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WATER SOFTENING PLANTS AND REDUCTION OF IRON AND MANGANESE BY MAGNETIC AND NANOBUBBLE CO_2 TREATMENT: A TECHNICAL AND APPLICATIVE ANALYSIS

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ABSTRACT

Human society and environment are based on water resources. Hard water with iron and manganese excess is spread across the world and softening of drinking water is widely applied for reasons of public health, client comfort, economic and environmental benefits. Also, from industrial or commercial point of view, using it produce scale deposits in water systems and equipment often result in ample technical and economic problems. Solutions of reducing its hardness and iron/manganese excess exists on the market, even with the substances presented in the work. The novelty this study brings comes from using high intensity permanent magnets arrangements and CO_2 nanobubbles treatment that increased the speed, the volume of treatment, while decreasing the energy and complexity of the installation, also decreasing the pollution mark of the system. The detrimental contributions of softening, in particular the use of chemicals and energy, are taken into account in the carbon footprint of the drinking water companies. The beneficial contributions have not been included in the carbon footprint. For carbon capture in the crystallized calcite and dissolution of CO_2 into the softened water, the carbon footprint is compensated by the net carbon benefit of softening.

Keywords: CO_2 nanobubbles water treatment, permanent magnet water treatment, hard water treatment, iron and manganese excess water treatment, carbon capture and decarbonization

INTRODUCTION

In addition to safe concentrations and limits for harmful inorganic components, albeit relatively higher than the legal limits, Fe and Mn are important secondary pollutants appearing with supply (natural water) alteration and pose various ecological, contamination, and management problems. The technical discipline concerning water treatment encompasses chemical and physical treatments with the goal of to reducing waste loads and stabilizing water quality. However, today the negative effects of the Fe and Mn complexes on clarity, water colour, and the excessive Mn content in natural waters, which have been the most surprising ones for the water industry in recent years, are the hallmarks of the surface water sources in summer crises [1].

The accelerated urbanization process has led to increased emissions and improper discharge of pollutants into various water sources, posing a significant economic and ethical crisis globally. Water scarcity could limit human development across diverse sectors, particularly in arid and rural areas. The main pollutants in water bodies are nutrients such as N, P, and organic matter, typically introducing excessive organic matter into water bodies. However, some inorganic water components also deteriorate aquatic ecosystems when present in excess, including manganese, iron in natural water, and optical inorganic components [2].

Background and Significance

If the water at the input of the process includes magnesium and iron salts in the form of hydroxide precipitate or it was cleaned with methods like centrifuge, flocculant, active carbon, cation synthetiser and flasks with physical or chemical methods, there is only one inexpensive method may be chosen: settlement. Therefore, the treated water contains a significant amount of the particulate matter and this is not acceptable for many industrial applications. For example, iron particulates polluted industrial water cannot be used even after it had been processed by active carbon and ozone treatment. Because, the precipitates are still present after these processing until completely oxidised. Likewise, flocculants, ion-exchangers or magnesium salt resins are used to delve into and remove ions from water [3].

Instead of single-elemental natural water, mostly iron and/or manganese will be present in the alluvial water or underground water which has high iron concentration in particular region. Water obtained from these sources without any treatment has brownish structure due to solvated Fe or/and Mn ions. But the issue that caused more concern is that during the use of such waters as agricultural irrigation, in the treatment of wastewater and production of drinking water, iron and manganese ions can be oxidized by oxygen and transferred to their hydroxide, oxide or carbonate forms. Their precipitation observed as reddish-brown solid particles in some parts of the pipeline, nozzles, and in the irrigated soils, and then blockage occurs and valuable plant growing can be prevented. Therefore, water should be treated for obtaining consumption. In that purpose, a method should be developed to separate these elements with an economically and industrially inexpensive method as much as possible [2].

