

# Recent Patents on Corrosion Control and Leak Detection Schemes in Boilers

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**Abstract:** For industrial processes, namely, power systems, chemical systems and oil refinery systems, the boilers play an important role in the overall plant operation. If they are operated continuously for an extended period of time, then due to chemical reactions, aging and stress caused by the heating process, there are problems of corrosion, slag precipitation and leaks in different components. This deterioration invariably leads to a reduction in the amount of steam generated, equipment damage and, in some cases, complete plant shutdown. This paper presents a survey on recent patents, which deals with monitoring and control of corrosion, slag as well as different leak detection schemes. The focus of this survey is on slagging and corrosion control in superheated tubes of the waste to energy (WTE) boilers as well as monitoring the corrosion of carbon steel in boiler-drum. For different leak detection schemes, it is well known that most of them generate false alarms. Therefore, some new inventions on the maximum number of false alarms tolerated by the system and the acceptable operation of the leak detection systems are also presented.

**Keywords:** Industrial boiler system, boiler corrosion problem, leak detection schemes, control applications.

## 1. INTRODUCTION

Industrial boilers are highly interconnected, whose main task is to generate steam for producing electricity and exporting the resulting electrical power to the grid [1,2]. The steam may also be sent to a nearby process plant, utilities or a housing complex. A schematic of a steam boiler system is shown in Fig. (1) [2]. The figure can be split into three parts: fire side, water side and electrical side. On the fire side, the heat used for steam generation may be obtained by burning fossil fuel or it may be derived from exhaust of a gas turbine. On the water side, the feedwater passes through an economizer (which is a heat exchanger between the incoming feedwater and outgoing flue gas) and is fed into the boiler drum. Then, it flows through the downcomers into the mud drum, where the mud drum distributes the water to risers and the heat supplied to risers cause boiling of the water. Gravity forces the saturated steam to rise in the risers, and leads to a circulation in the riser-drum-downcomer loop. The saturated steam is then separated from the water and leaves the steam drum into the primary and secondary superheaters to achieve a superheated steam (520°C). In between the superheaters, there is an attenuator, which sprays cold water to control the temperature. On the electrical side, the superheated steam passes through turbines to convert the heat energy into the mechanical energy and then to electrical energy in generators. The condensed steam from the low pressure turbines flows to a condenser (DM-makeup), low pressure heaters, deaerators (to remove air from water), high pressure heaters and feed control station, which then distributes it to an economizer. Hence, it is clear that the overall plant operation includes all primary disciplines chemical engineering, physics, thermodynamics, mechanical and electrical engineering. The overall operation is based on the well-known thermodynamic cycle of the power plant called *Rankine cycle* [2].

In this paper, the work is focused on surveying some recent patents on corrosion control and leak detection schemes in boilers. Although in steam boilers utilizing fossil fuels, corrosion in superheater tubes and leaking problem in downcomers/risers are very common, most of the patents we came across are mainly focused on waste to energy (WTE) boilers and black liquor recovery boilers. The WTE boilers uses solid waste, namely, refuse derived fuel (RDF) made from the municipal waste. Unlike fossil fuels, they are always available in vast amount, and are economical because there is no need for extra land for waste disposal [3]. Moreover, the electricity and the steam that the boiler produces can be useful in many other applications. However, due to the use of RDF and not fossil fuels, slagging and corrosion is a major issue in WTE boilers. The reasons for this concern are [3-5]:

1. Slag precipitation leads to draft loss, poor heat recovery, tube failure due to erosion and irregular operation in the power plants.
2. The municipal waste (plastics, non-recyclable materials) contains halogens, like chlorides, which is a main source of corrosion in the boiler tubes. It may require replacement of the tube or use of an expensive alloy to act as a protective shield, which are not economical.
3. In [6], the authors conclude that low NO<sub>x</sub> burners are the source of corrosion in the fire and the water side of the boilers. Usually, in the water inside, the boiler tubes are at high pressure, i.e. 2000 to 5000 psi. Therefore, the tubes may fail if their walls become thin due to corrosion.

On the other hand, black liquor recovery boilers uses black liquor as a fuel. It is an important liquid fuel, which is obtained from the byproduct of the paper making process. In the digestive process of pulping, when the cellulose fibers are completely cooked, then the byproduct is referred to as black liquor. As mentioned in [7]: “the escape or leakage of

