

GHGT-11

# CO<sub>2</sub> recovery from industrial hydrogen facilities and steel production to comply with future European Emission regulations

Bernd Holling<sup>a\*</sup>, Christine Kandziora<sup>a</sup>, Roland Ritter<sup>b</sup>

<sup>a</sup>Linde AG, Clean Energy Group, Seitnerstr. 70, 82049 Pullach, Germany

<sup>b</sup>Linde-Engineering Dresden GmbH, Bodenbacher Str. 80, 01277 Dresden, Germany

---

## Abstract

Next to large fossil fuelled power plants the industrial sector will face a need to implement CO<sub>2</sub> recovery systems to comply with the European Emission Trading Scheme.

Linde has a long track in designing, manufacturing and operation of hydrogen steam reformer units and CO<sub>2</sub> capture and purification units. Cooperation with customers in the refinery, chemical and metals sector trigger the activities to develop solutions to make CO<sub>2</sub> ready for transport, storage or utilisation.

© 2013 The Authors. Published by Elsevier Ltd.

Selection and/or peer-review under responsibility of GHGT

*Keywords:* Carbon capture and storage; hydrogen plants; steel plants; CO<sub>2</sub>; gas separation; European emission trading scheme

---

## 1. Introduction

The petrochemical and the metallurgical sector of the industry have a substantial portion of the global emission of greenhouse gases. In 2008 the industrial sectors (natural gas processing, hydrogen production, ethylene oxide, biomass conversion, cement, iron and steel, refineries) account globally for about 33 % of total emissions (7 Gt CO<sub>2</sub>) [1]. About 31 % of all industrial emissions are coming from the iron and steel industry, refineries account for approximately 10 % of the industrial emissions, thereof 20% resulting from hydrogen production units [1]. In the future we expect with the economic growth prognosis an even bigger increase of these industries emissions compared to other sectors like transportation and power generation. Compared to large scale fossil fired power plants there will be only a limited number

---

\* Corresponding author. Tel.: +49-89-7446-2561; fax: +49-89-7446-2371.

E-mail address: [bernd.holling@linde.com](mailto:bernd.holling@linde.com).

of large scale single point emitters in the industry sector. An initial focus will be on sources with high CO<sub>2</sub> partial pressure. That causes activities on larger hydrogen plants at refineries, petrochemical sites and on the blast furnaces and iron production facilities in the metals sector. In the European Union the European Emission trading scheme will start in 2013 with its 3rd trading period. Large emitters of these industries are already today part of the European Union Allowances (EUA) system with its national regulations for recording and certificating. Decisions to implement carbon capture and storage for the industry in Europe will strongly be influenced by the prices for EUA.

## 2. Hydrogen production from steam- methane reformers

### 2.1. Existing steam –methane reformers

Hydrogen is a key utility for the process industry. Refinery requirements of higher value products and changes in the crude oil qualities result in growing demand of hydrogen in the present and in the future. Single train units produce up to 150 000 m<sup>3</sup>/h hydrogen and emit about 130 t/h of CO<sub>2</sub> depending on plant configuration for feedstock, fuel and products. Industrial cluster regions develop plans to bundle the emissions to develop integrated solutions [2]. Natural gas is in many cases the choice of fuel for the furnace and the feedstock for the hydrogen production. The catalytic steam-methane technology is well proven. Key process steps are the feed pretreatment, the steam reformer, the CO- shift conversion and a pressure swing adsorption unit. The steam system and the waste heat recovery unit are important elements to design and operate the unit in best economic mode, see Fig. 1.

