Study and Optimization of the Industrial Water Circuits of the Alverca Plant

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Abstract

The reduced quality of demineralized water by an ion exchange system and the deficient performance of this system at ADP-Fertilizantes led to the need of this study and the search for solutions.

It was found that, due to the feed quality of the raw water in the system, from the active boreholes, the current treatment is not enough, since the ion exchange unit was designed to treat raw water from municipal sanitary water system of Vila Franca de Xira.

It was concluded that the resins currently used in the unit are the most indicated, so long as of an upstream reverse osmosis system, with pre-treatment, is installed to improve the quality of the feed water.

Part of the water leaving de reverse osmosis will be used as feed of the present ion exchange system, giving the desired quality, increasing the number of production cycles and decreasing regenerant consumptions.

The remaining water that leaves the reverse osmosis can also replace the demineralized water and Municipal System Water in particular areas in the plant, reducing this consumption too.

Finally, the total fixed investment necessary to improve the water treatment and the benefits it will bring were estimated. It was concluded that the benefits cover the initial investment after less than 18 months.

Key-Words: Ion Exchange, Reverse Osmosis, Membranes, Resins, Water Treatment, Separation Processes.

1. Introduction[1]

The proper running of a factory is guaranteed by the consumption of utilities, so that the process takes place under the desired conditions. The utilities used include saturated water vapor, natural gas, water, compressed air and electricity.

The study of the demineralized water necessary for the correct operation of the production processes, the correct functioning of the refrigeration circuits and the production of steam in the company ADP-Fertilizantes was essential.

The demineralized water obtained by the ion exchange system at the Alverca Plant does not present the desired quality and the performance of this system is not in accordance with its projection, with a considerable number of short production cycles occurring and consequently a high regenerant consumption.

To solve these problems the study of the existing ion exchange treatment and the consideration of the implementation of a reverse osmosis system upstream of this ion exchange was carried out. Finally, it was also essential to calculate the total fixed investment needed and the benefits resulting from increased water treatment at the plant.

For the previous points it was essential to know the various water circuits of the ADP-Fertilizantes water system.

This system consists of abstraction water, drinking water, cooling water, demineralized water and water from the fire network.

The abstraction water comes from the five active boreholes and it's immediately subjected to chemical treatment by the injection of sodium hypochlorite (NaOCl), which has as its objective the purification and disinfection of this water.

Drinking water comes from a pipeline of the municipal sanitary water system (SMAS) of Vila Franca de Xira and it's also subject to chemical treatment.

The demineralized water originates from the water treatment plant unit, U-445, and it's produced through an ion exchange system.

Water from the fire network is obtained through the abstraction water, the water from the SMAS and the purging of the cooling circuits.

The cooling system of this unit consists of three circuits: 2, 4 and 8.

The 2nd refrigeration circuit is normally supplied by the abstraction water, but if necessary it can be powered by SMAS drinking water.

The 4th cooling circuit is always supplied by the SMAS drinking water.

The 8th cooling circuit is supplied by the demineralized water, however it can be powered by water from the SMAS.

2. Theory

2.1. Ion Exchange [2][3]

The water treatment by ion exchange, through the use of resins, for the reversible exchange of cations and anions with water, began in 1935.

In the ion exchange process the resins are pre-saturated with a certain ion which will be exchanged for the undesirable ion in the water, with the removal of most of the undesirable cations and anions in the raw water in a semi-batch system. This operation is performed on ion exchange columns where the water to be treated is fed continuously until the undesirable ion concentration in the effluent reaches a certain value.

The ion exchange resins are named cation resins, when they exchange of cations, or anion resins, when they exchange of anions.

2.1.1. Cation Exchange Resins

Cation resins are in the hydrogen cycle if the ion exchanged by them is hydrogen, H^+, or in the sodium cycle if in this case is the sodium, Na^+. In ADP-Fertilizantes cation exchange resins are used in the hydrogen cycle, whose equations 1 and 2 represent the reaction relative to the treatment of raw water and to the regeneration carried out by hydrochloric acid, HCl, respectively. Regeneration may also be performed by sulfuric acid, H_2SO_4.

$$MX + 2HR \rightarrow MR_2 + H_2X \qquad (1)$$

$$MR_2 + 2HCl \rightarrow 2HR + MCl_2 \qquad (2)$$

R represents the resin and, for example, M = Ca^{2+} e X = SO_4^{2-}.

