# CHEMICAL TREATMENT OF WATER FOR STEAM BOILERS IN MINING POWER COMPLEX "OSLOMEJ" IN KICEVO

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**Abstract:** Mining power complex "Oslomej" in Kicevo is a thermal power plant that achieves an annual production of about 700 GW/h. Oslomej uses drinking water for operating of the steam boilers.. Since drinking water does not meet the required criteria for the working of steam boilers, it is necessary to be chemically treated. The chemical treatment is consisted of two different procedures: decarbonation and demineralization. Decarbonation is performed in quick concrete reactor - accelerator with a solution of $Ca(OH)_2$ and $FeCl_3$, and demineralization is performed using ion modifiers. As a result of the process of decarbonation, there is a partial water refill which reduces the conductivity. After applying the process of demineralization there is a complete removal of the mineral substances, so that the total water hardness is 0 degrees German (ºD), $SiO_2$ is less than 0,2 mg/L, and the conductivity (σ) is smaller than 0,5 μS/cm. Filtering is done using sand filters and the recommended intensity of the flow of filtered water is 40 - 60 $m^3$/h. The analyses of drinking, decarbonized and demineralized water are made daily. This paper describes the chemical treatment of water for steam boilers in "Oslomej". There are shown the results from the analysis of drinking, decarbonized and demineralized water in randomly selected days.

**Keywords**: decarbonation, demineralization, steam boilers, water

## 1. INTRODUCTION

About 96 % of the total domestic energy production in Macedonia is provided by AD ELEM. Power plants are used for production of approximately 5000 GW/h or 80 % of the total energy, while hydro plants contribute for about 1200 GW/h. The contribution of the mining - energy factories in Bitola and Kicevo is approximately 80 % of the total energy provided. These thermal plants use coal as primary fuel. The average calorific value is 7660 KJ/kg. "Oslomej", mining – energy plant in Kicevo, has installed capacity of 125 MW, and the net annual production is 700 GW/h [1].

This power plant uses drinking water for the steam boiler operating. According to its chemical composition, this water does not match the steam boilers needs. It contains ingredients that create a residue in boiler plants, cause corrosion of the boiler material and cause water foaming [2]. Therefore comes to lower utilization, higher costs and less job

security using steam boilers. Precipitate in boiler plants is due to the presence of soluble salts of calcium and magnesium in the water [3]. 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 the following conditions:

- Must not contain iron and copper, because the presence of hydrogen and oxygen causes corrosion
- Water fortress of low pressure steam boilers has to be <0,05 ºD, and for high pressure boilers <0,02 ºD
- The content of O2 has to be <0,02 mg/L because of caused corrosion of boiler
- Do not have to contain organic materials, because they cause water foaming and the level of water could not properly be controlled
- Free $H_2CO_3$ should not be included, because of the number of changes in pH
- $H_4SiO_4$ should not be included, because it creates a solid stone
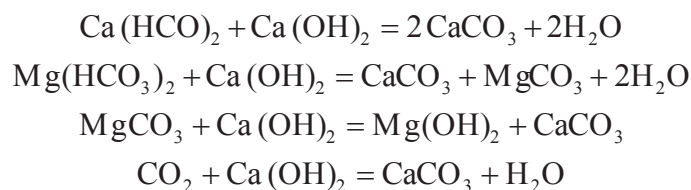- The most suitable pH for high pressure water boilers is 9,6

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 [4-7]. 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 ºD. 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: $Na_2CO_3$, NaOH, $Na_2CO_3$ and NaOH, $Na_3PO_4$, $Ca(OH)_2$, $Na_3PO_4$ and $Ca(OH)_2$, $Ca(OH)_2$ and $FeCl_3$ etc. Demineralization is performed using ion modifiers, which may be cationic and anionic. Cationic modifiers exchange the cations, while anionic modifiers exchange the anions [8,9].

## 2. MATERIALS AND METHODS

Mining - energy plant "Bitola" uses drinking water from the source "Studencica" as raw water. This water does not meet the required criteria for steam boilers and therefore is chemically treated [10]. The water is first collected in a concrete reservoir with a volume of 1000 $m^3$. 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 is performed the process of decarbonation. The capacity of the accelerator is 380-480 $m^3$/h. The speed which changes the capacity of the accelerator should not be higher than 20 - 40 $m^3$/h. If this speed is higher than 40 $m^3$/h, the deposition will not be successful and the water that comes out will occur greater amount of non-precipitated particles.

