Boilers and Steam Lines Chemical Cleaning

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Abstract*:- The aim of Chemical Cleaning is to is to safely remove all deposits from the inside of the boiler tubes. mill scale, oil, paint, preservatives, rust, welding slag's that would have entered during the assembly of new tubes. Steam piping must be cleaned by chemicals when either the product can react with oil left inside of the piping or in case it can lead to adverse effect to leave even very small parts of debris inside the piping. Proper neutralizing and flushing of these systems after the chemical attack are of utmost importance. After carrying out the process, the internal surfaces of the tubes are passivated by means of protective layer to prevent further rusting and corrosion. Proper chemical cleaning removes deposits from the inside of boiler tubes which improves the boiler heat rate, reduces tube failures and improves the stability of boiler chemistry. In Dangote Fertilizer Plant all Boilers are High Pressure boilers. In higher-pressure boilers, the major deposit removed is magnetite and some copper. The internal surfaces of a boiler in contact with water and steam must be kept clean and free of deposits to assure efficient heat transfer in the generation of steam. This article discusses when and how to chemically clean a boiler. Several methods can be used to determine the need to chemically clean a boiler. The high heat flux boiler tube surfaces mainly consist of magnetite and copper. The article outlines cost effective cleansing solvents for chemically cleaning boilers with magnetite deposits and copper. The chemical cleaning must be thoroughly planned. Criterion for determining the success of a chemical procedure and the effectiveness of the solvent in dissolving the deposit is covered in detail.

Keywords-Boiler, Steam lines, Chemical cleaning, Ammonia, Alkali, acid, effluents.

INTRODUCTION

Dangote Fertilizer Project consists in the realization of an Ammonia and Urea complex natural gas based plants with associated facilities. The Project under progress at LEKKI Free Zone in Ibeiju-Lekki Local Government Area of Lagos State, Nigeria. Ammonia and Urea complex includes: The normal flow rate of natural gas is 208695 Nm^3/hr. 2X2200 MTPD Ammonia Trains based on HTAS technology (and BASF technology for CO_2 capture in Ammonia Plants).2X3850 MTPD Melt Urea Trains based on Saipem Technology.2X3850 MTPD Urea Granulation Trains based on Udhe Fertilizer technology. Associated Utility Units. Commissioning activities under progress in which Boiler chemical cleaning successfully completed. Three numbers of auxiliary boilers and six numbers of waste heat boilers in ammonia plants train -1 & Train -2.

The Pre operational chemical cleaning was carried out for the steam generation equipment along with steam grids as detailed below:

1. 3 No's gas fired auxiliary boilers with the following operating parameters
   (a) Steam pressure -46 kg/cm^2
   (b) Steam production capacity each Boiler 200 MT/Hr
   (c) Temperature of super-heated steam produced - 385^{0}C
2. Ammonia Plant (Two streams) integrated process heat recovery unit comprising of:
   (a) Reformed gas boilers. Shell & tube construction with water on shell side
   (b) Process gas boiler downstream shift converter –Shell & tube construction with water on shell side
   (c) Process gas boiler downstream ammonia synthesis converter, Shell & tube construction with water on shell side.

All three boilers of each Ammonia plant stream are integrate with risers and down comers with single steam drum. The operating parameters for the process boiler packages are as below:
Operating pressure -120.5 kg/cm^2, Total combined steam generation with all 3 process boilers 559 MT/Hr, Steam temperature outlet (steam drum) -324 ^{0}C.

3. Very High pressure (KS) and High pressure (HS) steam network of the fertiliser complex is having steam networks at two operating levels. Very High pressure (KS) steam operating at 113 kg/cm^2 and 515^{0}C. This network is running in between the ammonia process boilers to the inlet of the steam turbines through a convective super heater coils. The chemical scoping shall include the full length of the saturated steam header, convective super heater coils including manifolds and up to inlet of the steam turbines.
4. High pressure (HS) steam network operating at 46 kg/cm^2 and 385^{0}C.This runs from the auxiliary boilers runs up to 3 No's steam turbines generators and also in ammonia plant.
5.

BRIEF DESCRIPTION OF THE PLANTS

In ammonia Plant ammonia is produced from synthesis gas containing hydrogen and nitrogen in the ratio of approximately 3:1. Besides these components, the synthesis gas also contains inert gases such as argon and methane to a limited extent. The source of H_2 is demineralized water (steam) and the hydrocarbons in the natural gas. The source of N_2 is the atmospheric air. The source of CO_2 is the hydrocarbons in the natural gas feed. Product ammonia and CO_2 is sending to urea plant. The main function of the plant is illustrated in the figure-1

