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# FAILURE AND REPAIR OF THE SECONDARY REFORMER – AN EXPERIENCE (a)

V. K. Bali\*, Indian Farmers Fertiliser Cooperative Limited (IFFCO), India

## 1. Summary

*The paper addresses the failure of large magnitude experienced in the Secondary Reformer of an Ammonia Plant after giving satisfactory service of about 13 years. Massive in-situ repair and the various examinations to establish the probable cause of the failure have also been discussed.*

## 2. Introduction

Located at Bareilly Uttar Pradesh in India, Indian Farmers Fertiliser Cooperative Ltd, operates two ammonia plants, each with name plate capacity of 1350 MTPD of ammonia. Both of these plants have been designed based on Haldor Topsoe technology with steam reforming of natural gas and/or naphtha.

Ammonia-I was commissioned in the year 1988 and has been operating normal since then without any major breakdowns.

Failure of large magnitude has been experienced in Oct. 2001 in secondary reformer of Ammonia Plant-I, after giving 13 years of service.

The paper highlights the incident of the failure, subsequent detailed inspection to establish the cause and extent of damage and in-situ repair of large magnitude in secondary reformer.

## 3. Secondary Reformer

The secondary reformer forms an integral part of the synthesis gas generation section of a conventional ammonia plant, and performs two useful functions within the ammonia production process. Firstly it is the point of introduction of the elemental nitrogen from the air, from which the product ammonia is synthesized and secondly it achieves a very high methane conversion, giving a low methane content gas for further processing before the final ammonia synthesis reaction.

Functionally, the secondary reformer consists of two distinct regions, the combustion zone and the fixed catalyst bed. The combustion is non-premixed, and since the feed gas is above its auto-ignition temperature ignition occurs automatically as the two streams mix.

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\*Executive Director (nitrogenous fertilizer)

Email: [vkbali@iffco.nic.in](mailto:vkbali@iffco.nic.in)

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## 4.2 The Process

Reformed gas from the primary reformer enters secondary reformer at the top portion. The gas enters at 800°C and 32 kg/cm<sup>2</sup>g and flows down through the annular space. The gases are directed downwards through a deflector and guide ring to enter the combustion zone of the reformer. Preheated air at 550°C is introduced to the air mixer burner. The process gas passing downward, comes in contact with the air jets. The air jet entrains the process gas on top and bottom side. It also entrains a large quantity of recirculating fluid, flowing upwards from the centre of the bed, which acts as a flame stabiliser ensuring ignition of process gas and air mixture. After the ignition, the hot gases at a temperature of about 1200°C pass through the catalyst bed.

The combustion reaction supplies the heat required for the endothermic reforming reaction that takes place in the catalyst bed. The temperature at the outlet of reformer is about 990 °C and pressure is 31 kg/cm<sup>2</sup> g. Methane at the exit is 0.3 mole %.

## 4.2 The Details

The secondary reformer for the plant was supplied in 1986 by Hyundai Heavy Industries, South Korea. The reformer operates under the most severe conditions of the process having a pressure of 32 kg/cm<sup>2</sup> (design shell pressure 38 kg/cm<sup>2</sup>) and extreme temperature reaching to 1200 deg. C. The normal shell temperature is about 160 deg. C. with design temp. of 350 deg. C. The shell of the reformer is made of low alloy steel CS SA204 Gr B (C-1/2 Mo) having a thickness of 80 mm and conical portion has a thickness of 92 mm. The thickness of neck portion and bottom dished end is 50 mm and 92 mm respectively. Due to high operating temperature. The shell is refractory lined from inside to minimise the heat loss and to keep the shell temperature less than 350 deg. C. Figure 1 shows the internal details of secondary reformer. Further, to warn against any possible refractory failure and high shell temperature, the shell is coated with Thermo Indicative Paint which changes colors at high shell temperature. Figure 2 shows the temperatures profile across the cross section of refractory and shell of secondary reformer.

### 3..1 Packing Details

Packing details from bottom to top of secondary reformer are as given below:

#### **Catalyst support:**

The catalyst support in the secondary reformer is a high alumina firebrick diffuser cone. Around the diffuser cone alumina lump of size ranging from 100-200 mm at the bottom and 50-100 mm at the top are placed. Above this to a height of 300-mm alumina lumps of size 25-50 mm are placed.

#### **Catalyst:**

Above alumina lumps, 39 m<sup>3</sup> of nickel based catalyst is charged. The height of catalyst bed is 2800 mm.

#### **Alumina lumps:**

Above the catalyst bed there is 250 mm high packing of 25-50 mm alumina lumps.

**Distribution tiles:**

On the top of alumina lumps, there is a 50-mm thick hexagonal refractory alumina tiles to distribute the gases.

In the middle of this arrangement of tiles, 37 hexagonal tiles are without holes. Around this, are arranged 1150 pieces of hexagonal tiles with nine hole each. On the periphery 92 tiles are arranged depending on the space left after arranging the hexagonal tiles.

**Circle bricks:**

Around this set of hexagonal tiles, 60 standard circle bricks are placed. The circle bricks are fitted tightly against the reformer lining.

**3..2 Refractory Lining:**

The first layer in contact with secondary reformer vessel is 200 mm thick insulating castable refractory (50-60% alumina). The next layer, which is in contact with insulating layer on one side and the high temperature process gas on the other side, is high alumina castable refractory (94% alumina). All these refractory are held together by stainless steel anchors which are welded to the vessel (**Refer Figure 3**).

**4. History of Secondary Reformer**

Secondary reformer of Ammonia-I has been operating satisfactorily since commissioning in the year 1988 without any major breakdown. Brief history of the vessel describing the repairs carried out on different occasions is as given below:

**4.1 The Refractory**

Refractory of conical and neck portions was inspected during every turnaround. Complete refractory of the secondary reformer was inspected during 1990,1992 and 1995 after emptying out all the catalyst. Most of the times the condition of refractory was found to be alright and only minor repair work was carried out except in 1992 as described below:

In 1992 the topmost ring of conical portion was found badly damaged and hot face refractory of about half of the conical portion had fallen down. There were five vertical cracks about 5-6 mm wide in topmost layer of cylindrical portion and there were gaps behind every segment of hot face refractory in conical portion. Total hot face refractory in the conical portion was replaced. Refractory was repaired in topmost segment (top 900 mm) of cylindrical portion and in top neck up to 200 mm from bottom of the neck.

## 4.2 The Catalyst

The catalyst RKS-2 7H (Vol-39m<sup>3</sup>) supplied by HTAS was charged in secondary reformer when the plant was commissioned in 1988. During 1990, 1992 and 1995 all the catalyst was removed and screened for dust removal to achieve reduction in pressure drop. Complete charge of original catalyst was replaced with new catalyst C-14-2 supplied by UCIL, in August 98 after achieving longevity of around 10 years.

## 4.3 The Air Mixer

The only major maintenance carried out on the air mixer was during 1992 when the mixer was found in heavily damaged/eroded condition. The holes of the air mixer had been enlarged and were having multiple cracks. The mixer assembly was cut and spare assembly was welded.

## 5. Failure of Secondary Reformer

### 5.1 Description of incidence

Ammonia-I was running normal at production rate of 1500 MTPD when on the evening of 18th Oct. 2001, gas leakage from one of the longitudinal weld joints in the conical portion of secondary reformer was observed. On close observation, it was found that the gas was leaking from a 10mm long crack and a pinhole at a distance of 10mm from the crack on the edge of one of the longitudinal weld seam of the cone. **Figure 4** depicts the various longitudinal and circumferential weld joints of secondary reformer.

Considering the critical process conditions of very high temperature and the process gas containing hydrogen, the Ammonia-I was immediately shut down for thorough inspection and repair.

### 5.2 Description of Failure

Initial inspection immediately after shutdown:

#### 5.2.1 Inspection carried out from outside

- **Magnetic particle test:** On inspection by magnetic particle testing, a crack of approximately 65-mm length (10 mm surface and 55 mm sub surface) was detected on the longitudinal seam L-1.
- **Ultrasonic testing:** On inspection by ultrasonic testing (UT) from outside, the length of the crack with varying depth was found to be around 1650 mm on the longitudinal seam L-1.

After having detected a long crack on L-1 seam, the other two longitudinal petal joints (L-2 and L-3) of the conical shell were also checked by UT from outside and similar cracks were found. The length of cracks was detected to be 1350 mm on L-2 seam and 2360 mm on L-3 seam with varying depth.

### 5.2.2 Inspection carried out from inside

After cooling of the secondary reformer, the refractory from the conical portion was removed for detailed inspection from inside. The crack on L-1 seam was visible with the naked eye to the same length as was indicated by UT test from outside. The other two longitudinal petal joints (L-2 & L-3) of the conical shell were also checked from inside after removing refractory and similar cracks were found as was indicated by UT test from outside.

