

# Getting of Industrial Water for Steam Boilers with Treatment of Drinking Water from the Spring "Studenčica"

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**Abstract.** The drinking water from the source Studenčica contains a high percentage of dissolved mineral salts and can not be used for the operation of steam boilers. It is therefore necessary this water to be physically and chemically treated. Physical treatment consists of the removal of mechanical impurities by means of sand filters, and chemical treatment is consisted of two different procedures: decarbonation and demineralization. Decarbonation is performed in quick concrete reactor - accelerator with a solution of  $\text{Ca}(\text{OH})_2$  and  $\text{FeCl}_3$ , and demineralization is performed using ion modifiers.

**Key words:** industrial water, drinking water, steam boilers, treatment

## 1. Introduction

"Studenčica" source provides drinking water to several towns in western Macedonia: Kičevo, Macedonian Brod, Prilep, Kruševo and settlements that gravitate around these cities. In April, the capacity of the water ranged from 2713 to 4293 liters per second [1]. Water from this source except for drinking is used for the operation of some industrial facilities.

Mining Energy Plant "Oslomej" from Kičevo is one of the largest consumers of water from this source. It produce 700 GW power per year, and its capacity is 125 MW [2]. Mining Energy Plant "Oslomej" the water from the spring "Studenčica" used to work on steam boilers

Drinking water contains very soluble components that increase the conductivity ( $\sigma$ ) of the water. Therefore, the conductivity of the water is one of the most important parameters for the quality of the industrial water. Water with high conductivity can not be used in industry [3]. In buildings that have steam boilers, heat generated during the combustion of fuel uses to generate steam from water, which further drives the steam turbine [4]. Boilers need much more effectively to convert water into steam.

Facilities with steam boilers use two types of water: demineralized and decarbonised. Demineralization is used to power boilers and decarbonised to power cooling devices [5].

Chemical composition of drinking water is not responsible for the operation of steam boilers.

It contains ingredients that create a residue in boiler plants, cause corrosion of the boiler material and cause water foaming [6]. Therefore there is lower utilization, higher costs and less job security using steam boilers. Precipitation in boiler plants is due to the presence of soluble salts of calcium and magnesium in the water [7]. The solid crystalline precipitate which occurs on the heated surface of the walls of the boiler is called boiler stone and colloidal irregular precipitate is called boiler mud.

The water used for steam boilers need to meet calcium and magnesium salts or its fortress has to be  $<0,05$  °D for low pressure steam boilers, and  $<0,02$  °D for high pressure boilers, because the creation of boiler stone. Dissolved gases such as  $\text{O}_2$  and  $\text{CO}_2$  cause corrosion, so they need to be removed. Copper and iron also cause corrosion.  $\text{H}_4\text{SiO}_4$  should not be included, because it creates a solid stone. Water does not have to contain organic materials, because they cause water foaming and the level of water could not properly be controlled.

There is a need of physical and chemical treatments to remove the unnecessary components from water or to reduce their amounts to the minimum acceptable value. Physical treatment comprises the processes of deposition and filtration, while the chemical treatment consists of two different procedures: decarbonation and demineralization [5], [8], [9].

Decarbonation is a process that removes carbonate salts. Decarbonized water can't be used for steam boilers, because the value of the hardness is 0,3 to 1 °D. It can be used in the technological and the process of cooling. Its usage in steam boilers

should be followed by the process of demineralization, or removal of all salts, carbonates and non carbonates.

Decarbonation can be made using different chemical elements:

$\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Na}_3\text{PO}_4$  and  $\text{Ca}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{FeCl}_3$  etc.

Demineralization is performed using ion modifiers, which may be cationic and anionic. Cationic modifiers exchange the cations, while anionic modifiers exchange the anions [10], [11], [12].

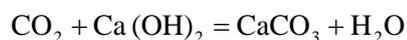
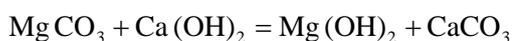
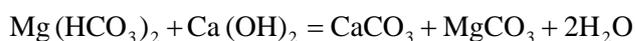
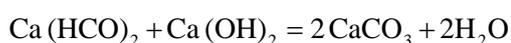
## 2. Materials and methods

Mining - energy plant "Oslomej" uses drinking water from the source "Studenčica" as raw water. This water has the same quality water as the population of the town of Kičevo use for drinking. It contains many dissolved minerals, metals and gases and therefore is required physical and chemical treatment [13]. The water is first collected in a concrete reservoir with a volume of 1000 m<sup>3</sup>. This reservoir is located above the Mining Energy Plant "Oslomej" and because of the gravity there is a movement of the water from the reservoir to the accelerator. The accelerator is a fast concrete reactor in which the process of decarbonation is performed. The capacity of the accelerator is 380-480 m<sup>3</sup>/h. The speed which changes the capacity of the accelerator should not be higher than 20 - 40 m<sup>3</sup>/h. If this speed is higher than 40 m<sup>3</sup>/h, the deposition will not be successful and the water that comes out will occur with greater amount of non precipitated particles.