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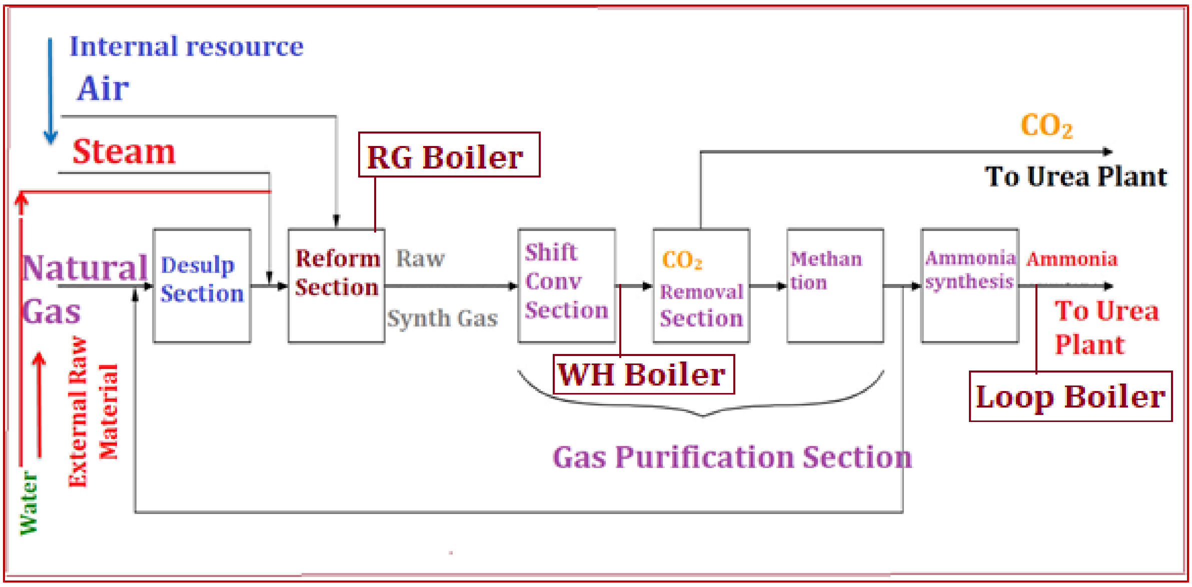

Fig.-1

The hydrocarbon feed is de sulphurized to the ppb level in the desulphurization section. The de sulphurized hydrocarbon feed is reformed with steam and air into raw synthesis gas (process gas). The gas contains mainly hydrogen, Nitrogen, Carbon monoxide, Carbon dioxide and steam. In the gas purification section, the CO is first converted into CO_2. Then the CO_2 is removed from the process gas in the CO_2 removal section. The CO and CO_2 residues in the gas outlet of the CO_2 removal unit are converted into methane by reaction with H_2 (methanation) before the synthesis gas is sent to the ammonia synthesis loop. The purified synthesis gas is compressed and then routed to the ammonia synthesis loop, where it is converted into ammonia. In order to limit the accumulation of argon and methane in the loop, a purge stream is taken. The liquid ammonia product is depressurised during which the dissolved gases, let-down gas and inert gas, are flashed off.
The complex contains three numbers of auxiliary boilers includes Boiler Feed Water preparation for Boilers feeding and for steam de-superheating, Very High Pressure Steam (KS), High Pressure Steam (HS) and Low Pressure Steam (LS) generation and distribution plus a dedicated steam sub-network) inside Urea Plant only, Condensates system, and Steam Power Generation System. The system has been conceived considering the maximum reliability and to allow the operation of plant on full range of ambient conditions.
The steam system network for each plant is independent and it can be segregated; two independent very high pressure steam header are provided (one for each ammonia/urea train) and, similarly, two independent high pressure steam header are provided (one for each ammonia/urea train) with a possibility of interconnecting.
Very High Pressure (KS) Steam KS steam is produced in the Waste Heat Boilers (Ammonia Process) at the following conditions:
Normal Pressure: 112 kg/cm2 (g)
Normal Temperature: 515 °C
Design Pressure: 128 kg/cm2 (g)
Design Temperature: 530 °C

The main users of KS steam in normal condition are here reported:

1. Synthesis Gas/Recirculation Compressor Steam Turbines
2. Ammonia Compressor Steam Turbines
3. CO_2 Compressor Steam Turbines.

The KS header is dedicated and limited to Ammonia Plant.
High Pressure (HS) Steam Turbines (Ammonia Compressor Steam Turbines) and (Synthesis Gas/Recirculation Compressor Steam Turbines) produce HS steam by discharging to the HS header: NH_3 Compressor Turbines are back pressure type, exhaust going to the high pressure network, Syngas compressor turbines are condensation type extracting steam to the same HS network. The produced HS Steam delivered to the high pressure steam grid together with the steam produced by three 100% Auxiliary Boilers are available for the other Turbine Users (STG generators; Process Air Compressor Turbines) and for process steam make-up requirements (Urea and Ammonia Plants). HS steam production/consumption depends on the working condition of complex, i.e. running condition of Ammonia / Urea Plants and the associated power requirement.

1. High Pressure Steam is produced at the following conditions:
2. Normal Pressure: 45.5 kg/cm^2 (g)
3. Normal Temperature: 385 °C
4. Design Pressure: 48/FV kg/cm^2 (g)
5. Design Temperature: 415 °C

The total power requirement of the complex is produced by three Steam Turbine Generators. The capacities of STGs cover the power requirement of Ammonia Unit, Urea Unit and Granulation Unit plus Utility facilities. Each Steam Turbine Generator produce approximately 41 MW (rated point) at 11 KV (island Mode); STGs use HS steam as motive fluid and work at the following operating conditions:

1. Normal Inlet pressure = 44 kg/cm^2 (g);
2. Normal Extraction pressure = 4.0 kg/cm^2 (g);

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3. Maximum Exhaust pressure = 0.2 kg/cm^2 (a).

WHY REQUIRED CHEMICAL CLEANING?

