Determination Of Cation And Anions In Industrial Boiler Water

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Abstract: The study was carried out to assess the cationic and anionic concentration in boiler water. The adverse impact of these ions on the surface of the boiler was also observed. The water samples were colleted from five industrial units and were compared with each other and with their corresponding outlets. The amounts of iron (Fe^{+2}), aluminum (Al^{+3}), sodium (Na^{+2}), potassium (K^{+1}), nitrate (NO_3^{-3}), silica (SiO_2) and sulphate (SO_4^{-2}) were calculated in ppm and noted that the ionic concentration gradually increased in the boiler outlet sample except that of silica which decreased in the outlet water. Presences of such ions in the boiler feed water cycle up and concentrate in the boiler. As a result, deposition takes place on internal surfaces of the boiler, particularly in the high heat transfer areas, which act as insulators and can cause overheating and failure. The outlet water containing high amounts of the concentrate, if discharged into the rivers or lakes or any agriculture area near the industrial unit, can effect human and plant life in a serious way.

Introduction

Steam is vaporized water, being part gas, part liquid. Steam itself is usually interspersed with minute droplets of water in its liquid state, which gives it a white, cloudy appearance. In industrial and process situations, steam is often generated using water boilers that are heated to create steam under controlled conditions. The energy generated is then transferred and used in many different ways. Steam is used as a heat transfer medium in several industries including food, paper, process, chemical manufacture etc. In industry steam is produced by water boilers, which come in all shapes, sizes, types and pressures and the water within them likewise. In extreme cases is has been known for steam boilers to explode causing much damage and even death. It is usually for the reason that the feed water used in the boiler is not pure or is contaminated (web. ref., 1). Source of feed water is usually natural water. Natural waters contain suspended matter, dissolved solids, and dissolved gases. Water being a universal solvent dissolves minerals, rocks and soil that come into contact with it. It dissolves gases from air and gases that are given off from organics in the soil. It picks up suspended matter from the earth. Additionally it may also be contaminated with industrial wastes and process materials. Dissolved minerals picked up by the water consist mainly of carbonates and sulfates of calcium and magnesium, silica , sodium chloride, hydrated sodium sulfate and smaller quantities of iron, manganese, potassium, aluminum, and other substances. The nitrates and phosphates found in water are usually due to sewage contamination (web. ref., 2). Water is said to be polluted when it is unfit for the purpose for which it is intended. This is due to the presence of physical substances and biological pathogens that make water unfit for human consumption. Many of the inorganic cations that we find objectionable in surface and ground water come from natural sources. Underground deposits of iron compounds are responsible for the presence of irons ions in certain ground waters. This ion reacts with hot water to form hydrated ferric hydroxide, which deposits as a brown stain on bathtubs and clothing (Odigure et al., 2005). Silica can form scale at pressures below 600 psig. Above 600 psig, silica starts to volatize, passing over with steam to potentially form deposits on the steam turbine diaphragms and blades. These deposits change the steam path components' profiles resulting in energy losses. Sodium can combine with hydroxide ions creating sodium hydroxide (caustic). Highly stressed areas of boiler piping and steam turbines can be attacked by sodium hydroxide and cause stress-corrosion cracks to occur. This was a problem in older boiler with riveted drums because of stresses and crevices in the areas of rivets and seams. While less

prevalent today, rolled tube ends are still vulnerable areas of attack as well as welded connections. High iron is not found in raw water but high concentrations can come from rusted piping and exfoliation of boiler tubes. Iron is found in condensate return in a particle form as it does not dissolve in water. The detrimental aspect of iron is called steam turbine solid particle erosion, which causes significant erosion of steam turbine steam path components. Raw water from reservoirs, lakes, rivers, and wells can have varying characteristics as provided below (Vogt Power Int. 2001)

Silica (SiO_2)	0.4 to 39 ppm
Iron (Fe)	0.0 to 2.1 ppm
Sodium (Na)	1.4 to 147 ppm
Potassium (K)	0.4 to 4 ppm
Sulfate (SO_4)	0.8 to 560 ppm
Nitrate (NO_3)	0.0 to 4.0 ppm