### 5.2.3 Detailed inspection after removal of refractory

Results of inspection (DP/MPI/UT) on various weld seams after removing refractory from inside the vessel are summarised as below:

<b>Weld seam No. L-1</b>
<ul style="list-style-type: none"> <li>1650 mm long crack at weld edge with depth varying from 10 mm to 92 mm from inside.</li> </ul>
<b>Weld seam No.L-2</b>
<ul style="list-style-type: none"> <li>1350 mm long crack at weld edge with depth varying from 12 mm to 62 mm from inside.</li> </ul>
<b>Weld seam No. L-3</b>
<ul style="list-style-type: none"> <li>2360 mm long crack at weld edge with depth varying from 12 mm to 62 mm from inside.</li> </ul>
<b>Weld seam No.L-4</b>
<ul style="list-style-type: none"> <li>A 65 mm long crack observed in UT at a distance of 290 mm from the lower edge of the weld seam. The same was confirmed by DP/MPI from inside. The depth of the crack was 6 mm to 7 mm.</li> </ul>
<b>Weld seam C-3</b>
<ul style="list-style-type: none"> <li>39 Nos transverse micro cracks were observed during DP test from inside on the weld and Heat Affected Zone. Depth of cracks was 5 to 6 mm.</li> </ul>
<b>Weld seam C-4</b>
<ul style="list-style-type: none"> <li>20 Nos circumferential cracks of varying length on the upper edge of the weld seam were revealed during DP test from inside which are distributed all along the circumference. Length of the cracks varied between 60 mm to 1020 mm totaling to 5045 mm. Many of the cracks were joined together by subsurface cracks as revealed during further testing by MPI. Similarly 16 Nos circumferential cracks were also observed at lower edge of the weld seam during DP test. The length of the cracks varied from 30mm to 1110 mm. The depth of these cracks ranged between 15 to 30 mm on average as estimated by UT from inside using angle probe. In addition to above, several fine transverse cracks were also observed on the weld. During UT of the circumferential cracks, the depth was found to be varying between 8 mm to 12 mm from inside.</li> </ul>
<b>Parent Metal</b>
<ul style="list-style-type: none"> <li>Several branched cracks observed on the internal surface of the shell which propagated to different depths varying from 6 mm to 15 mm. These branched cracks were mainly between L seams of the cone and near the C-3 and C-4 seam on knuckle area.</li> </ul>

From the above observation, it was evident that the failed weld joints (L-1, L-2, L-3 & C-4) had cracks from inside at the weld edge i.e. junction of the weld seam and the parent material in the HAZ area. However the upper circular weld seam C-3 had only transverse cracks and the lower circular seam C-4 had developed some transverse cracks in addition to major longitudinal cracks on the upper and lower weld edges. Photographs (PH-1, PH-2 & PH-3) show the cracks on longitudinal seams and photographs (PH-4 & PH-5) show the cracks on C-4 seam and the parent metal.

#### **5.2.4 Inspection after dehydrogenation of long seams**

Dehydrogenation and stress relieving of long seams (L-1, L-2 and L-3) was carried out for improving the weldability of joints. Subsequent to dehydrogenation treatment (DHT) of long weld seams at 620 Deg C, the original cracks further increased to 3135 mm, 2630 mm and 3135 mm respectively out of total length of 3250 mm of each seam. Figures 5 and 6 depict sectional view of the cone indicating cracks on longitudinal seams before and after dehydrogenation. The number of transverse cracks on C-3 and C-4 weld seams increased. The length of circumferential cracks on the edges of the C-4 weld also increased as some of the adjacent cracks joined together and few new cracks developed. Also several clusters of branched cracks were observed on the cone parent metal as well. The concentration of cluster of cracks was more in the lower 'knuckle' portion of the cone about 680 mm height above the C-4 weld. Also cluster of transverse cracks were observed in a 200 mm wide band below the C-4 weld. Average depth of cracks was 6-25 mm. Figure 7 shows the cracks on longitudinal weld seams L-1, L-2 and L-3 and Figures 8, 9 and 10 show the cracks on circumferential seams C-3, C-4 and on the parent metal in the conical portion of secondary reformer.

### **6. Repairs of secondary Reformer**

#### **6.1 Secondary Reformer Shell**

After initial inspection, the actual repairing job could be started after about 8 days from plant shutdown with the start of heat treatment for dehydrogenation. It was planned to do the dehydrogenation at higher temp of about 650 °C in place of temperature of around 350 °C normally used for dehydrogenation in order to improve the weldability of material.

Total affected area was considered for dehydrogenation. Complete heating, soaking and cooling cycle of about 99 hrs followed. During the dehydrogenation, the load of transfer line and neck portion of secondary reformer was supported on a mobile crane with chain blocks to facilitate free movement (thermal expansion) of the conical portion during heating. To avoid any undue stresses on weld joints between the transfer line and the vessel, the transfer line was jacked from bottom in proportion to the thermal expansion of the vessel during heating.

After completion of dehydrogenation, NDT inspection (full DPT and random MPT) of complete cone was taken up. It was observed that length of cracks on L-seams (L-1, L-2 and L-3) had increased covering almost full length. In addition to this, minor branched cracks were also found on the parent metal of cone.

The extent of damage and the repair job requirement was firmed up by detailed inspection carried out after the dehydrogenation.

Though the defects were mainly from inside but considering the major repairs requirement on the longitudinal seams it was decided to cut open all the weld seams to full thickness and carry out the welding from outside on account of difficulty in welding from inside in confined space and high temperature conditions. Figure 11 depicts the details of weld groove design adopted for repair.

Repair job was started with gas cutting of weld seams (L-1, L-2 and L-3) by automatic air gouging machine and weld edge preparation by grinding. After cutting, the cut edges and the adjacent parent metal surfaces showed that cracks are extended into the parent metal also. These cracks were ground off till there was no further indication of any remaining crack.

Fitting of back strips, compression plate, moon plate and stay pipes was carried out from inside on all three L seams (L-1, L-2 and L-3) to facilitate the welding up to depth of 50 mm from outside and to avoid distortion during welding (Refer Figure 12).

The conical portion was preheated up to 200°C before the start of welding as per the welding procedure. Buttering of 3 mm thick layer was applied on the grooves from outside to establish the weldability and achieve a homogeneous defect free surface for further weld deposition. MPT of buttering layer was done to confirm that it was defect free.

All the three grooves for L-1, L-2 and L-3 were welded by Manual Metal Arc (MMA) procedure up to 50 mm depth from outside using stringer bead technique. After welding, intermediate stress relieving of L-seams was carried out at 620-650 °C temperature with a soaking period of 1 hour. Stay pipes, moon plates and compression plates were removed after completion of 50 mm welding from outside.

Back strip was also removed by gouging, grinding and welding was carried out from inside to fill up the grooves. Subsequently DP test from inside and outside was done. Along with jobs on L-1, L-2 and L-3, grinding and welding of other parent metal cracks were done from inside of the vessel. Gouging, grinding and welding of longitudinal and transverse cracks of circumferential welds C-3, C-4 and heat affected zone were carried out simultaneously.

On completion of all welding jobs as described above, post weld heating of the cone was done at 300-350°C. After cooling down of the cone, radiography of weld joints was done.

After verifying the soundness of weld joints, balance outside welding was done followed by post weld heat treatment at 300-350°C. Finish grinding was done on all the weld joints for NDT.

After finish grinding DP & UT of all repaired joints were carried out from outside and inside of the secondary reformer. Final stress relieving was done at a temperature of 600-650°C.

Finally after stress relieving, the detailed inspection (PT, UT and hardness tests) of the complete repaired area were carried out and found satisfactory.

## **6.2 Refractory Lining**

Considering the criticality of refractory lining as a safeguard for shell against high temperature, the procedure for refractory lining was finalized in consultation with the experts in the field. External agencies were involved for carrying out the application along with technical assistance and supervising the refractory lining job.

Refractory lining job was carried out in top neck, conical portion and 450 mm of cylindrical shell and 800 mm inside the transfer line. Total job was carried out in eight stages for cold face refractory (200 mm thick layer) and another eight stages for hot face refractory (100 mm



thick layer) (Refer Figure 13). Refractory lining and dry-out of top dished end of secondary reformer was done separately.

Additional old hot face refractory lining to the extent of 125-150 mm (vertical height) was removed to make tongue and groove joint between old and new refractory. Complete cleaning of old refractory and the parting plane of old and new refractory was carried to achieve error free refractory surface. Casting of cold face refractory was carried out first and hot face refractory was applied over the cold face refractory layer after natural cooling of first layer. Studs were fixed to the bush by threading and tack welding. The tips of studs were wrapped with PVC tape and bituminous point was applied on the studs for expansion clearance. Tape was also wrapped on the retainer ring for clearance.

After casting cold face refractory up to 300 mm below the neck it was decided to complete hot face layer of lower portion first since further application of cold face refractory in neck portion would restrict the movement of men and material. Accordingly stud tips were opened, V portion of anchors was welded, PVC tape wrapped on V-tips, bituminous applied on the V portion and casting of the hot face layer started. After completion of job up to neck, the casting of refractory in neck and other areas was taken up in similar manner.

Total job was carried out in stage wise manner starting from the bottom using original available steel shuttering of 6 mm thick plates and 40 x 40 mm angle after modifying to meet the specific requirement. However during execution of jobs, it was felt that use of heavy metal shuttering within a restricted space was not the ideal choice for maintaining precise lining thickness as well as in controlling of leakage of water from the castable mix.

Total consumption of cold face refractory (200 mm thick layer) was around 16 MT and that of hot face refractory (100 mm thick layer) was around 17 MT.

The hot face refractory surface was finished by filling the gaps at joints between different stages and chipping of refractory wherever spilled out. Hot face refractory in neck portion required chipping thickness to achieve ID of 1080 mm. The cracks of old lining were patched using Tabcast-94 castable.

Hot curing of refractory was carried out after complete application of both cold face and hot face lining. A burner was provided at the bottom of secondary reformer and natural gas was used as fuel in the burner. A chimney was provided at top of secondary reformer to vent out the flue gases. The steps in the hot curing included rise of temperature up to 560 °C in steps with soaking in between followed by controlled cooling up to 150 °C and then natural cooling as per the laid down procedure. Thermocouples were provided for continuous monitoring of temperature during curing. The only difficulty experienced during refractory lining job was during removal of shuttering which was stuck to the refractory surface of hot face lining.

