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A review: Iron remove from natural mineral water

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Abstract

Iron and manganese are two mineral elements whose presence in water leads to serious effects on operation of mineral water bottling equipment and installations.

At same time, these two mineral elements negatively influence commercial value of product by forming bacteria in contact with oxygen, which in turn lead to formation of flakes. Both iron and manganese have no negative effects on health of consumers.

Current technologies in literature largely address removal of iron from drinking water. In this paper we propose an advanced method for removing iron from mineral waters. The proposed method can be easily adapted to removal of iron from drinking water.

Keywords: mineral water, iron, oxygen, automatic control

1.Introduction

Appearance and/or taste of water may indicate the presence of iron and manganese. For example, reddish-brown (iron) or black (manganese) particles may be visible in the water. These iron and/or manganese particles may come from corroded pipes or from the water supply itself. Formation of particles is due to presence of oxygen in sanitary installations it oxidizes and precipitates iron and manganese [1].

Removal of iron from water using ion exchangers. If water has not been exposed to oxygen, the softener resins will remove iron and manganese. Presence of dissolved oxygen in the water leads to clogging of the filters. Resin can be cleaned but with each cleaning process its efficiency is reduced. At the same time, the cleaning process is expensive [2].

Phosphate can be added to source to mask effects of high concentrations of iron in distribution system in case of drinking water. This is effective when the water is less than 0.3 ppm iron or 0.1 ppm manganese.

Phosphate aims to delay precipitation of manganese and oxidized iron, thus greatly reducing layer of limestone that forms on pipe. Effect is called sequestration. Iron or manganese ion is surrounded by a chain of phosphate molecules and is not allowed to precipitate in water [2].

Most methods of iron and manganese removing use oxidation/filtration processes. Oxidant chemically oxidizes iron or manganese (forming a particle) and removes ferruginous bacteria and any other disease-causing bacteria that may be present in water. Filter removes iron or manganese particles. Oxidation followed by filtration is a fairly simple method. Water source must be monitored to determine correct amount of oxidant, and treated water must be monitored to assess oxidation efficiency [3].

2.Method

2.1. Methods of oxidizing iron and manganese from water:

Oxidation with green manganese sand. Green manganese sand consists of a glauconite green sand that is able to reduce iron, manganese and hydrogen sulfide from water by oxidation and filtration.

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When oxidizing power of manganese green sand layer is depleted, bed is regenerated with a weak solution of potassium permanganate ($KMnO_4$).In cases where iron levels are high, potassium permanganate solution is dosed continuously to aid oxidation [4-8].

Oxidation with chlorine: Iron and manganese in water can also be oxidized by chlorine, resulting in ferric hydroxide and manganese dioxide. Precipitated material can then be removed by filtration. Speed of reaction depends on amount of chlorine. When using this process for water that contains organic substances, such as total organic carbon, the likelihood of creating disinfection by-products increases [4-8].

Oxidation by ozone: Ozone gas is produced in an ozone generator by means of high voltage passing through gas stream with oxygen content. Ozone will oxidize iron and manganese to form insoluble particles that can be easily filtered from water. After oxidation process for removal of iron and manganese, widely used sand filters are recommended due to the simple design and longevity of filter media [4-8].

Oxidation by aeration: Iron is slightly oxidized by atmospheric oxygen; less manganese, but aeration can provide dissolved oxygen needed to turn both iron and manganese from their soluble to insoluble forms. Oxidation of iron and manganese with air is the most cost-effective method, as there are no costs for purchasing reagents. However, it has some disadvantages. If there are high levels of manganese, oxidation process can be slow and the reaction tank must be large. In addition, small changes in water quality can affect the pH of the water, and rate of oxidation can slow down to a point where the removal capacity of iron and manganese is reduced [4, 6-8].

3.Results and discussions

Mineral water is collected from three sources as follows:

Partial degassing is the first operation in process of iron remove of natural mineral water, an operation in which concentration of carbon dioxide is reduced [9-11].

Partial degassing is carried out in closed containers to prevent the contact of mineral water with atmospheric air. Partially degassed mineral water with a low concentration of carbon dioxide, leaves degassing tank and enters cell filter with a pore diameter of 100 µm [9-11].

