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Boiler corrosion and suggestions for better efficiency

Mekala K.G.H, Ishara G.K.K

Faculty of Technology, University of Sri Jayewardenepura hmekala98@gmail.com

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Abstract: Corrosion is a critical issue in boiler systems, leading to reduced performance, increased maintenance costs and potential safety hazards. Boiler corrosion occurs when metallic components of a boiler system undergo deterioration due to electrochemical reactions in the presence of water, oxygen, and other contaminants. This review article aims to provide a comprehensive introduction to boiler corrosion, covering its types, causes, impacts on boiler performance and safety and also strategies for improving boiler efficiency.

Index Terms: Boiler components, Corrosion types, Metal surface, Corrosion prevention

1 WHAT IS THE BOILER

For most industrial facilities, boilers are the primary source of thermal energy. An enclosed vessel that produces steam through a heat transmission mechanism is called a boiler. When water is boiled, it turns into highly explosive steam, which increases in volume by 1600. As a result, the boiler is a device that needs to be maintained cautiously and safely to function without any problems [1].

Hero of Alexandria constructed boilers in the first century A.D., although they were primarily used as playthings. The potential of steam power for helpful work was given substantial consideration in the 17th century. Denis Papin of France created the first boiler with a safety valve in 1679; boilers were produced and utilized in England by the turn of the 18th century. When high pressure and temperature benefits were discovered, producers switched to steel from the wrought iron used in the early boilers. Alloy steel is used in modern boilers to endure high pressures and incredibly high temperatures [2].

Boilers come in a variety of designs and types. The two main categories it falls under as "Fire tubes" and "Water tubes." Boilers that use fire in tubes, also known as fire tube boilers, are those in which heated air is circulated long steel tubes of water that will eventually become steam. Fig. 1. Shows cross section of fire tube boiler. The Boilers with water flowing through the tubes and hot gases passing outside the tubes are referred to as "water tubes" or "water in tube" boilers. Fig. 2. Shows cross section of water tube boiler [3].



Fig. 1. Cross section of the fire tube boiler [4]



Fig. 2. Cross section of the water tube boiler [4]

2 GENERAL COMPONENTS OF BOILERS

Depending on the type of boiler, accessories may vary. However, the most common parts of any boiler are the firebox, burners, drums, tubes, an economiser, a steam distribution system, and a boiler feed water system.

Firebox

The main component of the boiler is the firebox, which supports the gas or oil combustion process to produce the required heat for steam generation. It comprises a refractory lining, burners, a conventional portion, a radiant section, fans, an airflow control unit, a stack, and dampers. It used to be insulated to prevent heat loss and improve the heat's transfer to the boiler's interior components [5].

Burners

In the burner, the combustion process is carried out by injecting fuel and air through a distribution system. Burners made of diesel, coal, biomass, or natural gas are commonly used in boilers to generate heat. The burner is made up of several parts. The main elements of a natural gas burner are the igniters, pilots, impellers, spuds, and spiders. The air/fuel mixture is made to spin above the burner by the impellers, which are mechanical devices. For combustion, a spud or spider injects fuel into the burner [1].

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Economizer

The economizer is merely a heat exchanger that uses the boiler feed water supply line and excess heat recovered from the flue gas stack to pre-heat the boiler input feed water before it enters the primary boiler system. The efficiency of the boiler system is increased by preheating. The economizer is often placed close to the boiler's stack gas line outlet. Before reaching the feed water inlet of the boiler, the feed water line travels via the economizer. For the pre-heating process, there is no need for an additional feed water control valve or stack gas control section. The primary function of the economizer is to recover waste heat that would otherwise be released into the atmosphere together with the hot flue gases [1], [5]. Fig. 3. shows Schematic diagram of the boiler with the economizer unit.



Fig. 3. Schematic diagram of the boiler with the economizer unit [6]

Drums

The mud and steam drums are the two primary types of drums in the boiler. The mud drum is the lowest and serves as a sediment collection area. Sludge is eliminated by blow-down from the mud drum's bottom. To minimise or remove the sediments at the bottom of the boiler, a technique known as "blow-down" involves withdrawing small volumes of water from the boiler. Part of the boiler water will decrease during the blow-down procedure, and additional water will be supplied to maintain the required water level. The steam drum, partially filled with water, is the upper drum of the boiler. The remaining overhead area keeps the boiler's vapour pressure constant. It provides a place for saturated steam to build up before passing through the distribution line and into the industrial process [5]. Fig. 4. Shows cross section of boiler drums.

