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Technical Guidance Document: Procedures for the Measurement of Carryover of Boiler Water into Steam

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This document outlines the considerations for periodic monitoring of carryover essential for chemistry control and the separation of mechanical carryover for guarantee purposes. Total carryover is determined by measuring the mass concentration of sodium in the boiler water and in steam. The mechanical carryover represents the fraction of water entrained from the boiler drum into the steam and is determined by correcting the total carryover for any contribution of vaporous carryover. This document gives procedures and covers practical aspects such as the choice of the sodium compound, test conditions, analytical procedures and plant parameters and operating conditions to be considered.

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1. Nomenclature and Definitions

Symbol	Physical quantity	Unit
T	Total Carryover	%
M	Mechanical Carryover	%
V	Vaporous Carryover	%
C_s	Sodium concentration in saturated steam (ppm)	mg kg^{-1}
C_b	Sodium concentration in boiler water (ppm)	mg kg^{-1}

Mechanical Carryover: fraction of boiler water droplets entrained in the steam (mass of drum water per mass of steam).

Vaporous Carryover: fraction of substances entrained from boiler water into the steam by the substance's volatility (mass concentration in steam per mass concentration in drum water).

Total Carryover: is the sum of mechanical and vaporous carryover, and is the measured carryover.

2. Introduction

Carryover from boiler water to steam is a path by which dissolved and suspended solids in boiler water can be introduced into steam. Steam drums are equipped with steam separation devices capable of mechanically reducing the moisture content of the steam. The total carryover into steam consists of two parts: a mechanical part and a vaporous part. The mechanical part (Mechanical Carryover) involves the carryover of boiler water droplets. The vaporous part (Vaporous Carryover) involves the partitioning of dissolved solids (salts, oxides, impurities and other chemicals) between water and steam and represents the physical volatility of the substance.

Only above a drum pressure of about 16 MPa (2300 psi) does vaporous carryover start to become significant for most of the solids dissolved in the boiler water. Below this pressure, it is nearly all mechanical carryover with the exception of a few substances like silica, the copper oxides/hydroxides, aluminum compounds and boric acid, which exhibit significant vaporous carryover even at relatively low pressures. For boilers below 18 MPa (2600 psi), vaporous carryover is typically less than 0.1 %.

There are two important and distinct aspects associated with carryover. The first, for the operators of drum units, is the concern about possible corrosion and fouling aspects in superheaters, reheaters and steam turbines associated with the total carryover. The second, for the boiler manufacturers, relates to the performance of a drum in relation to the efficiency of the steam/water separation components and in regard to mechanical carryover. Thus for operators, it is important to know and monitor the total carryover into steam. In contrast, manufacturers need to provide information on mechanical carryover. One rigorous methodology to determine the mechanical carryover is illustrated in a recent publication [1]. However, applying this methodology (described briefly in Section 4) has been found to be rather difficult because a complex computer code needs to be used to carry out the calculations [1]. So, some manufacturers have their own methods or use a default value of 0.1 % carryover for the vaporous component.

3. Scope

Provide a procedure for the measurement of total carryover, and a description of mechanical carryover from steam drums (fraction of boiler water droplets entrained in steam) and of vaporous carryover.

4. Mechanical Carryover vs. Total Carryover

The total carryover of boiler water impurities and conditioning chemicals in drum boilers determines the chemical purity of the steam. Carryover is a combination of two factors: vaporous carryover, due to the inherent volatility of the constituents in the boiler water, and mechanical carryover of droplets of boiler water into the steam. Once the total carryover is known, then boiler water limits can be set to limit the risk of initiating corrosion in the boiler, as well as steam limits to minimize the risk of initiating corrosion and deposition in the steam circuits, including the turbine. Thus, carryover needs to be measured to develop unit-specific cycle chemistry guidelines.

Total carryover of sodium is determined as the ratio of the saturated steam sodium concentration to boiler water sodium concentration. Mechanical carryover is determined by subtracting the vaporous sodium carryover in the steam at high pressures.

$$T = C_s / C_b * 100 \quad (1)$$

$$M = T - V \quad (2)$$

Mechanical carryover is the entrainment of water droplets in steam exiting the boiler. It depends on the condition of the water/steam separators, drum level control, and steady-state operating conditions. Mechanical carryover is a function of the density difference between water and steam phases at a particular pressure. An example of how mechanical carryover varies with pressure is shown in Figure 1, which illustrates that mechanical carryover can be significant; for example, at a pressure of 17.2 MPa (2500 psi), it may be as high as 0.2 %. The boiler manufacturer can supply the actual design data to be used for the respective boiler and such an example is also shown in Figure 1.

