

LESSON 1:

What Is Plant Cycle Chemistry and Why Is It Important for Steam and Power Generating Plants?

INTRODUCTION

The plant cycle of any fossil-fired steam or power generating unit consists of a multiplicity of cycle components made of different materials. All of them are in contact with water (condensate, feedwater or attemperator water) or steam (saturated, superheated, or wet steam). For those not familiar with the term *plant cycle*, it is important to note that two synonyms are often used as substitutes for this term: these are *steam/water cycle* or *water/steam cycle*. In this course, the term *plant cycle* will be used consistently.

The major fossil plant cycle components are the condenser, the feedwater heaters (low-pressure, LP, and high-pressure, HP, heaters) and the deaerator (feedwater storage tank), the steam generator (the boiler), and the turbine (often consisting of several parts, such as HP, intermediate-pressure, IP, and LP sections). [Figure 1](#) shows a very simplified schema of a plant cycle. The cycle depicted represents a high-pressure cycle with a drum-type boiler. Any other possible plant cycle configurations may be derived

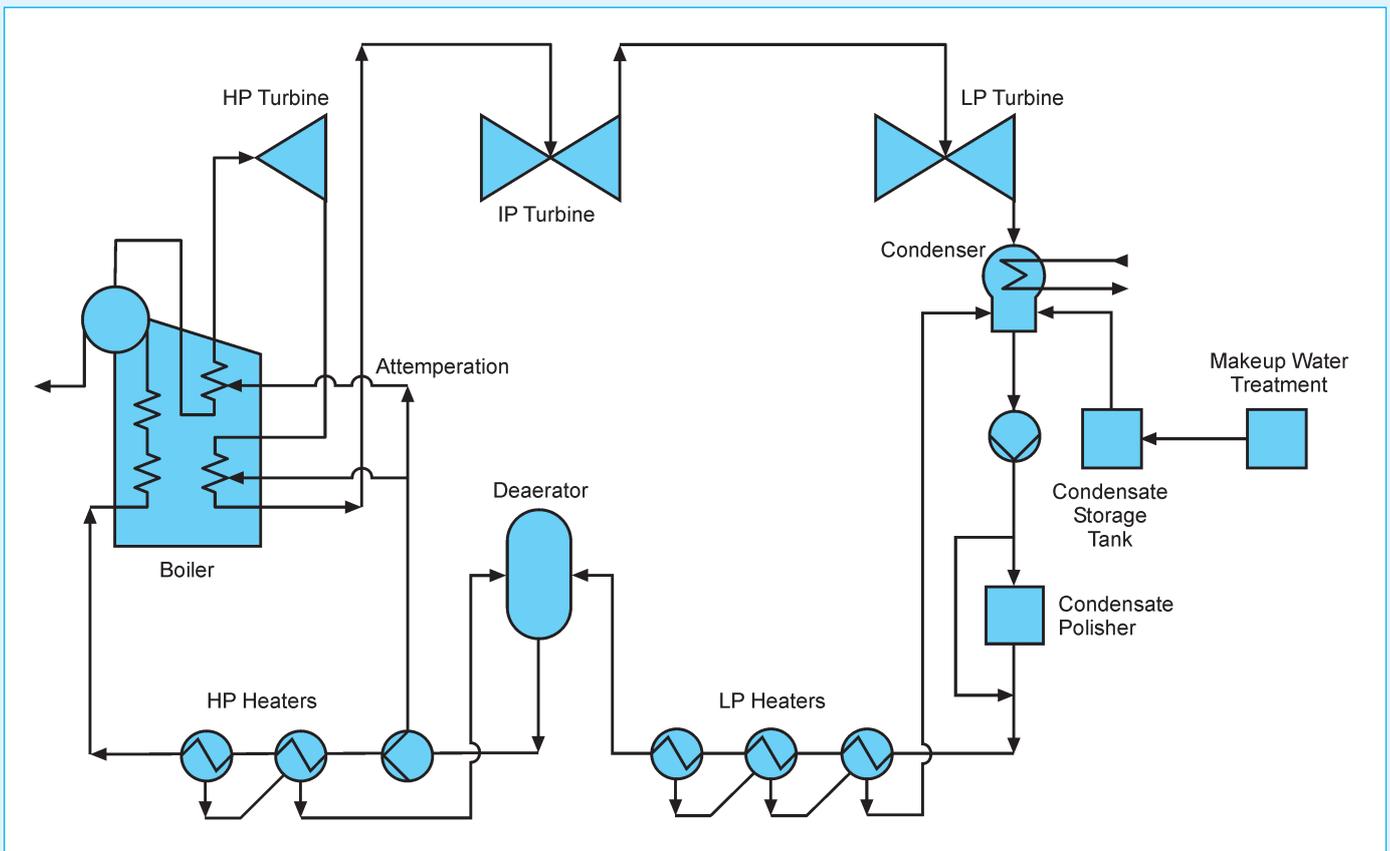


Figure 1:
Simplified schematics of a plant cycle with a drum boiler.