Common feed water contaminants that can form boiler deposits include calcium, magnesium, iron, copper, aluminum, silica, and (to a lesser extent) silt and oil. Most deposits can be classified as one of two type's scale that crystallized directly onto tube surfaces sludge deposits that precipitated elsewhere and were transported to the metal surface by the flowing water. Scale is formed by salts that have limited solubility but are not totally insoluble in boiler water. These salts reach the deposit site in a soluble form and precipitate when concentrated by evaporation. The precipitates formed usually have a fairly homogeneous composition and crystal structure. High heat transfer rates cause high evaporation rates, which concentrate the remaining water in the area of evaporation. A number of different scale-forming compounds can precipitate from the concentrated water. The nature of the scale formed depends on the chemical composition of the concentrated water. Normal deposit constituents are calcium, magnesium, silica, aluminum, iron, and (in some cases) sodium. The exact combinations in which they exist vary from boiler to boiler, and from location (Azani 2009).

Material and Methods
Sampling
For the purpose of estimation the samples were collected from various Industrial units in triplets. Random sampling was done for the collection of five samples. Samples (S_1, S_2, S_3, S_4, S_5) consist of inlets or "Boiler feed water" and their corresponding outlet samples. Samples were refrigerated at 4°C. Estimation was carried out through different spectroscopic techniques.

Sample Analysis
Determination of Aluminum and Iron

Spectrophotometer (Spectronic-21, Banch & Lomb) was used for the determination of Aluminum and Iron.
Determination of Potassium and Sodium
Flame photometer (Jenway PFP-7) was used for the determination of Potassium and Sodium.

Determination of Nitrates
To 5 ml of sample added 0.2 ml of 0.2 % brucine alkaloid solution and then added 10 ml of concentrated Sulphuric acid (H_2SO_4) followed by 10 ml of distilled water. Yellow coloration developed due to the presence of nitrates. Spectrophotometer (Spectronic-21, Banch & Lomb) was used. The instrument was previously set at zero point, reference point and wavelength of 470 nm. Noted the photometer reading for standard and samples, from the values obtained amount of nitrates was calculated.

Determination of Silica
Spectronic-21 (Banch & Lomb model) was used for the determination of silica. First of all a blank was prepared with sufficient standards. Then pipette out 10 ml of sample in a 50 ml of beaker, added 5 ml of 0.25 molar HCl, 5 ml of 5% ammonium molybdate and 5 ml of 1% Na(II)-EDTA, after 5 minutes added 10 ml of 17% Na_2SO_3. Mixed and allowed to stand for 30 minutes. The blue color appeared which became stable for several hours, after that time.

Results and Discussion
Results of the analysis carried out on boiler water showed that the amount of cation and anions increased gradually in the outlet water samples, as shown in table-1. The amount of silica showed varying results, as it decreased it the outlet water samples. The amount of iron in sample-1, increased from 0.7-10.4 showing a reasonable increase. Similarly in sample-2, there were no traces of sample in the inlet sample but an amount of 5.0ppm was obtained in the outlet samples. Sample-3, 4 and 5 showed a remarkable increase in the amount of iron. The reason may be the presence of rust in the boiler pipes or inside surface of the boiler. High iron is not found in raw water but high concentrations can come from rusted piping and exfoliation of boiler tubes. Iron is found in condensate return in a particle form as it does not dissolve in water. Aluminum also showed the same results, as its value increased in the outlet samples as compared to the inlet water samples. High amounts of aluminum were observed in samples-3, 4 and 5 (6.9, 7.2 and 9.8ppm) as were in the case of iron. Aluminum is one of the common contaminants in boiler feed water (Cotton 2000). Zeolite used for boiler makeup water is one of the possible sources for aluminum and sodium (or its substitutes, i.e., calcium