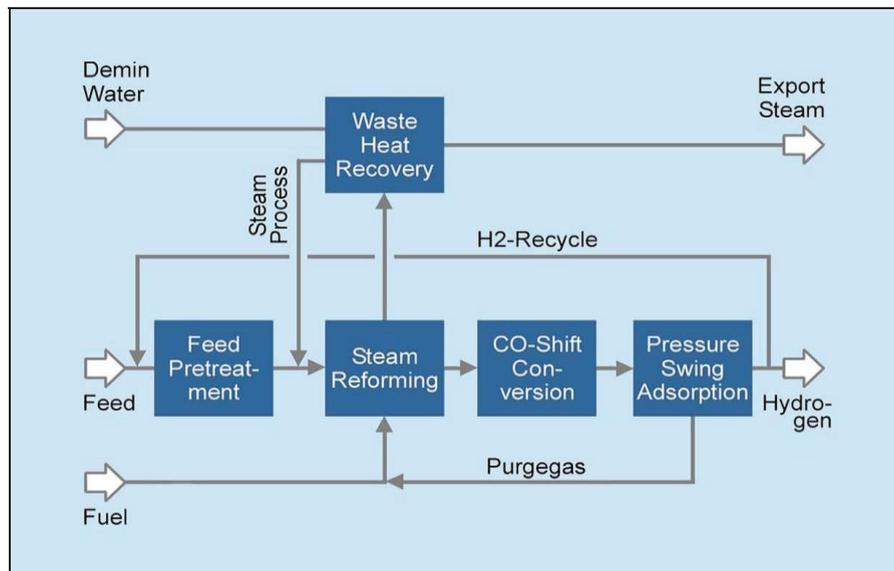


Fig. 1. Block diagram for a steam methane reformer for hydrogen production.

There are three options to capture CO<sub>2</sub> from the steam-methane reformer process (see Fig. 2)

- (1) medium pressure, low CO<sub>2</sub> content (Shifted gas)
- (2) low pressure, medium CO<sub>2</sub> content (Purge gas)
- (3) low pressure, low CO<sub>2</sub> content. (Flue gas)

The CO<sub>2</sub> content and the pressure of the syngas (1) favors absorption technologies like OASE<sup>®</sup> white /BASF as well as PSA technologies. See Fig. 3. A maximum recovery rate of 60% of the total CO<sub>2</sub> emissions is possible from the syngas. The choice for the CO<sub>2</sub> removal process will depend on the site specific costs for utilities (steam versus power).

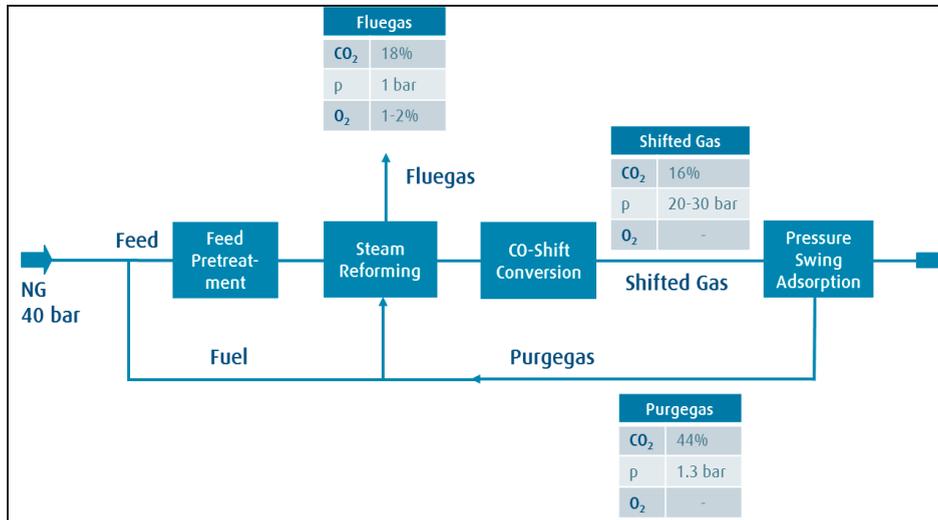


Fig. 2. Block diagram with typical process parameters for CO<sub>2</sub>.

