CHAPTER - I

INTRODUCTION TO Cr-Mo-V STEELS

1.1 General
1.2 Hydro Cracker Reactor
1.3 Material Selection for Hydrocracker Reactor

References
CHAPTER - 1
INTRODUCTION TO Cr – Mo - V STEELS

1.1 General

Steel is arguably the world’s most “advanced” material. It is a very versatile material with a wide range of attractive properties, which can be produced at a very competitive production cost. It has a diverse range of applications, and is second only to concrete in its annual production tonnage. Steel is not a new invention which leads to a common misperception that “everything is known about steel” amongst those outside its field. On the contrary, research within this field is probably the most challenging of all the material sciences. It is grounded on decades of research and much fundamental theory arises from the study of steel. Steel is generally defined as a ferrous alloy containing less than 2.0 wt. % C [1]. The complexity of steel arises with the introduction of further alloying elements into the iron – carbon alloy system. The optimization of alloying content in the iron – carbon alloy system, combined with different mechanical and heat treatments lead to immense opportunities for parameter variations and these are continuously being developed.

Through the last few decades a category of steels known as high strength steels have undergone constant research. As a direct result, steels with yield strengths greater than 1100 MPa combined with good toughness at low temperatures are available such as SSAB’s, Weldox 1100 containing 0.2 C, 1.4 Mn, 3 Ni and minor additions of Cr, Mo, Si, Cu, V, Nb, Ti, Al and B. Today, as new and greater challenges are presented to designers and engineers, these steels are increasingly employed in a diverse range of applications such as bridges, pipelines, submarines and cranes. Constructions with lower structural thickness and weight, with the
same load bearing capabilities are often possible with the employment of such steels.

In many of these applications it is essential to form strong joints that allow transfer of load between the different steel components. Generally, welding is the preferred joining method since it forms a continuous joint, it alleviates corrosion problems often associated with fasteners and it offers greater beauty to the application. In many circumstances, it is a structural requirement that the weld metal has over-matching strength in comparison to the steel in order to avoid design limitations. These requirements are possible to achieve under well-controlled conditions, gas tungsten arc welding (GTAW). However as strength levels increase it becomes more difficult to fulfil impact toughness requirements with flexible and productive welding methods such as shielded metal arc welding (SMAW), flux cored arc welding (FCAW), or submerged arc welding (SAW) [2–3]. This project encompasses the SAW-AC technique with a view to increasing impact toughness of steel weld metals while keeping yield strength greater than 690 MPa (100 ksi or 105 lb/in2).

All over the world, energy crisis is tremendous and particularly for India, which is a developing country and there is 10 to 15% annual increment of energy requirement. At present India rely mostly on thermal energy. One of the basic raw material of thermal energy is petroleum product for this, the most important equipment is hydrocracker reactor. This equipment uses Cr-Mo-V steel in its fabrication, this metal is very complex and difficult to understand during welding process. Therefore this project tries to evaluate the essential parameter, their mutual interdependence and to find out their relationship.
1.2 Hydrocracker Reactor

Flexibility of operation is the key word in the petroleum refining industry today. As the market demand have shifted from high to low sulfur fuels, and from fuel oil to lighter products, the refineries have no other option but to place an added emphasis on various alternative processes which are externally flexible and cost effective. Coupled with deterioration in average crude quality, this has inevitably led to increasing demand for residuum upgradation technology[1,10].

There are three widely used conversion processes for upgradation of heavy end of hydrocracker viz. Coking, Fluid Catalytic Cracking and Hydro cracking. While the first two processes are based on carbon rejection technique, whereas last process is based on breaking the C-C bond with simultaneous hydrogenation processes are as under:

Table 1.1 Comparisons of Hydrogenation Processes[1,10]

<table>
<thead>
<tr>
<th>SR NO.</th>
<th>VARIABLES</th>
<th>COKING</th>
<th>FCC</th>
<th>HC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Operating Pressure</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>2</td>
<td>Special metallurgy</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>Operating Flexibility</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>4</td>
<td>On stream Factor</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>5</td>
<td>Investment Cost</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>6</td>
<td>Feed preparation read</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>Conversion</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>8</td>
<td>Product Quality</td>
<td>Unstable</td>
<td>Unstable</td>
<td>Stable</td>
</tr>
<tr>
<td>9</td>
<td>Sulfur removal</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

FCC = Fluid Catalytic Cracking
HC = Hydro cracking
The major advantages of Hydro cracker over the other two alternatives are:

[1] Since Hydro cracking involves addition of hydrogen to the carbon atoms, distillate yield is much higher as compared to carbon rejection processes.

