**Induction**

Germany is now faced with tougher environmental legislations. The public concern about air quality and the reduction of pollutants requires refineries to modify fuel specifications and particular reduce the sulfurous content in gasoline and diesel. One way to achieve the targets is a higher desulfurization in hydrotreating process units. Hence some refiners are required to modify their existing hydrotreating facilities in order to meet these sulphur targets and increase their economic efficiency. TRM although a new and modern refinery was required to act to such business condition too.

The basic principle of the hydrotreating process is described in Figure 1. In principle the liquid feed is mixed with the hydrogen containing the treat gas, either make-up gas and/or recycle gas, heated in pre-heat heat exchangers and a furnace, then going into an adiabatic fixed-bed reactor in which the exothermic reaction will take place. The furnace controls the reactor inlet temperature; the outlet temperature is controlled by the exothermic reaction, which of course depends on the quenching possibilities inside the reactor. At relatively high temperature and pressure the catalyst beds crack the feedstock in such strongly exothermic reaction. The physical constraints, like the increasing temperature between start of run to end of run of a catalyst life are combined with the chemical constraints like the liberation of H₂S and coke formation.

The operating conditions of reactors vary from case to case. Basic requirement for a profitable operation is a highly efficient use of the catalyst, meaning good hydrodynamics, good mixing of the feed with the catalyst, high life time performance and a minimized pressure drop. The height to diameter ratio is one parameter to optimize the performance of a particular reactor. Other operational parameters are e.g. the catalyst activity, the hydrodynamics of the installed internal beds, grids and trays as well as operating condition and pressure drop. Naturally the operating conditions determine the design of the reactor.

![Figure 1: General design of a high-pressure hydrotreating unit](image-url)
The operating conditions of the reactor R-1001 in the TRM - Vacuumgasoil-Hydration-Unit (VGO-HDS-UOP-design) are in the range of 400°C temperature and 96 bar working pressure. The reactor shell is made of material grade 12.CrMo 9.10. according to VdTÜV Merkblatt 404 and TLT-requirements. The shell has a wall thickness of 172 mm and is weld overlayed with TP 347 (Niob-stabilized austenite) of thickness 5 mm. All the internals are made in austenitic material grade TP 321 (Titanium-stabilized austenite). The capacity is 233 m$^3$ and this reactor is one of the most expensive single equipment of the whole refinery, see Figure 2.

**Figure 2: VGO HDS Unit – R-1001 high-pressure hydrotreating unit**

### Metallurgical considerations

VGO-HDS-Reactors are not only subject to severe pressure and temperature but also to an specific corrosive environment caused by gases like H$_2$S, NH$_3$ and H$_2$ resulting from the hydrotreating reaction. Reactor design from a metallurgical point of view has to considered two important base conditions, viz. operating pressure and temperature. To face those boundaries modern design of high-pressure hydrotreating reactors choose as metallurgy either 1 ¼-Cr-1Mo, 2 ¼-Cr-1-Mo steel grades or even the advanced Cr-Mo-V-alloyed steel grades. These material grades are normally overlayed by austenitic weld material like TP-347 or TP-321.

The pressure and temperature constraint require good toughness and strength properties at elevated temperatures for the shell material. For the modern ferritic creep-resistant ferritic materials and their fabrication the J-and X-factor as well as the Hollomon-parameter are key issue for the selection among the different suppliers [1, 5]. Important for fabrication and repair if it becomes necessary are the right welding procedure and particular the heat treatment cycle. For example in Table 1 some of the metallurgical parameters applied for 2 ¼-Cr-1-Mo steel grades and used during the construction of the refinery are stated.
Requirements for 2 1/4Cr-1Mo with weld overlay