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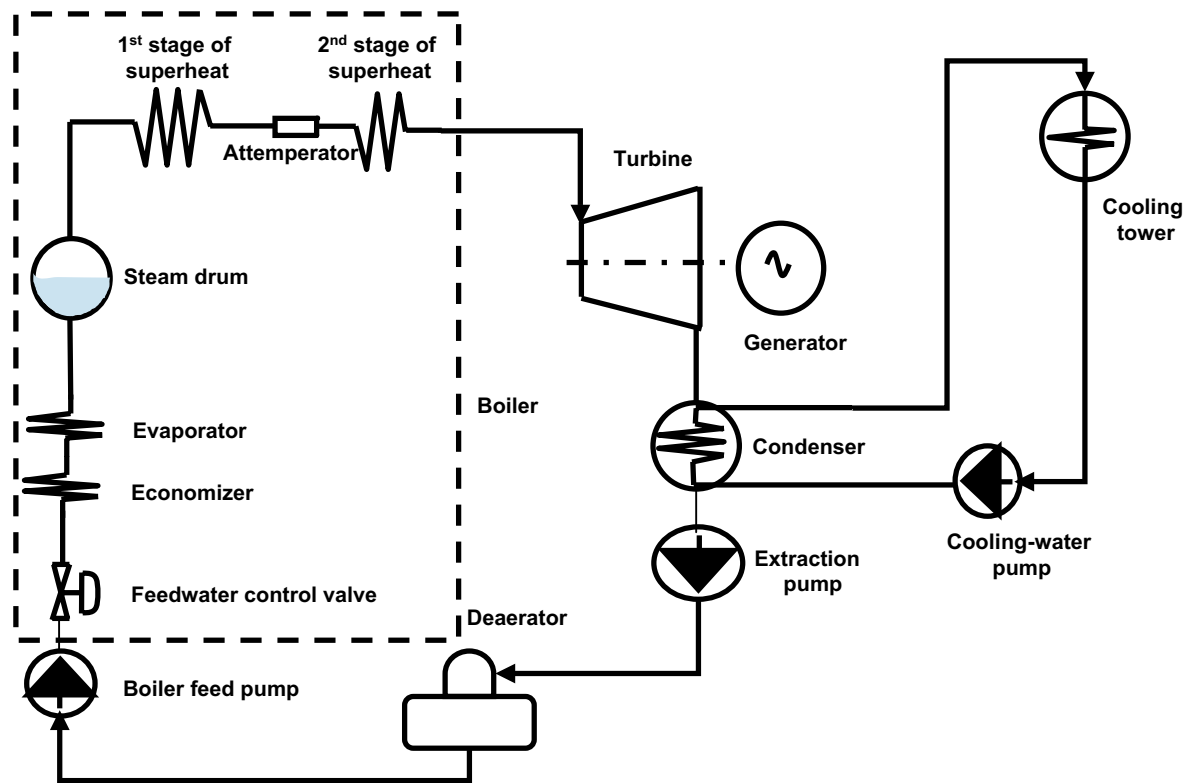


Fig. (1). Industrial boiler system [2].

aqueous temperature control liquid (in boiler drum) from the water side of the boiler into the hot, highly caustic fire side can result in violent explosions". Hence, a reliable leak detection system is required which can prevent the shutdown of the plant due to the aforementioned problem and loss of millions of dollars.

The rest of this survey paper is organized as follows. In section 2, the cause of slag and corruptions in different parts of the boilers are first introduced. It is then followed by different methods invented so far to overcome these problems. In section 3, we will go briefly through some leak detection schemes. Finally, section 4 offers some current and future developments.

## 2. SLAG AND CORROSION CONTROL IN BOILERS

Most of the contents of this section are based on the ideas of [3-5, 8]. The patent [4] was also published in [5]. The target of the corrosion engineers is to find the location of slagging and chloride corrosion control problem in different parts of the boilers and introducing suitable chemicals to overcome the same. They demand that the slag deposits can be easily crumbled to powder, so that it can be removed with less effort and little damage to the boiler tubes. Moreover, the corrosion monitor and the cost of the chemical reagent should not be expensive.

There are a number of theories available in recent patents [3-6, 9] on why corrosion occurs particularly on high temperature surfaces (based on chemical equations and intuitive/physical explanations). According to [9], corrosion may be caused by chlorine in the form of HCl, Cl<sub>2</sub> or by metal chlorides formed as a result of reaction between HCl and metal (Na, K, Zn, etc.) oxides. These metal chlorides may also react with SO<sub>2</sub>/SO<sub>3</sub> containing gas (in the presence

of moisture) to form metal sulphates. They found that at about 500°C, Cl<sub>2</sub> could react with the iron of the steel vessel to form FeCl<sub>2</sub>. The vapor pressure of this compound is relatively high at low temperature, which results in fragmentation of the protective oxide layer in the boiler tubes. These oxides are generally formed as a result of combustion and acts as a protective layer. In many cases [9], chlorine can cause a catalytic effect, in which FeCl<sub>2</sub>/FeCl<sub>3</sub> combines with oxygen to form iron oxide and liberate chlorine. This oxide layer is not very perfect, which causes the liberated chlorine to combine with the iron of the metal to form metal chlorides again, resulting in intensified corrosion. The following table [9] shows the temperature (T<sub>4</sub> °C) at which the vapor pressure of different metal chlorides reach 10<sup>-4</sup> bar.

