BEST AVAILABLE TECHNIQUES FOR HYDROGEN PRODUCTION BY STEAM METHANE REFORMING

PREPARED BY:

Amro FARID  AIR LIQUIDE
Jean GALLARDA  AIR LIQUIDE
Bernard MINEUR  AIR LIQUIDE
Stephen BRADLEY  AIR PRODUCTS
Wolfgang OTT  LINDE
Manfred IBLER  LINDE

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Table of Contents

1. Introduction .............................................................................................................................. 1
2. Scope and purpose .................................................................................................................... 1
3. Definitions ................................................................................................................................. 1
4. Hydrogen Production by Steam Methane Reformers .............................................................. 1
   4.1. The Steam Methane Reforming Process ............................................................................. 1
   4.2. Steam Methane Reforming Process: Environmental Advantages & Impacts ............... 2
5. Existing Best Available Techniques ...................................................................................... 3
   5.1. Low Excess Air ................................................................................................................. 3
   5.2. Energy Efficiency Management System Techniques ....................................................... 3
6. Additional BATs to Address Emissions to Air .......................................................................... 4
   6.1. Low NOx Burners ............................................................................................................. 4
   6.2. Utilisation of Sulphur Free Tail Gas ................................................................................. 5
   6.3. O2 and/or CO Monitoring ................................................................................................. 5
   6.4. Integrated Monitoring Scheme Rationalization ................................................................. 6
7. Generalized Noise Abatement Methodology ........................................................................... 7
8. Energy Efficiency ...................................................................................................................... 7
   8.1. Minimal Steam/Carbon Ratio & Associated Measurement ............................................... 7
   8.2. Air Preheat ........................................................................................................................ 8
9. Emissions to Water ................................................................................................................... 9
   9.2. Boiler Blowdown ............................................................................................................. 10
   9.3. Cooling Water Blowdown ............................................................................................... 10
10. Other Waste Aspects ............................................................................................................. 11
   10.1. Solid Wastes .................................................................................................................. 12
11. Environmental Management Systems ................................................................................... 13
12. References ............................................................................................................................... 14
1. Introduction

This EIGA publication provides guidance to EIGA members specifically to site managers, technical managers, and company environmental specialists on some best available techniques for hydrogen production by steam methane reforming. It represents the EIGA contribution to the Refineries BREF[1] being organized by the European IPPC[2] Bureau.

2. Scope and purpose

This document covers guidance on compliance with EC Directive 2008/1/EC Integrated Pollution Prevention & Control and associated BREFs. The main objective are

- To propose techniques deemed as “best & available” for Hydrogen production in refineries.
- To document data to support conclusions on Best Available Techniques.
- To encourage consistency with associated BREFs about Hydrogen production

3. Definitions

Steam Methane Reforming: steam methane reforming refers to the entire process in Figure 1. This name is commonly retained even when other feedstocks (e.g. naphtha) are used. Meanwhile, the steam methane reformer refers only to the fired chemical reactor in which Reaction 1-3 takes place.

4. Hydrogen Production by Steam Methane Reformers

The production of hydrogen in a refinery context is available through a number of processes[3]:

- Hydrogen recovery from refinery fuel gas or chemical plant off-gases by pressure swing adsorption (PSA) or membrane.
- Steam reforming of methane and other hydrocarbon feedstocks.
- Gasification/Partial Oxidation of heavier hydrocarbons.

While each of these provides their relative cost, capacity, and environmental advantages, this document seeks to focus solely on the steam methane reforming process. Specifically, it discusses its relative environmental impacts and advantages as a process choice and then describes some of the best available techniques that may be used to improve its environmental performance.

4.1. The Steam Methane Reforming Process

The steam methane reforming process can be used industrially to produce hydrogen, carbon monoxide and their mixtures. Depending on the quantities of the desired products, the elements of the process can be adapted. In its simplest form, the steam methane reforming process for pure hydrogen production consists of four stages as shown in Figure 1: a desulphurization unit, a steam methane reformer, shift reactor(s), and finally pressure swing adsorption[4].

