The Pebble-Bed High-Temperature Reactor as a Source of Nuclear Process Heat

Volume 4
System Considerations on Nuclear-Heated Steam Reformers

by
K. Kugeler, R. Schulten, M. Kugeler, H. F. Nießen, M. Röth-Kamat
H. Hohn, O. Woike, J. H. Germer
Berichte der Kernforschungsanlage Jülich – Nr. 1116
Institut für Reaktorentwicklung Jül - 1116 - RG

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K. Kugeler, R. Schulten, M. Kugeler, H. F. Nießen, M. Röth-Kamat
H. Hohn*)
O. Woike, J. H. Germer**)

A Common Study by
Kernforschungsanlage Jülich GmbH and General Electric Company

*) Institute for Reactor Development, Kernforschungsanlage Jülich, Germany
**) General Electric Company, USA
ABSTRACT

In this volume the design conditions for a helium-heated steam reformer in the primary circuit of a high-temperature reactor are explained as far as today's knowledge allows. For the realization of helium-heated steam reformers, some fundamental questions at first occur regarding the heating temperature, heat fluxes, suitable materials and design solutions for steam reformers. It is shown that following the development program, which has been carried out until now, solutions to these questions can be seen. Moreover, details are given about the heat transfer, the mechanical design and the behaviour of reformer materials in helium with regard to H₂- and T-permeation as well as corrosion. Furthermore, questions about the choice of the lay-out data, the design form, the arrangement in the helium circuit of the nuclear reactor and the necessary development steps are handled. Some design examples of heat exchangers for a 3000 MW(th)-plant are given, too.
INTRODUCTION

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INTRODUCTION

For the realization of helium-heated steam reformers, the following fundamental questions at first occur:

- Is a heating temperature of maximum 900 - 1000 °C sufficient in order to carry out the reforming process with adequate methane conversions?

- Are heat fluxes, comparable to those in conventional plants, obtainable in the reformer tubes?

- Are suitable materials available under the changed conditions of helium circuits?

- Are design solutions for steam reformers, which can be used in nuclear plants, thinkable?

Questions of the choice of the lay-out data, of the design form, of the arrangement in the helium circuit of the nuclear reactor and of the necessary developments steps are, next to the above, of special interest, too.
4.1 Status of Conventional Technology of Steam Reforming of Methane [1, 2, 3]

In the conventional process of the steam reforming of methane (see fig. 4.1-1), the starting materials (natural gas, liquid petroleum gas, refinery gas, light benzenes up to ~ 200 °C b.p.) are first desulfurized by hydrogenation and adsorption. After adding process steam in the desired ratio, the mixture is led to an externally heated steam reformer and reforming takes place in the tubes in the presence of a nickel catalyst. The tubes are heated externally mainly by radiation (maximum temperature ~ 1500 °C) by combustion of a sulfur-free fuel. The hydrocarbon/steam mixture is led to the reformer tubes at a temperature of 450 to 550 °C, pressures of 1 ... 30 b and with a steam/methane ratio of ~ 2/1 ... 5/1. The reforming temperature today lies between 750 and 850 °C depending on the application of the product gases. Depending on the pressure and the amount of steam, complete methane conversions are possible, excepting for a few percent "remaining methane". The waste heat of the flue gases and the product gases is utilized to produce process steam, for preheating of combustion air as well as for preheating of the applied hydrocarbon/steam mixture.

The cooled product gases are converted in a hydrogen production plant in 2 steps: in the first step the carbon oxide portion is converted to hydrogen at about 400 °C on an iron oxide catalyst. After cooling, nearly complete conversion of CO takes place (excepting for small traces) in a further step at about 200 °C on a

![Flow Scheme for Conventional Reforming of Methane](image_url)
copper catalyst. For removing the carbon dioxide of the converted product gas, there are a number of chemical and physical methods e.g. hot potash scrubbing, Purisol, Rectisol, MEA and DEA scrubbing.

If necessary, the remaining CO-content is reduced even further by methanation, as is the case in certain applications, where CO has to be reduced due to its being a catalyst poison.

In this step CO and CO\(_2\) react with H\(_2\) exothermically and are converted to methane at 300 °C on a nickel catalyst. Hydrogen is then cooled.
and is available as a product. The conventional plants are so constructed today that the centrifugally cast tubes (length: about 10 m, inner diameter: about 100 ... 130 mm, wall thickness: 15 ... 20 mm, material with 25 \% Cr/20 \% Ni) are hung in the reformer furnace (about 1 tube/m² floor space) and are heated by burners on the side wall and overhead. In a convection zone situated after the steam reformer, the waste heat of the flue gases is utilized below about 1000°C. The compensation of the deformation in elongation of the reformer tubes is normally so achieved that all the tubes are individually connected via so-called pigtails with a collecting pipe (see fig. 4.1-2).

This process is technically fully developed today and is applied worldwide for the production of gases for the ammonia- and the methanol synthesis as well as for the \( \text{H}_2 \) production for hydrocracking processes. The hydrogen produced has a pressure between 10 and 20 b and a purity of up to 99.5 \% (\( \text{CO} + \text{CO}_2 \sim 10 \text{ ppm}, \text{CH}_4 \sim 0.5 \% \)).

The energy consumption amounts to about 3600 ... 4000 kcal/Nm³H₂. Of this about 2200 kcal/Nm³H₂ is used as raw material (\( \geq 0.25 \text{Nm}^3 \text{CH}_4/1 \text{Nm}^3\text{H}_2 \)) and depending on the combination of the processes and the output pressure, 1400 ... 1800 kcal/Nm³H₂ as heat for the overall process (including gas purification). The substitution of the latter amount of energy by nuclear heat is the aim and the technical task in nuclear steam reforming.
4.2 Equilibria, Methane Conversion (Steam Reforming)

Many years of operation of commercial plants and the operation of the helium-heated steam-reforming plant in the Nuclear Research Centre Jülich (KFA), as well as the accompanying kinetic experiments, have confirmed that predictions can be made about the attainable methane conversion and gas analysis according to the equilibrium reactions. Fig. 4.2-1 shows gas compositions as a function of the steam-reforming pressure and temperature, and the ratio of steam/carbon, in parameter regions of interest for nuclear application. Accordingly, the attainable remaining methane content (dry) is shown in fig. 4.2-2.

Basic Equations

\[
\begin{align*}
&\text{CH}_4 + H_2O + CO + 3H_2 \\
&CO + H_2O + CO_2 + H_2 \\
\end{align*}
\]

\[
\begin{align*}
1) \quad K_1 &= \frac{p_{CO} \cdot p_{H_2}^3}{p_{CH_4} \cdot p_{H_2O}} \\
2) \quad K_2 &= \frac{p_{CO_2} \cdot p_{H_2}}{p_{H_2O} \cdot p_{CO}} \\
3) \quad \Sigma n_C &= n_{CO} + n_{CO_2} + n_{CH_4} \\
4) \quad \Sigma n_H &= 2n_{H_2} + 2n_{H_2O} + 4n_{CH_4} = b \cdot \Sigma n_C \\
5) \quad \Sigma n_0 &= n_{CO} + 2n_{CO_2} + n_{H_2O} = c \cdot \Sigma n_C
\end{align*}
\]

System of equations

\[
\begin{align*}
&\text{C : H : O = 1 : b : c, } x_i = \frac{p_i}{p}, \quad x_i = \frac{n_i}{\Sigma n_i} \\
1) \quad K_1 &= (x_{CO} \cdot x_{H_2}^3 \cdot p^2)/(x_{CH_4} \cdot x_{H_2O}) \\
2) \quad K_2 &= (x_{CO_2} \cdot x_{H_2})/(x_{H_2O} \cdot x_{CO}) \\
3) \quad x_{CO_2} &= (1 + 2\alpha)x_{CH_4} + (\alpha - 1)x_{H_2O} + \alpha \cdot x_{H_2}
\end{align*}
\]
4) $x_{H_2} = (2 - \beta)x_{CO} + (2 - 2\beta)x_{CO_2} - (1 + \beta)x_{H_2O}$

5) $x_{H_2} + x_{CO} + x_{CO_2} + x_{CH_4} + x_{H_2O} = 1$

$\alpha = 2(1 - c)/b, \beta = (4 - b)/c$

The choice of the steam-reforming parameters depends on the further use of the product $H_2$ or $H_2 + CO$ mixture. Typical examples for some of the regions of application foreseeable today are given in § 4.11. In general, for all applications which require a high operating pressure, a high steam-reforming pressure is advantageous. By compressing the gases before the steam-reforming process, compression energy can be saved. The disadvantage is that with increasing pressure, the backward reaction of methane conversion occurs, affecting the economy of the process. At a constant steam/hydrocarbon ratio and constant reforming temperature, the remaining methane content of the dry product gas increases with increasing pressure.

For typical parameters (reforming temperature = 800 °C, $H_2O/CH_4 = 3/1$) and for an initial steam reforming pressure of 30 b, the $CH_4$ conversion sinks by about 10 % for a pressure increase of 10 b and increases by a similar amount for a lowering in pressure. To produce the same amount of hydrogen, the total amount of reactants passing through the plant must be increased by about 10 % for an increase in pressure of 10 b. This naturally causes correspondingly higher production costs for the steam reformer and gas purification. Even after increasing the steam/carbon ratio, which favourably influences the $CH_4$-conversion, certain freedom still exists for the choice of pressure. However, the heat requirements and the input for heat recovery in the gas production thereby increase.

For heating the reforming plant with sensible heat of helium from the primary circuit of a HTR, a favourable coolant pressure for the nuclear reactor is to be chiefly considered. As this can be explained in detail, this pressure is appropriate at 40 b. So the reforming pressure should be maintained at $40 > b$ as far as possible, so that the pressure difference in the tube wall of the reformer tubes and hence the mechanical stresses are held as low as possible.
A steam/methane ratio of under 1.5/1 cannot be run without a risk of carbon deposition on the catalyst. The reforming temperature should not be raised above 850 °C in order to avoid tube wall temperatures of over 950 °C.
4.3 Kinetics of the Methane Reforming Reaction

All the experimental measurements given in literature indicate that the rate of conversion of methane is of first order in first approximation [4] and can be given by the following:

\[ V_{CH_4} \sim k(T) \cdot P_{CH_4} \]

Following these results, measurements were carried out in the KFA Jülich with a differential reactor whereby the interesting regions (600 \( \leq T \leq 800 \) \(^\circ\)C, 20 \( \leq p \leq 30 \) b, 2.5 \( \leq H_2O/CH_4 \leq 3 \)) were investigated. The following fig. 4.3-1 shows typical experimental results.

These results can be so interpreted that above a reaction temperature of about 600 \(^\circ\)C the reforming reaction occurs so fast that equilibrium is reached and that the limiting factor for the design is really the possibility of bringing in heat to the reformer tube. From the point of view of the reaction kinetics about e.g. 500 Nm\(^3\) CH\(_4\)/h \( \cdot \) tube could be converted (based on 600 \(^\circ\)C) while only approx. 100 Nm\(^3\) CH\(_4\)/h \( \cdot \) tube are converted limited by heat transfer (see later). This fast equilibrium adjustment has also been demonstrated by the reforming plant EVA as is seen in fig. 4.3-2 which shows the dependence of the experimental and calculated methane contents on the reforming temperature.

Fig. 4.3-1 Experimental Results on Reaction Kinetics [5]

Fig. 4.3-2 Remaining Methane Measured in the EVA Plant [6]
4.4 Temperatures, Heat Transfer and Heat Fluxes

The energy supply to conventional steam-reforming plants today is based upon the combustion of light sulfur- and ash-free hydrocarbons. Fig. 4.4-1 shows a schematic of the conventional process.

The fuel gases are burnt with preheated air in burners located at the top and side of the furnace. The combustion gas produced (flame temperature \( \sim 1500 \, ^\circ\text{C} \)) flows downward through the steam reformer in parallel with the flow of the process gas for the reforming process.

The process gas flows downward through the catalyst-filled tubes (10 m) and conversion takes place along the 10 m long reaction length according to the reaction: \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2; \Delta H = +49 \, \text{kcal/mole} \). The gas analysis depends on the pressure, temperature and composition (\( \text{H}_2\text{O}/\text{CH}_4 \)) of the reactants. In the upper section of the tube, the process gas receives large amounts of heat especially due to radiation, which lead to an extremely high heat flux density in this part of the reformer tube. For an end reaction temperature of 800 \( ^\circ\text{C} \), the enthalpy of the hot combustion gas can be utilized for the process down to a temperature of \( \sim 1000 \, ^\circ\text{C} \). The remaining enthalpy of the combustion gases is utilized in waste-heat boilers for preheating air and the feed gas, and for the generation of process steam.

In this process the heat transferred per unit area in the reformer tubes is very high in the upper region but decreases by a factor of 5 to 10 from the top to the bottom. However, because of the high temperature difference between the combustion gas and the process gas, the average heat flux over the total tube surface is relatively high (\( \sim 70,000 \, \text{kcal/m}^2\text{h} \)).

For heating the reformer tubes with nuclear heat, which is obtained from the primary circuit of a high-temperature nuclear reactor, a heat source with an upper temperature of about 950 \( ^\circ\text{C} \) is available. Furthermore only a certain part of the reactor power can be used for the reforming process as the inlet temperature of the reactor helium should be between 250 \( ^\circ\text{C} \) and a maximum of 450 \( ^\circ\text{C} \).
Nuclear Process

Conventional Process

Fig. 4.4-1 Flow Scheme and Some Fundamental Data of Heat Transfer for the Conventional and Nuclear Processes
The sensible heat of helium between this temperature and between about 600 ... 800 °C is used for the generation of steam.

An economical design of a steam reformer in a nuclear process leads to a prerequisite that similarly high average heat fluxes are obtained as in conventional processes. This aim is achieved in a helium-heated counterflow heat exchanger (s. fig. 4.4-1) in spite of the comparatively low temperature difference because helium under high pressure (40 b) shows excellent heat transfer properties. In this case the smaller temperature difference is compensated for by the high overall heat transfer coefficient for the process. The typical values for a helium-heated steam reformer shown in fig. 4.4-1 have been verified in the pilot plant EVA at the KFA Jülich, utilizing a single original-sized tube [7].

A certain disadvantage of conventional heating, viz. the unequal azimuthal heat flux distribution, which can show differences of up to 30 % based on the average value, is avoided in the heating with helium under pressure. Helium transfers heat nearly completely by convection and less than about 10 % is transferred by radiation in the observed temperature range. The given values for the heat transfer rate can be considerably increased by raising the outlet temperature of helium in the nuclear reactor above 950 °C, by increasing the reactor pressure above 40 b or by tolerating larger pressure losses on the inside and outside. A part of the measures requires some improvement in the status of material technology attained up to today.