Table 1. T<sub>4</sub> Temperatures of Metal Chlorides [9]

Metal Chloride	T <sub>4</sub> C
FeCl <sub>2</sub>	536
FeCl <sub>3</sub>	167
CrCl <sub>2</sub>	741
CrCl <sub>3</sub>	611
NiCl <sub>2</sub>	607

From this table, it is clear (as concluded by [5,9]) that iron base alloys have very less resistance against corrosion than nickel-based alloys, which have low volatility. Since, most of the temperatures in the table are well above 500°C, the corrosion effect should be considered and carefully

studied in superheater tubes, where the temperature of the steam should reach 520°C.

According to [6], the other reasons for corrosion at high temperature surfaces are:

- Reduced sulphur (in the form of FeS or FeS<sub>2</sub>), which is a result of the chemical reaction between the iron in the tube and the slag solution can react with the oxygen of the tube scale and decreases the effect of protective oxide layer.
- In some cases, if the protective layer is not present in the boiler tubes, then condensed phase chlorides may create cavities on the iron surface.

To overcome these problems, [4, 5] invented a new constant temperature probe to find the location and extent of corrosion as well as an inexpensive chemical agent (SO<sub>3</sub>) for corrosion treatment. In this work, the placement of probes and the original introductory parameters required to inject the chemical is determined based on computational fluid dynamics. The probe consists of a corrodible surface (can be worn away by chemical actions) and is attached to a fixed position in the superheater tube. It is then removed at regular intervals and its degree of corrosion is calibrated with the actual data obtained from other parts of the boiler (which are corroded at the same time). This helps to introduce the chemicals in appropriate amount and in suitable places. The preferred SO<sub>3</sub> reagent is in the form of sulphate salt, bisulphate salt or sulphuric acid. They are diluted with water, where the concentration from 10 to 90 weight percent is employed when the molar ratio of sulphur to chlorine (in combustion gases) are from 1:3 to 3:1. The chemical reaction  $2XCl + SO_3 + H_2O = X_2SO_4 + 2HCl$  helps maintain the chloride in gaseous form and avoids its solidification. It is clear that

this reaction converts the chloride salts into their sulphate forms, thus avoiding the formation of Cl<sub>2</sub> as a result of reaction between XCl and iron oxides (which is a major source of corrosion). The apparatus of this invention, where the aforementioned phenomenon occurs to maximize the combustion efficiency is shown in Fig. (2) [4, 5]. The corrosion-monitoring probe is labeled as 10 and source of cooling air (for cooling the probe and for maintaining it at a constant temperature in the presence of hot flue gases) is labeled as 14. The outer tube 16 is made up of a material similar to superheater tubes, which undergoes ultrasonic testing periodically to measure the corrosive effect of the flue gas. The probe consists of three thermocouples 18, 20 and 22 respectively. The controller 12 maintains the probe at a constant temperature by sensing the signals of the thermocouples and actuating the control valve 26 to supply the necessary air. Fig. (3) [4, 5] shows the wall thickness at different positions on the probe. It is clear that the effect of corrosion at high temperature surfaces is always more than other parts of the boiler.

In [3], an apparatus for simultaneously controlling the slag (in an efficient way) and corrosion is invented, as shown in Fig. (4). The corrosion is controlled in the same way as discussed above. However, since slag is a mixture of iron and silicon oxides (denoted as Fe<sub>x</sub>O<sub>y</sub>SiO<sub>2</sub> [6]), for controlling the slagging problem, magnesium oxide/magnesium hydroxide is used. Although, the invention of magnesium oxide/hydroxide is documented in [10], they are not found to be economical and also suffer environmental pollution problems. To overcome this issue, the apparatus in Fig. (4) is designed. In the Fig, (5) represent the WTE boiler, line 12 represents the points of injection of slag controlling chemical and the injectors are labeled by 13, 14 and 16, respectively.