from this diagram. Some of them will be markedly simpler; for example, the LP turbine and the condenser will be missing in industrial cycles with steam sendout and without any condensate return. Some will be more complicated; for example, combined cycles with heat recovery steam generators in which the steam generator itself may consist of up to three individual boilers operating at different pressures. However, this topic – the configurations of plant cycles – will be dealt with in another lesson of this course.

Let us follow the water and steam paths starting at the component with the lowest temperature of the operating medium in the cycle, the condenser. The condensate (low-pressure steam condensed in the condenser, which may be water-cooled as depicted in this diagram or air-cooled) is routed through a system of low-pressure heaters (where the condensate is heated up with steam extracted from the turbine (not shown in the diagram)) into the deaerator. The deaerator has several functions: it removes non-condensable gases (e.g., oxygen) from the condensate, works as a direct heater, and acts as receiver for the feed pump. This pump conveys the water (now called feedwater) through the HP heaters (again, heated up with steam turbine extractions) into the steam generator. The steam generator produces superheated steam, which drives the turbine. The steam generator depicted in the figure has a single reheat: the exhaust steam of the HP turbine is reheated in the steam generator and routed to the IP turbine. The exhaust steam of the last turbine section is condensed in the condenser.

The materials used in the plant cycles are in contact and interact with water or steam in over a very wide range of temperatures and pressures. In units with once-through fresh water or seawater cooling, the condensate temperature may be, depending on the particular season and climatic zone, very low. The superheated or reheated steam in modern HP boilers reaches temperatures in the region of about 500–600 °C (about 930–1 100 °F). The pressure range over which the individual plant cycle components operate is also very broad: from a vacuum in the condenser up to pressures higher than the critical pressure of the water substance. The critical data of water substance (rounded) are:

temperature	374 °C (705 °F)
pressure	22.06 MPa (3 200 psi)

It is quite obvious that the selection and behavior of materials, the component design, and the operation conditions including flow velocities, stresses, temperatures, pressures, operation modes, etc. are very complex and that they are crucial factors which decide the success or failure of the operation. This approach presupposes that the operating medium (water or steam) is always neutral and in no way affects the state of the materials or components. Unfortunately, this presupposition is incorrect.

PLANT CYCLE CHEMISTRY

Materials science, mechanical construction, dimensioning and design, thermodynamics, heat transfer, and many other scientific disciplines are involved in the design, construction and operation of a plant cycle. Yet the entire plant cycle and its operation may not seem to have anything to do with chemistry. However, as indicated above, this is not the case. Chemistry, or more precisely plant cycle chemistry, is the next science to be involved in the multidisciplinary approach to achieving optimal steam and power production.

Neglecting plant cycle chemistry when designing, constructing, and operating a steam or power generating unit unavoidably results in serious failures of or damage to major plant cycle components. However, these are not the only consequences of neglecting plant cycle chemistry: issues like plant cycle reliability, availability, and efficiency, among other things, are directly associated with and dependent on plant cycle chemistry.

Now, it would be appropriate to try to explain what power plant chemistry is at all. This generic term refers to all chemistry-related measures, actions and techniques to be applied in the entire plant cycle to ensure trouble-free, reliable, and economic operation of the entire plant cycle. In this lesson, only the most important items will be presented.

Makeup Water Treatment

In any plant cycle, water and/or steam losses occur. The causes are manifold. Here are some examples:

- during startup of a unit, steam which has not yet reached the parameters required for turbine operation cannot be used or completely reused;
- in coal- or heavy fuel oil-fired boilers, steam used for sootblowing in the furnace or in the convection banks is lost;
- any response of safety relief valves represents steam losses;
- in cycles with drum boilers, the boiler blowdown (required for concentration control of the boiler water) is a loss;
- in cogeneration units with steam sendout, the steam condensate is typically not completely returned or it is not returned at all or it is heavily contaminated and cannot be used in the plant cycle.