Research Objectives

The inventive concept behind technological lines is that any processed suspensions must contain a non-uniform concentration of macro- and micro-particles (including soft sulphide nanobubbles, S-HF) and monodisperse hydrosols (o-, o-hydrated and super hydration) as well as particles representing stiff magnetite nanoparticles (Fe_3O_4). As part of this work, we aim for an effective and eco-friendly combined iron and manganese removal technology from groundwaters, which in accordance with state standards contain excess of these metals. The innovative method uses CO_2 nanobubbles produced from water saturated with CO_2 at low pressure and a magnetic field operating directly in water that will reduce the operating costs for the removal of iron from the raw water and will not require any chemical dosing, which is typical for the most common methods in operation.

WATER HARDNESS AND IRON + MANGANESE CONTAMINATION

The WHO guidelines of 1 ppm as the maximum admissible for ferrous iron, are also respected. Even if iron determines problems mainly linked to the water appearance, sometimes associated with iron bacteria, heavy manganese occurrences can be found in natural water, especially when aquifers endure calcareous and sandstone formations.

Water hardness, primarily consisting of calcium and magnesium carbonates, represents a frequent problem in water management due to its precipitation and scaling potential in water pipes and electric conduits during heating.

The distribution of hard water in global underground and surface waters is generally reported by levels of the Hallay–Drömeland indices. Low values (4–<8 meq/L) characterize very soft and soft water, which is generally considered "good". High hardness levels (≈16–60 meq/L) have been found mainly (and not exclusively) in the arid regions of Western Asia, Africa and Australia (Kalahari Desert in South Africa, Zallantar in Syria). Groundwater in Italy indicates quite low Hallay– Drömeland values (around 18 meq/L) [4].

In Prahova County (Romania), close to Ploiesti city, there are sources of underground water with medium hardness (8-12 meq/L) and surface sources with high values (15-27 meq/L).

The global problem and its serious impacts on human society led the authors to develop and test a method based on CO_2 nanobubbles associated with magnetic water structures, that is able to increase water usability and to decrease water consumption. The findings present an innovative and sustainable approach to address water hardness issues, mainly for irrigation.

Causes and Impacts

Applications of chemical agents, such as potassium permanganate (for all types of manganese in raw iron compounds), $KMnO_4$:Cl_2, NaCl, and organic: Na_2S:KNO_3, are known. Nevertheless, the regimes of technological processes, including continuous replenishment of solution, wastewater neutralization or discharge into centralized networks, etc. Additional stages are performed at water preparation plants and require more resources and energy. Using CO_2 nanobubbles at the 200–500 nm scale and applying a lateral magnetic field creates a unique content of rotational flows. Increasing atomic oxygen content in the treated water allows increasing the biological oxygen absorption as well as lowering the water turbidity at sites without intensive fishery and oxygen consumption, and improving the microbial purification of water.

Many water sources contain high levels of iron and manganese that cause environmental damage and are unsuitable for human consumption. Iron is one of the most common metal pollutants in water and is therefore one of the most important parameters of water quality assessment.

Exceeding the maximum allowed concentration levels of both iron and manganese compounds leads to undesirable changes in water characteristics.

Their presence in drinking water results in lowered water quality, rusty water colour (an aesthetic problem), metallic bitter or astringent water taste, and potential damage to pipes and fixtures when exposed to oxygen [5].

CO_2 NANOBUBBLES TECHNOLOGY

The chemical reaction of CO_2 in water is described in the figure 1, where red spot is oxygen, black spot is carbon, grey spot is hydrogen.[6]

