

Acid Cleaning of Impurities in Natural Circulation High Pressure Drum Boiler

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Abstract : Acid cleaning operation has been employed to clean up undesired impurities (deposit) in boiler water wall tubes, (WWTs) boiler condenser, economizer, feed water lines, drum and other accessory pipelines for a natural circulation high pressure drum boiler unit, TIME - 206-COB, Russia ($158 \text{ kG}_f \text{ cm}^{-2}$) of a thermal power station in Bangladesh. The deposit contains highest Fe_2O_3 (96.91%). On area basis the maximum quantity (93 gm^{-2}) of deposit was measured at boiler WWTs. During cleaning operation the loose impurities were withdrawn at first by flushing ($100 \text{ m}^3 \text{ h}^{-1}$) with water. Acid cleaning operation was carried out by re-circulation of hot $115^\circ (\pm 5^\circ \text{C})$ cleaning solution $\text{H}_2 \text{SO}_4 (5.5 \pm 0.5\%)$, ($\text{N}_2 \text{H}_4 350 \pm 25 \text{ mg L}^{-1}$) at pH 1.5 for 36 hrs. The overall cleaning operation revealed that more than 90% of impurities were removed. The cleaning mechanism and passivation on clean surface of tubes by circulation of $500 \text{ mg L}^{-1} \text{ N}_2\text{H}_4$ and $0.5\% \text{ NH}_4 \text{ OH}$ (pH 11.2 ± 0.5) at $80^\circ (\pm 10^\circ \text{C})$ were found to be satisfactory.

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Introduction

Acid cleaning is essential after installation of a thermal power unit because the pipelines and other auxiliary equipment are contaminated by scale or corrosion, sediments, weld flash, different cutting, oil and greases, atmospheric dust particles like mud, SiO_2 , clay etc. If such impurities are not removed from boiler, these may cause further scaling or corrosion. Various techniques of boiler chemical cleaning are employed in different countries. Poulson [1] has studied the possibilities of stress corrosion cracking during boiler acid cleaning operation. French [2] has used hydrofluoric acid for boiler cleaning and Shenker [3] has described an economical method of boiler cleaning. Cherry [4] described a method to prevent boiler tube failure. Kotz [5] has shown relations and effects on controlling water side scales with boiler blow down. Krause [6] has shown the effects of sulfur on boiler tube metal. Phelan [7], Memet [8], Novitsky [9], Sohail [10], TEPCO, JICA, Japan [11], Changzheng [12-14], Yongshu [15], Flemming [16], Zhaoying [17], Wenyou [18] described different techniques for boiler chemical cleaning and corrosion protection.

The water wall tubes (WWTs), pipelines, and boiler accessories of a newly installed natural circulation high pressure drum boiler unit TIME-206-COB Russia, (capacity steam generation: 670 Ton h^{-1} , electricity: 210 MW) of Ghorasal Thermal Power Station (GTPS) unit No. 5, Bangladesh was attacked by natural deposit because these boiler water wall tubes and other boiler accessories were

exposed to natural environment for a long time before installation.

Prior to start cleaning action the following preparatory works were taken into consideration: scale analysis, scale dissolving test, water quality used for cleaning, heat source, electrical power, preparation of instruction, outline of boiler scope of cleaning and quantity of cleaning solution, types and required number of equipment and material for cleaning, injection point of boiler, concentration, quantity of cleaning agents and cleaning conditions (cleaning temperature, cleaning time), method for the determination of the end point of the cleaning solvent and time table for cleaning process.

In this presentation sulfuric acid and hydrazine hydrate have been employed for chemical cleaning of a newly set-up high pressure ($158 \text{ kG}_f \text{ cm}^{-2}$) boiler unit No. 5 of GTPS, Bangladesh. In this acid cleaning operation minimum amount of cleaning reagents have been used.

The plant-based investigations were carried out very carefully in the Central Chemical Research Laboratory of GTPS, Bangladesh Power Development Board (BPDB), Bangladesh.

Experimental

Chemicals used for cleaning operation were hydrazine hydrate (32% Russian origin), Sulfuric acid (98.5% Wata Chemical Ltd., Bangladesh) and compressed ammonia gas was procured from BCIC, Bangladesh.