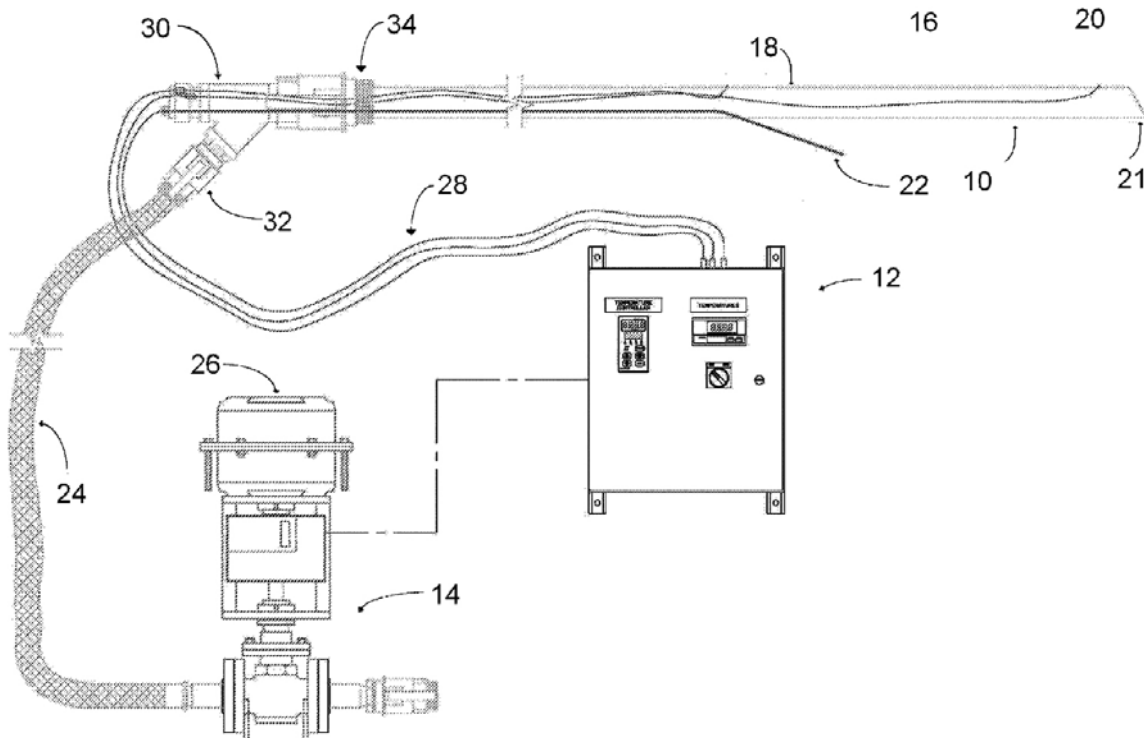


Fig. (2). Apparatus of the invention [4, 5].

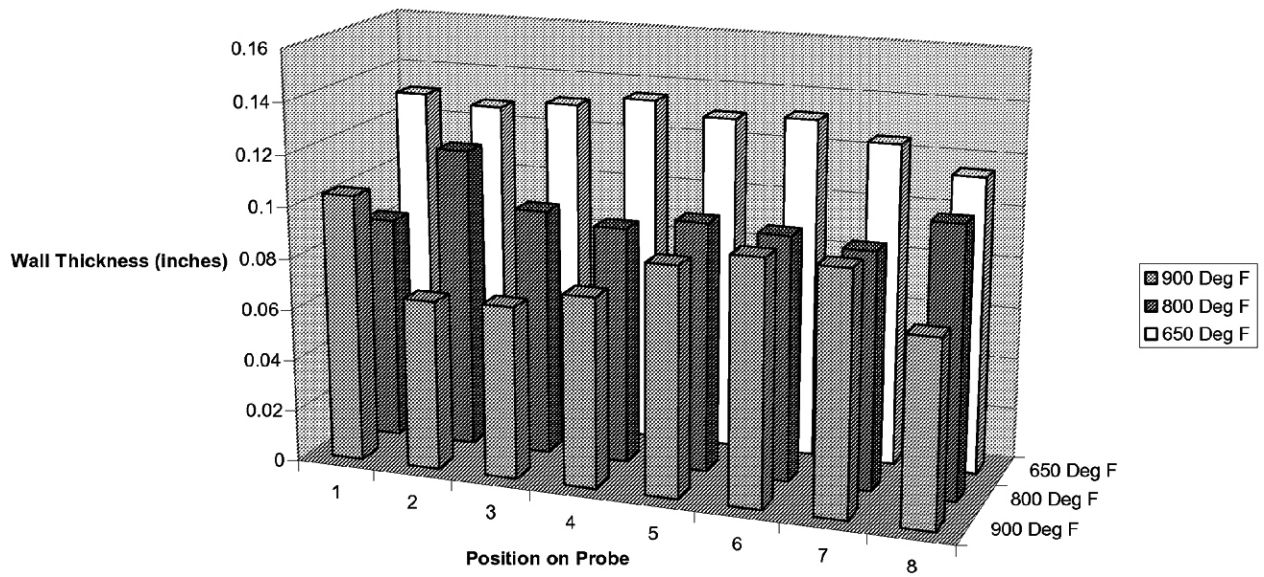


Fig. (3). Wall thickness at different positions on the probe [4, 5].

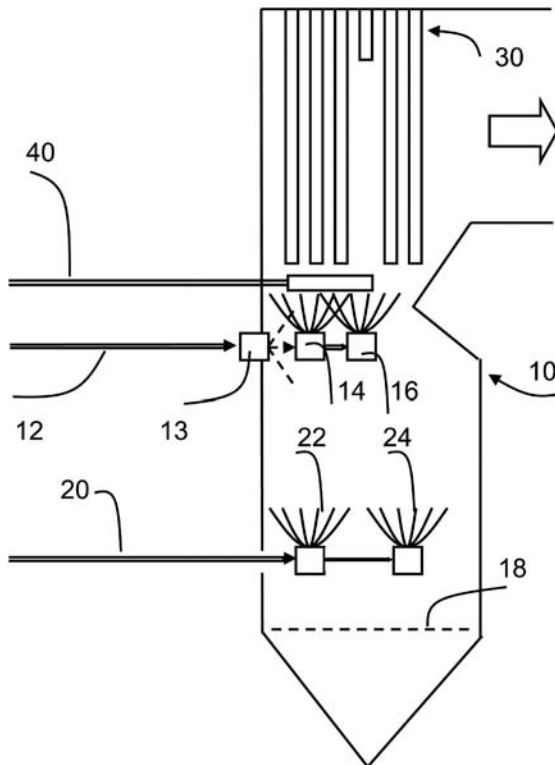


Fig. (4). Apparatus for slag and corrosion control [3].