![Figure 1. Hydrogen Production by Steam Methane Reforming](image_url)

The process uses a light hydrocarbon feedstock such as natural gas or naphtha. As a first step, this feedstock is desulphurized because the catalysts used in the steam methane reformer and the shift reactor are extremely vulnerable to sulphur poisoning. Next, the steam methane reformer provides the principle step of the process:
\[ C_nH_{m+n} + nH_2O \rightarrow nCO + (n+\frac{m}{2})H_2 \quad \Delta H < 0 \] (1)

\[ CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H = -206kJ/mol \text{ at } 15^\circ C \] (2)

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = +41.2kJ/mol \text{ at } 15^\circ C \] (3)

These equations apply for either methane or heavier feed stocks respectively[5]. These reactions are achieved by passing the steam/feedstock mixture through the reformer tubes filled with a (usually nickel-based) catalyst. Because the first two reactions dominate, the reaction overall is highly endothermic and high syngas outlet temperatures in the range of 750-1000°C are favoured. The heat necessary to compensate for the overall endothermic reaction is radiated to the reformer tubes by burners that may be mounted on the top, side or bottom walls of the reformer box. The burners may use as a fuel a combination of the feedstock, refinery fuel gas, and PSA tail gas. In the third step, the process increases the hydrogen product by shifting the H\(_2\)/CO product gas according to Reaction 3. This time, the reaction occurs at a lower temperature in the range of 200-450°C in the presence of a catalyst (e.g. iron-chromium, copper alloys) [4]. The last step separates the hydrogen from the product stream by pressure swing adsorption. The remaining PSA tail gas contains primarily CO, CO\(_2\), H\(_2\), and CH\(_4\) is usually fed to the reformer’s burners[4].

4.2. Steam Methane Reforming Process: Environmental Advantages & Impacts

When it is as exclusively or primarily as a hydrogen production process, the choice of steam methane reforming comes with a number of associated environmental advantages and impacts relative to other processes. A more comprehensive treatment of the environmental impact of steam methane reforming and other hydrogen production techniques is found in EIGA document 122[6]. First, the process generates few wastes, chemical storage, or liquid effluents. None of these are particularly hazardous[7]. The presence of a centralized waste water treatment facility on the refinery site further limits the impact on the aquatic environment. Sections 9 and 10 describe good practice to limit these environmental aspects while Section 11 introduces elements of an appropriate environmental management system.

Steam methane reforming is also advantageous from a product yield and energy consumption point of view. Figure 2 shows the product yield ranges for four industrial processes in terms of the ratio of hydrogen to carbon monoxide.

![Figure 2. H2/CO Ratio for Four Industrial Processes][8]
Depending on the chosen feedstock (and the chosen operating conditions), steam methane reforming typically yields 3 to 4 moles of hydrogen for every mole of feed stock[4], and so is advantageous when hydrogen production needs to be maximized.

These values, however, do not consider the potential reduction of air emissions that can be obtained from co-production synergies[9]. All of the processes in Figure 2 can be used within a refinery to export steam as a valuable product; thereby eliminating the need for dedicated steam production elsewhere. This translates directly into energy and CO₂ emissions savings. Furthermore, if there are other chemical facilities nearby, there may be demand for carbon monoxide which can be productively used instead of being emitted as CO₂. Steam methane reforming can benefit from these opportunities and also reduces the potential for CO₂ emissions with its requirement for lighter feed stocks. Steam methane reforming of natural gas typically has the smallest carbon-footprint of all hydrogen production processes[6]. Nevertheless, in the absence of co-production synergies, Reactions 2 and 3 show that by mass balance the process is limited to emit at least one mole of CO₂ for every four moles of hydrogen produced. The quantity of emitted CO₂ can be easily calculated from the quantity of feed & fuel consumed.

The remaining air emissions can be addressed individually. The use of light hydrocarbon feed stocks, and natural gas in particular, reduces in the potential for carbon monoxide, particulates and SOₓ emissions. SOₓ emissions are particularly reduced due to the necessary presence of the desulphurizer[7]. Finally, the process’ need for highly elevated temperatures increases the potential for NOₓ emissions[10]. This aspect is particularly affected by energy efficiency measures that often raise reformer temperatures further. However, this aspect is partially abated with the recirculation of CO₂-rich PSA tail gases which reduce flame temperatures in the reformer. Additional measures are described in the following section.

5. Existing Best Available Techniques

5.1. Low Excess Air

One existing best available technique for the abatement of NOₓ emissions is use a relatively small quantity of excess air. Steam methane reforming typically requires 5-10% excess air with the minimum value being limited by safety considerations. Further details on this technique can be found in the Large Combustion Plant BREF[11].

5.2. Energy Efficiency Management System Techniques

Description

Hydrogen plants should take advantage of co-production synergies wherever technically and economically feasible. This would lead to integration into energy management systems of nearby sites. Available energy sources (refinery gas, steam, heat, power, etc.) from nearby sites can also be used and exported back so as to be integrated in facility operations.

