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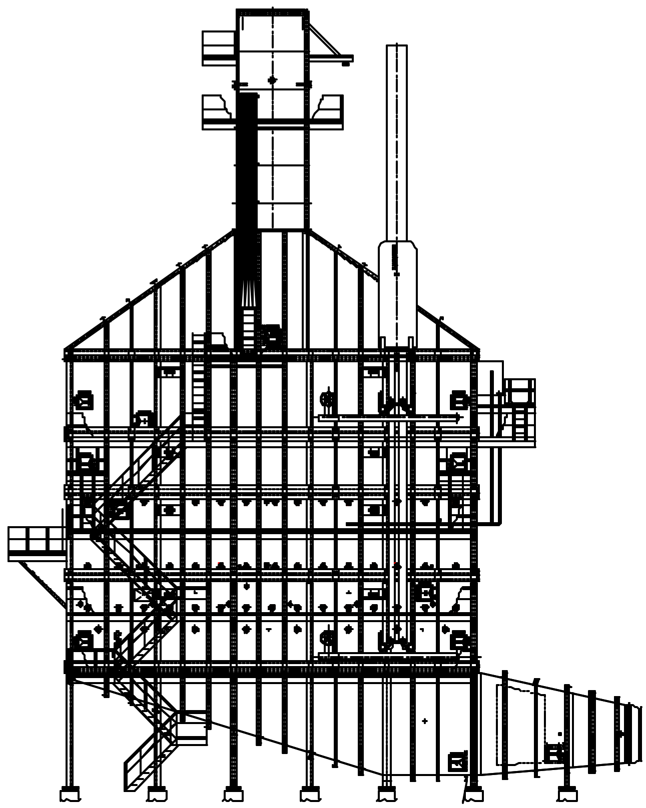

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VERTICAL GAS FLOW APPLICATIONS OF SCR'S WITH ONCE THROUGH HRSG'S

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ABSTRACT

The current environmental trend is to minimize atmospheric emissions such as nitrogen oxide (NO_x) emissions from combined cycle power plants. Selective catalytic reduction (SCR) systems have been successfully used by Hitachi to reduce NO_x emissions in combined cycle applications since 1981. SCR systems are most commonly placed in a horizontal gas path as in vertical tube, natural circulation heat recovery steam generators (HRSG's). Hitachi has extensive experience in vertical, down-flow SCR applications in coal fired applications. Innovative Steam Technologies (IST) integrates SCR's into vertical gas flow applications with their Once Through Heat Recovery Steam Generators (OTSG).

Vertical gas flow applications of SCR's with OTSG's provide many operating advantages over the standard HRSG arrangement that can benefit owners/operators. Operating advantages are provided during daily start/stop, part load operation and in elimination of soot deposits.

Many combined cycle plants are operating in a daily start/stop scenario. As emission restrictions are applied during these start ups, a quick start of the SCR system is imperative to minimize the emissions. The SCR system cannot start until a minimum temperature is established upstream of the SCR catalyst. The OTSG starts up dry, without any water in the tubing, allowing the SCR system to come on line faster than in a natural circulation or forced circulation HRSG application due to the absence of a water inventory.

Operating the gas turbine at part load conditions affect the gas inlet temperature to the SCR. Being above or below the desired gas temperature affects the SCR performance. Unlike the fixed steam flows for a given gas turbine condition associated with a natural or forced circulation HRSG, the OTSG can operate at various steam loads for a given gas turbine operating condition. This allows the owner/operator to control the gas temperature upstream of the SCR in order to maximize the efficiency of the SCR system.

Operation of SCR's with sulfur bearing fuels results in deposits of ammonium sulphate, ammonium bisulphate and sulphuric acid accumulating in the economizer section of the OTSG. Typical cleaning of HRSG's is completed with water washing of the pressure parts. As proven in testing, the dry running capability of the OTSG allows the deposits to be thermally decomposed and removed with compressed air.

NOMENCLATURE

OTSG – Once Through heat recovery Steam Generator
SCR – Selective catalytic reduction
NOx – Nitrous oxides
AIG - Ammonia injection grid
HP – High pressure section of OTSG
LP – Low pressure section of OTSG

CHARACTERISTICS OF ONCE THROUGH STEAM GENERATORS

The once-through steam generator, in its simplest form, is a continuous tube in which preheating, evaporation, and superheating of the working fluid takes place consecutively as indicated in Figure #1.

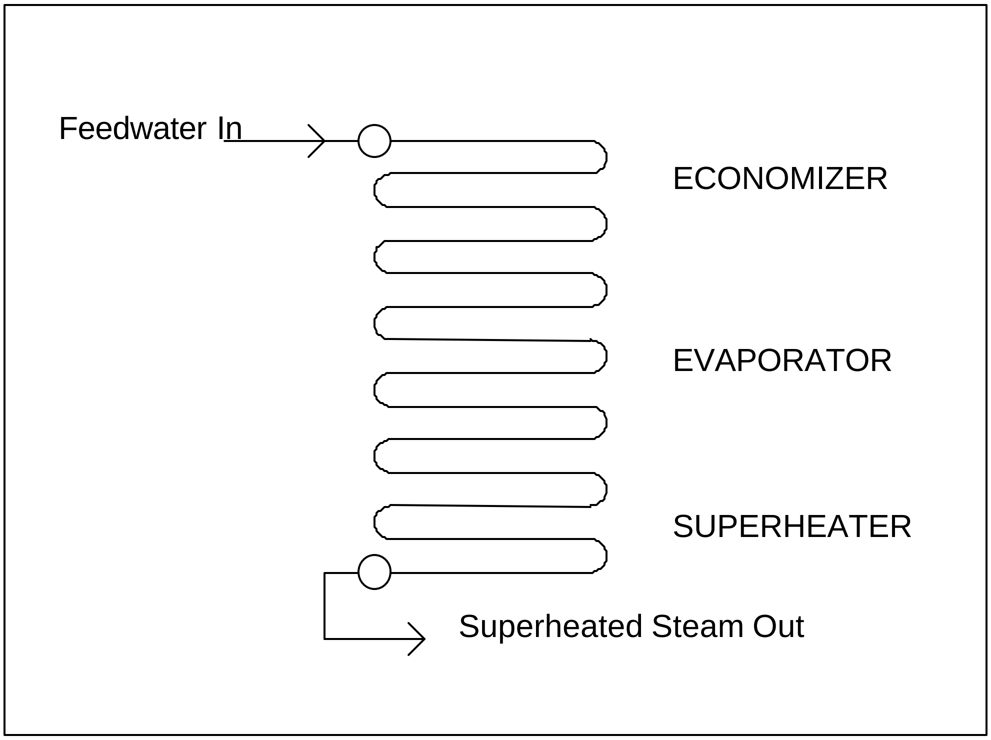


Figure #1 – Once through steam generator (OTSG)

In practice, of course, many tubes are mounted in parallel and are joined by headers thus providing a common inlet for feedwater and a common outlet for steam. Water is forced through the tubes by a boiler feedwater pump, entering the OTSG at the "cold" end. The water changes phase to steam midway along the circuit and exits as superheated steam at the "hot" or bottom of the unit. Gas flow is in the opposite direction to that of the water flow (counter current flow). The highest temperature gas comes into contact with water that has already been turned to steam. This makes it possible to provide superheated steam.

The advantages inherent in the once-through concept can be summarised as follows:

1. Minimum volume, weight, and complexity.
2. Inherently safe as the water volume is minimized by using only small diameter tubing.
3. Temperature or pressure control are easily achieved with only feedwater flow rate regulation.

The once-through steam generator achieves dissolved and suspended solids separation external to the steam generator by pre-treatment of the OTSG feedwater. Any solids remaining in the feedwater, either suspended or dissolved, can form deposits on the OTSG tubing and/or be carried over to the steam process. Dissolved oxygen control is not a critical issue for the IST OTSG, which is made of alloy tubing.