The analyses were carried out with a AAS (Model AA6650, Shimadzu, Japan), photoelectric colorimeter, (Model KFK-2 Russia) and Electro-

conductivity meter (digital Model Bibby England). pH and ionic strengths were measured with a pH and Ion meter (digital Model 130.04.1, Russia). Oven (model N-08, 76, Russia) and Furnace (Model Mn-2YM, Russia) were used during this work. Concentration (mg L^{-1}) of ionic impurities (Fe^{2+} , SiO_2 , Ca^{2+} , Mg^{2+}) in chemical solutions at different stages of boiler cleaning operation were measured by titrimetric and colorimetric analyses [19-22]. The iron in the cleaning solution was determined by titrimetric analysis as well as colorimetric analysis respectively.

Iron (II) reacts with 1,10-phenanthroline to form an orange red complex $[(\text{C}_{12}\text{H}_8\text{N}_2)_3\text{Fe}]^{2+}$, at pH range 2-9 and stable for long time (absorbance of the complex was measured at 515 nm). Iron (III) may be reduced to Iron (II) with hydroxyl ammonium chloride in presence of buffer sodium acetate. Both the Iron (II) and the iron (III) complexes have identical absorbance at 515 nm.

Ca^{2+} in cleaning solution was determined by titrimetric method using 0.1 M EDTA (Chelaton III) solution, 2-5 ml of 1M NaOH solution and Erochrome Black-T as an indicator. Mg^{2+} was determined by subtracting the result of Ca^{2+} from that of the total hardness. SiO_2 content in cleaning solution was determined by using 5% ammonium molybdate, 10M H_2SO_4 and stannous solution (absorbance 670 nm). The concentration of hydrazine was determined iodometrically using standard thio sulfate 0.1 N and starch as an indicator.

Scale dissolution laboratory test

Frequently 4%, 5% and 6% solutions of sulfuric acid were prepared separately in each beakers containing 200 mgL^{-1} hydrazine. Those were kept in water bath at $80^\circ (\pm 10)^\circ\text{C}$. Then measured amounts of scale samples were put in each beaker as per stoichiometric ratio and allowed to react for 12 hrs, for completion of the reaction. The beakers were then cooled and filtered using previously weighed (dry) filter paper. Afterwards filter paper containing un-dissolved matters were dried at 105°C in an oven and weighed. Careful investigation shows that 6% sulfuric acid solution containing hydrazine (200 mgL^{-1}) dissolves maximum deposit.

Corrosion laboratory test

Five specimens of steel having identical composition were collected from WWTs (Steel-20, Russia), economizer (Steel-20, Russia), boiler drum, LP heaters and feed water pipe lines. These specimens were cut into small pieces. These specimens were kept immersed in the $250 \pm 50 \text{ mgL}^{-1}$ N_2H_4 solution (100°C) for 8 hrs. Separately 4%, 5%, and 6% sulfuric acid solution (each 1000 ml) were prepared. Then 200 ml of 4% acid solution were taken into four separate beakers. In each beakers 100 mgL^{-1} N_2H_4 , 150 mgL^{-1} N_2H_4 , 200

mgL^{-1} N_2H_4 , and 250 mgL^{-1} N_2H_4 , were added separately. Therefore hydrazine treated steel specimens were kept immersed into the acidified hydrazine solution for 12 hrs at 100°C . Similar careful experiments were carried out separately with 5% and 6% acidified hydrazine solution. These solutions were analyzed for Fe and Cr content by colorimetric method followed by corrosion rate were calculated in $\text{mg/dm}^3/\text{day}$. Results indicate that hydrazine in acidic media containing above 200 mgL^{-1} yields least corrosion.

1. Measurement of deposits

The amount of deposit in boiler WWTs, pipelines and other auxiliary line, before and after cleaning operation were determined by rubbing out of a definite area ($3 \times 3 \text{ cm}^2$) of deposit from weighed sample and expressed in g m^{-2} . Compositions of deposits were determined by gravimetric, titrimetric and colorimetric analyses [12-15] of deposits. For each case multiple analyses were made and their averages are presented in tables.