or potassium). Copper-base alloys containing aluminum may be considered as another possible source for aluminum (Khajavi et al., 2007). The amount of sodium as shown in table-1, was very high even in the inlet water of sample-1, it means the water was taken from an already contaminated source. As the feed water was having a great amount of iron it may have affected the inside surface of the boiler and showed even a great increase (750ppm) in its outlet water. A low increase in the amount of sodium (25-98ppm) was observed in sample-2. Sample-3, 4 and 5 also showed great increase. Sodium as given above may exist in boiler water in combination with hydroxide ion, chloride or even as carbonates and sulphates. In its most of its forms it is a source of corrosion for the boilers, so is the reason for the high value of sodium in outlet samples. The amount of potassium also showed the same results as the previous three cations. The amount of potassium in the feed water of sample-1 was 13ppm, a very high value as compared to the other four samples. But the outlet water of sample-3 showed the highest amount as compared to the outlets of other four samples. Potassium chloride is one of the major impurities in the boiler system. It is well known that concentrated and accumulated sodium chloride and potassium salts not only act as inert substances which increase the circulation load of the chemicals and cause a reduction in economical efficiency due to an increased dead load, but also significantly enhance the corrodibility of the chemical recovery system. Especially in a sodium recovery boiler for burning spent liquor, the presence of sodium chloride and potassium salts enhances the corrodibility of the heat transfer tubes in the hot section of the boiler (web. ref. 3). The amount of nitrate as shown in table-2, was low in feed water of sample-2 (0.01ppm) and maximum in inlet of sample-1. In sample-5, the amount raised from 3.0-10.1 ppm. Sample-4 also showed the same level of increase from 2.0-9.1 ppm in the amount of nitrate. Nitrates are normally present in natural, drinking and waste waters. The outlet water from the boilers also contains Nitrates. Nitrates enter water supplies from the coordination of Nitrogen compounds in the industrial wastes including the boiler outlet water. Nitrate is an important control test for water supplies. Drinking water containing excessive amounts of Nitrates can cause methaemoglobnaemia in bottle feed infants (blue – babies) (web. ref. 4). The increased nitrate concentration in the boiler outlet samples may be due to the chemical process taking place inside the boiler. The amount of silica as shown in table-2, showed varying results as compared to the rest off ions. The amount of silica only increased in the outlet water of sample-2, as compared to the inlet water sample as 0.001-0.5ppm. In all other four samples its value

decreased in the outlet boiler water sample. Silica concentration was very high in the inlet water of sample-5 as it was 3.01ppm. It means that source of water was muddy and not good. Also the water was not treated before being used as feed water. The decreased concentration of silica in the boiler outlet water is not good for the boiler as most of the silica remained inside the boiler and will act its part in the destruction of the boiler surface or disturbing the chemical process taking place inside the boiler. Silica can vaporize into the steam at operating pressures as low as 400 psig. This has caused deposition problems in numerous boilers. The solubility of silica in steam increases with increased temperature; therefore, silica becomes more soluble as steam is superheated. As steam is cooled by expansion through the boiler, silica solubility is reduced and deposits are formed, usually where the steam temperature is below that of the boiler water. To minimize this problem, the quantity of silica in the steam must be controlled. Silica deposits are not a problem in most boilers where the silica content in the steam is below 0.02 ppm. Therefore, it has become customary to limit silica to less than 0.02 ppm in the steam (web. ref. 5). The amount of sulphates was very high in the feed water of sample-5; it was 22.0ppm as shown in table-2. It means that no perfect source of pure water was selected and no considerable conditioning was done before the introduction of water to the boiler. The sulphate concentration was very low (1.2ppm) in the case of feed water for sample-2, but a remarkable increase from 1.2-96.0 ppm was noted in this case and sulphate concentration reached its highest value in the outlet water as compared to all other samples. Sample-1, as shown in table-2, showed also shows an increase from 6.9-64.8ppm in the amount of sulphates. The sulphates in the form of calcium sulphate are considered to be scale producer, same as silica inside the boiler. Sulphate and silica generally precipitate directly on the boiler metal and are much harder to condition (web. ref., 2). The sulphate deposits are considered to be hard and difficult to be removed before proper conditioning. It means that the boiler of the industrial unit from where sample-2 was collected already contained sulphate deposits that mixed with the steam and were observed in the outlet water.