OTSG's can be supplied in both horizontal tube/vertical gas flow arrangements (Figure #2) as well as vertical tube/horizontal gas flow arrangements (Figure #3) to match customer requirements.

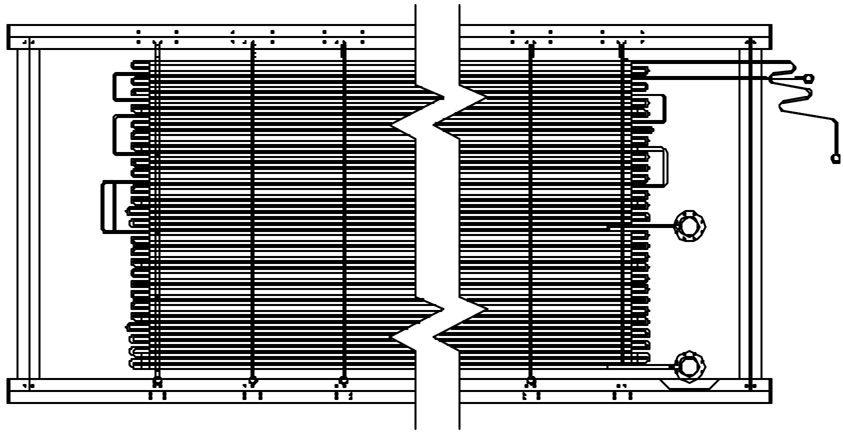


Figure #2 – Horizontal Tube/Vertical Gas Flow Arrangement

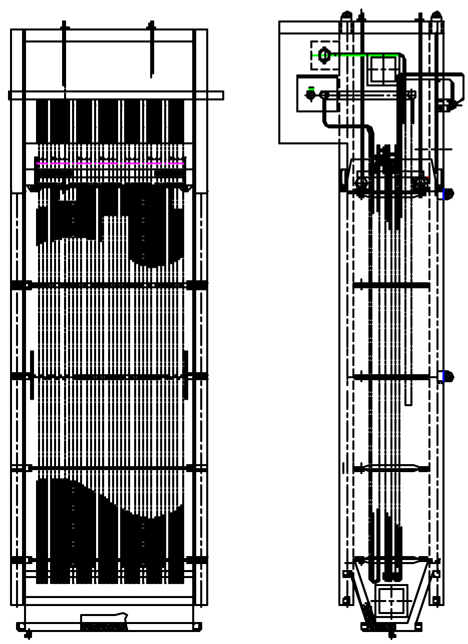


Figure #3 – Vertical Tube/Horizontal Gas Flow Arrangement

SELECTIVE CATALYTIC NO_x REDUCTION (SCR) PROCESS

Emissions

Nitrous oxides, principally NO and NO_2, result from high temperature combustion such as in the combustion of fossil fuels in gas turbines. Emission of these nitrous oxides (commonly referred to as NO_x) into the atmosphere have negative effects such as contributing to the formation of acid rain and smog. Under certain conditions, NO_x can react to form ozone. All of these results of NO_x can irritate the nose and throat and can also impair lung function. Processes have been developed to reduce these emissions in combined cycle power plants. Hitachi began developing NO_x removal systems in 1967. Today Hitachi is the leading Japanese manufacturer of NO_x removal systems with many systems successfully operating in North America, Europe and Asia.

Selective Catalytic Reduction (SCR) Process (ref. a)

The SCR NO_x removal system (also referred to as $DeNO_x$) is a dry process in which ammonia (NH_3) is used as a reducing agent, and the NO_x contained in the flue gas is decomposed into harmless into harmless N_2 and H_2O. See Figure #4 below for a diagram of the NO_x removal process reactions.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$
$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

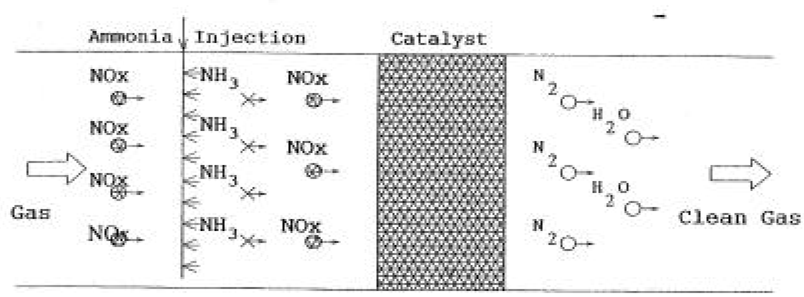
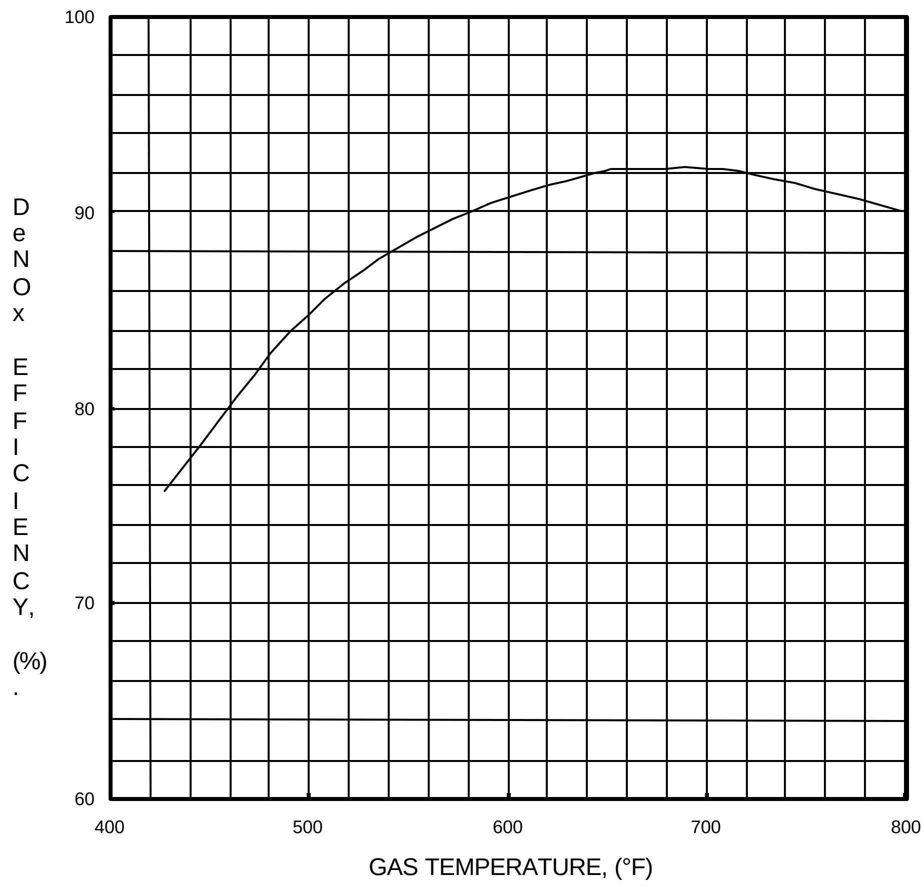


Figure #4 – NO_x Removal Process

Ammonia (NH_3) is injected into the flue gas upstream of the SCR catalyst, through a special injection grid to assure even distribution and mixing within the flue gas. The flue gas then passes through the catalyst layer.

SCR LOCATION

The SCR must be located in the appropriate gas temperature zone for maximum efficiency. A typical efficiency vs. gas temperature curve is shown in Figure #5. Typical medium temperature SCR catalyst maximum continuous operating temperature is 800°F with short temperature excursions up to approximately 870°F. Although the catalyst can operate at temperatures up to 870°F it is not recommended that the catalyst temperature exceed 800°F during continuous operation in order to maximize efficiency and catalyst life.