[2] Conversion to middle distillates in the case of hydrogen cracking is more than 80% against 40% in the case of catalytic cracking.

[3] Even though Catalyst cracking produces large quantities are far from Specification. But the products from hydro cracker are stable and free from sulfur and nitrogen compounds and hence no additive requirement for improvement in storage stability.

[4] A salient feature of hydro cracking is its flexibility with respect to Product pattern. Units are designed and operated to produce LPG, Naphtha, Gasoline, Middle distillates, lube base stocks, Ethylene plant feed and FCC feed.[1,10]

1.2.1 History of Hydro Cracking

Hydro cracking is one of the oldest hydrocarbon conversion processes and was commercially developed by I.G. Farben industries in 1927 for processing of lignite to gasoline. This technology was extensively used between 1935 and 1945. In early 1930's, this technology was used in USA for upgrading lube oils, diesel fuels and burning oils. These processes were primarily high-pressure processes. In early 1940's, the important of hydro cracking came down due to development of catalytic cracking processes and increased availability of middle east crudes[10,15].

By the end of 1950's, hydro cracking process have gained acceptability again due to various factors. Improved catalysts were developed later which permitted operation at relatively low pressure resulting in a reduction in the demand of
heavy petroleum products as a result of conversion of rail / road transport from steam to diesel and use of nature gas in the place of heating oil coupled with higher demand of gasoline placed the emphasis on the conversion of surplus fuel oil to distillate products. These factors together with the availability of relatively low cost hydrogen (from catalytic reforming) and advances made in mechanical engineering especially in the field of reactor design pushed up the case of hydro cracking[10,15].

Since then, the worldwide hydro cracking capacity has been increased steadily. Not all these units were true hydro crackers as it defined today. Many of them had the basic function of product and feedstock upgradation such as cycle oils, thermal and Coker gas oils and other heavy gas oils. With the improvement in catalyst, now a day hydro cracker has a broad range of products ranging from LPG to middle distillates, lube base stock, ethylene plant feed and FCC feed. It is now particularly recognized as a premium technology for products of high quality middle distillates demanded by market.

In advanced countries with high demand for gasoline, Catalytic cracking and hydro cracking have been employed as team. The catalytic crackers take the more easily cracked paraffin feed stock, while the hydro crackers use more automatic distillates as feed. Even though the new Zeolite catalyst have helped in improving gasoline yield and octane quality from catalytic crackers, it cannot crack the cycle stock to extinction. Such stocks find difficult application, but form excellent charge for hydro cracking. In addition to vacuum gas oil, cycle stocks etc., it is also possible to process residual oil and reduced crude by hydro cracking. The difference between the two types of processes is in the type of catalyst and operating condition[10,12]
1.2.2 Hydro Cracking

Hydro cracking processes has a wide range of application. The feed stocks can be straight run gas oils, thermally gas oil, cycle oils, cocker gas oils, thermally cracked stocks, solvent deasphalted residual oils, and straight run naphtha, cracked naphtha, atmospheric residue or vacuum residue. Its products states consists of LPG, MS, reformer feed, ATF, diesel fuels, heating oils, FCC or ethylene plant feed, lube oil base stocks etc. Large number of commercial processes and patents are available. In all these processes, hydro cracking as well as hydro treatment are carried out generally in fixed bed catalytic reactors in the presence of hydrogen under high pressure. Various types of catalysts such as Cobalt-Molybdenum or Nickel- Tungsten supported on Silica-Alumina or Zeolite are used in these processes. Depending upon the feed and the end products required, the operating condition and catalyst for hydrocraking may vary. Fig. 1.1 shows a fabrication procedure for reactor pressure vessels[10,15].

![Fabrication procedure for reactor pressure vessels](image-url)
Common Hydro cracker configurations are[15]:

[I] Single stage hydro cracking
[II] Two stage hydro cracking
[III] Series flow hydro cracking

When the treating step is combined with the cracking reaction to occur in one reactor, the process is called a SINGLE-STAGE PROCESS.

