Aluminum compound forms in the Al–H₂O system as applied to operating conditions of Dry Cooling Towers

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Abstract. One of important indicators of reliable operation of the steam-water cycle at power plants is water chemistry. Special chemicals are used to adjust properties of working fluids. At designing a new unit the chemicals are selected on the basis of parameters of water, steam and materials, used in different parts of the cycle. Another indicator is minimizing the cooling water loss. Typical loss of cooling water is about 5% of total water amount. This loss is associated with evaporation, droplet carry-over, and blowdown in cooling towers. For power plants, it is typically recommended to use dry cooling towers for minimizing the cooling water loss. In dry cooling systems, cooling water with low amount of impurities goes to mixing condenser, where turbine steam condensation occurs. Then one portion of mixed water flow at the condenser outlet is supplied to the boiler or steam generator feed water loop. Another portion is returned back to the cooling tower. Inside the cooling tower, water is cooled down by passing through air-cooled heat exchangers manufactured of aluminium or steel alloys. On the basis of Pourbaix diagram it is proposed to evaluate the influence of water chemistry on the forms of existence of aluminium compounds in dry cooling towers. The results of calculations are compared with the experimental data.

One of the features of modern utility industry is associated with increasing use of energy-efficient processes and technologies. Fossil fuel-based power generation is one of the major consumers of water, which is one of the most crucial natural resources. For example, at fossil power plants, 60 – 100 m³ of water is needed to condense 1 ton of steam [1]. Therefore, bulk of water at fossil and nuclear power plants (85 – 95%) is used for steam condensation in turbine condenser. At present, most of these power plants use evaporative cooling towers with circulating cooling water. Typical loss of cooling water is about 5% of total water amount. This loss is associated with evaporation, droplet carry-over, and blowdown in cooling towers. Some research works indicate that the amount of water loss due to evaporation during steam condensation at 100 MW unit is equivalent to water consumption of a city with population of 50000 [2, 3]. Countries with scarce water resources typically use dry cooling towers. In dry cooling systems, cooling water with low amount of impurities goes to mixing condenser, where turbine steam condensation occurs. Then one portion of mixed water flow at the condenser outlet is supplied to the boiler or steam generator feed water loop. Another portion is returned back to the cooling tower. Inside the cooling tower, water is cooled down by passing through air-cooled heat exchangers manufactured of aluminium or steel alloys [4].
Use of dry cooling towers (also known as Heller cooling towers) significantly reduces water loss at power plants due to cooling of water with air. Evaporative cooling towers need constant content of cooling water. In dry cooling towers it is not needed and, therefore, costs of water resources are markedly reduced.

The case study indicates that replacing the cooling system with two evaporative cooling towers by that with two dry and one evaporative cooling towers in the 1200 MW unit may result in more than 18-fold reduction in water losses (figure 1) [4].

![Figure 1](image.png)

**Figure 1.** Cooling Water Losses with Different Cooling System Arrangements [4].

The works [1 – 4] give comparison of cooling towers only from thermal standpoint, which does not provide complete picture on the potential use of dry cooling towers. At the same time, wide use of this technology is limited by some other factors; one of these is water chemistry used at power plants. This is related to the fact that in most cases heat exchangers used in Heller cooling towers are manufactured from aluminum alloys [5]. Presence of dissimilar materials – steel and aluminum – in power plant cycle makes water chemistry management more difficult, because minimum corrosion rate of steels at wide temperature range is at pH > 9 [6], and for aluminum alloys it is at pH 6.5 – 7.0 (figure 2).

Currently, the most widely used water chemistry at once-through units of power plants is oxygenated treatment with ammonia feed (OT) with pH 8.0 – 8.5. Some power plants use neutral treatment (NT) with pH 7.0 – 7.5. For drum-type units, pH is 9.0 ± 0.1 [13]. Therefore, under the above chemistries, the heat exchange surfaces manufactured from aluminum alloys are prone to failure: according to the data from [6], corrosion rate of aluminum alloys at pH 8.5 and temperature 25 °C was a. 0.1 mm/yr.
Estimation of behavior of aluminum alloys and their potential use in dry cooling towers at different water chemistries could be performed with Pourbaix Diagrams. These diagrams can determine forms of aluminum oxides on alloy surface as a function of pH and oxidation-reduction potential (ORP) [7]. This method was used for estimation of iron, chromium, and nickel oxide forms in field power plant conditions and showed very good agreement with test results [8].