Typical DeNOx Efficiency VS. Gas Temperature

Figure #5 – DeNOx Efficiency vs. Gas Temperature Curve

The flexibility of the OTSG allows for optimum placement of the SCR surface in the pressure parts in either the evaporator or superheater section of the OTSG as required for optimum operation of the SCR. As intermediate headers are not used, the tubes are simply jumpered over the SCR surface as shown in Figure #6.

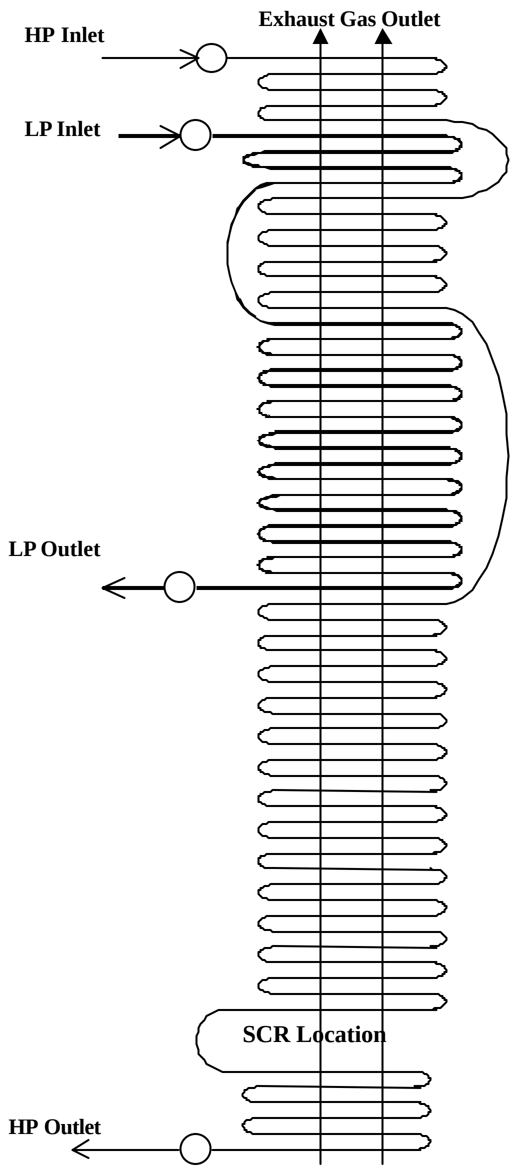


Figure #6 – SCR Catalyst Location in OTSG Tube Bundle

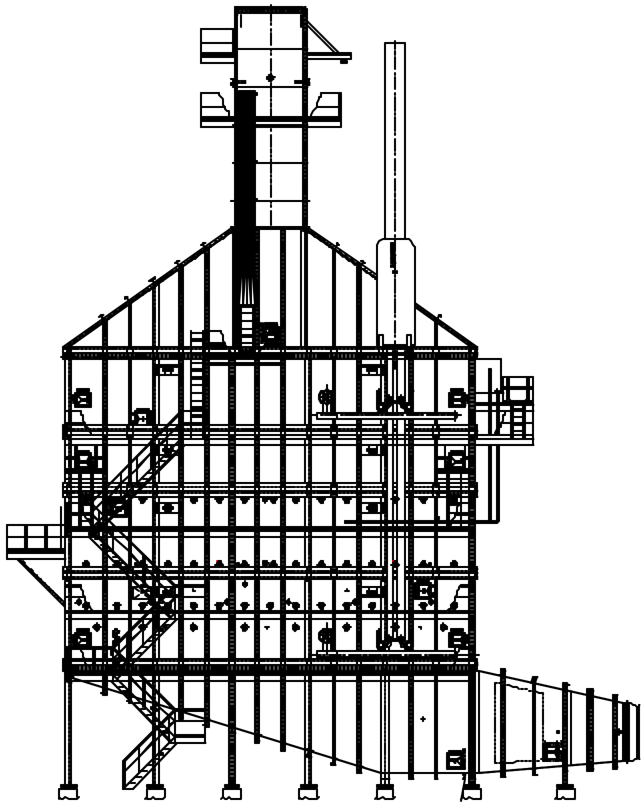


Figure #7 – General Arrangement of SCR in OTSG System

SCR SYSTEM COMPONENTS

The SCR DeNOx system is comprised of subsystems such as the ammonia injection system, air supply system and the SCR reactor.

Ammonia Injection System

Ammonia Supply System

Ammonia is supplied to the ammonia flow control unit (AFCU). The ammonia flows into the vaporizer and is diluted with air to achieve an air/ammonia volume ratio of approximately 19:1, in order to avoid a possible explosion of the air/ammonia mixture

Ammonia Injection Grid

The ammonia injection grid (AIG) is installed upstream of the SCR catalyst. The AIG consists of injection pipes and spray nozzles. Ammonia/air mixture injection is adjusted in accordance with NO_x concentration distribution through multiple holes. The design of the AIG is crucial to ensure proper operation of the SCR system. Flow modeling is required to ensure a uniform distribution of ammonia/flue gas mixture to the SCR catalyst.

Electric Heater and Aqueous Ammonia Vaporizer

An electric heater is equipped to heat up the dilution air. Uniform air flow (vaporized aqueous ammonia and dilution air) is achieved with a perforated plate.

Air Supply System

An ammonia dilution air fan is used as the supply source for dilution air. Mixing of the ammonia with air is achieved in the vaporizer and piping, and introduced to ammonia distribution manifold. The ammonia/air injection system consists of supply headers, grid of injection pipes and nozzles.

Each supply header is equipped with a manual throttling valve and flow orifice for obtaining a uniform distribution of the ammonia/flue gas mixture to the injection pipe grid. The manual throttling valves are set up by using the NH_3 and/or NO_x values obtained from sampling connections traversing the flue gas duct.

SCR Reactor

The SCR reactor is located in the flue gas duct downstream of the gas turbine. The SCR reactor uses a fixed bed, parallel passage type, vertical reactor. The reactor is a bottom supported steel structure. The reactor consists of an internally insulated exterior casing and internal catalyst support structure designed to sustain internal pressure, earthquake loading, wind gust loading, catalyst loading and thermal stress. Necessary seals are installed at the bottom, sides and top of the catalyst layer in order to prevent untreated gas bypassing.

Catalyst elements consist of support plates integrally coated with active catalyst on a titanium dioxide base. Flue gas flow is parallel to the catalyst elements to minimize pressure drop. Multiple plate elements are assembled into a catalyst unit, with catalyst units modularized into catalyst blocks for ease of shipment and installation. A typical catalyst unit assembly is shown in Figure #8.

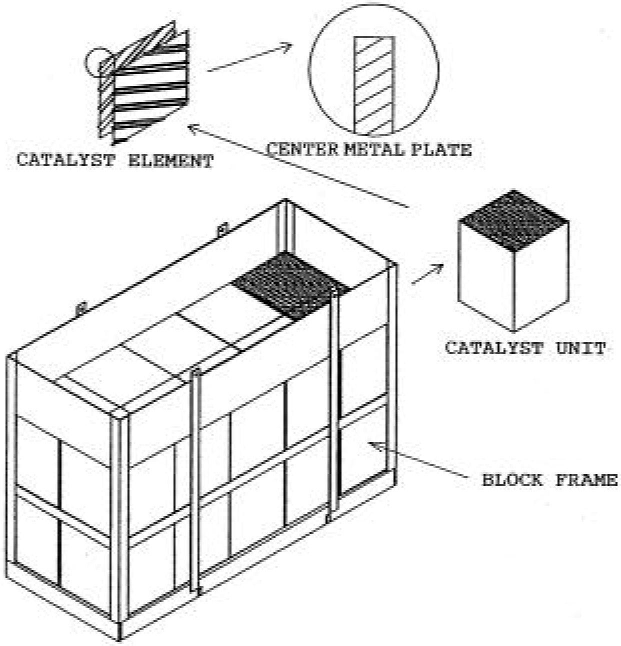


Figure #8 – SCR Reactor and Catalyst Units

The catalyst units are loaded through the access door located in the reactor casing. After lifting the catalyst units with a crane (or hoist), the catalyst units are placed onto a hydraulic carrier. The hydraulic carrier locates the catalyst blocks into the reactor casing. A typical loading procedure is shown in Figure #9.