[I] Single stage hydro cracking[10,15]

In this simplest of the hydrocracker configuration, the lay out of the reactor section generally resembles that of hydrotreating unit. This configuration will find application in cases where only moderate degree of conversion (say 60% or less) is required. The catalyst used in a single-stage process comprises a hydrogenation function in combination with a strong cracking function[10,15]. The hydrogenation function is provided by sulphided metals such as cobalt, molybdenum and nickel. An acidic support, usually alumina, attends to the cracking function. Nitrogen compounds and ammonia produced by hydrogenation interfere with acidic activity of the catalyst. In the cases of high/full conversion is required, the reaction temperatures and run lengths of interest in commercial operation can no longer be adhered to. It becomes necessary to switch to a multi-stage process, in which the cracking reaction mainly takes place in an added reactor. With regard to the adverse effect of ammonia and nitrogen compounds on catalyst activity, two versions of the multi stage hydrocracker have been developed: the TWO STAGE HYDROCRACKER and SERIES FLOW HYDROCRACKER[10,25].
In the first type, the undesirable compounds are removed from the unconverted hydrocarbons before the latter are charged to the cracking reactor. This type is called the TWO STAGE PROCESS. The other variety is often referred to as SERIES FLOW HYDROCRACKER. This type uses a catalyst with an increased tolerance towards nitrogen, both as ammonia and in organic form[10,22].

[II] Two stage hydro cracking

Fresh feed is preheated by heat exchange with effluent from the first reactor. It is combined with part of a not fresh gas/recycle gas mixture and passes through a first reactor for desulphurisation/denitrogenation step. These reactions, as well as those of hydrocracking, which occurs to a limited extent in the first reactor, are exothermic. The catalyst inventory is therefore divided among a number of fixed beds. Reaction temperatures are controlled by introducing part of the recycle gas as a quench medium between beds[10,17]. The ensuing liquid is fractionated to remove the product made in the first reactor. Unconverted, material, with low nitrogen content and free of ammonia, is taken as a bottom stream from the fractionation section.

After, heat exchange with reactor effluent and mixing with heated recycle gas, it is sent to the second reactor. Here most of the hydrocracking reactions occur[10,26]. Strongly acidic catalyst with a relatively low hydrogenation activity (metal sulphides, for example, amorphous silica-alumina) are usually applied. As in the first reactor, the exothermicity of the process is controlled by using recycle gas as quench medium the catalyst beds. Effluent from the second reactor is cooled and joins first stage effluent for separation from recycle gas and fractionation. The part of the second reactor feed that has remained unconverted is recycled to the reactor. Feedstock is thereby totally converted to the product boiling range.
Figure 1.2 Two Stage Hydro Cracking

[III] Series flow hydro cracking

The principal difference is the elimination of first stage cooling and gas/liquid separation and the interstage ammonia removal step. The effluent from the first stage is mixed with more recycle gas and routed direct to the inlet of the second reactor. In contrast with the amorphous catalyst of the two-stage process, the second reactor in series flow generally has a zeolitic catalyst, based on crystalline silica-alumina[10]. As in the two stage process, material not converted to the product boiling range is recycled from the fractionation section.
1.3 Material Selection For Hydro Cracker Reactor[5]

1.3.1 Introduction

Selection of materials of construction in chemical and petrochemical process industries is of considerable importance for economic operations of plants. Any material used has to satisfy certain basic requirements of physical, mechanical and corrosion resistance properties under the operating conditions. Once these are fulfilled, actual selection depends on number of factors which amongst others include available capital costs, type of equipment, code requirements, aggressiveness of environment, product purity requirement, cost of replacement and maintenance, safety aspects. For the selection of material following factors should be considered[5]

(I) Mechanical and physical properties of material.
(II) Ease of Equipment fabrication.
(III) Corrosion resistance
(IV) Material maintenance

(I) Mechanical and Physical Properties

Equipments should have mechanical stability at the operating pressure and temperature conditions. The factors which determine these are[18]:

(a) **Strength of material**: Higher the strength, lower the thickness of material used.
(b) **Ductility / Fracture toughness**: Material should be sufficiently ductile and tough to avoid any sudden failure because of defects or decrease in
ductility due to metallurgical changes. This property is dependent on alloy composition, heat treatment (hardening), metallurgical changes with time and temperature related degradations (graphitization, nitriding, carburizing, temperature embrittlement), etc.

(c) **Creep properties**: Above certain temperature creep properties become dominant. Higher the temperature and operating stresses more creep and oxidation restraint material are required.

(d) **Thermal conductivity**: This property is important in case of heat transfer service.

(e) **Thermal expansion / contraction**: Where temperature changes are substantial or where two materials have substantially different coefficient of expansion, this aspect is to be taken into consideration in the design.

(II) **Ease of Equipment Fabrication** [65]

In selecting any material of construction, the problems connected with fabrication and maintenance of equipment are also to be given due consideration. The various factors are[5,7]:

(a) Conformation to code requirements or code acceptable material.

(b) Adequate weldability of material.

(c) Expertise available for shop and field welding.

(d) Post weld heat treatment requirements.