2. Procedure of acid cleaning

After commissioning and start up of the mentioned boiler unit No. 5 at Ghorasal Thermal Power Station, acid cleaning operation and further boiler passivation was carried out carefully. The total inside volume of boiler cleaned was 500 m^3 with 1500 m^2 of surface area.

2.1. Hot water re-circulation in boiler (HWRB)

HWRB was carried out by introducing 500 m^3 of demineralized water into the boiler through make up pumps and circulated (flow $50 \pm 10 \text{ m}^3/\text{h}$) for 24 hrs. During hot water re-circulation operation temperature of the boiler was maintained at $(65^\circ\text{C} \pm 5^\circ\text{C})$ by injecting steam into the boiler water cycle. Water leakages from any valve, flange, pump glands, pipeline etc. (if found), was repaired.

2.2. Re-circulation of acid cleaning solution (RACS)

Hydrazine hydrate solution (32%) was gradually added to the boiler re-circulation water (during its circulation in the boiler) till its concentration reached $(350 \pm 25) \text{ mgL}^{-1}$. After completion of addition of hydrazine, the solution was circulated in the boiler for next 10 hrs while the temperature of the circulation solution was increased gradually to $(115 \pm 5)^\circ\text{C}$. Concentrated sulfuric acid (98%) was then dosed carefully for the next 6 hrs into the re-circulation cleaning solution with the help of a dosing pump till the pH of the solution was 1.5 (H_2SO_4 , $5.5 \pm 0.5\%$). The acid cleaning solution was re-circulated for 36 hours and the temperature of boiler was maintained at $115 (\pm 5)^\circ\text{C}$ by injecting steam and the pressure of boiler was controlled at $10 \text{ kg}_f/\text{cm}^2$. The

concentration of hydrazine in cleaning solution, acidity, pH as well as Fe^{2+} , Ca^{2+} , Mg^{2+} , SiO_2 in cleaning solution during cleaning operation were analyzed after every half an hour interval. After cleaning operation the cleaning solution was drained off into a neutralizing pond. The boiler was then washed by flushing (flow $100m^3 h^{-1}$) with demineralized water (required $3000 m^3$) till the pH of the flush solution attained a value of 6.7.

2.3 Neutralization and passivation of the boiler (NPB)

This operation of the boiler was made by introducing $500 m^3$ of demineralized water into the boiler and re-circulating it at $80(\pm 10) ^\circ C$ for 4hrs. Ammonia and hydrazine hydrate were then dosed into the boiler re-circulated water till the solution attained pH $11.2 (\pm 0.5)$, and N_2H_4 content of $500 mg L^{-1}$. The NPB operation was maintained for 8 hrs. After NPB operation, the boiler was cooled by reducing heat gradually. So that speed of the drum

temperature is not reduced by not more than $2.5 ^\circ C/minute$ and the difference between maximum and minimum is not more than $40 ^\circ C$. Later the cleaning re-circulated solution was drained off at $60 ^\circ C$ into a neutralizing pond.

Results and discussion

In order to cleanup the newly installed boiler unit No. 5 of Ghorasal Thermal Power Station, the superheaters (16 no. of tubes) and feed water pumps were disconnected from the boiler drum. The superheaters, platen superheaters (PSH), high pressure superheaters (HPSH), hot convective superheaters (HPCSH), low pressure heaters (first and second stage) etc. were not included into the acid cleaning operation but these were water and steam cleaned. For better cleaning performance a systematic temporary pipelines (as in Figure 1) were connected with the permanent pipelines as per technical demand. Few valves as shown in Figure 1 controlled the flow of acid cleaning operation.