After determining temperatures, pressure, tube dimensions and arrangement and gas ducting in the tube bundle, the thermodynamic design of a helium-heated reformer tube depends considerably on the choice of the velocities of helium and the process gas. An overall view showing the scope for determining these process parameters is given in fig. 4.4-2. The heat transfer coefficients and pressure drops on the process and helium sides are plotted as a function of the respective flow velocities.
Fig. 4.4-2 Heat Transfer for the Nuclear Process
Fig. 4.4-3
Principle of a Reformer Tube for Nuclear Applications

Table 4.4-4
Data of Reformer Tubes

<table>
<thead>
<tr>
<th>Helium side</th>
<th>600 ... 800 °C + 950 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperatures:</td>
<td>600 ... 800 °C + 950 °C</td>
</tr>
<tr>
<td>Pressure:</td>
<td>~ 40 b</td>
</tr>
<tr>
<td>Pressure loss:</td>
<td>~ 0.2 b</td>
</tr>
<tr>
<td>Mass flow:</td>
<td>0.15 ... 0.25 kg/sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process side</th>
<th>450 ... 300 °C + 800 ... 850 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperatures:</td>
<td>450 ... 300 °C + 800 ... 850 °C</td>
</tr>
<tr>
<td>End pressure:</td>
<td>41 b</td>
</tr>
<tr>
<td>Pressure loss:</td>
<td>3 ... 5 b</td>
</tr>
<tr>
<td>Mass flow:</td>
<td>100 ... 150 Nm³ CH₄/h + 200 ... 400 kg H₂O/h</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>10 ... 12 m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube length</td>
<td>10 ... 12 m</td>
</tr>
<tr>
<td>Inner diameter:</td>
<td>~ 100 mm</td>
</tr>
<tr>
<td>Wall thickness:</td>
<td>~ 15 mm</td>
</tr>
</tbody>
</table>
The calculations are based on a reformer tube with an inner diameter of 100 mm and a wall thickness of 15 mm. Fig. 4.4-2 shows the typical course of calculation for determining the heat transfer coefficients and pressure drops. For conventional plants flow velocities between 2 and 3 m/sec (based on the empty tube) are normally chosen today. A helium velocity of 30 m/sec provides a compromise between the size of the heat transfer areas and the necessary pumping power of the helium blowers. The attainable heat flux in the temperature interval from 950 - 700 °C for the reforming process is about 60,000 - 70,000 kcal/m²h.

The heat transferred to a reformer tube can be increased by utilizing an inner gas return duct (see fig. 4.4-3) for the hot product gas. Depending on the reforming temperature (800 ... 850 °C), the enthalpy of the product gas down to 650 ... 600 °C can be utilized for the process by heat transfer to the catalyst filling. This generally leads to a ~20 % increase of the heat transferred to the reformer tube.

Corresponding to the above considerations regarding heat transfer, pressure losses, conducting of the process and temperature requirements the following values given in table 4.4-4 are obtained for nuclear application. These values have been used in the designs shown later.
4.5 Mechanical Stresses in Steam Reformer Tubes

The stress in the tubes of a helium-heated steam reformer is characterized by the following limiting conditions:

- maximum tube wall temperature in operation: $T \leq 900\, ^\circ C$
- maximum tube wall temperature for short-time accident: $T \leq 950\, ^\circ C$
- azimuthal symmetrical heating for convective heat transfer
- maximum temperature gradient in the tube wall: $\Delta T \approx 30\, ^\circ C$
  (for $T_{\text{wall}} \approx 900\, ^\circ C$)
- maximum pressure difference in the tube wall for the hot part of the tube: $\Delta p \approx 1\, \text{bar}$ (for $T_{\text{wall}} \approx 900\, ^\circ C$)
- maximum pressure difference in the tube wall in the cold part of the tube: $\Delta p \approx 4\, \text{bar}$ (for $T_{\text{wall}} \approx 600\, ^\circ C$)
- no corrosion on the heating side (except for effects of a few ppm impurities in helium (see § 4.10))
- nearly constant heat flux in the axial direction
- no hot spots
- no constraining forces on the tubes when inner return ducts are used for the product gas

The course of the calculations for the design is given in the following pages.

The vessel formula is generally used for measuring the wall thickness of the reformer tubes. Thermal stresses are relieved at the existing high temperatures by the creep properties of the material and appear only when the heating and cooling processes take place too soon. Without getting rid of thermal stresses, it can be shown by a simple calculation that the design and operation of a steam reformer for the service life actually attained would not be possible.

Due to the temperature difference in the tube wall, there is a specification of $\approx 1\, ^\circ C/\text{min}$ for starting and stopping operation of the plant.

In the case of nuclear process heat applications, with the nuclear reactor helium pressure of 40 bar and the steam reforming pressure of $\approx 30...40$ bar, it is possible to design a reformer tube.
as follows: For the chosen dimensions in the hot part of the tubes (internal diameter \( D_i = 100 \text{ mm} \), wall thickness \( s = 15 \text{ mm} \), creep strength \( \sigma_{\text{allow}} \approx 0.5 \text{ kp/mm}^2 \)) the value of \( \Delta p_{\text{allowable}} \) has been calculated to be 15 kp/cm\(^2\). In comparison with this value, the actual maximum pressure difference is \( \approx 1 \text{ b} \) in the hot part of the tube and about 4b in the cold part of the tube (600 °C). This is in contrast to a conventional steam reformer where a novel problem occurs due to the pressure on the outside of the tube in the case of an accident (failure of the feed gas supply). It can be shown that in the case of the existing thick-walled tubes with relatively small inner diameters, buckling effects do not play a role here.

For the design of the reformer tubes the following calculations are carried out:

1) Design of the reformer tubes according to the vessel formula
2) Refined calculation (\( r \)-dependence)
3) Buckling effects in the tubes under pressure on the outside
4) Thermal stresses during operation
5) Thermal stresses during start-up and shut-down

At first the dimensions of the reformer tubes are calculated for the accident of total loss of coolant

\[
s = \frac{\Delta p \cdot D_i}{200 \cdot \sigma}
\]

\[
\Delta p = 40 \text{ kp/cm}^2
\]

\[
D_i = 100 \text{ mm}
\]

\[
\sigma \approx 1.5 \text{ kp/mm}^2 \text{ für 1000 h accident duration}
\]

From these considerations and with a safety factor in addition, a wall-thickness of 15 mm results for the reformer tube.

The checking of the reference stress in this thick-walled tube gives the following result:

\[
\sigma_t = p_i \left( \frac{r^2}{r_i^2} - \frac{1}{r_i^2} \right) - p_a \left( \frac{r^2}{r_i^2} + \frac{r^2}{r_i^2} \right)
\]

\[
\sigma_r = p_i \left( \frac{r^2}{r_i^2} + \frac{r^2}{r_i^2} \right) - p_a \left( \frac{r^2}{r_i^2} - \frac{r^2}{r_i^2} \right)
\]
\[ \sigma_a = \frac{1}{2} (\sigma_t + \sigma_r) \]

\[ \sigma_{\text{compar}} = \frac{1}{\sqrt{2}} \cdot \sqrt{(\sigma_t - \sigma_r)^2 + (\sigma_r - \sigma_a)^2 + (\sigma_a - \sigma_t)^2} \]

For \( P_a = P_i = 40 \text{ b} \), it follows: \( \sigma_t = -40 \text{ kp/cm}^2 \), \( \sigma_r = -40 \text{ kp/cm}^2 \), \( \sigma_a = -40 \text{ and } \sigma_{\text{compar}} = 0 \text{ kp/cm}^2 \)

The chosen tube dimensions guarantee safety against buckling from outside in the case of failure of pressure on the process side, as the following calculations show:

\[ P_k = \frac{E}{(n^2 - 1)c^2} \cdot \frac{s}{r} + \frac{E}{12(1-\mu^2)} \cdot \left\{ (n^2 - 1) + \frac{2n^2-1-(1-\mu)}{c} \right\} \left(\frac{s}{r}\right)^3 \]

\( P_k = \text{critical pressure} \)

\( C = 1 + \left(\frac{n-L}{n-P_r}\right)^2 \)

\( s = \text{wall thickness} \)

\( r = \text{mean radius} \)

\( n = \text{number of waves for circumference} \geq 2 \)

\( (n \text{ is so chosen that } P_k = \text{minimum}) \)

\( L = \text{tube length} \)

\( E = \text{Youngs' Modulus} \)

For \( \frac{1}{r} \to \infty \), it follows \( C \to \infty \) and \( \mu = 0.3 \)

\[ P_k = 0.09 \cdot E \cdot (n^2 - 1) \left(\frac{s}{r}\right)^3, \quad n = 2 \]

For \( r = 5.8 \text{ cm}, s = 1.5 \text{ cm}, E = 1.15 \cdot 10^6 \text{ kp/cm}^2 \) the value of \( P_k \) is 5500 kp/cm\(^2\), i.e against an external excess pressure of 40 kp/cm\(^2\) there is a safety factor of < 100 against buckling.

In the case of failure of the helium heating, the following consideration can be employed:

\[ \sigma_t = P_i \frac{y^2 + 1}{y^2 - 1}, \quad \sigma_r = -P_i, \quad \sigma_a = \frac{P_i}{y^2 - 1}, \quad y = \frac{r_a}{r_i} = 1.3 \]
\[ \sigma_{\text{red}} = p_i \cdot 1.73 \cdot \frac{y^2}{y^2 - 1} = 170 \text{ kp/cm}^2 \]

This value is tolerable for a short duration \( \tau \) of the accident (i.e. assuming \( \tau < 1000 \text{ h during the lifetime} \)).

The thermal stresses are relieved during steady operation. The following calculation shows that without relieving these stresses, it would not be possible to design a reformer tube.

\[
\begin{align*}
\sigma_r &= C \cdot (r_a^2 \cdot \ln \frac{r_a}{r_i} + r_i^2 \cdot \ln \frac{r_i}{r_a} - \frac{r_a^2}{r_i^2} \cdot \ln \frac{r_a}{r_i}) \\
\sigma_t &= C \cdot (r_i^2 (1-\ln \frac{r_i}{r_a}) - r_a^2 \cdot (1-\ln \frac{r_a}{r_i}) + \frac{r_i^2}{r_a^2} r_a \ln \frac{r_a}{r_i}) \\
\sigma_a &= \sigma_t \\
C &= \frac{\alpha \cdot E \cdot (T_a - T_i)}{2(1-\mu) (r_a^2 - r_i^2) \ln \frac{r_a}{r_i}}
\end{align*}
\]

Maximum values of the tangential stress occur e.g. for

\[ r = r_a \text{ and } r = r_i : \]

\[ \sigma_t (r = r_a) = \frac{\alpha \cdot E \cdot (T_a - T_i)}{2(1-\mu)} \left( \frac{2r_i^2}{r_a^2 - r_i^2} - \frac{1}{r_a \ln \frac{r_a}{r_i}} \right) < 0 \]

\[ \sigma_r (r = r_a) = 0 \]

\[ \sigma_t (r = r_i) = \frac{\alpha \cdot E \cdot (T_a - T_i)}{2(1-\mu)} \left( \frac{2r_a^2}{r_a^2 - r_i^2} - \frac{1}{r_a \ln \frac{r_a}{r_i}} \right) > 0 \]

\[ \sigma_r (r = r_i) = 0 \]

For \( \alpha = 1.67 \cdot 10^{-5} \text{ }^{\circ} \text{C}^{-1} \), \( E = 1.15 \cdot 10^6 \text{ kp/cm}^2 \), \( \mu = 0.3 \),

\( T_a - T_i \approx 40 \text{ }^{\circ} \text{C} \), \( r_i = 5 \text{ cm} \), \( r_a = 6.5 \text{ cm} \), a compressive stress of 600 kp/cm² results on the inner side of the reformer tube. This calculated value of \( \sigma_t \) is higher than the stress value used for calculation by a factor of 8, if the thermal stresses had not been relieved.

Actually this is not the case and the reformer tubes have a service life of more than 70 000 h. In the course of heating up, the ther-
mal stresses are relieved by the creep properties of the ma-
terial structure [8].

However, the starting and shut-down of the operation of the steam
reformer has to be done sufficiently slowly in order to avoid
thermo-shock. For a rate of temperature change $v_T$, the stress
occurring can be given approximately by:

$$\sigma_T = \frac{E \cdot \alpha}{1 - \mu} \frac{v_T \cdot C \cdot \gamma}{3\lambda} \cdot s^2 \cdot (0.43 \frac{s}{t} + 0.57)$$

$C$ = specific heat $= 0.14 \text{ kcal/kg}^{0}\text{C}$
$\alpha$ = coefficient of expansion $= 1.65 \cdot 10^5 \text{ }^{0}\text{C}^{-1}$
$s$ = wall thickness
$E$ = Youngs' Modulus $= 1.15 \cdot 10^6 \text{ kp/cm}^2$
$\gamma$ = specific weight $= 7.8 \text{ g/cm}^3$
$\lambda$ = thermal conductivity $= 20 \text{ kcal/mh}^{0}\text{C}$

For a constant allowable stress $\sigma_T$, the permissible rates de-
crease with increasing wall thickness as fig. 4.5-1 shows.

Fig. 4.5-1  Interrelation Between the Wall Thickness of the Re-
former Tube and the Permissible Rate of Heating Up and
Cooling Down

One possibility for considerably reducing the tube wall temperature,
in order to obtain a larger strength factor and less hydrogen
diffusion, is to operate with parallel flow instead of counter-
flow between helium and the process gas. With counterflow, the
maximum tube wall temperature is about 900 °C, whereas with parallel flow it would be reduced to about 800 °C on the outer wall. The allowed material strength is thus increased by a factor of 2, and the hydrogen diffusion rate is reduced by a factor of 3. However, if parallel flow is employed, the helium outlet temperature from the reformer tube region has to be at least 800 °C and higher, in order to obtain similar mean thermal fluxes as with counterflow heat exchangers. The amount of process heat available is thus smaller. The axial asymmetry of the thermal flux is much larger. Furthermore, immense difficulties occur during the supporting of the reformer tubes and the advantageous technique of using inner return gas ducts for the product gas cannot be employed. These disadvantages prohibit the use of the parallel flow principle.

Fig. 4.5-2 Tube Wall Temperatures in the Reformer Tube
a) Counterflow
b) Parallel Flow

Fig. 4.5-3 Limitation of the Mechanical Design

An increase of the maximum helium temperatures in the steam reformer to over 950 °C leads to tube wall temperatures of over 900 °C in steady operation. This moves away from the region of known and tested centrifugally cast materials. Improved materials have to be used here (fig. 4.5-3).
4.6 Materials for Reformer Tubes

The creep strength of some of the steels used in the steam reformer can be seen in the following fig. 4.6-1 and 4.6-2, which show the behaviour of the materials as a function of the lifetime and the temperature of operation. From the Larson-Miller diagram an extrapolation can be made from the short-time behaviour to the long-time behaviour of materials and the method is thus suitable to make predictions about the creep strengths to be expected for materials for 100000 hours of operation as well as for short-time stresses due to accidents. Actually operation times of more than 70000 hours have been attained for a sufficiently large number of reformer tubes [10, 11].