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Fig. 4. Cross-section of the boiler drums [7]

Steam Distribution System

The valves, fittings, pipework, connectors, and steam traps are the components of the steam distribution system that are used the most frequently. The pressure at which the steam is produced in the boiler should be sufficient to move it to the process. If steam is being used in the industrial process, the pressure is lower than when steam is used in the steam turbine to generate power. In order to serve both the needs of producing energy and the uses for the process, steam must be created at a much greater pressure than the required pressure for that process.

In order to lessen the steam pressure needed by the turbines that power process pumps and compressors, which require lower-pressure steam, steam is first utilised to power steam turbine generators to produce energy. In an industrial operation, the bulk of the steam condenses into water. When it comes to feeding water, it is crucial to recover the condensate return and use it as feed water. Typically, condensate is recycled as boiler-feed water through condensate return systems. As the feed water is already clean and free of minerals and carbonates, this lowers the cost of feed-water treatment. Consequently, substituting condensate return for the makeup water demand will result in significant cost savings for feed water supply and feed water treatment chemicals.

A steam trap is one of the most crucial parts of the steam distribution system, which is utilised to collect condensate from the steam system. Mechanical and thermostatic traps are the two primary varieties of steam traps. The thermostatic trap uses the change in temperature to work, while the mechanical trap uses the difference in density. The interior floats of the mechanical trap are connected to mechanical linkages. The condensate will be separated from the steam by the trap's opening, which depends on the condensate level. The separation concept is slightly different in the thermostatic trap, though. As the temperature of the steam is higher than that of the condensate, the bimetallic element will move or alter its position as a result of thermal expansion to separate the two. The bimetallic element moves the other way when the condensate separates, leaving only steam [3], [5].

Boiler Feed-water System

The feed-water supply segment is considered the most crucial part of the boiler process. To keep the boiler's water level at the required level when steam is supplied to an industrial operation, makeup water must be provided. Minerals and other dissolved pollutants that can harm the boiler tubes should not be present in the water supply to the boiler. As a result, the boiler process should include the feed-water treatment step [5].

Draft fan

A draft fan is used to regulate the air intake to the boiler, either forcing the air through the boiler (forced draft) or pulling the air through the boiler (pulled draft) (induced draft) [5].

Downcomers and riser tubes

A downcomer moves water from the steam drum to the mud drum while the firebox's temperature is measured. Riser tubes simultaneously enable the transfer of water or steam from the lower drum to the upper drum [1].

3 BOILER CORROSION

Boiler corrosion can be defined as the deterioration of a boiler's metal surfaces due to chemical or electrochemical interactions with its surroundings. The water wall, screen, and superheater tubes of the boiler, which are its hottest parts, can experience many corrosion issues. Deaerators, feedwater heaters, and Economisers are other frequent sources of problems. Many corrosion control procedures are employed, depending on the type of corrosion discovered. The most prevalent sources of corrosion include dissolved gases (mainly oxygen and carbon dioxide), under-deposit attack, low pH, and assault on places weakened by mechanical stress, which leads to stress and fatigue cracking. Many issues, such as decreased efficiency, leakage, and even boiler failure, can be brought on by boiler corrosion. As a result, it's crucial to keep an eye on corrosion and avoid it with frequent maintenance and appropriate water treatment [8].

Corrosion can occur in several places in a boiler, including the water-side and fire-side surfaces, depending on its type and source.

Water-side corrosion - Dissolved gases like oxygen and carbon dioxide in the water contributed to this corrosion. The interaction of these gases with metal surfaces has the potential to cause oxidation and the growth of rust. Another source of corrosion is caused by dissolved salts, which can cause scaling and pitting on metal surfaces.

Fire-side corrosion happens when the fuel burns inefficiently and releases combustion byproducts that are acidic, like sulfur dioxide and nitrogen oxides. These corrosive gas products can react with metal surfaces to generate sulfates, nitrates, and rust.