Cation resins are classified into strong acid cation resins or weak acid cation resins.

During the water treatment in this type of resin occurs the formation of carbonic acid, equation 3, which decomposes easily into carbon dioxide, CO_2, and water, equation 4, then removed by aeration through a degasifier.

$$M(HCO_3)_2 + 2HR \rightarrow MR_2 + 2H_2CO_3 \qquad (3)$$

$$H_2CO_3 \rightarrow CO_2 + H_2O \qquad (4)$$

2.1.2. Anion Exchange Resins

The water treatment from the anion exchange resins is shown below by equations 5 and 6, which correspond to the reaction relative to the treatment of decationized water, and the reaction relative to the regeneration carried out by sodium hydroxide, NaO. The presence of a degasifier in the system before the anion column allows the reduction of the consumption of this reagent.

$$HX + ROH \rightarrow XR + H_2O \qquad (5)$$

$$XR + NaOH \rightarrow ROH + NaX \qquad (6)$$

R represents the resin and, for example, X = HCO_3, Cl, SO_4.

Anion resins can be classified into strong base anion resins type I, II or III or weak base anion resins.

2.1.3. Demineralization System

A demineralization system consists of a cation column, a degasifier, an anion column and a mixed bed. This bed contains cation resin and anion resin for the final thinning of the production of demineralized water.

Typically, this system has a downstream production flow and an upward regeneration flow, which is the case of ADP-Fertilizantes.

2.1.4. Performance and Lifetime of Ion Exchange Resins

The use of resins is designed for a considerable period of time, however there are several factors that influence the lifetime of these and their capacity.

Temperature, a highly oxidative environment, fouling, osmotic shocks and the movement of the resin are some of the factors that lead to a loss of resin capacity, inability to produce water with the desired quality and the increase of the pressure drop during the process.

2.1.5. Capacity and Selectivity of Ion Exchange Resins

The capacity of an ion exchange resin refers to the number of exchangeable equivalents per unit volume of resin, eq/L. [4] The operational capacity is the practical quantity of exchangeable equivalents during an operation and can be obtained from equation 7, where t is the cycle time, C_0 is the concentration of the species to be removed, the water flow rate to be treated, the capacity of the resin and V_r the volume of resin. [5]

$$t \times C_0 \times Q = q \times V_r \qquad (7)$$

The selectivity of a resin to a given ion relative to another represents the order in which the ions are adsorbed by the resin.

In ADP-Fertilizantes the order of affinities for the cation resin used in relation to the hydrogen ion is given by: $Ca^{2+} > Mg^{2+} > Na^{+} > H^{+}$, for the anion resin used in relation to the hydroxide ion is given by: $SO_4^{2-} > Cl^{-} > H_3SiO_4^{-} > HCO_3{}^{-} > OH^{-}$.[6][7]

2.1.6. Ion Exchange System at ADP-Fertilizantes

The imposed initial conditions of service were the need for regeneration of the cation columns and anion columns after 24h of operation and regeneration of the mixed beds every 15 days, with a flow rate of 60 m^3/h.[1]

In this unit the cation resins used are of the strongly acid cationic type with a capacity of 2.00 eq/L. The anionic resins are type II in the anion and type I columns in mixed beds, with capacity equal to 1.25 eq/L and 1.20 eq/L, respectively. [9][10]

2.2 Reverse Osmosis [11][12][13]

Reverse osmosis is a separation process with membranes which began to be used upstream of the ion exchange treatment in order to reduce the frequency of regenerations required in the latter.

2.2.1 Reverse Osmosis System

The mechanism of separation in reverse osmosis is the transfer of mass through a semipermeable physical barrier, the membrane, by the application of a driving force, the pressure. The membrane is placed between two phases, the upstream phase is constituted by the feed and the downstream phase is constituted by the permeate, the stream which continues to flow upstream of the membrane after separation of the components is called the concentrate stream.

In water treatment the goal of reverse osmosis separation is to obtain water with less salts that constitutes the permeate, the undesirable compounds are retained in the concentrate.