An efficiency evaluation at the plant design stage should be used to identify these issues and input into the design process, referring to the range of energy efficiency techniques are described in Refinery BREF (Section 4.10.1.3 Heat integration/recovery and Section 4.10.1.4 Steam management)[1]. The main techniques are optimised waste heat recovery to minimise fuel consumption, and integration into the energy system of the refinery or nearby site. In addition, energy efficiency can be improved by either optimising the conversion of the feed and/or the combustion efficiency.

Plant control and the maintenance system should be designed to ensure that energy is used as efficiently as possible, with the constraints of the safe and reliable operation of the plant and the design energy import and export requirements. Further guidelines on energy management system techniques can be found in the energy efficiency BREF[12].

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[1] Assuming that both direct and indirect emissions are counted, and that the energy mix of electricity production of the EU is used.
Achieved environmental benefits
These measures optimise the energy efficiency of the overall facility and its associated hydrogen plant, therefore minimising the external effects such as CO₂ emissions.

6. Additional BATs to Address Emissions to Air

6.1. Low NOₓ Burners

Description
Low-NOₓ burners are used to burn PSA tail gas and other gaseous fuels. This technology in steam reformers (SMR) for hydrogen production is considered to be a BAT. Air staging, fuel staging and flue gas recirculation as described in the Large Combustion Plants BREF[11] are not as such applicable for the furnace design of SMRs but are applied in the low-NOₓ burner design. For further information on low-NOₓ burner types see Chapter 4.10.4.1 of Refineries BREF[1]. Further SMR specific aspects to be considered for burner type selection are described in the section on operational data below.

Achieved Environmental Benefits
The use of low-NOₓ burners as a process-integrated measure provides a significant reduction of NOₓ emissions compared with conventional burner designs based upon the same fuel.

Cross-Media Effects
No negatives. The application of gaseous fuel also minimise SO₂ emissions.

Operational Data
In order to provide stable operation of the SMR, low NOₓ burners design has to be selected carefully with regard to operating conditions required for the specific cases. Applicable low-NOₓ burner type and achievable emission levels depend on the specific situation. The following constraints have to be considered:
- SMR reaction requires high temperatures (around 750-1000 °C)
- specific fire box geometry (long heated tubes, rectangular box etc.)
- turndown rate
- feed composition flexibility
- extend of air preheating
- even air/fuel mixing to prevent CO and unburned hydrocarbon emissions
- composition range of available supplementary fuel gas

Due to these aspects NOₓ emission levels achievable in a SMR are higher than those of boilers and other fired heaters.

Typical NOₓ emission values (calculated as NO₂ in dry flue gas with 3 vol-% O₂) when the fuel does not include significant N₂ content:
- i) without air preheat: 100 to 140 mg/Nm³ (50-70ppmv).
- ii) with air preheating: up to 200 mg/Nm³ (100ppmv).

The application of low-NOₓ burners does not cause additional energy or other utility consumption.

Applicability
Low-NOₓ burners are most suitable for gas-fired-based SMRs. Application is straightforward for new installations. Applicability of retrofitting of low-NOₓ burners for existing installations requires detailed evaluation with regard to existing fire box geometry and required operating conditions. Reference is made to Chapter 4.10.4.1 of Refineries BREF[1].

Economics
The investment cost of low NOₓ burners is typically in the range of 105 to 150% of that of conventional gas fuel burners.

Driving Force for Implementation
Reduction of NOₓ emissions.
Example Plants
There are many examples of SMRs using PSA tail gas in combination with Low-NOx-burners.

Reference Literature
Large Combustion Plant BREF[11]

6.2. Utilisation of Sulphur Free Tail Gas

Description
The steam methane reforming process requires the desulphurization of the feed so as to prevent catalyst poisoning. As a result, the tail gas from the PSA is free of sulphur. As it forms up to 90% of the fuel, SOx emissions are correspondingly reduced. They depend on the sulphur content of the supplementary fuel.