4 Types of corrosion

- Oxygen corrosion (Oxygen attack)
- Stress corrosion
- Galvanic corrosion
- Hydrogen corrosion (Hydrogen embrittlement)

- Phosphate corrosion
- Cold end corrosion
- Sulfur-Induced Corrosion
- Hot corrosion
- Crevice corrosion
- Caustic corrosion
- Acidic corrosion

Oxygen Corrosion

An oxygen attack is a type of corrosion brought on by dissolved oxygen in water on a metal surface. As an illustration, internal boiler corrosion, which typically results from oxygen attack or low pH and is potentially harmful due to the pressures and temperatures involved with a functioning boiler, is caused by these factors.

The boiler system's entire metallic surface is open to oxygen attack. Pits are small, confined areas of corrosion caused by oxygen. Oxygen pits have the ability to rapidly "drill" through metal surfaces, causing the metal to become worn out and fail. The surface of the iron dissolves as oxygen corrodes the boiler's metal. It also sends dissolved iron into the boiler, which weakens the metal site. The boiler tubes may become deposited with this dissolved iron, which could lead to tube failure and overheating.

Three critical factors govern the onset and progress of oxygen attack or corrosion:

- Presence of moisture or water
- Presence of dissolved oxygen
- Unprotected metal surface

Water becomes more corrosive with rising temperature, rising dissolved solids, and falling pH. Oxygen levels tend to rise along with aggressiveness. In most cases, controlling oxygen involves both mechanical and chemical steps. By boiling the water to lower its solubility, the majority of the oxygen in the boiler feedwater is typically lowered to less than 20 parts per billion (ppb). Although a deaerator eliminates the majority of the oxygen in feedwater, small amounts may still be present and lead to corrosion-related issues. To eliminate the tiny amount of oxygen that leaks from the deaerator, oxygen scavengers are introduced to the feedwater, ideally in the feedwater storage tank [8].

Stress Corrosion

The corrosion process is accelerated when mechanical strains are present along with a corrosive environment. Stress-corrosion cracking (SCC) is the first form where corrosion and stress interact. This type of corrosion occurs when a structure that could withstand the same stress in a non-corrosive environment fails due to static tensile stress in a susceptible metal. These stresses may be external or residual stresses, such as those after cold working or welding [9]. SCC may also result from corrosion products in a small or enclosed area [10].

Corrosion fatigue is a different type of corrosion where stress plays a part. This is distinguished by a variable load well below the yield threshold. Corrosive media have an impact on the fatigue behaviour of metals. Fig. 5. uses an S-N curve to show how corrosion affects fatigue behaviour. As can be seen, failure



occurs for a given load in fewer cycles, and a fatigue limit is no longer apparent [11].

Fig. 5. S-N curve illustrating the influence of corrosion on fatigue behaviour [11]

Sodium sulfite is the most commonly used oxygen scavenger. Sodium sulfite is affordable, efficient, and simple to measure in water.

Galvanic Corrosion

A galvanic cell is formed, and a potential difference exists between the two metals when two dissimilar metals are electrically connected and come into contact with an electrolyte. The anode, the metal with the lowest potential in this bimetallic pair, will begin to corrode. The more noble metal will act as a cathode, and its surface won't be altered [09].

The potential of metal in this situation is also influenced by the properties of the electrolyte; this fact must be emphasised. As a result, it is conceivable for two dissimilar metals to act differently in different electrolytes. For example, one metal may behave cathodically toward another metal in one electrolyte, whereas the other metal may behave anodically toward it. A single metal may also experience galvanic corrosion due to surface deposits of metal, regional variations in the electrolyte's chemistry (such as those found in an oxygen concentration cell), or local flaws [12].

Hydrogen corrosion (Hydrogen Embrittlement)

Hydrogen embrittlement is one of the numerous potential causes of a carbon steel boiler tube breaking. Molecular hydrogen precipitation close to the grain boundary is the primary cause of cracking. This reaction between the carbon in the steel and the dissolved hydrogen results in the production of methane. Hydrogen cracks have a very different morphology from cracks brought on by either short-term or long-term warming. During hydrogen embrittlement, steel's plasticity declines. Another concomitant process is the intense hydrogen decarburisation of the waterside surface of the tube. Deposits that could accumulate on the waterside of the tube, particularly in a small area, may significantly impact the likelihood that hydrogen will precipitate on grain boundaries and produce cracks. The heat transmission process and the intensity and localisation of the hydrogen attack process are all greatly influenced by the disruption of the boiling regime and departure from nucleate boiling occurring in a specific area of waterwall tubing [13].