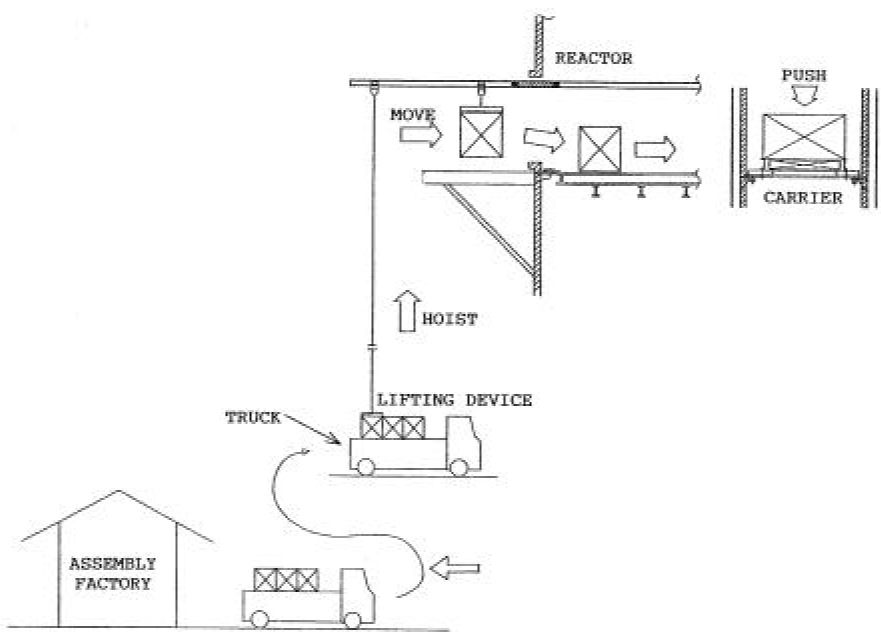


Figure #9 – Loading of Catalyst Units into the SCR Reactor

SCR CONTROL SYSTEM

The fundamental philosophy of the SCR $DeNO_x$ control system is to provide the required ammonia flow required to maintain a constant outlet NO_x level. The product of the inlet NO_x concentration and flue gas flow rate yields the NO_x flow signal. This signal is then multiplied by the required ammonia/NO_x mole ratio to give the basic ammonia flow demand signal.

Ammonia Injection Flow

The ammonia injection flow is regulated by the following equation:

Ammonia injection flow = $GF \bullet GNOx \bullet M \times 10^{-6}$ (Nm^3/hr)

Where, GF = Gas turbine flue gas flow (Nm^3/hr – dry)
GNOx = NO_x concentration (ppmvd)
M = modified mole ratio

The calculated demand signal for ammonia flow is sent to a controller, where the demand is compared to the actual ammonia flow. The resultant error signal is conditioned via proportional plus integral action and used to position the ammonia flow control valve.

The controller maintains a constant outlet NO_x by controlling the ammonia flow via an ammonia flow control valve. An emergency shut-off of ammonia flow is provided in the ammonia supply line. Any one of the following interlock functions, which are furnished to secure safe operation and prevent catalyst damage, will activate the shut-off valve.

1) Low inlet flue gas temperature
2) High inlet flue gas temperature
3) High ammonia dilution ratio to air

Dilution air supply

The dilution air flow to the vaporizer is set manually using a damper. The air flow rate is based on approximately 5% design ammonia dilution ratio at the maximum ammonia flow. At lower loads and NO_x levels, the ammonia concentration will decrease below 5%. The air flow rate signal is compared to the ammonia flow rate signal to yield the dilution ratio interlock for flammability limits.

Ammonia/air mixture supply

Mixing of aqueous ammonia with air is achieved within the vaporizer. The ammonia/air mixture flows into the distribution manifold, and is distributed to each injection pipe via supply headers. Each header contains a manual throttling valve and local flow indicator to ensure even distribution of the ammonia/air mixture to the injection pipes.

DAILY START/STOP OPERATION

In most applications, the combined cycle plant is required to come on line as quickly as possible but at the same time start the boiler in a manner that minimizes the amount of NO_x emitted to atmosphere. The SCR system can not be initiated until a minimum gas temperature is attained. Traditional drum type HRSG's are limited in their fast response and transient capability by the steam drums and associated water inventory and mass of metal which require heating. Using an OTSG and eliminating the drums and interconnecting piping, the fast start capabilities are vastly improved. The following start up procedure is typical of a daily cycling application with a dual pressure OTSG and LM6000 gas turbine.

GT/SCR Start-up

The gas turbine is initially ramped to a predefined load to initiate SCR operation. As indicated in Figure #5, the gas temperature upstream of the catalyst face determines the NOx removal efficiency. Although the optimal SCR gas temperature is around 700°F, higher or lower temperatures may still meet the required NO_x conversion levels since the NO_x levels on a lb/hr basis are lower at reduced gas turbine loads.

The gas turbine is initially ramped to approximately 800°F. As the gas turbine is ramped up, the exhaust gas energy will initially be absorbed by the lower tube rows upstream of the SCR catalyst. Due to the dry starting capability of the OTSG and absence of steam drums, the time required to reach the initiation temperature is minimized. SCR operation is started within approximately 5 to 8 minutes following gas turbine initiation.

The gas temperature into the SCR is monitored. When the gas temperature reaches the minimum allowed (450°F), ammonia is injected for NO_x control. Once the SCR is operational, OTSG steam production is initiated. The OTSG water ramp sequence can be started once the inlet gas temperature and stack exhaust temperature register 500°F and 350°F, respectively.

The OTSG high pressure start up sequence is given below.