Lines and equipment cleaning is intended to eliminate welds rods and slags, abrasive dusts, oxides grease and in general other substances which might impede the normal unit operation or damage the equipment (valves, pumps, compressors, turbines, etc.), The layers of corrosion product are made on pure iron as shown in the figure- 2, that layers must be removed by chemicals cleaning.

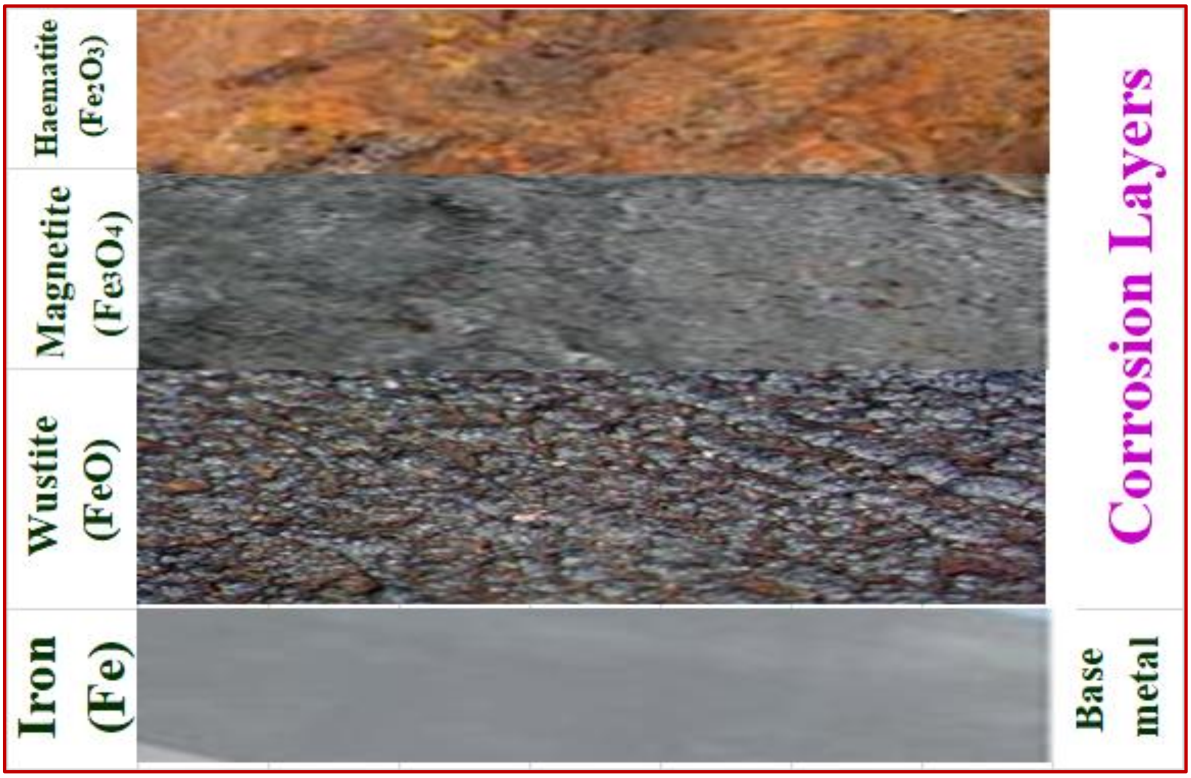

Fig -2

CHEMICAL CLEANING OF BOILERS

Preparation of Temporary Circuit*.*

The cleaning carried out by circulating the specified chemical solutions in the specified sequence and conditions. Temporary piping, pumps and suitable capacity, fittings, flanges, tanks, gaskets, heating arrangement, valves, test coupons, spares, laboratory facilities with all accessories required for conducting tests during cleaning operation, chemicals and safety accessories for operation, personnel etc., made available at site prior to cleaning operation. Quantity of chemicals required calculated based on the hold-up volume of the temporary circuit.

Material and Method.

All Chemicals used for chemical cleaning was inspected on receipt. Method for transportation of materials, storage, checked as per Material Safety Data sheet. The Batch / Lot No, Expiry Date of Chemicals was verified with Batch Certificates. Temporary boiler for heating /Heating Tank/mix Tank: Capacity 20 M^3

Circulation Pump: Capacity 200 M^3 /hour, Head: 50 m

Temporary waste water Pond: 2200 M^3

Potable Analytical Laboratory: pH meter, Conductivity meter, Turbidity meter etc. Balance and test coupons, Gauges: Temperature, Pressure, level, Necessary Pipes for fabrication of temporary circuit, Necessary valves, flanges, bends and gaskets, Tool & Tackles, all required Personnel Protective Equipment's, Hoses, Bolts, nuts and gaskets, Air compressor, Electricity or diesel generator, Diesel fuel, Consumables, Scaffolding where required, Waste water tanks, HDPE sheets for waste water tanks.

Provision was made to establish a circulation path through the steam generating section. Integrated chemical cleaning for high pressure and medium pressure headers considering one as the feed header and the latte as return header within ammonia plant having a separate cleaning loop for the medium pressure header from auxiliary boilers to steam generators and yard piping. Hook up temporary piping to these connection points. An external circulation pump required to circulate the chemicals through these steam generators and steam network in separate circulation paths. Provision also made for the necessary atmospheric vent lines, sampling connection with valve which was installed and appropriately tagged (as per figure No.-3) All pressure parts were carefully inspected for obstructions and the necessary hydrostatic tests were made.