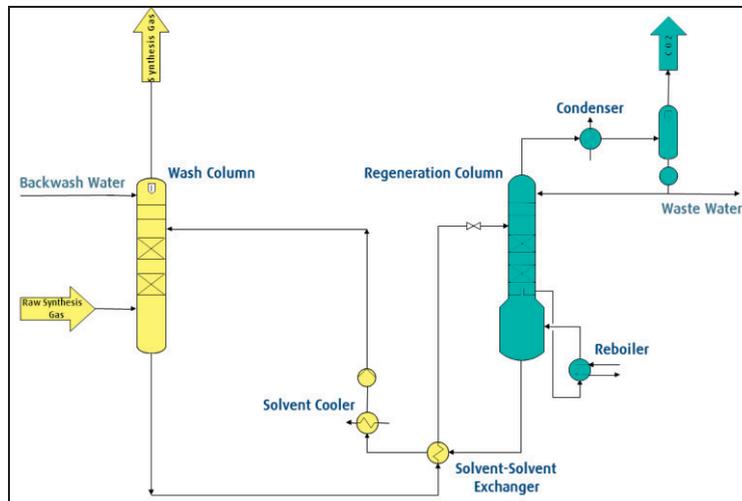


Fig. 3. Typical diagram for a CO<sub>2</sub> absorber process

From the hydrogen PSA-tailgas (2) CO<sub>2</sub> can be captured with a traditional PSA process. This has been several times applied for the production of liquid CO<sub>2</sub> for the industrial gas market. See Fig 4 and Fig 5. A maximum recovery rate of 60 % of the total CO<sub>2</sub> emissions is possible.

Due to the low pressure and low CO<sub>2</sub> content in the flue gas (3) traditional post combustion capture technology can be applied.

There are a number of post combustion capture technologies under development and in testing in laboratory and pilot plant scale. The absorber solvents have to fulfill technical, commercial and safety requirements.

Linde has cooperated with BASF and RWE to develop and test new amine based solvent systems for several years. Results of this cooperation are presented on the 10<sup>th</sup> and 11<sup>th</sup> GHGT conference [3]. The BASF OASE<sup>®</sup> blue amine system to process flue gases is ready for industrial implementation. The low pressure flue gas requires large installations for absorption and regeneration.

The captured CO<sub>2</sub> has to be dried and compressed for pipeline transport. The final moisture content of the CO<sub>2</sub>, cooling water availability and the ambient conditions will influence the selected processes for drying and compression. According to our study the specific capture costs from syngas or PSA-tailgas are lower than from flue gas.

However if transport costs are also considered the total cost for carbon capture and storage could be lower if flue gas capture is applied to the system. The reasons are lower specific transportation costs at higher CO<sub>2</sub> volumes. In a steam-methane reformer based carbon capture study the CO<sub>2</sub> capture costs were calculated in the range of 50-70 Euros per ton CO<sub>2</sub> including CO<sub>2</sub> compression.

The above described methods for CO<sub>2</sub> capture are suitable to fulfill CO<sub>2</sub> specifications for storage as well as for Enhanced Oil Recovery.