Achieved environmental benefits
Hydrogen SMRs have minimal SOx emissions.
Minimisation of use and disposal of desulphurisation catalyst

Cross Media effects
Utilisation of tail gas with its hydrogen content has the effect of increasing NOx formation

6.3. O2 and/or CO Monitoring

Description
The monitoring of oxygen and/or carbon monoxide content in the steam methane reformer's flue gas can be use to limit the emission of carbon monoxide and unburned hydrocarbons. This is achieved when the appropriate fuel/air ratio is maintained. The fuel gas quantity is fixed by the required duty in the reformer. The combustion is typically controlled to get 2% excess O$_2$ in the flue gas corresponding to approximately 10% excess air flow. So by monitoring the excess O$_2$ content in the flue gas complete combustion is maintained. As incomplete combustion results in an increased CO content in the flue gas, also monitoring the CO concentration in the flue gas can be applied for combustion control. In the event that the plant has natural draft air, the operator manually adapts the quantity of excess air.

Achieved Environmental Benefits
The monitoring of oxygen and/or carbon monoxide content in the steam methane reformer's flue gas can be use to control combustion efficiency and thus limit the emission of carbon monoxide and unburned hydrocarbons.

Cross-Media Effects
None.

Operational Data
To ensure good combustion efficiency, approximately 10% excess air is used to maintain approximately 2% excess oxygen in the flue gas.

Applicability
Many new and existing plants in Europe use this technique.

Economics
None available.

Driving Force for Implementation
Continuous oxygen monitoring is common industrial practice to control the combustion efficiency.
6.4. Integrated Monitoring Scheme Rationalization

Description
Installation of adequate sample ports in the flue gas stack of gas-fired methane based steam reformers (SMR) for hydrogen production is considered to be BAT with regard to emission monitoring.

As the SMR operation is a very stable process and due to the low sulphur gas firing only NOₓ and CO has to be considered as relevant emission components. Occasional measurements for compliance verification is recommended for SMR's not subject to Directive 2001/80/EC[13] on the limitation of emissions of certain pollutants into the air from large combustion plants.

EN 15259[14] regulates detailed design aspects for the installation of sample ports and measurement planning. Main aspects are sufficient number of sample ports, adequate sample port location and accessibility. With respect to accessibility also mobile scaffolding may be considered with regard to the low measurement frequency required.

Achieved Environmental Benefits
The possibility of direct measurement for verification of compliance with emission limit values or for other reasons, e.g. periodic environmental reporting.

Cross-Media Effects
None.

Operational Data
For gaseous fuel firing facilities, relevant emission components to be considered for design of sampling ports are NOₓ and CO. Also O₂ measurement (for calculation of emissions to reference conditions) shall be considered.

In the event that flue gas flow monitoring is required, it is preferable to calculate the flue gas flow on the basis of the fuel flow measurement and its heating value.

The PSA tail gas usually applied as fuel gas is sulphur free and also other supplementary gaseous fuels applied are usually of low sulphur type, thus measurement of SOₓ normally need not to be considered. Due to clean gas firing and related low dust emissions also specific precautions for sample ports regarding particulate measurement (isokinetic sampling) normally need not to be considered.

Applicability
Application is possible for new installations.
Applicability for existing installations requires case specific evaluation with regard to existing duct geometry.

The SMR process is very stable. Therefore, following the methodology provided in the monitoring BREF, occasional measurements (e.g. once every 3 to 5 years) can be regarded sufficient.

Economics
Investment costs for sample ports:
- approx. 1000€ per required sample nozzle
- approx. 20000€ for platform with access ladder (very much depending on detailed size and equipment arrangement.

The cost of analysis may be significant depending on the required frequency and local authorities’ requirements.

Driving Force for Implementation
Ensure possibility of direct measurement for verification of compliance with emission limit values or for other reasons, e.g. periodic environmental reporting.

Example Plants
There are many examples of SMRs using occasional direct emission measurements for compliance verification.
7. Generalized Noise Abatement Methodology

Description
A noise evaluation for the plant should be considered at the design stage. A methodology (e.g. IPPC Noise guidance note H3 parts 1[16] and 2[17] Sept 2002- Environment Agency, Attachment of the German TA-Lärm issued August 26th 1998[18]) could be used to evaluate the potential for noise impact on local receptors on and off site.

The Refineries BREF[1] refers to the ‘bubble concept’, where total noise contributions for the whole site are evaluated to establish the most economically efficient ways of reducing noise to minimise nuisance. Where necessary and practical the noise impacts of the hydrogen SMRs should be integrated into this assessment, for example depending on the location of the SMR relative to the main site.

Continuous contributors to the noise profile of hydrogen plants when in operation include process equipment such as compressors, the PSA unit, the steam methane reformer, & cooling towers. Non-continuous sources include start up and shut down noise, alarm testing and venting/gas flaring.

