

STRATEGIC ENERGY TECHNOLOGY PLAN

Scientific Assessment in support of the Materials Roadmap enabling Low Carbon Energy Technologies

Fossil Fuel Energies Sector, including Carbon Capture and Storage

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Preamble

This scientific assessment serves as the basis for a materials research roadmap for fossil fuel energy technology including Carbon Capture and Storage, itself an integral element of an overall "Materials Roadmap Enabling Low Carbon Technologies", a Commission Staff Working Document published in December 2011. The Materials Roadmap aims at contributing to strategic decisions on materials research funding at European and Member State levels and is aligned with the priorities of the Strategic Energy Technology Plan (SET-Plan). It is intended to serve as a guide for developing specific research and development activities in the field of materials for energy applications over the next 10 years.

This report provides an in-depth analysis of the state-of-the-art and future challenges for energy technology-related materials and the needs for research activities to support the development of fossil fuel energy technology including Carbon Capture and Storage both for the 2020 and the 2050 market horizons.

It has been produced by independent and renowned European materials scientists and energy technology experts, drawn from academia, research institutes and industry, under the coordination the SET-Plan Information System (SETIS), which is managed by the Joint Research Centre (JRC) of the European Commission. The contents were presented and discussed at a dedicated hearing in which a wide pool of stakeholders participated, including representatives of the relevant technology platforms, industry associations and the Joint Programmes of the European Energy Research Associations.

Section 1: Technology and System State of the Art and Challenges (Martin De Jong, Trevor Drage)

The development and deployment of technologies for the clean and sustainable use of fossil fuels for power generation and the industrial sector is key to achieve the aims of the SET Plan. A range of technology penetration scenarios have been developed for the deployment of SET-Plan technologies [1]. Most appropriate to this section is the potential deployment of between 6 and 80 GW of CCS technologies by 2030 based on the low or high penetration scenarios. Materials, both structural and functional are required, with future development in some cases, to achieve either of these levels of deployment, the discussion of which forms the focus of this chapter.

Fossil fuel power generation

1.1. Key structural materials

The principal state of the art fossil fuel power generation technologies are high efficiency PF Power plants (USC), Integrated Gasification Combined Cycle Power plants (IGCC) and Combined Cycle Power plants (CC).

For the present high efficiency PF power plant design, the following specification are applicable: coal-fired, achieving an efficiency of up to 55 % with steam parameters up to 700°C/720 °C at 350 bar[2]. The creep rupture should be at least 100 N/mm², over 100,000 hours of operation.

In order to reach the steam temperatures > 700°C, higher strength ferritic steels for waterwalls, and higher strength austenitic steels and nickel-based superalloys for the pressure parts are required and applied. In the steam turbine, the high-pressure/intermediate-pressure rotors, rotating blades, bolting, and inner cylinder are exposed to the highest temperatures and are or will be constructed from superalloys[3].

For the radiant and convective zones, the alloys must be resistant to sulphide and chloride attack. Depending on the boiler design, the higher strength ferretic steels can or will be protected by an overlay coating. In the case of co-firing biomass or solid recovered waste fractions, the fouling/slagging propensities are becoming more predominant factors influencing plant integrity.

The hot section of the (gas) turbine, applied in IGCC's and CC's, requires materials of construction that are able to resist oxidation, hot corrosion, creep, fatigue, and wear. The current generation of nickel- and cobalt-based superalloys are able to withstand sustained metal temperatures of up to 1100-1200°C, requiring internal cooling as well as thermal-barrier and oxidation-resistant coatings to meet today's turbine performance requirements.

1.2. Description of the main challenges for current technologies related to structural materials.

For the USC boilers the research activities in this area are mainly concentrated on nickel-based materials, since these possess a suitably high creep rupture strength potential, while the processing of the materials is also important (manufacturing of pipes and weldability). However austenitic and ferritic steels have been developed and tested up to 620-650°C. Some USC plant initiatives have been

¹ EU energy trends to 2030-Update 2009, DG- Energy [2010]

² Project information1, www.ad700.dk

³ C.A. Powell, B.D. Bryan, Materials Challenges in Advanced Coal Conversion Technologies, MRS bulletin, volume 33, april 2008

put on hold because the long term creep data turned out to be less promising than short term data suggested.

The manufacturing of large scale and thick walled castings and forgings is still challenging in terms of quality control. Also the quality control of large weldments is challenging at this moment. For all industries the advanced manufacturing and joining (cost reduction, increased performance and integrity) is challenge that will always remain. Another challenge is the development of data generation and life evaluation methods for components and design by modelling.

It is envisaged a future increased use of low-grade fuels, including both biomass and indeed low-grade fossil fuels (e.g. lignite). Fuel flexibility is often reported for future power plants and flexible fuel operation will present materials challenges, as will cyclic operation (for accommodating renewables/smart-grid operation). Fuel flexibility is better accommodated in fluidised bed systems, for example as being demonstrated at the 460 MWe Lagisza plant in Poland. There are different materials challenges to FB systems as it is mentioned in the section on chemical looping.

Structural materials will form a key requirement of any CO₂ transport network and infrastructure for CCS. The size of these transport networks dictate that low cost steel will be required for construction to keep costs of the pipeline to an economically acceptable level. In this area, regulation and control of the composition of the piped CO₂ is more of a consideration than materials development.

CO₂ Capture

1.3. Key functional materials.

The application of functional materials in the fossil energy sector is principally related to gas clean up, whether it be the removal of trace acid gases for example SO_x and NO_x using well established technologies, such as flue gas desulphurisation and selective catalytic reduction respectively, or more recent developments for materials for CCS.

The principal CCS technologies are pre, post combustion capture and oxyfuel combustion. To be successful, capture technologies need to operate with, a minimum energy penalty on power plant, with reasonable cap-ex and op-ex and plant footprint as well as to achieve capture targets and produce CO₂ in a state pure enough to meet the requirements and legislation for transport and storage. The ultimate goal is to meet the targets for efficiency and costs of electricity proposed to make CCS attractive commercially [4, 5] Whilst initially the development and deployment of CCS is focussed on the electricity generation sector, there is potential to adapt this technology to operate on gas streams from industrial processes, for example iron and steel production.