<table>
<thead>
<tr>
<th>Requirement</th>
<th>TLT Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Material - Temper embrittlement = J-Factor</td>
<td>( J = (\text{Si} + \text{Mn}) \times (\text{P} + \text{Sn}) \times 10^4 \leq 120 )</td>
</tr>
<tr>
<td>Weld metal - Temper embrittlement = X – Factor and PE-Factor</td>
<td>( X = (10 \times \text{P} + 5 \times \text{Sb} + 4 \times \text{Sn} + \text{As}) / 100 \leq 15 )</td>
</tr>
<tr>
<td>PE = C + Mn + Mo + Cr/3 + Si/4 + 3.5 ( \times (10 \times \text{P} + 5 \times \text{Sb} + 4 \times \text{Sn} + \text{As}) )</td>
<td>( \leq 3.5 )</td>
</tr>
<tr>
<td>Base metal - Stress relief cracking = dG – Factor</td>
<td>For info</td>
</tr>
<tr>
<td>dG = (%Cr) + [3.3 \times (%Mo)] + [8.1 \times (%V)] - 2</td>
<td></td>
</tr>
<tr>
<td>Steel making / Heat treatment: Electric furnace, vacuum degassed / normalized and tempered (grain size max. 5)</td>
<td></td>
</tr>
<tr>
<td>Chemical analysis restrictions [%]: Ti, Nb, Sn, Vmax. 0.010; Pmax. 0.005; Smax. 0.002; Asmax 0.012; Sbmax. 0.004; Almax 0.02; Cmax. 0.15; Nimax 0.020</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: TLT-Limits of diverse metallurgical parameter of low-alloy steels for reactor

On the other hand reactor design has also to consider the corrosion aspect. In hydrotreating refining operation there are basically three main corrosion mechanism which need to be dealt with, viz.: high temperature sulfidic corrosion, hydrogen-related degradation mechanisms, like embrittlement and cracking, and as specifically related to shutdowns, the low-temperature polythionic acid corrosion. The use of austenitic materials as lining has the advantage that the material is better protected against the hydrogen attack, to be remembered is only the difference in the diffusion coefficient of austenitic and ferritic materials, but also provides a better corrosion resistance against the \( \text{H}_2\text{S} \) and \( \text{H}_2\text{S} / \text{H}_2 \) – attack compared with the properties of the ferritic materials. Here the reference is made to the well-known relationships described by McConomy and Couper-Gormann. However there are also some disadvantages of the austenitic weld overlay. Problems arise at the interface between the weld overlay stainless steel and the low-alloy material of the shell. Due to welding and thermal cycling a hard thin martensitic bands with precipitated carbides are formed. The resulting precipitates have a higher absorption for hydrogen than the surrounding metal zones and increase the brittleness of this zone. The weld deposition is not 100%-austenitic but contains sigma-ferrite inclusions. Due to several the thermal cycles within the reactor operation these ferritice bands convert at a faster rate the brittle sigma phase than the austenite. Therefore the permissible ferrite range during fabrication is restricted normally in the range of 3 - 10% (Schaeffler / Ferritscope) [1, 5]. However there are Company related tougher restrictions in order to prevent the hot cracking problem during welding, here the lower limit is also very important.

The brittleness of this zone is of particular concern. Disbonding of the weld overlays from the low alloy Cr-Mo-steel shell is not uncommon. Metallurgical deterioration of the weld overlay itself can be caused by the elevated temperature exposure and the post-weld-heat-treatment required for the fabrication of the reactor, causing sigma-phase formation of the stainless steel. The sigma phase, a hard and brittle Fe-Cr-phase can cause particular concern:

- During cooling down there is a difference between the thermal expansion coefficients and the ductility of the different zones in the weld overlay / shell material
- Stainless steel becomes more sensitive to polythionic attack

Reactors internals like support beams for the fixed catalyst beds are made of full austenitic grades and welded onto the weld overlay of the reactor shell. Their structural integrity depends to a large scale on the integrity of the weld overlay, i.e. bonding properties of the overlay / shell materials.