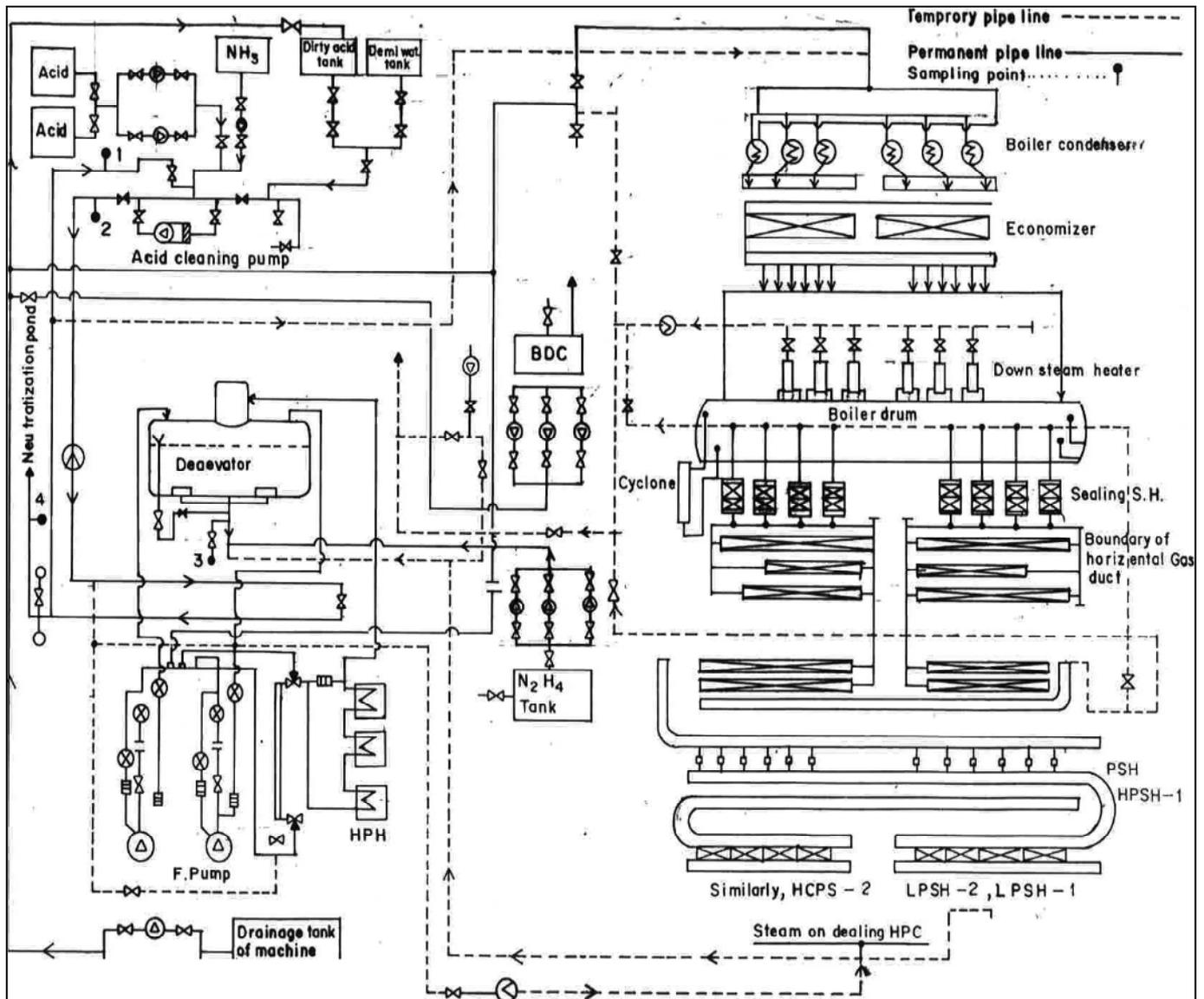


Figure 1 : Flow diagram for acid cleaning of a natural circulation water wall tube high-pressure drum boiler.

Table 1 : Chemical composition (%) of deposits measured at different location of boiler before cleaning operation.

Identity	Composition (%)			
	Fe ₂ O ₃	SiO ₂	MgO	CaO
Front wall p-3, T-12	96.81	1.94	0.48	0.98
Back wall p-4, T-16	96.42	1.93	0.42	0.92
Economizer	96.12	1.97	0.48	0.84
Superheater	96.91	2.01	0.87	0.91
LP heater	96.42	2.03	0.63	0.96

Table 2 : Average compositions of deposits (mixing of same mass of deposits from different sites of high pressure boiler) before cleaning operation.