In fact, oxidation of divalent iron and permanent maintenance under control at minimum required level of this operation is essential aspect in technology of iron remove from mineral waters [9-11].

After degassing and filtration, proposed technology comprises an oxidation to dissolve in water oxygen strictly necessary for transformation of divalent iron into trivalent iron, a contact volume to ensure time required for chemical oxidation reactions of 50-60% of divalent iron, sand filtration in a single step, in which oxidation is continued up to 100% and trivalent iron is retained [9-11].

Figure 1. shows technological diagram to iron remove from mineral water

Technological process aims to eliminate possible losses of carbon dioxide and to avoid contact with atmospheric air. It is verified that superior results are obtained in reducing carbon dioxide losses if only 25 to 30% of the deferential water flow is oxidized more intensively, which is then mixed with the rest of the water, so as to obtain the desired dissolved oxygen concentration [9-11].

Oxidation is performed by blowing air into a closed oxidizing vessel, in which water to be oxidized is sprayed.

Air used for oxidation is filtered through felt and filter cardboard for dusting and disinfection followed by diffusion in an oxidizing liquid such as: chlorine water, chlorogenic solution, hydrogen peroxide, etc. [9-11].

Thus, in the case of oxidation by blowing air, a Raschig ring compartment or other inert filler material is used in the oxidizer.

The volume of the contact and settling tank must ensure a natural mineral water flow time of 100 min. [9-11].

Air flow and the water flow to be aerated must be adjusted so that water to be filtered will contain the oxygen necessary for oxidation of 50% of divalent iron and the concentration of dissolved oxygen necessary for oxidation of remaining 50% in filters [9-11].