Conclusion:
The results obtained revealed that the inlet water samples-1, 3, 4 and 5 were less suitable for boiler feed as the samples contained appreciable amount of ions. When these sample used as inlet samples, affected various parts of the boiler and to some extent the reaction taking place inside and as a result, contaminated outlet water was obtained. Sample-2 was collected from a good source and its feed water was having fewer amounts of contaminating ions but its

outlet water showed a reasonable amount of sulphates in it.

Comparison of different ions in the inlet and outlet boiler water can be seen in the Figure-3 and table-3.

Table-1: Amount of Cations in various Inlet and Outlet Boiler Water Samples

No. of sample	Iron 'Fe'		Aluminum 'Al'		Sodium 'Na'		Potassium 'K'	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
(1)	0.70	10.4	0.10	5.8	212.0	750.0	13.0	46.0
(2)	0.00	5.00	0.02	3.2	25.00	98.00	2.00	14.0
(3)	0.10	30.0	0.85	6.9	20.00	301.0	5.00	48.0
(4)	0.05	33.0	0.93	7.2	12.00	356.0	1.00	26.0
(5)	0.30	33.0	0.64	9.8	62.00	264.0	3.00	32.0

*The cations concentration in ppm

Table-2: Amount of Anions in various Inlet and Outlet Boiler Water Samples

No. of sample	Nitrate 'NO$_3$'		Silica 'SiO$_2$'		Sulphate 'SO$_4$	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
(1)	5.00	2.60	0.060	0.16	6.90	64.8
(2)	0.01	4.40	0.001	0.50	1.20	96.0
(3)	2.60	6.00	2.600	0.80	12.0	34.5
(4)	2.00	9.10	2.040	0.80	11.0	31.1
(5)	3.00	10.1	3.010	0.90	22.0	31.1

*The anions concentration in ppm

Table-3: Comparison in %age of different parameters of inlet and outlet boiler water samples

Ions	Inlet Samples (%)	Outlet samples (%)
Iron (Fe^{+2})	0%	5%
Aluminum (Al^{+3})	1%	1%
Sodium (Na^{+2})	76%	75%
Potassium (K^{+1})	6%	7%
Nitrate (NO$_3^{-3}$)	3%	1%
Silica (SiO$_2$)	2%	0%
Sulphate (SO$_4^{-2}$)	12%	11%

Figure-1: Amount of Cations and Anions in Various Inlet Boiler Water Samples
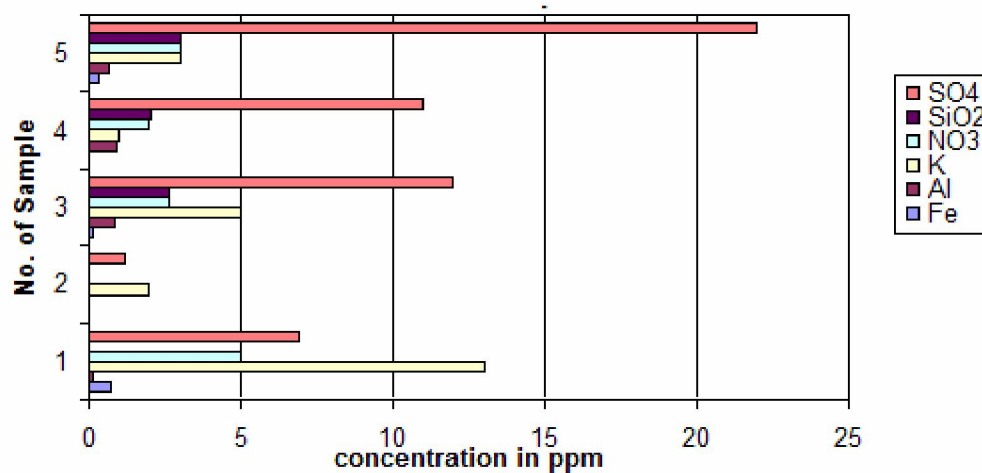