The total repair of secondary reformer comprising of i) Inspection, ii) Heat Treatment iii) Shell Repair and iv) Refractory lining, as carried out at various stages are summarized below:

### INSPECTION

- Initial inspection immediately after shutdown (without breaking refractory) and subsequent refractory removal from inside.
- a) Inspection carried out from outside
  - Dye penetration test
  - Magnetic particle test.
  - Ultrasonic testing
  - Inspection carried out from inside
  - Visual inspection
  - Magnetic particle test (MPT)
  - Dye penetrant test (DPT)
  - Ultrasonic flaw detection (UFD)
- Inspection after dehydrogenation treatment to establish the final welding requirement.
  - Dye penetrant test (DPT)
  - Ultrasonic flaw detection (UFD)
- Inspection after buttering of 3mm thick layer of L-1, L-2 & L-3
- MPT of buttering layer at 200°C to establish the weldability and to achieve a homogeneous defect free surface for further weld deposition.
- Inspection after filling 50mm depth of weld groove.
  - Intermediate Stress Relieving.
  - DPT after grinding
- Radiography (RT) of weld joints (L-1, L-2 & L-3) after completion of 50mm welding from outside and complete welding from inside.
- Inspection after completion of welding and post heat treatment.
  - DPT & UT from outside
  - DPT & UT from inside
- DPT & UT of all repaired 'L' & 'C' seams after final Stress Relieving and Hardness testing

### HEAT TREATMENT

(Coils and thermocouple arrangement for heat treatment are depicted in Fig-14 & 15)

- Dehydrogenation after initial inspection at a temperature of 620 – 650° C with 1.5 hrs soaking.
- Preheating up to 200°C before starting any welding job.
- Post weld heating up to 300-350°C after each stage of welding for 3 hours.
- Intermediate stress relieving of L-1, L-2 & L-3 after 50 mm welding from outside and weld edge preparation from inside at a temperature of 620- 650 °C for period of 1 hour.
- Cooling down to facilitate inspection after each stage of welding.
- Final stress relieving at 600-650 °C after completion of all welding jobs with 2.5 hours soaking time and subsequent controlled cooling.

### REPAIRS

- Gas cutting of weld seam (L-1, L-2 & L-3) by automatic air gouging machine and weld edge preparation by grinding.
- Fitting of back strips, compression plate, moon plate and stay pipes to avoid distortion of cone during welding.
- Buttering of 3 mm thick layer at 200°C from outside
- Welding by Manual Metal Arc (MMA) procedure up to 50mm depth from outside on L-1, L-2 & L-3 after preheating up to 200 °C followed by intermediate stress relieving.
- Removal of stay pipes, moon plates, compression plate after welding of 50 mm depth from outside and post weld heating up to 300-350 °C.
- Back strip gouging & grinding.
- Welding from Inside by Manual Metal Arc (MMA) procedure after preheating up to 200 °C.
- Gouging, grinding & welding longitudinal and transverse cracks of C-3 & C-4 weld and HAZ.
- Grinding and welding of other parent metal cracks on cone away from the weld.
- Balance welding from outside of L seams after preheating up to 200 °C.
- Finish grinding of weld surface from inside and outside for NDT (DPT, UT & Hardness) after completion of all welding jobs & final stress relieving.

### REFRACTORY LINING

- Refractory lining job was carried out in top neck, conical portion and 450 mm of cylindrical shell and 800 mm inside transfer duct.
- Removal of additional hot face refractory lining of 150 mm to make tongue and groove joint.
- Fixing of studs in the bushes by threading and tack welding.
- Application of cold face refractory in cylindrical and conical portions up to 300 mm below neck.
- Welding of V-portion of anchors.
- Application of hot face refractory in cylindrical and conical portions up to 300 mm below neck after natural cooling of cold face refractory
- Application of cold and hot face refractories in balance areas of neck, cone and transfer line.
- Finishing of hot face refractory surface.
- Hot curing of refractory.

### 6.3 Resource Mobilisation

Initial inspection of the secondary reformer revealed that there was extensive damage in the conical portion of the equipment and the same shall involve detailed inspection to ascertain the extent of repairs required, machining, heat treatment and refractory lining jobs.

It may be noted that there was no spare material available on-site, when the incident occurred, either for repair of the shell or for the refractory lining, all of which was to be arranged from outside to enable the job to be carried out.

Keeping in view the volume of job a separate site office was created with availability of engineers and other technical staff on round the clock basis. The job was monitored at highest level at plant as well as corporate office.

Outside parties were mobilized for supply and installation of refractory, supply of welding electrodes, DP test material, skilled manpower, hiring of radiography equipment, material and manpower for heat treatment, etc. Experts were contacted for carrying out the diagnosis and supervision of repairs.

Total repairing job was carried out involving manpower from different disciplines. In the Mechanical discipline 1500 man days of supervisory staff, 670 man days of welders, 200 man days of fitters and fabricators and 725 man days of riggers were utilized. At a time six welders (two on each L-seam) were involved in welding.

In the Inspection discipline a total 400 man days were utilized which include the man hours of inspection staff from other fertilizer units also.

In the Civil discipline 200 man days of both supervisory and subordinate staff were utilized for removal and installation of refractory.

The Electrical discipline personnel were utilized for providing lighting and other power connections for heat treatment, welding machines, grinders etc.

12 welding machines, 300 sanding discs, 300 grinding wheels, 2108 kg of electrodes, 800 M3 of BSL scaffolding material, and 2 cranes were utilized in the repair job.

In addition to above, DP material (60 cans of penetrant, 150 cans of developer & 300 cans of cleaner), 3 ultrasonic flaw detectors, 2 magnaflux MPI units, 30 curie strength source (Iridium-192) in a remote operated radiography camera were utilised for inspection activities.

The job involved extensive arrangement of heating coils, heating machines and controllers for heat treatment job. Thermocouples were provided at all critical points and the readings were brought to a central place for precise control of temperature. For this purpose, 81 heating coils (Total length – 80 meters) and 42 thermocouples were employed. Peak power consumption (220 Volts supply) for heat treatment during final stress relieving was to the tune of 1 MW.

## **7. Schedule of Repairs**

Not many references of in-situ repair of such a failure in secondary reformer were available. In the absence of that tentative schedule of various activities was planned.

The overall repair time from the date of incident to the secondary reformer going back into service was estimated to be around 50-55 days whereas the actual time achieved was 73 days as per the breakup given below:

➤ Cooling down, removal of catalyst and refractory lining and initial inspection	8 days
➤ Dehydrogenation and detailed inspection to identify the extent of damage.	12 days
➤ Preparation and repairs including heat treatment and inspection	33 days
➤ Refractory lining, catalyst loading and startup	20 days
<b>Total duration</b>	<b>73 days</b>

To carry out repairs in the shortest possible time, adequate resources were mobilized and the repair work was carried out on round the clock basis. The services of experts in the field, available in India, were requisitioned and all out efforts were made to repair the equipment satisfactorily by following the laid down procedure.

The enormity of the job can be judged by the fact that around 2108 Kg of electrodes were consumed in the welding of cracked weld seams and defects in parent metal. In addition to above around 33000 Kg of refractory material was consumed in relining of repaired portion of secondary reformer.

## **8. Probable Causes of Failure**

Before analysing the probable causes of failure, it will be interesting to note the various facts regarding the secondary reformer:

- Secondary reformer service in an ammonia plant can be characterised as an easy catalytic duty under difficult mechanical conditions.
- The failure of refractory, damage to air burner and RG boiler downstream of the reformer are common but incidences of shell cracking and weld failure are very much isolated.
- Secondary reformer operating conditions are basically defined by the process, leaving the operator little flexibility to change operating conditions.
- Normally monitored parameters in secondary reformer typically provide no indication of developing internal problems.
- No specific requirements of inspection for secondary reformer have been stipulated by the Consultant/supplier of the equipment, other than inspection of Air Mixer Nozzle, Refractory and Catalyst.
- Secondary reformer operating in high temperature and high pressure hydrogen environment is susceptible to damage due to hydrogen picked up by the metal.

### **8.1 Effect of hydrogen environment on metals**

Any damage to equipment operating in high temperature high pressure hydrogen environment is due to hydrogen picked up by the metal. In addition, any hydrogen dissolved in the metal during the welding process also adds to it. The two major forms of hydrogen damage which are of concern are hydrogen attack and hydrogen embrittlement. While the former occurs during prolonged operation at high temperature, the latter adversely affects the material at lower temperatures, i.e., during start up and shut down.

#### **8.1.1 High temperature hydrogen damage**

Hydrogen attack of steel results in grain boundary fissuring and/or decarburisation. Both these damages result in the weakening of the metal. The susceptibility to this form of attack increases with increase in hydrogen partial pressure and temperature. To increase resistance to attack, the metallurgy is upgraded by the addition of chromium and / or molybdenum. For the present reactor C-0.5Mo was used as the design temperature of the shell was 350 °C. Intergranular fissure / crack and methane bubbles are detected when metal is damaged by hydrogen attack.

#### **8.1.2 Hydrogen embrittlement**

Hydrogen embrittlement is a phenomenon whereby ferritic steels fail in the presence of hydrogen and stresses in the metal. The failure is by cracking followed by further growth of cracks. The hydrogen picked up during welding and also during service can cause this type of damage. The susceptibility to cracking increases with increase in strength of material, hydrogen content and stresses. The welds and HAZ have maximum hardness (higher strength) and therefore the weldments are most susceptible to this type of damage. The mode of failure can be both transgranular or intergranular.