![Fig. 4.6-1. Creep Strength Curves for Various Materials as a Function of Temperature [8, 10]](image1)

![Fig. 4.6-3 Larson-Miller Diagram for Material Nr. 1 [8]](image2)
The creep strength value of 0.5 kp/mm² for 100 000 h, which was used in the previous calculation, seems to be conservative for 900 °C as compared with the given values. However, it should be mentioned that the data given in the literature varies a lot (+30 %) and so justifies the assumption of \( \sigma_{\text{allow}} \sim 0.5 \text{ kp/mm}^2 \).

Further development of steam reformer materials for higher temperature or higher creep strength is thinkable, but are not principally necessary, when the maximum heating temperature of the process is fixed at 950 °C, due also to the previously mentioned reasons. Consideration would have to be given especially to the problem of increased corrosion in helium with impurities at higher temperatures.

For all the applications of the helium-heated steam reformer discussed here, an acceptable solution is a design with a maximum tube wall temperature of 900 °C with nearly zero pressure difference in the hot tube part. The only exception is the special direct reduction variant, which requires a hot product gas at low pressure in which the hot gas would go directly into the reduction shaft. A design with a wall temperature of about 900 °C and a pressure difference of 35 b in the hot part would be necessary for this. According to the status of material technology today, this specification requires a decrease in the lifetime to about 5 years or a modification of the materials.
4.7 Hydrogen Permeation

The combination of process heat exchangers with helium circuits of high-temperature reactors has the new and specific problem of hydrogen permeation from the secondary process into the coolant circuit of the nuclear reactor. It is well-known that pure hydrogen permeates at a considerable rate through high-temperature metal walls. The core and the fuel elements of the HTR consist of graphite, which can be corroded by the hydrogen present in the coolant circuit.

Through the reaction $C + 2H_2 \rightarrow CH_4$, about 265 g carbon are removed per $1 \text{Nm}^3$ of hydrogen from the hot regions of the core and its internals. The allowable amount of carbon removal in the 30 years lifetime is of the order of 0.1 mm thickness. Furthermore, there is the risk that the methane formed will decompose under carbon deposition in the different heat exchangers and cause changes in the material structure due to carburization. Hydrogen permeation is therefore a basic consideration in an overall process heat system, if an intermediate circuit is not used.

Experiments to clarify the behaviour of reformer tube materials were started very early, and first results from long-time tests on small test bodies are already existent. These experiments were carried out with a mixture of hydrogen and steam on the inside of the tube at high wall temperatures, and with argon as scavenging gas on the outside. Hydrogen was found as impurity in the argon gas. Fig. 4.7-1 shows the measured "permeation rate" as a function of wall temperature and with gas composition as the parameter [12].

The well-known fact is again demonstrated that pure hydrogen permeates at a very high rate through a metallic wall. The rate was very much less in a mixture of hydrogen and steam. This indicates that a diffusion barrier is formed by oxides of chromium and iron, which form an increasingly impermeable layer. The influence of the absolute pressures of a mixture of hydrogen and steam could only be assessed so far (up to 2 kp/cm$^2$). However, experiments indicate that the form of the rate of permeation
\( R \propto p^{1/2} \ldots 1 \) is appropriate.

For possible process heat applications the experimental assumption \( P_{H_2O}/P_{H_2} \propto 1 \) is practically always fulfilled so that the results shown here can be considered to be representative.

Next to the exact form of the pressure dependence of the permeation rate, the behaviour of the above-mentioned chromium and iron oxides when thermal expansion of the reformer tubes occurs as well as mechanical stress due to catalyst movement, start-up and shut-down are yet be investigated.

The hydrogen, which according to the present experimental results would enter the core, is limited in amount and is tolerable. The amount of \( H_2 \) is of the order of magnitude of the tolerated water leakages from steam generators.

---

**Fig. 4.7-1**
Dependence of Hydrogen Permeation on the Temperature [12]

**Fig. 4.7-2**
The total amount of hydrogen permeating $R_{\text{tot}}$ into the helium circuit can be estimated according to the following:

$$R_{\text{tot}} = NR \cdot \frac{T_1 - T_2}{T_1 - T_3} \cdot \frac{1}{k \cdot \Delta T} \cdot \frac{1}{n} \cdot \sum_{i=1}^{n} x_i r_i$$

$$\sum_{i=1}^{n} x_i = L$$

$\text{ET} \approx 200 \, ^\circ\text{C}$

$\Delta T = 200 \, ^\circ\text{C}$

$L = 10 \, \text{m}$

$p = 40 \, \text{b}$

$X_{H_2} \approx 0.4 \, \text{at} \, \text{40 b}/800 \, ^\circ\text{C}/\text{H}_2 \text{O}/\text{CH}_4 = 3/1$

$S_{\text{expt}} = 3.3 \, \text{mm}$

$S_{\text{techn}} = 15 \, \text{mm}$

With the help of the above data a value for $R_{\text{tot}} \approx 0.3 \, \text{Nm}^3 \, \text{H}_2/\text{h}$ follows. This value is tolerable as corresponding considerations for graphite corrosion in the core show (see Vol. 3).
4.8 Tritium Permeation

Tritium is found in the HTR from three different sources:

- through nuclear fission with a yield of $1.1 \times 10^{-4}$ tritium nuclei per fission. This calculates to be $1.43 \times 10^{-2}$ Curies tritium per day and per MW(th). Converted to the 3000 MW(th)-plant the amount is 43 Ci daily.

- through the $\text{Li}^6 (n, \alpha)\text{T}$ reaction of the lithium in the fuel elements and the structural graphite. About 10 Ci tritium per day are produced. A lithium impurity of 0.2 ppm in the fuel element graphite with a $\text{Li}^6$-content of 7.4 % and a mean neutron flux in the core, which corresponds to a mean power density of 5 MW/m$^3$, is thereby assumed.

- through the $\text{He}^3 (n, \alpha)\text{T}^0$ reaction of the helium present in the coolant. 30 Ci tritium per day are produced. It is thereby assumed that a $\text{He}^3$ concentration of $1.3 \times 10^{-7}$ is realizable and that a helium filling per year is lost through leakage. A neutron flux distribution in the core corresponding to a mean power density of 5 MW/m$^3$ is assumed here also.

The location of the tritium from the various sources varies. Nearly all the tritium produced by fission remains in the fuel elements; a pessimistic estimation shows 10 % of the tritium from fission to enter the coolant circuit [14].

A similar percentage can be assumed for the tritium produced by $\text{Li}^6$ transformation in graphite.

Of the tritium produced by $\text{He}^3$ transformation in the coolant circuit itself, about 90 % is adsorbed by the graphite of the core according to present experience [15].

The result is that for a 3000 MW(th)-plant about 8 Ci/d is actually released ($\equiv 2.6 \cdot 10^{-3}$ Ci/MWd). This value can be correlated to that of 40 Ci/a ($\equiv 2.7 \times 10^{-3}$ Ci/MWd) obtained in the AVR experiments [16, 17].
For a product gas flow of \( \sim 3 \times 10^7 \text{Nm}^3/\text{day} \), the amount of tritium is about \( 2.7 \times 10^{-7} \text{Ci/Nm}^3 \) in the product hydrogen or correspondingly \( \sim 8.0 \times 10^{-7} \text{Ci/Nm}^3 \) in the product synthetic methane (\( \sim 10^7 \text{Nm}^3 \text{CH}_4/\text{day} \)).

A tritium content of \( 2.89 \times 10^{-6} \text{PCurie/cm}^3 \) is the present allowable limit in the air. The maximum (pessimistic) limits assumed above for both hydrogen and methane production are thus a factor of 10 times lower than the allowed values. In addition, the combustion of methane generally takes place under the addition of air, which leads to a further factor of 10 due to this dilution. Hydrogen is also diluted by a similar factor in all cases of its application, so that no problems are expected as far as the present tritium specifications go. In the closed circuit of nuclear long-distance energy, however, an enrichment of the isotope by tritium removal must be prevented.

However, tritium is oxidized in any case along with hydrogen, in the CuO beds of the purification installation in the primary helium circuit of the nuclear reactor and is removed from the system by molecular sieves. The size of the purification by-pass is of great importance as regards the possible tritium removal. The aim should be to let about 3% of the total amount of helium pass through the purification system. In this way the amount of tritium which can diffuse through the steam reformer tube walls is reduced by a factor of 2 - 3.

Investigations on hydrogen permeation through the reformer tube materials at high temperatures, show that for certain limiting conditions i.e. excess of steam on the process side, an oxide layer is formed, which acts as a diffusion barrier. This effect would also hinder tritium permeation. Furthermore, hydrogen on the process side has a preventive influence on tritium permeation. Quantitative results can, however, only be obtained after adequate experiments, which have already been started, are completed.
4.9 Contamination of Steam Reformer Tubes

A deposition of solid radioactive fission products on the walls of the reformer tubes could hinder access to the catalyst filling vent, if the fission product release from the fuel elements was intolerably high. Special attention should be paid to the isotopes Cs-137 and Ag-111, as shall be mentioned in detail in Vol. 3. Cs-137 has a half-life of about 10 years, Ag-111 has an unexpectedly high exit rate from the coated particles. (However, this isotope is of special importance only in the low-enriched fuel cycle due to the high content there through fission). It has to be guaranteed that for a change of catalyst, which will probably be necessary every four years, a manipulation of long duration is possible above the supporting construction of the reformer tubes. As the carrier-plate can always be made to form a gas-tight termination of the space containing primary circuit helium, the assumption is justified that only irradiation can occur in the steam reformer caused by fission products on the tube walls. The carrier-plate of 0.5 m thickness then operates as a very effective shield.

About 5 to 100 Ci Cs-137 per annum are set free using the desired particle concept for ball-shaped fuel elements with a low uranium contamination (see Vol 3) in a 3000 MW reactor plant with a mean gas outlet temperature of the core of 980 °C [18]. This means that between 0.3 and 5 µCi/cm² are deposited for a typical overall surface of the reformer tubes of 18 000 m². However, it is very pessimistically assumed here that all the Cesium found in the helium circuit is deposited in the steam reformer.

Recent calculations [19] show that probably only about 10% of the total amount remain in this spot of the circuit. Most of the cesium is deposited in the steam generator. In addition to Cs-137, a similarly large additional activity coating will occur on the reformer tubes due to Ag-111 and some other solid fission products.

The dosis, which is to be expected in the vicinity of the catalyst filling vent, can be estimated according to fig. 4.9-1.
A numerical treatment can be approximately achieved in that it is assumed that all the Cs-137 deposited on the steam reformer bundle is concentrated in the form of a surface source under the tube carrier-plate.

**Flux in P₁:** \[ \phi = \frac{A}{2} \left[ E₁(\mu\cdot s) - E₁(\mu\cdot s \cdot \sqrt{1 + \left(\frac{a}{s}\right)^2}) \right] \]

\[ E₁(y) = \int_{y}^{\infty} e^{-\frac{t}{\mu}} dt \]

**Flux in P₂:** \[ \phi = \frac{A}{2} \left[ E₁(\mu\cdot d) - E₁(\mu d \cdot \sqrt{1 + \left(\frac{a}{s}\right)^2}) \right] \cdot K(a₁, a₂, s) \]

\[ K(a₁, a₂, s) = \frac{a₂}{s} \cdot \frac{a₁}{\sqrt{a₂ - a₁}} \cdot \cos \frac{a₁}{a₂} - a₁ \cdot \sqrt{\frac{a₂}{s} - a₁} \]
Data: \( \mu = 0.6 \text{ cm}^{-1} \)
\( s = 30 \text{ cm} \)
\( d = 8 \text{ cm} \)
\( a_1 = 6.5 \text{ cm} \)
\( a_2 = 6.6 \text{ cm} \)
\( A = 0.6 \cdot 10^{-3} \text{ Ci/cm}^2 \) (Assumption: 1000 Ci Cs-137 after 10 a
\( \equiv 83 \text{ Ci/heat exchanger after an operation time of 10 yrs for 12 loops} \)

allowed value: \( 5 \cdot 10^3 \frac{\text{γquants}}{\text{cm}^2\text{sec}} \) for 60 mrem per 8 h-day

(for 0.66 MeV-γquants) [20]

Flux in \( P_1 \): \( \phi \sim 1.2 \text{ P}_{\text{hot/cm}^2\text{sec}} \)

Flux in \( P_2 \): \( \phi \sim 1.3 \times 10^3 \text{ P}_{\text{hot/cm}^2\text{sec}} \)

Thus the allowed value is not exceeded at any spot above the supporting construction. In any case, the assumption that all the cesium deposited in the steam reformer is concentrated in the form of a surface source, is very pessimistic. The change of catalyst can thus be carried out without any difficulty. However, even at the uranium contamination of \( 2.5 \times 10^{-4} \) attainable today i.e. release of 10 000 Ci Cs-137 in 10 years, the problem of accessibility can be satisfactorily solved by a slight increase in the value of \( d \).
4.10 Corrosion of Tube Materials in Impure Helium

Whereas according to the existing experience no corrosion worth mentioning takes place on the inner side of reformer tubes in gas atmospheres typical for the steam reforming of methane, as long as the tube wall temperature remains under 900 °C, consideration should be given to the corrosion of reformer tube materials in impure helium according to investigations of the DRAGON project [21].

Helium, itself, is chemically inert and does not participate directly in gas/metal surface reactions. However, small traces of impurities (H₂, H₂O, CO, CO₂, CH₄, O₂) can cause changes in properties of the materials.