**Physical treatment** - This treatment is removal of mechanical impurities from water. He performed with sand filters. The capacity of the filter depends on the consumption of water. Sand filters are filled by gravel whose granulation is 2,0-3,0 mm, and the amount of sand filtration is 1,4 m. When water passes through the sand filter, mechanical impurities are retained between sand grains. If the water contains more impurities it impedes the passage of water through the filter. Therefore it is necessary to rinse the filter. The filter is rinsed by decarbonized water that is worn by the pump from the decarbonized water tank. The recommended intensity of the water flow is 40-60 m<sup>3</sup>/h.

**Chemical treatment** – This treatment consists of two processes: decarbonation and demineralization. The process of decarbonation is performed using  $\text{Ca}(\text{OH})_2$  and  $\text{FeCl}_3$  as coagulants. The solution of  $\text{Ca}(\text{OH})_2$  is prepared in separate

tanks and its concentration is about 3,6 %. The density of this solution is approximately 1,055 g/cm<sup>3</sup>. The accelerator solution of  $\text{Ca}(\text{OH})_2$  is transferred by pumps from these tanks. Prepared solution of  $\text{Ca}(\text{OH})_2$  should always be mixed using special blenders. For 24 hours around 700-1300 kg solution of  $\text{Ca}(\text{OH})_2$  is spent. The greatest amount of  $\text{Ca}(\text{OH})_2$  is consumed in summer and the lowest in winter. The reason is that in summer the highest amount of decarbonated water for cooling the plants in "Oslomej" is consumed. Dosing the solution of  $\text{Ca}(\text{OH})_2$  in the accelerator must be carried out continuously. Changing the amount of solution of  $\text{Ca}(\text{OH})_2$  depends on the change of the capacity of the accelerator. Dosage amount of solution of  $\text{Ca}(\text{OH})_2$  in the accelerator depends on the value of alkalinity "p" and alkalinity "m" of the water in the accelerator, which is constantly monitored. Alkalinity "p" of the water in level 1 should range from 0,2 - 0,4 mVal/dm<sup>3</sup>. When  $2p = m$ , the decarbonation is properly executed and  $\text{Ca}(\text{OH})_2$  is exactly balanced. When  $\text{Ca}(\text{OH})_2$  is added in excess,  $2p > m$ , and when  $2p < m$ , there is added a smaller amount of  $\text{Ca}(\text{OH})_2$  than necessary. Under the condition of excess of  $\text{Ca}(\text{OH})_2$  there is a reaction between  $\text{Ca}(\text{OH})_2$  and atmospheric  $\text{CO}_2$ , which creates  $\text{CaCO}_3$ . When  $2p < m$ , or  $\text{Ca}(\text{OH})_2$  is added less than necessary, decarbonation is incomplete and follows a process of salt precipitation in the condenser, thus reducing thermal alteration. Using the process of decarbonation there is mainly a removal of calcium and magnesium bicarbonates, according to the following reactions:



$\text{FeCl}_3$  is a coagulant and it should be added continuously. If you stop adding  $\text{FeCl}_3$ , the outlet water from the accelerator will skyrocket the amount of sediment. If decarbonation is done correctly, the water that comes out of the accelerator is clear and its fortress is less than 3,5 °D.  $\text{FeCl}_3$  is prepared in the form of a solution with a density of 1,006 g/cm<sup>3</sup>. For 1 m<sup>3</sup> raw water 20-30 g  $\text{FeCl}_3$  is spent as coagulant. For 24 hours, depending on the quality of raw water, about 75-90 kg coagulant is consumed. Sludge removing is performed in every 4 hours. The precipitate is removed simultaneously from both holes and is collected in two reservoirs. The volume of one tank is 30 m<sup>3</sup>. Piping after removing sludge should be rinsed using decarbonized water to avoid their blockage. To reduce the water losses there is a need for the clear water reservoir to be turned back to

the accelerator after sludge removing. Sediment from the bottom of the tank is discharged.

