Some power plants use dry cooling towers with aluminum alloys. Presence of two alloys in the cycle – steel and aluminum - makes water chemistry more difficult, because minimum corrosion rate is provided by two different pH values: 6.5-7.0 for aluminum and >9.0 for steel [1, 2].

For power plants with dry cooling towers two chemistries are the most acceptable: NOT (pH ca. 7.0) for once-through boilers and phosphate treatment (pH = 7.0-7.5) for drum boilers [2]. Higher pH values are not advisable, because corrosion rate of aluminum alloys increases drastically. Also, two types of water chemistry for power plants with dry cooling towers are mentioned in foreign publications: NOT (pH ca. 7.0) and alkaline treatment (pH = 8.0-8.5) with feed of hydrazine, morpholine, or ammonia.

The operating experience of high- and supercritical units shows that aluminum compounds in the cycle may deposit in the turbine flowpath. High-pressure turbine deposits at three Russian power plants had more that 10% of aluminum [3]. It was suspected that aluminum enters the condensate with cooling water in-leakage in form of aluminum silicates, which are decomposed in boiler at high temperature and carried over with steam to the turbine.

For establishment of optimum water chemistry of fossil plants with dry cooling towers, a number of laboratory and field studies were performed [4-6]. Large-scale test program was executed at 200 MW unit, Razdan power plant. This unit is equipped with high-pressure boiler (14 MPa) and steam output 640 t/h. The dry cooling tower had 57,120 aluminum tubes (internal diameter 14 mm, wall thickness 1 mm). Cooling water flowrate was 22,000 t/h. The makeup water was prepared with two-stage demineralization; its flowrate was 20-40 t/h. During the tests the unit had 50% condensate polishing.

Initially both feedwater and cooling water were operated with alkaline treatment at pH=9.0 [6]. But with this chemistry significant corrosion of aluminum alloys in the cooling tower occurs (Figure 1); aluminum level in the cooling water was 70-80 ppb and in the feedwater – ca. 50 ppb. When water chemistry with hydrazine feed (pH = 8.2-8.4) was applied, aluminum concentration reduced by 25-30% (51 ppb in cooling water and 38 ppb in feedwater).

![Figure 1: Dependence of concentration aluminium from pH.](image)

a - in a cooling water; b - in a feedwater

After that the feedwater train of the unit was converted to NOT, and aluminum level in the feedwater reduced down to 20 ppb. Based on these studies, the NOT with oxygen level 150 ppb was recommended for power plants with dry cooling towers [7]. It was found that the “transit” value of aluminum concentration in supercritical turbine steam is 5 ppb [8].

There are lots of literature data on the effect of different factors, both thermophysical and chemical, on corrosion rate of aluminum alloys [9-12].

Relatively high corrosion resistance of aluminum alloys is explained by formation on its surface during contact with water of protective
multi-layer film of different forms of aluminum oxides. These films in general include aluminum hydroxide (Al(OH)$_3$) and oxyhydroxide (AlOOH), which structure largely depends on temperature. There are some literature data [13, 14], which show that in the temperature range of 40-300 °C oxide films formed on aluminum or aluminum alloy surface in contact with distilled water consist of two layers. The inner uniform layer over the above-mentioned temperature range consists of fine-crystalline aluminum hydroxide with boehmite structure. The outer layer, which contacts with water, at temperatures up to 80 °C mainly consists of aluminum hydroxide crystals with bayerite structure $\gamma$-Al$_2$O$_3$·3H$_2$O; in the temperature range 80-110 °C thin plates with boehmite structure are formed on the inner layer surface.

At temperatures above 300 °C the outer layer consists of columnar crystals of diaspore, which is high-density modification of aluminum oxyhydroxide.

Difference in corrosion rates of aluminum in aqueous environment with unequal composition of impurities is explained by the composition of the outer layer on the metal surface and solubility of this layer [15]. In particular, inhibiting effect of phosphate-ions is explained by the changes that occur in the outer layer of the film under action of phosphate. For example, at temperature 195 °C in solution with 5 ppm of PO$_4^{3-}$, the film consists of augelite Al$_2$PO$_4$(OH)$_3$. Corrosion rate of aluminum alloys also depends on alloy composition [11]. Rate of uniform corrosion is limited by outer, not by inner, oxide layer. It is assumed that the outer layer does not influence on the rate of intercrystalline corrosion, which is typical for elevated temperatures.

Water impurities determine composition and protective properties of the film on aluminum surface. Film solubility, in turn, depends on composition of film and water, in particular, on pH. Some researchers highlight importance of solubility in calculation of mass transfer of corrosion products in water-steam cycle [12, 16]. The data on solubility of aluminum compounds in water are very limited [17, 18]. Available literature data indicate that solubility of aluminum compounds strongly depends on pH: minimum solubility is observed at pH = 5.0-5.5; at pH values below and above this range solubility of aluminum compounds sharply increases (Figure 2).

The pattern of solubility of different aluminum corrosion products (Al(OH)$_3$, Al$_2$O$_3$, Al$_2$O$_3$·3H$_2$O) vs. pH is the same, but absolute solubility values are different. The highest solubility of the studied oxygen-containing aluminum compounds is attributed to Al(OH)$_3$. Some researchers confirm the same pattern of solubility of different aluminum compounds vs. pH at high temperatures and pressures also (Figure 3) [18, 19].