Vaporous carryover occurs due to the inherent volatility of the compounds present in the boiler water. Some compounds, *e.g.*, ammonia and amines, are deliberately added to the water/steam circuit as conditioning chemicals, because they are volatile and can protect various parts of the boiler water/steam circuit during operation and off-load conditions. Except for these plant conditioning chemicals and a few substances like silica, copper oxides/hydroxides, aluminium compounds and boric acid, vaporous carryover at pressures less than about 16 MPa (2300 psi) is negligible.

Molecular impurities in boiler water can evaporate with steam (vaporous carryover). The degree of vaporous carryover is expressed as a distribution ratio of concentration of the compound or impurities in the steam to that in the boiler water. The distribution ratio is a function of:

- boiler drum pressure
- boiler water dissolved solids concentrations, and
- boiler water pH and interactions between the species present.

Thus, information is required on the volatility of the salts and their corresponding acids and bases likely to be present in boiler water, such as sodium chloride, hydrochloric acid, sodium hydroxide, ammonia, ammonium chloride, sulfuric acid, sodium hydroxide, and sodium and ammonium sulfates and bisulfates, over the range of temperatures of interest. This can then be used to model the chemistry around the water/steam circuit under the chemical regime at any temperature, pH or composition of the boiler water. The allowable impurity concentrations in boiler water can then be calculated from those of the steam and the amounts of mechanical and vaporous carryover.

Previously, the vaporous content (*V*) of the total carryover was estimated from a distribution ratio diagram (commonly referred to as the “ray” diagram). However, monitoring in numerous plants showed that the “ray” diagram had severe shortcomings and a more rigorous method was required. After over 15 years of research initiated through IAPWS, most of the partitioning constants for the important boiler water compounds have been investigated. Figure 2 shows one such compilation with others being illustrated in references [1] and [2]. At the highest pressures, the vaporous carryover

can be derived from the partitioning constants of the species using an appropriate set of equations. Manufacturers have their own methods for calculating the vaporous carryover or, because of the complexity of using the partitioning constants and a computer code to implement the equations, they simply use a default of 0.1 %.

5. Description of the Method

A sample of saturated steam is withdrawn through an isokinetic sample nozzle in the connecting links (off-takes) leading from the steam drum to the primary superheater. The steam sample is condensed and the concentration of sodium in the sample is measured. A sample of boiler water from the steam drum is obtained at the same time, and its sodium concentration is also measured. The steam sodium concentration divided by the boiler water sodium concentration represents the total carryover.

The boiler water sample is obtained from the continuous blowdown line that comes from the steam drum. The blowdown water is a fairly homogenous mixture of the feedwater (distributed along the drum length) and the returned water/steam mixture from the evaporator tubes/risers also distributed along the drum length. The fossil boiler steam drum is long and relatively narrow, so mixing hasn't usually been a problem. Drum internals and components can be installed improperly, but these problems are typically discovered and resolved during the commissioning process. Usually there are sampling devices that obtain water/steam samples above and below the water level. These are sometimes (and temporarily) installed in new units to calibrate or resolve problems with water level controllers. These can be used to obtain samples of water that is in more immediate contact with steam, but the difference in the carryover measurements has not been significant enough to warrant the permanent installation of these devices.

6. Use of Sodium to Determine Total Carryover

Sodium salts, such as Na_3PO_4 and/or NaOH , are used for boiler water treatment (primarily in fossil plants). These have good solubility in boiler water and a low volatility in steam, which makes them suitable tracers for determining the total carryover.

The sodium concentration is typically 1-5 mg/kg (ppm) for phosphate treated boilers and up to 1 mg/kg (ppm) for NaOH treated boilers. These levels are usually sufficient to permit the carryover measurements (primarily an accurate measurement of the trace sodium concentration in the steam), especially if the concentration is maintained toward the higher end of the range. Additional dosing of sodium is not required for boilers operated on NaOH or on phosphate treatments. For boilers on oxygenated treatment (OT) or all-volatile treatment (AVT), pressure-dependent sodium concentration should be stated as the maximum tolerable concentration of sodium in the boiler water. The experience base with these tests is large, mature and comprehensive.

Any hideout or other transient behavior associated with sodium addition should be normalized by performing the tests at stable and fixed operating conditions. In other words, the system is brought to steady-state conditions and then samples are obtained. If concerns arise as to the time lag in obtaining/analyzing samples, other options exist such as obtaining/analyzing samples at close proximity to the steam drum.