You could easily add other water and steam losses yourself. However, the reasons are not important. The fact that any water or steam losses have to be replaced by treated makeup leads us back to the item *makeup water treatment*.

Water as available in nature in wells, rivers and lakes (or in the form of treated municipal wastewater, which is increasingly being reused in dry regions) cannot be directly used in a high-pressure plant cycle. (Low-pressure cycles do not have as strict requirements on the makeup as high-pressure cycles do. At the moment, this difference can be abstracted away from for our purposes.) Before it can be used, all suspended solids, ionic substances and dissolved gases have to be removed. In many cases, a high content of organic substances (natural or anthropogenic) could cause problems in the plant cycle (decomposition of organics resulting in acidic decomposition products). For this reason, the content of organic substances also has to be markedly reduced via makeup water treatment.

The requirements on the makeup quality are specified in all major industry guidelines. High-pressure or supercritical cycles require nearly chemically pure water without any contaminants. The precise data will be discussed later in another lesson. At this point, we only want to state that the raw water has to be treated (in a makeup water treatment installation). Physical and chemical techniques are implemented in the makeup water treatment process. The selection of individual processes or subprocesses depends on the raw water quality; a generally valid indication cannot be given. However, ion exchange is a widely applied process in makeup water treatment.

Condensate Polishing

Condensate polishing is a further part of fossil plant cycle chemistry. Why? Is the condensate, in fact distilled water, not pure enough to be used – after heating in feedwater heaters and degassing in a deaerator – as feedwater for the steam generator? As always, the question is very simple; the answer, however, is a bit complicated. Perhaps the answer should be split into two parts: the first part considering typical utility cycles, the second considering the specific conditions in cogenerating units, in particular in those in industry (e.g., in refineries, sugar and paper mills, and the chemical industry).

In a utility, the condenser is a component in which ingress of contaminants into the cycle may occur. Any leak in the condenser tubing results – due to the pressure difference between the vacuum part of the condenser and the cooling water pressure – in cooling water ingress into the cycle. Depending on the amount of cooling water entering and its salinity, the consequences of such an event may be very serious. Two major cycle components, the steam generator and the turbine, may be affected. For this reason, high-pressure or supercritical cycles are equipped with condensate polishers. The polishers remove suspended solids, ionic impurities and silica from the condensate contaminated with cooling water and make sure that the quality of the polished condensate is in accordance with the strict quality requirements for the particular plant cycle. Typical

condensate polishers are mixed beds, in which cation and anion exchangers are combined in one charge. Mixed beds or mixed-bed demineralizers are not only capable of removing ionic impurities and silica, but they also act as mechanical filters.

In cogenerating units, the return condensate may be contaminated with substances from the actual industrial process. For this reason, it is necessary to treat (to clean) the return condensate using various processes and equipment, the type of which depend on the type of the possible contaminations.

Feedwater Treatment

In the condensate or feedwater train (the part of the cycle between the condenser and the steam generator), condensate and feedwater (and steam in feedwater heaters and in the deaerator) are in contact with particular materials. The surfaces of the feedwater tubing comprise the majority of the surface area in the feedwater train. Such tubing is made either of carbon steel, low-alloyed steel, and stainless steel or of copper-based materials. Except for stainless steel, these materials may be subject to corrosion or flow-accelerated corrosion. The operating medium – feedwater – is then contaminated with corrosion products and transports them into the steam generator.

This occurrence has a very negative impact on plant cycle components:

- corrosion damage to feedwater heater tubing;
- deposition of corrosion products in the boiler resulting in underdeposit corrosion of boiler tubes;
- transport and deposition of corrosion products in the superheater and in the turbine. Turbine deposits may cause significant capacity losses and diminish the turbine (the whole cycle) efficiency.

Chemical measures focusing on the optimum protection of the feedwater train and on the reduction of the suspended corrosion product transport are typically called *feedwater treatment*. The feedwater treatment has to be selected in consideration of all materials used in the respective condensate/feedwater train. All typical feedwater treatment chemicals are volatile substances. For this reason, they may also be used in cycles with once-through steam generators.

Four feedwater treatments are applied in plant cycles. The first three are typically used in utilities and at industrial steam and power generators with high-pressure units. The fourth treatment is mainly applied in industrial steam and power generation, very often in units operating at pressures lower than those used in utilities.