The process of demineralization is also called softening of the water. These are the important parameters for demineralised water: pH, conductivity, SiO<sub>2</sub>, Cl<sup>-</sup>, total hardness (TH). Demineralized water for system water-steam must fulfill the conditions given in Table 1 [3].

Table 1. Recommended value of demineralized water for system water-steam

| Parameters              | Recommended value |
|-------------------------|-------------------|
| pH                      | 9                 |
| TH                      | 0                 |
| Cl <sup>-</sup> (µg/L)  | 10                |
| SiO <sub>2</sub> (µg/L) | 20                |
| σ (µs/cm)               | 0,2               |

The demineralization is performed using ion modifiers. Various types of cationic and anionic modifiers are used. Over the period of the analysis, the cationic modifier K-1 is used filled by ionic modification table LEVATIT S-100 and anionic modifier A-1 filled by ionic modification table VOFATIT SBK. The height of cationic modifier is 1 m, and the amount is 0,8 m<sup>3</sup>. The height of the anion

modifier is 1 m and the amount is 1,1 m<sup>3</sup>. Ion modifiers are regenerated, cationic are regenerated by concentrated HCl, and the anionic are regenerated by concentrated NaOH [14].

### 3. Results and discussion

The Mining - energy Plant "Oslomej" daily performs analysis of raw, demineralized and decarbonized water. Raw water is drinking water that is collected in concrete tanks over mining - energy Plant "Oslomej". There is an analysis of the following parameters: conductivity, pH, alkalinity "p" and "m", total hardness (TH), calcium hardness (CaH), magnesium hardness (MgH), carbonate hardness (KH), Fe<sup>3+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SiO<sub>2</sub>, KMnO<sub>4</sub> etc.

Table 2. shows the values of the parameters analyzed in rough water.

In Table 2. is shown that the raw water from 28.03.2013 has the highest value for SiO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Fe<sup>3+</sup> and the lowest for σ, pH, TH and p/m for the three analyzed waters. It is because at this time of the year there is a greatest rainfall and snow melting, which increases the amount of water in the sources.

Table 2. Analyzed parameters in raw water

| Date       | σ (µs/cm) | pH  | TH (°D) | p/m (mVal/L) | Fe <sup>3+</sup> (mg/L) | Cl <sup>-</sup> (mg/L) | SO <sub>4</sub> <sup>2-</sup> (mg/L) | SiO <sub>2</sub> (mg/L) |
|------------|-----------|-----|---------|--------------|-------------------------|------------------------|--------------------------------------|-------------------------|
| 28.12.2012 | 157       | 8,1 | 6,2     | 0,00/2,14    | 0,022                   | 2,1                    | 15,8                                 | 2,70                    |
| 13.02.2013 | 144       | 8,0 | 6,3     | 0,00/2,2     | 0,018                   | 2,2                    | 17,4                                 | 2,95                    |
| 28.03.2013 | 135       | 7,8 | 5,2     | 0,00/2,1     | 0,039                   | 12,2                   | 18,1                                 | 3,19                    |

Raw water is taken in accelerators where the process of decarbonation is performed. Every 2 hours take sample for analysis. The sample is collected from three different places: level 1, level 2 and level 3. Level 1 is the lowest level, and level 3 is the highest level of the accelerator. In every 2 hours there are monitored these parameters for all the 3 levels: σ, pH, p/m and TH. The process of decarbonation follows these parameters to be accurately dosed Ca(OH)<sub>2</sub> and FeCl<sub>3</sub>. Apart from these parameters, once in the month there are made analyzes of water decarbonation just like those for the raw water.

Table 3 provides the results of measurements of water decarbonized in three different days and different times of the day.

When the decarbonation is properly executed, 2p=m. Table 3 shows that on 27.01.2012 and 10.02.2013, 2p> m, which means that Ca(OH)<sub>2</sub> was added in excess or there was not enough coagulant FeCl<sub>3</sub>. In this case FeCl<sub>3</sub> coagulant is added to get the required terms of p and m. On 07.03.2013 at 11 am, just in the first level, 2p=m, while in the second and third level 2p < m. The relationship between p and m in this case is corrected by adding Ca(OH)<sub>2</sub>. Because of this, we monitor the basic parameters in every 2 hours.