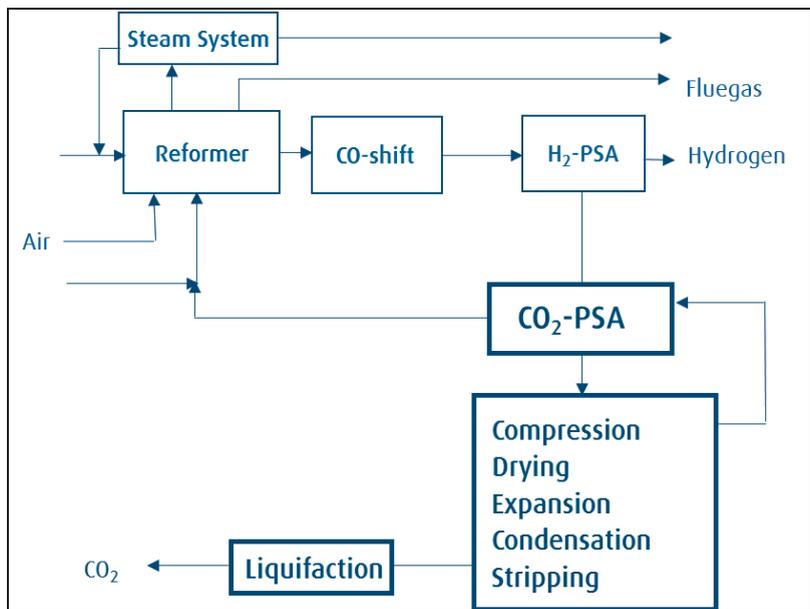


Fig. 4. CO<sub>2</sub> recovery with PSA system.



Fig. 5. CO<sub>2</sub> recovery with PSA system at a Finland refinery hydrogen plant (valve skid)

## 2.2. Alternative hydrogen production from renewable fuels (electrolysis, biomass conversion)

Fossil sources to produce hydrogen can be replaced by renewable biomass that goes into a gasification process for producing a "green syngas". Up to now these processes have to show their commercial viability. The European Union supports these innovative technologies by the actual NER 300 funding program for CCS technologies and renewable energy solutions to demonstrate. The conversion from biomass to "green fuel" is a subcategory in this actual funding. Several applicants of the EU program plan to produce green syngas that will be converted in different routes to fuels like methanol, diesel, SNG or others. Hydrogen will also be a possible product. The operation of these European demonstration projects is planned in 2015 and 2016. The recovery of the associated CO<sub>2</sub> of these renewable energy processes and its storage will be counted as a negative CO<sub>2</sub> balance element.

Electrolysers for hydrogen production are industrial proven for a long time. With the use of renewable energy as power source the hydrogen can be considered as CO<sub>2</sub>-free. Up to now the capacities of these units and the power costs for operation of the hydrogen units limit the application of the electrolysers.

### 3. CO<sub>2</sub> recovery from iron and steel

#### 3.1. General situation

The global demand for steel has tripled in the last 45 years to 1.5 bln tons per year, see Fig. 6.

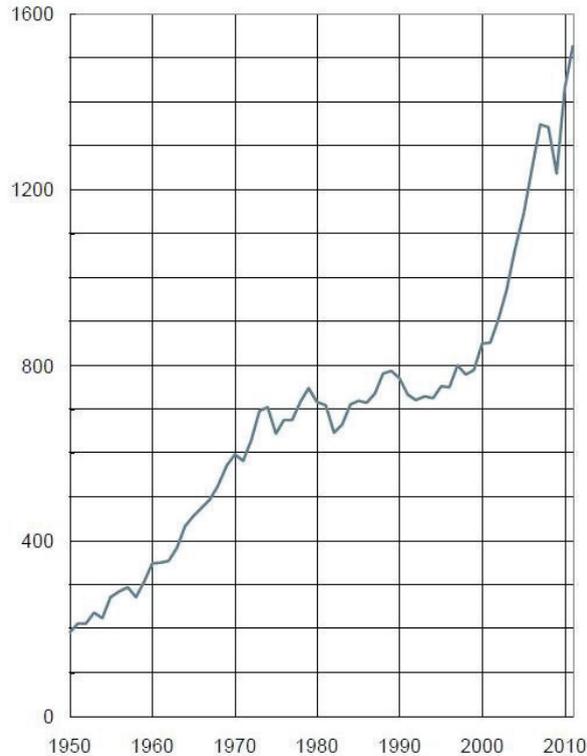


Fig. 6. World crude steel production, 1950-2011 [4]

Two third of the steel is produced on the blast furnace production route; one third comes from electric arc furnaces (EAF) [5]. The annual growth in steel production is 3-5 % per year on a global basis. On average ca. 1.7 t of CO<sub>2</sub> are produced per t of steel. Blast furnaces have a rate of roughly 2.3 t CO<sub>2</sub> per t of steel compared to electric arc furnace route where it is just 0.6 t CO<sub>2</sub> per t of steel [6]. Blast furnaces consume large amount of coke and coal, EAF use recycled steel (scrap) as feed. With attractive natural gas prices in several regions of the world direct reduced iron (DRI) processes can significantly reduce the carbon foot print of the production of steel.