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QUANTITY OF CHEMICALS CONSUMED.

Sr. No.	Chemicals	Quantity
1	Non Ionic wetting Agent	180 kg
2	Inhibitor	270 kg
3	Citric Acid	3600 Kg
4	Ammonia (NH_4OH)	2110 Kg
5	Sodium Nitrite	650 Kg
6	Anti-foaming agent	20 Lit
7	Sulphamic acid(NH_2SO_3H)	750 Kg
8	Caustic Soda Flaks(neutralization)	1750 Kg
9	Lime(Neutralization)	300 Kg

Table-1

RO WATER CONSUMPTION FOR THE ENTIRE PROCESS

Sr. No	Description	RO water m^3
1	Temporary pipe leak Test	70 m^3
2	Cold RO water Flushing	360 m^3
3	De greasing and citric Acid pickling	120 m^3
4	Passivation	60 m^3
5	Ammoniated RO water rinse	240 m^3
6	Neutralization pit Dilution	90 m3
	Total	**940 m^3**

Table-2

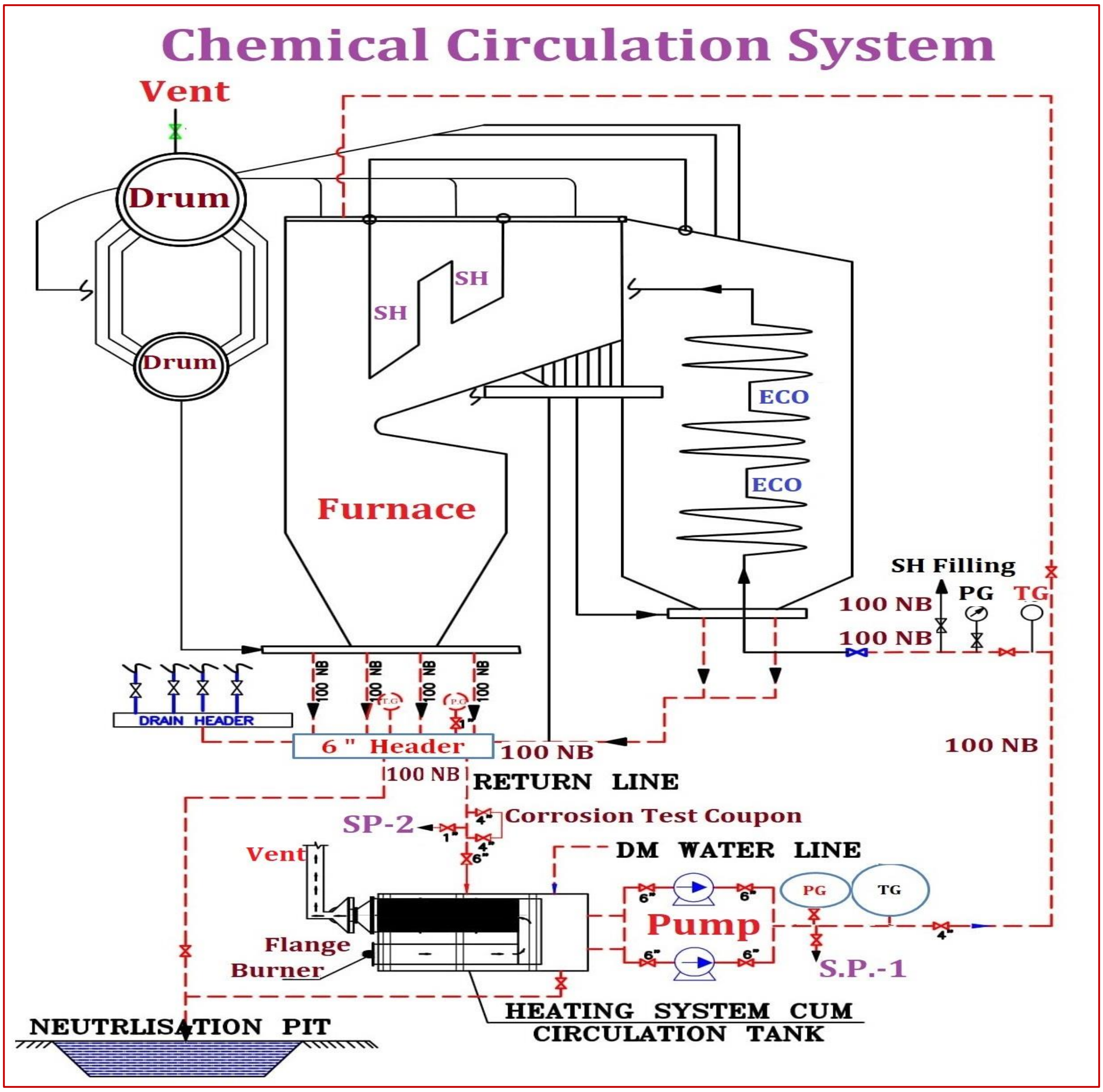

Fig. 3

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CHEMICAL CLEANING OF BOILERS.

The cleaning was done by circulation technique using external pumps in a **“SINGLE FILL METHOD”**. The sequence of the cleaning step like Degreasing, inhibited Citric acid cleaning and Passivation is done in one single fill method.

Each system was done in sequence in separate circulation path.