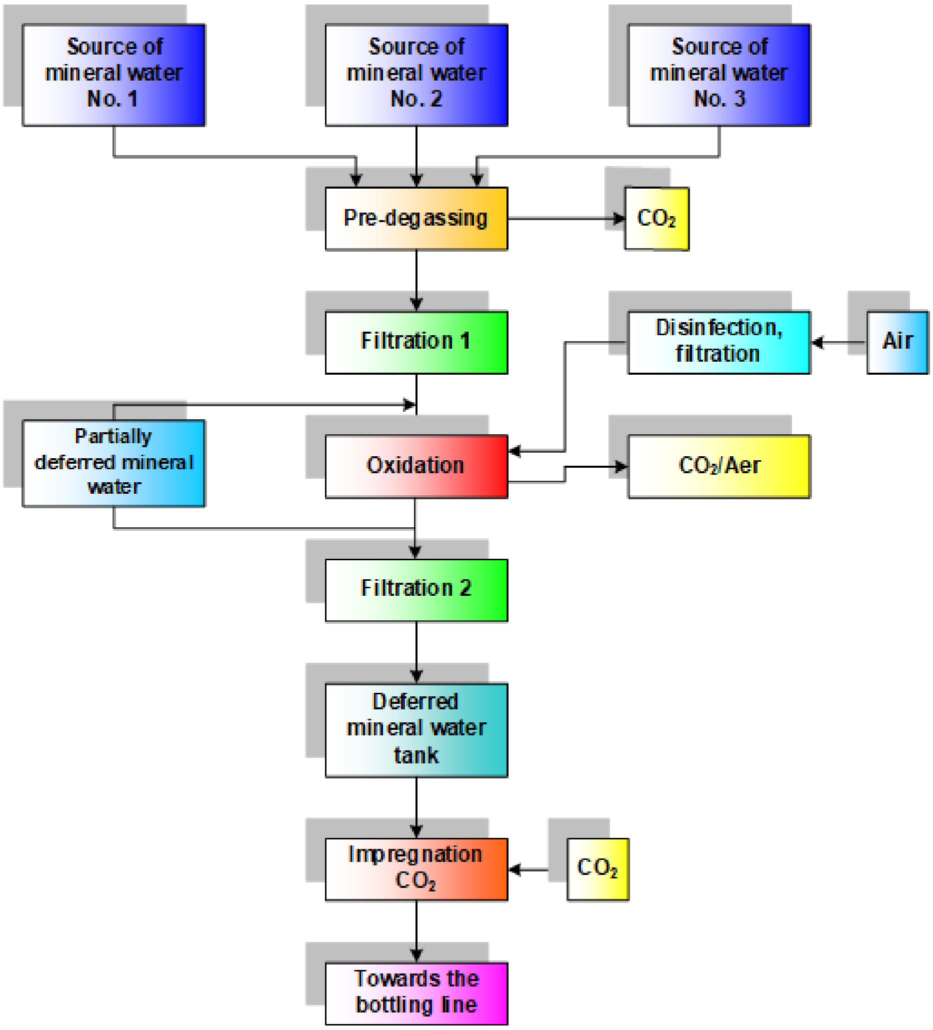

Figure 1. Technological diagram to iron remove from mineral water [9, 10]

Sand with a grain size of 1 to 2.5 mm will be used at first filtration stage, and between 0.6 and 1.2 mm at second filtration stage. Filtering speeds may be different at two filtering stages, but for practical reasons filtering containers of same size are used and as such result equal speeds, which are chosen between 6 and 8 m / h [9-11].

During operation, it must be checked whether water contains divalent and trivalent iron in approximately equal amounts and dissolved oxygen in concentration necessary for oxidation, when passing through sand filter, of remaining divalent iron [9-11].

If percentage of divalent iron is higher, contact time must be increased, and if dissolved oxygen is in an inadequate concentration, oxidation of water must be intensified or reduced for further oxidation of divalent iron [9-11].

Excessive dissolved oxygen content and excessive reduction of dissolved free carbon dioxide should not be allowed, as this can lead to difficulties in decanter and filter operation through chemical water imbalance and intensive carbonate deposition [9-11].

Filtration should be done in pressure filters also in order to avoid contact of water with atmospheric air, but also to reduce release of carbon dioxide favored by passage of water through porous medium at low pressure. In order to obtain a good efficiency of filtration operation, a layer of 0.8 ... 1.2 m of granular sand with dimensions between 0.8 and 1.5 mm must be used. Filtering speed can reach up to 8 m/h, but for safety it is recommended not to exceed 6 m/h [9-11].

3.1.Automatic control diagram

As the automatic management of existing mineral water production facilities has some deficiencies, which of course do not ensure desired performance of their operation, we have proposed an automatic control diagram of our own design for mineral water, which is presented below. This new automation diagram obviously implies a new strategy for operating mineral water iron removal process. Table 1 show the equipment used in automating the process of iron removal mineral water and their role [10].

Table 1. Equipment used in the automation of the water iron remove process [10]

Current number	Equipment used	Role of equipment	
1.	Buttons	P – starting AP (PLC) O – stop / reset AP (PLC) PP1 – start pump P1 OP1 – stop pump P1 PP2 – start pump P2 OP2 – stop pump P2 PP3 – start pump P3 OP3 – stop pump P3 PP4 – start pump P4 OP4 – stop pump P4 PP5 – start pump P5 OP5 – stop pump P5	
2.	Selectors	S1 – three-position selector – M – O – A (Manual - Off - Automatic) S2 - two position selector - D - I – valve VM1 S3 - two position selector - D - I – valve VM2 S4 - two position selector - D - I – valve VM3 S5 - two position selector - D - I – valve VM4 S6 - two position selector - D - I – valve VM5 S7 - two position selector - D - I – valve VM6 S8 - two position selector - D - I – valve VM7 S9 - two position selector - D - I – valve VM8 S10 - two position selector - D - I – valve VM9	
3.	Confirmation of automatic valves	K1 – confirmation VA1 open K2 – confirmation VA2 open K3 – confirmation VA3 open K4 – confirmation VA4 open K5 – confirmation VA5 open K6 – confirmation VA6 open K7 – confirmation VA7 open K8 – confirmation VA8 open K9 – confirmation VA9 open K10 – confirmation VA10 open K11 – confirmation VA11 closed K12 – confirmation VE1 works	
4.	Transducers	Pressure transducers type PC – 400 Gi1/4A1M – ARX – B1151: [12]	TP1 – pump outlet P4 (after VA1) TP2 – pump outlet P5 (after VM9) TP3 – column entry 1 (after VA2) TP4 – column entry 2 (after VA4) TP5 – column entry 3 (after VA6) TP6 – column entry 4 (after VA8)
		Level transducers type RN 300/400/500 NS1 [13]	TN1 - minimum level in pre-degassing tank; TN2 - minimum level in pre-degassing tank; TN3 - maximum level in the pre-degassing tank
		Flow transducers type PSF 100 [14]	TQ1 – output flow transducer column 1 TQ2 – output flow transducer column 2 TQ3 – output flow transducer column 3 TQ4 – output flow transducer column 4