There are a number of well established techniques that should be evaluated to reduce the potential for noise nuisance from these sources. Reference should be made to EIGA document 85 Noise Management[19] for a suitable list of techniques for consideration.

Achieved environmental benefits
Minimisation of the nuisance potential

8. Energy Efficiency

8.1. Minimal Steam/Carbon Ratio & Associated Measurement

Description
One essential design technique for improving the global thermal balance is the minimization of the molar ratio of steam to hydrocarbon feedstock (S/C) entering the reformer. As described in Section 4.1, steam reacts with hydrocarbons to produce hydrogen. However, not all of the steam is depleted as Reactions 2&3 defines the composition of the wet reformed gas. If the steam flow is higher than optimal, as defined by the products ratio, the unreacted portion will effectively be heated up only to be cooled again with the steam methane reformer. As a result, too high of S/C reduces the thermal efficiency of the plant. Too low S/C ratio increases the quantity of un-reacted methane; thus reducing the hydrogen output and increasing the risk of carbon deposition[20]. In order to compensate, the reformer outlet temperature is raised[21]. In operation, the S/C ratio is maintained by continual measurement of the steam and hydrocarbon flow variables.

The optimum operating range is mainly defined by the H₂/CO ratio of the product gas and the customer requirements for co-production (e.g. steam export). For example, in cases where exported steam is considered a valuable product, a reduction of the S/C ratio allows the system to use less steam and produce very efficiently a larger quantity of export steam, thus improving the thermal efficiency.

Achieved Environmental Benefits
The limitation of the S/C ratio maximum operating range results in an improved thermal efficiency by reducing the consumption of fuel (firing heat), cooling water (amount of low temperature heat) and electricity (fans power). While a number of references provide indicative numerical results[21], the relative and absolute values depend strongly on the parameters above.
Cross-Media Effects
The optimum adjustment of the S/C ratio in combination with the reformer outlet temperature has an effect on NO\textsubscript{x} formation. The concentration of some by-products (e.g. methanol, acetic acid) will increase.

Operational Data
A molar S/C value of three is typical for an \( \text{H}_2 \) plant with both an SMR and shift reactor. While lower values are feasible, they are highly context dependent as described in the applicability section below\[22\].

Applicability
The S/C ratio can not be reduced indefinitely to a stoichiometric level due risks within both SMR and the shift reactor. In the shift reactor, there is the risk of producing various types of by-products, e.g. alkanes and alcohols. This tendency depends on the chosen catalyst\[23\]. In the SMR, there is the risk of carbon deposition (coking) by the three equations below\[5\]:

\[
\begin{align*}
2\text{CO} & \leftrightarrow \text{C} + \text{CO}_2 & \Delta H = 172 \text{kJ/mol} \quad (4) \\
\text{CH}_4 & \leftrightarrow \text{C} + 2\text{H}_2 & \Delta H = -75 \text{kJ/mol} \quad (5) \\
\text{C}_n\text{H}_m & \leftrightarrow n\text{C} + \frac{m}{2}\text{H}_2 & \quad (6)
\end{align*}
\]

Such carbon deposition leads to breakdown of the catalyst, further carbon deposits, blockage of the tubes and the development of “hot spots”\[5\]. To prevent such a scenario, the S/C ratio must be maintained sufficiently high. At a given temperature, the risk of carbon deposition is greater for heavier hydrocarbon feedstock and so the critical S/C ratio is higher in this case\[5\]. The maximum reformer outlet temperature is limited by mechanical constraints of the reformer tube at high temperature. The S/C ratio and reformer outlet temperature must be controlled to ensure safe and reliable operation.

Economics
For a given quantity of \( \text{H}_2 \) product, reducing the S/C ratio reduces both operating and investment costs. While case studies have been reported, the relative and absolute cost improvements depend on production capacity, and the valuation of co-products (e.g. steam) amongst other variables\[21\].

Driving Force for Implementation
The minimal S/C is a point of continual technological improvement because it results in some case in product and cost efficiencies. However, on a plant-by-plant basis the S/C must be optimized depending on the required \( \text{H}_2/\text{CO} \) ratio and steam valuation.

Example Plants
Many plants in Europe use this technique, although the final S/C ratio depends on all the factors mentioned above.

8.2. Air Preheat

Description
The application of air preheating in steam methane reformers (SMR) with forced air draft for hydrogen production as described as a BAT option for increasing furnace efficiency in Chapter 4.10.3.1 of the Refinery BREF\[1\] needs to be evaluated carefully with regard to the resulting increased NO\textsubscript{x} production.