In nuclear steam generators with All-volatile Treatment and low concentrations of alkali in the boiler water, radioactive tracers may be used. A common tracer is Na-24 in the form of Na_2CO_3 or NaNO_3 , applied in very low chemical concentration.

Other alkali such as lithium hydroxide could also be used, however there is a lack of information about the volatility of lithium species at high pressures. They would be selected on consideration of a low volatility (vaporous carryover).

7. Sampling

Drum boilers can have several steam purity sample nozzles (up to six off-takes) located in the connecting links between the steam drum and primary superheater inlet. These nozzles can be individually fitted with sample lines and isolation valves. For normal operation, the sample lines typically discharge into a collection header, and pass through a sample cooler to a single monitor in the chemical sampling/instrumentation panel.

The preferred procedure when evaluating steam purity (especially for the first time) is to separate the sample nozzle lines and analyze a sample from each line. The initial performance tests should include a characterization of the carryover behavior. Therefore, saturated steam samples should be obtained at least at each quarter point along the length of the drum. This will also help to establish sampling needs for future tests and requirements for the continuous steam purity sample. This permits the steam purity to be evaluated along the length of the drum, and helps to identify variations that may exist and may be the cause for these variations. A “switched” sampling device that can rotate around the various off-takes will ensure that a false impression is not provided by simply taking samples from only one off-take. Numerous examples exist of steam turbine and boiler feed pump turbine damage in such situations.

The steam nozzles should be designed for isokinetic sampling [3-7]. The nozzle sample flow must be controlled to provide isokinetic conditions at the nozzle inlet. This sample flow rate must be varied to match the steam velocity variation in the saturated steam link with boiler load.

8. Analytical Methods

On-line sodium analyzers for steam and boiler water samples have proven to be successful when sodium salts (or hydroxide) are used for boiler water treatment [7]. It is also possible to analyze by ion chromatography.

In a typical test, the sodium concentration in the boiler water is on the order of 1 to 5 mg/kg (ppm), and the sodium concentration in the steam is typically on the order of 2 to 10 $\mu\text{g}/\text{kg}$ (ppb). In some cases, the sodium concentration in steam is as low as 0.4 to 2.0 $\mu\text{g}/\text{kg}$ (ppb). In all cases, the sodium level should be in agreement with the pressure-dependent sodium levels in boiler water as specified in the applicable guidelines. Contamination of the samples by contact with ambient air, sample bottle walls, or through manipulation can give erroneous results. The advent of the selective ion electrode has

improved the measurement of these low concentrations. The sample can be withdrawn through tubing directly to the measurement station without significant contamination from external sources. A second improvement in the measurement ability is the connection of the measurement station to a PC data acquisition system that displays trends of the concentration with time, permitting the operator to determine that an equilibrium condition was achieved when deciding whether to include data as a test point.

The isokinetic sample flow usually does not match the flow required by a sodium analyzer. Generally, sodium analyzers typically require less sample than an isokinetic nozzle sample can deliver. For this reason, the sodium analyzer should be operated in a by-pass; the sample surplus can be sent to drain.

A second sodium analyzer is required for the boiler water sample from the steam drum. The residence time needs to be calculated for the sample line size and length to determine the drum sample time for water compared to the sample time for the saturated steam sample. These sample times should be within 5 minutes of each other. The sample flow for the boiler water and analyzer are similar to those of the steam sample thus requiring the same arrangement. It is also possible to analyze the sodium in the boiler water by other methods than an on-line analyzer, because the higher concentrations make the sample less susceptible to errors by contamination.

9. Test Procedures

In order to fully characterize the behavior of the boiler, samples should be taken over an extended period. For the first hour after establishment of a new operating condition (load, drum water level, etc.), the data may be subject to transient effects and may not be fully representative. Major changes in carryover can occur at steady load in some boilers; if this is observed, then thorough investigation of the cause will be required. Continuous flow selective ion analyzers will permit an observer to determine the exact flush time requirement. The samples should not be taken for one hour after setting the required boiler operating conditions to permit the unit to reach equilibrium. The sample flow rates should be adjusted to an isokinetic sample flow. If grab samples are used for the measurements, then the blowdown and steam samples should be flowing for at least three hours before the samples are taken.

