The Technologies Optimization for the Treatment of Underground Water with Iron and Arsenic Content – A Case Study

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Abstract. Generally, in Romania, the water treatment aimed at removing the classic compounds of iron, manganese, ammonium, nitrates / nitrites, etc. by the known classical technologies (chemical coagulation, precipitation, decantation, slow / fast filtration with free / under pressure, disinfection). When in the raw water, besides the classical compounds, heavy metals semi-metals are also found, together with the classical treatment technologies, advanced technologies are required combined, known as hybrid processes (Electro-coagulation / EC, oxidation, adsorption / exchange ions, membrane filtration -UF / NF / RO), which can lead to the desired results. Along with iron, manganese, ammonium, nitrites / nitrites, arsenic is a naturally occurring element in the Earth's crust. Arsenic in drinking water is a global problem affecting the population worldwide because the arsenic and its components have carcinogenic properties. Regarding the elimination of arsenic (As) found in the water especially collected from the underground, the studies and researches applied were much more restricted and the applications completely isolated, at present the subject being more intensely approached. This situation is also caused by the fact that the Water Framework Directive no.98_83_CEE, transposed into national legislation, lowered the Arsenic (As) chemical indicator limit to 10 μg As / L (from 50 μg As / L). An alternative / complementary technology with low maintenance costs for underground treatment is Electro-oxidation/coagulation (EC), which has been of increasing interest in the last decade. The use of pilot stations / equipment for studying potential treatment technologies is essential for optimizing the treatment schemes and in order to avoid the implementation of costly technologies that cannot work for various reasons. In this case study, it was analysed comparatively from the efficiency point of view combining and optimizing oxidation-coagulation-filtration technologies in a pilot station for water treatment with iron, manganese and arsenic content, coming from the medium depth underground source (western Romania). In the initially provided technological flow (oxidation with ozone, multimedia filtration and disinfection with hypochlorite for the remanence), an electro-coagulation / oxidation (EC) cell was introduced upstream of the multimedia filter. This process aimed at eliminating the use of chemicals (ferric chloride) from the coagulation process that would have caused the rapid alteration of the multimedia filter and consequently increased operating costs. The results showed that compared to conventional technologies, the EC advantage includes high disposal efficiency, a compact treatment plant and the possibility of complete automation.
1. Introduction
Currently, in Romania and around the world, for the elimination from water of iron, manganese, ammonium, nitrates / nitrates and other physical-chemical compounds there are quite numerous studies, researches, experiences and applications / treatment stations [1, 2].

Regarding the removal of arsenic (As) from groundwater, the studies and researches applied were much more restricted, and the applications completely isolated. Currently, the subject is being more intensely addressed [3, 4]. This situation is also caused by the fact that the Water Framework Directive no. 98_83_CEE transposed into national legislation (L.458 / 2002 completed by L.311 / 2004) lowered the chemical indicator Arsenic (As) limit to 10 μg As / L (from 50 μg As / L). When arsenic is also found in raw water, classical treatment techniques should be combined or mixed with other techniques (hybrid processes) for the elimination of arsenic compounds, either independently or concomitantly with the elimination of iron, manganese and ammonia. [1, 2, 5-9]

The chemical processes of coagulation (CC) and adsorption are the most promising for the elimination of arsenic from the water which has high arsenic content, due to the low cost and the high efficiency. These processes are widely used in developed countries [1, 2, 5-9]. An alternative technology for providing low-cost, low-maintenance water treatment services is electro-coagulation (EC). The EC advantage over conventional technologies is high disposal efficiency, a compact treatment plant and the possibility of complete automatization. However, there are some limitations, such as high energy consumption on a large scale, optimization of EC reactor configuration and passivation of electrodes. [8, 9].