Phosphate corrosion

The phosphate treatment program and the background of phosphate programs in high-pressure boilers must be covered in detail in order to explain the process of phosphate corrosion. Boiler water has been treated with phosphate since the 1950s. In various boiler water treatment procedures, sodium phosphate salts are purposefully introduced to boiler water at certain concentrations for internal chemical treatment. Residual phosphate treatment programs are typically employed in relatively low-pressure boilers with softened makeup water to control scale. They can be used with or without synthetic polymers as a conditioner and dispersion.

To effectively treat residual phosphate, boiler water must have a predetermined orthophosphate content and a controlled degree of free hydroxide. This control ranges change depending on the operating pressure of the boiler drum. For any hardness pollution of the feedwater, residual phosphate treatment is typically utilised as a precipitating treatment chemical. The calcium and magnesium are intended to precipitate as calcium hydroxyapatite and magnesium hydroxide, respectively. This treatment permits a significant concentration of free hydroxide ions in the boiler water to aid in the precipitation of the magnesium. It is often employed in boilers operating at 1000 psi (6.9 MPa). High-purity feedwater boiler systems occasionally use this treatment as well. Nonetheless, numerous additional pH and phosphate control strategies have been utilised in higher-pressure boilers requiring more feedwater purity. These programs' primary purposes are pH buffering and corrosion control. On steel surfaces, proper pH management ensures the creation and retention of passive, protective magnetite coatings. Coordinated phosphate control, congruent phosphate control, equilibrium phosphate treatment, and lastly, what has been referred to as phosphate continuum treatment are some of the pH and phosphate control schemes employed in high-pressure boilers.

When significantly concentrated, free hydroxide in the boiler water can produce several potentially corrosive situations. If there is a leak at a mechanical rolled tube junction, for instance, carbon steel drum materials may experience caustic stress corrosion and cracking. On waterside heat-transfer surfaces that are highly contaminated by moderately porous metal oxide deposits, under-deposit caustic corrosion may also happen). To reduce the amount of free hydroxide in the boiler water, several phosphate/pH control approaches have been developed. The initial program was known as coordinated phosphate chemistry, and the boiler water's sodium-to-phosphate molar ratio was maintained at less than 3.0:1. In order to reduce the number of free hydroxides in the boiler water, this was done. Unfortunately, this attitude was insufficient to stop the production of free hydroxide because it was discovered that sodium orthophosphate precipitates inconsistently under dry-out conditions. To minimise the presence of free hydroxide in the boiler water, the subsequent pH/phosphate control philosophy, known as congruent phosphate, was developed to control the upper molar sodium-to-phosphate ratio in the boiler water between the congruent ratio of 2.6:1 at high pressure and 2.85:1 at lower pressures. The exact boiler water phosphate control range is determined by the pressure at which the boiler drum operates. Although this treatment chemical has been in use for a while, it was discovered to be susceptible to a condition known as phosphate hideaway. Phosphate is eliminated from boiler water solutions, as the name implies because it can be found on surfaces in high-heat transfer regions of the boiler. Phosphate storage became an increasingly critical challenge as boiler drum operating pressures rose over time. To limit the possibility of phosphate hiding, phosphate control ranges are required to be lowered as a function of operating pressure [14].

Cold end corrosion

The catalytic oxidation of sulfur dioxide to sulfur trioxide and subsequent sulfuric acid condensation at the dew point cause cold-end corrosion, which manifests itself. When burning, the sulfur in the fuel oxidising at SO_2 . During combustion, a tiny amount of SO_2 is converted to SO_3 , but the SO_3 concentration then rises due to the metallic surfaces' catalytic activity. Sulfuric acid emerges and condenses as the flue gases in the pre-heater cool and reach the dew point, causing what is known as "cold end corrosion." First, air excess determines the SO_3 generation yield for a particular fuel (Fig. 5). The SO_3 concentration in the flue gas and, indirectly, the extra oxygen depend proportionally on the dew point, which controls the corrosion conditions (Fig. 6) [15].