It is possible to determine the concentration of feed, a, permeate, p, and concentrate, r, in the reverse osmosis process from equation 8, in steady state.

$$\begin{cases} Q_a = Q_p + Q_r \\ Q_a C_a = Q_p C_p + Q_r C_r \end{cases} \tag{8}$$

Q and C represent the flow rate and the concentration, respectively.

In a reverse osmosis water treatment process the recovery represents the percentage of feed that appears as permeate and the rejection refers to the percentage of solute concentration removed from the feed water by the membranes.

2.2.2. Performance of Reverse Osmosis Membranes

The most important criteria for determining the performance of the reverse osmosis process are permeate flow and salt rejection, both are influenced by the pressure, temperature, recovery and feed water composition.

There are some factors that influence the performance of membranes, such as fouling, scaling, oxidative process by chlorine attack, freezing and back pressure.

The usage of a pre-treatment before the reverse osmosis system allows the increase of efficiency and lifetime of the membranes, its projection depends on the type of feed water and its composition.

3. Experimental Methods

For the study of the existing ion exchange system, samples were collected in the unit and subjected to laboratory analysis.

There were two tests, one prior to the annual plant shutdown and one after, in order to see if there had been any improvements resulting from maintenance. During this maintenance occurred the addition of new resins in the cation and anion columns.

The production cycle of the first test lasted 3 hours and 40 minutes and the second test lasted 4 hours.

In both test, were drawn samples of raw water, of the cation column outlet, of the degasifier outlet, of the anion column outlet and of the mixed bed outlet, which corresponds to the end of the treatment.

These samples were subjected to analysis of some laboratory parameters taking into account that the cation resin column captures sodium, calcium and magnesium ions, the degasifier removes carbon dioxide and the anion resin column captures sulfate, chlorine, carbonate and silica ions.

Laboratory determinations included: determination of pH, conductivity, sulfate content, alkalinity, silica content, calcium content, total hardness and chloride content.

Water whose pH is approximately 7 the sodium content is obtained by the difference between cations and anions present in the water, equation 9. However, since the water at the exit of the cation column presents a low pH the sodium is obtained through the pH, equation 10.

$$[Na^+] = [HCO_3^-] + [Cl^-] + [SO_4^{2-}] - [Ca^{2+}] - [Mg^{2+}] \tag{9}$$

$$[Na^+] = [HCO_3^-] + [Cl^-] + [SO_4^{2-}] - [H^+] - [Ca^{2+}] - [Mg^{2+}] \tag{10}$$

4. Results and Discussion

4.1. Characterization of Ion Exchange Resins

From the analysis of the water of the first test, it was found that the cation resins were showing the expected behavior, first captured the calcium, then the magnesium and finally the sodium. However, the anion resins did not exhibit the expected behavior, because in the first place it removed chlorine, then silica, then the sulfates and finally the bicarbonates.

As the resin gets older the ionic leaks begin to be higher due to the appearance of kinetic problems, the ion sulfate is the first to suffer ionic leakage, since its ionic size is superior to the other ions, thus explaining the unexpected behavior of the anionic resin. [14]

The mixed bed has also a cation resin with expected behavior, however the anion resin of this bed presented the same behavior as the previous one.

In general, the production cycle corresponding to the first test had an expected cation removal and an unexpected removal of anions, and the sulfates ended up being the least anion removed.

In the second test it was found that the cation resins also showed an expected behavior. However, the anion resins did not present an expected behavior, like during the first test cycle.

The cation resins of the mixed bed also showed an expected behavior, the same did not happen with the anion resins of this bed.

In general, the production cycle corresponding to the second test had an expected cation removal and an unexpected removal of anions, and the sulfates ended up being the least anion removed too.

In comparison, it was verified that the production cycle corresponding to the second test had a longer duration and a larger volume of treated water, resulting in an improvement from the maintenance performed during the annual shutdown.

In both tests the cation resins exhibited an expected behavior and in the second test occurred an improvement in cation removal. The anion resins in the second test also showed an improvement in the removal of anions, being more noticeable in relation to the sulfates.