A key component of all CCS technologies is gas separation, CO₂ and N₂ in the case of post-combustion capture, CO₂ and H₂ for pre-combustion capture and O₂ from air in oxyfuel combustion. Dependent upon the type and location within a power plant, each of these gas separations will be performed under different physical and chemical conditions. The principal gas separation techniques for CCS are listed in Appendix 1. The selection of the capture technology dependent upon the state, pressure, CO₂ partial pressure and volume of gas to be separated with a wide range of materials developed depending upon the point of capture within the power plant. At present, the most mature technologies to be used in CCS demonstration plant are solvent based, with physical and chemical

⁴ J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, *Int J Greenh Gas Con*, 2008, **2**, 9-20.

⁵ Communication from the commission to the european parliament, the council, the european economic and social committee and the committee of the regions on Investing in the Development of Low Carbon Technologies (SET-Plan): A Technology Roadmap. 2009.

based solvents being the current preferred technology for pre and post combustion capture respectively. First generation oxyfuel combustion relies on more traditional cryogenic air separation technologies to provide a stream of pure O₂. Whilst solvent based technologies (pre and post CC) and cryogenic separation (oxyfuel) are the most developed for CCS application and the closest to market and deployment, the energy penalties associated with these technologies has led to research and development of a range of alternative, or second and third generation CO₂ capture technologies. Examples of which include, advanced solvents, solid adsorbents, membranes, ionic liquids, SEWGS (Sorption-Enhanced Water-Gas Shift) as well as novel combustion technologies such as chemical looping, OTM (Oxygen Transport Membranes) cycles [4]. Many of these technologies are currently at the laboratory / fundamental level of research in terms of materials and process development for CCS.

1.4. Description of current materials manufacturing processes for functional materials

Current manufacturing techniques are related to the stage of development of each of the technologies. Whilst solvent are produced at large scales by principal chemical companies. Materials for the 2nd and 3rd generation techniques are at more of an early stage of development and materials are currently only produced at a small or pilot scale. However it should be noted that many of the materials types, for examples zeolites, activated carbons, are currently produced at scale for other industrial processes. If these technologies are to be demonstrated at large scale, linking of laboratory to industrial production scale at an economically attractive cost will be required if appropriate materials and processes are developed.

1.5. Description of the main challenges for current technologies related to functional materials.

The precise performance requirements of functional materials for carbon capture are going to be specific for each technology. However, in general, for separation techniques materials are required to have a high selectivity, fast reaction kinetics to achieve separation to the required purity, at an acceptable energy penalty, whilst minimising the size of the capture or separation plant. The principal stability challenges will be ability of the material to function in the aggressive chemical environments of fuel derived gas streams, physical demands of the process, as well as to be durable and continue to perform over numerous cycles if material replacement rates are to be economic. The principal challenges of which are defined in further detail in Appendix 2.

CO₂ Storage

1.6. Description of the main challenges relating to well technologies

Wells are necessary to gain access to the reservoir, both to inject CO₂ and to characterise or monitor subsurface rocks and formation fluid properties. New wells should be designed carefully for long-term zonal isolation and instrumented according to purpose. Existing wells should be managed to avoid leakage. Such wells may include active wells which may be converted into new uses or wells which have been plugged and abandoned, possibly many years previously and to unknown standards.

Existing technologies to design, build, repair and abandon wells in oil and gas reservoirs appear to be broadly sufficient to guarantee safe, long-term CO₂ storage. There is therefore no need for a revolutionary approach for well construction, maintenance and closure in CO₂ environment, but rather for a natural evolutionary progress in the technology to improve well reliability over the life of a CO₂ injection project.

Experience from oil and gas wells – especially those that have been exposed to sour gas (CO₂ and/or H₂S) either through production or through injection to improve hydrocarbon recovery – suggests that catastrophic leaks can be avoided except in cases of gross negligence.

However, existing wells penetrating the storage reservoir (true in particular for depleted oil and gas field as opposed to deep saline formations) have to be considered as an important factor in the overall leakage risk. This is because it is difficult to estimate the long term reliability of wells given the relatively short time span of oil and gas exploration experience in the field and the knowledge gained from laboratory studies. Current lab experiments are limited in applicability since they generally consist in the immersion of cement samples in CO₂-rich fluids, which is not entirely representative of field conditions. Indeed, it is widely accepted, based on experience with oil and gas wells, that integrity is overwhelmingly lost through mechanical defects (e.g. micro fractures, debonding at interfaces), which, when connected, can create a leakage path.

Current materials technology development efforts focus on the development and deployment of corrosion-resistant materials, such as chromium steel alloys, composite materials and CO₂-resistant cement systems. Some effort is also dedicated to testing the feasibility of truly inert materials as well as materials and methodologies to repair failed completions.

1.7. Description of the main challenges related to mitigation and remediation

The EC directive on the geological storage of CO₂ establishes the obligation on the operator to take corrective measures in case of significant irregularities or leakages, on the basis of a corrective measures plan submitted to and approved by the competent national authority. The operator also has the obligation to assess the effectiveness of any corrective measures taken.

Such corrective measures mainly stem from the past efforts in the field of:

- Oil and gas industry, in particular natural gas storage activities;
- Wellbore integrity engineering,
- Pollution engineering, as CO₂ leakage plumes show, in particular, similarities to volatile organic compound vapour plumes.

At wellbores, conventional procedures to correct potential irregularities in the structure integrity remain, to some extent, well-established at an engineering level, but still require to be validated considering the specificity of long term storage of CO₂. In the geological domain, interventions practices based on reservoir and pollution engineering methods to correct significant irregularities, such as CO₂ leakage or abnormal fluid displacement, still require further developments regarding the uniqueness of CO₂ geological storage activities, whether it is in terms of time scale (from decades to centuries), or of large spatial scale impact (up to the geological basin scale), and also of the properties of the injected CO₂ stream (buoyancy effect, geochemical reactivity, presence of potential impurities). (In this context, further research efforts should be undertaken to develop materials (foam / gel / etc) that can cost effectively be used, at the injection, post- injection and post-closure phases of the storage project.