2. Case study
This study refers to a compact water treatment plant having a nominal flow rate of 15 m³ / h, designed to obtain drinking water in the centralized system and to eliminate the contamination with arsenic, iron, manganese, ammonium, suspensions, organic substances, etc., so that the parameters of the drinking water obtained after the final processing are in accordance with the legal norms (Directive 98/83 CEE transposed in the national legislation L.458 / 2002 updated by L.311 / 2004). The water comes from a deep well, F1 (more than 100 m deep) which is from a locality by western Timis county [10]. According to the water sample analyse (Table 1), higher values of the parameters are observed compared to the legal norms.

| Nr. crt. | Parameter  | Determined value | UM | Value allowed by Law no. 458/2002 republished | Test method                  |
|---------|------------|------------------|----|---------------------------------------------|-----------------------------|
| 1       | Arsenic    | 55               | μg/l | 10                                          | SR ISO 15586:2004          |
| 2       | Ammonium   | 1.85             | mg/l | 0.5                                         | SR ISO 7150-1:2001         |
| 3       | Manganese  | 65               | μg/l | 50                                          | SR ISO 15586:2004          |
| 4       | Total iron | 270              | μg/l | 200                                         | SR ISO 6332:1996/C91:2006  |

It is observed that the value of the arsenic in the water is 5.5 times higher than the allowed value (a very high value) and of the ammonia 3.5 times higher than the allowed value. It can be observed also exceeding the value of total iron and manganese. At the same time, the presence of hydrogen sulphide was found, and the pH of the water was 7.7. In order to correct the exceeding parameters and the disinfection of the water, in the project of the treatment station, it was initially proposed a water treatment flow composed of:

- The oxidation with ozone of the pollutants from the water source in order to oxidize and precipitate them, so that they can be eliminated from the water.
• Water filtration in a multimedia filter and biological mineralization.
• Water Oxygenation - Disinfection using residual nitrogen recovered after the first ozonation step.
• Disinfection of water using sodium hypochlorite.
• Storage of drinking water in a suspended stainless-steel tank.
• Water distribution in the distribution network through a pumping group.

The first ozonation step has the following purposes:
• Water oxygen enrichment in order to mineralization in the filter, especially of the ammonium ions.
• Iron oxidation from the bivalent valence Fe2 to the trivalent oxidation state Fe3 (Fe (OH) 3) that is retained in the multimedia filter.
• Manganese oxidation at a higher valence in order to bring it to a filterable form.
• Arsenic oxidation from valence +3 to valence +5 which is a filterable form.
• Decompose of large molecule organic substances (which are generally non-biodegradable) into smaller molecule substances that are used in the demineralization step from the filter.

The ozone necessary for the operation of the compact drinking water station was obtained on the spot using atmospheric oxygen. The obtained ozone was then injected into the treated water (depending on the particularities of the chosen technology), at two injection points using two ozone compressors, followed by the reaction of the ozone with the pollutants present in the water.

During the time of the water ozonation, the ozone molecule is decomposing and will release a free oxygen atom which will, in turn, reacts with substances dissolved in water, producing their oxidation. Ozone is an oxidant whose oxidation potential is high (2.07 V), according to (Table 2).

Table 2. The electrochemical potential of oxidation of different oxidants

| Oxidant                  | Oxidation potential <Volt> |
|--------------------------|-----------------------------|
| Hydroxyl radical OH⁻     | 2.8                         |
| Ozone O₃                 | **2.07**                    |
| Hydrogen peroxide H₂O₂   | 1.78                        |
| Potassium permanganate KMnO₄ | 1.7                 |
| Hipoclorit de sodium NaOCl | 1.49                   |
| Chlorine Cl₂             | 1.36                        |
| Chlorine dioxide ClO₂    | 1.27                        |
| Oxygen O₂                | 1.23                        |

As shown in Table 2, the ozone oxidation potential is exceeded by that of the hydroxyl radicals, which have an oxidation potential of 2.8 V. With an electrochemical potential higher than ozone, the hydroxyl radicals (OH⁻) can produce higher oxidation of substances dissolved in water and at a higher speed. This is important in the oxidation process of arsenic. In order to eliminate from the process, the use of ferric chloride (FeCl₃) for the chemical coagulation of arsenic (causes the clogging and rapid degradation of the multimedia filter) was analysed the possibility of optimizing the treatment scheme by adding in the process an alternative and complementary technology, namely electro-oxidation/coagulation (EC). Electrocoagulation (EC) (Figure 1) is a complex and interdependent process, strongly dependent on the chemistry of the aqueous environment. EC uses the electrochemical process to produce in situ chemical coagulants as needed. EC uses electricity to dissolve metals (M), such as aluminium and iron, to destabilize colloidal suspensions that lead to flocculation and flotation of pollutants [8, 9].
Electrocoagulation is an electrochemical process that simultaneously removes heavy metals, suspended solids, organic emulsions and many other water pollutants, using electricity and sacrificial metal plates (electrodes) instead of expensive chemical reagents. Sacrificial anodes corrode/passivate to release active coagulation precursors (usually aluminium or iron cations) into solution. Electrolytic reactions at cathodes are accompanied by gas (usually hydrogen bubbles) [7, 8] (Figure 1).