The treated water obtained during the production cycles of these tests had an higher silica concentration than the desired one, being undesirable in the formation of steam in the boilers, and a pH lower than desired, what can cause corrosion in the boilers, thus not being the expected water quality.

In order to complete the study of the behavior of the resins, their operational capacity was calculated and compared with the capacities of the data sheets, table 1. [8] [9]

Table 1 – Operational capacity and data sheet capacity for cation resins (CAT) and anion resins (ANI) at ADP-Fertilizantes

	Capacity ANI (eq/Lresin)	Capacity CAT (eq/Lresin)
1st Test	0,56	0,43
2nd Test	0,60	0,49
Data Sheet	1,25	2,00

Table 1 shows that the operational capacities are quite apart from those mentioned in the data sheets, however there was an improvement in capacity after the annual shutdown, 2nd test, due to the addition of new resin.

From these operational capacities it was determined, by equation 7, what is the necessary volume of these resins to remove the maximum value of compounds in the water and consequently to obtain treated water with the desired quality.

The required volumes of cation resins (CAT) and anion resins (ANI), for a real ADP-Fertilizantes production cycle, are shown in Table 2 and 3 respectively, and were obtained through the Lenntech simulator and from calculations in Excel. [15]

Table 2 - Volume of cation resin required, for each test, for a current cycle

		Volume CAT (Lresin/cycle)
1st Test	**Excel**	3367,57
	Lenntech	3348,78
2nd Test	**Excel**	3501,72
	Lenntech	3511,17

Table 3 - Volume of anion resin required, for each test, for a current cycle

		Volume ANI (Lresin/Cycle)
1st Test	**Excel**	1603,46
	Lenntech	1526,04
2nd Test	**Excel**	1727,77
	Lenntech	1629,49

Tables 2 and 3 show that for a current cycle it is required a volume higher than the used in the unit, since the volume of cation resin in the UFAA was 2700L in the first test and 3000L in the second test, and volume of anion resin was 1475L for the first test and 1650L for the second test.

In order to the unit functions at ideal cycle which it was designed, 60 m^3/h for 24h, with the operational capacity the resin volumes shown in tables 4 and 5 are required.

Table 4 - Volume of cation resin required, for each test, for an ideal production cycle

		Volume CAT (Lresin/cycle)
1st Test	**Excel**	42537,75
	Lenntech	42302,22
2nd Test	**Excel**	35262,09
	Lenntech	35357,23

Table 5 - Volume of anion resin required, for each test, for an ideal production cycle

		Volume ANI (Lresin/Cycle)
1st Test	**Excel**	20254,23
	Lenntech	19277,12
2nd Test	**Excel**	17398,51
	Lenntech	16408,81

From tables 4 and 5 it was found that using the resins, with the unit's operational capacities, to obtain an ideal cycle would be required an extremely large volume of resins for which the unit is not prepared.

Since the treatment of treated water in the unit is not showing the desired qualities and that a very high volume of resins would be required for the use of production cycles designed in the projection of the unit, it is necessary to study options for water treatment at ADP-Fertilizantes.

4.2 Options for Water Treatment at ADP-Fertilizantes

4.2.1 Comparison between Ion Exchange Resins

The comparison between the type of resins supplied by the market and the type of resins present in ADP-Fertilizantes is interesting for the possibility of exchange of these resins by others that can improve the performance of the UFAA ion exchange system.

Since strong acid cation resins are used in cation columns and in mixed bed and as they are able to remove a larger amount of cations in the raw water compared to the weak ones, it will not be preferable to change the type of cation resins present in the unit.

Since type II and type I anion resins are used in the UFAA, resin type modification will not be necessary, since the use of type II in anion column followed by the use of type I in the mixed bed is the best possible combination, since type II resin has a higher operational capacity than type I, and the latter has a higher affinity for silica, which leads to the removal of previously existing silica leaks.

Although weak base anion resins have higher operational capacity than strong ones, their use is not preferable in this unit, since the removal of silica is one of the main parameters to be taken into account in the treatment of UFAA waters. The use of type III resin is also not favorable, because although it has positive aspects its operational capacity is inferior to the type I and II used in the unit. [9] [10] [16]

4.2.2 Reverse Osmosis

The consideration of a reverse osmosis system before the ion exchange system is a possibility to improve the performance of water treatment, so that the water arrives with better quality leading to an increase in production cycles and a decrease in the number of necessary regenerations.