Section 2: Material Supply Status and Challenges (Marco Falzetti, Niklas Hedin)

In the recent past, several relevant initiatives on Raw Materials and Rare Elements with emphasis on the future clean energy market took place in EU [6,7,8,9], USA [10,11], and Japan. All these initiatives

⁶ Improving Framework Conditions for Extracting Minerals for the EU – EU report, European Commission, DG Enterprise – July 2010

⁷ Annex V to the Report of the Ad-hoc Working Group on defining critical raw materials – EU report, European Commission, DG Enterprise – July 2010

⁸ Commission Staff Working Document The Raw Materials – Meeting our Critical needs for Growth and Jobs in Europe - European Commission - 2008

dealt with the analysis and assessment of the technological and strategic implications of material supply that will be critical for achieving the expected goals for new technologies related to clean energy.

As far as the new or improved Clean Coal Technologies (CCT) is concerned, the major improvements are related to possibilities to develop new materials able to show improved mechanical, thermal and corrosion resistance properties, without a sustainable cost increase. Mandatory conditions for the European energy sector are future safe, affordable, and available improved materials such as HSS, austenitic steels, and nickel based alloys and others more exotic materials.

At the request of the EU Competitiveness Council, the European Commission commenced the development of an EU strategy for raw materials. In November 2008 it submitted an initiative for raw materials being necessary for meeting critical needs for growth and jobs in Europe. That initiative was based on three pillars: securing access to raw materials on world markets at undistorted conditions, fostering sustainable supplies of raw materials from European sources, and reducing the EU's consumption of primary raw

This strategy is particularly true for the energy sectors, for which the new Societal Grand Challenges ask for radically improved technologies to be developed and implemented in the medium and long-term future. Most of these technological improvements are based on the availability of enhanced or totally new and advanced materials, typically: metal alloys, polymers, and ceramics. These are compounds of elements/substances showing supply criticalities, due to market, geopolitical, and environmental implications. Interruptions to this supply can jeopardise the competitive position of companies within these industrial sectors, thereby threatening the functioning of the EU economy.

Demand for mass raw materials (so-called commodities) with a broad spectrum of uses such as iron, steel, copper, and chromium is apt to be driven more strongly by global economic growth in the future, whereas demand for high-tech metals such as gallium, neodymium, and indium will more likely be driven by technological advances. In the case of the platinum metals, tantalum, silver, titanium, and cobalt, both economic growth and technological advances will likely have a similar impact on demand.

As far as concern the materials needs for the CCT area, the distinction between structural and functional materials strongly characterise the supply strategies and problems. In the case of structural materials the problem are related to critical supply of special and some time rare metals/elements which are the base of the most advanced and future metal alloys for the production of plant components operating at high temperature and pressure in very harsh environments. Concerning the functional materials the risks are less concerned with natural resources problem, but much more to the market structure that could be critical for assuring the suitable and timing supply of future materials in the volumes and costs requested by a strong development and exploitation of CCT technologies.

2.1. Structural Materials - Metals Alloys

In the case of coal-fired power plants, components and parts made of steel or other metals alloys determine maximum efficiencies for operation by limiting the temperatures and pressures in steam sections. The use of metals alloys with high performance (steels and non ferrous) that can resist steam with high temperature and yield high efficiencies for the power plants, is the preferred way to retrofit existing coal-fired power plants and to build new supercritical plants.

⁹ Commission Staff Working Document - Analysis of the competitiveness of the non-energy extractive industry in the EU - European Commission - 2007

¹⁰ Critical Materials Strategy - USA Department of Energy – December 2010

¹¹ Trans-Atlantic Workshop on Rare Earth Elements and Other Critical Materials for a Clean Energy Future – USA and EU join initiative – December 2010 (Proceedings not yet officially published)

In a context of this technological reference, the role of metals alloys play is outstanding for CCT; and consequently the supply and market strategies related to the elements entering in such alloys become crucial elements to control. Among these elements, especially significant is: Nickel (Ni based alloys and austenitic steels), Chromium, and other elements used in small quantities but being crucial for the final mechanical, thermal and corrosive-resistance performances, such as Cobalt, Tungsten, Rhenium, Vanadium, Molybdenum, and Niobium. Information about the main criticality related to these different elements is reported in Appendix 6.

| Structural Materials# | Main producing countries# | Main EU import sources# | Import dependence# | Supply Risk factor ¹² # |
|-----------------------|---|--|--------------------|------------------------------------|
| Nickel | Russia 18%, Canada 17%, Indonesia 12% | Australia 90%, Norway 4%, Turkey 4% | 55 | 0.25 |
| Chromium | South Africa 41%, India 17%, Kazakhstan 15% | South Africa 79%, Turkey 16%, Albania 2% | 46 | 0.9 |
| Cobalt | Dem. Rep. Congo 41%, Canada 11%, Zambia 9% | Dem. Rep. Congo 71%, Russia 19%, Tanzania 5% | 100 | 1.1 |
| Tungsten | China 78%, Russia 5%, Canada 4% | Russia 76%, Bolivia 7%, Rwanda 13% | 73 | 1.8 |
| Rhenium | Chile 49%, USA 14%, Kazakhstan 14% | Taiwan, USA, Malaysia and Canada | 100 | 0.85 |
| Vanadium | China 36%, South Africa 36%, Russia 26% | South Korea 90%, Japan 7%, Venezuela 3% | 100 | 0.7 |
| Molybdenum | China 38%, USA 25%, Chile 16% | USA 47%, Chile 32%, China 10% | 100 | 0.45 |
| Niobium | Brazil 92%, Canada 7% | Brazil 84%, Canada 16% | 100 | 2.85 |

In addition to the metals included in the Table, Ruthenium is used for Ni-base SC superalloys for applications in advanced gas turbine and coatings. Ruthenium, one of the Platinum Group of Metals (PGMs), is one of the materials included in the group of critical materials for emerging technologies [¹³] There is no primary production of PGMs in the EU. The main sources for PGM for the EU are South Africa (about 60%) and the Russian Federation (over 30%). Boron is important for the optimization of martensitic steels (9-12%Cr) to be applied in steam generator plants operating at USC conditions Other metal of this group, Platinum, or some coating with platinum –metal oxides is applied in production of synthetic fuels from H₂ and CO₂.