The advantages in Single fill method when compared to other multiple fill method is

1. Reduce DM water quantity.
2. Reduce Waste water volume.
3. Reduce cleaning time.
4. Safe Operations.
5. Reduce chemical cost.
6. Excellent results after cleaning with citric acid and sodium nitrite passivation.

SEQUENCE OF OPERATION

The cleaning of piping was carried out in the following sequence in a Single fill method.as shown in the figure-4

1. Cold water Flushing with potable water to remove dirt, dust, loose rust and foreign matter.
2. Degreasing with Non-ionic wetting agent.
3. Circulating with ammoniated inhibited citric acid.
4. Circulating with Sodium Nitrite ($NaNO_2$).
5. Drain.
6. Rinse with Ammoniated water.
7. Drying & Inspection

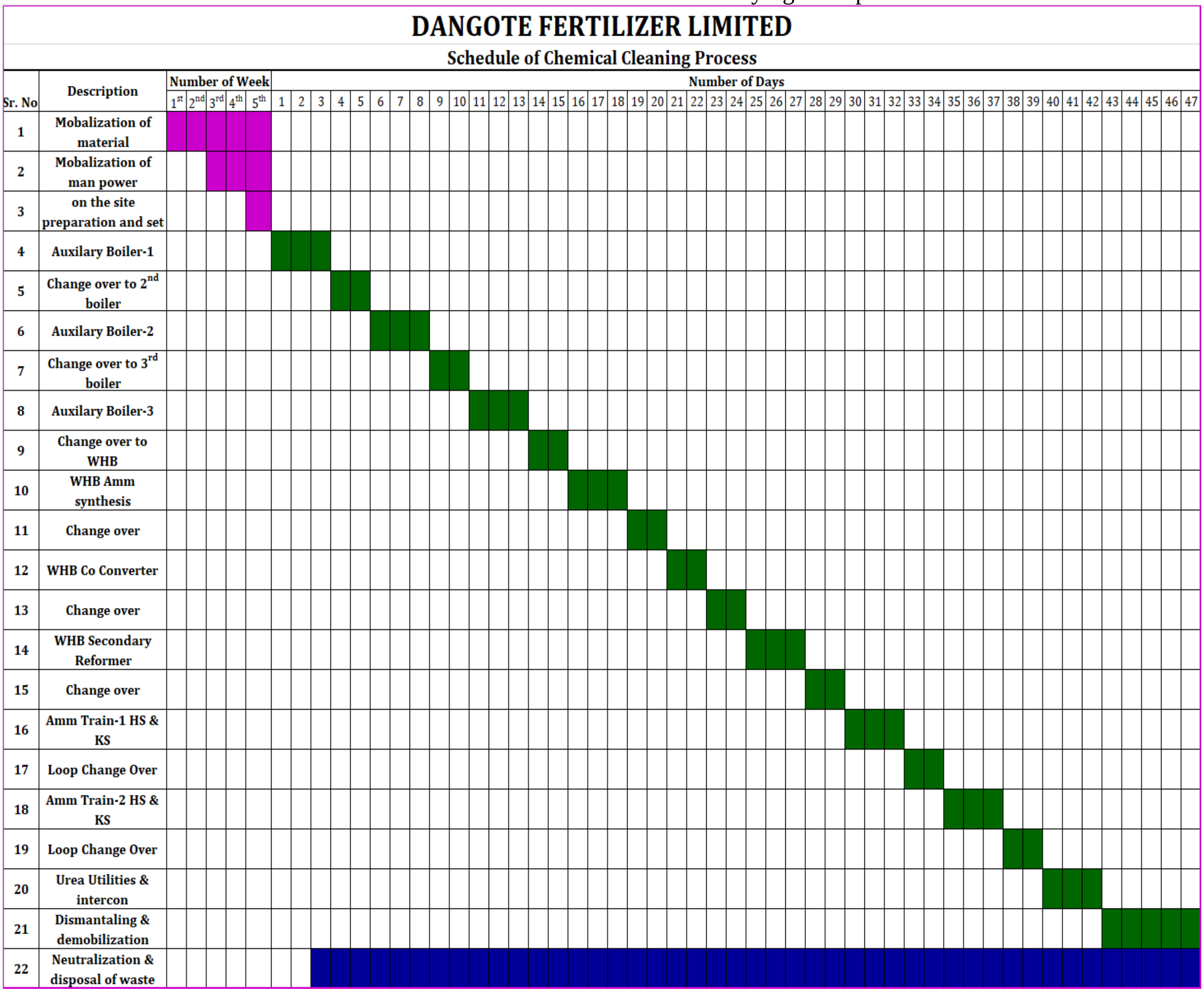

Fig-4

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Fig.-5

COLD WATER FLUSHING & LEAK TEST

Closed all drum manhole. Filled the system with Demineralised water drum Normal working level.

1. Once the boiler is filled start open flushing to flush out temporary bottom Header stubs connecting lines, return line and drain lines (Economiser, water tubes & bottom header) till the drain water is visually clear. At completion of flushing close temporary drain valves.
2. Circulate water in the system by temporary chemical cleaning pump Temporary system along with Boiler was hydraulically tested by using temporary Chemical cleaning pump at head pressure for 30 mins.
3. The mentioned flushing and leak test was performed for all temporary piping and its connection to endure that there were no leakages to the ambient or adjacent systems.
4. Ensure no leaks in temporary system via full walk down. Walk down was conducted from bottom to top to make sure all critical points are inspected and signed.
5. After the completion of the hydro test, the boiler was depressurized and walk down to inspect casing (external and internal side) thoroughly for any leaking tube, sweating tube or weeping tubes.
6. The flushing of the sections to be cleaned was executed with the maximum possible flow rate. The minimum velocity of the flow was 0.5m/s in each part of the system and 1 m/s in vertical pipes with flow going upwards.