The process of decarbonation is performed using $Ca(OH)_2$ and $FeCl_3$ as coagulants. The solution of $Ca(OH)_2$ is prepared in separate tanks and its concentration is about 3,6 %. The density of this solution is approximately 1,055 $g/cm^3$. The accelerator solution of $Ca(OH)_2$ is transferred by pumps from these tanks. Prepared solution of $Ca(OH)_2$ should always be mixed using special blenders. For 24 hours it is spent around 700-1300 kg solution of $Ca(OH)_2$. The greatest amount of $Ca(OH)_2$ is consumed in summer and the lowest in winter. The reason is that in summer is consumed the highest amount of decarbonated water for cooling the plants in " Oslomej". Dosing the solution of $Ca(OH)_2$ in the accelerator must be carried out continuously. Changing the amount of solution of $Ca(OH)_2$ depends on the change of the capacity of the accelerator. Dosage amount of solution of $Ca(OH)_2$ 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 $mVal/dm^3$. When 2p = m, the decarbonation is properly executed and $Ca(OH)_2$ is exactly balanced. When $Ca(OH)_2$ is added in excess, 2p> m, and when 2p <m, there is added a smaller amount of $Ca(OH)_2$ than necessary. Under the condition of excess of $Ca(OH)_2$ there is a reaction between $Ca(OH)_2$ and atmospheric $CO_2$, which creates CaCO3. When 2p <m, or $Ca(OH)_2$ 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:

$$Ca(HCO)_2 + Ca(OH)_2 = 2\,CaCO_3 + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 = CaCO_3 + MgCO_3 + 2H_2O$$
$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3$$
$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$$

$FeCl_3$ is a coagulant and it should be added continuously. If you stop adding $FeCl_3$, 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 ºD. $FeCl_3$ is prepared in the form of a solution with a density of 1,006 $g/cm^3$. For 1 $m^3$ raw water it is spent 20-30 g $FeCl_3$ as coagulant. For 24 hours, depending on the quality of raw water, it is consumed about 75-90 kg coagulant. 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 $m^3$. Piping after removing sludge should be rinsed using decarbonized water to avoid their blockage. To reduce the water losses there is a need the clear water reservoir to be turned back to the accelerator after sludge removing. Sediment from the bottom of the tank is discharged.

Purification of water by mechanical impurities is done by sand filters. The capacity of the filter depends on the consumption of water. Sand filters are filled by gravel which 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 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 $m^3$/h.

The demineralization is performed using ion modifiers. There are used various types of cationic and anionic modifiers. Over the period of the analysis, it is used the cationic modifier K-1 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 $m^3$. The height of the anion modifier is 1 m and the amount is 1,1 $m^3$. Ion modifiers are regenerated, cationic are regenerated by concentrated HCl, and the anionic are regenerated by concentrated NaOH [11].

## 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: $\sigma$, pH, alkalinity "p" and "m", total hardness (TH), calcium hardness (CaH), magnesium hardness (MgH), carbonate hardness (KH), $Fe^{3+}$, $Cl^-$, $SO_4^{2-}$, $SiO_2$, $KMnO_4$ etc. table 1 shows the values of the important parameters in rough water.

Table 1. Important parameters in raw water

| date | $\sigma$ ($\mu$s/cm) | pH | TH (ºD) | p/m (mVal/L) | $SiO_2$ (mg/L) |
|---|---|---|---|---|---|
| 28.12.2012 | 157 | 8,1 | 6,2 | 0,00/2,14 | 2,70 |
| 13.02.2013 | 144 | 8,0 | 6,3 | 0,00/2,2 | 2,95 |
| 28.03.2013 | 135 | 7,8 | 5,2 | 0,00/2,1 | 3,19 |

In table 1 is shown that the raw water from 28.03.2013 has the highest value for $SiO_2$, and the lowest for $\sigma$, 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. Raw water is taken in accelerators where the process of decarboxylation is performed. The process of decarbonation is taking samples for analysis in every 2 hours. 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: $\sigma$, pH, p/m and TH. The process of decarbonation follows these parameters to be accurately dosed $Ca(OH)_2$ and $FeCl_3$. Apart from these parameters, once in the month there are made analyzes of decarbonation water just like those for the raw water. Table 2 provides the results of measurements of decarbonized water in three different days and different times of the day.

Table 2. Important parameters in decarbonized water

| Levels in the accelerator | Important parameters measured on 27.01.2012 in 13$^{30}$ hour | | | |
|---|---|---|---|---|
| | σ (µs/cm) | pH | TH (ºD) | 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 in 11 hour | | | |
| | σ (µs/cm) | pH | TH (ºD) | 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 in 11 hour | | | |
| | σ (µs/cm) | pH | TH (ºD) | 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 |

When the decarbonation is properly executed, 2p=m. Table 2 shows that on 27.01.2012 and 10.02.2013, 2p> m, which means that $Ca(OH)_2$ was added in excess or there was not enough coagulant $FeCl_3$. In this case $FeCl_3$ 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 $Ca(OH)_2$. Because of this, we monitor the basic parameters in every 2 hours.

In table 3 are given the values of p/m and TH at different times of the day. These values are exactly the same for all 3 levels.