(e) Expertise available in plant or with local contractors for maintenance repairs.
(III) Corrosion Resistance

Once mechanical aspects are taken care of, the life of a vessel is governed primarily by corrosion behavior of the material in the environment to which it is exposed[5,15]. Selection of material for resistance to corrosion needs following considerations.

(a) Operating conditions: Corrosion rate at operating temperature, pressure and types and concentrations of corrosive constituents.
(b) Modification of environment: Whether corrosion can be minimized by incorporating suitable corrosion control methods in the system, e.g. neutralization, inhibitor addition, pH control, etc.
(c) Type of corrosive constituents:
   (a) In presence of aqueous phase-acid, alkali, salts, H2S, So2.
   (b) In absence of aqueous phase H2S, fuel ash, naphthenic acid, etc.
(d) Type of attack: Uniform pitting, stress corrosion cracking, de-alloying, hydrogen damage, etc.
(e) Product purity: Allowable metallic impurities in product.

(IV) Material Maintenance

Maintenance plays a vital role to get optimum performance from any vessel. With best of material selection vessel life will be affected if maintenance and operation are inadequate. On the other hand, with good maintenance and operation practice an economic life can be obtained even if less corrosion resistance material is used. Maintenance involves multi-disciplinary approach and a good maintenance practice requires the following important inputs[5]:

i) Mechanical inspection/condition monitoring.
ii) Preventive and predictive maintenance.
iii) Regular turn-around.
iv) Input of vessel experience.
v) Input of expertise in various related fields.
vi) Keeping abreast with latest developments.
vii) Failure and success analysis.

The older vessels were designed considering maintenance at periodically. This approach has changed and the present trend is to increase period of continuous determined performance with in between maintenance period of 2 to 3 years. This approach requires that no breakdown will occur during this period due to material failure. The emphasis has therefore shifted to specifying better material, better inspection and maintenance practices, close control on operation and involved corrosion control practices.

1.3.2 Development Stages of Reactor Material [3]

Hydrogen reactors are used for several kinds of processes in refineries and petrochemical plants, such as desulphurisation of hydrocarbons and cracking of heavier hydrocarbon fractions into lighter molecules. These processes are carried out at high temperatures and pressures in the presence of a catalyst.

For more than last 30 years, conventional low-alloy chromium-molybdenum 2.25Cr-1Mo steel has been extensively used for the reactor vessels; to a lesser extent 3Cr-1Mo steel has been also applied. The reactors generally have been operated at temperatures lower than 454°C with hydrogen partial pressure above 10Mpa growing demands for higher service temperatures/pressures and increased reactor sizes resulted in larger and heavier reactors with a unit weight up to 1500 metric tons. Many problems with transportation and construction of such reactors were encountered. Moreover, due to the process temperature increase close to the
position of 2.25Cr-1Mo curve according to API 941 (Nelson diagram)[13], high
temperature hydrogen attack was possible to occur during the reactors’ service.
In order to solve these problems, new generation of vanadium modified Cr-Mo
steels was developed. The steels are standardized according to ASME Boiler and
Pressure Vessels Code, Section VIII Division 2:

- 2.25Cr-1Mo-0.25V steel, approved as Code Case 2098-1 in 1991,
  allowing several grades with additions of niobium, calcium, titanium and
  boron,
- 3Cr-1Mo-0.25V-Ti-B, approved as Code Case 1961 in 1992,
- 3Cr-1Mo-0.25V-Nb-Ca, accepted as Code Case 2153 in 1993.

First two reactors made of 3Cr-1Mo-0.25V-Ti-B steel by Japan Steel Work were
completed in 1990 [17], and the reactors made of 3Cr-1Mo-0.25V-Nb-Ca were
manufactured in 1994 at Kobe Steel, Tagasako Works in Japan [4]. The first
2.25Cr-1Mo-0.25V reactor was fabricated by Nuovo Pignone in Italy in 1995. By
the end of 2001 year, 98 vanadium-modified vessels had been fabricated all over
the world.

The evolution of modern hydroprocessing reactors can be demonstrated through
the following generations.[15,25]

(I) First Generation - Pre World War II To Mid 1960s.

Forged monobled and multilayer reactor construction for hydrogenation
plants using 2.25% to 3.8% chrome moly alloys. Generally, little regard was
given to impact toughness.

The birth of modern hydro processing reactors manufactured from heavy wall 2.25% chrome moly alloys with 54 joule impact toughness (TT54) at -10°C with no requirements for temper embrittlement control[15].

(III) Third Generation-1970s to 1980s.