10. Test Conditions

The performance of the steam drum internals (and total carryover) is primarily dependent on load (steam flow rate), operating pressure and water level. The steam flow rate and pressure affect the fluid velocity and thus the performance of the separators. Carryover is usually fairly low (considerably below design limit) and constant until the steam flow (for a particular design pressure) approaches full load conditions, at which point it begins to increase. This increase is usually progressive, but in some boilers it can occur suddenly and/or intermittently. It is important for the operators to be aware of the drum internals performance as a function of drum water level. An increase in water level above the normal level reduces the height between the water surface and final separators (dryers) thus reducing gravity separation of water droplets from the steam. This can have

a detrimental effect on the effectiveness of the separators. Mindful of the water level (*i.e.*, low water level) impact on boiler performance, the water level targets for the carryover tests should be selected to be well within safe boundaries established by level control alarms and experience.

A number of aspects about carryover need to be considered: a) a drum may show distinct periods lasting a few hours at a time when serious carryover is occurring, interspersed with periods of acceptable operation; b) small changes of load, burner pattern, or drum water level can all influence the performance of the drum; c) in long, narrow drums it is known that carryover taking place along part of the length can occur; and d) any chemicals present that influence surface tension can have a major effect on the carryover.

The steam purity tests can therefore be performed at various conditions. An example to show the impact of various factors is shown in Table 1. However, for the purpose of determining the design or predicted performance of the steam drum or separator system, the carryover tests should be performed at full load conditions.

Carryover testing conducted between every six and twelve months is a satisfactory interval for boilers not experiencing carryover-related problems. Greatly preferable is to perform continuous measurements using continuous on-line instruments, switched between off-take sampling points, especially during periods when load/pressure changes are occurring.

11. References

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4. *Standard Practice for Sampling Steam*, ASTM D1066.
5. *Standard Practice for Flow Control and Temperature Control for On-Line Water Sampling Analysis*, ASTM D5540.
6. *Standard Guide for Equipment for Sampling Water and Steam in Closed Conduits*, ASTM D1192.
7. *Standard Test Methods for Continuous Determination of Sodium in Water*, ASTM D2791.

12. Tables and Figures

Table 1. An example of test conditions for the measurement of the Total Carryover (MCR = maximum continuous rating)

Test No.	Unit Load % MCR	Drum Operating Pressure MPa	Water Level, Deviation. from Normal mm
1	100	Maximum	0
2	100	Nominal	0
3	100	Nominal	+100
4	100	Nominal	+50
5	100	Nominal	-50
6	100	Nominal	-100
7	105 (peak)	Nominal	0
8	75	Corresponding	0
9	50	Corresponding	0