Table 3. p/m and TH of decarbonized water at different times of the day

| hour | 05.02.2013 | | 06.02.2013 | | 08.02.2013 | |
|---|---|---|---|---|---|---|
| | p/m (mVal/L) | TH (ºD) | p/m (mVal/L) | TH (ºD) | p/m (mVal/L) | TH (ºD) |
| 7$^{00}$ | 0,30/0,60 | 2,5 | 0,35/0,70 | 2,4 | 0,45/0,90 | 2,5 |
| 9$^{00}$ | 0,35/0,70 | 1,5 | 0,30/0,60 | 1,9 | 0,40/0,80 | 2,4 |
| 11$^{00}$ | 0,35/0,70 | 1,4 | 0,30/0,60 | 1,7 | 0,30/0,60 | 2,2 |

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 $Ca(OH)_2$ or $FeCl_3$. In table 3 is shown TH value that over time which is constantly declining for the three days. Although TH in decarbonizated water is much smaller than TH in the rough water, this is not enough to be used for "Oslomej" steam boilers. It is therefore necessary to perform demineralization that will remove all mineral materials and TH will be 0.

Table 4 shows the values of σ, pH, p/m, TH and $SiO_2$.

Table 4. Important parameters in raw, dacarbonized and demineralized water

| Type of water | Important parameters measured on 28.12.2012 | | | | | |
|---|---|---|---|---|---|---|
| | $\sigma$ ($\mu$s/cm) | pH | TH (ºD) | p/m (mVal/L) | $SiO_2$($\mu$g/L) | $\sigma$ ($\mu$s/cm) |
| Raw | 157 | 8,1 | 6,2 | 0,00/2,14 | 2 700 | 157 |
| Decarbonized | 70 | 10,2 | 1,5 | 0,25/0,5 | 2 080 | 70 |
| Demineralized | 0,8 | 7,2 | 0,000 | 0,00/0,05 | <10 | 0,8 |
| | Important parameters measured on 13.02.2013 | | | | | |
| | $\sigma$ ($\mu$s/cm) | pH | TH (ºD) | p/m (mVal/L) | $SiO_2$($\mu$g/L) | $\sigma$ ($\mu$s/cm) |
| Raw | 144 | 8,0 | 6,3 | 0,00/2,2 | 2 900 | 144 |
| Decarbonized | 61,7 | 9,9 | 2,1 | 0,25/0,5 | 2560 | 61,7 |
| Demineralized | 0,3 | 7,8 | 0,000 | 0,00/0,05 | <10 | 0,3 |
| | Important parameters measured on 28.03.2013 | | | | | |
| | $\sigma$ ($\mu$s/cm) | pH | TH (ºD) | p/m (mVal/L) | $SiO_2$($\mu$g/L) | $\sigma$ ($\mu$s/cm) |
| Raw | 135 | 7,8 | 5,2 | 0,00/2,1 | 3190 | 135 |
| Decarbonized | 60 | 9,6 | 2,0 | 0,2/0,4 | 2628 | 60 |
| Demineralized | 0,5 | 7,7 | 0.000 | 0,00/0,05 | <10 | 0,5 |

Table 4 shows that the conductivity of the water is greatly reduced during the processes of decarbonation and demineralization. Raw water's conductivity is about 140 µs/cm and it is reduced by more than a half of its value, to the value of around 60 µs/cm. After the process of demineralization, σ value is less than 0,5 µs/cm. The conductivity decreases because many ions and many salts are removed by the processes of dekacarbonation and demineralization. Besides conductivity, reducing salts affect the overall hardness of the water. Raw water's total hardness is 5,2- 6,3 ºD. This value for the decarbonation water varies from 1,5 to 2,5 ºD, and for demineralization water is equal to 0,00 ºD. The amount of $SiO_2$ is slightly reduced during the decarbonation and it is almost completely removed in the process of demineralization.

## 4. CONCLUSIONS

Steam boilers in "Oslomej" mining - energy plant are using drinking water. This water is chemically treated before using, because it does not fulfill the required criteria. Chemical treatment is comprised of decarbonation and demineralization. Decarbonation is performed by $Ca(OH)_2$ and $FeCl_3$. In every 2 hours there is a monitoring of parameters "p" and "m" to see whether these assets are properly dosed. When 2p> m, there should be added $Ca(OH)_2$, and when 2p <m, $Ca(OH)_2$ is in excess and there should be added $FeCl_3$. The ion modifiers are used for the process of demineralization which removes all mineral material. The chemical treatment is carried out continuously and therefore we perform daily analyzes of crude, decarbonation and demineralization water. The daily monitor is important for the parameters σ, pH, TH and p /m, while there is once a month monitoring for analyzing all parameters in the water. The results show that σ 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 6ºD, in decarbonation water this value is around 2ºD, and in demineralization water it is 0ºD. The results show that the amount of $SiO_2$ is extremely reduced in the process of demineralization while in the process of decarbonation the reduction is very small.

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