Reactors with temper embrittlement control to limit the embrittlement factor (J) to and with increased (TT54) toughness to below-18°C[17]. In addition, this generation included consideration of the long term susceptibility to temper embrittlement measured by the transition temperature curve shift due to embrittlement. In this generation, precautions against weld overlay disbonding were introduced.

(IV) Forth Generation-1980s to 1990s.

Temper embrittlement control reduced by limiting the J factor to 100. The long term susceptibility to temper embrittlement also further reduced. This generation saw the (TT54) toughness temperature decreases to below -32°C.

(V) Fifth Generation-1990s.

New grades of vanadium modified 2.25% to 3% chrome steels were introduced for service with higher strength levels, increased hydrogen attack resistance and TT54 toughness reduced to below -40°C.

1.3.3 Characteristics of Cr-Mo-V Steels[12]

ASME VIII-2 Code Cases requirements for chemical composition of vanadium modified steels are given in Table 1.2. Advanced steel making processes, such as a process based on pig iron production in the blast furnace by steel refining in the BOF converter, ladle metallurgy and vacuum treatment are
necessary. They provide an extraordinary low content of tramp elements, such as
tin, arsenic, antimony and low level of phosphorus, sulphur and oxygen.

The three modified alloys utilize vanadium addition to enhance tensile
strength at elevated temperature and creep rupture strength, and to improve
resistance to in-service degradation phenomena, such as temper embrittlement,
high temperature hydrogen attack (HTHA) and hydrogen embrittlement[22]. The
effect of vanadium content on the mechanical properties of 3Cr-1Mo steel is
shown in Fig. 1.3. The elevated temperature tensile strength and creep rupture of
3Cr-1Mo-0.25V-Nb-Ca are improved by the addition of Niobium. By the addition
of calcium into Cr-Mo steels, calcium sulphides form instead of manganese
sulphides. In opposite to manganese sulphides, stable calcium sulphides do not
dissolve during welding that results in a decreased susceptibility of weldments to
stress relief cracking caused by grain boundary segregation of sulphur.

Table 1.2 Chemical requirements for V modified Cr-Mo steel[15]

<table>
<thead>
<tr>
<th>Composition, wt. %</th>
<th>2.25Cr-1Mo-0.25V Code Case 2098-1</th>
<th>3Cr-1Mo-0.25V-Ti-B Code Case 1961</th>
<th>3Cr-1Mo-0.25V-Nb-Ca Code Case 2151</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.10 - 0.15</td>
<td>0.10 - 0.15</td>
<td>0.10 - 0.15</td>
</tr>
<tr>
<td>Mn</td>
<td>0.30 - 0.60</td>
<td>0.30 - 0.60</td>
<td>0.30 - 0.60</td>
</tr>
<tr>
<td>P</td>
<td>max. 0.015</td>
<td>max. 0.015</td>
<td>max. 0.015</td>
</tr>
<tr>
<td>S</td>
<td>max. 0.010</td>
<td>max. 0.010</td>
<td>max. 0.010</td>
</tr>
<tr>
<td>Si</td>
<td>max. 0.1</td>
<td>max. 0.1</td>
<td>max. 0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>2.00 - 2.50</td>
<td>2.75 - 3.25</td>
<td>2.75 - 3.25</td>
</tr>
<tr>
<td>Mo</td>
<td>0.90 - 1.10</td>
<td>0.90 - 1.10</td>
<td>0.90 - 1.10</td>
</tr>
<tr>
<td>Cu</td>
<td>max. 0.25</td>
<td>max. 0.25</td>
<td>max. 0.25</td>
</tr>
<tr>
<td>Ni</td>
<td>max. 0.25</td>
<td>max. 0.25</td>
<td>max. 0.25</td>
</tr>
<tr>
<td>V</td>
<td>0.25 - 0.35</td>
<td>0.20 - 0.30</td>
<td>0.20 - 0.30</td>
</tr>
<tr>
<td>Nb</td>
<td>max. 0.07</td>
<td>-</td>
<td>0.015 - 0.070</td>
</tr>
<tr>
<td>Ca</td>
<td>max. 0.015</td>
<td>-</td>
<td>0.0005 - 0.0150</td>
</tr>
<tr>
<td>Ti</td>
<td>max. 0.030</td>
<td>0.015 - 0.035</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>max. 0.0020</td>
<td>0.001 - 0.003</td>
<td>-</td>
</tr>
</tbody>
</table>
Fig. 1.3 Effect of Vanadium content on mechanical properties of 3Cr-1Mo steel [12]

The intentional addition of boron in 3Cr-1Mo-0.25V-Ti-B steel increases the hardenability and assures uniform distribution of mechanical properties throughout most heavy cross sections. The addition of titanium helps to maximize the effect of boron [34].