Analysis report Cold water Flushing

Date/ Time(Hrs) 14/02/2020	Outlet pH	Conductivity(μ/s) outlet	Turbidity(outlet)
09.45	7.15	57	61
10.15	7.07	51	47
10.45	6.47	46	29
12.45	6.91	45	18
13.30	6.89	42	10
14.30	6.87	44	7
14.45	6.85	44	3
15.05	6.83	44	1

Table-3

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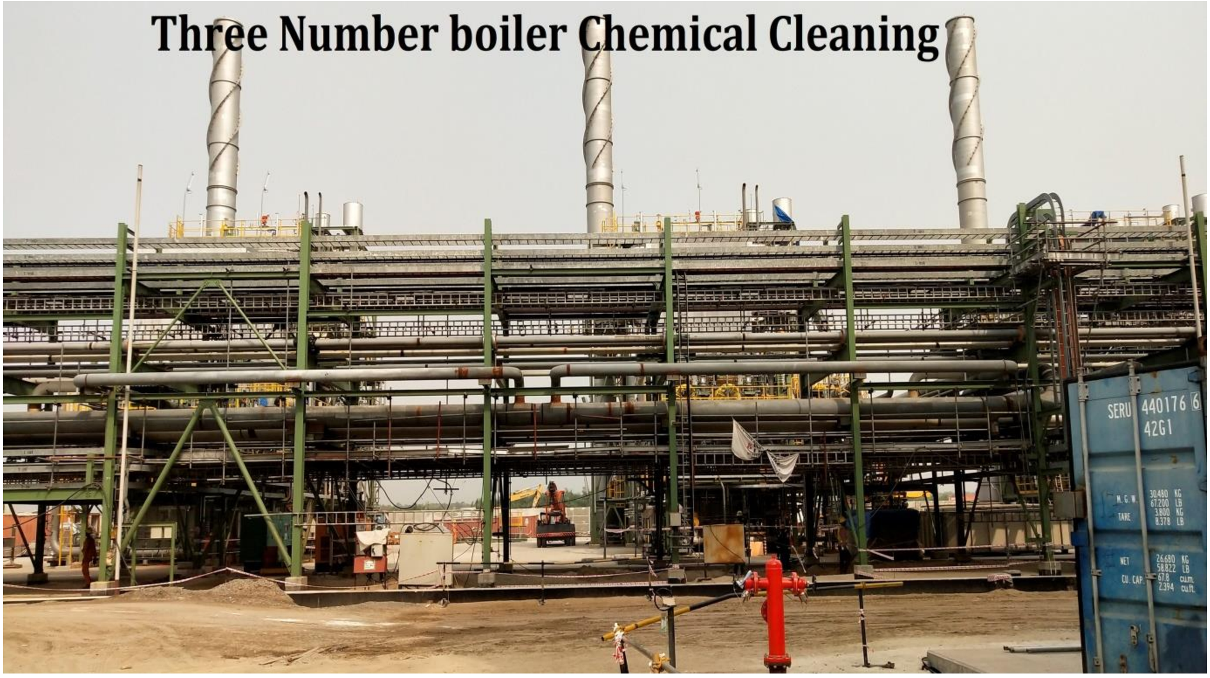

Fig.-6

DEGREASING:

Immerse the piping in a caustic bath at a temperature of about 70/80°C for a period of at least 30 minutes, depending on the condition of the material, to remove all grease, dirt, oil or paint. Piping and/or solution is agitated to ensure the flow of solution through the piping. The batch may be a solution of 6 % wt. of sodium hydroxide in water with detergent. Remove piping from caustic bath and immediately rinse with cold water. For degreasing added 4.6 kg/m3 of tri sodium phosphate and 3.1 kg/m3 of bi-sodium phosphate. For passivation Fill the boiler with BFW using filling up valve up to normal. Ensure that passivation chemicals (Hydrazine) is injected in the line between deaerator and boiler in order to treat also the economizer. The suggested concentration is 1.0 litre of hydrazine per cubic meter BFW.

1. The system was Fill with Demineralised water drum Normal working level. Heated up the circulating water by temporary auxiliary boiler or Heating system to approximately 65 ºC - 70 ºC. Insert to chemical circulation tank the desired chemicals.
2. Added 0.15% Non-ionic wetting agent to prepare the surface for Pickling. For degreasing added 4.6 kg/m3 of tri sodium phosphate and 3.1 kg/m3 of bi-sodium phosphate.
3. The circulation was continued for min 4 hours.
4. The chemical was dissolved with DM water in the main circulation tank. Ensure proper mixing of chemicals.
5. All Operators and workmen was involved in chemical cleaning process was born all PPE, rubber aprons, Protective Boots, Face shields, and Hand gloves and to avoid contact with chemical.
6. The chemicals were filled solution through the external piping on the economiser inlet for each section. When the economiser is full, close the vents.
7. Circulation was established with the external pump from the inlet connection on the Economiser and the connections on the manifold drains. The water level in the drum was kept from going out of sight in the gauge glasses. The readings tabulated as per table No. 4