Table 1. Equipment used in the automation of the water iron remove process (*continued*) [10]

Current number	**Equipment used**	**Role of equipment**	
5.	Elements of execution	Pumps (P)	P1 – supply pump P2 – supply pump P5 – filter column supply pump P3 – supply pump P4 – reaction tank supply pump
		Ventilators	VE1
		Valves controlled automatically (VA); [15]	VA1 – towards the columns VA2 – column power supply 1 VA3 – column emptying 1 – for reverse washing operation VA4 – column power supply 2 VA5 – column emptying 2 – for reverse washing operation VA6 – column power supply 3 VA7 – column emptying 3 – for reverse washing operation VA8 – column power supply 4 VA9 – column emptying 4 – for reverse washing operation VA10 – transition to buffer tank VA11 – empty columns after reverse wash.
		Manual valves	VM1 – feeding VM2 – feeding VM3 – feeding VM4 – emptying the pre-degassing tank VM5 – supply pump P4 VM6 – emptying reaction tank VM7- supply pump P5 – exit to the filter columns VM8 - water recirculation route to improve the oxidation process VM9 – feed filter columns

In order to use as efficiently as possible at a maximum productive efficiency of the installation, in the conditions of ensuring the imposed quality of the final product, an automatic management diagram of the three specific processes has been designed:

- pre-degassing;
- reaction;
- filtering.

Following the literature study carried out regarding the iron remove of mineral waters as well as the mathematical models obtained in the modeling chapter of iron removed process, synthetic automation diagram presented in figure 2 was elaborated. It was named in order to highlight the groups of elements specific to this process management system, namely:

- buttons and selectors;
- transducers;
- confirmations;
- execution elements;
- signals.

Complete automation diagram of mineral water iron removed process is presented in figure 3a and figure 3b respectively [10].

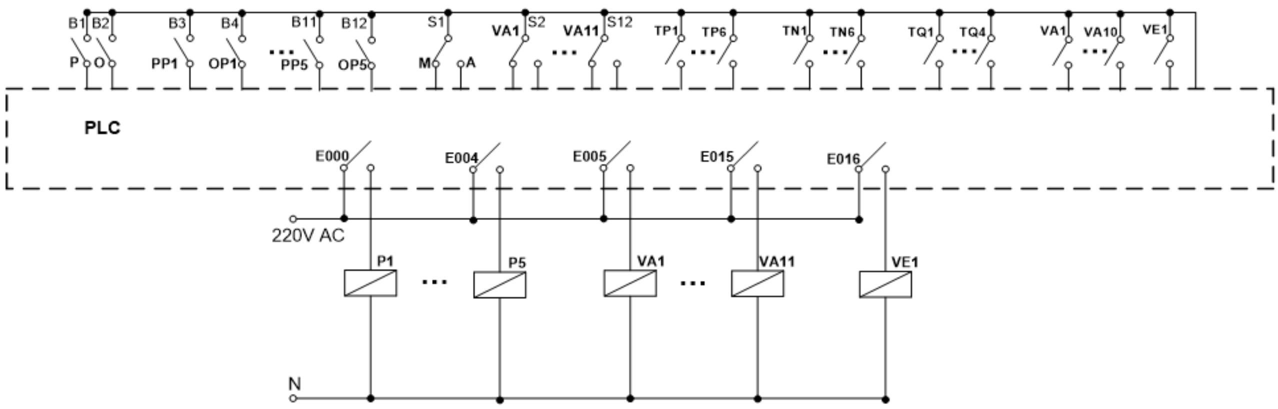

Figure 2. Synthetic automation diagram [10]