2.2. Ceramics

¹² the "supply risk" is a factor which takes into account the political-economic stability of the producing countries, the level of concentration of production, the potential for substitution and the recycling rate. It is defined accordingly to the model proposed in *Report of the Ad-hoc Working Group on defining critical raw materials* – EU Commission, DG ENTER

¹³ Critical raw materials for the EU. Report of the Ad-hoc Working Group on defining critical raw materials. Version of 30 July 2010

Ceramic components will certainly have a role in the future developments for the vast area of CCT technologies, for both structural and functional applications. The structural use of ceramic will be mainly concentrate in specialised coatings with enhanced thermal (TBC) and corrosion resistance. Among these solutions the zirconia based ceramics, stabilised with yttrium oxide and including others element like Cerium and Lanthanum are the most promising ones. Also functional use of ceramics is foreseen: examples are supports for ceramic membranes eg for Pd H₂-separating membranes, full ceramic membranes, eg. sol gel, zeolite or mixed ion electron conductors for gas separation, and chemical looping oxygen carriers supports

From a point of view of the supply, Cerium and Lanthanum belong to the so call Rare Earth Elements (REE) that could experience serious supply problems due to the large numbers of future expected uses in many different advanced materials/sectors. Nowadays, almost all the world production is from China and European import is strongly dependent from this country. Despite the current China dominant position, REE are present in many other areas and it is expected that new extraction sites (United States, Canada, India, Australia and Malawi,) will be opened in the future following an increase of the expected China internal request.

2.3. Functional materials

•*Absorbents.* The supply of simple amines and alkanolamines are not seen as a problem, their synthesis is straightforward and scalable to very large amounts. Amines are a health threat and after reaction with SO₂ in combustion plants they are hazardous waste. Other absorbents like amine salts are less dangerous and tested in first field test. Their consequent development should be prioritized. A potential scale up problem can exist for more exotic absorbents such as ionic liquids. Supply issues may occur for ionic liquids as special care is needed for their preparation and purification [14].

•*Adsorbents.* Many type of adsorbents are available today, zeolites, activated carbons, carbon molecular sieves, mesoporous silica, aluminumphosphates, etc. No distinct supply issues for these are expected as their syntheses are established and that they consist of very common elements. For other more exotic adsorbents, e.g. metal organic frameworks with Lanthanide metal ions, titanium silicates, one could foresee potential for supply problems. Adsorbents are important for IGCC technique because of their advantage when higher CO₂ partial pressures are available.

•*Membrane materials:* Depending on the application, there are many different membrane materials for gas purification and separation. These can be ceramic, metallic, polymeric, or hybrids thereof.[15] Palladium based membranes are commercialized for hydrogen purification and could very well be important for pre combustion carbon capture. Palladium is one of the metals included in the PGMs and its production in 2006 was estimated at 267 t, whereas the demand of Palladium for emerging technologies is estimated at 77 t for 2030 [13]. Inorganic membranes in general are only used to a small extent and it is still to be seen, if such can be commercialized for post combustion carbon capture. Mixed ionic–electronic conducting (MIEC) ceramic membranes are developed for oxygen and hydrogen separation. Some promising ones have compositions containing significant amounts of Lanthanides, for which supply is already today constrained. Polymer membranes, on the other hand has been commercialized since the 80:ies for natural gas processing.[16] Similar membranes could be potentially be derived for different versions of carbon capture. Typical polymers for today’s gas

¹⁴ A. K. Burrell, R. E. Del Sesto, S.N. Baker, T. M. McCleskey, G. A. Baker, ‘The large scale synthesis of pure imidazolium and pyrrolidinium ionic liquids’, Green Chem., 9, 449-454, 2007.

¹⁵ D. Dortmund, K. Doshi, Recent developments in CO₂ removal membrane technology, UOP LLC (1999).

¹⁶ Richard W. Baker and Kaaeid Lokhandwala, Natural Gas Processing with Membranes: An Overview, Ind. Eng. Chem. Res. 2008, 47, 2109-2121

upgrading membranes are polyimide, cellulose acetate, perfluoro polymers silicone rubber, and polysulfone. The polymer industry in EU is still rather strong, however, manufacturing of polymer membranes appear to be mainly placed outside of EU, even if the mother companies are within EU.

Chemical looping combustion: In such combustion metal/ metal oxide or metal carbonate/oxide/sulphide/sulphate pairs allows fuel to be oxidized without air in the fuel reactor. We can not see any supply constrains on these particular pairs of metal/ oxides etc.

Catalysis will play an important role in many different phases of the carbon separation processes and in fuel/gas denitrification and other clean fuel manufactures such as synfuels. *Catalysis* could also play a significant role in dissolution of CO₂ in storage reservoirs and for in situ mineralisation.

This will require a relevant increase of use of materials as catalysts. Fabrication of synthetic fuel from CO₂(or/and CO obtained by the reverse water gas shift reaction) and H₂ needs catalysts to accelerate the syntheses, such as platinum. Chemical processing catalysts account for approximately 20% of the total catalyst demand in volume. It is expected to grow more than double fast than petroleum refining catalysts which represent today the largest volume market for catalysts. The market demand will increase to 214 thousand tonnes by 2012 and reach 243 thousand tonnes by 2015. Within this frame it is important to monitor the evolution and prepare a proper European industrial and market strategy to avoid possible problems of access to the high value catalysts market. The supply problems could be generated starting from 2020 due to the significant increase of green processes/applications on the way, which will be based on the use of ‘precious’ catalysts most of them based on the use of transition metals, which suffer of well know supply risks and market constraints.

Tracers: Material to track the front or the tail of the movement of the CO₂ plume may become interesting as a tool to account for the behaviour of the stored volumes.

Section 3: On-going Research and Actors in the Field of Material Research for Energy Technology Applications and Challenges (*Trevor Drage, Martin De Jong*)

3.1. On-going research in structural materials in fossil Fuel power generation

On-going research in the field of high efficiency FP power plants is already focussing on steam and metal temperatures far beyond 700 °C [17]. To temper the increase beyond 700 °C by reducing carbon capture and in the same time meeting the CO₂ emission goals set by the EU, biomass will be co-fired on a larger scale to reach the targets. Reviewing the likely process environments, and results from the early laboratory and rig trials, there are significant concerns that the materials used in existing boilers, and those being specified for future plant may not be able to deliver the reliability expected from modern power stations, principally due to the increased risks of excessive rates of fireside corrosion and steam side oxidation. One of the potential responses is to develop a new generation of protective coatings for both the fireside and steam-side of boiler tubing and pipework. As far as Oxy Combustion is concerned, the degradation rates affect severely both the metallic components and refractory parts due to the high oxygen level, aiming for demanding materials characteristic [18].