The superheater tubes are denoted by 30, the point of injection of the corrosion control chemical (line 20) lies above the grate 18 and the corresponding injectors are labeled as 22 and 24, respectively. Hence, all injections are performed anterior to the superheater tubes. It was claimed in [3] that the compressive yield points of the slag deposits (after treatment) are less than 10 psi and, in some cases, even less than 1 psi in comparison to 1000 psi without any treatment. The contribution of this invention lies in finding appropriate nozzles, proper droplet size, its velocity and direction in the spray, which can interact with the flue gases in right time

and avoids loss of excessive chemicals. This is economical and the average size of the droplet to achieve these objectives is found to be within the range of 20 to 1000 microns (using laser light scattering and Doppler techniques).

In [6], an interesting method of corrosion control is proposed, as shown in Fig. (5). It utilizes the fact that corrosion is an electrochemical process during which an electrochemical noise is produced. It was long recognized in [11] that this noise can be used for monitoring corrosion and he developed an apparatus for measuring corrosion rate in pipes, storage tanks, heat exchangers and valves. However, as mentioned in [6], the author has not taken the initiative to monitor furnaces, where the corrosion occurs due to chloride reactions, and metal oxidation/reductions in wet slag. In [6], it is explained that if we consider the fire side of the boiler, then during the normal operation the oxide layer on the tube gets coated with the slag solution. In the presence of low NO<sub>x</sub> burners, the iron from the tubes moves to the liquid slag solution, resulting in corrosion. Since, the movement of the iron and its dissolution into the slag solution is electrochemical, it produces electrochemical signals and noise, which can be measured. The phase change of the slag solution from solid to liquid is an indication of the starting point of corrosion. In Fig. (5) [6], the probe to measure the rate of corrosion is shown which includes two electrodes 12 and 14 surrounded by an insulator 13. The wires are represented by 26 and 27, which are made up of copper and the insulator is a titanium oxide material. The corrosion monitor converts the electrochemical noise into a corrosion rate. After detecting the corrosion rate, the furnace operator utilizes this real time measurement to change the fuel/air ratio (i.e. burner air setting), slot and fan settings, etc. Since low NO<sub>x</sub> firing is a cause of boiler corrosion, changing the burner settings change the amount of NO<sub>x</sub> and SO<sub>x</sub> exiting the combustion chamber. In general, several burners are adjusted simultaneously when corrosion is detected and if by increasing the NO<sub>x</sub> emissions the corrosion rate is decreased,

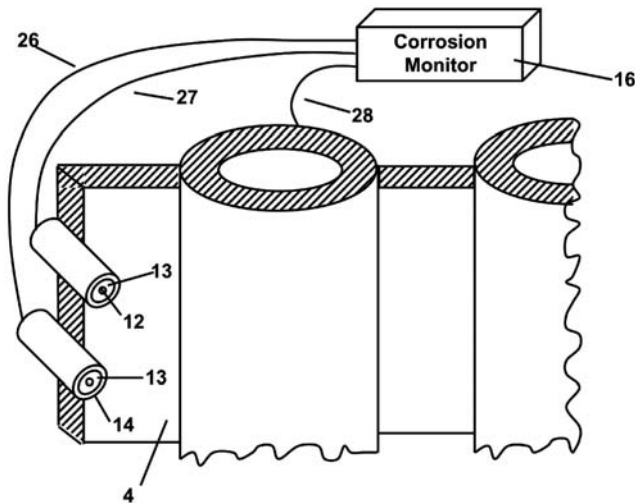


Fig. (5). Corrosion control in WTE boilers [6].

then proper adjustment of the reburn injectors should be done to remove the excess  $\text{NO}_x$  from the combustion chamber. The probe in Fig. (5) is one of the three preferred types of probes that the inventors have used.

We came across many other patents, where chemicals are added to the fuel or to the furnace for solving the corrosion problems. In [10] a survey is provided, which deals with introducing chemicals on the fire-side of the black liquor recovery boilers for reducing slagging and corrosion. Paper industry produces tons of black liquors and the combustion of these chemicals generates sodium and potassium salts of sulphate and chloride. To overcome this problem, magnesium oxide and hydroxide are widely used. They react with the deposit forming compounds to raise their ash fusion temperature, resulting in a less friable deposit. As mentioned in [10], other chemicals were also used in this regard, namely, sodium bentonite by [12] and magnesium dioxide or cupric oxide is added to react with the sodium sulphide content of the black liquor in [13]. The invention in [10] includes many other interesting features: identifying the location of corrosion, finding the temperature and gas flow conditions in the furnace, selecting appropriate amount of chemical (slurry of magnesium oxide/hydroxide) and volume of water to act as a carrier and calculating droplet momentum required to inject the chemical to the desired slagging locations. Concentration of the chemical in the slurry is selected to be around 1-80%.

