates (French physicists and chemists Anri Lui Le Shatelle and others).

Further researches of gaseous hydrates (up to 30^{th} years of 20^{th} century) have pure academic character. From 1940 a lot of perspective offers are being published and patented on using gaseous hydrates in different technological processes and in particular how to desalinate water, desalination of sea water, concentration and division of water solutions and others.

Great success was achieved in Great Britain, where was created skilled-industrial installation for obtaining hydrates productivity 1 ton a day. In Japan were erected semi-industrial installations for obtaining ice-gas hydrating pills which can save and convey in low temperatures [12]. The subsequent researches were conducted by many scientists [6, 7, 12-18, 20, 24, 25].

By summarizing it can be noted that it is the list of researches on gas hydrates, their practical value is great, they consist of scientific-technical base for hydro ecological, hydro chemical, hydrological, geological and ecological researches.

Afterwards much attention was paid to that gas hydrates can be used in different industrial technologies (separating gases, dispersion of fogs, clouds, demineralization of water and others).

1.2. Analysis of technologies of demineralizing water

As Kireycheva and others noted that, mineralized drainage water is the waste of hydro meliorative systems. Its utilization is the serious problem of the modern science (1999). Underground water of the deep bed is salted and can be used in the conditions of desalination.

Modern level of the science and techniques demand for working out the ecological and economical technology of demineralizing water. At present for the purpose of demineralizing water, are being applied different methods of cleaning: distillation, activation; physical and chemical; floatation, extraction, coagulation, sorption, electrodials, reverse osmosis, gaseous hydrates; biological and bio chemical aerobic and anaerobic microorganisms, microfits, hydro macrofits, sorbents.

The method of the ionic exchange is used for demineralizing water with contents of salt 1.5-10 g/l. however, in desalination of the mineralized water expenditures of chemical reagents increase and consist of 3-5 percents of the desalinated water. [10]. As L.A.Koreneva and M.K.Adilova notice that the desalinating technologies demand the application of expensive equipments and materials, therefore, the problem of working out cheap technologies is very important. Comparing technical-economical parameters of different methods, the most ecological-economical technology was gas hydrate. The importance of this technology is that in the contact of gas hydrate producer with sewage water in favorable temperatures and pressures gas hydrate is formed, in which only gas and unsalted water enter, but the salts stay in the solution, as their molecules are too large and aren’t located in the stripes of water molecules. After separating crystals of the hydrate from the pickle they are washed and arrange with the form of fresh water and gas, which direct towards the cycle. In the industrial installations of the firm “Coppers” as gas hydrating producer is used propane [19].

Low power-consumption of hydrate technology for demineralizing natural and sewage water is based on that the main process is carried on at the temperature interval from $0\text{-}10^0$ C.

The existing lack of this method is mainly connected with the selection of gas hydrating producer, as well as this gas determines the last result, and also parameters and the effectiveness of all links of the technological chain. In this method, as mentioned above, as a gas hydrate producer is used propane. However, this gas is first of all, inflammable and explosive. For the second, it is scarce, mainly in countries and regions, not having own oil and gas deposits.

Propane comprises the following deficits of the technological plan. As a gas and a liquefied form, propane is bad soluble in water, that negatively affects to the kinetics of hydrate producer. Gas hydrate of this hydrocarbon occurs in the very short interval of the positive temperature, and also puts a limit it to use in technological process.

2. Results and discussion of the research.

The main problem, being solved by us, is to remove the above-mentioned deficits. The suggested solution includes obtaining has hydrate in contact the gas hydrate producer with water, separating crystals of the hydrate, washing them and decomposition with the form of fresh water and gas, moreover, as a gas hydrate producer is used gas in water solution. Of its parameters the most advantageous for these purposes is carbon dioxide (CO_2). The form of gas hydrate of the carbon dioxide occur in the interval of the temperatures 275-179 ^{0} under the pressure 1400 2500 Pa.

At present, there are great number of gases, forming hydrates. However, all the gases aren't advantageous for occurring the hydrate process of demineralizing water. As a criteria of the selection of optimal gas hydrate producer can be used the followings: first, hydrate must be formed in positive temperatures, contacting with liquid water, in the high atmospheric pressure (with the exception of hit to the air system), but no more than 20-25 Mpa (for decreasing the metal capacity of the construction, proceeding from the conditions of the solidity); second, the preferable gas good soluble in water; third, gas hydrate producer must correspond to the hygienic and ecological conditions.