The modified steels are supplied in quenched and tempered condition. Tempering is carried out at 690-710°C in order to reduce the strength level and to improve impact properties of the quenched steels. The tempering process is performed after the final post weld heat treatment cycle of the reactor. The steels exhibit some decrease in low temperature toughness compared to the conventional steels: 54 J transition temperature (54 J TT) is -29°C and -40°C, respectively.

Design properties of the conventional Cr-Mo steels and vanadium modified Cr-Mo steels are summarized in Table 1.3. Higher room temperature strength properties of the modified steels are presented. Increased mechanical properties
allow for higher design stresses, leading to a decreased wall thickness and a reduced weight of the reactors[4].

According to API 941, 0.25 wt.% of vanadium in 2.25Cr-1Mo steel protects the material from HTHA (High Temperature Hydrogen Attack) under hydrogen partial pressure 13.79 MPa up to 482°C, compared to 454°C for the conventional 2.25Cr-1Mo alloy[80]. However, despite the vanadium addition, the maximum design temperature permitted by ASME VIII-2 for modified 3Cr-1Mo steels is 454°C at the present time. These steels cannot meet the Division 2 creep rupture requirements at 482°C. It is indicated in Table 1.3 that application of the modified steels results in lower unit weight of the reactors at a comparable cost.

Due to the more wall thickness, the high hardenability and the severe service conditions of the reactors made of vanadium modified Cr-Mo steels, welding needs precaution and careful processing. Welds are always post weld heat treated before service. Generally, 54J TT of weld metal and base metal are 20°C to 30°C higher than those of the conventional 2.25Cr-1Mo steel, but the transition temperature of heat affected zone is sufficiently low enough compared with those of base metal and weld metal.

1.3.4 ASME Code Requirement for Hydrocracker.

Since hydro processing reactors generally operate in the temperature range of 400°C to 454°C with hydrogen partial pressures above 10 MPa, API 941 has dictated that as a minimum requirement, the material for the construction of these reactors be 2.25Cr-1Mo steel[17]. As indicated earlier, 2.25Cr-1Mo alloys have been extensively used for the construction of hydro processor reactors in the present time. 3 Cr-1 Mo material has also been used to a lesser extent where process conditions dictated a requirement for the higher alloy content in the steel.
However, the need for higher stress intensity values resulting in reduced wall thickness reactors has been the driving force for the development of alternate higher strength materials and this development gained momentum in the early 1980s.[11]

As a result, the following conventional and newer alloy steels can be used for hydro processor reactors today.

(I) Conventional 2.25Cr-1Mo Alloys

This material has been the alloy material of choice for almost all of the hydro processing reactors that have been constructed during the past 30 years. The property requirement and values are given in Table 1.3.

(II) 2.25Cr-1Mo Alloy (ASME Code Case 1960-3)

This material is basically the same material as conventional 2.25Cr-1Mo material except that the final tempering (Final post weld heat treatment) temperature is limited to assure a higher tensile strength. This restriction results in higher permissible design stress intensity values (9% over conventional 2.25 Cr-1Mo material)[13]. The limitations of this material include a potential for higher hydrogen embrittlement and hydrogen attack susceptibility as well as a maximum design temperature limitations of 454°C. Because of these limitations, this alloy has found limited acceptance and only a relatively small number of reactors have been built to date utilizing this code case.
(III) 2.25Cr-1Mo-0.25V Alloy (ASME Code Case 2098-2)[3,4]

Because of vanadium addition and increased tensile strength, this material achieves the highest permissible design stress intensity values of all these materials under discussion (12% increases at 454°C and 39% increases at 482°C over conventional 2.25Cr-1Mo material). Vanadium addition generally increases the tensile strength, creep rupture strength and hydrogen attack resistance of these alloys[11]. This material has proven to have an excellent resistance to hydrogen attack through extensive testing during its development. This resistance to hydrogen attack can be attributed to finely dispersed stable vanadium carbides. The addition of vanadium enhances the creep rupture life of 2.25 Cr-1Mo alloy to a greater degree than that for 3Cr- and Cr 1 Mo alloys.

The API 941 committee recently voted to elevate this material to the same level as 3 Chrome 1 Moly alloy on the Nelson Curve. Because of its better creep rupture properties and hydrogen attack resistance, this material is the only vanadium enhanced material permitted by the ASME Sec-VIII, Div. 2 code which can be used with design temperature up to 482°C with hydrogen partial pressure 11.7 MPa, that are typical in hydro processing reactors. ASME Code Case 2098-1 permits this material use up to 482°C.