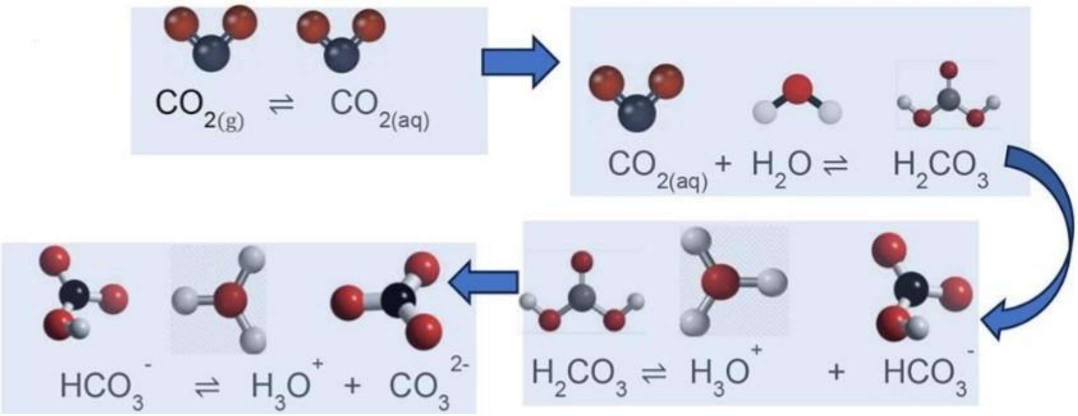

Figure 1 *CO_2 chemical reactions with water*

Dissolution of CO_2 in water produces natural bicarbonate system in aquatic chemistry. This system typically involves three physico-chemical processes: gas-liquid transfer, reaction of CO_2 with water yielding carbonic acid, and the acid-base equilibrium of carbonic acid as weak acid. Therefore, CO_2 is an acid gas that modifies the pH of water by reducing it. [7] attained pH 4.5 for CO_2-nanobubbles and CO_2-microbubbles after 5- and 25-min generation time. In another study, pH of CO_2-nanobubbles decreased with generation time [8]. Main CO2-nanobubbles diameter proved to be 350nm had a lifespan of 5 days [9]. Schematics of a nanobubbles CO_2 system is in the figure 2

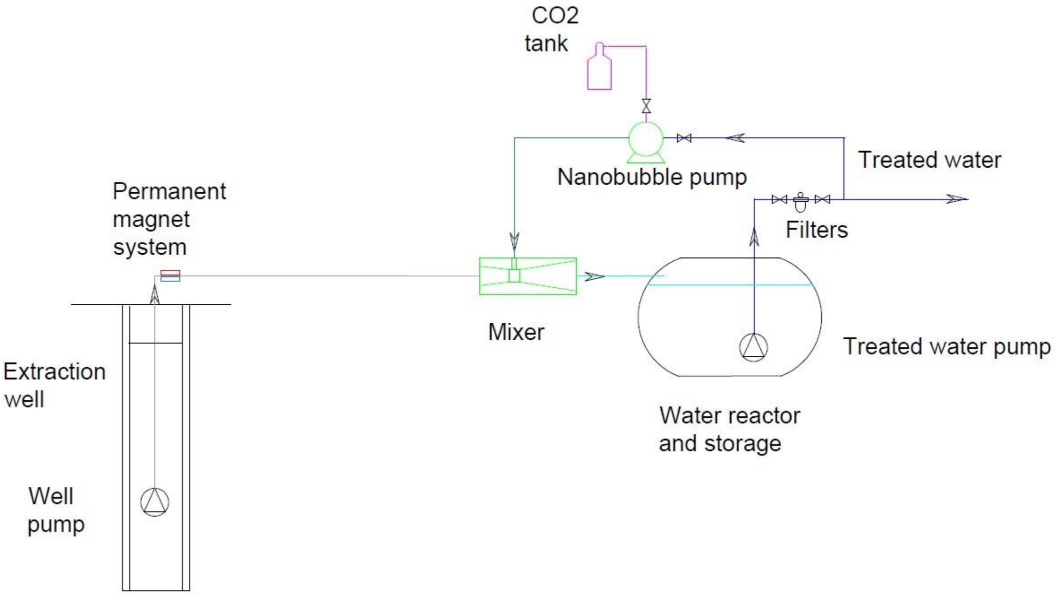

Figure 2*. Schematic of nanobubble system with CO_2 gas for water treatment*

The nanobubble pump is supplied with clean water from the output filtered water of the treatment system, and it combines with the CO_2 gas supplied by a gas tank. The purity of the gas is 99% so no other gases will be presented in the treated water. The output of the nanobubble pump is supplied to a Venturi device where the hard and iron/manganese excess water is very well mixed with the nano-bubbled water. The liquid mix is then supplied to the reaction and storage tank, where the CO_2 reacts with water to form an acid solution which attacks the iron and manganese ions and salts in water.

Manganese precipitates out faster with higher pH-values and greater concentration of oxidant.