Because of sulfuric acid condensation, the corrosion process requires extra steps. The production of ferric sulfate on the metallic exchange surface. The corrosion layer is porous and has a low coefficient of heat transmission.



Fig. 5. The SO3 formation yield vs sulfur content of the fuels and oxygen concentration in the burned gases [15]



Fig. 6. The dew point values vs oxygen in burned gases sulfur content in fuels

During the creation of sulfuric acids, water vapors from the burnt gases spread and hydrolyse. During the attack on fresh metal components, the hydrolysis of ferric hydroxides and oxides continues. The reactions quicken when the corrosion zone comes into contact with the cold air. Corrosion enters the tube and spreads throughout it, causing warm, burned gases and cold air to mingle [15].

Sulfur-Induced Corrosion

The most common form of sulfur in fuel ash is sodium sulfate. It dissociates as a result of the subsequent reaction when heated up.

 $Na_2SO_4 \longrightarrow Na_2O + SO_3$

The reaction byproducts will change the molten ash deposits' basicity. Sulfur and sodium in the melt interact, influencing the concentration of Na_2O and, in turn, the rates of corrosion. Deposit melting spans from 480 to 900 0C and is influenced by the Na + S/V ratio. The mechanical characteristics of the tube metal decrease when the intergranular corrosion of the fireside surface of the tubes rises. Under these conditions, if the tube's temperature and pressure rise unusually for some reason, the tube will rupture [9].

Hot corrosion

Hot corrosion (also known as rapid corrosion) is caused by the presence of salt impurities (Na_2SO_4 , NaCl, and V_2O_5) that combine to generate molten deposits that harm the surface oxides that are meant to defend against corrosion [16].

Hot corrosion can be broadly divided into Type I, or high-temperature corrosion, and Type II, or low-temperature corrosion. Many factors, including alloy composition, contaminants, temperature, flux rate, velocity, temperature cycles, the erosion process, and the thermo-mechanical state, may influence the development of these two forms of hot corrosion.

Type 1 hot corrosion - It happens at high temperatures between 850 and 950 °C (above the melting point of Na₂SO₄) [17], [18]. It starts with the condensation of fused alkali metal salts, such as sodium sulfide, sodium carbonate, sodium acetate, etc., on the surface of the exposed components at high temperatures. The chemical reaction then starts, attacking the protective oxide film at first before steadily lowering the amount of chromium (Cr) in the substrate materials. The extensive peeling of metallic components and notable colour changes are frequent features of the macroscopic appearance of type I hot corrosion. The surface of metals also takes on a greenish tone as a result of NiO production in the area of rapid assault. A sulfidation and depletion area beneath the porous, non-protective scale characterises the morphology of Type I hot corrosion under a microscope. Oxide precipitates scattered in the salt layer are typically visible in the reaction results [19].

Type II hot corrosion - It occurs in a 650–800 °C environment (less than the melting point of Na_2SO_4 in the presence of small amounts of SO_3) [20], [21]. It has a pitting assault with a weaker attack underneath. Low melting-point eutectic combinations of sodium sulfate (Na_2SO_4) and cobalt sulfate ($CoSO_4$) in this form of hot corrosion result in the typical pitting in the limited sections. Localised failure of the scale due to erosion, heat cycling, and chemical reactions is related to the localised nature of type II hot corrosion. Microscopic sulfidation and chromium depletion are typically not seen in low-temperature hot corrosion [22]. Even though the temperature is the primary determinant of the hot corrosion mechanism. As the temperature rises, type II hot corrosion becomes type I hot corrosion in the attack [23].