C-0.5 Mo during welding can develop transformation products (like bainite) which are more susceptible to hydrogen embrittlement than the base metal. However, with proper weld procedure and PWHT, the structure can be tempered to reduce its strength (i.e. hardness) within the non-susceptible range. As far as excessive hydrogen in the metal is concerned, there are two possible sources, namely (i) hydrogen dissolved during welding because of inadequate pre-heating and use of consumables containing high amount of moisture and (ii) hydrogen picked up from the process gas reaching the metal surface through damaged refractory lining.

At the operating hydrogen partial pressure in the present case, a stable crack may grow over a period of time under the influence of both the residual and operating stresses and dissolved hydrogen. The embrittlement effect is likely to be more at lower temperatures. As the reformer shell temperature is considerably low (around 160° C max), the cracks will grow along the susceptible path. Once the less susceptible areas of low hardness/ low strength are reached, the cracks are likely to be arrested.

## **8.2 Inspection carried out to find the cause of failure**

Insitu metallography and replica testing were carried out on the cracked area of longitudinal seams of conical portion to find out the cause of the failure. The replica taken at the four locations were examined at higher magnification under microscope as described below:

### **8.2.1 Outer Surface**

On the cracked area of longitudinal weld seam and HAZ microstructure was examined. Uniform grains were observed in the weld metal. HAZ showed fine grains of ferrite and pearlite. The crack was observed at 1.5 mm from the weld fusion line on the HAZ. The crack was parallel to the weld seam and was of transgranular in nature. The microstructure of base material near the longitudinal seam showed banding of ferrite and pearlite.

### **8.2.2 Inner Surface**

On the cracked area of longitudinal seam the microstructure showed main crack with secondary crack. The crack was longitudinal and located in the HAZ.

The microstructure of base material near the longitudinal seam showed banding of ferrite and pearlite and was similar to the base material microstructure as observed on the outer surface.

The weld metal microstructure from inside showed incomplete dendrites of ferrite and carbide which are not properly tempered. The HAZ showed bainitic structure. Also, the polished and etched cross section of the weldment showed that weld bead profile and HAZ were not visible on outer diameter side whereas the weld bead profile and HAZ were visible on inside diameter side which indicated that the outside portion was normalized whereas the inside portion had not undergone complete normalizing heat treatment. Thus it is probable that PWHT, re-normalizing and tempering treatment of the hot formed conical shell portion of the secondary reformer might have been inadequate due to non-uniformity of temperature along the length and across the depth of the weld and the base metal thickness which made the cone more susceptible to hydrogen assisted cracking during service.

Besides in-situ metallography, the samples of defective material were taken for metallurgical examination. Photographs PH-6 and PH-7 show several cracks on the sample piece cut from the weld and the HAZ of longitudinal seam L-1.

The following tests were carried out on the sample pieces to ascertain the cause of the problem and the condition of shell material

- 1) Visual examination
- 2) Metallography examination
- 3) Hardness test (Weld, HAZ & parent metal)
- 4) Microhardness test
- 5) Chemical analysis
- 6) Tensile and impact test
- 7) Fractography

Visual examination of the fracture surface of the samples showed brown to dark brown color and brittle type of failure. The direction of fracture observed on sample removed from inside surface of longitudinal seam showed that the cracks had started from inner surface of cone and propagated towards the outer surface. Also, there were radial marks starting inside surface which are characteristic of brittle fracture. After the brittle fracture, some quasi-cleavage type of fracture was observed. Metallography examination revealed that cracks had started from heat affected zone at the toe of the weld and propagated into base material. The cracks are fine and transgranular in nature indicative of hydrogen assisted cracking.

The hardness in HAZ of sample removed from the inside surface of the longitudinal seams showed very high hardness values. The hardness in the outer surface and inner surface of weld metal and HAZ shows a large variation. Hardness of the weld metal on outer surface of longitudinal seam is lower than the hardness of weld metal on inner surface of longitudinal seam. Hardness of the HAZ is very high. With increase in hardness, the notch sensitivity of material increases making it more susceptible to brittle failure, especially in hydrogen environment where temperature and pressure are high. Figures 16 and 17 depict the hardness and micro-hardness test results on weld, HAZ and base metal.

The polished and etched cross section of the weldment showed that weld bead profile and HAZ were not visible on OD side whereas the weld bead profile and HAZ were visible on ID side which indicated that the outside portion was normalized whereas the inside portion had not undergone complete normalizing heat treatment.

Spectroscopic chemical analysis carried out on inside and outside surfaces of both base and the weld material met the specification requirement of SA 204 Gr. B. The carbon content of base material is found to be on maximum limit i.e. 0.25 %. The carbon equivalent calculated showed value of 0.57 which make the steel highly hardenable. High hardness was observed in the banded area of base material which makes steel susceptible for cracking.

Tensile test for both weld and base material were carried out and were meeting the requirement as per SA204 Gr B. Transverse impact test specimens were machined from weld metal. The impact energy values were found to be satisfactory. However, it was found that impact energy of weld metal near ID shows much lower values (22-27 joule) as compared to weld on OD (around 55 joule) and base material (around 45 joule), indicating embrittlement effect due to hydrogen.



Fractography of the sample using Scanning Electron Microscope was made to study the nature of cracking. The fractographs of the sample indicated that the main cracking which resulted in failure was of brittle mode and the cracks were intergranular in nature indicating towards hydrogen embrittlement as cause of the failure.

Based on various in-situ metallography tests and metallurgical examinations, cracking due to hydrogen embrittlement or hydrogen assisted cracking appears to be the most likely cause of failure which is evident from the facts as summarized below:

- 1) Microscopic examination of specimens from the cracked knuckle area and the welds indicate that the cracks had started from the HAZ and weld regions from inside surface of the vessel and propagated further into base material and to outer surface by formation of voids/bubbles, a mechanism typical of hydrogen assisted cracking.
- 2) Non-uniformity of temperature control during PWHT, normalizing and tempering of the hot formed cone during fabrication making it susceptible for in-service cracking.
- 3) Cracking had occurred on the inside surface of the weld having low hardness values i.e. 213 to 238 VHN.
- 4) The presence of hairline cracks on many locations on weld, HAZ and base material even at low hardness levels indicates the severity of hydrogen attack.
- 5) The tensile test of the base material indicated reduction in the percentage elongation from 37% to 27% on the mid thickness sample of outside surface.
- 6) Impact testing showed reduction in impact values on the inside surface weld samples as compared to outside surface samples indicating embrittlement effect due to hydrogen pick up.
- 7) The fractography of the sample indicated the brittle mode cracking.

## 9. Conclusions

While the failure of refractory, damage to air burner and problems in RG boiler down-stream of reformer are fairly common, the problem encountered in the secondary reformer of IFFCO Aonla (India) is certainly an isolated case if not unique.

Considering all the available information, it is difficult to come to a very definite conclusion regarding the cause of the failure. However, cracking due to hydrogen embrittlement or hydrogen assisted cracking appears to be the most likely cause of failure.

Our experience brings out the following facts about operation and maintenance of secondary reformer which are worth considering by all operators of ammonia plant:

- Visual inspections of the hot face lining are misleading and give practically no indication of the condition of the refractory lining behind.
- It is important not to wait for a catalyst change out or actual refractory damage before inspecting the secondary reformer.
- Spray of water on the outer surface of secondary reformer during normal operation is likely to misguide regarding the condition of inside refractory as the hot spot may not be visual during initial stage of refractory damage.
- Time and money spend in inspection and maintaining the vessel in healthy condition will always be paid back. Further it can save you from expensive if not catastrophic failure.
- Periodic inspection of the secondary reformer shell and its weld joints from outside can give fairly good idea about the health of the vessel.