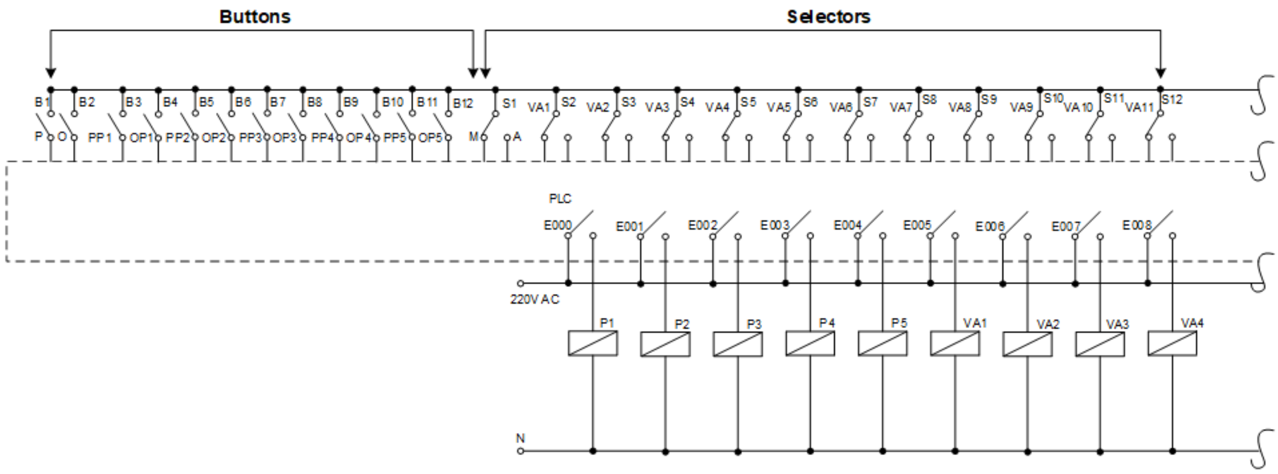

Figure 3a. Complete automation diagram - Part I [10]

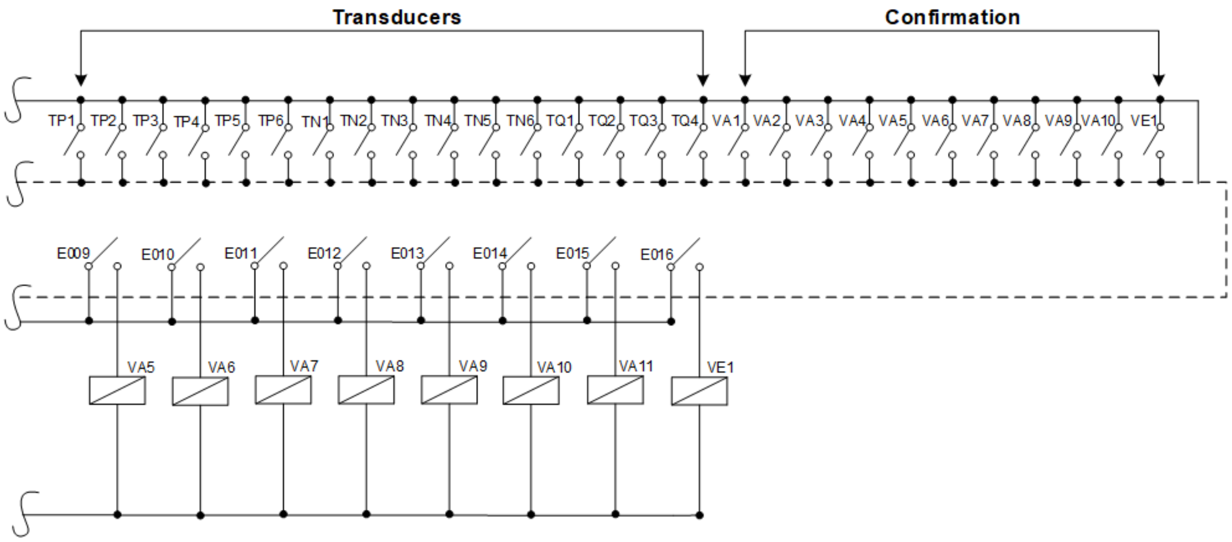

Figure 3b. Complete automation diagram - Part II [10]