Usually steam is produced in the waste heat recovery unit (WHRU) of an SMR which contributes to the total steam production for the refinery or nearby site and increases also significantly the energy efficiency of the SMR furnace. Thus, air preheating may be replaced by optimised steam production in the WHRU as adequate alternative, when the steam production is required anyhow at a specific site.

Achieved Environmental Benefits
Increasing energy efficiency and thus reducing green house gas emissions (overall balance)
Cross-Media Effects
Increased combustion air temperatures increase NOx emissions from the combustion. Optimised steam production and export to refinery consumers have to be evaluated carefully as adequate alternative without increased NOx emissions. Reference is also made to the large combustion plant BREF Chapter 7.4.2[11] and the energy efficiency BREF Chapter 3.1.1[12].

Operational Data
Achievable overall energy efficiency and thus reduction of greenhouse gas emissions is depending on the specific project situation.

Positive effect of air preheating on CO2 emissions has to be balanced against the negative effect on NOx emissions. Reference is made to Chapter 3.1.1.1 of the energy efficiency BREF[12].

Waste heat recovery by optimised steam production shall also be considered as adequate alternative, if steam production is required.

Applicability
Application is possible for new installations. Applicability of installation of air preheating for existing installations requires detailed case specific evaluation with regard to existing flue gas duct geometry and required operating conditions. Reference is made to the energy efficiency BREF Chapter 3.1.1.1[12]. This technique is not applicable for natural draft reformers.

Economics
Investment as well as operational costs and potential savings for air preheating as well as for optimised steam production depend on the specific project situation and have to be evaluated carefully.

Driving Force for Implementation
Increasing energy efficiency and thus reducing greenhouse gas emissions

Example Plants
There are many examples of installed SMRs including air preheating.

Reference Literature
Energy efficiency BREF [12]
Large combustion plant BREF[11]

9. Emissions to Water

While hydrogen production by steam methane reforming does generate a number of liquid effluent streams, they are not sufficiently unique from many other industrial processes to warrant process-specific abatement techniques[6, 7]. Instead, a waste water management strategy can be used to prevent and control the impurities in the different waste water streams. This section describes such a strategy before highlighting specific issues related to the blowdowns from the boiler and the cooling tower.


As stated previously, facilities that produce hydrogen by steam methane reforming do not generate any particularly unconventional waste water streams. Additionally, these facilities generally exist to serve other industrial facilities (e.g. refineries) with liquid effluents that are more challenging to treat. Therefore, a Centralized Waste Water Treatment (CWWT) plant often is part of such industrial facilities in order to meet applicable environmental standards. In such a scenario, the most environmentally effective and financially most available solution is to divert the liquid effluents from the hydrogen production facility to the CWWT plant for final treatment.

Such action, however, does not absolve the hydrogen production facility from action on-site. Instead, prevention techniques should be used to minimize the load on the CWWT plant. An effective strategy begins during the design stages and can be completed in three parts:
1. **Stream Identification** – The prevention of waste water stream contamination begins with the identification of all water streams entering and leaving the facility. These streams enter the facility with varying levels of contamination, and then accumulate different quantities of contaminants throughout the facility. Addressing these streams collectively requires an understanding of the source and level of contamination for each stream.

2. **Stream Segregation & Collection** – These streams must be maintained separate so as to prevent the needless contamination of otherwise unpolluted streams. In such a way, each stream can be addressed individually in terms of the appropriate collection technique.

3. **Minimization of Stream Flow & Contamination** – Once each stream has been identified, segregated, and routed to the appropriate destination, attention can be given to reduce the flow and level of contamination in each stream. Such efforts usually require evaluation of possibilities for process alterations with the aim of avoiding or recycling waste water flows or the minimisation of flow and contamination level. Also, monitoring the level of contamination in each stream and reducing the causes for its elevation within the constraints of the process may be considered.


Given this strategy, for an SMR-based hydrogen production unit, the following types of liquid effluent streams may have to be considered[6]:
- Demineralized water production unit effluents (if within system boundary)
- Boiler blowdown & other process condensates
- Cooling water blowdown
- Process condensates from synthesis gas cooling
- Rain/Surface water
- Domestic water
- Oily water from base plates of pumps and machinery

Additional liquid effluents may have to be considered for other process plant constellations, e.g. application of liquid feed or co-generation of carbon monoxide.