**PHOTOGRAPHS SHOWING CRACKS**



**PH-1: L-1 SEAM**



**PH-2: L-2 SEAM**

**PHOTOGRAPHS SHOWING CRACKS**



**PH-3: L-3 SEAM**



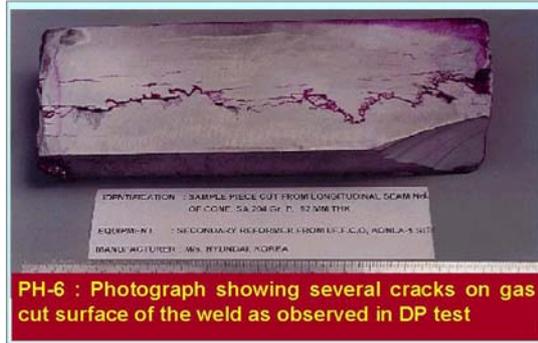
**CRACKS IN C-4 SEAM**

**PH-4**

**PH-5**

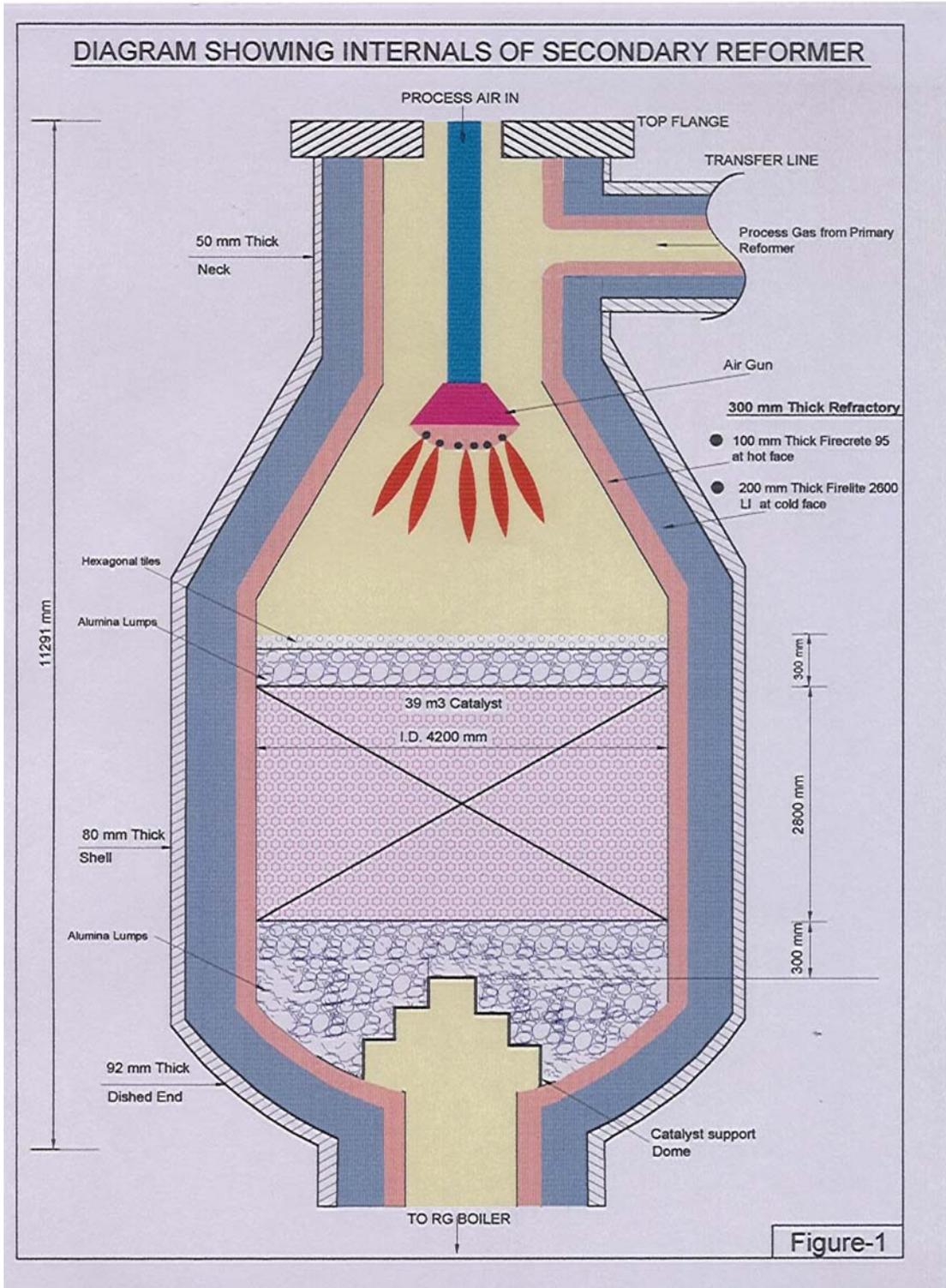


### Sample Piece Cut From Longitudinal Seam: L-1

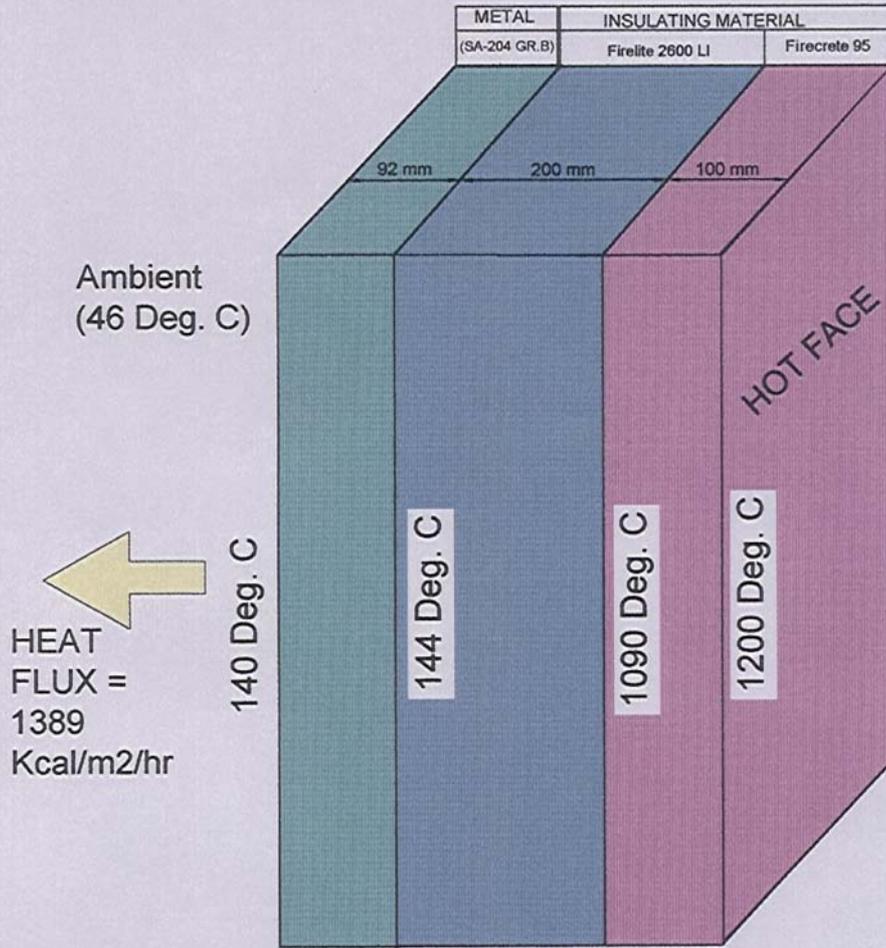


### Sample Piece Cut From Longitudinal Seam: L-1





**SECONDARY REFORMER:- SURFACE TEMPERATURES AT INTERFACES**



FIRECRETE 95	High Alumina Castable refractory Material: Al <sub>2</sub> O <sub>3</sub> : 94.1%, SiO <sub>2</sub> < 0.1%, Fe <sub>2</sub> O <sub>3</sub> : 0.1 %
FIRELITE 2600 LI	Insulating Castable refractory Material: Al <sub>2</sub> O <sub>3</sub> : 58%, SiO <sub>2</sub> : 31.4 %, Fe <sub>2</sub> O <sub>3</sub> : 0.7%