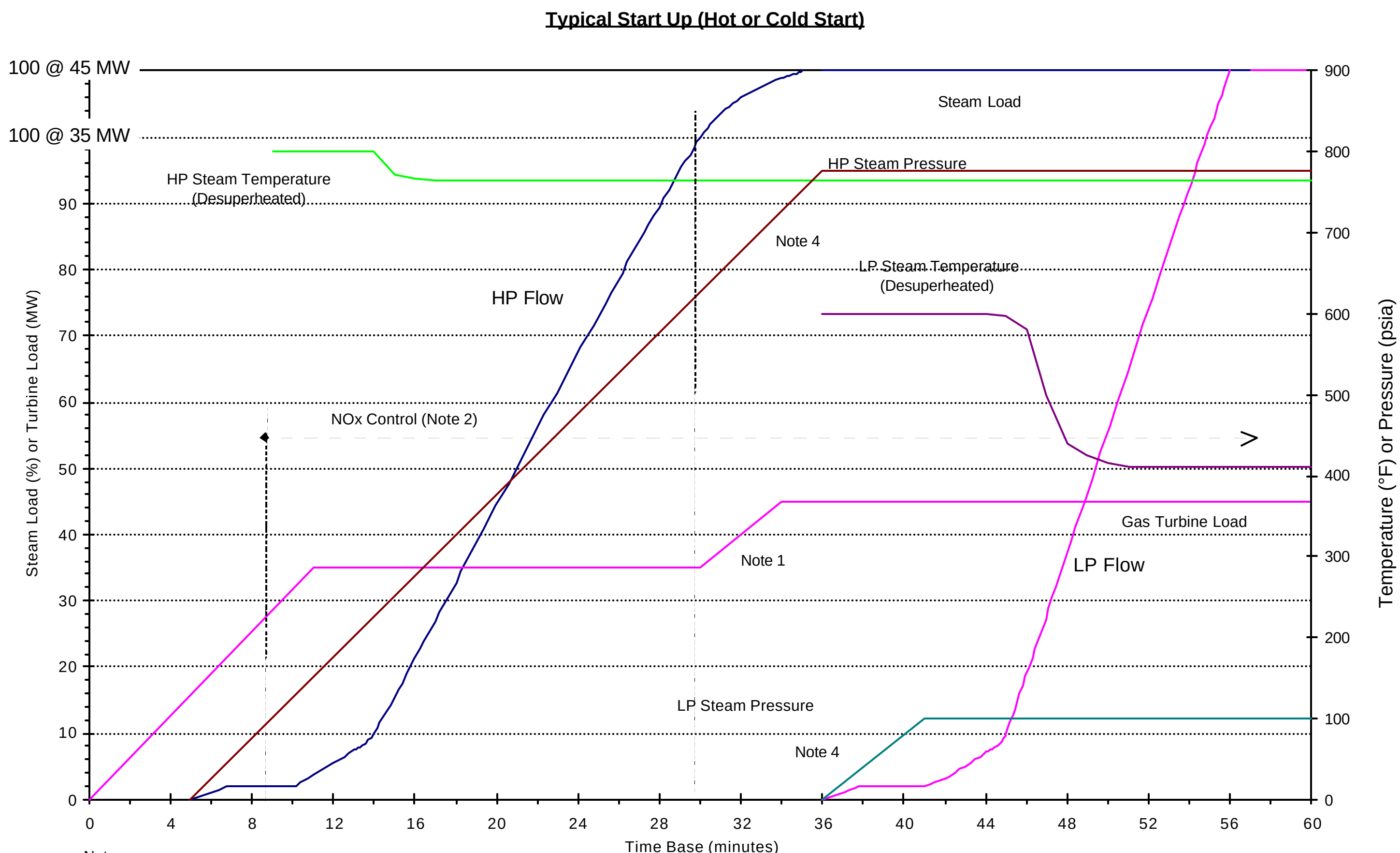
i) Ramp water flow at 1% of full flow / minute for 2 minutes
ii) Hold water flow steady for 3 minutes
iii) Ramp water flow at 2% of full flow / minute for 4 minutes
iv) Ramp water flow at 6% full flow / minute for 15 minutes.

The HP section of the OTSG attains 100% load in approximately 25 minutes.

As soon as the HP ramp is complete, the gas turbine load can be increased to full load. As the engine mass flow and temperature increases, the patented OTSG feedforward algorithms will anticipate the increased energy input and will signal the OTSG to increase the water flow. The OTSG will then ramp up to the new required water flow at 6% full flow / min to bring the flow in line with the flow required for steam temperature control. During this final gas turbine ramp, the gas turbine ramp is trimmed according to the gas temperature entering the catalyst.

The LP circuit ramp sequence can be initiated once the HP circuit has reached 100% flow. The LP sequence is the same as (i) to (iv) above and takes the same amount of time.

A typical GT/SCR/OTSG start up curve is provided below (Figure #10) indicating full load is achieved after approximately 50 to 60 minutes following gas turbine initiation. This applies for either a hot or cold start of the OTSG and SCR systems. This duration may be shortened in a hot start if a stack damper is used to maintain heat during the shutdown period.



Notes:
1. GT Ramp will be based on maintaining a pre-determined gas temperature into SCR. OTSG water flow is ramped as GT load increases (Maximum ramp rate is 6% / minute).
2. Ammonia can be injected once gas temperature entering SCR exeeds 500°F.
3. Time 0 is GT ramp start
4. HP & LP steam pressure rise at a rate of 25 psi / minute max

Figure #10 – Startup Curve for GT/SCR/OTSG System

PART LOAD OPERATION

Unlike traditional natural circulation or forced circulation HRSG's, the OTSG does not have a steam drum. Water enters at one end of the OTSG through the inlet header and exits the other end of the OTSG as superheated steam through the outlet header. The evaporator section is free to move throughout the bundle depending on the operational load. In traditional natural circulation (Figure #11) or forced circulation HRSG's, the steam drum forms a distinct boundary between the economizer, evaporator and superheater.

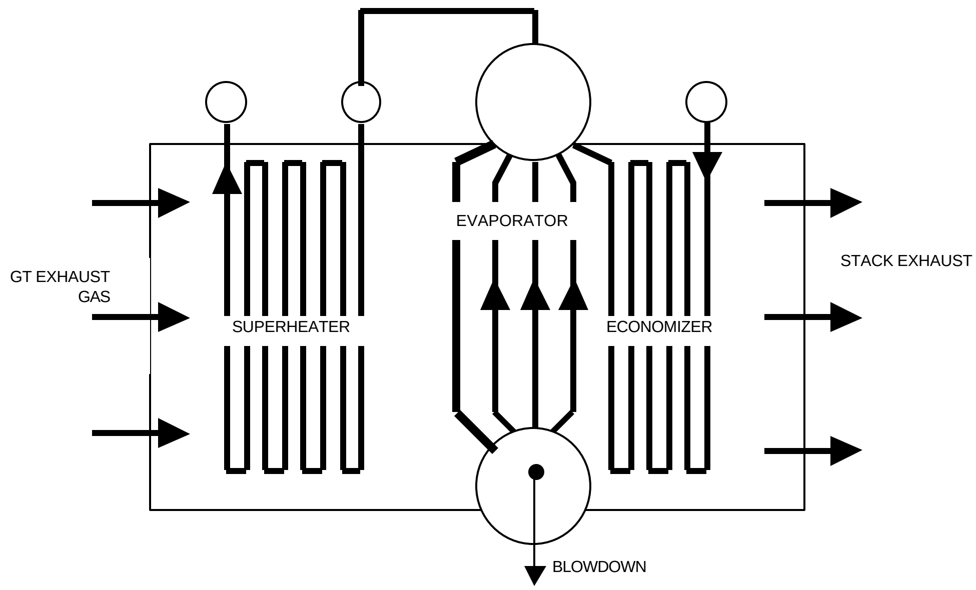


Figure #11 Drum -Type HRSG

Without a boundary for the steam generator, there is ultimate flexibility in steam production levels. This allows the OTSG to vary water/steam flow to maintain the required gas temperature entering the SCR catalyst section at off load cases.

This flexibility is indicated with the table below. Table #1 illustrates the ability of the gas temperature at a section of the OTSG to be controlled by modulating feedwater flow.

	Fired Full Load	Unfired Full Load	Unfired Part Load
Exhaust Gas Flow (lb/hr)	1,112,400	1,112,400	1,112,400
Gas Temperature (F)	839	839	839
Duct Firing Temperature (F)	1022	N/A	N/A
Stack Temperature (F)	316	332	346
Steam Flow (lb/hr)	200,409	139,750	119,000
Steam Outlet Temperature (F)	475	475	759
Gas Temp Into SCR (F)	690	613	694
	See Figure #12	See Figure #13	See Figure #14

Table #1 – Load Comparison for OTSG

For a fixed gas turbine load the OTSG can operate at part load conditions without the requirement for gas or steam bypassing. By throttling back the feedwater flow to the OTSG and desuperheating at the outlet header, the OTSG can adapt to wide load swings.