The addition of vanadium was originally thought to present disadvantages in terms of hardenability and weldability and a higher susceptibility to reheat or stress relief cracking[15]. These effects have not been found to be significant. Recent studies have indicated that low impurity vanadium enhanced 2.25Cr-1Mo steel has similar susceptibility to stress relief cracking as the conventional steel. Other inherent disadvantages of this material in the past included limited availability of welding consumables and the suggested need for intermediate stress relief at 600°C in lieu of a dehydrogenation treatment usually conducted at
315°C[8]. In spite of extensive testing programs that have taken place over a number of years in the development of this alloy, the first commercial reactor is only now being constructed by Nuovo Pignone in Italy. A number of weld manufactures have now also developed welding consumables which give good metal strength, toughness and creep rupture properties.

(IV) Conventional 3Cr-1 Mo alloy:

This material has been used for the construction of hydro processor pressure equipment on a limited basis where process requirements indicated a need for a higher chromium content. The disadvantages of this material in comparison of convention 2.25Cr-1Mo material include internal stress rupture properties above 426°C and, therefore, lower permissible design stress intensity values (13% lower at 454 °C and higher material costs.)[3]. Further more, the ASME section VIII Division 2 Code limits the maximum design temperature of vessels constructed from this material to 454 °C. Because of the limited use of this material, welding consumables are generally not readily available.

(V) 3 Cr-1Mo-0.25V-Ti-B (Formerly C.C. 1961) and 3Cr-1Mo-V-Cb-Ca alloys (Formerly C.C.2151)

These newer alloys, are similar in opportunities with yield of 414 MPa and minimum and maximum tensile strengths between 586 MPa and 758 MPa. Both of the alloys are susceptible identically in chemical composition except that the first alloy contains intentional addition of limited amounts of titanium and boron and the second alloy contains limited amounts of columbium and calcium.

It is to be noted that both alloys utilize vanadium addition (0.5%V nominal ) to enhance creep rupture strength and hydrogen attack resistance. However despite
the vanadium addition, the maximum design temperature permitted by the ASME Section VIII Division 2 Code at the present time is 454° C because experimental data suggests that these alloys cannot meet the Division 2 creep rupture requirements at 482°C. At 454°C, these material have approximately 9 % higher allowable stress intensity values than the conventional 2.25Cr-1Mo material.

Intentional addition of boron in the C.C. 1961, material increases the hardenability of the material and assures uniform distribution of mechanical properties through out most heavy cross sections. The addition of titanium helps to maximize the effect of boron (Kimure et al 1993)[11]. The C.C.2151 alloy utilizes columbium for enhancing tensile strength by precipitation of columbium carbides (CbC) and minimizes reheat cracking by decreasing intergranular micro segregation of sulphur (Kobe steel, 1993)[30].

The C.C. 1961 alloy, now patented in the U.S., was developed in the early '80s and was adopted an ASME code material in 1992. The first commercial reactor was constructed in 1990 by Japan Steel Works (J.S.W) to date twenty two commercial reactors have been built by J.S.W and five more are presently under construction. The same welding consumables originally developed by the weld wire decision of Kobe steel have been used for both materials.

**Table 1.3** indicates the relative tensile strength and the ASME Section VIII Division 2 design intensity stress values of these materials along with other relevant data. Each of the alloys characteristics related to the design and construction of hydro processing reactors are available in either plate or forging product forms[12]. Also included in **Table 1.3** is relative cost/weight figures based on a typical nominal 1,000 ton hydro processor reactor fabricated from each of the alloy discussed. At a design temperature of 454°C, the enhanced 2.25Cr-
1Mo alloys provides a marginally lower total cost over the conventional 2.25Cr-1Mo steel and the vanadium modified steels[10]. However, the limitations of this material have precluded its general acceptance. The vanadium-modified steels provide,

- The lightest reactors, which can be a significant benefit in foundation design, transportation and erection.
- At a design temperature of 482°C, 2.25Cr-1Mo-0.25V steel offers a very substantial advantage from reduced weight and cost considerations.
- Higher tensile strength at room and design temperature thereby allowing higher allowable stress, which in turn results in thinner wall thickness.
- Better elevated temperature properties.
- Better hydrogen embrittlement and hydrogen attack resistance.
- Better temper embrittlement resistance.
- Good weldability.