<u>Mechanism of hot corrosion</u> - The protective oxide layer's failure, which allows the molten salt to get direct access to the substrate material (metal or alloy), is what causes high-temperature, hot corrosion to start. Thermal stresses, chemical reactions, erosion, erosion-corrosion, and erosion may all have contributed to this failure. The sulfidation-oxidation process and the salt fluxing mechanism are the two distinct mechanisms proposed for type I hot corrosion propagation phases [20]. Initially, Goebel and Pettit et al. [24], [25] proposed the salt fluxing process and hypothesised that the surface oxide layer's effectiveness as a barrier would be compromised by the layer's fluxing in molten salt. Fluxing can be either basic or acidic. In contrast to acidic fluxing, which is induced by the breakdown of oxides into the respective cations and

 O_2 , basic fluxing can be caused by the interaction of oxides with O_2 to form anions [26], [27]. Because it causes a far more severe oxidation reaction than basic fluxing, acidic fluxing happens when the O2 activity in the molten salt is significantly reduced. In contrast to basic fluxing, acidic fluxing has the potential to be self-sustaining since the displacement of the salt from stoichiometry does not worsen during the course of the reaction [22].

Stages of hot corrosion - Superalloys are subject to three separate stages of heat corrosion [28].

i) First stage (incubation stage): the reaction proceeds at a rate similar to normal oxidation.

ii) Second stage (initiation stage): the corrosion is accelerated

iii) Third stage (propagation stage): rapid corrosion takes place.

The final failure of a component occurs after this point.

Crevice corrosion

Crevice corrosion can be known as another intense and dangerous form of localised corrosion caused by a local environment different from the bulk environment. Oxygen can be depleted in crevices or shielded areas with stagnant liquid. This difference in oxygen concentration has an impact on the beginning of crevice corrosion. Crevice corrosion can also start as a result of the presence of chlorides. When the crevice narrows and the cathode area has increased, the rate of corrosion increases [9].

Caustic Corrosion

Both localised boiling beneath porous deposits on tube surfaces and steam blanketing, which allows salts to concentrate on boiler metal surfaces, can result in the concentration of caustic (NaOH). When iron comes into contact with boiler water, magnetite is created, continuously regenerating the protective coating. The magnetite is constantly dissolved, though, so long as there is a high caustic concentration, which results in a loss of base metal and eventual failure. The condition known as "steam blanketing" is when a layer of steam forms between the boiler water and the tube wall, preventing enough water from reaching the surface of the tube to effectively transfer heat and causing the water that does reach the overheated boiler wall to rapidly evaporate, leaving behind a concentrated caustic solution that is corrosive. High boiler water concentrations can also develop due to porous metal oxide deposits. Water enters the deposit, and when heat is given to the tube, the water evaporates, leaving a highly concentrated solution. Once more, corrosion might happen.

Acidic Corrosion

Acidic assault on metal surfaces in the pre-boiler and boiler system can be seriously exacerbated by low makeup or feed-water pH. Feed-water can become acidic due to system contamination even if the original makeup or feed-water pH is not low. Incorrect use or control of de-mineralized cation units, condensate contamination from processes (such as sugar contamination in food processing industries), and condenser-related pollution of cooling water are a few examples.

Prevention of corrosion

Using the following steps, these conditions may be managed:

• Keeping the right alkalinity and pH levels

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- Contamination of the boiler feed water and oxygen
- Mechanical strains are decreased.
- Operating within design parameters, particularly for pressure and temperature.
- The right material selection is one of the most crucial factors in preventing the corrosion of a boiler in a particular fluid.
- Appropriate precautions during start-up and shutdown. The best metal should be used since some metals are more suitable for a given environment than others.
- Good supervision and management

For a boiler to be reliable, corrosion control monitoring must be effective. The following should be part of a well-planned monitoring program:

- Appropriate sampling and monitoring at key system nodes
- Totally representative sampling
- Using proper test techniques.
- Comparing test findings to predetermined boundaries.
- A course of action that must be taken right away if test results go outside of predetermined ranges
- A backup plan in case of serious disruptions
- A system for quality improvement and evaluation of outcomes based on testing and inspections [8]

5 CONCLUSION

Boiler corrosion is a significant issue that can result in equipment failure, safety risks, and costly repairs. To guarantee the long-term functioning of boiler systems, however, efficient corrosion management and preventive measures can be applied. The techniques covered in this review article, such as water purification, material selection, protective coatings, and corrosion inhibitors, are widely applied in the sector to avoid corrosion in boiler systems. Overall, boiler operators can ensure the safe and effective functioning of their equipment, increase the lifespan of their boilers, and save on long-term maintenance and repair costs by putting effective corrosion management and prevention measures into practice.

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