Figure-2

TYPICAL ANCHOR INSTALLATION FOR THE TWO LAYERS OF REFRACTORY

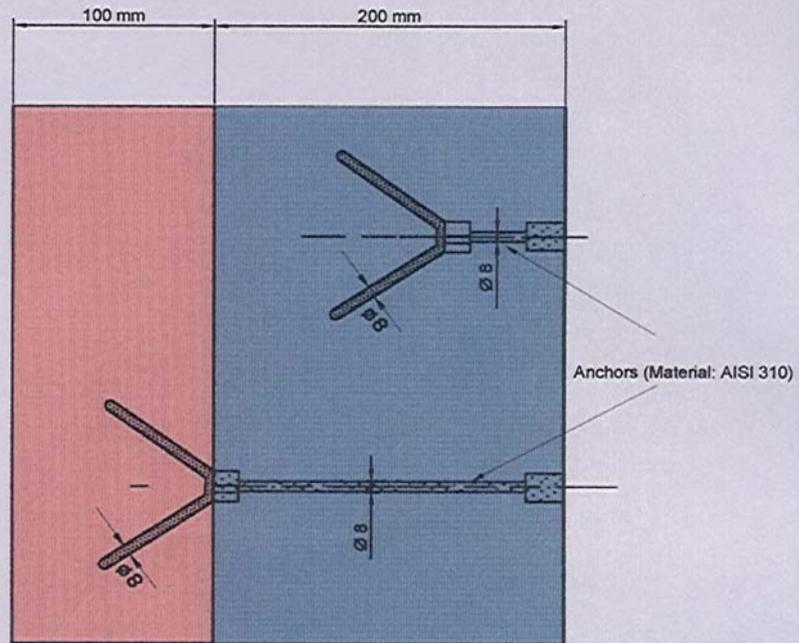
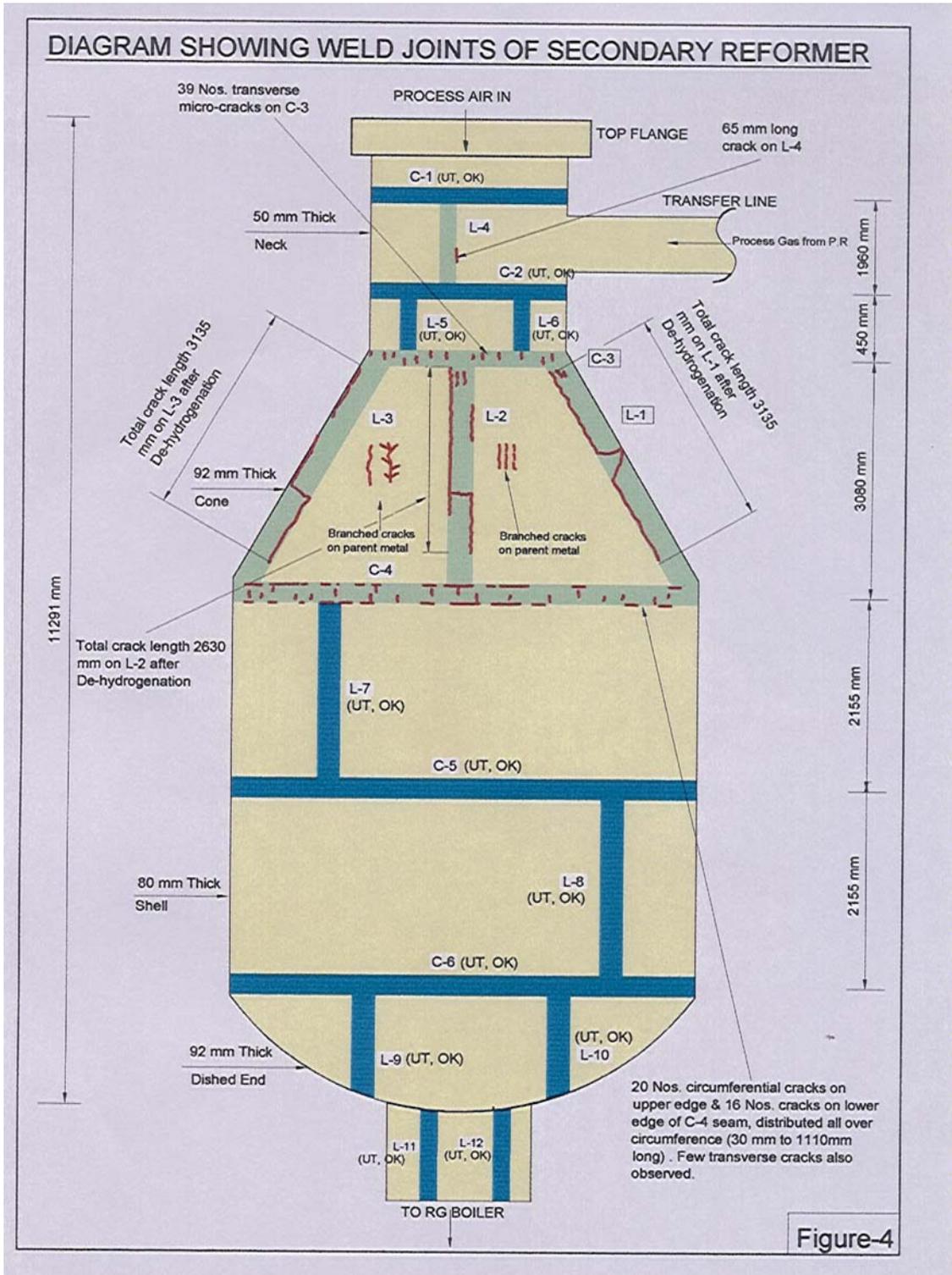
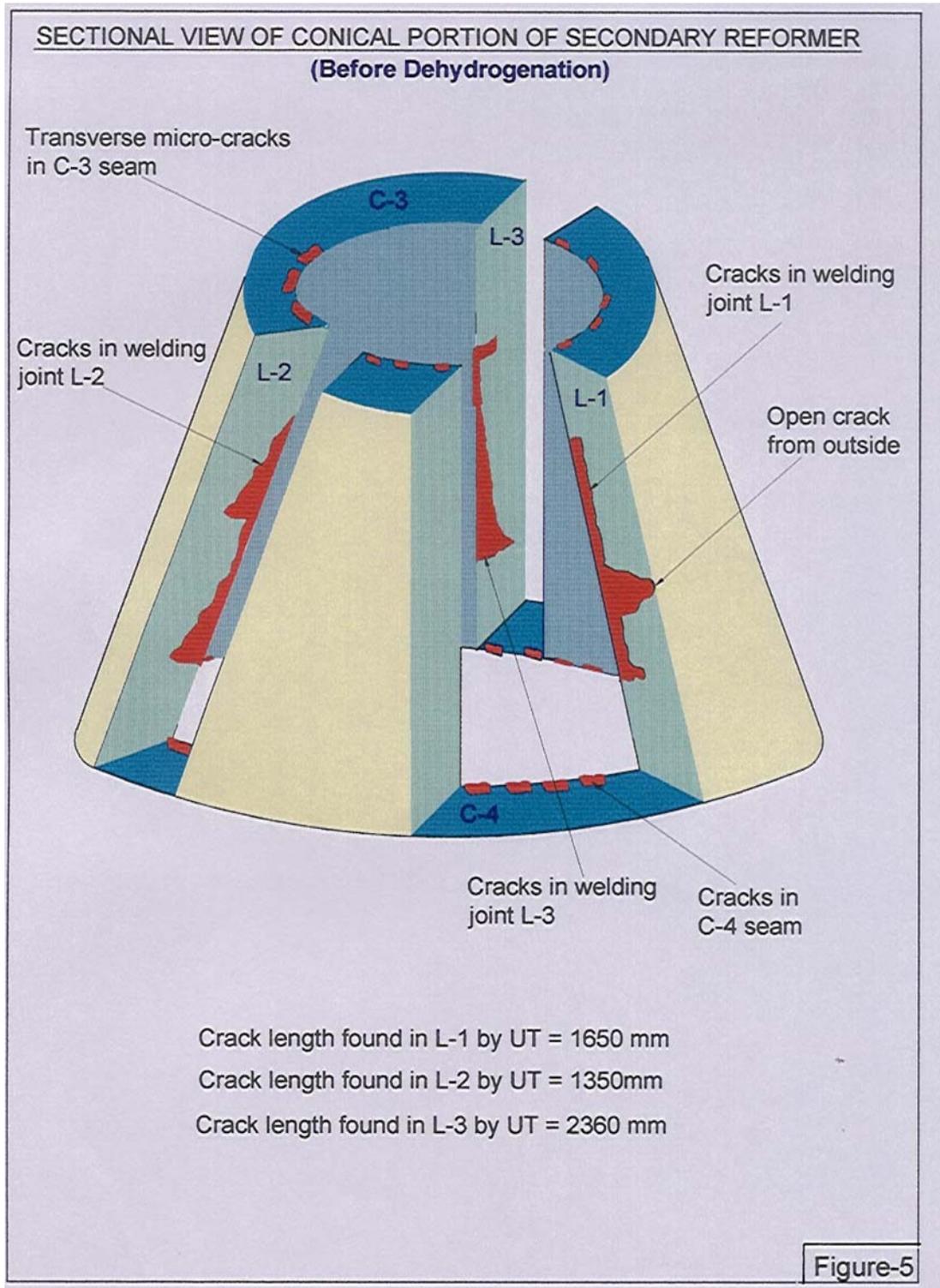
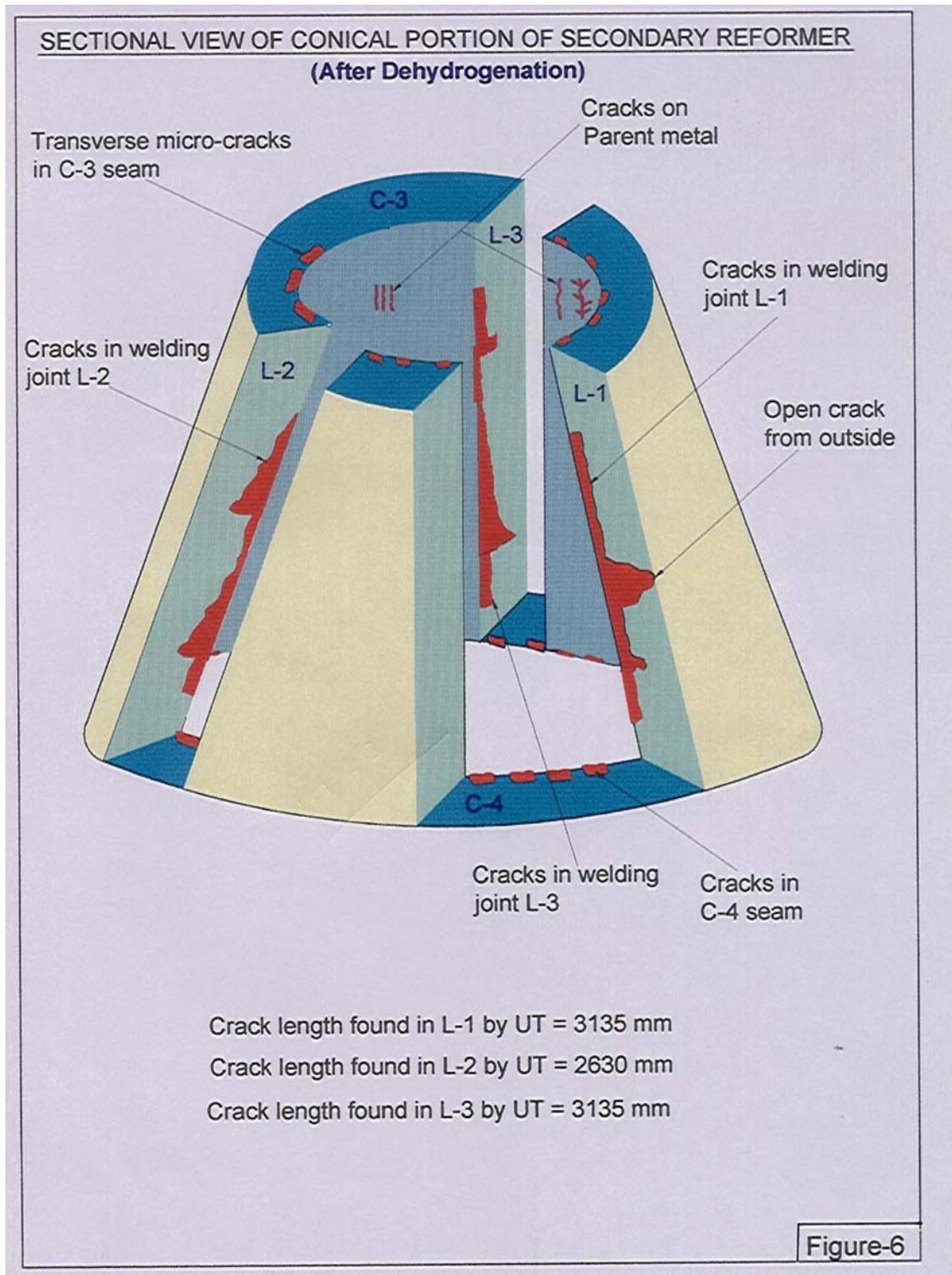