- oxygenated treatment (dosing of oxygen and ammonia), applicable only in all-ferrous systems;
- all-volatile treatment (dosing of ammonia) without an oxygen scavenger, also applicable only in all-ferrous systems;
- all-volatile treatment (dosing of ammonia) with additional dosing of an oxygen scavenger (typically hydrazine). This treatment is an absolute must for units with mixed metallurgy (steel and copper-based materials in the feedwater train);
- all-volatile treatment based on the use of different amines and in some cases with the parallel application of an oxygen scavenger (hydrazine substitutes).

Boiler Water Treatment

In drum-type boilers, even trace amounts of contaminants concentrate in the boiler water. Boiler blowdown helps to control the concentration below the pressure-dependent limits. Nevertheless, in most cases the additional use of chemicals to ensure an optimal operation environment in the waterwalls is required. This measure is called *boiler water treatment*; the chemicals are injected into the boiler water. It is only possible to do without the additional boiler water treatment in the case of very high operation pressures under the condition that the feedwater (and the resulting boiler water) is extremely pure. In this case, it is very common to designate this type of operation as all-volatile boiler water treatment or oxygenated boiler water treatment although no additional chemicals are used besides those already present in the feedwater.

The most common boiler water treatments are:

- phosphate treatment (also called phosphate continuum);
- sodium hydroxide treatment (also called caustic treatment);
- amine and/or polyamine treatment, primarily used in industrial steam and power generation.

Plant Cycle Chemistry Monitoring

Successful cycle chemistry operation requires reliable surveillance. For this reason, sampling points are installed around the plant cycle and equipped with appropriate instruments. This is an indispensable condition to controlling the cycle chemistry parameters at the predetermined target values. As a rule, the most important chemistry-related parameters not only have to be recorded (with data storage), but should also be alarmed in the main control room of the unit. Only in this way can the operation staff (very often neither chemists nor people trained in chemistry) make the correct decisions.

Plant cycle chemistry monitoring is an area which is frequently the victim of imprudent cost savings. This is a pity since "flying blind" with respect to cycle chemistry does not pay. If the actual value of an important parameter is not known, it is not possible to control this value at its optimum.

SIGNIFICANCE OF PLANT CYCLE CHEMISTRY FOR PLANT OPERATION

Operating experience teaches that there are very complex interactions or interferences between materials (component design and material processing included), strains (stresses, flow velocity, temperature, heat transfer, operation mode, etc.), and local environments (concentration of contaminants and plant cycle chemistry treatment chemicals, pH, redox potential, etc.) occurring in plant cycle components. Even if there are optimal material selection and component design, as well as strains within tolerable ranges, a detrimental local environment (outside of chemistry specifications) will unavoidably result in damage to the component.

The most serious consequences may be expected for the steam generator and for the turbine. For example, the typical boiler tube failure mechanisms in fossil-fired steam generators related to improper cycle chemistry are:

- Corrosion fatigue
- Hydrogen damage
- Acid phosphate corrosion
- Caustic gauging
- Flow-accelerated corrosion
- Pitting
- Stress-corrosion cracking

A similar statement may be made with respect to heat recovery steam generators.

Figures 2–4 show hydrogen damage failures in heat recovery and conventional steam generators.

As to the turbine, there are two chemistry-related problems: deposition in the turbine and damage due to incorrect chemistry:

- Deposits in the turbine always result in decreased unit capacity and efficiency;
- Incorrect cycle and in this way steam chemistry may be the root cause or an important component of a damage mechanism, for example
 - damage in turbine blades and the blade-disc attachments,
 - pitting,
 - crevice corrosion,
 - corrosion fatigue of LP turbine blades,
 - stress-corrosion cracking in turbine blades or blade attachments, and
 - flow-accelerated corrosion.

Figures 5–7 imposingly depict consequences of incorrect plant cycle chemistry in turbines.

In both cases, boiler tube failures and damage to the turbine, chemistry-related problems are not exclusively related to the component operation. In many cases, the shutdown environment and its chemical composition may be the cause of later damage.

Regarding high reliability, availability, and optimum efficiency of fossil plant cycles, plant cycle chemistry has to be acknowledged as one important condition for reaching these goals. Sufficient attention to cycle chemistry as well as adequate manpower and resources to achieve cycle chemistry optimization is a reasonable policy.