The main source of water pollution by aluminium is corrosion process. That's why it is necessary to decrease the rate of corrosion. It is known that one of the ways of decreasing the rate of corrosion of aluminum alloys is the injection of phosphates into the water [12]. In this connection it is of particular interest to study the influence of phosphates on solubility of aluminium corrosion products in water and saturated steam.
Figure 4: Experimental rig

1 – deaerator; 2 – ion exchange columns; 3 – pump; 4 – water heater; 5 – heater; 6 – steam-boiler; 7 – steam heater; 8 – bubler; 9 – heat exchanger; 10 – initial solution tank; 11 – steam; 12 – condensate of steam.

The tests to study influence of phosphates on solubility of aluminium corrosion products in boiling water and equilibrium saturated steam were performed at an experimental rig shown on Fig 4. It consisted of a system for preparation of demineralized and deaerated water; heat exchangers; a bubler and a system for preparation of solutions to be studied.

It is necessary to note, that all parts of experimental rig, including, pumps, steam generator, bubler and sampling lines were manufactured from a titanic alloy.

The phosphate level in the boiling water was controlled by the feed of Na₃PO₄ solution in the feedwater. During the tests the steam and water sampling was performed for determination of phosphate and aluminium concentration and measurement of pH value.

The test results are shown in Tables 1 and 2, and on Figures 5 and 6.

**Table 1: Effect of pH on Solubility of Aluminum Compounds in Water and Saturated Steam at Phosphate Level ca. 1.4 ppm (average data)**

<table>
<thead>
<tr>
<th>Concentration of phosphates, ppm</th>
<th>pH</th>
<th>Concentration of aluminium, ppb</th>
<th>Distribution ratio of aluminium compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,52</td>
<td>7.30</td>
<td>50.0</td>
<td>4.8</td>
</tr>
<tr>
<td>1,36</td>
<td>7.85</td>
<td>88.0</td>
<td>4.0</td>
</tr>
<tr>
<td>1,40</td>
<td>8.64</td>
<td>310.0</td>
<td>4.0</td>
</tr>
<tr>
<td>1,30</td>
<td>8.76</td>
<td>372.0</td>
<td>5.0</td>
</tr>
<tr>
<td>1,60</td>
<td>9.40</td>
<td>838.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

**Table 2: Effect of pH on Solubility of Aluminum Compounds in Water and Saturated Steam at Phosphate Level ca. 4.6 ppm (average data)**

<table>
<thead>
<tr>
<th>Concentration of phosphates, ppm</th>
<th>pH</th>
<th>Concentration of aluminium, ppb</th>
<th>Distribution ratio of aluminium compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.10</td>
<td>6.88</td>
<td>88.0</td>
<td>4.0</td>
</tr>
<tr>
<td>4.40</td>
<td>6.95</td>
<td>90.0</td>
<td>4.0</td>
</tr>
<tr>
<td>4.60</td>
<td>7.36</td>
<td>180.0</td>
<td>4.8</td>
</tr>
<tr>
<td>4.40</td>
<td>7.80</td>
<td>250.0</td>
<td>4.2</td>
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<td>4.53</td>
<td>8.20</td>
<td>600.0</td>
<td>4.5</td>
</tr>
<tr>
<td>5.10</td>
<td>8.90</td>
<td>1098.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Figure 5: Effect of pH on Solubility of Aluminum Compounds in Water with Phosphate

1 – PO₄³⁻ = 1.4 ppm; 2 – PO₄³⁻ = 4.6 ppm; 3 – (x) without PO₄³⁻.

Figure 6: Effect of pH on Distribution ratio of Aluminum Compounds between Water and Steam with Phosphate (p = 7.0 MPa)

1 – PO₄³⁻ = 1.4 ppm; 2 – PO₄³⁻ = 4.6 ppm
These data show that at temperature 285 °C (psat = 7.0 MPa) solubility of aluminum compounds in boiling water increased with pH at phosphate levels in boiling water ca. 1.4 and 4.6 ppm. Comparison with the data shown in Figure 3 [18] indicates that increase in phosphate level in water up to 1.4 ppm has almost no effect on solubility of aluminum corrosion products in water; but further increase in phosphate levels up to 4.6 ppm results in rise of solubility of aluminum compounds. Apparently, this phenomenon is related to the change in form of existence of aluminum compounds in water.

The pH dependence of distribution ratio of aluminum between water and steam at pressure 18 MPa with no phosphate in boiling water is shown in Figure 7 [20]; maximum value of distribution ratio of aluminum (0.35) is at pH = 8.5.

Comparison of literature results with the data produced in this study indicates that at pH ~ 8.5 phosphate present in water reduce significantly the distribution ratio of aluminum: at phosphate level 1.4 and 4.6 ppm it was respectively six and twelve times lower compared with no phosphate addition. Some testing of the phosphate effect on distribution ratio of aluminum was performed at pressure 14 MPa. At this pressure the distribution ratio of aluminum was also lower in presence of phosphate.

It is known that contamination of saturated steam due to solubility is governed by the form of existence of impurity in water. Presence of phosphate in water results in formation of aluminum phosphate compounds resulting in change of distribution ratio.

Conclusions

- The review of literature data showed that behavior of aluminum corrosion products depended on temperature and composition of impurities in water.
- Study of solubility of aluminum compounds in water and steam at temperature 285 °C (psat = 7.0 MPa) and pH 6.88-9.40 with phosphate.
- Increase in phosphate levels in water up to 1.4 ppm has almost no effect on solubility of aluminum corrosion products in water. Further increase in phosphate levels up to 4.6 ppm results in rise of solubility of aluminum compounds over the studied pH range.
- Presence of phosphate in boiling water reduces distribution ratio of aluminum in water.

References

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