Figure-3

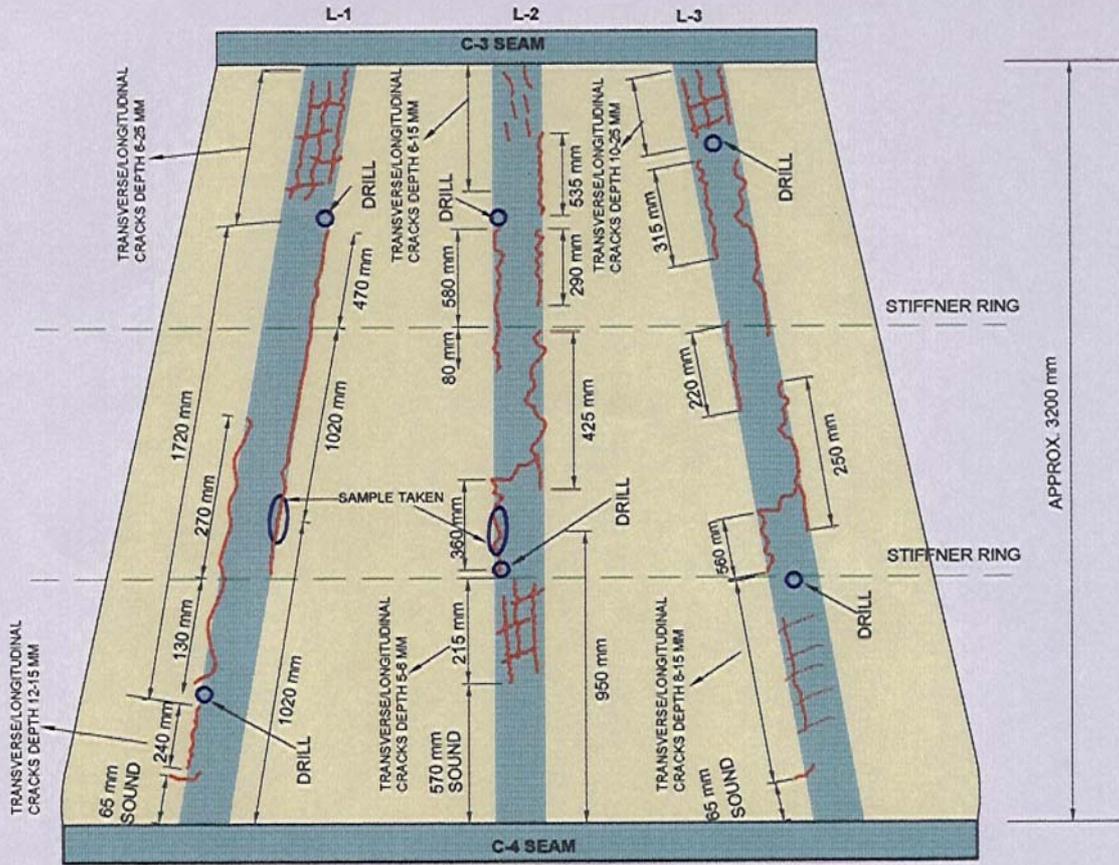








### LOCATION OF CRACKS ON L- SEAMS



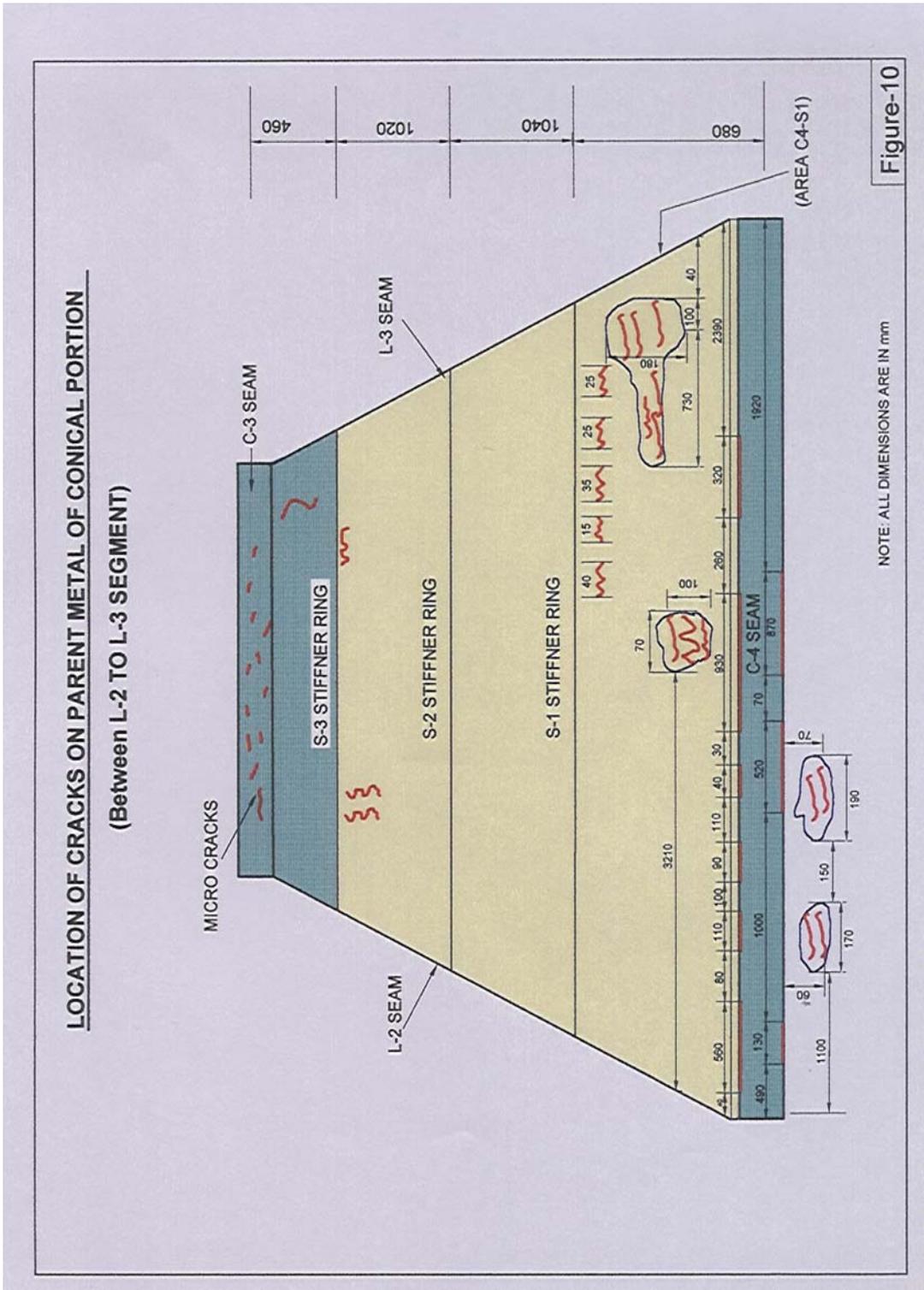
**NOTE:**

- Depth of transverse cracks observed in U.T in the range of 6-8 mm .
- Depth of longitudinal cracks observed in U.T in the range of 10-15 mm & at few locations 25 mm .