The measured values of the impurities for the existing test HTRs and estimated values for larger HTRs are given in table 4.10-1. The impurities originated from the residual content of air after filling up the system with helium, leakages of water from the steam generators, hydrogen from the steam reformer as well as from the desorption of gases from carbon stone when it is used. The penetration of air during repairs is also a source of new impurities.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>H₂O</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
<th>CH₄</th>
<th>P₉e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peach Bottom</td>
<td>10</td>
<td>200</td>
<td>10</td>
<td>-</td>
<td>15</td>
<td>24</td>
</tr>
<tr>
<td>DRAGON</td>
<td>1</td>
<td>20</td>
<td>10</td>
<td>0.4</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>AVR</td>
<td>30</td>
<td>300</td>
<td>300</td>
<td>100</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>THTR</td>
<td>150</td>
<td>600</td>
<td>600</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Process Heat Reactor</td>
<td>10</td>
<td>700</td>
<td>700</td>
<td>100</td>
<td>10</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 4.10-1: Impurity Content (μatm) in the Helium Circuit of Different Reactor Systems (Guiding Values with Larger Scattering Region).
<table>
<thead>
<tr>
<th>Material</th>
<th>Test Conditions</th>
<th></th>
<th>Atmosphere</th>
<th>Layer thickness (µm)</th>
<th>Penetration depth at grain boundary (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (h)</td>
<td>Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type 347</td>
<td>2,300</td>
<td>650</td>
<td>CIIR dry</td>
<td>0.8</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5,000</td>
<td>750</td>
<td>CIIR dry</td>
<td>4.8</td>
<td>0</td>
</tr>
<tr>
<td>Type 321</td>
<td>5,000</td>
<td>750</td>
<td>CIIR dry</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>16,000</td>
<td>700-750</td>
<td>Dragon</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>5,000</td>
<td>750</td>
<td>CIIR dry</td>
<td>2.0</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>5,000</td>
<td>850</td>
<td>CIIR dry</td>
<td>4.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Nimonic 75</td>
<td>2,500</td>
<td>850</td>
<td>Air</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>5,000</td>
<td>850</td>
<td>CIIR dry</td>
<td>6.0</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>12,000</td>
<td>750-830</td>
<td>Dragon</td>
<td>10.0</td>
<td>34.0</td>
</tr>
<tr>
<td>IN-523-NX</td>
<td>2,800</td>
<td>850</td>
<td>CIIR moist</td>
<td>7.0</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>16,000</td>
<td>850</td>
<td>Dragon</td>
<td>7.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Nimonic 105</td>
<td>2,800</td>
<td>850</td>
<td>CIIR moist</td>
<td>7.0</td>
<td>80.0</td>
</tr>
<tr>
<td></td>
<td>5,000</td>
<td>950</td>
<td>Dragon</td>
<td>3.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Incoloy 800</td>
<td>2,800</td>
<td>850</td>
<td>CIIR moist</td>
<td>7.5</td>
<td>28.0</td>
</tr>
<tr>
<td></td>
<td>5,000</td>
<td>750</td>
<td>CIIR dry</td>
<td>3.0</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>5,000</td>
<td>850</td>
<td>CIIR dry</td>
<td>6.0</td>
<td>30.0</td>
</tr>
<tr>
<td></td>
<td>2,500</td>
<td>750</td>
<td>CIIR very dry (Variab)</td>
<td>5.0</td>
<td>carburization 19.0</td>
</tr>
<tr>
<td></td>
<td>12,000</td>
<td>950</td>
<td>Dragon</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Impurity content (µ atm)</th>
<th>Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>CO</td>
</tr>
<tr>
<td>CIIR Loop</td>
<td></td>
</tr>
<tr>
<td>moist</td>
<td>400</td>
</tr>
<tr>
<td>dry</td>
<td>100</td>
</tr>
<tr>
<td>very dry</td>
<td>50-100</td>
</tr>
<tr>
<td>Dragon</td>
<td></td>
</tr>
<tr>
<td>normal</td>
<td>10</td>
</tr>
<tr>
<td>during water injection experiments</td>
<td>200</td>
</tr>
</tbody>
</table>

Table 4.10-2: Corrosion Behaviour of Various Materials in Helium Loops and in the Dragon Reactor [22]
These traces of impurities in the coolant of a HTR act strongly corrosive on some alloys. Corrosion in helium differs from that in air mainly in that here no protecting oxide layers are formed [21].

The following table 4.10-2 shows some results of the Dragon Project [22]. According to this, Incoloy 800, which is an interesting material for reformer tubes, has a lower creep strength in helium than in air. This is due to the oxidation of the traces in Al and Ti. The penetration depth of oxidation is about 19 μm after 12000 h in the Dragon atmosphere at 950 °C. The following statements are important:

- Al and Ti are strongly corroded, Al₂O₃ especially separates at the grain boundary.
- The oxide layer consists of Cr-oxides as well as Mn-, Si- and Ti-oxides. Besides, Ti- and Al-oxides separate at the grain boundary. The rate of corrosion is higher in moist helium than in dry helium.

On the whole these effects need a general explanation, broad programs have to be carried out before a possible application of reformer tubes in nuclear plants takes place. In any case, the thick-walled reformer tubes (15 mm) seem to have less problems due to their composition than the thin-walled materials for gas ducting systems or heat exchanger ducts for intermediate circuits.

Next to the actual corrosion, a further problem exists in the design of plant components which are operated in helium. During storage or for friction spots which occur in a normal atmosphere, a direct contact between the materials is prevented by oxide layers. This is also the case when the lubricating film ruptures temporarily.

In a high-temperature reactor which, to prevent corrosion of graphite, is operated with practically pure dry helium (i.e. the H₂O- and O₂-concentrations lie in the region of a few ppm), no new
protective layer can, however, be formed after the initially existing oxide layers are worn away. The touching materials then have direct metallic contact, which leads to increased friction values and finally to the so-called fretting and "wearing out" of the metals.

If the temperature of the friction spot lies above 200 °C, it is not possible to use grease lubrication. Solid lubricants, like e.g. molybdenum sulfide (MoS₂), however, have sufficiently low friction values and can be used in reactor coolant circuits for a temperature range of up to 400 °C. Without lubrication, operation with friction spots in dry helium can only then take place when suitable material coupling is chosen or if the friction spots concerned are improved by coating them with protective layers. There are a number of material pairs known today which can be used in helium circuits without any risk of too high friction or tendency of wearing out. In general, the rule holds good that the same materials should not be put together. Also the bearings should be oversized as far as possible.

Fig. 4.10-3: Friction Values for a Useable Material Pair at High Temperatures (Inconel 625 on Al₂O₃) [24]

In fig. 4.10-3 some results are shown of several investigations [24] for a useable material pair at high temperatures. In table 4.10-4 material pairs, which are not useable, are given.
The CVD technique (chemical vapour deposition), which has been developed in recent years, can also be used. Gaseous compounds are thereby deposited at higher temperatures as solid layers on the carrier-materials. These layers possess some properties which are especially interesting for their application in the helium technology: They have very high coefficients of hardness (e.g., titanium carbide ~ 4000 kp/mm², titanium nitride ~ 2500 kp/mm²), they are very resistant to corrosion, they adhere well to base materials especially when they contain chromium. The adhesive strength is sufficiently large for a thickness of the vapour-coated layers of 10 µm, so that through bending and denting of these coated construction elements, there is no fear of the protective layer peeling off. The possibilities for application and the advantages of such a protective layer for sliding and rolling strain have been demonstrated in the meantime in the space technology. It is justified to assume that protective layers can be applied in the helium technology with similar success.

Attention has to be paid to these problems of friction in steam reformer designs especially for gas ducting (gas deflector, baffle installations).

<table>
<thead>
<tr>
<th>Material pairs</th>
<th>Test conditions</th>
<th>Friction Velocity</th>
<th>Friction path</th>
<th>Friction value</th>
<th>Characteristic of the surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel 625/Aluminum oxide</td>
<td>20-050 1000</td>
<td>2</td>
<td>5.2</td>
<td>0.4-0.6</td>
<td>smooth, no abrasion</td>
</tr>
<tr>
<td>Nimocast 713LC/Nimonic 75</td>
<td>20-050 1000</td>
<td>2</td>
<td>0.1</td>
<td>&gt;1.5</td>
<td>total welding</td>
</tr>
<tr>
<td>Colmanoy 6/Celimanoy 6</td>
<td>20-600 5000</td>
<td>2</td>
<td>5.2</td>
<td>0.5-0.6</td>
<td>smooth friction surface, no welding</td>
</tr>
<tr>
<td>Nimocast 713 LC/Incoloy 800</td>
<td>20-850 1000</td>
<td>1</td>
<td>2.5</td>
<td>0.2-1.0</td>
<td>formation of grooves</td>
</tr>
<tr>
<td>Nimocast 713 LC/Colmonoy 6</td>
<td>20-350 1000</td>
<td>1</td>
<td>2.5</td>
<td>0.3-0.7</td>
<td>smooth friction surface</td>
</tr>
<tr>
<td>Nimocast 713 LC/Inconel 625</td>
<td>20-050 1000</td>
<td>1</td>
<td>2.5</td>
<td>0.8-0.95</td>
<td>grooves, but no welding</td>
</tr>
<tr>
<td>Nimocast 713 LC/17 Cr Mo 55</td>
<td>20-480 100</td>
<td>1</td>
<td>2.5</td>
<td>0.3-0.75</td>
<td>grooves</td>
</tr>
<tr>
<td>Ho TZM/17 Cr Mo 55</td>
<td>20-480 100</td>
<td>1</td>
<td>1.5</td>
<td>0.5-1.2</td>
<td>local welding</td>
</tr>
</tbody>
</table>

Table 4.10-4: Some Results of Friction Testing at High Temperatures [24]
4.11 Requirements of the Steam Reformer Process Based on the Subsequent Processes

For the several processes shown in table 4.11-1 the following specifications are given:

Regarding:
4.11.1 Ammonia Synthesis

For the ammonia synthesis, a hydrogen/nitrogen mixture ratio of 3/1 is required. Therefore, a high steam dilution (4/1 ... 5/1 moles H₂O/mole CH₄) is chosen in order to keep the remaining methane content as low as possible. The product gas from the steam reformer is directed to a secondary reformer, in which an addition of air partially oxidizes the residual methane as well as carbon monoxide with the help of a catalyst. The result, after removal of CO₂, is a mixture containing practically only nitrogen and hydrogen. The process parameters are so chosen as to produce the desired stoichiometric mixture of 3 moles H₂ per mole N₂. In order to keep the energy consumption for the gas compression before the synthesis low, an operation pressure of over 30 bar is desirable.

Regarding:
4.11.2 Methanol Synthesis

The methanol synthesis is carried out with a mixture of 2 moles H₂ per mole of CO. Therefore the amount of CO₂ produced should be held at a minimum. This is accomplished under the following reaction conditions:

a) low steam dilution corresponding to 1.5/1 ... 2.0/1 moles H₂O/mole CH₄
b) highest possible reaction temperature
c) recycling of a part of the CO₂ product as a substitute instead of steam to the steam reformer and thus to obtain a shift of the chemical equilibrium in the direction of CO.

In this process, a shift reaction or conversion does not occur. The CO₂ contained in the product of steam reforming is removed in a scrubber. In a low temperature separation, three fractions are obtained: H₂, CO + H₂, and CH₄, whereby the actual product CO + H₂ has the desired specification.
<table>
<thead>
<tr>
<th>Process</th>
<th>Ammonia Synthesis</th>
<th>Methanol Synthesis</th>
<th>Hydrogasification</th>
<th>Coal Hydrogenation</th>
<th>Hydrocracking</th>
<th>Direct Reduction of Iron</th>
<th>Chemical Heat Pipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction in following process</td>
<td>( \text{H}_2 + 3\text{H}_2 = 2\text{NH}_3 )</td>
<td>( 2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH} )</td>
<td>( \text{C} + \text{Zn} = \text{CH}_4 )</td>
<td>( \text{C} + \text{H}_2 = -\text{CH}_2^- )</td>
<td>( \text{CH}_2 + \text{H}_2 = \text{CH}_4 )</td>
<td>a) ( \text{Fe}_2\text{O}_3 + 3\text{H}_2 = 2\text{Fe} + 3\text{H}_2\text{O} )</td>
<td>CO = CH&lt;sub&gt;4&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Input to following process</td>
<td>( \text{H}_2 + \text{H}_2 )</td>
<td>( \text{CO} + \text{H}_2 )</td>
<td>Coal</td>
<td>Coal</td>
<td>Distillate residue</td>
<td>Iron-Ore</td>
<td>CO + H&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Temperature of following process</td>
<td>400 °C</td>
<td>250 ... 300 °C</td>
<td>800 °C</td>
<td>500 °C</td>
<td>350 ... 450 °C</td>
<td>a) 500 °C</td>
<td>20 °C</td>
</tr>
<tr>
<td>Pressure in following process</td>
<td>500 b</td>
<td>50 ... 200 b</td>
<td>50 ... 100 b</td>
<td>300 ... 700 b</td>
<td>50 ... 150 b</td>
<td>a) 30 ... 40 b</td>
<td>70 b</td>
</tr>
<tr>
<td>Desired gas analysis in the following process</td>
<td>( \text{H}_2/\text{H}_2 = 3/1 )</td>
<td>( \text{H}_2/\text{CO} = 2/1 )</td>
<td>95 % ( \text{H}_2 )</td>
<td>98 % ( \text{H}_2 )</td>
<td>98 % ( \text{H}_2 )</td>
<td>a) 98 % ( \text{H}_2 )</td>
<td>not specified</td>
</tr>
<tr>
<td>Feed material to Steam Reformer</td>
<td>( \text{CH}_4, \text{C}_n\text{H}_m )</td>
<td>( \text{CH}_4, \text{C}_n\text{H}_m )</td>
<td>( \text{CH}_4 )</td>
<td>( \text{C}_1 \ldots \text{C}_4 )</td>
<td>( \text{C}_1 \ldots \text{C}_4 )</td>
<td>( \text{CH}_4, \text{C}_n\text{H}_m )</td>
<td>( \text{CH}_4 )</td>
</tr>
<tr>
<td>Temperature in Steam Reformer</td>
<td>850 °C</td>
<td>850 °C</td>
<td>800 ... 850 °C</td>
<td>800 ... 850 °C</td>
<td>800 ... 850 °C</td>
<td>a) 800 ... 850 °C</td>
<td>800 ... 850 °C</td>
</tr>
<tr>
<td>Pressure in Steam Reformer</td>
<td>30 ... 40 b</td>
<td>30 ... 40 b</td>
<td>30 ... 40 b</td>
<td>30 ... 40 b</td>
<td>30 ... 40 b</td>
<td>a) 30 ... 40 b</td>
<td>30 ... 40 b</td>
</tr>
<tr>
<td>( \text{H}_2/\text{CH}_4 )-ratio</td>
<td>4/1 ... 5/1</td>
<td>1,5/1 ... 2/1</td>
<td>3/1 ... 4/1</td>
<td>3/1 ... 4/1</td>
<td>3/1 ... 4/1</td>
<td>a) 4/1</td>
<td>1,5/1 ... 3/1</td>
</tr>
<tr>
<td>Specific gas production</td>
<td>2200 ( \text{Nm}^3\text{H}_2 ) / ( \text{t} \text{CH}_4 )</td>
<td>2300 ( \text{Nm}^3(\text{CO}+\text{H}_2) ) / ( \text{t} \text{CH}_4 )</td>
<td>1,5 ( \text{Nm}^3\text{H}_2 ) / ( \text{t} \text{CH}_4 )</td>
<td>2000 ... 2600 ( \text{Nm}^3\text{H}_2 ) / ( \text{t} \text{CH}_4 )</td>
<td>400 ... 500 ( \text{Nm}^3\text{H}_2 ) / ( \text{t} \text{CH}_4 )</td>
<td>600 ... 700 ( \text{Nm}^3(\text{CO}+\text{H}_2) ) / ( \text{t} \text{CH}_4 )</td>
<td>2000 ( \text{Nm}^3(\text{CO}+\text{H}_2) ) / ( \text{t} \text{CH}_4 )</td>
</tr>
<tr>
<td>Total gas from</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A similar process is used for the synthesis gas of the oxosynthesis, but with a desired gas analysis \( H_2/CO = 3/1 \).

Regarding:

4.11.3 Hydrogasification (Production of SNG)

Too high a concentration of methane in hydrogen during the hydrogenating gasification causes an undesired displacement of the equilibrium. Therefore, to obtain high conversion of coal, it is necessary to produce hydrogen with a CH\(_4\)-concentration of less than 5 vol %. This is only possible by insertion of a low temperature separation. As the hydrogasification will be carried out at a pressure of at least 40 bar, a reforming pressure of 40 bar is desirable.