Constituents	Fe ₂ O ₃	SiO ₂	MgO	CaO
Average %	96.41	2.24	0.94	0.67

The qualitative and quantitative analyses of the adhesion scale inside the pipelines and other accessories for a natural circulation vertical water wall tubes in high pressure boiler has been estimated. The supplied pipelines and accessories used for boiler WWTs, low pressure heaters, high pressure heaters, collectors, economizer, boiler condenser, boiler drum and deaerator, feed water lines were attacked by considerable amount of undesired deposit or scale (Table 1) consisting of Fe₂O₃, CaO, MgO and SiO₂ (Table 2).

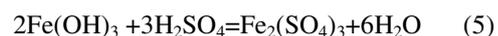
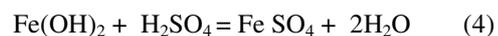
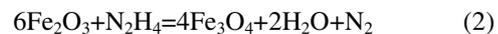
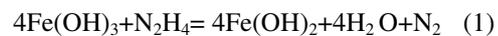
The maximum quantity of deposit (93 g m⁻²) was found in the boiler water wall tubes (carbon steel -St.- 20, Russia) followed by LP heaters (68 g m⁻²), collector (67 g m⁻²), economizer (58 g m⁻²) and superheaters (45 g m⁻²) respectively (Table 3). The formation of deposit in such a type of boiler is due to natural oxidation of metallic tubes and accessories.

Circulation of cleaning solution (denoted by arrow signs in Figure 1) was carried out by forcing the cleaning solution through the system by pumps of existing temporary facilities. This method is most frequently used because it is easy to maintain a uniform concentration and temperature of the cleaning solution and the cleaning effect can be improved by increasing flow rate of the cleaning solution.

The laboratory scale dissolution and corrosion tests confirm that 6% sulfuric acid with (300 ± 25) mgL⁻¹ N₂H₄ at 100 °C produce good cleaning with no corrosion. Hence during cleaning operation slight excess (350 ± 25) mgL⁻¹ N₂H₄ has been used

to avoid any corrosion risk. In cleaning solution hydrazine reacts with loose deposits of Fe₂O₃ and FeO, to form ferrosferric oxide Fe₃O₄ and Fe; and cleaned off with circulated solution and after a while hydrazine itself also reduces and formed a thin coat of Fe₃O₄ on cleaned metallic iron surfaces, which protect corrosion. Therefore hydrazine itself takes part both as a cleaning reagent as well as a corrosion inhibitor in the acidic media.

The followings are the probable chemical reactions that take place in the boiler during cleaning operation.



It should be noted that that during acid cleaning operation temperature of the cleaning solution should not exceed 250 °C. This is because at higher temperature hydrazine rapidly breaks down into ammonia and nitrogen.



During acid cleaning operation various metals remains in the scale were dissolved in cleaning solution. Oxidative ions such as ferric ions were also included among them. Oxidative ions reacts with ferrous metal in an acid solution as shown in the following equation,



The presence of oxidative ion in the acid cleaning solution greatly accelerates the corrosion of the base metal. Hence a strong reducing agent

such as hydrazine has been employed to reduce the oxidative ions and to make the process harmless. In absence of reducing agent steel corroded in proportion to the concentration of the ferric ions. It was observed that during acid cleaning operation the concentrations of Fe^{2+} , Ca^{2+} , Mg^{2+} , SiO_2 in the cleaning solution increase gradually, while the acid concentration decreases but up to a certain extent. This is the end point of the cleaning operation under prevailing conditions (Figure 2 and Figure 3). The cleaning solution was then drained off into the neutralization pond.

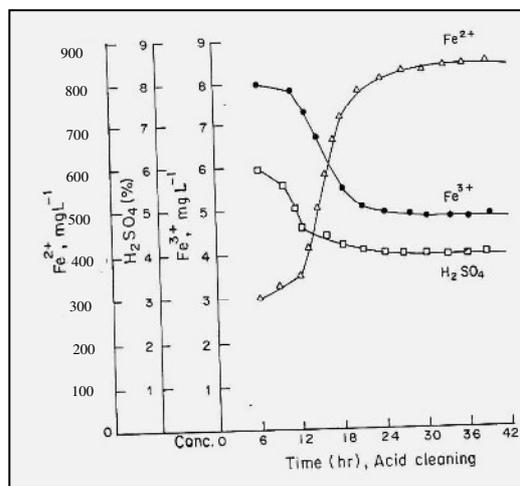


Figure 2 : Concentration of iron Fe^{2+} in acid cleaning solution with time.