Figure-7







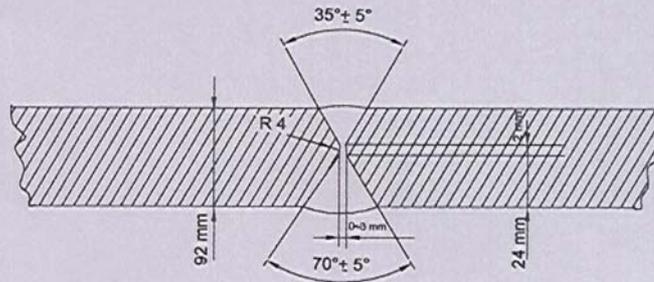
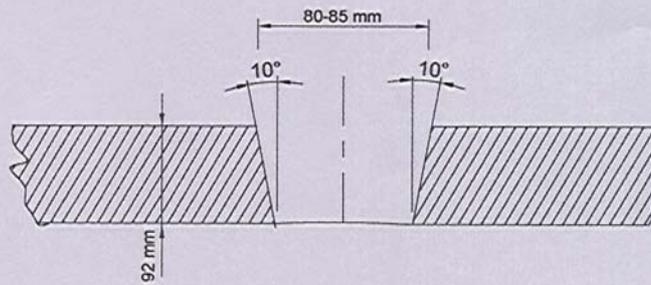
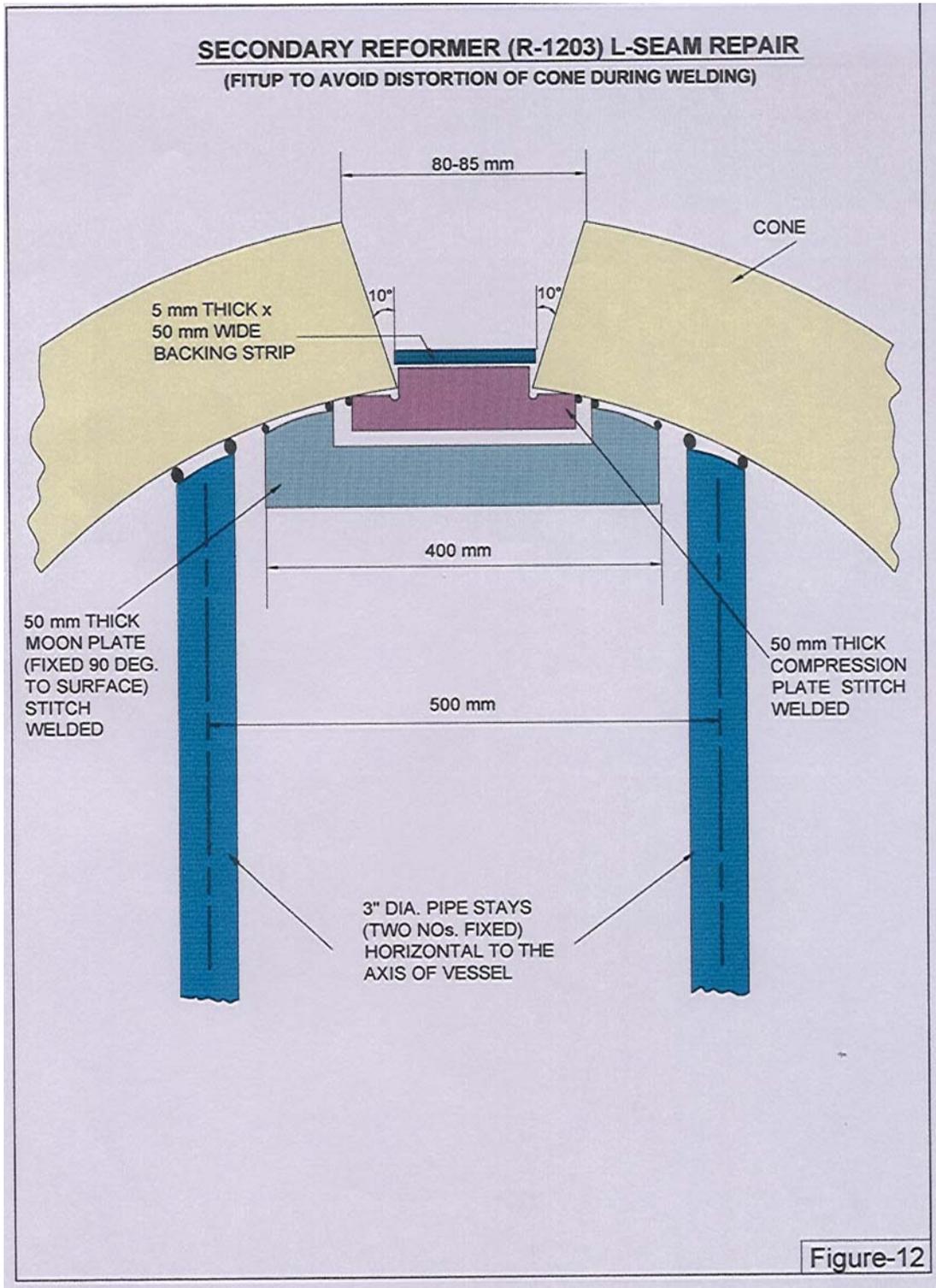
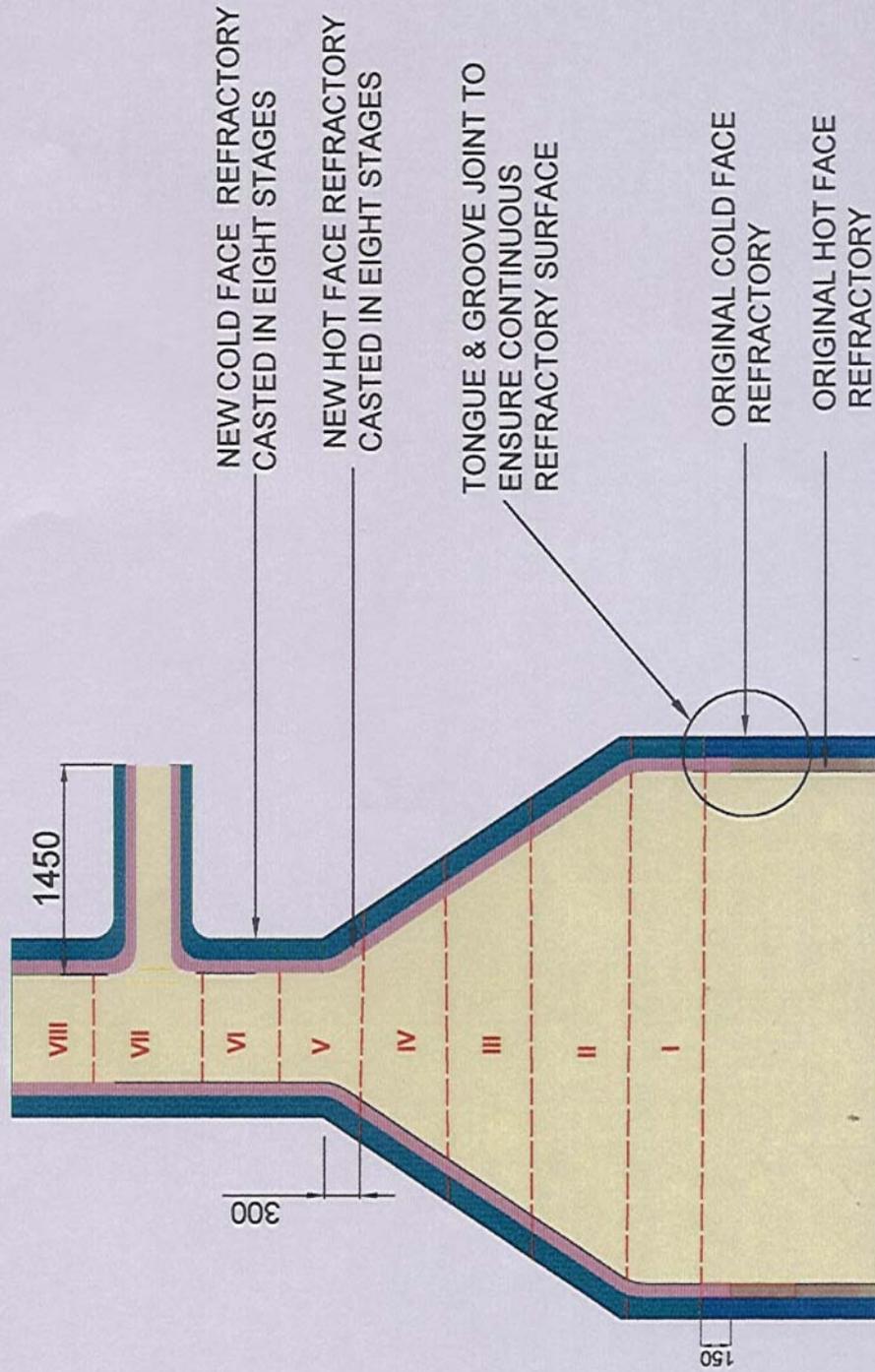
**WELD GROOVE DESIGN OF LONGITUDINAL SEAM****ORIGINAL WELD GROOVE DESIGN****ADOPTED WELD GROOVE DESIGN FOR REPAIR**

Figure-11





### DIAGRAM SHOWING REFRACTORY LINING JOB

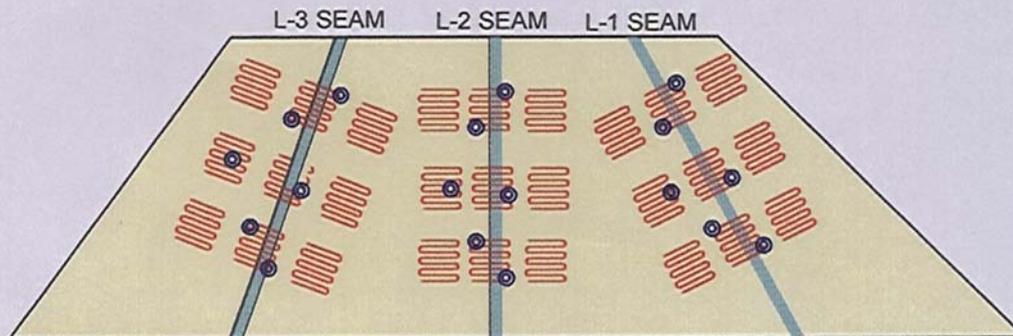


ALL DIMENSIONS IN MM

Figure-13

## DEHYDROGENATION OF L-1,L-2,L-3 SEAMS

(COIL & THERMOCOUPLE ARRANGEMENT FROM INSIDE & OUTSIDE)



- 6 NO. THERMOCOUPLES ON EACH SEAM (TOTAL 18 NOS. INSIDE & 18 NOS. OUTSIDE)
- 9 NO. 80 VOLT COILS ON EACH SEAM (TOTAL 27 NOS. INSIDE & 27 NOS. OUTSIDE)

Figure-14

PREHEATING FROM OUTSIDE FOR INSIDE WELDING OF  
L-1,L-2,L-3,C-3,C-4 SEAMS (80V)