Regarding:

4.11.4 and 4.11.5 Coal Hydrogenation and Hydrocracking

For both processes there are high specifications regarding the carbon monoxide content in the hydrogen used for hydrogenation (CO < 10 ppm), as CO acts as a catalyst poison. Therefore, conversion as well as methanation are necessary. The methane content in the hydrogen is not chemically disadvantageous; however, it gives rise to a considerably larger circuit and hence increased compressor power for the recycle hydrogen as the methane content builds up. A purity of 99 vol % \( H_2 \) is therefore desirable. A high reforming pressure and a high \( H_2O/CH_4 \) ratio in the steam reforming of methane are favourable for these processes.

Regarding:

4.11.6 Direct Reduction of Iron Ore

a) H-Iron

In this process, the required purity of the hydrogen used for reduction is 98 % by volume. Therefore, a conversion (shift reactor) and a low temperature separation are necessary. There are no specifications regarding the remaining CO-content. A high steam dilution of the inlet gas (\( H_2O/CH_4 \approx 4/1 \ldots 5/1 \)) is advantageous here.
b) Korf-Midland-Ross

For this subsequent process the gas should have a high reduction factor \((\text{CO} + \text{H}_2)/(\text{CO}_2 + \text{H}_2\text{O}) \approx 20\) and a pressure of approx. 3 b as well as a temperature of 800 °C. Therefore, the steam reformer has to be operated at a low steam dilution ratio (1.2 ... 1.5 moles \(\text{H}_2\text{O}/\text{mole CH}_4\)) so that carbon deposition, which is harmful to the catalyst, is just prevented. A further limitation is the allowed content of remaining methane (< 3%). This gas specification can be attained using the following two techniques:

1) Reforming at high temperature (850 °C) and low pressure (5 b), so that a larger pressure difference results across the tube wall (and thus higher stresses occur in the reformer tube).

2) Reforming at high temperature (850 °C) and a pressure of 30 - 40 b. In a subsequent gas processing including separation of methane, the necessary gas specifications are attained. A part of the carbon dioxide is also used as raw material in the steam reformer, in order to obtain a ratio of \(\text{H}_2/\text{CO} \approx 2/1\).

Regarding:
7. **Nuclear Chemical Heat Pipe (Long-Distance Energy)**

The design specifications of the steam reformer in this case of application is determined only by the efficiency of heat utilization and not by chemical product specifications. The remaining methane content has to be considered in the optimization calculations as it causes larger transportation costs. For reforming temperatures of 800 °C to 850 °C, the optimum steam dilution inlet ratios are 3.0/1 ... 1.5/1 moles \(\text{H}_2\text{O}/\text{mole CH}_4\). An operation pressure of 40 b is appropriate as the long-distance transportation of the gases occur at a pressure of \(\approx 70\) b.
4.12 Splitting Up of Nuclear Reactor Heat for Methane Reforming (Process Heat) and for Steam Generation

The splitting up of nuclear heat is basically possible in a wide range depending on the mean reactor outlet temperature \( T_1 \), the reactor inlet temperature \( T_3 \) as well as the inlet temperature \( T_2 \) of helium in the steam generator. This is only limited by the temperature \( T_2 \) (inlet temperature in the steam generator), which should not be under 600 ... 650 °C, so that the heat flux surfaces in the steam generator as well as in the steam reformer tubes are not too large. Furthermore, the reactor inlet temperature should not be raised above 450 °C. The reasons for this will be explained elsewhere (vol. 3 § 6).

\[ \frac{N_{PW}}{N_{ges}} = \frac{T_f - T_2}{T_f - T_3} \]

![Diagram showing possible proportion of high-temperature process heat to overall reactor heat](image)

Fig. 4.12-1 Possible Proportion of the High-Temperature Process Heat to the Overall Reactor Heat

The magnitude of the reactor outlet temperature depends on the status of development of the fuel elements, on the hot-gas ducting and on the material of the reformer tubes. Without an intermediate circuit, values of 900 - 950 °C are reasonable for the steam reforming of methane; if an intermediate circuit is used the values
Because of the differences in the amount of heat utilized from the upper $(T_1 \ldots T_2)$ and lower $(T_2 \ldots T_3)$ temperature range of helium, a detailed consideration has to be made to carry out a suitable split up of reactor heat for every process discussed in connection with nuclear-heated steam reformers.

a) Hydrogen production (e.g. direct reduction by the H-Iron method, hydrocracking, hydrogenation of coal, synthesis of NH$_3$).

The energy needed for steam reforming as also for the superheating of process gas between 450 and 800 °C amounts to about 700 kcal/Nm$^3$ H$_2$ (at $T_{\text{reforming}} = 825$ °C, $p = 40$ bar, H$_2$O/CH$_4$ = 3/1). This energy is extracted from a so-called HT-range (High-Temperature range $T_1 \ldots T_2$). The energy required for process gas preheating from 20 °C to 450 °C is about 800 kcal/Nm$^3$ under the chosen process conditions. The waste heat contained in the product gas is just sufficient to provide energy for the gas purification steps up to the end product (H$_2$ with 98 % purity and at a pressure of 20 b).

$$Q = \dot{m}_H^2 \cdot (a + b) + \frac{N_{\text{el}}}{n}$$

$$Q = \dot{m}_{\text{He}} \cdot C_{\text{p,He}} \cdot (T_1 - T_3)$$

$$\dot{m}_H^2 = \frac{Q}{a} \cdot \frac{T_1 - T_2}{T_1 - T_3}$$

$$N_{\text{el}} = n \cdot (Q - \dot{m}_H^2 \cdot (a + b)) = n \cdot Q \cdot (1 - \frac{a + b}{a} \cdot \frac{T_1 - T_2}{T_1 - T_3})$$

$$\frac{\dot{m}_H^2}{N_{\text{el}}} = \frac{1}{a \cdot n} \cdot \frac{T_1 - T_2}{\frac{a + b}{a} T_2 - T_3 - \frac{b}{a} T_1}$$

$Q$ = nuclear reactor power (3000 MW)

$\dot{m}_H^2$ = amount of hydrogen produced (Nm$^3$H$_2$/h)

$a$ = specific high-temperature heat consumption (700 kcal/Nm$^3$H$_2$)

$b$ = specific low-temperature heat consumption (800 kcal/Nm$^3$H$_2$)

$N_{\text{el}}$ = net electrical power

$n$ = efficiency for electricity generation (40 %)
Fig. 4.12-1: Dependence of Hydrogen Production and Generation of Electrical Energy on the Splitting Up of Heat in the Primary Circuit of the Nuclear Reactor

Depending on the available peak temperature of helium and the re-entry temperatures in the nuclear reactor, the ratio of gas production to generation of electrical energy can be varied in a wide range by varying the steam generator inlet temperature.

A nuclear reactor with a peak temperature of 850 °C, for example, could thus produce the same amount of hydrogen as a reactor with a peak temperature of 950 °C. The preconditions would, however, be that the re-entry temperature in the nuclear reactor is raised from 250 to 400 °C and the helium inlet temperature in the steam generator is simultaneously lowered from 800 to 750 °C (see fig.).
Such measures have a number of consequences, which are discussed in Vol 3, § 7.

From the figure it is seen that also other split ups are possible, in which only so much electrical energy is produced as is necessary for internal consumption.

The following table is obtained for the processes discussed here using known consumption values, assuming a closed energy balance i.e. no net generation of electricity.

Table 4.12-4: Possible Split Up of Heat for the Various \( \text{H}_2 \)-Consuming Processes

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Steel from H- Iron Process or Korf-Mid- land-Ross</th>
<th>( \text{NH}_3 )-Synthesis</th>
<th>Hydro- Cracking</th>
<th>Hydro- genation of Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen consumption Nm(^3)/t</td>
<td>700</td>
<td>2200</td>
<td>450</td>
<td>2200</td>
</tr>
<tr>
<td>consumption of electrical energy/steam kWh/t</td>
<td>650</td>
<td>self- sufficient (steam)</td>
<td>self- sufficient (steam)</td>
<td>self- sufficient (steam)</td>
</tr>
<tr>
<td>high-temperature heat/t product Gcal/t</td>
<td>0.49</td>
<td>1.54</td>
<td>0.315</td>
<td>1.54</td>
</tr>
<tr>
<td>low-temperature heat/t product Gcal/t</td>
<td>1.96</td>
<td>1.76</td>
<td>0.36</td>
<td>1.76</td>
</tr>
<tr>
<td>methane used/t product Nm(^3)/t</td>
<td>175</td>
<td>550</td>
<td>112.5</td>
<td>550</td>
</tr>
<tr>
<td>Total energy consumption Gcal/t</td>
<td>2.45</td>
<td>3.3</td>
<td>1.76</td>
<td>3.3</td>
</tr>
</tbody>
</table>

For the \( \text{NH}_3 \)-synthesis, for hydrocracking and for the hydrogenation of coal a suitable temperature split up would be 950 ... 625 ... 250 °C or e.g. 950 ... 670 ... 350 °C, for the process of direct reduction a split up 950 ... 810 ... 250 °C or 950 ... 830 ... 350 °C has to be chosen, if electrical energy is not to be pro-
duced as a by-product. However, it has to be tested from case to case, which split up is the most favourable solution. In all these combined methods, the operation of a counterpressure extraction-turbine is especially desirable, by which the generation of electricity can occur more efficiently.

b) in hydro-gasification the following representative energy consumption values can be used:
1500 kcal/Nm³CH₄ from the upper helium temperature range
4500 kcal/Nm³CH₄ from the lower helium temperature range
(included are steam and electricity consumption for the total process).

![Graph](image)

Fig. 4.12-5 Regarding the Split Up of Heat in Hydrogasification

According to fig. 4.12-5 the process is just self-sufficient regarding energy, when the steam generator inlet temperature is chosen to be about 770 °C (at T₁ = 950 °C, T₂ = 250 °C).
c) **Long-Distance Energy** (Chemical Heat Pipe)

Table 4.12-6  Split Up of Heat for Nuclear Long-Distance Energy

<table>
<thead>
<tr>
<th>$T_3 \ldots T_2 \ldots T_1$ ($^\circ$C)</th>
<th>Long-Distance Energy Output (Gcal/h)</th>
<th>$P_{LD}$ $P_{reactor}$</th>
<th>$P_{el, net}^+$</th>
<th>$P_{el, net}$ $P_{reactor}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>350...600...950</td>
<td>1522</td>
<td>0.59</td>
<td>309</td>
<td>0.10</td>
</tr>
<tr>
<td>350...600...1000</td>
<td>1600</td>
<td>0.62</td>
<td>279</td>
<td>0.09</td>
</tr>
<tr>
<td>450...600...1000</td>
<td>1909</td>
<td>0.74</td>
<td>175</td>
<td>0.06</td>
</tr>
</tbody>
</table>

$^+$ after substraction of internal energy consumption for helium circulators and feed water pumps.

For obtaining a long-distance energy quota as high as possible, the reactor outlet temperature as well as the reactor inlet temperature have to be raised. An increase of the long-distance energy portion to a maximum of about 75% would thus be technically realizable. A further increase in the reactor outlet temperature has no added advantages, as the heat in the lower temperature region of the helium cycle must be enough to evaporate the necessary reaction water ($H_2O/CH_4 \approx 1.5$ is chosen here).

4.13  **Power Density of the Steam Reformer**

The split up of the available heat of the nuclear reactor in a high-temperature and a low-temperature region has considerable effects on the attainable heat fluxes and thus on the design volume of the steam reformer and the steam generator. In the following table three typical divisions are discussed in detail. The logarithmic temperature differences for the steam reformer are based on a reforming temperature of 825 $^\circ$C and a process gas inlet temperature of 450 $^\circ$C. The effect of the inner pigtails on heat transfer was not taken into account for this consideration.
Because of the comparatively low volumetric power the steam reformer as compared to the steam generators, the placement of the heat exchangers is difficult when a low value of $T_2$ (600 °C) is chosen. This requires an increase in the number of loops. In the case of reactor vessels of the pod-boiler type, the diameter of the vessel would then greatly increase.

<table>
<thead>
<tr>
<th>Data</th>
<th>Dim.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Split Up</td>
<td>$^\circ$C</td>
</tr>
<tr>
<td>Power for Process Heat</td>
<td>$H_{th}$</td>
</tr>
<tr>
<td>AT for Steam Reformer</td>
<td>$^\circ$C</td>
</tr>
<tr>
<td>k-Hr. for Steam Reformer</td>
<td>kcal/m$^2$°C</td>
</tr>
<tr>
<td>Heat Flux Density for Steam Reformer</td>
<td>kcal/m$^2$°C</td>
</tr>
<tr>
<td>Required Heat Transfer Area</td>
<td>$m^2$</td>
</tr>
<tr>
<td>Heat Transfer Area per Tube</td>
<td>$m^2$</td>
</tr>
<tr>
<td>Number of Tubes</td>
<td>-</td>
</tr>
<tr>
<td>Number of Tube per $m^2$ Heat Exchanger Cross Section</td>
<td>$/m^2$</td>
</tr>
<tr>
<td>Power Density in Steam Reformer</td>
<td>$MN/m^3$</td>
</tr>
<tr>
<td>Number of Loops for Steam Reformer</td>
<td>-</td>
</tr>
<tr>
<td>Diameter of Steam Reformer</td>
<td>-</td>
</tr>
<tr>
<td>Power of Steam Generator</td>
<td>$H_{th}$</td>
</tr>
<tr>
<td>AT for SG</td>
<td>$^\circ$C</td>
</tr>
<tr>
<td>k-Hr. for SG</td>
<td>kcal/m$^2$°C</td>
</tr>
<tr>
<td>Heat Flux Density for SG</td>
<td>kcal/m$^2$°C</td>
</tr>
<tr>
<td>Required Heat Transfer Area SG</td>
<td>$m^2$</td>
</tr>
<tr>
<td>Heat Exchange Area SG</td>
<td>$m^2/m^3$</td>
</tr>
<tr>
<td>Heat Exchange Volume SG</td>
<td></td>
</tr>
<tr>
<td>Power Density SG</td>
<td>$MN/m^3$</td>
</tr>
<tr>
<td>Req. Volume SG</td>
<td>$m^3$</td>
</tr>
<tr>
<td>Weight of SG</td>
<td>$m$</td>
</tr>
<tr>
<td>Cross-Section of SG</td>
<td>$m^2$</td>
</tr>
<tr>
<td>Diameter of SG</td>
<td>$m$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Data</th>
<th>Dim.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power for Process Heat</td>
<td>$H_{th}$</td>
</tr>
<tr>
<td>AT for Steam Reformer</td>
<td>$^\circ$C</td>
</tr>
<tr>
<td>k-Hr. for Steam Reformer</td>
<td>kcal/m$^2$°C</td>
</tr>
<tr>
<td>Heat Flux Density for Steam Reformer</td>
<td>kcal/m$^2$°C</td>
</tr>
<tr>
<td>Required Heat Transfer Area</td>
<td>$m^2$</td>
</tr>
<tr>
<td>Heat Transfer Area per Tube</td>
<td>$m^2$</td>
</tr>
<tr>
<td>Number of Tubes</td>
<td>-</td>
</tr>
<tr>
<td>Number of Tube per $m^2$ Heat Exchanger Cross Section</td>
<td>$/m^2$</td>
</tr>
<tr>
<td>Power Density in Steam Reformer</td>
<td>$MN/m^3$</td>
</tr>
<tr>
<td>Number of Loops for Steam Reformer</td>
<td>-</td>
</tr>
<tr>
<td>Diameter of Steam Reformer</td>
<td>-</td>
</tr>
<tr>
<td>Power of Steam Generator</td>
<td>$H_{th}$</td>
</tr>
<tr>
<td>AT for SG</td>
<td>$^\circ$C</td>
</tr>
<tr>
<td>k-Hr. for SG</td>
<td>kcal/m$^2$°C</td>
</tr>
<tr>
<td>Heat Flux Density for SG</td>
<td>kcal/m$^2$°C</td>
</tr>
<tr>
<td>Required Heat Transfer Area SG</td>
<td>$m^2$</td>
</tr>
<tr>
<td>Heat Exchange Area SG</td>
<td>$m^2/m^3$</td>
</tr>
<tr>
<td>Heat Exchange Volume SG</td>
<td></td>
</tr>
<tr>
<td>Power Density SG</td>
<td>$MN/m^3$</td>
</tr>
<tr>
<td>Req. Volume SG</td>
<td>$m^3$</td>
</tr>
<tr>
<td>Weight of SG</td>
<td>$m$</td>
</tr>
<tr>
<td>Cross-Section of SG</td>
<td>$m^2$</td>
</tr>
<tr>
<td>Diameter of SG</td>
<td>$m$</td>
</tr>
</tbody>
</table>