It is well known that the boiler drum in steam generator is made up of carbon steel (C-steel). In spite of focusing only on the fire side of the boiler, [8] proposed an interesting method of monitoring the corrosion in C-steel of the vessel. It was long recognized that the vessels in the nuclear power plant are required to be cleaned to remove deposits, such as magnetite. There are various chemicals available for cleaning process, which utilizes the fact that when magnetite is removed and the chemical comes in contact with the material of the vessel, a hydrogen gas is released. However, as mentioned in [8], these methods cannot establish the extent of cleaning, because if the chemical reaches the C-

steel in one specific part of the vessel, then also the hydrogen is released even if most of the other parts are not cleaned and are covered with magnetite. To overcome this problem, [8] introduced a complexing agent that includes  $\text{NH}_3$ -EDTA and Hydrazine. When the vessel is being cleaned using this chemical, then in addition to hydrogen gas, nitrogen is also produced. The volume or the quantity of nitrogen indicates the current intensity of the cleaning process and the quantity of hydrogen indicates the extent to which the C-steel of the vessel came in contact with the complexing agent. Hence, if the ratio between the two volumes (hydrogen and nitrogen) exceed, then the drawbacks are more than the cleaning process and the cleaning should be stopped. The invention measures the gas/vapor mixture of hydrogen and nitrogen using a gas chromatograph. A threshold value of 1.4 is selected as the volumetric ratio between the hydrogen and the nitrogen, above which the cleaning should be interrupted. It was claimed that the method could even measure the rate in mm/h at which the C-steel of the vessel is subjected to the chemical.

### 3. LEAK DETECTION SCHEMES

It is well researched that detecting leaks in boiler tubes (caused by aging and stress) is very important for normal and safe operation of the boilers. This kind of water/steam leakage in the risers and downcomers occur very frequently, but there are only few patents available in this regard. In [7], a leak detection system is invented, which consists of a boiler drum containing a temperature control liquid (shown in Fig. 6). It is assumed that the boiler has an automatic liquid level control mechanism. In this temperature control liquid, additional feedwater is added and the following fundamental equations are useful for understanding the underlying principle of leak detection.

The water mass balance in the drum is given by [7]:

$$\frac{dM}{dt} = I - O - U,$$

where  $M$  is the mass of the water in the drum,  $I$  is the input rate of water,  $O$  is the water output rate removed as blowdown, main steam and sootblower steam and  $U$  is the leak. Usually, the input and output water rate follows the relation [7]:  $I = a \times O + c$  (due to calibration mismatch), and if the boiler system has an automatic level control mechanism, then  $\frac{dM}{dt} = b \times \frac{dI}{dt}$  [7] (since the level in the drum is not

changing). Here, the constants  $a$ ,  $b$  and  $c$  can be calculated on the basis of curve fitting on the boiler data. Based on these relations, [7] found that the leak can be modeled as

$$U = I - a \times O - b \times \frac{dI}{dt} - c$$

and measuring it in real time leads to the conclusion that if leak is present, then  $U$  is greater than zero. It should be noted that during the normal operation of the boiler, the feedwater is controlled to maintain the desired volume of the temperature control liquid and to overcome the loss of water from blowdown and steam. Therefore, the change of mass of the temperature control fluid can be determined by measuring the rate of feedwater input ( $I$ ). In some cases, a desired quantity of the liquid is also removed and the corresponding amount of feedwater is added. As the