“$Mn^{2+} + CO_3^{2-} + H_2CO_3 = Mn^{2+} + 2HCO_3$, $Mn^{2+} + 2HCO_3 = Mn(HCO_3)_2$ (1)

$Mn(HCO_3)_2 = MnO + H_2O + CO_2$ (2)

$2H_2CO_3 + Mn^{2+} = Mn(CO_3)_2 + H_2$ (3)

$2Mn(HCO_3)_2 + H_2O + O_2 = 4Mn(OH)_4 + 4CO_2$ (4)

Iron reaction in CO2 nanobubble in water is:

$Fe^{2+} + 2HCO_3 = Fe(HCO_3)_2$ (5)

$4Fe(HCO_3)_2 + H_2O + O_2 = 4Fe(OH)_3 + 8CO_2$ (6)

$Fe^{2+} + CO_3 = FeCO_3$ (7)

$4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2$ (8)

$2Fe^{2+} + 2H_2CO_3 + O_2 = 2FeCO_3 + 2H_2O$ (9)

Also, oxidation of iron directly goes to insoluble compound:

$4Fe^{2+} + O_2 + 2H_2O = 4Fe^{3+} + 4OH^-$ (10)

$4Fe^{3+} + 4OH^- + 8H_2O = 4Fe(OH)_3 + 4H^+$ (11)

$4Fe^{2+} + O_2 + 10H_2O = 4Fe(OH)_3 + 8H^+$ (12)

Contaminated iron and manganese compounds lead to insoluble products:

$2Fe(HCO_3)_2 + MnO_2 + H_2O = Fe(OH)_3 + MnO + 4CO_2 + H_2O$” [10] (13)

So, the solid particles from iron and manganese excess that are deposited on the bottom of the tank are carbonates of iron and manganese, oxides of iron and manganese, hydroxide of iron and manganese which are precipitate, too. If there are insoluble particles entrained by the tank pump, the filters installed after the tank will stop these components, the output of the system being a reduced concentration of manganese and iron water. [11]

Producing potable water with low cost and high technology, the principle being easy instead of complicated, and practical instead of congested, has always been an important objective of the scientific world. In CO_2 nanobubble technology, if the microorganisms, suspended particles, and chemicals, such as iron and manganese, present in water, are coated with a greater number of CO_2 nanobubbles, they not only lose functionality but also decreases in solid particles (SPs). This results in increasing the dissolved oxygen (DO), one of the basic parameters, and therefore, a low DO can be changed to high in a short time. Due to the data obtained from Field Emission Scanning Electron Microscopy (FE-SEM), Transmission Electron Microscopy (TEM), UV–Vis spectrophotometry, and

X-Ray Diffraction (XRD) analyses, it was concluded that the proposed CO_2 nanobubble system can be considered as the environment-friendly and environmentally suitable nanotechnology, and can also find industrial area of applications. There is great potential for this stable, eco-friendly CO_2 nanobubble dispersion; in the future, it could also be useful in a variety of nanotechnological applications such as iron and manganese removal from geothermal water by proposed NF separation membranes [12].

Principles and Applications

Magnetic water treatment (MWT) has been proposed for water conditioning in several different systems, for removing scales, in greenhouses, in pool areas, in feedlots, for agriculture purposes, in oil treating/refining, for pipe-line applications and among other purposes [13]. tested the effect of MWT on the formation of scales and deposits as well as the bacterial growth inside tubing in an air conditioning system using water as a refrigerant (chilled water system). According to the authors, “The application of MWT on a recirculating water loop has been proved to suppress the formation of scales and deposits and to inhibit the growth of algae and microbial matter inside the tubes. The application has also resulted in energy savings”. This mechanism is the results of Lorentz forces—forces acting on a moving charged particle in continuous flow fluid.