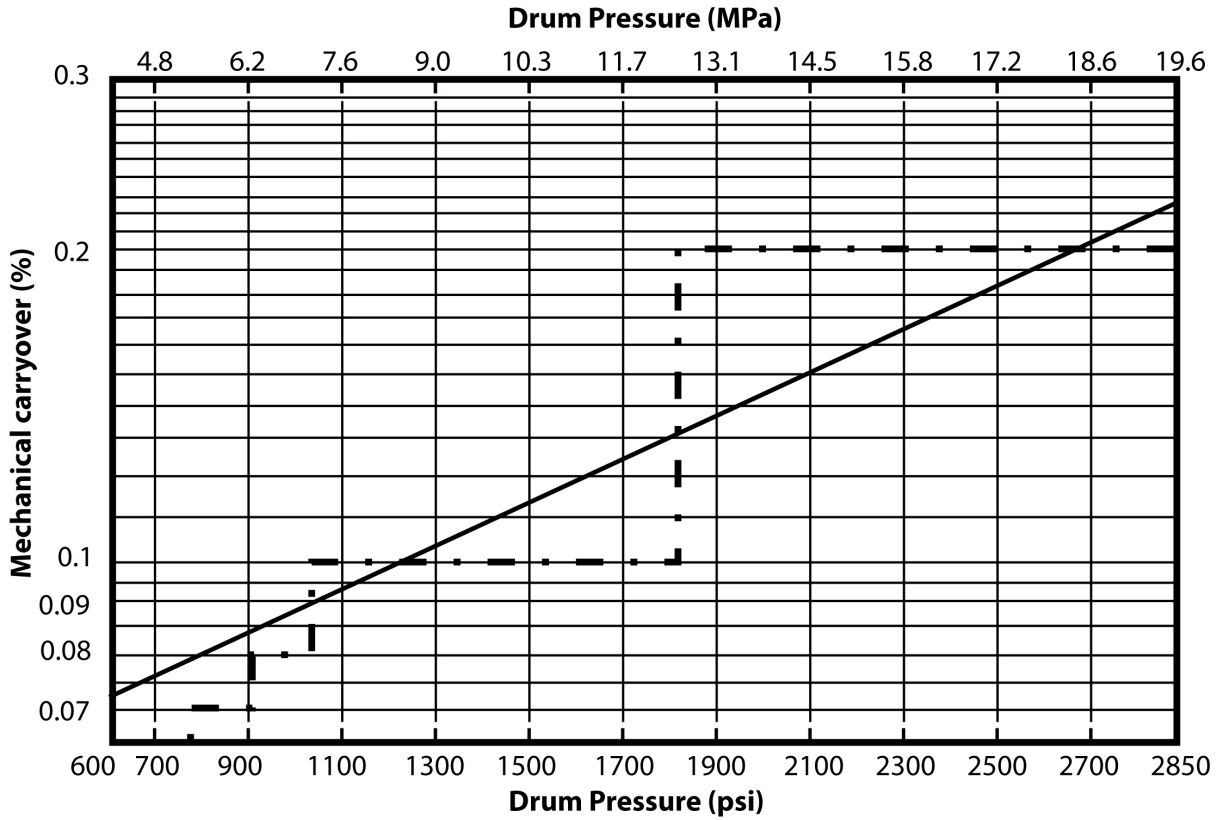


Figure 1. Example of percentage of mechanical carryover as a function of the boiler pressure (solid line) [1]. Information for a specific boiler that is more precise can be provided by the boiler manufacturer: the dotted line shows an example.

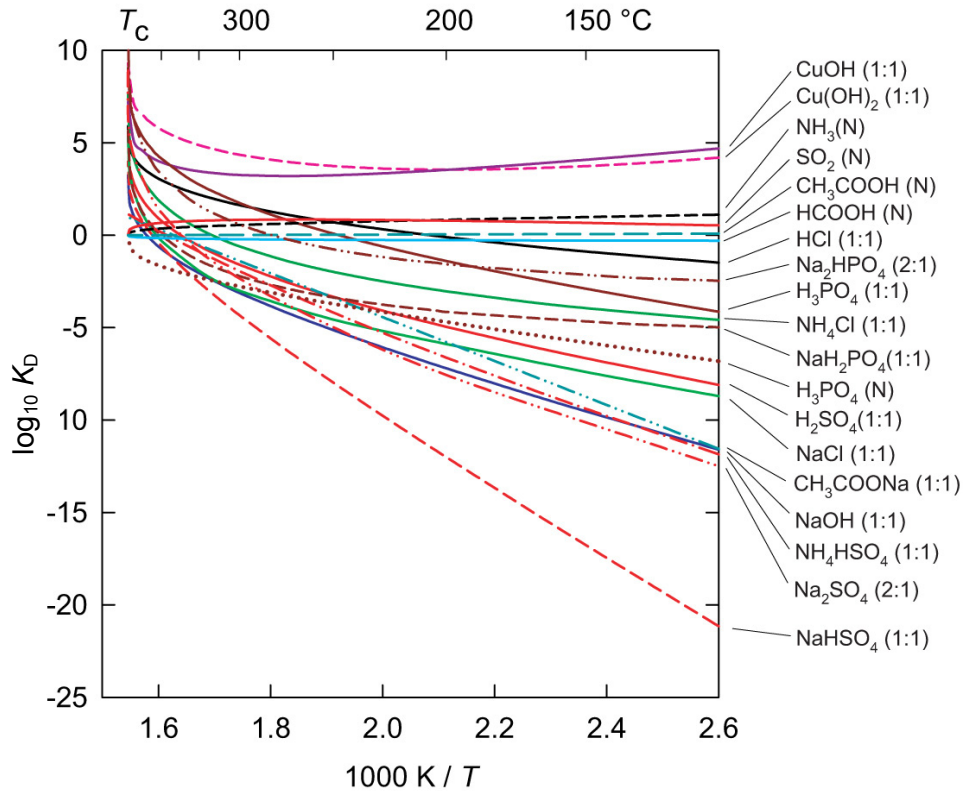


Figure 2. Partitioning constants (K_D) for some species plotted against reciprocal temperature (kelvin). It should be noted that the volatility of neutral (N) compounds can be compared directly with other neutral compounds on this figure, 1:1 compounds with other 1:1 compounds, and 2:1 compounds with other 2:1 compounds. But neutral compounds cannot be compared directly with 1:1 or 2:1 compounds [1,2]. Other examples of distribution coefficients can be seen in references [1] and [2].