Fig. 4.13-1 Dependence of Power Densities in Steam Reformers and Steam Generators on the Helium Temperatures
4.14 Design Forms of Nuclear-Heated Steam Reformers

4.14.1 Survey of the Degrees of Freedom in the Design

For the design of helium-heated steam reformers there are a number of possibilities of realization as Tab. 4.14-1 shows. After answering the question of the necessity of an intermediate circuit and after determining the special circuit (s. Vol 3, § 5), the volumetric power and hence the size of the steam reformer is determined mainly by the choice of the thermodynamical design parameters. The arrangement of the reformer tubes and the steam generator heat flux areas in the primary circuit of the nuclear reactor depends considerably on the split up of reactor heat for methane reforming and for steam generation as well as on the concept underlying the reactor vessel (see Vol 3, § 7). The type of reformer tube, the form of gas ducting in the tube bundle as well as the form of suspending the reformer tube are technical questions, which permit a plurality of solutions; however, they have still to be supported by experiments on a technical scale.

A large number of different high-temperature alloys from the conventional as well as nuclear technology are available for the choice of materials for the reformer tubes, for the process gas inlet and outlet ducts, for insulations, carrier-plates and gas ducting systems. An important predecision will be the determination of whether centrifugally cast or rolled materials are to be used for the reformer tubes. The necessary qualification tests, which permit such a decision, will be described in detail elsewhere (s. §4.17).

4.14.2 Arrangement of Steam Reformers and Steam Generators

As fig. 4.14-2 shows, there is considerable freedom in the arrangement of steam reformers and steam generators, which is only limited by the chosen vessel concept and by the heat split up. The various arrangements are to be investigated and rated regarding the following features:
Tab. 4.14-1: Criteria for the Design of Helium-heated Steam Reformers
- the construction height upwards and downwards is limited (relative to the hot-gas ducting of the reactor vessel)
- the hot-gas ducting and distribution in the steam reformer should be as short and as regular as possible
- all gas baffle installations have to be cooled by cold helium in counterflow
- pressure losses in the gas ducting should be held as small as possible
- the filling vent of the reformer tubes should be accessible without difficulty due to the necessary change of catalyst
- temperature and energy losses in the gas ducting should be as low as possible
- compensation problems should be solvable by placing compensators possibly in the cold construction parts.

Fig. 4.14-2: Possibilities of Arrangement of Steam Reformers and Steam Generators
The variants 2 and 4 are not appropriate for an integrated arrangement and probably also for the system due to their large construction height.

Variants 1 and 3 differ only as regards the form of the connection between the steam reformer and the steam generator. Both are equally suitable for being placed in pod-boiler or loop systems.

Variant 5 has the advantage of having a larger number of identical units due to the common arrangement of the heat flux areas in a vessel. This permits the use of e.g. small compressors (e.g. corresponding to THTR 300). The complicated helium ducting is disadvantageous.

Variant 6 can only be used for higher inlet temperatures of the coolant in the nuclear reactor ($T > 450\,^\circ\text{C}$). This is because the use of steam generator heat flux surfaces can then be dispensed with.

4.14.3 Choice of Reformer Tube Forms or Alternative Forms

Several geometrical forms are possible for the design of the reformer tubes. Some basic designs are shown in the following fig. 4.14-3.

![Possible Tube Forms for Helium-heated Steam Reformers](image)

The reformer tube (1) is the one that is used in conventional furnaces today. Longitudinal thermal expansion from cold to operating
temperature is about 20 cm, and this is accommodated by flexibility in the form of the pigtail. In a nuclear reformer furnace, the pigtail can, for example, be constructed in the form of a thin coiled tube (internal diameter \( \approx \) 2.5 cm). The filling vent must be wide enough \( (d_i \approx 5 \text{ cm}) \) for removal of the catalyst.

The geometry of the reformer tube (2) is commonly used in steam generators. The disadvantage here is the complicated gas ducting on the helium side, whereas compensation problems can be solved somewhat more easily.

In the reformer variant (3), the process gas is led back in a thin coiled tube inside the reformer tube.

The design has a number of considerable advantages:

- heat of the process gas from 800 ... 850 °C to about 650 °C is given up to the catalyst filling. This means that the reformer tube heat flux area is reduced up to 20%.
- the hot areas of the pigtail lie within the reformer tubes. Hydrogen and tritium permeation are thereby considerably reduced.
- the longitudinal expansion of the reformer tube causes no problem; space, which would be required for the hot pigtail in the reformer tube vessel, is saved.
- the penetrations for the process gas through the pressure vessel have to be made only for \( \approx 650 \) °C instead of for the reforming temperatures.
- in case of rupture of the pigtail, it is of advantage from the technical safety point of view that the process gas cannot enter the helium gas and vice versa.
- an additional defective spot, where the weld pigtail/reformer tube would occur (in the hot region in the case of an outer return duct!), is avoided.
- for a possible removal of the tube, it is not necessary to detach the pigtail at the lower end of the reformer tube.

Variant (4) differs from all usual arrangements in that the hot helium gas flow within tubes, while the catalyst is located in immersion-heater type of heating coils. The amount of tubing...
material for heat transfer areas in such a construction is naturally very low, since tubes with small diameters are used. The design of the pressure vessel, however, is complicated, especially, when there is a pressure difference between the heating and process sides.

Internal insulations are then necessary, which cause the dimensions of the overall heat exchanger pressure vessel to be considerably enlarged. The penetrations of the helium ducting tube through the pressure casing, which has the catalyst filling, are only possible with special constructions (heat bridges). There is the possibility of plugging off individual tubes on both sides after accidents; however, for this purpose manipulation inside the primary circuit has to occur. The change of catalyst for this variant could occur relatively simply, possibly even continuously.

Considering all the advantages and disadvantages, variant 3 seems to be the most favourable solution.

A completely new variant for the reforming of methane, apart from the thick-walled reformer tube, has been suggested and tested on a laboratory scale at the IRB of the KFA Jülich [25]. Hereby, a methane/steam mixture is reformed on the inner walls of a strongly nickel-containing tube without catalyst filling. The conversions were approximately the same as in the EVA reforming plant. The use of tubes with small dimensions ($d_a < 20$ mm) opens up the prospect of producing very compact heat exchangers for the reforming of methane. However, the long-time behaviour of the material and desactivation processes possibly occurring have not been investigated as yet.

4.14.4 Type of Gas Ducting in the Reformer Bundle

Fig. 4.14-4 shows the different possibilities of helium ducting in the reformer tube bundle. The basic condition for all the proposals is that sufficiently high helium velocities are attained and thus adequately large $\alpha$-numbers. This can be achieved by the
following measures:
- Use of concentric gas ducting tubes for each reformer tube
- Displacement bodies in the wedges between the reformer tube
- Longitudinal ribs on the reformer tubes in order to decrease
  the wedges
- Placement of the reformer tubes in blocks of Al₂O₃ with holes,
  which give rise to sufficiently small ring-shaped crevices
- Use of baffle installations to produce cross-counterflow
- Very dense arrangement of reformer tubes without special
  measures

These variants can be rated according to the following scheme:

- How many reformer tubes can be accomodated per m², how large
  is the volumetric power of the steam reformer?
- How much material is required for the reformer tubes and for
  the gas-ducting systems?
- Which production and testing problems occur?
- How does the tube bundle behave after the fall-out of individu-
  al tubes?

When the different variants are more exactly worked out, it

can be ascertained that some arrangements (e.g. very dense arrange-
ments) cannot be realized at all functionally because e.g. the

tube base cannot be reached or the welding-in of the tube is

hindered by problems due to space. Other proposals (e.g. arrange-
ment in ceramic structures) are disadvantageous, as the volumetric

power of such steam reformer aggregates is lessened (only about

20 reformer tubes/m² can be accomodated) and is prohibitive for

an installation in integrated reactor vessels.

Again, other variants (e.g. baffles) have to be tested more exact-
ly on a large scale regarding friction problems between the tubes

and the baffle installations.

Also, the casting or welding on of ribs on the outer side is

not without problems regarding the formation of dissymmetries in

the mechanical stresses. Therefore, before a basic recommendation
Fig. 4.14-4 Different Possibilities of Helium Ducting in Steam Reformer Bundle [28]
can be made, tests should be undertaken in a large reforming plant, where the different variants can be tried out.

4.14.5 Suspension of the Reformer Tubes

A number of solutions can be considered for the suspension of the reformer tubes:

- the tubes can be inserted into a tube-plate and be welded above this carrier-plate
- the tubes can be welded onto the carrier-plate in a butt-joint from below
- instead of a carrier-plate, a cooled supporting beam system can be used, in which the reformer tubes are suspended and to which they are welded
- by using ceramic gas-ducting structures, the reformer tubes are sufficiently far apart, so that when prestressed cast steel vessels are used they can in principle be made to penetrate the vessel lid and be welded on compactly from the outside.
4.15 Heat and Mass Balances for Typical Steam Reformer Processes

The reference steam reformer system is shown schematically in fig. 4.15-1, and is described in detail below. A detailed tabulation of the hydrogen mass balance is given in table 4.15-2. This system is based upon a reactor having a thermal power of 3000 MW and a helium temperature range of 950 - 250 °C. The steam reformer utilizes 1071 MW heat from the helium over a temperature range of 950 - 700 °C, while the remainder of the heat is used for steam generation.

Table 4.15-2 Mass Balance for Hydrogen Production

<table>
<thead>
<tr>
<th>Inlet Mass Flow Rate</th>
<th>Outlet Mass Flow Rate</th>
<th>Mass Converted to Hydrogen</th>
<th>Scrubber portion from the low temperature separation</th>
<th>Methane Recycled in methane production</th>
<th>Hydrogen produced from methane production</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg/h</td>
<td>kg/h</td>
<td>kg/h</td>
<td>kg/h</td>
<td>kg/h</td>
<td>kg/h</td>
</tr>
<tr>
<td>H₂</td>
<td>406</td>
<td>108474</td>
<td>122446</td>
<td>624</td>
<td>121416</td>
</tr>
<tr>
<td>CH₄</td>
<td>384528</td>
<td>135968</td>
<td>135968</td>
<td>704</td>
<td>30528</td>
</tr>
<tr>
<td>CO</td>
<td>11620</td>
<td>238588</td>
<td>42980</td>
<td>224</td>
<td>31136</td>
</tr>
<tr>
<td>CO₂</td>
<td>-</td>
<td>326876</td>
<td>634260</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>1297782</td>
<td>884430</td>
<td>758682</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1694336</td>
<td>1694336</td>
<td>1694336</td>
<td>635812</td>
<td>183080</td>
<td>116762</td>
</tr>
</tbody>
</table>

4.15.1 Process Design

The following reaction conditions are chosen:
- reformer temperature: 825 °C
- reformer pressure: 40 b
- steam/methane ratio: 3:1
The product analysis is then:

<table>
<thead>
<tr>
<th></th>
<th>Vol %</th>
<th>Vol % (dry i.e. without water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>42.4</td>
<td>68.4</td>
</tr>
<tr>
<td>CH₄</td>
<td>6.7</td>
<td>10.8</td>
</tr>
<tr>
<td>CO</td>
<td>6.7</td>
<td>10.8</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.8</td>
<td>9.5</td>
</tr>
<tr>
<td>H₂O</td>
<td>38.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

The methane conversion is 64.6%.