Assume the SCR is located in the OTSG bundle based upon the full load fired point of operation. The SCR would be located at a gas temperature of approximately 690 F where the SCR will operate at maximum efficiency (Figure #12).

During unfired full load operation, the SCR will now be located in a gas temperature zone of approximately 613 F (Figure #13), which is not at the maximum efficiency of the SCR. By reducing water flow to the OTSG, the gas temperature at the SCR can be increased to the maximum efficiency temperature of approximately 694 F (Figure #14).

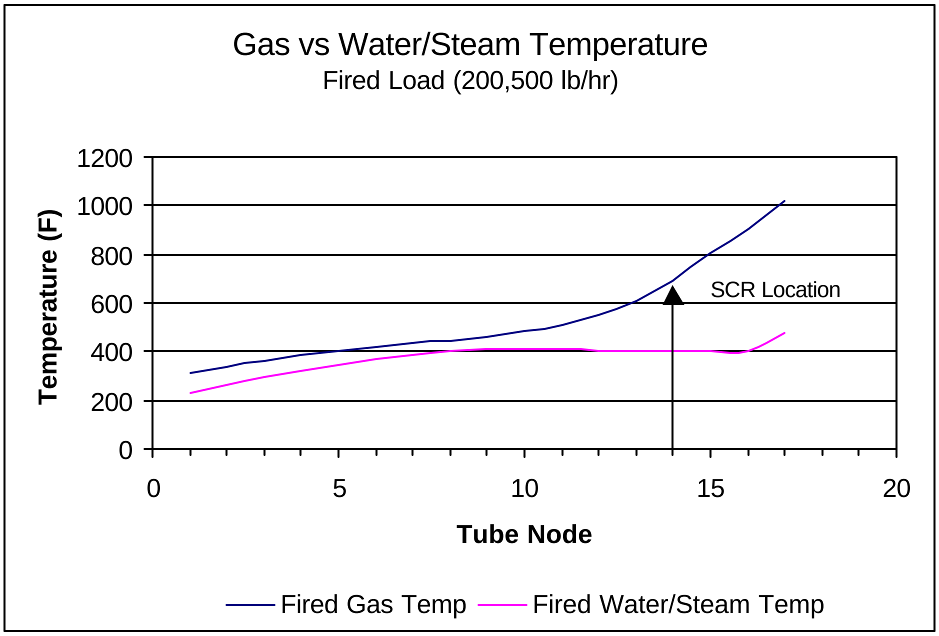


Figure #12 – Fired Full Load Operation

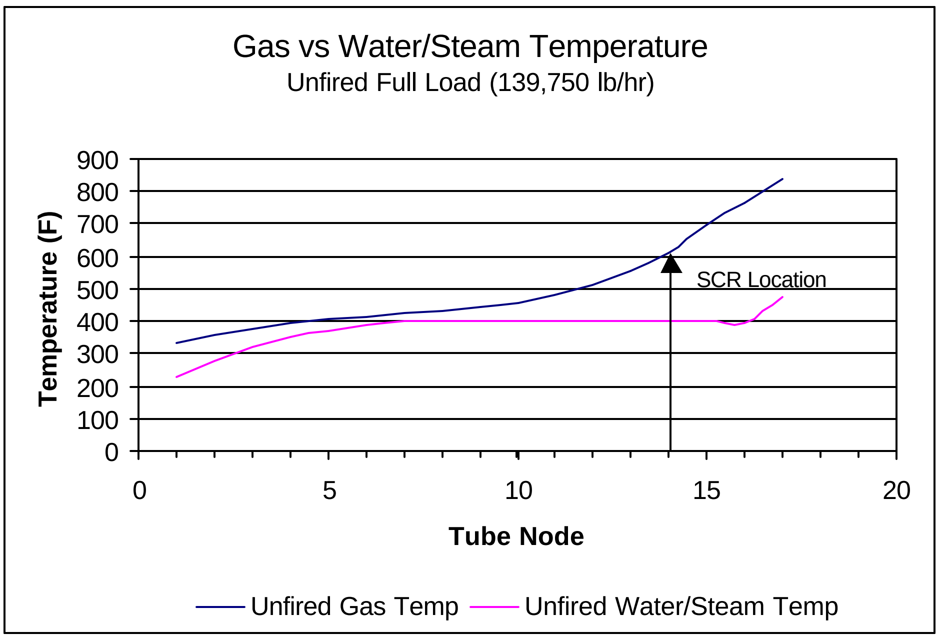


Figure #13 – Unfired Full Load Operation

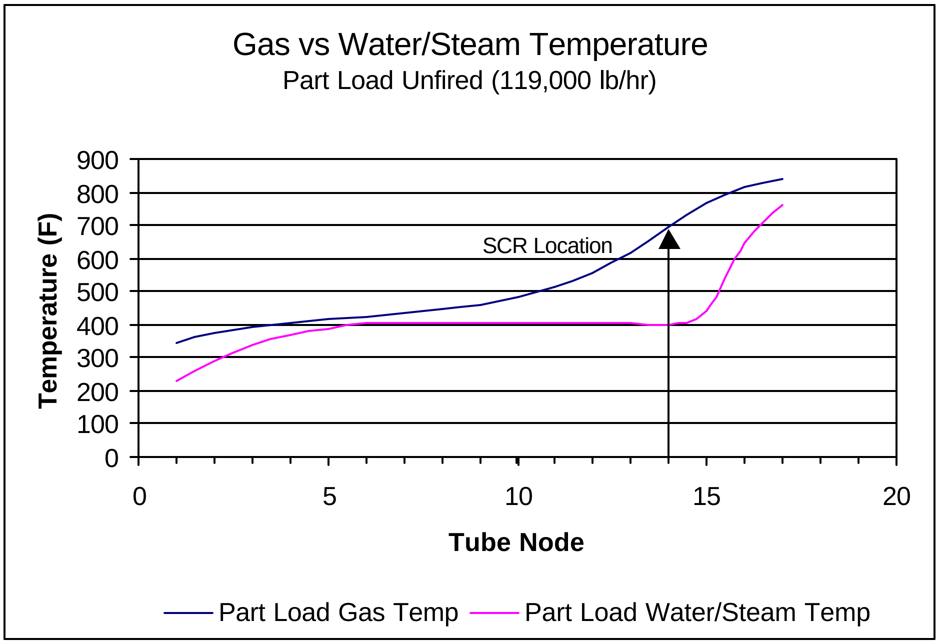


Figure #14 – Unfired Part Load Operation

CONTAMINANTS IN SCR APPLICATIONS

There are many sources of contaminants in SCR applications, which can cause premature corrosion of pressure part surfaces and ducting components. As described above, ammonia is injected into the exhaust gas as necessary to remove the NO_x compounds. This ammonia can combine with the sulfur in the exhaust gas to form ammonium sulphate and/or ammonium bisulphate. The type of contaminant formed depends on the amounts of ammonia and sulphur present in the exhaust gas along with the local temperatures. In most gas turbine combined cycles applications operating on natural gas with ammonia slip levels of 10 ppm or less, ammonium sulphate is the most common contaminant. In oil fired applications with increased levels of sulphur, ammonium bisulphate can precipitate onto the pressure parts. Depending on incoming fluid temperatures, sulfuric acid and ammonium hydroxide can also form. All of these contaminants must be considered in the selection of pressure part materials of the HRSG's.