Figure 1. Electro-coagulation scheme

By inserting into the treatment hydraulic circuit, an ozonation step followed by a hydroxyl radical generation step (Electro-oxidation/coagulation- EC), an ozonation step is obtained whose characteristics are superior to simple ozonation. In the technical literature, it is called ADVANCED OZONIZATION. Considering the high concentration of arsenic in the water source, the first ozonation step was transformed into an advanced ozonation (ozone and hydroxyl radicals obtained by electric means - EC) (Figure 2).

Figure 2. Process Diagram - EC insertion point- according to reference [10]
Advanced oxidation takes place in the presence of hydroxyl radicals and ozone in water. Hydroxyl radicals are generated both by direct decomposition of ozone and in the electric field, according to reaction (1). The overall reaction results in the production of two $\text{OH}^0$ molecules from three ozone molecules.

$$3\text{O}_3 + \text{OH}^- + \text{H}^+ \rightarrow 2\text{OH}^0 + 4\text{O}_2$$ (1)

The first step consists of electrochemical (EC) treatment equipment (in which there is an advanced oxidation followed by the production of hydroxyl radicals in water) and then a vertical static mixer (the first mixing column).

Configuration and operation of EC equipment (Figure 3):

The electrochemical treatment chamber is made of stainless steel (1.4162) with a diameter of $\Phi$ 219 mm x 3 mm, length 420 mm, in which 6 titanium electrodes with 99.6% purity are fixed. The electrodes are covered with rhodium for corrosion. They have the dimensions of 400 mm x 85 mm x 3 mm. In the electrochemical treatment chamber, electrodes are placed in the form of a mesh, placed transversely on the flow of processed water, electrodes fed from a pulsating electricity source.

The pulsed electricity source ensures the galvanic separation between the electrical network and the supply voltage of the electrodes. It consists of a three-phase frequency converter that supplies a three-phase electrical transformer with the power of 3 kVA, at the output of which is a pulse-forming circuit followed by a contactor for changing the polarity of power supply to the electrodes. The supply voltage of the hydroxyl radical generation electrodes in the water is adjustable in the range 10 ... 48 V at a maximum frequency of 400 Hz, the sampling frequency of the inverter is greater than 6 kHz.

During the test period, the ozone production of the generator was kept constant at 40 g O$_3$ / h, and the ozone dose applied in the first step was 3 g O$_3$ / m$^3$ of water at a constant water flow rate of 10 m$^3$ / h. At the same time, the voltage applied to the EC was in the range of 30 ÷ 40 V and the effective electric current density on the electrodes was 16 mA / cm$^2$ at the same value of the water flow during the test period of 10 mc / h. The advanced ozonation step is followed by the filtration step, which takes
place in a stainless-steel filtration tank, on multiple layers of quartz sand/greensand and activated carbon/adsorbent Titansorb (Figure 3). The filtration step has the role of separating the dispersed solids from the water. At the top of the filter, the gas is separated from the water, which is then redirected to the ozone destroyer, and the ozone dissolved in the water is transformed into oxygen by the activated charcoal, which is the first filter layer. The sulphur hydrogen is retained in the active carbon layer. Iron retention is performed in the sand layer after it has been transformed by ozone into ferrous hydroxide [Fe (OH)\textsubscript{3}] which precipitates. Manganese (MnO\textsubscript{2}) and arsenic (As (OH)\textsubscript{5}) are also retained in the sand layer. After a certain time of filter, the washing process appears. The pollutants retained in the filter are eliminated in the washing water, which reaches a settling tank. The settling tank is placed outside of the treatment plant.

In the second step, ozonation is simple and takes place in the second mixing column. In this step, oxygenation and disinfection of water are performed (Figure 2). The process works correctly if the water redox potential (ORP) after the second ozonation step is greater than or equal to the value of +750 mV, potentially measured by the on-line sensor in the water treatment line.