The magnitude of this force is defined by the following equation:

$$|F_L| = q|v \times B| = qvB \sin\theta \quad (14)$$

where q is the quantity of charge, v is its velocity, B is the magnetic induction, and θ is the angle between v and B vectors. Since this force can stimulate all charged species in the electrolyte solution/dispersion traversing the EMF, including the surface charge, ions in the electrical double layer near charged surfaces, and free ions in the solution. [14] According to the authors, “Magnetic treatment reduces dramatically the growth of biofilms, and fungi on the pipe wall, decreases the strength of the scale formation, and, in turn, reduces the intervals of pipe-cleaning in the pipeline network of the university”. They argue that the useful effects of MWT are to raise the super-saturation state in the fluid, by disrupting the nucleation phase.

MAGNETIC FIELD APPLICATION IN WATER TREATMENT

There are two configurations of a magnetic device used in water systems: permanent magnet and solenoid coil, as presented in figure 3.

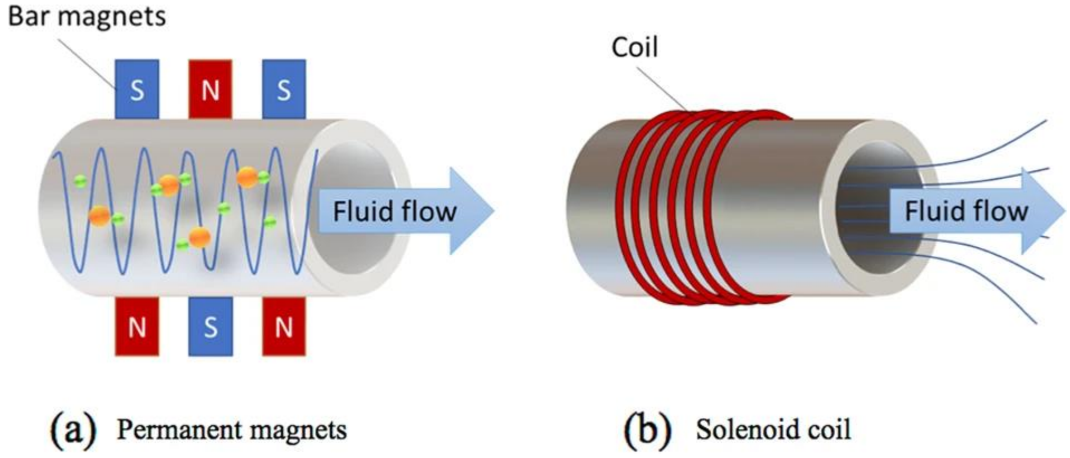

Figure 3. *Permanent magnets system on pipe and coil on pipe for water treatment*

Permanent magnets are made of iron-based, nickel-based, cobalt based or rare element-based compounds ferromagnets and the configuration depends on the number and arrangement of the said magnets. They can bd arranged with alternating poles of magnets or without alternation, depending on the application. Another magnetic field application in water treatment is with solenoid of electrical conducting wire that generates the magnetic field. Depending on application in order to produce field strength, the arrangements can vary the number of coils, or the thickness of their wire.[13]

“Surface tension can be defined as the surface energy per unit area, and in the aqueous system, the surface energy of a solid–liquid state is more than that of a liquid–liquid state. The presence of colloidal particles increases the surface energy at the water–colloid interface, thereby declining the surface energy at the water–reactor surface.”

It has been also reported that $CaCO_3$ crystallization on a pipe wall declined through permanent magnets treatment and the precipitation of $CaCO_3$ increased 11% form no magnet situation [14].

These bulk magnets produce a magnetic field density of 1 to 2 T. In this research, two water channels containing iron balls were placed in the strong field to trap magnetized flock in contaminated water. The bulk magnet system achieved performance values of 100% removal, showing a higher separation for Fe(II); Mn(II) Removal: Fe (98.7%); Mn (92.5%) [15], [16].

The magnetic treatment efficiency is better on higher flow rates (1-2 m/s) [17], on low pH (<6.5 pH) measuring 17% increasing in precipitation regarding no magnetic treatment [18]. Of great interest for the author of the paper is the observation that magnetic treatment is very effective on heat exchanger deposition reduction with more than 20% [19], [20].