PRESSURE PART MATERIALS FOR SCR APPLICATIONS

Standard materials of construction in the condensing section (fluid inlet temperature below water dew point) of OTSG's consist of Incoloy 825 tubing and 316 stainless steel fins. The stainless steel fins are bonded to the pressure parts in a proprietary brazing process using a BNi2 braze material. The chemical compositions of these materials are as follows:

	Incoloy 825	316 SS	BNi2
Nickel	38.0 – 46.0	11.0 –14.0	Balance
Iron	22.0 min.	Balance	3.0
Chromium	19.5 – 23.5	16.0 – 18.0	7.0
Molybdenum	2.5 – 3.5	2.0 – 3.0	n/a
Copper	1.5 – 3.0	n/a	n/a
Titanium	0.6 – 1.2	n/a	n/a
Carbon	0.05 max.	0.08 max.	0.06 max.
Manganese	1.0 max.	2.00 max.	n/a
Sulfur	0.03 max.	0.03 max.	n/a
Silicon	0.5 max.	0.75 max.	4.5
Aluminum	0.2 max.	n/a	n/a
Phosphorous	n/a	0.040 max.	n/a
Boron	n/a	n/a	3.2

All of these materials of construction are very resistant to sulphuric acid, ammonium sulfate, ammonium bisulphate and ammonium hydroxide.

SOOT REMOVAL

Various methods (water washing, CO_2 blasting) have been used with varying success to remove any deposits that do accumulate over time. While water washing can be used, the waste stream can be considered a hazardous chemical and can also corrode surfaces below the SCR housing.

Another option exists that is limited to the OTSG and its dry running capability. Dry running refers to the OTSG operating without water/steam flowing through the pressure parts. The result is the pressure parts heat up to local gas temperature. The advantages of dry running have been proven in liquid fired gas turbine applications such as diesel oil.

A series of tests were conducted on OTSG's in the early 1980's (ref. b). Following soot fouling tests in which soot was accumulated on the cold section of the OTSG, cleaning tests were completed. The cleaning tests involved running the OTSG at elevated gas temperatures without feedwater flowing through the OTSG. Dry running tests were run at 840 F for 60 minutes and 900 F for 60 minutes and 100 minutes. Heat transfer performance was fully recovered by performing a dry boiler burnoff at 900 F for 100 minutes.

Similar tests have been completed in an attempt to remove the corrosive products associated with SCR operation (ammonium sulphate and ammonium bisulphate). While gas temperatures of 800 F to 1000 F were used in the testing, current limitations of medium temperature SCR catalysts are in the range of 870 F to 900 F. Innovative Steam Technologies completed the testing using the services of Bodycote Materials Testing Canada Inc. located in Cambridge, Ontario, Canada. (ref. c)

Finned tubes were manually covered in mixtures of ammonium sulphate and ammonium bisulphate. The tubes were photographed before exposure, after exposure and after blowing with compressed air to remove loose deposits. Compressed air is used in lieu of water washing to eliminate the concern of corrosive mixtures depositing on the surfaces below the SCR housing.

Figures 15 shows photographs of tubes coated with ammonium sulphate before exposure for four hours at 1000°F, after exposure and after blowing with compressed air. It can be seen that the dry running and compressed air blowing was very successful at removing the ammonia sulphate deposits.

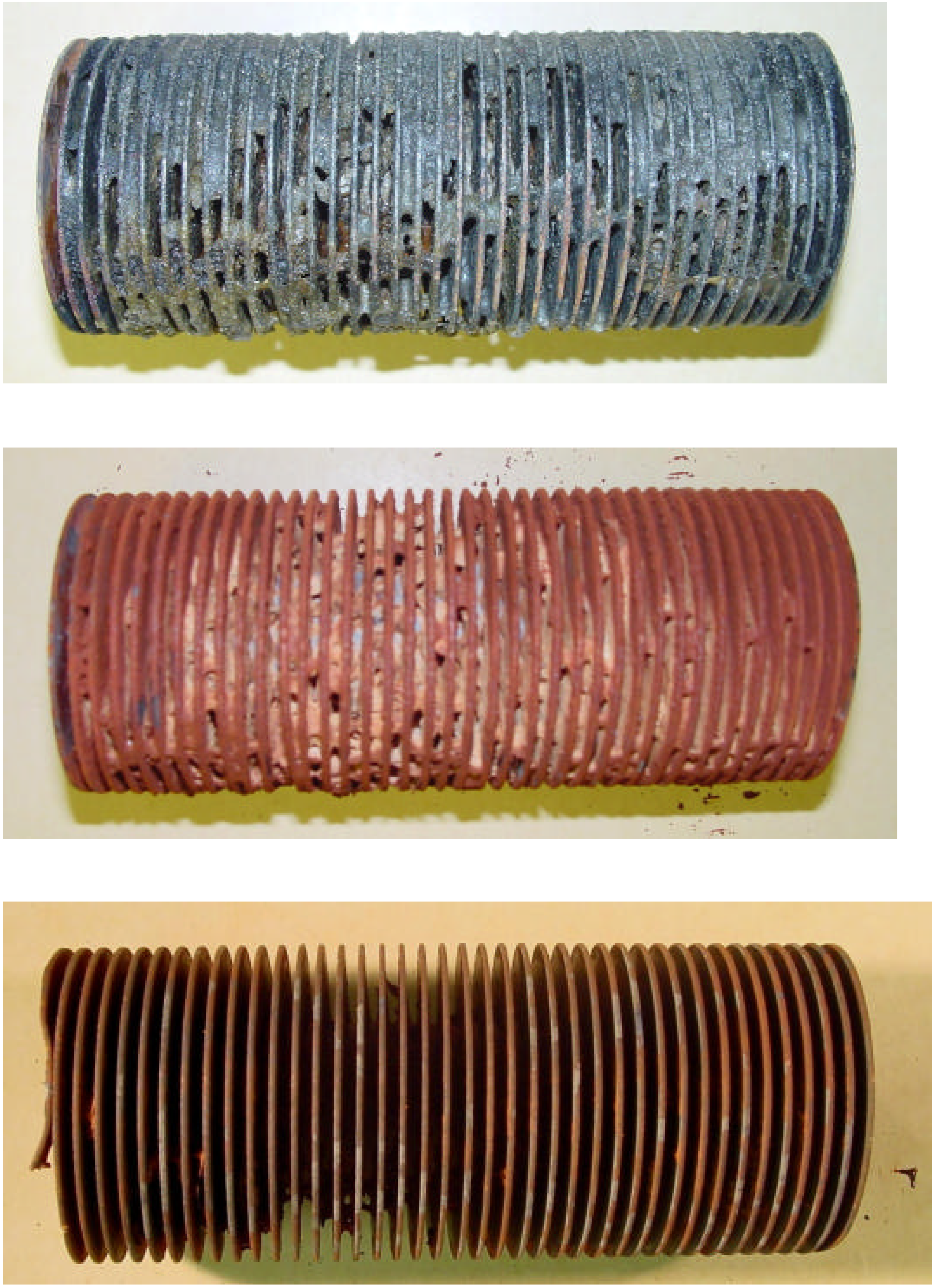


Figure 15: Tube coated with ammonium sulphate, after heating at 1000° F for four hours and after blowing with compressed air.

Similar results were obtained with dry running at 900 F. Figure 16 shows photographs of tubes coated with ammonium sulphate before exposure for four hours at 900°F, after exposure and after blowing with compressed air.