De- Greasing Analysis Report

Date/Time	Outlet pH	Total alkalinity(ppm) as $CaCO_3$	Oil & grease ppm	Temperature(^{0}C)	
				inlet	outlet
04/02/2020					
22.00	8.41	37.5	9.6	75	70
23.00	8.36	42.5		76	72
05/02/2020					
00.00	8.31	45	22.4	76	73
01.00	8.36	47.5		74	71
02.00	8.40	47.5	30.2	73	70
03.00	8.37	47.5		75	72
04.00	8.6	47.5	30.4	74	71

Table-4

INHIBITTED CITRIC ACID PICKLING

For inhibited citric acid pickling the R.O water heated by electric heater up to 72-75^{0}C in the tank and then inhibitor added about 270 kg, Citric acid also added to control the solution p^H. Following chemicals were added. First the citric acid pickling was carried out up to 6 hrs with closed circulation. After that the system was partially (30-40%) drained into neutralization pit and the effluent well neutralized by caustic flaks up to pH about 7.06. during the process pH and temperature were recorded as shown in the table No-5

1. Inhibitor-270 kg.
2. Citric acid -3600 kg.
3. Ammonia -70 kg.

Date & time	pH Outlet	Citric Acid outlet(%)	Fe^3(ppm)	Fe^2(ppm)	Total Iron (ppm)	Temperature(^{0}C)	
						In	Out
5/02/2020							
06.30	3.2	3.1	84	783	867	78	75
07.30	3.64	3.43	118	2256	2374	77	74
08.30	3.66	3.36	223	2430	2653	76	74
09.30	3.68	3.29	223	2831	3044	75	73
10.30	3.69	3.15	223	3295	3518	74	72
11.00	3.70	3.15	223	3323	3546	73	71
11.30	3.69	3.15	223	3323	3546	73	71
12.00	3.70	3.15	223	3323	3546	73	71

Table-5

ALKALINE CLEANING

Alkaline cleaning (flush/boil-out) solutions are basically tri sodium phosphate and surfactant. Tri sodium phosphate concentrations typically range from 0.1 to 1%. Disodium phosphate and/or sodium hydroxide may be added. Sodium nitrate is often added when caustic is used, as a precaution against caustic embrittlement. Sodium sulphite is occasionally used to prevent oxygen corrosion. Although mill scale removal is not one of the purposes of alkaline cleaning, the addition of chelating agents may remove enough mill scale to eliminate the need for further chemical cleaning. However, where mill scale removal is specifically desired, acid or chelant cleaning should follow alkaline cleaning. Commercial alkaline cleaning products may include chelants and other compounds specifically formulated to provide effective cleaning. Alkaline cleaning should follow procedures that boiler manufacturers furnish for their specific boilers. During cleaning, boilers are fired at a low rate, but not enough to establish positive circulation. Boil-out pressure is usually about half the operating pressure. Several times during the alkaline boil-out, half of the boiler water was blown down. Alternate valves was used where there is more than one blowdown connection. The boiler is refilled close to the top of the glass after each blow. Super heaters and re heaters are protected by backfilling with a properly treated condensate. Each chemical cleaning stage lasts was carried out for approximately 6 to 24 hr. When alkaline cleaning was completed, the unit is slowly cooled, the alkaline solution was drained to the disposal area and neutralized by acid effluent which was collected in acid cleaning steps and the unit was flushed with good-quality condensate. Flushing, with intermediate blowdown, was continued until flush water conductivity is less than 50 mhos and phosphate is less than 1 ppm. Alkaline cleaning was repeated if organic or residual oil-based contaminants are found upon inspection of the unit.

AMMONIA AND RO WATER RINSE

System was filled with RO water and added ammonia about 20 kg, and flushing started again added 20 kg ammonia and system was continued. This flushing was carried out in open and spent collected and neutralized with caustic flaks. During the process the pH were tested and tabulated in table no.- 6 after that the system was fully drained spent ammoniated RO water solution was neutralized with Sulphamic acid.

PASSIVATION

Date & Time	pH		Temperature(^{0}C)	
	In	Out	In	Out
05/02/2020				
17.30	9.86	9.84	58	55
18.30	9.84	9.85	59	56
19.30	9.76	9.79	58	55
20.30	9.7	9.72	57	55
21.30	9.71	9.67	59	56
22.30	9.65	9.61	58	56
23.30	9.58	9.59	59	55
06/02/2020				
00.30	9.55	9.56	57	54

Table-6

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NEUTRALIZATION OF SPENT CITRIC ACID & PASSIVATION SOLUTION

Date & time (Hrs)	pH neutralization pit	Remarks
05/02/2020		
12.50		Caustic soda flaks-1000 kg added in the neutralization pit
16.30	5.52	
		Caustic soda flaks-750 kg added in the neutralization pit
22.00	8.45	
06/02/2020		
03.00		Sulphamic Acid-400kg added in the neutralization pit
10.15	8.07	
15.00		Sulphamic Acid-350 kg added in the neutralization pit
17.30	7.52	
07/02/2020		
09.30		Lime added -300 kg added in neutralization pit
11.45	8.35	