Table 3. Important parameters in decarbonized water

| Levels in the accelerator | Important parameters measured on 27.01.2012 at 13 <sup>30</sup> hour |      |                           |              |
|---------------------------|--|------|---------------------------|--------------|
|                           | $\sigma$ ( $\mu\text{s/cm}$ )  | pH   | TH ( $^{\circ}\text{D}$ ) | p/m (mVal/L) |
| Level 1                   | 68,2   | 10,4 | 2,5                       | 0,35/0,5     |
| Level 2                   | 69,3   | 10,5 | 2,5                       | 0,3/0,5      |
| Level 3                   | 69,0   | 10,4 | 2,9                       | 0,35/0,5     |
|                           | Important parameters measured on 10.02.2013 at 11 hour               |      |                           |              |
|                           | $\sigma$ ( $\mu\text{s/cm}$ )  | pH   | TH ( $^{\circ}\text{D}$ ) | p/m (mVal/L) |
| Level 1                   | 65,1   | 10,2 | 2,9                       | 0,35/0,5     |
| Level 2                   | 64,2   | 10,4 | 2,7                       | 0,35/0,5     |
| Level 3                   | 63,7   | 10,3 | 2,8                       | 0,35/0,5     |
|                           | Important parameters measured on 07.03.2013 at 11 hour               |      |                           |              |
|                           | $\sigma$ ( $\mu\text{s/cm}$ )  | pH   | TH ( $^{\circ}\text{D}$ ) | p/m (mVal/L) |
| Level 1                   | 61,5   | 9,7  | 3,2                       | 0,3/0,6      |
| Level 2                   | 60,6   | 9,67 | 2,7                       | 0,4/0,9      |
| Level 3                   | 61,7   | 9,5  | 2,5                       | 0,3/0,65     |

In Table 4 are given the values of p/m and TH at different times of the day and different level.

In all the three selected days, at different times of the day  $2p=m$ , which means decarbonization is properly executed and there are not necessary any adjustments by adding  $\text{Ca}(\text{OH})_2$  or  $\text{FeCl}_3$ . In table 4

TH value is shown that over time which is constantly declining for the three days. Although TH in decarbonized water is much smaller than TH in the rough water, this is not enough to be used for "Oslomej" steam boilers.

Table 4. p/m and TH of decarbonized water at different times of the day and different level

| Hour             | Level   | 05.02.2013   |                           | 06.02.2013   |                           | 08.02.2013   |                           |
|------------------|---------|--------------|---------------------------|--------------|---------------------------|--------------|---------------------------|
|                  |         | p/m (mVal/L) | TH ( $^{\circ}\text{D}$ ) | p/m (mVal/L) | TH ( $^{\circ}\text{D}$ ) | p/m (mVal/L) | TH ( $^{\circ}\text{D}$ ) |
| 7 <sup>00</sup>  | Level 1 | 0,30/0,60    | 2,5                       | 0,35/0,70    | 2,4                       | 0,45/0,90    | 2,5                       |
|                  | Level 2 | 0,30/0,60    | 2,5                       | 0,35/0,70    | 2,4                       | 0,45/0,90    | 2,5                       |
|                  | Level 3 | 0,30/0,60    | 2,5                       | 0,35/0,70    | 2,4                       | 0,45/0,90    | 2,5                       |
| 9 <sup>00</sup>  | Level 1 | 0,35/0,70    | 1,5                       | 0,30/0,60    | 1,9                       | 0,40/0,80    | 2,4                       |
|                  | Level 2 | 0,35/0,70    | 1,5                       | 0,30/0,60    | 1,9                       | 0,40/0,80    | 2,4                       |
|                  | Level 3 | 0,35/0,70    | 1,5                       | 0,30/0,60    | 1,9                       | 0,40/0,80    | 2,4                       |
| 11 <sup>00</sup> | Level 1 | 0,35/0,70    | 1,4                       | 0,30/0,60    | 1,7                       | 0,30/0,60    | 2,2                       |
|                  | Level 2 | 0,35/0,70    | 1,4                       | 0,30/0,60    | 1,7                       | 0,30/0,60    | 2,2                       |
|                  | Level 3 | 0,35/0,70    | 1,4                       | 0,30/0,60    | 1,7                       | 0,30/0,60    | 2,2                       |

It is therefore necessary to perform demineralization that will remove all mineral materials and TH will be 0. If the value of m is decreased to 0,2 mVal/L regeneration of the cationic modifiers is necessary. Regeneration is performed using a 5-8% solution of HCl. For successful regeneration 320 dm<sup>3</sup> of 30% HCl is needed. Through coil demineralized water flow of 1,5 dm<sup>3</sup>/h is passed, and 5% is added HCl. Regeneration is carried out in 60-70 minutes depending on the concentration of the solution. For the regeneration of anionic modifiers

150 dm<sup>3</sup> of 40% NaOH is required. If the solution for regeneration is 4 %, regeneration ends in 50 min. The temperature of the solution for regeneration should not be higher than 40°C. After regeneration of both modifiers, cationic and anionic are rinsed with decarbonised water in 30 minutes.