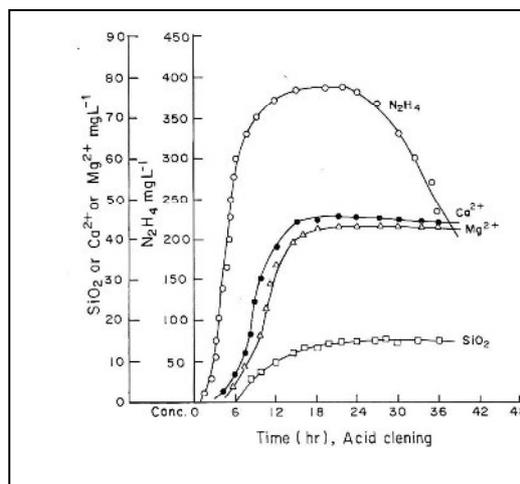


Figure 3 : Concentration of Ca^{2+} , Mg^{2+} and SiO_2 in acid cleaning solution with time.

Table 3 : The quantitative range of deposits measured (g m^{-2}) in boiler pipeline and boiler accessories before cleaning operation.

Location	impurities/sediment
BWWTs	35-93
Superheater	36-50
LP heater	35-68
Collector	40-67
Economizer	30-59

Table 4 : Average concentrations (mgL^{-1}) of ionic impurities attained in chemical solution and % impurities removed at different stages of cleaning operation.

CS	CSol. M^3	pH	N_2H_4	Ionic impurities removed				% impurities removed			
				Fe	Ca	Mg	SiO_2	Fe	Ca	Mg	SiO_2
HRB	500 ± 0.5	6.9 ± 0.2	Nil	0.8	4.0	2.4	0.62	1.4	2.8	1.8	1.68
RACS	500 ± 0.5	1.7 ± 0.2	350 ± 25	818	47	46	14	90.6	89.1	88.0	70.4

CS- Cleaning stage. C Sol - cleaning solution

The percentage of impurities (ionic stage) removed from the boiler measured at different stages of chemical cleaning operation is given in Table 4.

Passivation on clean surface was carried out very carefully because after acid cleaning operation the metal surface remains in a activated stage. The metal, especially carbon steel, under this condition is readily rusted. Ammonia and hydrazine (500 mgL^{-1}) pH 11 (± 0.5) were used for stabilization of the surface of steels after the operation owing to its good property of protecting crystalline magnetite film formation. The film formed is found to be soft but stable. After completion of cleaning, the manholes of boiler drum, deaerator, bottom water walls headers were opened. Inspection revealed that in the drum, deaerator, and in headers end points solid sediments (sludge, scale particles, weld flash, cutting) were not present, In two location of headers very little sediment was observed. The average quantity of residual deposit (g m^{-2}) remained in boiler pipelines and accessories after cleaning operation was found highest in back wall (panel-4 and 16; 18 g m^{-2}) followed by front wall (Panel 3 and 12, 14 g m^{-2}), LP heater (11 g m^{-2}) and economizer (10 g m^{-2}) respectively. After completion of acid cleaning and passivation operations the average composition of deposits remained on the inside surfaces of the boiler WWTs and other pipe lines depicted maximum amount of Fe_3O_4 97.4% (as a very thin brownish-

black coloured thin and powdery coating) followed by SiO_2 0.87%; CaO 0.89% and MgO 0.42% respectively

Conclusion

The overall investigated results of the present acid cleaning operation suggested that not less than 90% of deposits and impurities have been removed. The cleaning process is found to be very effective .A remarkable uniform brownish-black coloured (Fe_3O_4) passivation due to hydrazine in the presence of ammonia on the inside metal surfaces of the boiler pipelines were attained, which was found to act as strong protector against corrosion.

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