9.2. **Boiler Blowdown**

Boiler blowdown is the generally used method to divert to soluble contaminants accumulated in the boiler water to avoid scaling and corrosion. As in other industrial plants, it presents a significant effluent stream in an SMR facility[25]. Corrosion is one of the main causes for compromised boiler reliability and safety while scale significantly inhibits boiler heat transfer rates; thus reducing energy efficiency. As with boilers in other industrial plants, these risks are alleviated by altering the boiler chemistry with chemical additives. Corrosion is prevented when various chemicals (e.g. tri-sodium phosphate Na₃PO₄, ammonia) are used to raise the boiler water pH to a well-defined alkaline range. These additives also prevent calcium-based scale. The relative high pH value also serves to prevent magnesium-based scale because magnesium hydroxide precipitates as well. In addition to such a treatment program, polymers and chelants may be added for improved corrosion and scale prevention. Well-known industrial guidelines for the quantities of these additives have been provided[25-28].

Process condensates from the dearator stream will also appear in the boiler blowdown. Their volume is low and contains similar contaminants to the rest of boiler blowdown. In addition, low levels of ammonia and biodegradable organics result from the reuse of the process condensates as make up water to the dearator.

Given these constraints, the environmental objective of minimizing the steam contamination translates into the task of appropriately monitoring and controlling the boiler chemistry such that these guidelines are followed. Feed water sources of higher quality would also serve to reduce the need for chemical additives. Such opportunities can be investigated upon integration with nearby industrial facilities.

9.3. **Cooling Water Blowdown**

The cooling water blowdown can be found as an effluent stream when the facility has decided to use a semi-open recirculating system. The emissions are required to balance corrosion, scale, and bio-
fouling. These objectives are further complicated by efforts to reduce water consumption. Many of the best available techniques to minimize these emissions can be found in Sections 4.4 and 4.6 of the Industrial Cooling Systems BREF[27, 29].

10. Other Waste Aspects

The impact of waste from SMR-based hydrogen production units does not warrant process-specific abatement techniques[27, 30]. Instead, the appropriate common industrial practice is described here.

Description
Due to its process and design SMRs generally have little potential for waste generation. To meet legal obligations and requirements it is necessary to define the categorization and type of waste together with the requirements for waste storage, handling, transfer and disposal (European Waste Catalog Code and Labeling[31]).

Appropriate waste management has to be applied, i.e. selecting the highest practicable option from the following waste hierarchy:

- Prevention and minimization of waste at source
- Maximum recycling and reuse of materials and energy
- Safe disposal of waste that cannot be reused or recycled in the following order of options:
  - Physical, chemical or biological treatment
  - Incineration
  - Landfill

Achieved Environmental Benefits
Waste management reduces waste quantities, and the release of pollutants into the environment.

Cross-Media Effects
None

Operational Data
To meet legal obligations and requirements it is necessary to:

- describe the waste in sufficient detail to provide enough information to enable any subsequent handlers of the waste to manage it correctly and safely
- define the categorization and type of waste (European Waste Catalog Code and Labeling[31])
- define waste quantities generated
- define the requirements for waste storage & handling
- define waste treatment, transfer and disposal

In addition to above assessment liquid spills have to be managed by application of additional measures.

Plant areas in which liquid spills could occur have to be appropriately designed to collect such spills and to prevent any soil contamination. Such appropriate design means for example:

- spill resistant ground sealing (concrete plate, paving or plastic covers) with pits accessible for regular controls (leakage inspections)
- appropriate containments and storage facilities for oil, lubricants or other liquid chemicals
- avoiding underground storage vessels or tanks (since these can not be properly controlled or inspected)

In the event of spillage of liquid waste adequate procedures and emergency plans have to be available. These should regulate how for example:

- spillage has to be contained as quickly as possible (using, for example, spill kits)
- to prevent spillage entering the drainage system (and to inform the relevant authorities immediately in such a situation)
- materials which were used to adsorb spillage are stored and disposed of correctly.

Minimization of wastes should consider the following aspects:

- applied methods of catalyst performance monitoring
- design for and adherence to extended lifetimes of each type of catalyst
- major plant overhaul frequencies
- volumes of each type of catalyst
- used waste catalyst removal methods
waste catalyst disposal/recycling methods

Applicability
All

Economics
In general, an adequate waste management system leads to overall cost savings and improved economics.