Economically, the magnetic treatment of water reduces chemical costs, transport, storage, addition and monitoring system for chemicals, maintenance and training reduced operation costs, reduce control of scale formation, frequent and aggressive cleaning and/or replacing the failed components, reduce energy consumption input, reduce chemical pollution of the treatment in amount of 13% in capital costs and 18% in energy savings.

Mechanisms and Benefits

CO_2 nanobubbles combined with a magnetic field has been used for the effective treatment of hard and Iron + Manganese excess water and to increase the mineral ions and Iron + Manganese dissolution from the loaded filter bed. [6]. The combined application of CO_2 nanobubbles and magnetic field can be expanded to other fields that utilize mineral ions and metals. The schematic of a water extracted from a well with permanent magnets and nanocarbon CO_2 treatment for iron and manganese excess system is presented in figure 2.

CASE STUDIES AND RESULTS

After carbonation, the iron cations are effectively transferred to the carbonate fractions, which precipitate without any oxidation ($Fe^{2+} \rightarrow Fe^{3+}$). Moreover, the deposition of the Zn^{2+} fraction, for example, or it is obvious that the hardening process also removes Zn^{2+} ions. In an industrial environment, additional magnetization / demagnetization of the Orawa spring water leads to the precipitation of Contaminating ions, e.g., iron, during water hardening. Water from the Orawa spring is artificially deposited by soda, for drinking purposes, but it poses a threat of sedimentation of insoluble $Fe(OH)_3$ on the pipes or fittings, which in turn will promote suspension to the very high iron concentration ions reaching the tap water. In order to protect against this danger, the application of magnetically hardened water was suggested.

The deposition of metals is inertial and depends purely on the conditions of flow termination and does not require any increase in release and may beneficially extract the burdened metal ions from the water. Temporary hardeners are by Mg^{2+} ions and Fe^{2+} and combine with the sulphate ions and bicarbonates in the spring water [21]. Apparently, their solubilization in mineral water is purposeful due to their positive effect on human health when consumed in small amounts. The disturbing factors appeared, however, when it turned out that the Fe^{2+} ions dissolved in water can oxidize to $Fe(OH)_3$ at the water's surface or the wall of the pipeline. A common method of water hardening involves carbonation, the reaction of CO_2 with hydroxyl and bicarbonate earth cations, including Fe^{2+}. The effect of carbonation of Orawa spring water by a traditional method of agitation of degassed water in laboratory beakers or by using a magnetic reactor is presented [22].

Field Applications and Performance Data

The design of a treatment system to measure performances of a 10 m3/h is presented in figure 4.