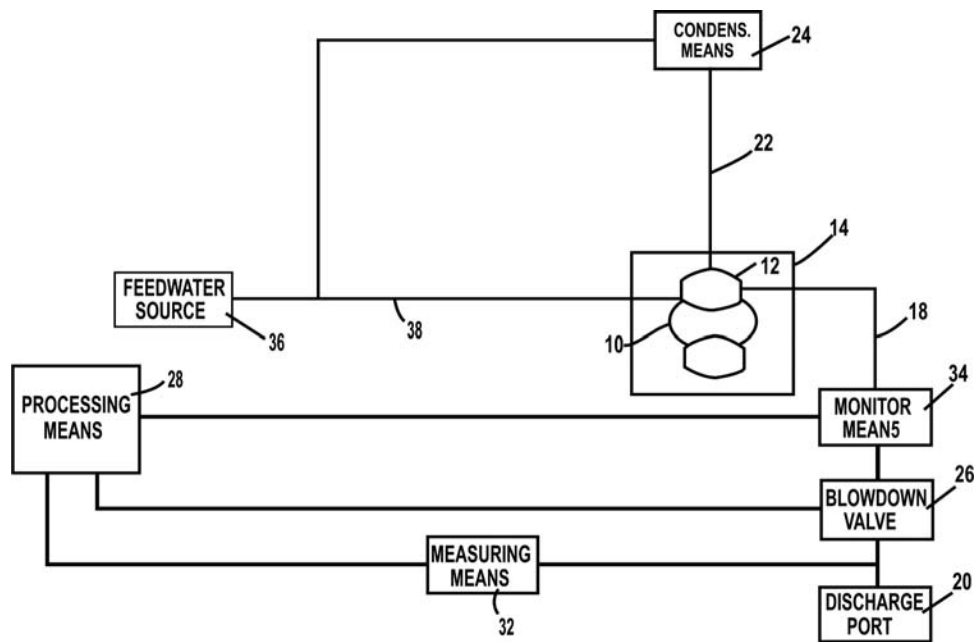


Fig. (6). Leak detection scheme in black liquor recovery boilers [7].

water comes out of the drum in the form of steam and blowdown, the sensor measures it and the level control mechanism adds feedwater to overcome the fall in liquid level.

In Fig. (6) [7], the boiler (labeled as 10) contains a temperature control liquid 12 and is in contact with a furnace 14. The blowdown line is represented by 18, the steam line by 22 and the feedwater line by 38. The steam gets condensed in 24 and the blowdown is controlled through actuating the blowdown valve 26. The monitor means 34 provides the information of the blowdown flow rate, and the processing means processes (filtering, bandwidth selection) the measured data. To conclude, this method [7] can be useful to monitor any kind of system to which a liquid is added and from which it is subsequently removed and also involves an automatic water level control mechanism.

In [14], to get a more accurate indication of the leak than the aforementioned approach, a method of adding a tracer to the temperature control liquid is introduced and the change of its concentration is measured in real time, shown in Fig. (7) [14]. In addition to the jobs performed in [7], the apparatus in Fig. (7) measures the feedrate and the concentration of the chemical tracer in the temperature control liquid as well as in the blowdown. In the figure, the measuring means 32 is an analyzer based on UV/visible spectroscopy to measure the concentration of the tracer. As explained in [14], for the case of a molybdate tracer and phosphate tracer, a FPA 800 analyzer manufactured by Tytronics and a Hach series 5000 phosphate analyzer can be used, respectively. The drawdown assembly 46 provides the measurement of the flow rate of the tracer to the processing means, which controls the speed of the pump to direct the appropriate amount of the tracer to the drum directly (through line 44) or adding it to the feedwater line 38 through 42. The tracer, which is preferred in this invention consists of a transition metal compound such as sodium

molybdate with the property of [14]: 1) being easily soluble to feedwater, temperature control liquid and blowdown, 2) thermally stable, non-volatile and 3) absorb or emit amounts of light in proportion to the amount of the tracer present and/or when the blowdown is mixed with a certain reagent, then the reaction of the reagent and the tracer produces a color which is indicative of the amount of tracer present.

According to [14], this method also offers advantage over the previous inventions, where only the measured reading is compared with the calculated concentration of the tracer in the boiler. They may require long time duration for alarm generation, and, moreover, false alarms may be generated if the operating conditions of the boiler suddenly changes leading to a change in the boiler water mass, which in turn causes the actual tracer concentration to be different from the calculated value.

An interesting invention can also be seen in [15], which is simple, economical and measures the boiler leak based on the average difference of fluid input into the recovery boiler system and the fluid output from the recovery boiler system. The apparatus of the invention is shown in Fig. (8) [15]. The figure clearly states the normal operation of the boiler, where the first monitor measures the mass flow rate of feedwater into the boiler, the second monitor measures the flow rate of blowdown, the third monitor measures the attemperator fluid flow rate, the fourth monitor measures the steam flow rate out of the secondary superheater and the fifth monitor measures the drum water level. These measurements help avoiding false alarms caused by the shrinking and swelling of the drum level. When the steam out of the drum is more than the feedwater input, then swelling occurs. The monitor may interpret it as a leak and generate false alarms if the swelling and shrinking problem has not been carefully treated. The controller 36 performs three different tasks [15]: 1) providing control signal to the alarm, 2) supplying input control signal to the warming lamp and 3) controlling a two