The global demand for steel has resulted in many new installations of blast furnaces in the world, especially in emerging countries.

#### 3.2. Blast furnaces solutions

European steel producers have joint their forces to develop new technologies in steel making with lower carbon foot print. The ULCOS initiative has developed several technologies that are now under

more detailed investigation and testing. The Top Gas Recycling (TGR) concept is one of the advanced processes that are ready for large scale demonstration [7]. One of these projects in France is applying for funding in the European NER 300 CCS program.

The coke consumption can be reduced by advanced modified utilization of the blast furnace top gas. The blast furnace top gas shows good reduction properties and is recycled to the blast furnace. The separated CO<sub>2</sub> has to be processed for later transport and storage, the most obvious process for the CO<sub>2</sub> separation is the PSA process, see Fig. 7.

The blast furnace process will operate with oxygen instead of air. So nitrogen will not act as inert gas, which had to be processed or separated in the recycle loop.

The PSA unit to purify the recycle gas has commercial references from other iron making processes. Important is a high quality particle filtering process to avoid mechanical problems in the valves operation of the PSA. Applying oxygen and a PSA unit in the TGR process will –even without CO<sub>2</sub> storage – already lower the CO<sub>2</sub> emission of the blast furnace. A complete CCS solution requires the processing of the purge gas of the adsorption unit.

The PSA purge gas contains 75-80 % CO<sub>2</sub> that has to be concentrated to fulfill storage requirements. The purification process is very similar to the technology used for production of industrial liquid CO<sub>2</sub> that Linde owns and operates worldwide.

Another reference for a purification unit is the Linde built pilot scale Oxyfuel CCS installation next to a power plant in Germany that has been in operation for several years.

Most of the impurities are non-condensable gases and so a cryogenic separation process is applied. The recovery rate is close to 90% of the processed CO<sub>2</sub>. The total power consumption rate depends on the final compression of the CO<sub>2</sub> gas.

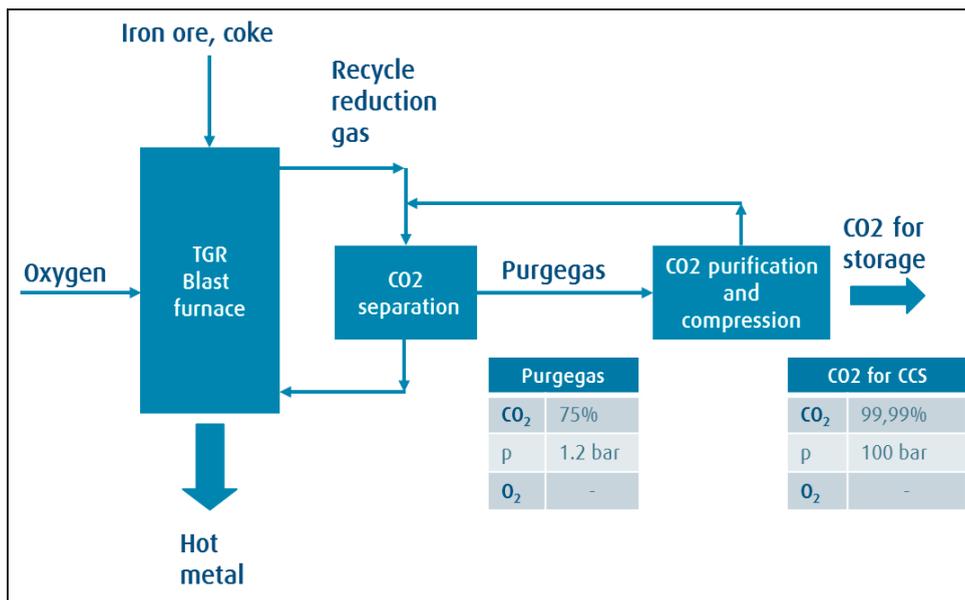


Fig. 7. Top Gas Recycling for blast furnace for carbon capture.