High steam and metal temperatures also require the further development of new materials systems, such as Ni-alloys and coating for long time service life beyond 700°C. Also the further development of

¹⁷ www.nextgenpower.eu

¹⁸ MACPLUS project : Component Performance-driven Solutions for Long-Term Efficiency Increase in Ultra Supercritical Power Plants

austenitic and ferritic steels is part on-going research in order to be able to use these materials at temperatures beyond 620°C. Tailored micro/nanostructures of particular materials are being used to obtain desired properties. Research is also focussed on large weldments and the manufacturing of large (full scale) components.

In the field of gas turbine applications (for IGCC and CC), the following items have been identified: fuel flexibility, by enabling the burning of back-up fuels, such as natural gas, without adversely affecting the reliability and availability. Improved materials systems with advanced coatings able to protect hot path components exposed to different temperatures and compositions of exhaust gases. Cost-effective materials and coatings technologies will be developed to overcome the component life-limiting problems of overheating and of hot corrosion resulting from the higher temperatures and residual contaminants in the syngas, including validation of materials performance data, life prediction and monitoring methods. Simulation tools for estimating performance and lifetime of materials systems will also be enhanced to suit the new operating environments [19]

While biomass co-firing in existing pulverised fuel power plants means grinding to small particles, in the bioenergy field there is lot of on-going work on producing bio-coal (i.e. torrefaction of biomass to produce a dry, easily grindable fuel) for power plants. Torrefaction is described in detail in the Bioenergy report.. The consequences of using large fractions of torrefied biomass on power plant structural materials are not yet known and research is needed on this topic.

New plants or plants under construction will be designed and built based on the latest proven materials specifications. However, except for the combined cycles, most plant concepts are designed for full load operation. The trend is already visible that with respect to the competitiveness in electricity market, one should expect that the most efficient and cleanest power plants will be the main players for power generation in the very near future. However, other electricity market driven influences may interfere, forcing the large PF power plants or IGCC's to be operated in cycling mode as well.

In European research projects, the implications of this potential trend or maybe thread on the residual lifetime of critical components may be not sufficient covered by any mechanical testing research. This magnitude of the impact of cycling operation mode should be part of future research projects.

3.2. On-going research in functional materials for carbon capture.

The following section describes in more detail the key research challenges for functional materials for CO₂ capture. Functional materials for carbon capture can be broadly separated into solvent technologies which have been developed to a large scale and are in commercial development and alternative or 2nd and 3rd generation capture technologies, which are more commonly at a small or bench scale.

3.2.1. Solvents and Advanced Solvents

Current state of the art amine solvent technology uses a range of alkanolamine solvents, and has been applied for many years in the removal of acid gases from natural gas. Research is underway to make these systems more efficient and cost effective through both solvent and process modifications and optimisation. The development of improved solvents can be considered a key development in functional materials [20], with principal aim is of developing solvents with lower parasitic power demand for the CO₂ capture compared to the benchmark solvent monoethanolamine (MEA). These aims can be achieved by developing solvents which compared to MEA have; higher capacity for CO₂,

¹⁹ www.h2-igcc.eu

²⁰ A. B. Rao, E. S. Rubin, D. W. Keith and M. G. Morgan, *Energy Policy*, 2006, **34**, 3765-3772.

lower energy for regeneration, higher adsorption / desorption rates. Another important consideration is the development of solvents that have lower volatility and improved stability in the presence of flue gas and less corrosive such that higher concentrations can be used [21]. Industrial developers (example the; Fluor Daniel Econamine FG Plus, Mitsubishi Heavy Industries) have developed their own proprietary systems and solvents which are being tested at various scales. This work has also involved the development of various anti oxidation and foaming additives for the solvents. Academic research in this field has investigated the use of a range of amines, for example secondary amines [22], sterically hindered amines [23] as well as blended solvent mixtures [24, 25]. Other solvent types have been explored for example ammonia [26], amino acid salts and other basic carbonate solutions. Solvent development has been extensively reviewed [21].

Physical solvents for pre-combustion capture are at an advanced state of development with a number of full scale demonstration plants proposed. The two leading technologies are the SelexolTM and Rectisol® process, although these have not been used for capture in electric power plants at present, because both systems are not working economical in steam power plant flue gas. They are beneficial in IGCC technology. Development of alternative physical solvents aims to increase the CO₂ capacity and reduce the heat of absorption of physical solvents. There is also a drive to develop solvents that capture CO₂ at a higher temperature and pressure than current systems, reducing the cooling requirement of current capture systems. One such material that is being explored for this application is ionic liquids.

In addition to the development of organic solvents, Ionic liquids (ILs) are a potentially attractive route to carbon capture. ILs form a liquid salt composed of usually of an organic cation paired with either an inorganic or organic anion [27]. This leads to a large diversity of potential compounds based on a range of cations and anions that can be mixed. IL properties are favourable for CO₂ capture based on their negligible volatility, high intrinsic physical solubility for CO₂ and flexibility in the chemical functionality can be added to the liquids to tune properties for specific applications. Process design is a principal challenge of IL use due to their inherent high viscosity. ILs have the potential to absorb large quantities of CO₂, potentially at high temperature [28, 29], which is advantageous for application in pre-combustion capture at high pressure. It is proposed that though the use of it is possible to achieve better performance than traditional physical solvents and aqueous amines. Development and chemical modification of ILs for different temperature and applications is described in Appendix 3. At present ILs are commercially available, however, the ones most suited to CO₂ separation have only been synthesised in small quantities at laboratory scale [30].

3.2.2. Solid Sorbents

A key motivation for the development of solid adsorbents for carbon capture is the potential energy saving shown by theoretical studies [31]. Solid adsorbents have been developed based on a range of materials for different temperatures of application.

²¹ R. M. Davidson, 2007. Post-combustion carbon capture from coal fired plants - solvent scrubbing. IEA Clean Coal Centre.

²² A. Veawab and A. Aroonwilas, *Corrosion Science*, 2002, **44**, 967-987.

²³ A. Aroonwilas and A. Veawab, *Ind Eng Chem Res*, 2004, **43**, 2228-2237.

²⁴ R. Idem, M. Wilson, P. Tontiwachwuthikul, A. Chakma, A. Veawab, A. Aroonwilas and D. Gelowitz, *Ind Eng Chem Res*, 2006, **45**, 2414-2420.

²⁵ S. Bishnoi and G. T. Rochelle, *Ind Eng Chem Res*, 2002, **41**, 604-612.