Very many gases-hydrate producers, wholly corresponding to the one of the criteria, completely don't meet requirements of the others. So, hydrates of haloid hydrocarbons (phreons) occur in the temperature till 21^{0}C (for example, chlorine methyl CH_3Cl) and in pressure not higher than 1.6kPa (methyl bromide CH_3Br). However, freons are dangerous from the point of ecological view (destroys the ozone layer of the earth), and also very expensive.

The very used one of the metals is chlorine. This gas is very good soluble in water (461 ml in 100 g water in 0^{0}C). besides that, it has very high critical temperature of gas hydrate forming (28.7 ^{0}C). However, chlorine is high toxic and is strong corrosion agent.

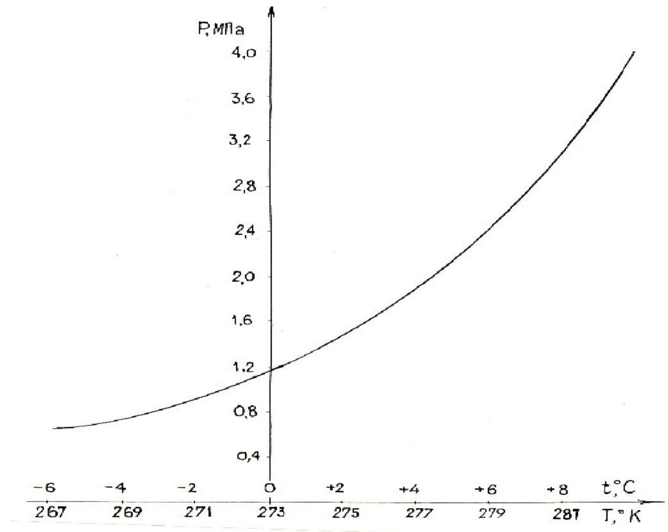
Regarding the above-mentioned , the most suitable one is carbon dioxide. This gas has the certain advantages, comparing with gas, using the method of the USA (propane).

First, carbon dioxide in very good soluble in water (in temperature 0^{0}C in 100 g water is solved 171.3ml CO_2). Second, hydrate of carbon dioxide is formed in the wide interval of the positive temperature. For CO_2 the maximal temperature for occurring hydrate is equal to 283.1^0 K, the interval of the positive temperature in gas hydrate producer is as two times as propane hydrate.

Carbon dioxide is not dangerous in treatment (in contrast with the burning and exploding propane), water solutions of CO_2 is not toxic for the human, that's why it isn't necessary to remove it from the final product (fresh water). Carbon dioxide is more wide-spread in nature and cheaper gas, comparing with propane. The formula of the hydrate of the carbon dioxide changes from $CO_2 \cdot 6H_2$ till $CO_2 \cdot 17H_2O$ (in the pressure till 70 MPa). The low kvadrupolnaya point of the system CO_2+H_2O (gas-hydrate-ice) is characterized by the following parameters: T=273.1^0 K; P=1250 kPa, and the high _________________ point (gas-hydrate-water-liquid hydrate porducer) – parameters: T=283.1^o K, P=4490 kPa. Under the normal atmospheric pressure (P=101.3 kPa) the balanced temperature of occurring the hydrate T=218.1^0 K (-55^{0}C).