Meaning of buttons, selectors, confirmations, execution elements and signals is shown in Table 1. In order to ensure an optimal development (in terms of quality, quantity and economy) of technological process of obtaining mineral water, proposed automation diagram has a number of features in terms of process management. Thus, for individual testing of the components iron removal process of mineral water, in addition to the operation performed in automatic mode, possibility of manual operation was also provided. Automatic control and possible component testing is designed around the PLC (Programable Logic Controller) MELSEC FX1N of company Mitsubishi Electric [16].

A first step before starting automatic operation is proper positioning of manually operated valves (VM) to make it possible to create mandatory preconditions for operation [16].

TN1, TN2 and TN3 level transducers monitor the water level in the pre-degassing tank. From the point of view of their indications, operation is permitted provided that the water level is between the working minimum (TN2) and the working maximum (TN3). TN1 detects a minimum level whose damage is equivalent to a malfunction and it will be treated according to specific procedures.

If water level in tank falls below set value to TN2, it is ordered to start one of the pumps P1, P2 or P3 according to specific criteria and conditions. Pump feeds the pre-degassing tank until the maximum working level (TN3) is reached, after which it is ordered to stop.

PLC verifies that the above level conditions are met and then controls the VA1 valve to allow water to be pumped to the reaction tank. Opening valve VA1 (confirmed by the closing of K1) allows control actuation of the pump P4 which ensures (according to general diagram of automatic control of mineral water iron removal process shown in figure 4) supply of reaction column. Simultaneously with control of VA1 valve, VE1 fan starts, which will introduce countercurrent air into reaction tank. Water level in reaction tank is monitored similarly to that in pre-degassing tank, with transducer TN4 (minimum level), TN5 (maximum level) and TN6 (maximum working level) [10, 16].