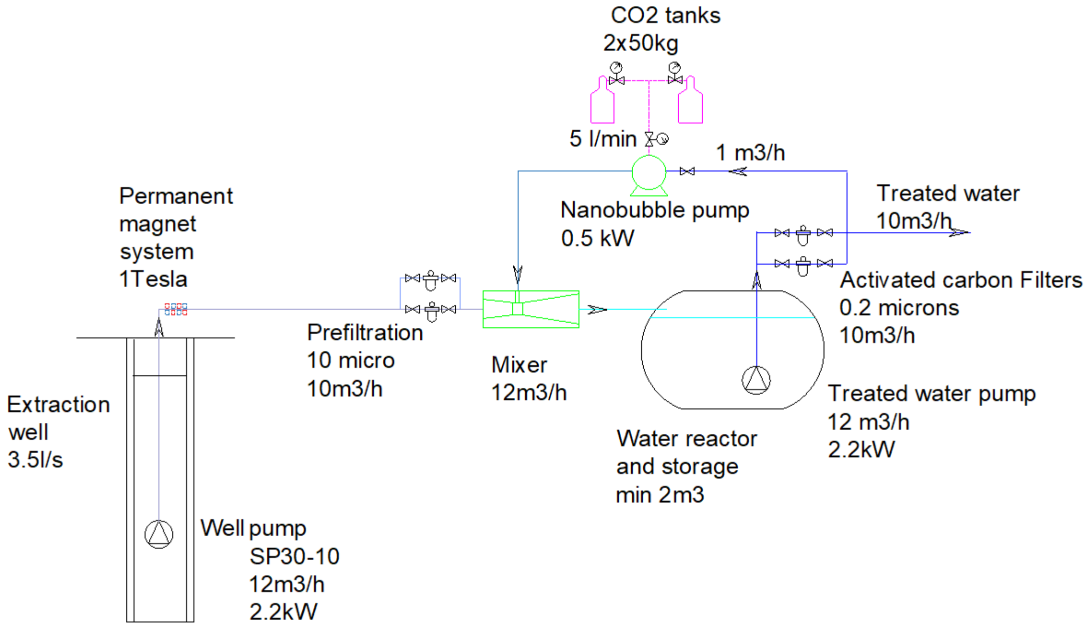

Figure 4. *Schematics of designed 10m3/h water treatment with* CO_2 *nanobubbles and permanent magnets*

The system is realized with a well pump of 10 m^3/h type Grundfos SP30-10, extracting from 40m deep water from the 95m deep well, through a 65mm HDPE pipe. This water is hard, presenting excess Fe and Mg ions and needs treatment to become potable and usable for heat pump heating systems. At start from the well, a group on Permanent neodymium magnets realizing 1Tesla magnetic field. According to presented studies, magnets will block Ca, Fe and Mg at least 60%, making the CO_2 task easier. The system continues with a pair of filters to arrest particulate greater than 10 microns coming from the well. A filter is active while the other is in self-cleaning state and then in stand-by until the first one is charged.

The CO_2 is insured by 2 tanks of 50l, one working, the other in standby, each tank having liquid CO_2 at initial pressure of 57bar, 50l weighting 37.5kg of CO_2, the pressure is reduced in 2 valve system to 5l/min flow. The output pressure of the CO_2 must be 0.2 bar bigger than the pressure of the water at the inlet of the nanobubble pump. The water inlet of the nanobubble pump is from the output of the treatment water unit. The 0.5kW nanobubble pump produces CO_2 nanobubble in a clean water flow of 0.1 m^3/h that forms the reactor for the hard with Fe and Mg excess water. The water to be treated is mixed in a Venturi mixer with the nano-bubbled CO_2 water and released in the storage/reactor tank. In order to ensure the reaction time, which is 12 minutes, the volume of this tank must be minimum 2 m^3. The treated water is sent to the 2 carbon active filters through a 10m^3/h pump, the filters being one in service, the other regenerating/self-cleaning and standby till the first one is charged, of 0.2 µm rating and 10 m^3/h capacity. The output of the filters are 0.1 m^3/h to nanobubble pump and the rest of nearly 10m^3/h to potable water network or heat pump thermal system.

The treatment system is automatized with a smart PLC system, sensors for CO_2, flow rate, water quality, differential pressure and calculator to command, maintenance, store data and present the system on the internet.

Active systems: well pump 2.2 kW, nanobubbles generator 0.37kW, clean water pump 2,2kW, Digital system 0.33kW. Total energy power: 5.1 kW.

Potential production per year: 83.000 m^3,

Energy consumption: 42.33 MWh and cost 11.000 euro/year

CO_2 consumption 830 kg and cost 1830 euro/year

Maintenance cost 500 euro/year

Total costs per year: 13.300 euro

Cost per unit of treated water: 0.16 euro/m^3.

Cost per unit of extracted water to National Water Administration: 0.2 euro/m^3

Total cost of water and its treatment: 0.36 euro versus the cost of unit network water 1.2 euro, nearly 4 times bigger.

The system presents no pollution, and the CO_2 that it consumes is 1toCO_2.

CONCLUSIONS

Water softening plants, combined with modern iron and manganese reduction technologies such as magnetic treatment and the use of CO_2 nanobubbles, represent promising solutions for ensuring drinking and industrial water quality. The treatment of hard water and excess Fe and Mg ions from the well is advantageous regarding the cost of water from network. Not to mention the cost of maintenance and replacement of pipes, installation that are clogged with hard and Fe and Mg ions excess deposits.

Although there is ignorance and fear about upfront costs and the need for maintenance, the advantages of these systems make them a viable option for a wide range of applications. Continuous innovations in the field promise significant improvements in the efficiency and sustainability of these technologies in the future.

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