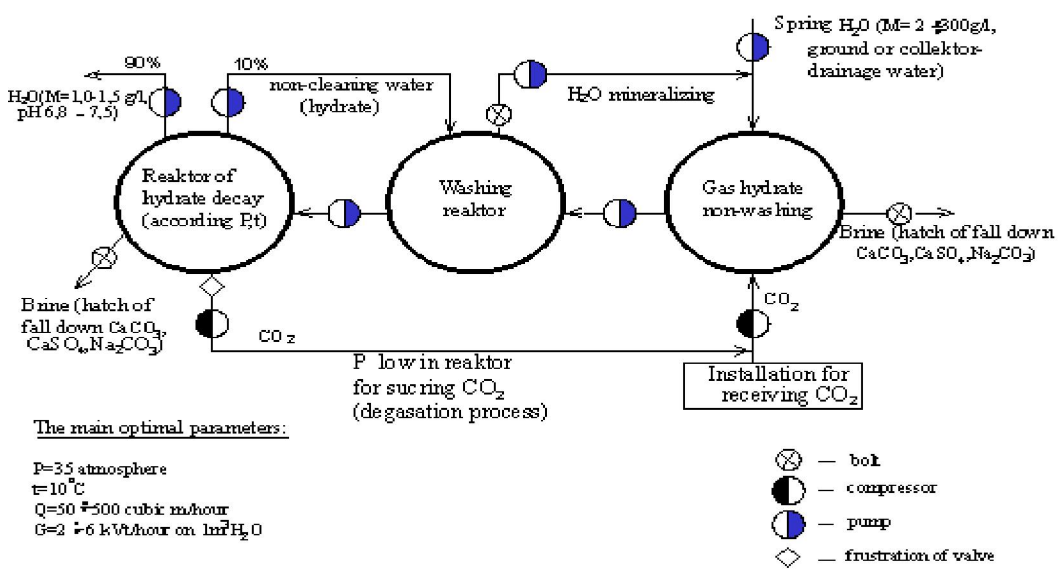
For realizing the elaborated method, P-T condition of hydrate forming is very important, as they determine the regime characteristics of the technological process of demineralization of water, and also selection of pumps, compressors and materials of the constructive elements of the using equipments and installations. On the base of generalizing the odd literature data and conducting experimental researches, and also carrying on the accounts, the following conditions were achieved for forming hydrate CO_2 in the system of CO_2+H_2O (Picture 1).

From the experimental data, as an optimal temperature interval was obtained from 275 till 279^{0}K, which corresponds to the balanced pressure of hydrate forming from 1400 to 2500 kPa. Temperature intervals 273.1 274.9^{0}K and 279.1 283.1^{0}K comprise a certain regime supply of stability (they join the high and low point, near which the process of hydrate forming is suddenly weakened; besides that, they are necessary for regulating the process of thermal changes). The suggested method of demineralization of collector-drainage water include obtaining gas hydrate in contacting gas-hydrate producer with mineralized water, separating of crystals of hydrate, washing them, and decomposition with forming fresh water and gas, moreover, as a gas-hydrate producer is used the solution of gas carbon dioxide in water, but the process of hydrate forming occur in the interval of temperatures 275-279^0 K and under pressure 1400-2500 kPa.



Picture 1. Conditions of forming hydrate of carbon dioxide in the system CO_2+H_2O. The crooked line is the form of hydrates.

The technological scheme of demineralization is described in Picture 2.



Picture 2. Technological scheme of demineralization of water.

Here is reflected all kinds of processes. On the base of is elaborated the modern technological scheme of the installation.

The elaborated scheme of improving the installation differs from that as a source for forming hydrates CO^2 is suggested condensed or liquefied carbon dioxide under the pressure that it simplifies the construction.

One more property of the suggested modernized decision is its universality.

So demineralization can be achieved by underground, collector-drainage, lake and other sewage water in the very wide spectrum of the indexes: pH 3:12;

Mineralization – from 2-3 to 200-300g/l (by the way in April 2009, salting in the East Aral reached to 253 g/l [24]); it obtains selectivity, the type of pollution – as an inorganic and organic. For the final product demineralization is fresh water. Hydrate technology imposes the following functions on it: pH 6.8+7.5; dry residue – not higher than 1.0 -1.5 g/l; by chemical, bacterial content, containing suspension and physical properties of water correspond to the active normative. It is popular that mineralized water from 0.7 to 2.0 is considered well according to the quality for irrigation [26].

The projected power of industrial installation is from 50 to 500 m^3/h.

Conclusions

Demineralization of collector-drainage, underground and lake water is considered as the most cardinal variant of solving the problem of regeneration of them, utilization and increasing the water-stable regions.

The suggested ecological and economical method of gas hydrate technology of demineralization of water corresponds to the modern level of science and techniques, increases the safety of work, decreases the deficiency of gas-hydrate producer, and also power-consumption and increases the technology of processes; accelerates hydrate forming and widens the interval of positive temperature of hydrate forming. This solution of the problem is called both by the society and the nature.

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