The areas of stable oxide films for different materials depend not only on fluid parameters, but also on temperature and pressure [10, 11]. In this regard, estimation of aluminum oxide film stability area change with temperature is important. In contrast to well-studied iron and copper oxide films, properties of aluminum oxide films change significantly with small temperature changes [12]. It needs to be emphasized that condensate temperature at the dry cooling tower inlet could be 50 – 70 °C, and at the outlet it is 25 – 30 °C. The primary aim of the study was to determine pH and ORP ranges that correspond to formation of stable protective film on aluminum alloy with varying condensate temperature. The knowledge about aluminum compound forms is particularly important in cases when dry cooling towers are used at drum-type units, because condensate polishing at these units is not available, and aluminum compounds can be carried over to steam and deposit on steam turbine blades [9].

In this study, three basic stable forms of aluminum compounds in Al–H₂O system are considered: ionic forms Al⁺³ and AlO₂⁻, and aluminum oxide Al₂O₃. The latter can be produced according to three basic reactions:

\[
2Al + 3H_2O \leftrightarrow Al_2O_3 + 6H^+ + 6e^-
\]  \( \text{(1)} \)

\[
2Al^{3+} + 3H_2O \leftrightarrow Al_2O_3 + 6H^+
\]  \( \text{(2)} \)

**Figure 2.** Effect of pH on material corrosion rate at temperature 25 °C.
One of the assumptions is that alloying additions of Mg, Mn, Si, and Cr with total content of up to 5% have no influence on reactions (Eq. 1 – 3) for the Al–H₂O system.

The Pourbaix Diagrams were compiled assuming the presence of aluminum alloy corrosion products in ionic form in the amount of 10 ppb at a pressure 0.1 MPa [12] (figure 3).

\[ 2\text{AlO}_2^- + 2\text{H}^+ \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \]  
\hspace{1cm} (3)

Analysis of results shows that at a temperature of 25 °C and aqueous ionic concentration of \( \text{Al}^{3+}/\text{AlO}_2^- \), protective aluminum oxide film is formed in pH range of 3.9 – 8.6 and ORP range of -0.5 – 1.0 V. Further increase in pH value results in formation of \( \text{AlO}_2^- \) ion. At temperature of 75 °C, \( \text{Al}_2\text{O}_3 \) exists at ORP from -0.26 to 0.87 V for pH 3.5, and at ORP from -0.42 to 0.71 V for pH 5.8. Comparison of the data on areas of \( \text{Al}_2\text{O}_3 \) existence indicates that with temperature increase from 25 to 75 °C, the area of that oxide shifts towards acidic pH values. The produced results also demonstrate that pH exerts major effect on formation of protective film compared to ORP.

Thus, formation of protective film in dry cooling towers with OT and NT chemistries occurs at a temperature of 25 °C. An increase of water temperature to 75 °C reduces the possibility of formation of \( \text{Al}_2\text{O}_3 \) film. These results are in very good agreement with the data on corrosion rates of aluminum alloys.

References
[1] Laptev A G and Vedgaeva I A 2004 Layout and Design of Industrial Cooling Towers. (KGEU, Kazan)
[2] Sabo Z 2000 Breakthrough System of Indirect Dry Cooling. (Energetik, Special Issue) pp. 8-12.
[3] Balog A and Takach Z 2002 Indirect Dry Cooling System for Modern Power Plants. (Energetik, Special Issue), pp. 13-21.
[4] Bergmann D Possible 2012 Use of Heller Dry Cooling Towers in Combination with Peak Evaporative Cooling Towers for Cooling of LAES-2 Units. (International Public Forum-Dialogue “Nuclear Energy, Society, Safety 2012”. St. Petersburg, Russia, September 5-6)
[5] Sabo Z 2004 Increase in Efficiency of Water Use in Power Plant Cooling Systems
[6] Mamet A P 1951 Power-Generating Equipment Metal Corrosion and Protection. Doctor of Technical Science Thesis
[7] Garrels R M, Christ Ch L and 1968 Solutions, minerals, equilibria. (Moscow: Mir)
[8] Petrova T I, Selivanov E A 2017 J. Phys.: Conf. Series 891 012262
[9] Vasilenko G V, Zenkevich Yu V and Mazurova O K 1978 Features of Fossil Power Plant Chemistry with Aluminum Alloy Heat Exchangers. (Water Treatment, Chemistry, and Chemical Monitoring at Steam Power Units vol 6) pp. 28-31.
[10] Petrova T I, Rogalev A N and Selivanov E A 2016 The choice of structural materials and chemical water-treatment for thermal electric power plants with supercritical parameters. (New in the Russian electric power industry vol 7), pp 22 - 31.
[11] Petrova T I 1976 Fundamentals of the method for constructing diagrams of the state of iron and copper (Moscow: MEI Publishing house)
[12] Babaev V A 1984 Decrease in intensity of formation of deposits of corrosion products in a condensate-nutritive path of fossil power plants with air cooling condenser. Ph.D. of Technical Science Thesis
[13] Rules for technical operation of power plants and networks of Russian Federation Ministry of Energy of Russia 2003 (Moscow: SPO ORGRES)