²⁶ J. T. Yeh, K. P. Resnik, K. Rygle and H. W. Pennline, *Fuel Processing Technology*, 2005, **86**, 1533-1546.

²⁷ J. H. Huang and T. Ruther, *Australian Journal of Chemistry*, 2009, **62**, 298-308.

²⁸ J. L. Anderson, J. K. Dixon and J. F. Brennecke, *Accounts of Chemical Research*, 2007, **40**, 1208-1216.

²⁹ M. J. Muldoon, S. N. V. K. Aki, J. L. Anderson, J. K. Dixon and J. F. Brennecke, *Journal of Physical Chemistry B*, 2007, **111**, 9001-9009.

³⁰ J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, *Int J Greenh Gas Con*, 2008, **2**, 9-20.

³¹ M. L. Gray, Y. Soong, K. J. Champagne, H. Pennline, J. P. Baltrus, J. R. W. Stevens, R. Khatri, S. S. C. Chuang and T. Filburn, *Fuel Processing Technology*, 2005, **86**, 1449-1455.

Based on the assumption that low temperature solid sorbents can achieve the required cyclic CO₂ capacities they have the potential to reduce the energy penalty of capture by 30-50% compared with amine solvent systems [32]. This potential energy saving is based on avoiding the need for large quantities of water present in solvent systems. Overall, to achieve these potential savings solid sorbent materials need to be developed that can achieve high adsorption capacities, fast reaction rates and stability in flue gas environments [33, 34] and also the ability to withstand the physical challenges associated with the capture process, for example temperature swing and attrition. A wide range of materials have been developed for this application, for example supported amines [35,36,37,38,39], activated carbons [40,41,42,43], hydrotalcites [44] zeolites [45], and more recently MOFs (Metallic Organic Framework) [46], all of which have] been extensively reviewed [47]. Low temperature solid sorbents can also be applied to CO₂ capture pre-combustion capture. This requires materials that, similarly to solvents involve physisorption. A range of materials are being explored for this application, for example activated carbons, zeolites, MOFs, with high surface area and pore volume would be suitable. Solid sorbents have the advantage of being able to capture CO₂ at higher temperature than current state of the art physical solvents and could potentially reduce syngas cooling requirements. Whilst solid adsorbents have been used extensively in industry for PSA gas purification, their application into CCS is a new [48]. Amine salts are developed from RWE and in a field test in the Power Plant Staudinger near Frankfurt. The next field test will start in Canada.

A number of materials have been tested for high temperature capture of CO₂, at approximately 250 – 600 °C, which have an application in both pre and post-combustion capture applications. Calcium oxide (CaO) sorbents commonly derived from limestone can be repeatedly cycled between two vessels resulting in carbonation reaction with CO₂ in the flue gas, followed by calcination where CaO is reformed. The main materials challenges associated with high temperature sorbents are the sintering of the sorbent and interaction with other flue gas species resulting in a loss of capacity [49]. As a result a number of modified CaO adsorbents and other ceramic type materials is being developed (appendix 4). This process will produce thousands of tons CaCO₃. Transport and storage cost and energy for transport should be carefully evaluated.

³² M. L. Gray, K. J. Champagne, D. Fauth, J. P. Baltrus and H. Pennline, *Int J Greenh Gas Con*, 2008, **2**, 3-8

³³ S. Sjoström and H. Krutka, *Fuel*, 2010, **89**, 1298-1306.

³⁴ A. R. Millward and O. M. Yaghi, *J Am Chem Soc*, 2005, **127**, 17998-17999.

³⁵ T. J. Tarka, J. P. Ciferno and D. J. Fauth, *Abstr Pap Am Chem S*, 2006, **231**, -

³⁶ X. C. Xu, C. S. Song, J. M. Andresen, B. G. Miller and A. W. Scaroni, *Energ Fuel*, 2002, **16**, 1463-1469.

³⁷ X. C. Xu, C. S. Song, J. M. Andresen, B. G. Miller and A. W. Scaroni, *Micropor Mesopor Mat*, 2003, **62**, 29-45.

³⁸ X. C. Xu, C. S. Song, B. G. Miller and A. W. Scaroni, *Ind Eng Chem Res*, 2005, **44**, 8113-8119.

³⁹ D. J. Fauth, T. P. Filburn, M. L. Gray and M. J. Keller, *Abstr Pap Am Chem S*, 2006, **231**, -

⁴⁰ A. Arenillas, T. C. Drage, K. Smith and C. E. Snape, *J Anal Appl Pyrol*, 2005, **74**, 298-306.

⁴¹ T. C. Drage, A. Arenillas, K. M. Smith, C. Pevida, S. Piippo and C. E. Snape, *Fuel*, 2007, **86**, 22-31.

⁴² C. Pevida, T. C. Drage and C. E. Snape, *Carbon*, 2008, **46**, 1464-1474.

⁴³ M. G. Plaza, C. Pevida, B. Arias, J. Feroso, A. Arenillas, F. Rubiera and J. J. Pis, *J Therm Anal Calorim*, 2008, **92**, 601-606.

⁴⁴ E. L. G. Oliveira, C. A. Grande and A. E. Rodrigues, *Sep Purif Technol*, 2008, **62**, 137-147.

⁴⁵ P. Xiao, J. Zhang, P. Webley, G. Li, R. Singh and R. Todd, *Adsorption*, 2008, **14**, 575-582.

⁴⁶ A. Torrisi, R. G. Bell and C. Mellot-Draznieks, *Cryst Growth Des*, 2010, **10**, 2839-2841

⁴⁷ R. Davidson, 2009. Post-combustion carbon capture – solid sorbents and membranes. IEA Clean Coal Centre.

⁴⁸ T. C. Drage, O. Kozynchenko, C. Pevida, M. G. Plaza, F. Rubiera, J. J. Pis, C. E. Snape and S. Tennison, *Greenhouse Gas Control Technologies* 9, 2009, **1**, 599-605

⁴⁹ J. Blamey, E. J. Anthony, J. Wang and P. S. Fennell, *Progress in Energy and Combustion Science*, 2010, **36**, 260-279.