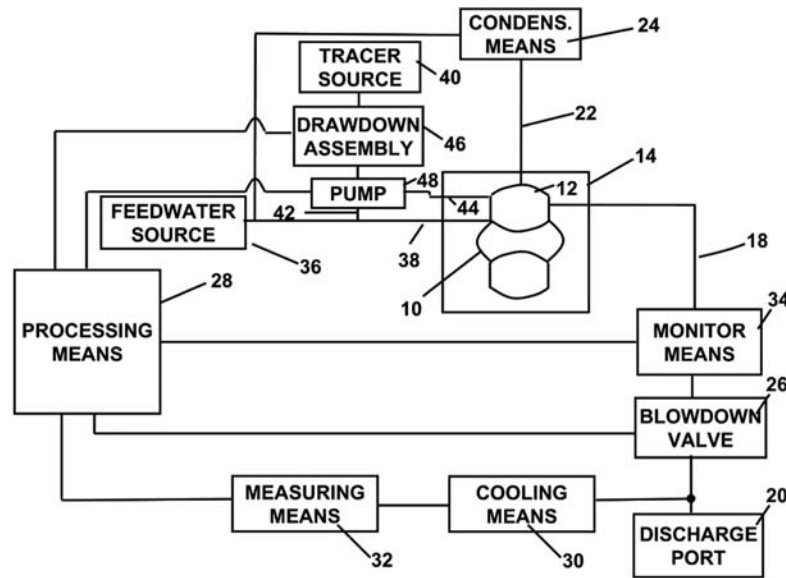


Fig. (7). Leak detection scheme in black liquor recovery boilers using a chemical tracer [14].

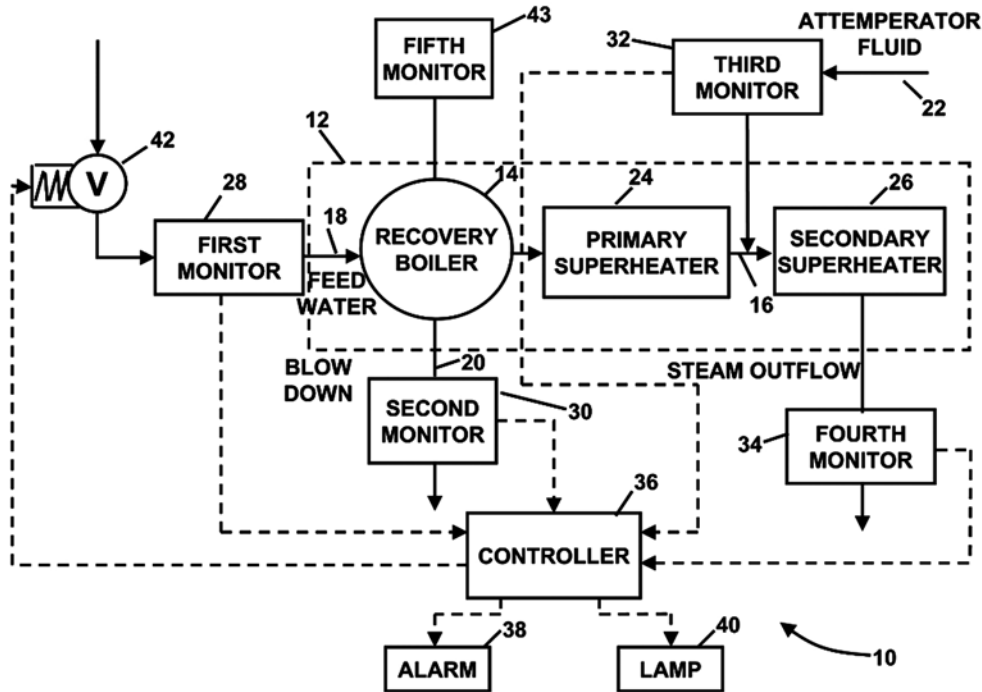


Fig. (8). Leak detection scheme in recovery boilers [15].

position shut off valve 42, which in turn controls the feedwater flow rate for drum level control.

The advantages of this invention are manifold that includes [15]: 1) using different time frames for calculating the average difference between the input and output fluid flow rate, 2) overcoming the effect of swelling and shrinking phenomenon and 3) generating alarms only when significant difference between the input fluid flow rate and the output fluid flow rate occurs.

### 3. CURRENT & FUTURE DEVELOPMENTS

This paper presents some recent state-of-art on overcoming the corrosion problem and false alarms due to leaks

in boilers. The task consists of identifying the location of slag, corrosion and leak in different components and introducing suitable inexpensive chemical reagent to minimize the corrosion and slugging effects. After treatment, the slag deposits can be easily crumbled to powder, so that it can be removed with less mechanical effort and little damage to the boiler tubes.

In recent patents, most of the corrosion monitoring problems are focused only on the fire side and the water side of the boilers. However, in the electrical side, the presence of oxygen in the water (stator cooling water) also leads to corrosion problem. Although, mechanical deaeration and oxygen scavenger addition are widely used now a days, they

require maintenance of sensor membranes and regular replacement of the electrolyte. Their performances are not always acceptable, because of delay of the signals the sensors may produce and other maintenance issues. To overcome these problems, new inventions based on optical techniques should be developed for online oxygen monitoring. For the case of corrosion monitoring using a constant temperature probe presented in this paper, additional cooling fluid and maintenance are required which are not always economical. In this situation, new luminescent technologies should be useful. For leak detection schemes, most of the techniques developed so far are interesting, but they are heuristic. Researchers demand some analytical techniques, based on stochastic approach and/or least squares for producing fast response and avoiding false alarm generations.

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