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**Inspection of reactors**

Inspection of valuable equipment like reactors has to be performed with a high efficiency. Because of the reactor size the 100%-coverage is impractical and so critical areas must be selected based on previous experience and inspection records. The past operational history has to be taken into account as well. The experience for reactors showed, that there specific damages to be considered in the inspection work, see Figure 3. They are obviously related to the metallurgical aspects and specific corrosion mechanism in such environment. The JSW-Surveys [3] shows for example that the majority of the observed failures are related to specific areas of concern, like:

- Cracks at ring joint type gasket groove due to hydrogen embrittlement or sigma-phase formation
- Cracking due to stress concentration combined with hydrogen embrittlement and sigma-phase formation on welds of external lugs, welds on nozzles or attachment welds of skirt
- Imperfections of the main weld seams due to temper embrittlement or hydrogen attack
- Disbonding of weld overlay due to hydrogen attack
- Cracking of weld overlay due to sigma phase formation (embrittlement)

![Figure 3: Important areas of inspection activities for hydrogenation reactors [3, 4]](image)
For such failure mechanism there are proven and reliable non-destructive inspection methods available. Mainly the ultrasonic method, shear-wave, straight-beam or even the backscatter techniques are applied. Proper calibration and the use of the right calibration pieces that are representative for the actual conditions are to be applied. However one should not forget that quite often the inlet / outlet piping system has also to be considered. This piping is normally made in full stainless steel grades joint either with stabilized or unstabilized welding consumable. Here the information about possible sensitation behavior that is important for the risk of polythionic acid corrosion can only be achieved with advanced techniques like the EPR-method or by microstructure analysis provided with SSAM-technique.

In Figure 4 one example is given about TRM experience with failures related to cracking of ring joint type gasket groove. The austenitic forging of question is located between the reactor inlet piping and the reactor flange.

![Cracking of RTJ-groove made in 2-1/4Cr-1Mo cladded with E-347 Crack starts in corner](image)

**Figure 4: Failure on RTJ-ring joint gasket / Inlet of reactor**

**Reactor differential pressure problem**

Although a lot of attention is paid to the pressure-retaining envelope due to obvious safety reasons one has also to consider the integrity of the reactor internals. Since hydrotreating reactors designed as fix-bed reactors the pressure drop over the reactor beds is an important operating parameter. The reactor beds are normally resting on beams and grids which have among other basic things the task to prevent a breakthrough of catalyst into other systems further down in the processing unit chain. The final result of such scenario would have been a filling of the further down located heat exchanger, vessels and piping systems by catalyst with all the safety and maintenance consequences, providing also a situation where the exothermic reaction inside the reactor might less controllable too.
That possible scenario had been faced the refinery in Spring 2002, shortly after the revamp of the unit which was performed in order to meet the new sulphur targets. Part of the revamp were modifications of the reactor internals. The reactor R-1001 observed a sharp and rapid increase in the pressure differential in the second bed of the first hydrotreating reactor, see Figure 5. The observed pressure drop showed such a behaviour that would require an unplanned repair long before the original planning. The consequence the refinery was faced with, would have been a shutdown of the unit. Other units of the refinery would be affected as well, causing with the so-called “domino-effect” even more severe financial losses. The leading scenario because of the pressure drop was related to a rupture of the welded area associated with the catalyst bin beams support brackets. This rupture may cause the either above-mentioned catalyst breakthrough and also make necessary repair by welding difficult, to mention only the preparation of surfaces for welding, i.e. removal of sulphur-containing components from the surface or the heat treatment after welding as per code and regulation. The repairs of weld overlays in such environments are cost- and time intensive.

The information by the licensor of the unit stated a limit of 6.3 bar pressure drop of the reactor based on their design calculations. The obvious question for the operator was if the true strength of the brackets welded on the weld overlay of the reactor could be established and so the pressure drop limit could be expanded.

Figure 5: Pressure drop problem on VGO-HDS – Reactor R-1001, second bed
The general layout of the reactor and the internals of the second bed are shown in Figure 6. The main beams of the internals are resting on support brackets that are welded onto the weld overlay of the reactor shell. As per design the shear strength or bonding properties of the ferritic and austenitic material is the governing factor for the integrity of the internals.