Table 5 shows the values of  $\sigma$ , pH, p/m, TH and SiO<sub>2</sub> in raw, decarbonized and demineralized water.

Table 5. Important parameters in raw, decarbonized and demineralized water

| Type of water | Important parameters measured on 28.12.2012 |      |                           |              |   |
|---------------|---|------|---------------------------|--------------|---|
|               | $\sigma$ ( $\mu\text{s}/\text{cm}$ )        | pH   | TH ( $^{\circ}\text{D}$ ) | p/m (mVal/L) | $\text{SiO}_2$ ( $\mu\text{g}/\text{L}$ ) |
| Raw           | 157   | 8,1  | 6,2                       | 0,00/2,14    | 2 700                                     |
| Decarbonized  | 70  | 10,2 | 1,5                       | 0,25/0,5     | 2 080                                     |
| Demineralized | 0,8   | 7,2  | 0,000                     | 0,00/0,05    | <10                                       |
|               | Important parameters measured on 13.02.2013 |      |                           |              |   |
|               | $\sigma$ ( $\mu\text{s}/\text{cm}$ )        | pH   | TH ( $^{\circ}\text{D}$ ) | p/m (mVal/L) | $\text{SiO}_2$ ( $\mu\text{g}/\text{L}$ ) |
| Raw           | 144   | 8,0  | 6,3                       | 0,00/2,2     | 2 900                                     |
| Decarbonized  | 61,7  | 9,9  | 2,1                       | 0,25/0,5     | 2560                                      |
| Demineralized | 0,3   | 7,8  | 0,000                     | 0,00/0,05    | <10                                       |
|               | Important parameters measured on 28.03.2013 |      |                           |              |   |
|               | $\sigma$ ( $\mu\text{s}/\text{cm}$ )        | pH   | TH ( $^{\circ}\text{D}$ ) | p/m (mVal/L) | $\text{SiO}_2$ ( $\mu\text{g}/\text{L}$ ) |
| Raw           | 135   | 7,8  | 5,2                       | 0,00/2,1     | 3190                                      |
| Decarbonized  | 60  | 9,6  | 2,0                       | 0,2/0,4      | 2628                                      |
| Demineralized | 0,5   | 7,7  | 0.000                     | 0,00/0,05    | <10                                       |

Table 5 shows that the conductivity of the water is greatly reduced during the processes of decarbonation and demineralization. Raw water's conductivity is about 140  $\mu\text{s}/\text{cm}$  and it is reduced by more than a half of its value, to the value of around 60  $\mu\text{s}/\text{cm}$ . After the process of demineralization,  $\sigma$  value is less than 0,5  $\mu\text{s}/\text{cm}$ . The conductivity decreases because many ions and many salts are removed by the processes of decarbonation and demineralization. Besides conductivity, reducing salts affects the overall hardness of the water. Raw water's total hardness is 5,2- 6,3  $^{\circ}\text{D}$ . This value for the decarbonation water varies from 1,5 to 2,5  $^{\circ}\text{D}$ , and for demineralization water is equal to 0,00  $^{\circ}\text{D}$ . The amount of  $\text{SiO}_2$  is slightly reduced during the decarbonation and it is almost completely removed in the process of demineralization.

#### 4. Conclusions

Drinking water from the spring "Studenčica" except for drinking is used as industrial water for the operation of steam boilers. This water is necessary to be physically and chemically treated before using. The physical treatment is removal of mechanical impurities by filtration through sand filters. Chemical treatment is comprised of decarbonation and demineralization. Decarbonation is performed by  $\text{Ca}(\text{OH})_2$  and  $\text{FeCl}_3$ . The ion modifiers are used for the process of demineralization which removes all mineral material. The chemical treatment is carried out continuously. Daily analysis we perform of crude, decarbonation and demineralization water. The daily monitoring is important for the parameters  $\sigma$ , pH, TH and p /m, while there is once a month monitoring for analyzing

all the parameters in the water. The results show that  $\sigma$  is the largest in the rough water. In the process of decarbonation this value is almost halved, while the demineralization water gives the smallest and has negligible value in terms of raw water. The total hardness of water is the most important parameter of the water for its use in steam boilers. TH value in the raw water is around 6 $^{\circ}\text{D}$ , in decarbonation water this value is around 2 $^{\circ}\text{D}$ , and in demineralization water it is 0 $^{\circ}\text{D}$ .

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