The study of the reverse osmosis system required in ADP-Fertilizantes was carried out from the design software ROSA (Reverse Osmosis System Analysis), available by the company DOW, which in addition to making the design of the system also presents the parameters referring to quality of the water resulting from this treatment.

For the design of the reverse osmosis system, an operating temperature of 20ºC and a desired permeate flow rate of 60 m^3/h was considered. [17]

The determination of the best reverse osmosis design to be used included the projection of a single-stage system, a single-stage system with recycling, a two-stage system, a three-stage system, a two-stage system with recycling and a three-stage system with recycling.

It was verified that the system with the best permeate quality is the single-stage system, however as its recovery rate is only 50% a large amount of feed water was required, leading to a considerable waste of water. The next system that presented better permeate quality was the two-stage system, with a recovery rate of 75%, which is the system to be implemented at the plant.

Since the water obtained by the reverse osmosis two-stage system represents a superior quality to the water of the SMAS it can be used in the 4th circuit and in the 8th circuit. Therefore, only the production of demineralized water is required for the nitric acid plant and for the steam generator unit.

Once this water at the exit of the reverse osmosis will serve as a feed to the ion exchange system, it is possible to obtain the duration of the new production cycles of this system, taking into account the total removal of the existing compounds in the water, table 6.

Table 6 – Duration of future production cycles

		1st Test	**2nd Test**
Time (h)	**CAT**	264,43	348,42
	ANI	185,95	229,34

Table 6 shows a significant increase in the duration of production cycles, as expected due to the better quality of feed water, with the shortest time being 185,95 h.

With the increase in the duration of the production cycles there is a decrease in the number of regenerations and consequently a decrease in the consumption of regenerants, as can be seen in table 7.

Table 7 - Consumption of regenerants per day current and future

	Only Ion Exchange	**Ion Exchange after Reverse Osmosis**
HCl (kg/day)	3240,00	63,89
NaOH (kg/day)	1505,45	29,68

In order to increase the efficiency of the reverse osmosis system and to reduce fouling, scaling and membrane degradation it is necessary to use a pre-treatment.

This pretreatment includes a multimedia filter, an activated carbon filter, a scale inhibitor and a microfilter.

5 Economic Analysis[18]

The economic analysis included the calculation of the required total fixed investment and economic benefits from the implementation of the reverse osmosis system, considering that one year is composed by 365 days and that the unit will be subject to a total shutdown of 30 days per year.

The total fixed investment required is 345.8k€ and included the calculation of direct and indirect costs. Direct costs for this system include the costs of the base equipment, piping, control equipment, electrical installations, buildings and assemblies. The indirect cost for this system only refers to the provision for contingencies.

The total benefit from the reverse osmosis system is 240.2k€/year and includes the benefit of reducing regenerant consumption and the decrease of the water consumption of SMAS and the operating costs of this system.

Thus, it is possible to conclude that the value of the total fixed investment will be recovered through the total benefit after 1 year and 161 days.

5. Conclusion

Sampling during the production cycles of the ion exchange system in ADP-Fertilizantes allowed us to conclude, as expected, that the water obtained does not have the desired quality.

Although the resins used in the unit are the most indicated, they are not sufficient for the treatment of the current feed water of the ion exchange system, and it is necessary to implement an upstream reverse osmosis system to improve the water quality of ion exchange.

The reverse osmosis system to be implemented at the plant will be a two-stage system with a recovery rate of 75% and a permeate flow rate of 60 m^3/h, with an upstream pretreatment.

The water produced by reverse osmosis has a superior quality than SMAS water, so it can be used in the 4th and 8th circuits, reducing the consumption of drinking and demineralized water.

Since the water leaving the reverse osmosis system serves as a feed to the ion exchange, there is an increase in the duration of the production cycles and a reduction in the consumption of regenerants, as well as obtaining demineralized water with the desired quality.

For this improvement in ADP-Fertilizantes water treatment, a total fixed investment of 345,8 k€ will be required with a total benefit of 240,2k€/year, with the investment being recovered in less than 18 months.

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