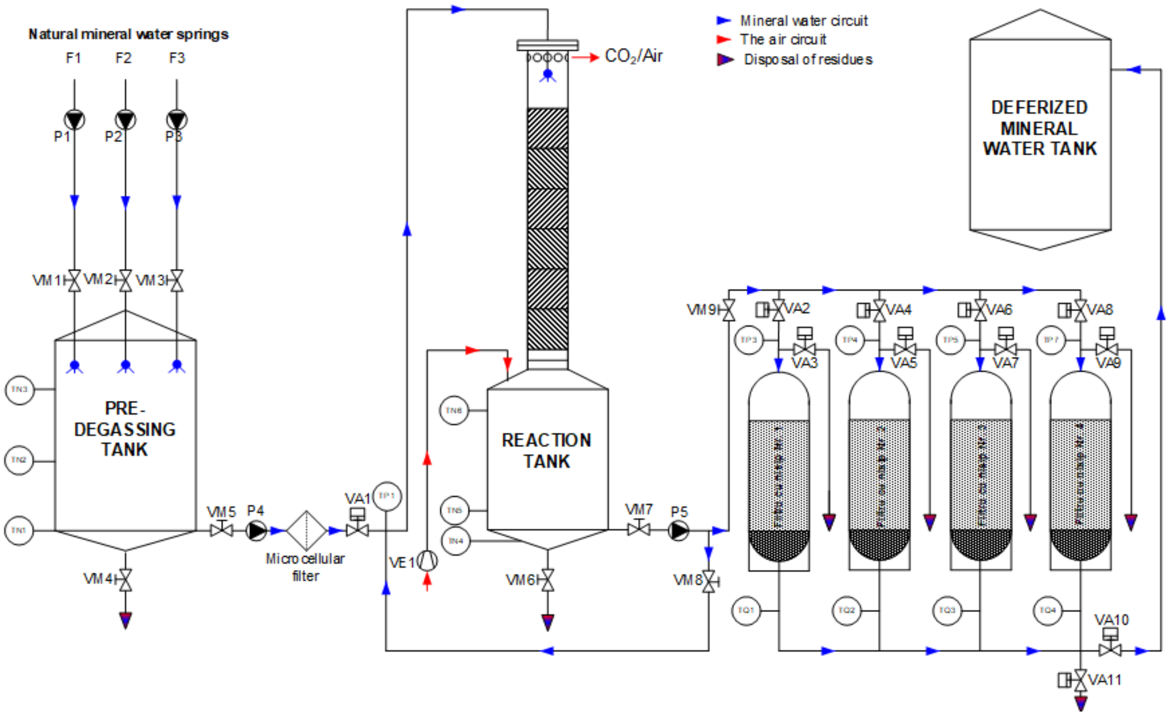

Figure 4. General diagram of automatic management of iron remove process of mineral waters [10]

If water level is within permissible operating range, open valves VA2, VA4, VA6, VA8, VA10 and close valve VA1. Confirmation above operation allows automatic release of P5 pump actuation control [10, 16].

According to the (manual) regulation VM8 valve, an amount of about 25-30% water is recirculated and brought to reaction tank, where it is mixed with partially degassed water to reduce CO_2 losses. Larger amount of mineral water reaches the filtration columns, passes through them, a process by which the trivalent iron is retained, after which it passes into the buffer tank of treated water. If a longer time has elapsed since the last stop of filtration than indicated, for safety reasons, in order to avoid unfavorable filtration of mineral water, reverse process of washing the filters is started. This operation is performed by simultaneous actuation, with the control of opening valves VA2, VA4, VA6 and VA8 for a time interval (calculated for technological reasons) and opening valve VA11 and closing valve VA10. After this time, VA10 valve is opened and VA11 valve is closed [10, 16].

From this point on, the plant transfers iron remove from water to tank. An essential aspect of the iron remove process solved in this paper is the automatic performance of the reverse wash operation. Tripping of this operation is based on information provided by flow transducers mounted at the outputs of filter columns. With their help, the flow is measured at the exit of each column and by comparing them reciprocally with the prescribed value, the decision is made to start the reverse washing procedure of the column considered to be clogged in the established proportion. To perform this operation, PLC will generate following commands [10, 16]:

1. It is ordered to close the supply valve of column to be washed in reverse (VA2 in column 1, VA4 in column 2, VA6 in column 3 and VA8 in column 4).
2. After closing, open reverse wash flush valve of affected column (VA3, VA5, VA7, VA9). Simultaneously close VA10 valve.

From moment VA10 valve is closed, actual operation of reverse washing of selected column is performed, with water flowing through other columns.Time required to perform reverse wash is determined experimentally on basis of technological and economic considerations.

After the reverse wash time has elapsed, the sequence of return to working filtering is triggered, as follows [10, 16]:

1. It is ordered to close the supply valves of the columns that provided the water for washing.
2. After closing them, open VA11 valve
3. After this operation, it is necessary to simultaneously open the supply valve of the column that has been washed and close the drain valve. As a result, the entire flow of water will pass through the column that was washed backwards, and will eliminate by intensive direct washing the iron residue III retained in the filter pores [10, 16].
4. After the direct washing time has elapsed, it is ordered to open the supply valves of the columns that ensured the washing. This eliminates any traces of Fe III from all pipes.
5. Valve VA10 is opened and valve VA11 is closed after confirmation of opening. From this moment, the operation of delivering the iron remove from water to the buffer tank is resumed [10, 16].

4.Conclusion

Personal automation diagram implemented in technological process of iron removed from natural mineral waters, can ensure obtaining of following advantages:

- achieving a unitary management of process to iron removed of mineral water from the source to the final product - deferized mineral water;
- making a communication connection through a USB port with a PC with help of which process can be programmed, monitored and / or modified;
- finding an objective criterion for choosing the moment of starting the reverse wash by measuring the flow at the output of the filter columns as well processing/comparing their values;
- elaboration and implementation of an algorithm for cleaning filters by reverse washing with water saving (closing the direct wash of the columns that contributed to the reverse wash of the selected column);
- operation without local operator, with supervision and management through the computer.

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human or animal subjects (if exist) respect the specific regulation and standards.

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