### 3.3. DRI process

Direct reduction processes are applicable for iron production if hydrocarbons like natural gas are available at competitive cost. In the Middle East, Russia and in Latin America several plants are in operation and more are in planning phase. A generated syngas with reduction potential goes in direct contact with the iron ore. Recirculation of the reduction gas requires a removal of the CO<sub>2</sub>. Figure 8 shows the general block diagram of the DRI process.

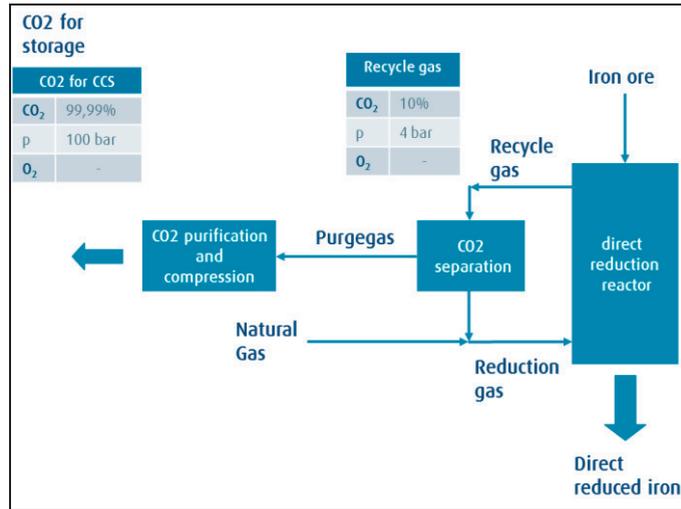


Fig. 8. DRI process with Carbon Capture Solution.

An amine process for the CO<sub>2</sub> separation is applicable. Figure 9 shows a reference in Middle East for the capture of ca. 350,000 tpy of CO<sub>2</sub> from a DRI unit of about 1.4 Mtpy of produced direct reduced iron. The OASE<sup>®</sup> white technology from BASF was selected for the capture process.



Fig. 9. CO<sub>2</sub> Absorption Unit in a DRI plant.

The separated CO<sub>2</sub> can be processed to get pure CO<sub>2</sub> for industrial applications or to bring it to a CCS solution as it is planned in Abu Dhabi's Masdar initiative [8].

The advantage of the applied DRI technology is the integration of the capture process as a core element of the iron production and the generation of a concentrated CO<sub>2</sub> stream that can be purified, dried and compressed on relative low costs.

#### 4. Purification of CO<sub>2</sub>

There are a number of separation processes that result in a CO<sub>2</sub> stream that needs further purification. One example is the oxygen driven combustion processes like in ULCOS.

An other well recognized example is the coal fired Oxyfuel CCS pilot plant in Schwarze Pumpe, Germany. It shows that multiple impurities from the feed stream and non-condensable components are removable on a stable operation. The low pressure CO<sub>2</sub> rich gas has to be compressed, pretreated to remove process sensible components like particles and moisture. The cryogenic process will partially liquefy the feed gas and by partial condensation and rectification the required purity of the CO<sub>2</sub> will be adjusted. High efficient plate fin heat exchangers support the compact design and minimize the amount of refrigeration. The cryogenic process is supported by a gas turbo-expander to deliver the refrigeration. See Fig 10.