In addition to use in gas separation, high temperature CO₂ adsorbents have a role in enhanced water gas shift reaction [50,51]. This process provides many potential benefits over more traditional pre combustion capture technologies in that WGS and CO₂ capture can occur simultaneously in a single reactor. This can be achieved using a solid sorbent or through the use of a membrane system in conjunction with a catalyst. Extensive research of this technology is currently being undertaken at ECN. A range of high temperature adsorbents would be applicable to this technology, for example hydrotalcites [52, 53].

3.2.3. Membrane systems

Membranes have potential for CCS in that they potentially have: low energy consumption; possibility to carry out separation continuously; mild process conditions; easy scaling up; absence of additives; possibility to combine with other separation technologies. However, important disadvantages are, depending on the specific membrane type, fouling tendency, low membrane lifetime and depending on the material low selectivity or CO₂ flux make them less applicable to large scale application. Key performance parameter against which membrane performance is benchmarked is the selectivity and permeability of the membrane, which determines the CO₂ purity and transfer rate through the membrane respectively. Membranes can be classified into two principal categories, dense and porous membrane systems, both of which find application in CCS. Specific membrane materials, for example polymeric, ceramic, zeolitic, and metal can be selected for a certain applications, depending on the temperature and pressure regimes of the separation gas. The material and type of membrane is task specific (pre, post combustion and air separation), with the key type and developments summarised in Appendix 4. Finally, membranes find application in oxyfuel production as a route to advanced oxygen production and offer an alternative and potentially lower energy penalty compared to cryogenic air separation. Two membrane systems have been developed based on ion transport membranes (ITMs) and oxygen transport membranes (OTMs), which use pressure difference and chemical potential respectively to separate oxygen from air. For these systems the stability in contact with flue gas components is not demonstrated. Therefore they are still in the state of material development. Their mechanical reliability during load changes is low. Load changes will be necessary to compensate wind to electricity conversion up- and downturns. The development is risky and testing of small systems, before power plant systems, are in the focus of development. This technology will not be available before 2050.

3.2.4. Chemical Looping Combustion

Chemical looping combustion is a way of combusting coal or gas, without the energy penalty usually associated with the gas separation of carbon capture, and can be applied to gasification and combustion of fuels [54, 55, 56]. Chemical looping combustion requires materials development in the form of a solid oxygen carrier which must withstand being cycled between oxidation and reduction. Materials

⁵⁰ E. R. van Selow, P. D. Cobden, R. W. van den Brink, J. R. Hufton and A. Wright, *Greenhouse Gas Control Technologies* 9, 2009, 1, 689-696

⁵¹ E. R. van Selow, P. D. Cobden, P. A. Verbraeken, J. R. Hufton and R. W. van den Brink, *Ind Eng Chem Res*, 2009, 48, 4184-4193.

⁵² S. Walspurger, L. Boels, P. D. Cobden, G. D. Elzinga, W. G. Haije and R. W. van den Brink, *Chemoschem*, 2008, 1, 643-650.

⁵³ P. D. Cobden, P. van Beurden, H. T. J. Reijers, G. D. Elzinga, S. C. A. Kluiters, J. W. Dijkstra, D. Jansen and R. W. van den Brink, *Int J Greenh Gas Con*, 2007, 1, 170-179.

⁵⁴ J. S. Dennis, C. R. Muller and S. A. Scott, *Fuel*, 2010, 89, 2353-2364.

⁵⁵ S. A. Scott, J. S. Dennis, A. N. Hayhurst and T. Brown, *Aiche Journal*, 2006, 52, 3325-3328.

⁵⁶ M. M. Hossain and H. I. de Lasa, *Chem Eng Sci*, 2008, 63, 4433-4451.

with high surface areas to achieve good contact with the combusting fuel and therefore fast reaction kinetics are also required. Oxygen carriers for chemical looping combustion can be either cheap, natural materials e.g. ilmenite ore ($\text{FeTiO}_3/\text{Fe}_2\text{TiO}_5$) or highly-reactive synthetic materials (for example $\text{Co}_3\text{O}_4/\text{CoAl}_2\text{O}_4$, $\text{CuO}/\text{Al}_2\text{O}_3$ [57, 58] and $\text{Fe}/\text{Al}_2\text{O}_3$ and mixed oxide oxygen carriers [39]). Materials challenges for this technology involve developing materials that can sustain numerous cycles, avoiding degradation by reaction with species such as sulphur and ash in coal, present fast reaction kinetic. The gap is the knowledge in thermodynamic and kinetic of reactions: Nucleation from the gas phase and growth of phases. On the basis of current knowledge the development is an trial and error development with all risks combined with this kind on work.

Chemical looping is far away from commercial availability. The slow reaction kinetic, ageing of the reactive material, loss of capacity with cycles, high temperatures, corrosion in conjunction with erosion have to resolved. This technology should be demonstrated in the KW and low MW technical scale.

3.3. Ongoing research on storage and transport technologies

The key materials related issues when dealing with new storage development , such as in deep saline aquifers, is linked to well completions: casing, production strings, packers, filters/send filters, cementing and placement of sensors or other monitoring equipment within the injection or monitoring wells. Corrosion resistance is a prime consideration, combined with material choices safeguarding against unwanted chemical or biological reactions at the well interface to the storage reservoir. Such reactions have been known to block filters and near-wellbore permeability as well as mobilise fine-grained formation particles with subsequent loss of injectivity.

Corrosion resistant material such as steel, composite material and cements are of particular importance ver the long term, i.e. with operational life-time of a storage operation of 30-40 years followed by 30 years of monitoring or more, this could become an issue approaching a century. This is also valid for old, abandoned wells which are common in depleted oil or gas fields, but also may exist in saline aquifers. The precise materials and abandonment procedures for such wells may be poorly know and may in some cases necessitate re-drilling and an abandonment at today's practice. Such remediation is generally very expensive and best avoided if possible. Efficient methods – including improved abandonment materials – are expected to become a prime consideration when deploying CO_2 storage at a wider scale, when the most favourable storage sites have been engaged.

Controlling the flow of fluids in the subsurface has been carried out in oil and gas oprations for decades. High permeability zones may be partially or fully plugged by foams or gels, while low-flow zone may be stimulated by acid treatment. This may be supplemented by fracturing of selected interval and fractures may be propped by various material in order to stay open and allow permeability enhancement to last longer. Current research is developing agents which, when added to the CO_2 plume and subjected to unexpected changes in reservoir conditions – i.e. pressure change – may act as leakage preventions tools.