It is the only material, which can be used hydrogen partial pressures above 11.7 MPa.[10,4]
Table 1.3 Comparison of Hydro processing reactor materials [4]

<table>
<thead>
<tr>
<th>Alloy Types</th>
<th>Conventional 2.25Cr-1Mo</th>
<th>Enhanced 2.25Cr-1Mo</th>
<th>225Cr-1Mo-0.25V</th>
<th>3Cr-1Mo-0.25V-Ti-B</th>
<th>3Cr-1Mo-V-Cb-Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old ASME Code Case</td>
<td>NA</td>
<td>1960 vs 3</td>
<td>2096-2</td>
<td>1951</td>
<td>2151</td>
</tr>
<tr>
<td>ASME Material Specifications</td>
<td>SA336 F22</td>
<td>SA541 CL2 Cl2b</td>
<td>SA336 F22V</td>
<td>SA536 F3V</td>
<td>SA336 F3V</td>
</tr>
<tr>
<td>ASME Sec VIII Div. 2 Max Allowable Temp (Deg. C)</td>
<td>192</td>
<td>464</td>
<td>462</td>
<td>454</td>
<td>454</td>
</tr>
<tr>
<td>Room Temp. UTS (Mpa)</td>
<td>517-689</td>
<td>585-760</td>
<td>585-760</td>
<td>585-760</td>
<td>585-760</td>
</tr>
<tr>
<td>Room Temp. YS (Mpa)</td>
<td>310 Min</td>
<td>375 Min</td>
<td>411 Min</td>
<td>414 Min</td>
<td>414 Min</td>
</tr>
<tr>
<td>Design Stress Intensity as per ASME Sec VIII Div. 2 (Mpa)</td>
<td>159 @ 454 C</td>
<td>164 @ 454 C</td>
<td>169 @ 454 C</td>
<td>164 @ 454 C</td>
<td>164 @ 454 C</td>
</tr>
<tr>
<td>Nelson Curve for Max Temp in H2 Service</td>
<td>451°C-pp=211 MPA</td>
<td>451°C-pp=211 MPA</td>
<td>412°C-pp=12.4 MPA</td>
<td>454°C-pp=212.4 MPA</td>
<td>454°C-pp=212.4 MPA</td>
</tr>
<tr>
<td>Typical Vessel Thickness as per ASME Sec VIII, Div. 2 for a 1000MT Reactor</td>
<td>5380mm @ 454°C</td>
<td>307mm @ 154 C</td>
<td>298mm @ 454°C</td>
<td>307mm @ 454°C</td>
<td>307mm @ 454°C</td>
</tr>
<tr>
<td></td>
<td>442mm @ 482°C</td>
<td>NA @ 482 C</td>
<td>NA @ 482 C</td>
<td>NA @ 482 C</td>
<td>NA @ 482 C</td>
</tr>
</tbody>
</table>

All the alloys described are supplied in the quenched and tempered condition with vacuum degassing to achieve high impact properties. Quenching is usually carried out in a water-filled quench tank fitted with high capacity re-circulating pumps to agitate the water for maximum possible quenching effects. Tempering is normally carried out at 690°C - 704°C for the conventional alloys and 704°C - 718°C for vanadium-modified alloys in order to soften and reduce the strength level of the quenched steel and to improve its impact properties. The tempering process is carried out during the final post weld heat treatment cycle of the reactor. The steel is usually ordered on the basis of allowing for two additional post weld heat treatment cycles for future weld repairs or modifications in the field if needed[4].

All the above discussion leads to one important point that selection of hydro cracker reactor material needs lots of economical and technical consideration.
References:

1. I. Detemple, F. Hanus, and G. Luxenburger, Dillinger Hutte, “ADVANCED STEEL FOR HYDROGEN REACTORS”


5. Dr. A.K. Lahiri, Kiribhco Ltd., Hazira, Surat, Gujarat, “Material Selection And Performance In Fertilizer Industries”.

6. Joanna Hucinska, “ADVANCED VANADIUM MODIFIED STEELS FOR HIGH PRESSURE HYDROGEN REACTORS”


8. Yamada, M., Sakai, T., nose.: “Development of Cr-Mo-Ve-Cb-Ca steel for higher pressure and high temperature hydrogenation reactors, in application of 2.25Cr-1Mo-V Modified steel for hydro processing pressure vessels.” Kobe steel, Limited tag sago, Japan, 1996.


10. S.Y. Khedekar and C. Manoharan, Gujarat Refinery, IOCL, Baroda “Hydrocracking Process to Maximise Middle Distillate”


15. Lesile P. Antalffy Senior Director, Process Department, Fluor Daniel, Inc. Sugar Land, Texas & Pran M Chaku, Chief Metallurgist / Senior Technologist, ABB Lumas Global, Houston Texas. "MODERN HYDROPROCESSING REACTORS"


40. JSW, Data Provided by Japan Steel work in a Private Communication Dated February 19, 1994.