The power consumption is dependent on the CO<sub>2</sub> content in the feed gas and the discharge pressure of the produced CO<sub>2</sub> and is usually in the range of 160-180 kWh/t of CO<sub>2</sub>.

Linde has a long experience in designing and manufacturing of CO<sub>2</sub> purification and -liquefaction plants to produce up to food grade CO<sub>2</sub>.

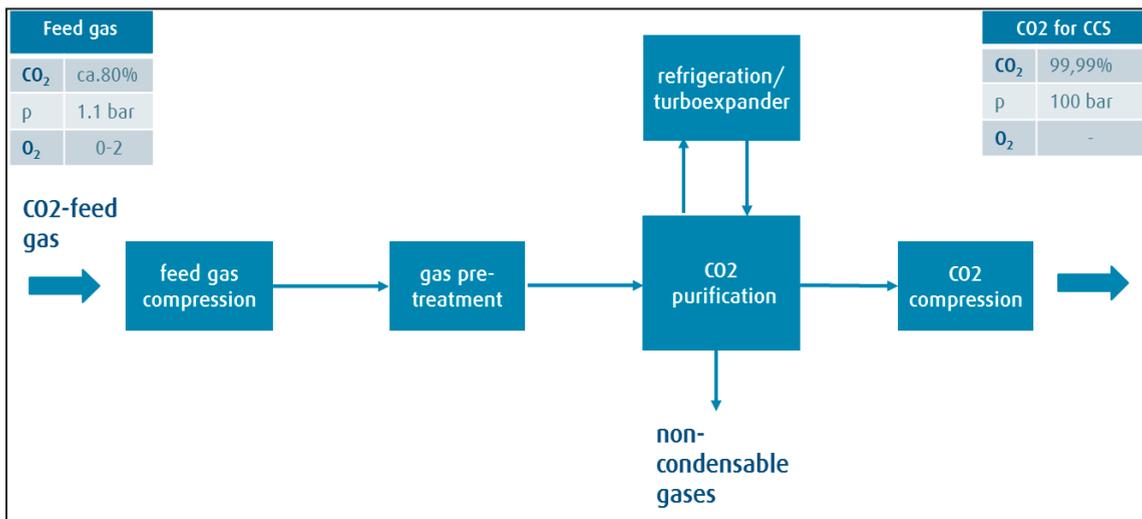


Fig. 10. CO<sub>2</sub> purification for CCS application.

## 5. Conclusions

The implementation of CCS has to start now to achieve the targets in the limitation of global warming by control of the greenhouse gas emissions. Refineries, the petrochemical and steel industry will play an important role to achieve the reduction of greenhouse gases. The processes to produce large volumes of hydrogen and steel will also in future require the utilization of carbon containing feedstocks or utilities like hydrocarbons and coke. The need to implement new technologies is a chance for engineering companies and operators to identify new business opportunities like the EOR application for the recovered CO<sub>2</sub>.

With Linde's current portfolio of steam-methane reformer technology as well as adsorptive and absorptive carbon capture technologies we can offer a wide range of solutions for refineries and the petrochemical and steel industry.

## References

- [1] ZEP technology roadmap. Carbon capture and storage in industrial applications 2011.
- [2] Rotterdam climate initiative –CO<sub>2</sub> capture and storage in Rotterdam 2011.
- [3] Moser et al., "Enhancement and long-term testing of optimized post-combustion capture technology – Results from the second phase of the testing programme at the pilot plant Niederaussem", GHGT11
- [4] E.Basson, "Sustainable steel at the core of a green economy-) World Steel Association , Rio 2012
- [5] World Steel association 2012 , World Steel in Figures
- [6] J.P. Birat, "low CO<sub>2</sub>-steel making-" at Industrial Technologies 2012" workshop, Aarhus 2012
- [7] A. Hirsch, "Top gas recycling Blast Furnace (ULCOS) , Stahl 2012 conference
- [8] Masdar Media Centre press release on 18.01.12 "Masdar and ADNOC on CCU &S "