---

**Fig. 4.15-1 Flow Schematic for the Reference Nuclear Steam-Reforming Process**

The steam/methane mixture is introduced into the steam-reformer tubes at 450 °C. In the reformer tubes the gas is heated to a temperature of 825 °C. The product gas is led out of the reformer tube through a pigtail. As this occurs, heat is transferred to the colder reaction mixture. Because of the heat transfer, the product gas is cooled to 600 °C. The following is a specific heat balance for 1 kg-mole methane (≈16 kg ≈ 22.4 Nm³ CH₄).
Heat of reaction  \( 3.127 \times 10^4 \) kcal

Sensible heat  
(450 \( \rightarrow \) 825 °C)  \( 1.619 \times 10^4 \) kcal

Heat recovery by inner pigtail  
(825 \( \rightarrow \) 600 °C)  \(-1.058 \times 10^4 \) kcal  
\[ \frac{-1.058 \times 10^4}{3.688 \times 10^4} \] kcal

With this summation, the flow rate will be \( 2.498 \times 10^4 \) kmole CH\(_4\)/h
\( \equiv 396.600 \) kg/h \( \equiv 5.5954 \times 10^5 \) Nm\(^3\)/h,

4.15.2 Thermodynamic Data of a Single Reformer Tube

### Helium Side

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>950 °C</td>
</tr>
<tr>
<td>Outlet temperature</td>
<td>700 °C</td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>39.4 b</td>
</tr>
<tr>
<td>Outlet pressure</td>
<td>39.2 b</td>
</tr>
<tr>
<td>Mass flow rate</td>
<td>0.1846 kg/sec</td>
</tr>
<tr>
<td>Heat available</td>
<td>2.059 \times 10^5 \text{ kcal/h}</td>
</tr>
</tbody>
</table>

### Process Side

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>450 °C</td>
</tr>
<tr>
<td>Reforming temperature</td>
<td>825 °C</td>
</tr>
<tr>
<td>Outlet temperature (pigtail)</td>
<td>600 °C</td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>46 b</td>
</tr>
<tr>
<td>Outlet pressure</td>
<td>40 b</td>
</tr>
<tr>
<td>Methane inlet flow rate</td>
<td>125.1 Nm(^3) CH(_4)/h</td>
</tr>
<tr>
<td>Steam inlet flow rate</td>
<td>290 kg H(_2)O/h</td>
</tr>
<tr>
<td>Product gas flow rate (moist)</td>
<td>640 Nm(^3)/h</td>
</tr>
<tr>
<td>Gas production rate</td>
<td>314 (Nm(^3) CO + H(_2))/h</td>
</tr>
<tr>
<td>Amount of heat required</td>
<td>2.058 \times 10^5 \text{ kcal/h}</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Inner diameter of the tube</td>
<td>100 mm</td>
</tr>
<tr>
<td>Outer diameter of the tube</td>
<td>130 mm</td>
</tr>
<tr>
<td>Helium flow area per tube</td>
<td>92 cm²</td>
</tr>
<tr>
<td>Active tube length</td>
<td>10 m</td>
</tr>
<tr>
<td>Inactive tube length</td>
<td>1.0 m</td>
</tr>
<tr>
<td>Helium velocity in the tube bundle</td>
<td>13.5 m/s</td>
</tr>
<tr>
<td>Film coefficient of heat transfer on the helium side</td>
<td>810 kcal/m²h °C</td>
</tr>
<tr>
<td>Film coefficient of heat transfer on product side</td>
<td>1000 kcal/m²h °C</td>
</tr>
<tr>
<td>Thermal conductivity of the tube wall</td>
<td>23 kcal/m h °C</td>
</tr>
<tr>
<td>Overall heat transfer coefficient</td>
<td>304 kcal/m²h °C</td>
</tr>
<tr>
<td>Log. mean temperature difference</td>
<td>180 °C</td>
</tr>
<tr>
<td>Heat flux</td>
<td>54,720 kcal/m²</td>
</tr>
<tr>
<td>Effective heat transfer area per tube</td>
<td>4.08 m²</td>
</tr>
<tr>
<td>Heat transferred per tube</td>
<td>2.235 x 10⁵ kcal/h</td>
</tr>
<tr>
<td>Maximum wall temperature of the tube</td>
<td>900 °C</td>
</tr>
<tr>
<td>Pressure drop across tube wall at maximum wall temperature</td>
<td>1 b</td>
</tr>
</tbody>
</table>

4.15.3 Data of the Steam Reformer System

4.15.3.1 General Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclear reactor thermal power</td>
<td>3000 MW</td>
</tr>
<tr>
<td>Temperature range in nuclear reactor core</td>
<td>280 ~ 980 °C</td>
</tr>
<tr>
<td>Mass flow rate of helium</td>
<td>820 kg/sec</td>
</tr>
<tr>
<td>Maximum heat available (950 °C ~ 700 °C)</td>
<td>9.211 x 10⁸ kcal/h</td>
</tr>
<tr>
<td>Heat consumed in the process per unit of gas production</td>
<td>655 kcal/Nm³(CO + H₂)</td>
</tr>
<tr>
<td>Gas production rate</td>
<td>1.406 x 10⁶ Nm³(CO + H₂)/h</td>
</tr>
<tr>
<td>Number of steam reformers</td>
<td>8</td>
</tr>
<tr>
<td>Maximum heat available (700 °C ~ 250 °C)</td>
<td>16.69 x 10⁸ kcal/h</td>
</tr>
<tr>
<td></td>
<td>≡ 1929 MW(th)</td>
</tr>
</tbody>
</table>
Steam produced (540 °C/195 bar) 2678 t/h
Steam flow rate used in process 905 t/h
Number of steam generators 4

4.15.3.2 Steam Reformer Data

Number of units 8
Total thermal power produced per unit 134 MW(th)
Mass flow rate of helium per unit 102.5 kg/sec
Number of reforming tubes per unit 559
Gas production rate per unit 176,000 Nm³ (CO + H₂)/h

4.15.3.3 Data of a Steam Generator

Number of units 4
Total thermal power produced per unit 482 MW(th)
Mass flow rate of helium per unit 205 kg/sec
Steam flow rate per unit 670 t/h

4.15.4 Waste Heat Utilization (see flow diagram fig. 4.15-1)

4.15.4.1 Superheater for Feed Gas(≠ 5)

The heat of the product gas leaving the steam reformer is utilized in a heat exchanger to superheat the feed gas.

DATA:

Product Side
Inlet temperature 600 °C
Outlet temperature 465 °C
Inlet pressure 40 b
Outlet pressure 39.7 b
Inlet Gas

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>320 °C</td>
</tr>
<tr>
<td>Outlet temperature</td>
<td>450 °C</td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>47 atm</td>
</tr>
<tr>
<td>Outlet pressure</td>
<td>46.4 atm</td>
</tr>
<tr>
<td>Steam mass flow rate</td>
<td>1298 t/h</td>
</tr>
<tr>
<td>Methane mass flow rate</td>
<td>397 t/h = 5.59 x 10^5 Nm^3/h</td>
</tr>
</tbody>
</table>

4.15.4.2 Process Steam Generation (**# 6**)

The product gas is further cooled to 350 °C, and through this heat transfer process, steam is produced at a rate of 188 t/h. The heat for this process is: 1.27 x 10^8 kcal/h.

4.15.4.3 Conversion (shift Reactor (**# 7**))

The product gas now undergoes a shift reaction. This exothermic reaction causes a temperature increase of 58 °C.

<table>
<thead>
<tr>
<th></th>
<th>Inlet Vol %</th>
<th>Outlet Vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>moist</td>
<td>dry</td>
</tr>
<tr>
<td>H₂</td>
<td>42.4</td>
<td>(68.9)</td>
</tr>
<tr>
<td>CH₄</td>
<td>6.7</td>
<td>(10.8)</td>
</tr>
<tr>
<td>CO</td>
<td>6.7</td>
<td>(10.8)</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.8</td>
<td>(9.5)</td>
</tr>
<tr>
<td>H₂O</td>
<td>38.4</td>
<td>(-)</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>(100.0)</td>
</tr>
</tbody>
</table>

4.15.4.4 Process Steam Generation and Methane Preheating (**# 8 + **# 9**)

The product gas stream is now divided into 2 parts: The heat of one part is used for the production of steam, while the other is used to preheat methane. The product gas is thus cooled to 200 °C.
Process Steam Generation

Steam flow rate 205 t/h
Heat required 13.87 x 10^7 kcal/h

Preheating of Methane

Methane flow rate 397 t/h
Heat required 8.01 x 10^7 kcal/h

4.15.4.5 Preheating of Feed Water (## 10)

The product gas is further cooled to 140 °C. The heat produced is utilized to preheat the feed water from 40 + 180 °C.

Q = 37.57 x 10^7 kcal/h

4.15.4.6 CO₂ Scrubber (Sulfinol Washing) (## 11)

After further cooling to approximately 50 °C, the gas is led to the CO₂ scrubber. The wash contains Sulfinol, a mixture of Sulfolan (Tetrahydrothiophene dioxide) and "Adip" (Diisopropanolamine).

For regeneration, the following is required:

Amount of steam 2.8 - 3.0 kg/(Nm³ CO₂)
Electrical energy 0.05 kWh/(Nm³ CO₂)
Steam flow rate 950 t/h
Electrical power 17 MW

4.15.4.7 Low-Temperature Separation (## 12)

The remaining mixture of H₂, CH₄, CO, is cooled to a temperature of -166 °C after drying. Most of the methane is then condensed and separated as a liquid. To obtain the necessary amount of cooling, the methane portion is expanded through an orifice, while the H₂ portion is expanded in a turbine to 17 bar. Both product portions are heated in a heat exchanger, where the above-mentioned gas mixture to be separated passes in counterflow.
4.15.4.8 Methanation (13)

The hydrogen portion is purified by methanation (\(\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}\)). The composition of the mixture after the separation of the water produced in the reactor is:

- \(\text{H}_2\) 95.0 vol. %
- \(\text{CH}_4\) 5.0 vol. %

4.15.4.9 Recycle Compressor (14)

The methane portion is compressed to 48 b in a 2-stage compressor. An electrical power of 17.6 MW is needed for a compressor efficiency of 85 %.
4.16 Design Examples of Steam Reformers

Some typical arrangement possibilities are described in the following:

The hot helium enters the hot-gas tube of the coaxial ducts from the hot-gas plenum (see arrangement in fig. 4.16-1) at a maximum temperature of 980 °C. In the lower part of the gas-ducting construction of the heat exchanger, the helium flow is deflected and then enters the reformer tube region. It is led into the intermediate space between the reformer tubes and the upper carrier-plate. The temperature thus falls up to 700 °C and is utilized for the superheating of the feed gas and for the steam-reforming process itself.

Under the carrier-plate construction there is a space enlargement for the helium gas which here is lead via a second coaxial duct to the steam generator. The temperature drop up to 250 °C is utilized for the production of process and turbine steam. The gas is then led to the circulators, after flowing along the walls of the steam generator, the coaxial ducts and the reformer tubes. It is then compressed and conducted into the outer concentric duct, which leads to the reactor.

Through this type of flow system chosen here, all the pressure-withstanding walls of the heat exchangers, circulators and outer tube of the coaxial ducts are in contact with helium at a temperature of 250 °C and so only have to be protected by a thin insulation layer.

Furthermore, due to this arrangement, the construction components of the hot-gas ducting system are held at a maximum temperature of 500 °C using the counterflow principle. The coaxial ducts are additionally internally insulated and through this their wall temperature only reaches about 300 °C. There is no special problem regarding the mechanical design as the occurring pressure differences are only due to the pressure drop in the individual heat exchanger sections (reformer tube zone and steam generator zone). They therefore are in the order of magnitude of 0.3 kg/cm² respectively. The velocities in the gas-ducting system are so low that the pressure differences are tolerable. Mechanical vibration
of the outer gas-ducting system is prevented by hardening the walls, which is necessary in any case in order to obtain uniform flow conditions.

The upper carrier-plate and a carrier ring, which are welded onto the pressure vessel wall just above the concentric connecting ducts between the steam generator and the steam reformer, act as fixed points in the overall gas-ducting construction.

This variant is designed so as to be as similar as possible to the conventional reformer tube technique and the experiment in the single-tube test reformer plant by using centrifugally cast steel. The "active" length of 10 m is chosen on the conservative side. The inner diameter of 100 mm as well as the wall thickness of 15 mm is in accordance with the data in use today. The product gas is led back through thin helical ducts which are placed inside the catalyst-filled reformer tubes ("inner pigtails").

There is a gas plenum above the carrier construction, which is gas-tight in the upper part of the pressure vessel. This spatial separation is suitable in order to separate the catalyst inlets in the reformer tube from the region of the primary gas flow. Also, in the case of plate-out, this upper region can be accessible by having corresponding screening. The upper region is constantly held at the same helium pressure as the bordering primary system. For a change of catalyst, only the upper manhole lid of the pressure vessel has to be demounted.

Feed gas (preheated methane and steam) is led to the reformer tubes and the product gas is then led through pigtails, which pass outwards through the vessel lid. The connections do not have to be dismounted for changing of catalyst as the upper manhole is large enough to allow this to be done. In this construction, the catalyst is removed by means of a vacuum-cleaner, after first opening the reformer tube lid, and it is then replaced.

The plurality of the reformer tube connections ensures that in the case of a tube rupture, a large tube cross-section is not set free
Fig. 4.16-2 Design of a Steam Reformer Furnace for the Loop System
(Steam Reformer and Steam Generator in one Vessel)
from the technical safety point of view. The reformer tubes themselves are made of one of the usual materials (e.g. DIN material no. 4848) by the centrifugal casting method.

The heat exchanger surfaces in the steam generator are made of curved meander-formed tubes in parallel arrangement. They are arranged from bottom to top in the sequence: economizer, evaporator and superheater. The economizer and evaporator operate in counterflow, while the superheater has continuous flow in order to keep the tube wall temperatures low. All the curved tubes are welded on to the cold feed water ducts. The latter are placed between the heating tubes and lead downwards. The inlet of feed water as well as the outlet of steam occurs via 86 ducts through the vessel lid. Through this arrangement, the amount of water penetrating into the primary circuit in the case of rupture of the steam generator tubes is held at a minimum. Furthermore, a plugging off of the damaged tubes is facilitated. The external collecting system for feed water and fresh steam have a large redundancy as is customary in steam generating techniques. The vibration of the tube bundle is prevented by welding it on to the feed water ducts.

Fig. 4.16-2 shows a schematic design in which the reformer tube zone and the steam generator zone are agglomerated inside the same vessel. In the dimensions shown here for a subdivision of the reactor heat (950...700...250 °C), 12 such units would be required for a 3000 MW plant. The central region contains a steam reformer. The steam generator bundle is located outside. All heat exchanger bundles are cooled by cold helium at 250 °C. This design could be inserted in a pod-boiler or in a loop design. In fig. 4.16-3 there is a third possibility for the arrangement of the steam reformer and the steam generator, which could be used in connection with a loop design for a 3000 MW(th) plant or in a pod-boiler design too. The splitting up of reactor heat in this example is 950 ... 800 °C for the steam reforming process and 800 ... 250 °C for the steam generation process. If necessary these heat exchangers can be surrounded by an additional burst protection.
Fig. 4.16-3  Design of a Steam Reformer Furnace for the Loop System
(Steam Reformer and Steam Generator in Separate Vessels)
The design data of nuclear-heated and conventionally heated steam reformers are similar, excepting for the different form of heating and the connected special questions (pressure differences, hot spots, corrosion), as the following table 4.17-1 shows.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conventional Plants</th>
<th>Nuclear Plants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube length</td>
<td>8 ... 12 m</td>
<td>10 m</td>
</tr>
<tr>
<td>Internal diameter</td>
<td>100 ... 150 mm</td>
<td>100 mm</td>
</tr>
<tr>
<td>Wall thickness</td>
<td>15 ... 20 mm</td>
<td>15 mm</td>
</tr>
<tr>
<td>Product gas removal</td>
<td>outside reformer tube</td>
<td>within reformer tube</td>
</tr>
<tr>
<td>Reforming pressure</td>
<td>1 ... 25 b</td>
<td>40 b</td>
</tr>
<tr>
<td>Reforming temperature</td>
<td>800 ... 850 °C</td>
<td>800 ... 850 °C</td>
</tr>
<tr>
<td>Heating pressure</td>
<td>1 b</td>
<td>40 b</td>
</tr>
<tr>
<td>Heat transfer</td>
<td>Radiation</td>
<td>Convection</td>
</tr>
<tr>
<td>Space utilization</td>
<td>&lt; 1 tube/m²</td>
<td>~ 45 tubes/m²</td>
</tr>
<tr>
<td>Max. heating temperature</td>
<td>1400 ... 1500 °C</td>
<td>950 °C</td>
</tr>
<tr>
<td>Max. tube wall temp.</td>
<td>900 °C</td>
<td>900 °C</td>
</tr>
<tr>
<td>Max. pressure difference across tube wall</td>
<td>0 ... 25 b</td>
<td>1 bar (hot part)</td>
</tr>
<tr>
<td>H₂O/CH₄ ratio</td>
<td>2/1 ... 5/1</td>
<td>2/1 ... 5/1</td>
</tr>
<tr>
<td>Mean heat flux</td>
<td>60 000 kcal/m²h</td>
<td>60000 ... 70000 kcal/m²h</td>
</tr>
<tr>
<td>Heat flux max./min</td>
<td>10/1</td>
<td>1.5/1</td>
</tr>
<tr>
<td>Rate of gas flow</td>
<td>~50000 Nm³ H₂ + CO/m²h</td>
<td>~50000 Nm³ H₂ + CO/m²h</td>
</tr>
<tr>
<td>Service life aim</td>
<td>100,000 h (60,000 h attained today)</td>
<td>&gt;100,000 h</td>
</tr>
<tr>
<td>Reformer tube materials</td>
<td>G-X40 CrNiNb 2524 (W.-No. 1.4855; IN 519)</td>
<td>(as in the conventional plants)</td>
</tr>
<tr>
<td></td>
<td>G-X45 NiCrCoWNb 4625(IN 643)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G-X45 NiCrCoWNb 3626(IN 638)</td>
<td></td>
</tr>
<tr>
<td>Product gas tube materials</td>
<td>Incoloy 800, Incoloy 807</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.17-1: Comparison of Data for Conventionally Heated (Flue Gases) and Nuclear-Heated (Helium) Steam Reformers
Tube length:  
The tube length in the nuclear steam refomer should be chosen to be as short as possible from the chemical reaction point of view because the height of the reactor vessel is limited.