10.1. Solid Wastes

Description
The SMR generates relatively few solid wastes which can be clustered as follows[6, 32]:
- Catalysts, Absorbents, & Adsorbents:
  - Feed Hydrogenation Catalyst
  - Feed Purification Catalyst
  - Feed Purification Absorbent
  - Reforming & pre-reforming Catalyst
  - Shift Catalyst
  - PSA Adsorbents
- Technical Materials:
  - Insulation (Rockwool, Ceramic Fibre,..)
  - Refractory (reformer, WHRU)
  - Scrap metals (Piping, etc.)
  - Electrical (Motors, cable, lighting,..)
  - Instrumentation (Transmitters, modules, etc.)
  - Used equipment (e.g. reformer tubes, end-of-life equipment)
- Sludges:
  - Oil interceptor sludge
  - Cooling tower basin

Typically these wastes are generated during a plant maintenance period and strict industry standard controls are implemented to deactivate used catalysts and to minimise any uncontrolled release to the environment.

Achieved Environmental Benefits
Waste management reduces waste quantities, and the release of pollutants into the environment.

Cross-Media Effects
Depending on the waste disposal method applied, cross-media may have to be evaluated.

Operational Data
The principle of all waste management is to avoid when possible and to minimize the generation of wastes. Hence, appropriate process design and catalyst performance monitoring methods have to be applied to prolong catalyst lifetime.

Typical waste disposal/recycling methods:
- Feed Hydrogenation Catalyst: Recovery as raw material feedstock in production of Mo and Co Ferro Alloys. Care must be taken in handling these catalysts as they can be pyrophoric.
- Feed Purification Catalyst: Recovery as raw material feedstock in production of Road Aggregate or Cement
- Feed Purification Absorbent: Recovery as raw material feedstock in production of Zn Metal or Zn Chemicals.
- Reforming Catalyst: Recovery as raw material feedstock in production of Ni, Ferro Nickel or Stainless Steel.
- Shift Catalyst: Recovery as raw material feedstock in production of Ferro Alloys, Cu and Zn Metal/Cathodes. Care must be taken in handling these catalysts after use as they are pyrophoric.
- Product Purification Adsorbent: Disposal to landfill
- Product Purification Activated Carbon: Disposal to landfill
Catalysts & Others: Spent catalysts/adsorbents (material) should be disposed of immediately or stored in a manner that will not impact the environment until disposal can be arranged. It is recommended that spent material be stored in discrete containers such as drums or portable containers for each different material type. If containers are not feasible, spent material should be stored on an impermeable surface such as concrete, asphalt or plastic sheeting that is heat and chemical resistant. It is recommended that spent material be protected from rainfall to prevent the possibility of generating contaminated storm water runoff. If water flooding has been used during unloading operations, additional spill prevention and controls such as temporary dikes may be needed to contain free liquid that may be generated when the spent material is unloaded.

- Insulation Materials (Rockwool, Ceramic Fibre): Disposal to landfill
- Scrap metals (Pipework, etc.): Recovery as raw material feedstock in production of new metals
- Electrical (Motors, cable, lighting): Recovery as raw material feedstock in production of new metals
- Instrumentation (Transmitters, modules, etc.): Recovery as raw material in production of new metals when feasible.
- Batteries: Separate collection and recovery.

Applicability
All

Economics
Typical costs/savings associated with catalyst disposal/recycling are country dependent.

Driving Force for Implementation
To reduce solid waste to landfill – increasing costs & regulation

Reference Literature
Catalyst Supply & Recovery vendor literature provide generic information on appropriate handling and disposal methods.

11. Environmental Management Systems

Description
The essential elements of an environmental management system are described in many sources. A summary for the industrial gases industry is found in EIGA document 107 Guidelines on Environmental Management System[33], which provides a guide to implementation of an environmental management system according to EN ISO 14001[34] into the existing quality system according to EN ISO 9001[35].

EIGA document 122 Environmental Impact of a Hydrogen production plant[6] identifies specific important environmental aspects and impacts to be identified and managed in operation and guidelines for so doing including:

- Energy
- Noise
- Emissions to air and water
- The consumption of natural gas feed and water consumption,
- Use and management of waste catalyst material,
- Use of consumables such as lubricants, nitrogen, compressed air, other utilities, adsorbent materials,

Additional guidance is provided in EIGA document 88 Best Environmental Management Practices[27].

Achieved environmental benefits
The overall effective management of the installation minimises environmental and other impacts.
12. References


14. EUROPEAN COMMITTEE FOR STANDARDIZATION, Air quality — Measurement of stationary source emissions — Requirements for measurement sections and sites and for the measurement objective, plan and report. 2007: Brussels, Belgium