The gas resulting from the ozonation reactions (in which ozone unreacted with water is also found) is discharged from the treated water by means of two degassing valves. It is then sent to an ozone destroyer, which contains an ozone destruction catalyst.

After the second ozonation, the water is taken over by an on-line pump that sends it to the storage tank. The storage tank is made of stainless-steel. In the water, sodium / calcium hypochlorite is dosed in order to ensure water disinfection in the water distribution network. The dose of hypochlorite introduced into the water is chosen so that the concentration of the free chlorine ion in the water in the storage tank does not exceed the value of 0.5 mg / l Cl\textsuperscript{-}, a value imposed by the legal norms and measured by the online free chlorine sensor (measuring cell with gold and copper electrode). At the end of the water distribution network, the value of the free chlorine concentration should be greater than 0.2 mg / l Cl\textsuperscript{-}.

From the storage tank, the water is taken over by a pumping group consisting of three pumps with the power of 6 kW each, which have the role of raising the water pressure in the distribution network in the range 3 ... 5 bar. The treatment station operation is completely automatized due to the PLC, the sensors, the HMI interface and the SCADA program implemented [10].

3. Results and discussions
Among the measurements made were those in which the residual ozone concentration in the water was measured after the first ozonation step, if the electrochemical step was stopped or it worked at the following parameters - advanced ozonation and ozonation:

- the water flow was kept constant at 10 m\textsuperscript{3} / h.
- the ozone production of the generator was kept constant at 40 g O\textsubscript{3} / h, and the ozone dose applied in the first step was 3 g O\textsubscript{3} / m\textsuperscript{3} of water.
- the stage of electrochemical treatment in operation consumed from the electrical network power of 250 W / h and the effective electric current density on electrodes was 16 mA / cm\textsuperscript{2}.

When the electrochemical step (EC) has been worked, hydroxyl radicals (OH-) are generated in the water. Their reaction rate with pollutants and ozone is high so in their presence the rate of reaction and decay of ozone increases. Thus, taking samples from the same place, under the same conditions, after the same time since ozone dosing, the lower ozone concentration in the presence of EC shows that it was a higher reaction rate (Table 3).
As shown in Table 3, the average residual ozone concentration in the absence of electrocoagulation step is 0.75 mg O3 / l, and in the presence of EC, the average residual ozone concentration is 0.24 mg O3 / l. The reaction rate for two chemical species can be written in the form of relation (2):

$$\frac{d[O_3]}{dt} = -k_{O_3-Mn} * [O_3] * [Mn]$$ (2)

Where: - [Concentration of a chemical species];
- Ks - reaction rate between two chemical species.

The initial concentrations of ozone and manganese were the same in both cases, differing only in the final concentrations, where it follows that when using the EC step the reaction rate k was higher, and the final concentrations of ozone and manganese were lower (Figure 4).

![Figure 4](image)

**Figure 4 – Values Step 1 - Simple oxidation / Advanced oxidation**
Table 4. Parameters values of treated water

| Nr. crt. | Parameter    | Determined value | UM | Value allowed by Law no. 458/2002 republished | Test method           |
|---------|--------------|------------------|----|---------------------------------------------|-----------------------|
| 1       | Arsenic      | 1,32 µg/l        |    | 10                                         | SR ISO 15586:2004     |
| 2       | Ammonium     | 0,06 mg/l        |    | 0,5                                        | SR ISO 7150-1:2001   |
| 3       | Manganese    | 2,9 µg/l         |    | 50                                         | SR ISO 15586:2004     |
| 4       | Total iron   | <10 µg/l         |    | 200                                        | SR ISO 6332:1996/C91:2006 |

4. Conclusions

The application of advanced oxidation (ozone + EC) can be a low-cost alternative technology that can be widely applied in many water treatment applications, in combination with other classical or advanced technologies. However, it requires a thorough analysis of the water to be treated as it is highly dependent on the chemistry of the aqueous environment and also requires tests in prior and meticulous laboratory conditions before being applied in situ. The dimensions and configuration of the EC, as well as the material and arrangement of the electrodes, electrode polarity time change on the arsenic removal, flow rate, pH evolution, are aspects that need to be studied very carefully.

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