**Numerical Calculations**

In order to get more information about the true strength of the reactor internals the refinery asked the MPA University of Stuttgart to perform a numerical analysis of the situation and depending of the outcome to perform pertinent experimental work. The calculations of the reactors internals were made idealizing the support grid as beams (Euler-Bernoulli-Theory) with pinned or fixed kinematics boundary conditions. The load was determined by using the weight of the catalyst and the pressure drop; a trapezoidal load for the intermediate main support grid was idealized. There was no need for a finite element analysis due to obvious restrictions. The material properties for the calculation were determined according to ASME Section II Part D and compared with the German code KTA 3211.2. The results of calculations showed that the weakest part of the whole reactor internals and therefore critical was the lower beam of the second bed. The maximum calculated shear strength of \( dp = 8.2 \text{ bar} \) gives only a safety margin of 1.15, for a \( dp = 6.2 \text{ bar} \) the safety coefficient was 1.5 for this piece of internal equipment. The safety coefficient of 1.15 is not in line with the pertinent rules and regulations. This was not acceptable for the refinery and consequently an experimental verification was necessary [2].
Experimental part

Subject of the experiment was a K-weld between the support bracket made of austenitic materials and the simulated shell made of a ferritic base material and an austenitic weld overlay. The support bracket had to be welded on the weld overlay, indirectly on the reactor shell. The simulated shell as well as the bracket was made as per original design of the reactor. Hence the aim of the experiment was to establish the maximum shear strength of the K-weld between bracket and shell at a reactor operating temperature of 400°C and calculating from that achieved value the maximum allowable pressure drop over the second bed of the reactor. The welding test conditions are the same as applied for the original welding. The chosen ferritic shell material with grade 22 NiMoCr 3.7. has the same strength properties at the elevated temperature range of interest compared to the original material 12 CrMo 9.10.. The same is valid for the chosen material of the bracket. The weld overlay and the weld seam between bracket and weld overlay / shell has the same specification as the original design. The welding joint was designed with a not complete penetration of the weld toe.

![Experimental arrangement for evaluation of shear strength of support brackets](image)

*Figure 7: Experimental arrangement for evaluation of shear strength of support brackets [2]*
The test body was heated up within 16 hours to a temperature of 450°C. The temperature during heating was permanently measured. During the whole test the temperature dropped about 100°C. After removal of the heating insulation the test body was subject to a vertical force provided by a press in order to define the maximum shear strength. Figure 7 and 8 are showing the test configuration.

In Figure 9 the relationship between force and vertical displacement as well as temperature can be seen. The increase in force was done in successive steps in order to simulate a possible creep-dependent behavior. It can be seen in the graph that till a load of 1200 KN linear behavior exists, behind that load the non-linear behavior dominates which is typical for austenitic materials. The test was abandoned by a maximum load of 2500 KN because of safety reasons for the press. There was no shearing-off of the brackets and a maximum displacement of 9 mm was achieved.

The transfer from linear to non-linear behavior (1200 KN limit) can be considered the elasticity limit and combined with a safety coefficient of 1.5 gives a pressure drop of 16 bar. This is more 2.5 times more than the limit given by the designer. This result was quite acceptable for the operator [2].
The liquid penetrant inspection of the welded connection showed no indication of cracking or crack formation.

Metallographic examination was performed afterwards, cutting the welding connections into several slices. In Figure 10 the slip lines that are commonly observed for such load can be seen. As expected too there are crack starters originating from the imperfection of the weld toe. During the next planned shutdown the reactor and specifically the support brackets have been inspected. The results of inspection showed that there was no pertinent repair work required and the reactor beds, their beams and grids were in an acceptable condition.
Conclusion and Summary

The help of the numerical analysis and the experimental verification made it possible to expand the original mechanical limits for hydrotreating reactor. The observed pressure drop over the reactor was expanded to 16 bar instead of the original 6.3 bar. Due to this increased margin it was possible to run the unit until the planned shutdown. Substantial financial losses could be avoided.

The experimental part showed that the behavior of the weld overlay on a ferritic material provides sufficient shear strength that is much higher than the pertinent numerical calculations showed. The case also puts the attention to problems that are normally not related to the pressure-retaining components of such equipments. The structural integrity of internals is also important issue for operation of reactors.

In order to prove the experimental part the reactor internals were thoroughly inspected during the general shutdown of the refinery in September 2002. Particular attention was paid to the weldments of the reactor internals and possible deformation of beams and support grids. The inspection made confirmed the results of the analysis, there was no deviation observed.
Literature


[4] Hattori K., Aikawa S.: “Scheduling and planning inspection of Cr-1/2-Mo equipment using the new hydrogen attack tendency chart”, Fuji Oil Company, Chiba, Japan