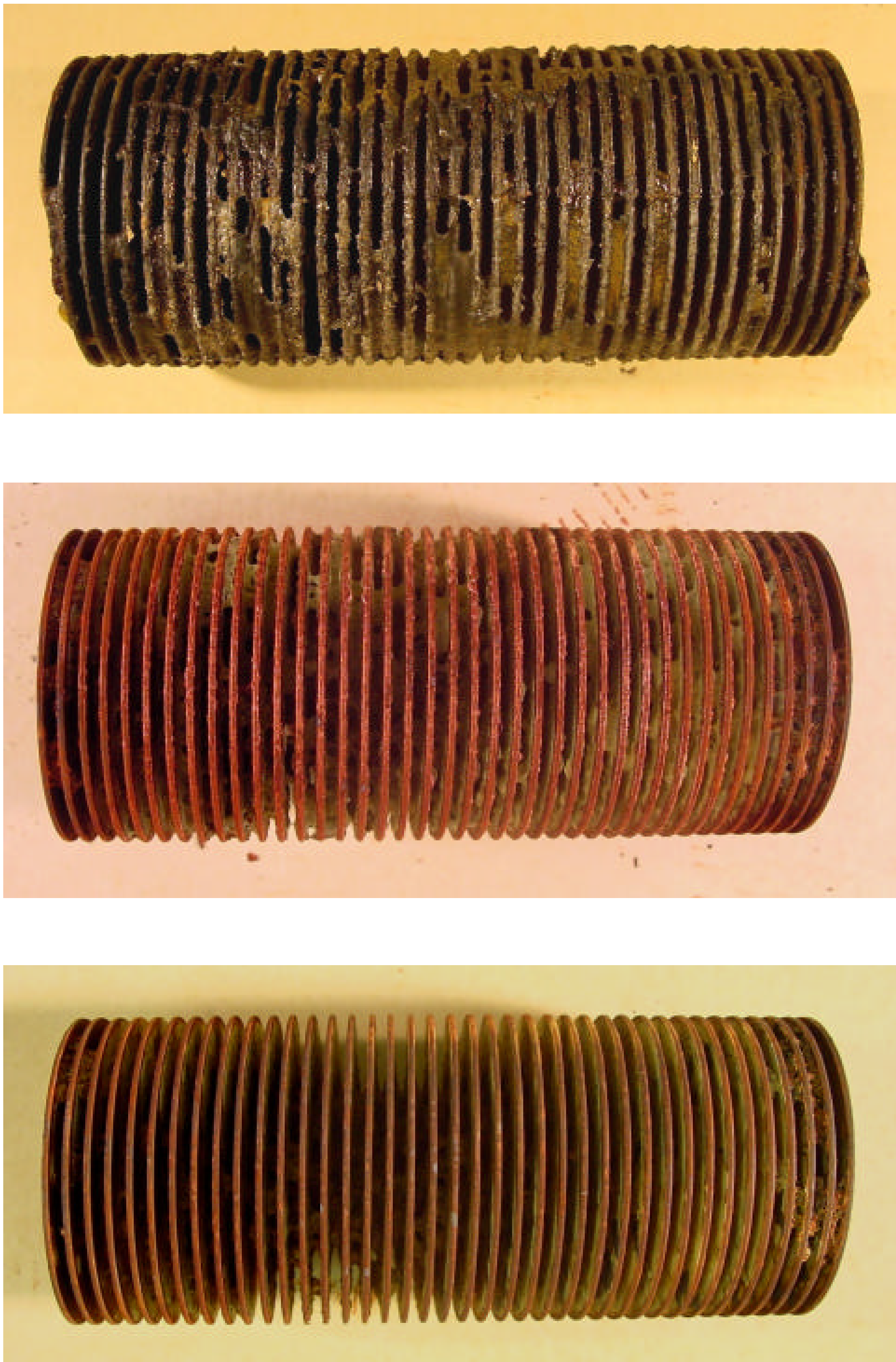
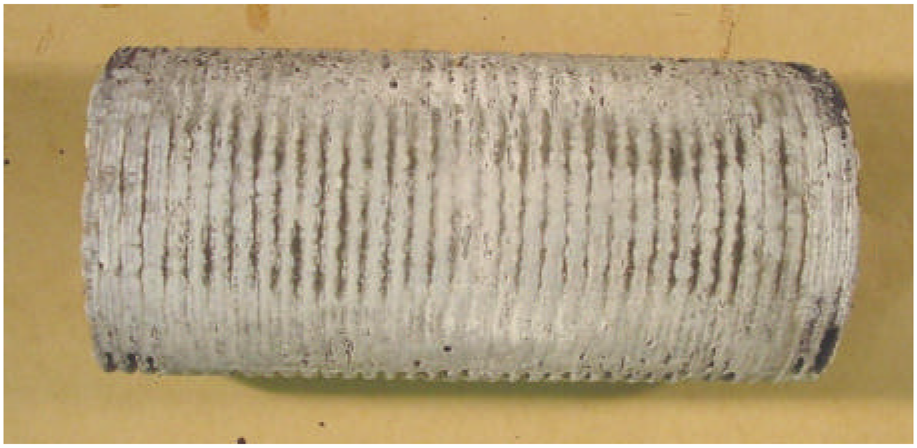


Figure 16: Tube coated with ammonium sulphate, after heating at 900° F for four hours and after blowing with compressed air.

Figure 17 shows photographs of a tube coated with ammonium bisulphate before exposure for two hours at 1000°F, after exposure and after blowing with compressed air.



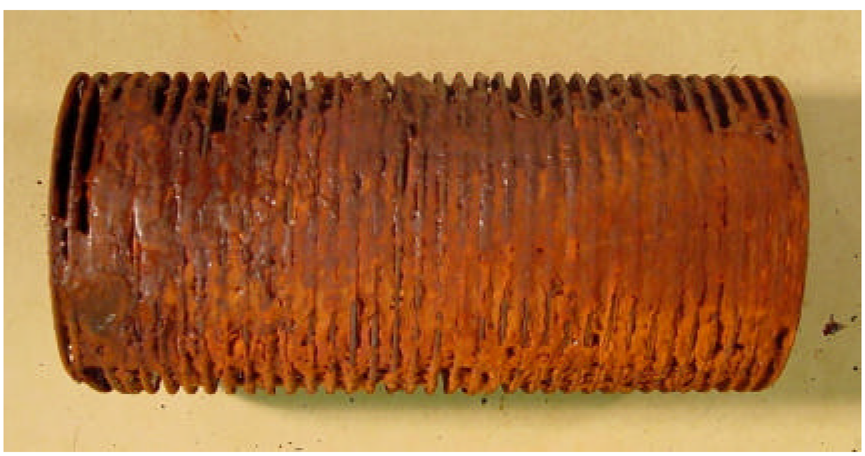


Figure 17: Tube coated with ammonium bisulphate, after heating at 1000° F for two hours and after blowing with compressed air.

The ammonium bisulphate appears to be more difficult to remove. This may be partly due to the selection of carbon steel finned samples for the testing. Actual units have been supplied with stainless steel fins. The yellow residue remaining on the samples at 900°F and 1000°F are likely ferric sulphate or iron disulphide which would be unaffected by the exposed temperatures. The physical properties [Lange's Handbook of Chemistry, 12^{th} Edition, 1979, Table 4.1] of ammonium sulphate, ammonium bisulphate, ferric sulphate, sulphur and iron disulphide are listed below:

Compound	Colour	Melting Point	Boiling Point
Ammonium Sulphate	colourless	d 230°C (446°F)	
Ammonium bisulphate	colourless	146.9°C (~297°F)	350°C (662°F)
Ferric sulphate	yellow	d 1178°C (~2156°F)	
Sulphur	yellow	115°C (239°F)	445°C (833°F)
Iron disulphide	yellow	1171°C (~2140°F)	

Heating the tubes to 900°F for a period of up to four hours followed by blowing with compressed air appears capable of removing the bulk of the ammonium sulphate deposits. Ammonium bisulphate deposits seem to be more difficult to remove with the dry running procedure. Frequent cleaning during scheduled shutdowns may be required to ensure the deposits do not accumulate.

A procedure is being developed and operating experience will be available in the next few months on the effectiveness of dry running to remove deposits.

CONCLUSION

While traditional SCR applications for combined cycle power plants have used vertical tube/horizontal gas flow drum type HRSG's, the horizontal tube/vertical gas flow OTSG provides many operating advantages. Advantages exist in start up times, part load flexibility and in removal of soot deposits.

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