Figure-2: Amount of Cations and Anions in Various Outlet Boiler Water Samples
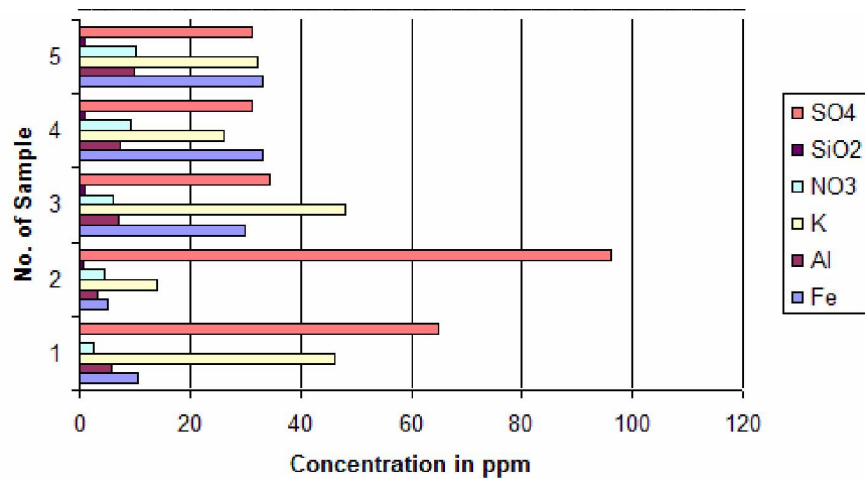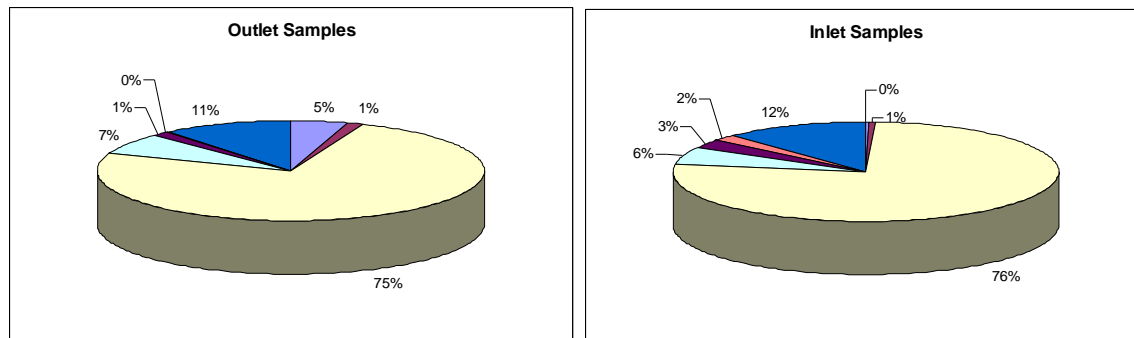

Figure-3: Comparison in %age of different parameters of inlet and outlet boiler water samples.

Data Analysis:

Data analysis was done by using the computer program "SPSS", the results are shown in table-4

Table-4: Statistical Analysis of the inlet and outlet boiler water samples

Name of Samples		Mean	Standard Deviation	SE Mean
Iron	Inlets	0.23	±0.286	0.128
	Outlets	22.28	±13.50	6.038
Aluminum	Inlets	0.50	±0.432	0.189
	Outlets	6.50	±2.39	1.069
Sodium	Inlets	66.20	±83.732	37.446
	Outlets	353.80	±241.487	107.996
Potassium	Inlets	4.80	±4.816	2.154
	Outlets	33.20	±14.184	6.3435
Nitrate	Inlets	2.52	±1.799	0.804
	Outlets	6.44	±3.145	1.4066
Silica	Inlets	1.5422	±1.422	0.636
	Outlets	0.632	±0.303	0.135
Sulphate	Inlets	10.620	±7.6506	3.421
	Outlets	51.5	±28.628	12.80

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