Inner diameter:  
From the point of view of mechanical design, the diameter should be small; however, with respect to the inner pigtail and the dimensions of the catalyst, there is a limitation.

Wall thickness:  
has to be calculated for accident of pressure loss at one side in a given time (for instance 100 h) and will be in the order of values used today to reach more safety.

Pigtail location:  
Inner pigtails have a lot of advantages, for instance:
- saving in space for compensation
- heat transfer back to process
- hot surface lies within process tube, important for hydrogen and tritium permeation
- influence of impurities in helium on thin-walled material prohibited
- if outlet temperature of reformer gas is 600 °C...650 °C instead of 800...850 °C, penetrations in closures can be made in same way as penetrations for steam.

Reformer pressure:  
higher than in conventional tubes so that reforming pressure same as reactor pressure (40 b). This can be advantageous for all processes which need high pressures.

Reformer temperature:  
The same in both cases.
Heat transfer, space utilization:
Heat transfer by radiation in conventional plants needs a lot of space for the tubes. In helium at 40 b very good heat transfer by convection, this needs high velocities, that means tubes must be as narrow as possible.

Heating gas temperature:
Has to be very high in conventional plants to get high heat fluxes. Therefore, for mistakes in operation, hot spots occur in the tube walls; this causes failures in tube material. In helium-heated steam reformers, the helium temperature of 950 °C can never be exceeded. This is advantageous for the lifetime of the tubes.

Wall temperature:
This value is a little bit lower in nuclear-heated plants; therefore, higher creep stress values can be tolerated or a longer lifetime is possible.

Pressure difference across tube wall:
Smaller in the nuclear case because helium at 40 b. Higher safety factor possible.

Heat flux, heat flux max/min:
Mean heat flux can be nearly the same in conventional and nuclear plants. Possibility to attain higher heat fluxes in nuclear plants with higher pressure drops on helium side. Because of sharp decrease of temperature profile on heating side, high variations in heat flux occur about tube length in conventional plants which cause difficulties in stress distributions. In nuclear case, heat flux is relatively constant about the whole length of the tube.

Gas production:
The same for same mean heat flux.

H₂O/CH₄-ratio: the same
Expected lifetime of reformer tubes:

Estimation that the same lifetimes can be realized. This seems, however, to be a pessimistic assumption for the nuclear-heated tubes, because:

- Pressure difference across wall is smaller (1b in hot part)
- Wall temperature is lower
- Heat distribution in z-axis and circumference is constant
- No hot spots can occur
- Practically no corrosion on outside

The data of helium-heated nuclear plants is confirmed through many years of operation of the EVA plant at Jülich. The reformer tube has dimensions which can be varied as follows: length $L = 10 \ldots 15$ m, internal diameter $D_i = 100 \ldots 150$ mm. It is heated by helium under pressure and at temperatures of up to 1000 °C. Fig. 4.17-2 and 4.17-3 show the schematic as well as the experimental results of this plant (temperatures and gas analysis).

![Fig. 4.17-2 Schematic of the EVA-plant [7]](image-url)
Main design data
Electrical power $\sim 1$ MW

**Helium side**
- Maximum temperature 1000 $^\circ$C
- Maximum pressure 50 b
- Maximum mass rate of flow 0.4 kg/sec

**Process side**
- Inlet temperature 550 $^\circ$C
- Maximum pressure 35 b
- Maximum CH$_4$ input 200 Nm$^3$/h
- Maximum steam input 500 kg/h

The experience which has been gained from the single-tube reforming plant (EVA), with the help of accompanying kinetic experiments as well as from laboratory experiments on hydrogen and tritium permeation can be summarized as follows:

- The kinetics of the methane reforming is such that the process is only limited by heat transfer. The theoretically calculated equilibria are attained.
- A maximum helium temperature of 950 $^\circ$C is sufficient in order to obtain heat fluxes as in conventional plants (60,000 ... 70,000 kcal/m$^2$h).
- If the process parameters are so chosen that $p \sim 40$ b, $T \sim 800 ... 850$ $^\circ$C and H$_2$O/CH$_4$ $\sim 2/1 ... 4/1$, the methane conversion is sufficiently high (60 ... 65 %) and the stresses in the tube walls are controllable.
- The materials available today have sufficient strength values of 0.5 ... 1 kp/mm$^2$ for a lifetime of $10^5$ h. A very safe design is thus possible for a stress at 900 $^\circ$C wall temperature and $\Delta p \sim 1$ bar in the hot region.
- If the ratio of H$_2$/H$_2$O in the reforming process is about 1/1 ... 2/1, hydrogen permeation for a 3000 MW(th)-plant is limited to the order of magnitude of $\sim 1$ Nm$^3$H$_2$/h. This value is tolerable for graphite corrosion.
- Similar behaviour is expected for tritium. Even if all the
tritium occurring in the coolant is released into the process gas, the tritium content of this gas is within allowed limits.

- because of the convective heat transfer by helium, the reformer tube heat exchangers have to be constructed very compactly. According to the various possibilities of ducting helium in the reformer tube bundle, the number of reformer tubes/m² can be 20 - 45. This corresponds to a power density of \( \approx 0.7 \ldots 1.5 \text{ MW/m}^3 \) in the steam reformer.

- Tests have been started, which investigate the behaviour of metal corrosion by impurities in helium (H₂, CO, CO₂, H₂O, CH₄). However, considerably more experimental data on this effect is necessary.

- the reformer tube materials have to be qualified for application in nuclear plants by extensive material programs.

- the reformer tubes should, in any case, have inner return ducts for the product gas.

- the life span of the reformer tubes should be \( 10^5 \text{ h} \) or possibly longer, as the stress in helium at maximum temperatures is considerably lower than in conventional plants. (No hot spots in the tube wall at \( T > 950 \text{ °C} \); no pressure difference in the hot part during normal operation; no large azimuthal and axial dissymmetries for heat fluxes; no corrosion by flue gases).

- from the safety point of view, the reformer tubes can be arranged in the primary circuit of the nuclear reactor without an intermediate circuit, as the amount of gas, which enters the helium circuit in case of rupture of tubes, is limited to very small values (production of one tube \( \approx 400 \text{ Nm}^3 \text{ H}_2 + \text{ CO/h} \)).

- an intermediate circuit for the steam reforming of methane seems to have no advantages according to present knowledge; it should, however, be developed as a back-up solution.

- the contamination of the reformer tubes is probably low enough after \( 10^5 \text{ h} \), so that the tube bundle can be removed without any great difficulty (estimated deposition of Cs 137: < 10 \( \mu \text{Ci/cm}^2 \) after 10 years).
While the work done up to now has shown that the helium-heated steam reforming of methane is basically possible, the technical feasibility of a large tube bundle has to be proved. This test has to be carried out for a plant with 30 helium-heated reformer tubes. Fig. 4.17-4 shows a flow scheme of this plant, which should be ready at Jülich by 1978 [27]. Based on circuits, which will be typical for nuclear process heat plants, the helium circuit consists of a steam reformer, a steam generator, the helium compressor as well as an electro-heater, which simulates the nuclear heat source. The helium stream is heated in an electro-heater to a temperature of more than 950 °C at a pressure of 40 b. The temperature drop on the helium side between 950 and 600 °C is utilized in the steam reformer for superheating of the process gas from 450 °C to the reaction end-temperature of 825 °C as well as for carrying out the reforming of methane. In the steam generator, the remaining enthalpy of helium between 600 and 350 °C is utilized for the production of steam at 325 °C. After compensation of the pressure losses in the circuit by the compressor, helium enters the electro-heater again at a temperature of approx. 350 °C. The total power of the electro-heater amounts to 10 MW. The reforming of methane occurs at an inlet ratio of methane/steam = 1/3 as well as a reaction end-temperature of 825 °C and an end-pressure of 40 b. The product gas at a temperature of 825 °C is led away by inner return ducts in the reformer tubes. Sensible heat of the product gas between 825 °C and 600 °C is thereby transferred to the catalyst bed in the tubes and so regained for the process. The enthalpy of the product gas below 600 °C as well as the heat of condensation of excess water are utilized in various waste heat exchangers following the reformer plant. The dry product gas is compressed and led to the methanation plant.

In order to avoid the flaring-off of large amounts of product gas (∼ 9600 Nm³/h) as well as the buying of large amounts of natural gas (∼ 3000 Nm³/h), a methanation plant is used, in which a reversal of the reforming reactions occurs (CO + 3H₂ → CH₄ + H₂O, CO₂ + 4H₂ → CH₄ + 2H₂O). The proposed circuit scheme represents a demonstration of nuclear long-distance energy (nuclear chemical heat
Schematic of the Reformer Tube Plant for the Demonstration of a Reformer Tube Bundle

pipe) on a technical scale. The product gas of the reforming process which is preheated to 80 °C, is converted to methane and water in a 3-step methanation plant. After each methanation step, the heat of reaction is utilized. The maximum temperature of methanation ensured today from experience is limited to a value of 480 °C. Methane is dried and compressed and finally led to the reforming plant again.

An example of a possible construction design of the overall plant is shown in fig. 4.17-5. In this variant, the heater is placed in a boiler made of prestressed cast steel blocks and the whole of the remaining helium circuit is arranged in two steel boiler vessels. The vessels are connected by coaxial ducts.

The gas ducting is such that in the heater, helium streaming downwards is heated from 350 to 950 °C by resistance heating rods. It is led to the reformer tube vessel through the hot-gas duct of the ceramic coaxial duct. In the fig.所示 here a ceramic gas-
Fig. 4.17-5 Technical Design of a Helium-heated Steam Reformer Plant for the Demonstration of a Reformer Tube Bundle [28]
ducting system is also used for the reforming region. After giving up heat in the steam reformer, helium at 600 °C is led to the steam generator, in which helium is cooled to 350 °C in counterflow. Helium is then fed to the compressor and the pressure loss in the overall circuit is compensated for. Helium at 350 °C is then led to the heater in counterflow to the hot gas. The principle of counterflow cooling of the vessel wall by cold helium is used in all vessels. All gas-ducting walls, which border on hot helium, are surrounded by cold helium at higher pressure.

The plant should be built so flexibly that a compact metallic tube bundle can also be put into the vessel for the steam reformer. In this arrangement of the reformer tubes, metallic installations, which cause cross-counterflow, make the necessary high heat transfer coefficient on the helium side possible.

On the whole, the following technical insight can be attained according to present considerations based on the operation of this plant:

- testing of technical details of reformer tube bundles (suspension of tubes, carrier-plates, gas ducting, pigtails, pigtail ducting, behaviour of a compact tube bundle in hot helium, study of start-up and shut-down processes, behaviour of individual tubes for fall-out of the heating).
- investigation of handling of catalyst under simulated difficult conditions
- when carbon stone is used, the testing of this material as insulator, for vessel walls as well as a material for coaxial gas ducting.
- by choice of a design which is as near as possible to the reactor technology thinkable today for large-scale nuclear plants, testing of cold-gas collecting chambers in graphite installations
- possible application of a prestressed cast steel block vessel which is typical, e.g. in its dimensions, for a heat exchanger of a 3000 MW(th)-plant
- testing of methanation on a large scale, testing of the catalyst for over 4000 h and more. Later demonstration of steam generation in methanation plant possible. Investigation of problems regarding control
- measurement of hydrogen permeation under realistic conditions
- testing of a steam generator set in the helium circuit
- study possible for over $10^4$ h of the behaviour of reformer tubes in helium with impurities.
This plant should render sufficient experience and should be large enough in order to be able to take the step from here to a nuclear demonstration plant and then to later commercial plants. In table 4.17-6 some important data of the development of helium-heated reformer plants are given, which allow an estimation about the extrapolation steps.

<table>
<thead>
<tr>
<th>Plant &amp; Extrapolation Steps in the Development of the Helium-heated Steam Reformer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat source</td>
</tr>
<tr>
<td>Power</td>
</tr>
<tr>
<td>Number of loops</td>
</tr>
<tr>
<td>Maximum helium temperature</td>
</tr>
<tr>
<td>Helium throughput</td>
</tr>
<tr>
<td>Maximum helium pressure</td>
</tr>
<tr>
<td>Refining temperature</td>
</tr>
<tr>
<td>Refining pressure</td>
</tr>
<tr>
<td>H₂/CH₄-ratio</td>
</tr>
<tr>
<td>Diameter of reformer tubes</td>
</tr>
<tr>
<td>Status</td>
</tr>
</tbody>
</table>

As is foreseeable today, for a qualification of the reformer tube material on a technical scale the following tests are to be carried out:

- measurement of H₂ permeation rates
- measurement of T permeation rates
- behaviour of oxide layers for nonsteady processes, vibrations, shock stress
- corrosion of metals in helium with impurities, influence of metal structure, change of typical material characteristics
- measurement of creep strength in helium for various temperatures up to 3 x 10⁴ hr
- measurement of creep behaviour in a helium atmosphere
- measurement of breaking tension (elongation) in helium
- behaviour of materials under periodic strain (low-frequency and high-frequency fatigue)
- investigation of friction welding, finding suitable materials pairs at high temperatures
- investigation of weldability of reformer tube materials after long duration in helium
- working out of testing methods and investigation of possibilities for repetitive tests
- working out of specifications for tubes, inner gas ducting and closures, working out of tests for acceptance.

Some of these activities have been part of the current development program since years (H₂ and T permeation measurements), others like e.g. the investigation of the metal corrosion in helium with impurities are being tackled. The remaining qualification tests on selected tube materials, which are nearly always long-time tests, have to be started soon.
List of References


[19] Inniotakis, N.: Private Mitteilung


[26] Harth, R.: Private Mitteilung