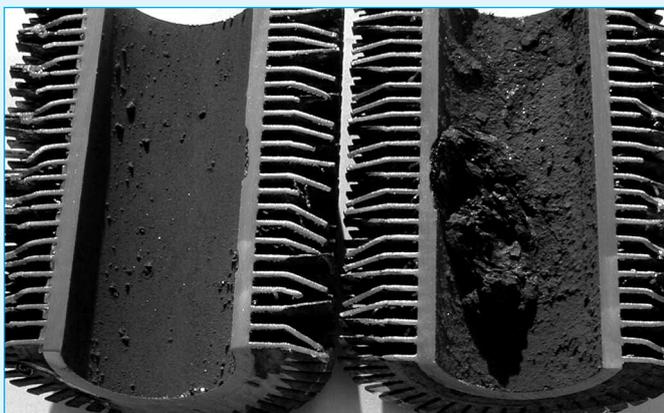


Figure 2:
Hydrogen damage in an HP evaporator of a heat recovery steam generator.
Courtesy of R. B. Dooley (Structural Integrity Associates, Inc.).

CLOSING REMARK

This lesson is intended and should be understood as the introductory lecture of this course. For this reason, this lesson does not include any details on the terms or operations presented. This is reserved for the following lessons, which will deal with the individual issues mentioned in this lesson.



Figure 3:
Hydrogen damage in an HP evaporator of a heat recovery steam generator.
Courtesy of R. B. Dooley (Structural Integrity Associates, Inc.).



Figure 4:
Hydrogen damage in a waterwall tube of a conventional boiler.
Courtesy of R. B. Dooley (Structural Integrity Associates, Inc.).



Figure 5:

Blade failure in the zone of first condensation of an LP turbine. Condenser leakage with seawater was inadequately purified in the condensate polishers, leaving an excess of chloride. In the boiler this chloride passed over into the steam. It subsequently condensed in the first condensate to a concentrated solution, which supported corrosion attack, in this case by corrosion fatigue.

Courtesy of R. Svoboda (Alstom Power, Ltd.).

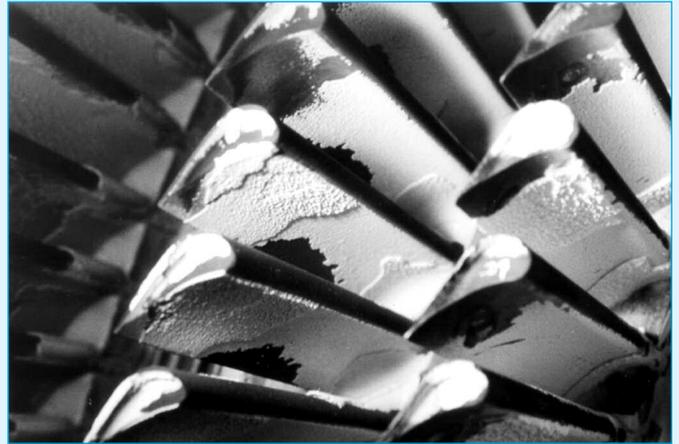


Figure 7:

Silica deposits in the turbine. A large quantity of silica was introduced into the plant cycle due to a regeneration failure in the makeup plant. Subsequently about 12 kg of silica deposited in the steam turbine. The turbine exhibited a loss in steam-swallowing capacity and the development of axial thrust. It had to be opened and cleaned by sandblasting. The picture was taken before cleaning. It can be seen that part of the deposits had already flaked off.

Courtesy of R. Svoboda (Alstom Power, Ltd.).

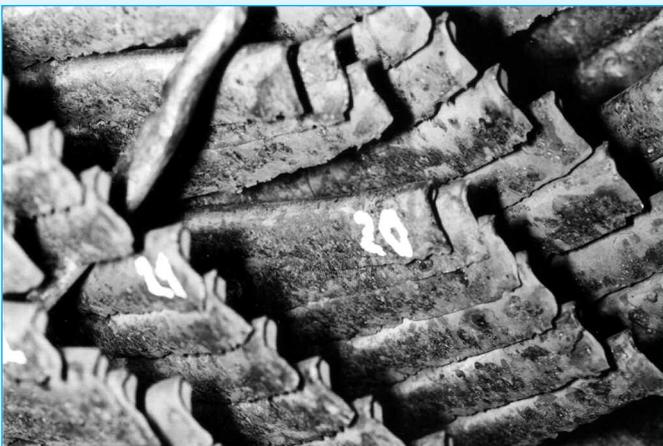


Figure 6:

Severe pitting damage of low-alloy steel stationary blades in an industrial turbine. The pitting was caused by salt deposits and moist shutdown conditions.

Courtesy of R. Svoboda (Alstom Power, Ltd.).