Table-7

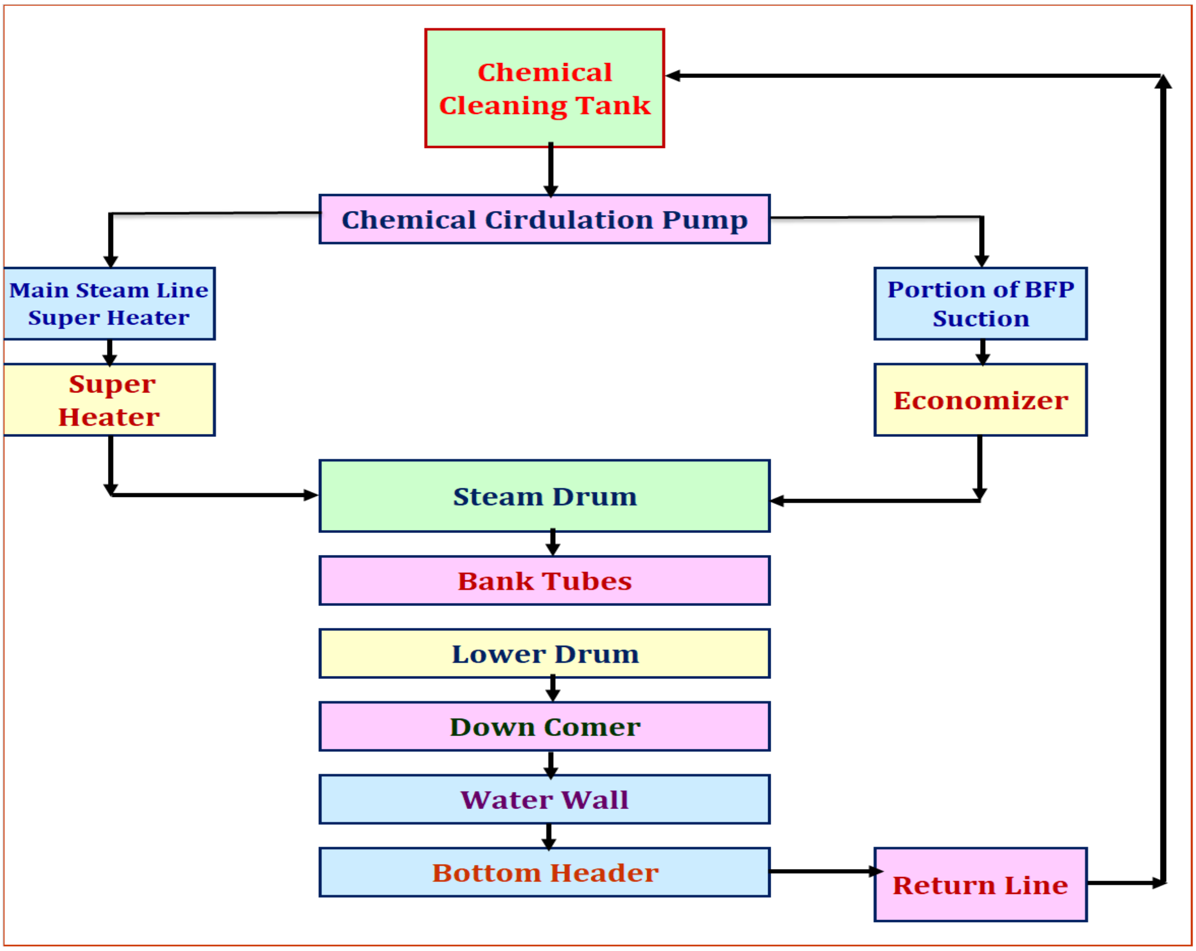

Fig-7

PASSIVATION

To minimize deterioration of the active surfaces produced by acid cleaning, a final passivation stage is an essential part of the overall cleaning process. Passivation is the process of treating the metal with acids in order to remove the free iron from the surface of the metal and coat it with this corrosion-preventing oxide layer. This passive layer gets damaged through heat or chemical cleaning damage due to high humidity levels. After the steel surfaces have been chemically cleaned, they are very 'active' and subject to rapid rusting. It is, therefore, necessary to passivate the cleaned metal surfaces to prevent their deterioration. Operation immediately after passivation is the best means of establishing the protective oxide film. Before steam blowing Complete chemical cleaning of your system to ensure piping is ready for operation Complete hydraulic testing of lines, ensure all system parts, components and plates are properly set up for steam blowing.

CONCLUSION

The chemical cleaning of boilers has proved to be rapid and efficient method of removing deposits from the water side of the boiler. In many boilers this is the only method available today to clean some areas of the equipment. From a corrosion viewpoint, this method can be made a satisfactory procedure when all the factors involved are properly understood and controlled; however, caution should be the password at all times. Steam blowing comes with hazards, such as high thermal stress on your boiler. We take great care to use the minimum necessary pressure, closely monitor every detail and ensure a safe process. we take safety, health and the environment seriously. After chemical cleaning of the system "Steam blows" are required on large industrial/utility boilers prior to commissioning. conducting and completing "steam blows" The basic concept of a steam blow is to subject the boiler system to a flow with a "mass-momentum" higher than that it will ever see during normal operation. Cleaning is accomplished by a combination of steps. For some boilers it may not be necessary to use all the cleaning steps, since the degree of contamination will vary from one boiler to another.

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