Storage reliability is enhanced when increasing volumes of CO_2 become dissolved in the resident formation brines. Reserch indicated that this process may be accelerated by physical mixing – exposing CO_2 to 'fresh' formation fluid – and by addition of catalysts which may also increase the formation of new minrals, immobilising the CO_2 . The proper management of these processes require accurate monitoring of the storage reservoir and the resident fluids, and down-hole probes with very long life-times will be a key tools in this context (pH, pressure, temperature, salinity/conductivity).

⁵⁷ S. Y. Chuang, J. S. Dennis, A. N. Hayhurst and S. A. Scott, *Combustion and Flame*, 2008, **154**, 109-121.

⁵⁸ A. M. Kierzkowska, C. D. Bohn, S. A. Scott, J. P. Cleeton, J. S. Dennis and C. R. Muller, *Ind Eng Chem Res*, 2010, 49, 5383-5391.

3.4. Main Research on functional materials

Large EU consortia have been funded through FP7 to develop and test functional materials for CCS. A summary of the principal projects and their scope is available (<http://www.co2net.eu/public/linksongoing.asp>). The most appropriate programmes for materials for CO₂ capture include CACHET II, CAESAR, CATO. Many of the research groups active in the development of functional materials for CO₂ capture are also involved in EERA (<http://www.eera-set.eu/>) which is based on the 10 leading European research institutes. A summary of the key EU research institutes involved in materials for CCS is presented in Appendix 5.

Outside the EU, the principal research programmes developing functional materials in CCS are the USA and Australia. The USA has a large programme on the development of technologies for CCS funded through the US Department of Energy in collaboration with NETL. A report on the key research developments in this field was recently published and covers many one the materials discussed in this report [30]. The Australian research in Australia is bases around the CO2CRC (<http://www.co2crc.com.au/>) and has a research focus into a range of functional materials for carbon capture, for example solid sorbents, membranes and cryogenic systems.

3.4. Main Research on structural materials

A summary of key EU research institutes and industrial players involved in the development of structural materials is presented in Appendix 5. Large EU-projects funded through FP7 and entirely focussed or dealing with aspects of structural materials include NEXTGENPOWER [59], COMTES [60], H2-IGCC [19], RECOMBIO[61], MACPLUS [18] and ENCIO [62]

Outside the EU, the principal research programs developing structural materials for high efficiency power plants are the USA and Japan (although China and India are also to some extent active in this field). The USA has a large programme on the development of materials for USC boilers funded through the US Department of Energy [63]. In Japan, long term R&D projects have been initiated to reduce the amount of CO₂ emission by adopting a double reheating system with the main steam temperature higher than 700°C and the pressure of 35Mpa. The USC-A Power Plant Project is described as challenging for the metallurgists since none of the ferritic and austenitic steels developed seems to survive in such a hostile environment, and there is no experience on Ni-Co based alloys for large diameter heavy wall thick piping application mainly due to their sensitivity to relaxation cracking, poor toughness, fatigue resistance and workability⁶⁴

Section 4: Materials Specification Targets for Market Implementation in 2020/2030 and beyond 2030 (Frans Snijkers, Dolores Gómez-Briceño)

⁵⁹ Annex I, www.nextgenpower.eu

⁶⁰ http://ec.europa.eu/research/research-for-europe/energy-comtes700_en.html

⁶¹ <http://lib.bioinfo.pl/projects/view/13606>

⁶² European Network for Component Integration and Optimisation

⁶³ R. Viswanathan and J. Shingledecker, Proceedings of 6th International Conference on Advances in Material Technology for Fossil Power Plants, 2010, session 1-05

⁶⁴ A.Iseda, M.Igarashi, H. Semba, M. Yonemura. Proceedings of 6th International Conference on Advances in Material Technology for Fossil Power Plants, 2010, Session 1-02

Performance levels relating to materials for CCS and fossil fuel conversion are discussed. Quantification of performance levels of materials for CCS, and future fossil fuel conversion, are discussed to the extent possible. There are too many trade-offs and technological variations, to make very specific specification targets. These variations make it impossible to bridge the gap between, on the one hand quantitative specifications for the materials and on the other hand, implementation of the related technology on the market. In order to specify quantitative material performance, full scenarios and data sets are needed for the technology that uses the material. The specification targets for the (post-combustion) adsorbent, CO₂ membrane separation technologies, (oxy-combustion) chemical looping technologies, oxy- and pre-combustion H₂ and O₂ separation membrane technologies and catalyst materials are presented for market implementation in 2020-2030 and in 2050.

4.1 Specification targets for Market Implementation in 2020/2030 and beyond 2030

4.1.1. Functional materials

1. Absorbent liquids

Amines like MEA, DEA and MDEA are well know materials for use in scrubbing processes for gas cleaning. For 2020-2030 they need to fulfil requirements with regard to CO₂ capacity, fast kinetics for (economic) regeneration, stability over a high number of cycles, resistant to poisoning by H₂O, Hg, SO_x, and NO_x, service life and economy, including environmental and safety cost, low energy penalty for the process, fast CO₂ absorption at low temperatures and fast desorption at slightly higher temperatures. This also includes research in better temperature control and heat transfer management.

In 2020 absorbent liquids must be expected to be mature materials and thus are projected for implementation in 2020-2030.

2. Adsorbent materials

Several classes of adsorbent materials are recognised. Zeolites and carbon belong to the physi-sorption based adsorbents. Chemi-sorption is found for a wider range of adsorbent materials: inorganic metal-based, mainly Ca-, Mg-oxide, and hydrotalcite (for pre and post combustion) and organic, mainly amines (MEA, DEA, MDEA) that can be in solution or impregnated on silica (molecular baskets) or covalently bonded, supported on carbon, resins and carbon-nanotubes, and finally metal organic frameworks or MOF's. Solid adsorbents can occur in a variety of structural configurations, namely monolith, laminar, foam, fabric or other structure [65].

Many factors determine the quality of CO₂ adsorbents in post-combustion flue gas treatment. In reality, all practical adsorbents have trade-offs. Generally, an ideal (hypothetical) adsorbent can defined by fast adsorption and desorption kinetics, large adsorption capacity, infinite regenerability and stability, and a wide yet tunable window of operating conditions. It is unlikely that all these requirements will be covered by one single absorbent material.

Consequently, it will rather be necessary to evaluate each adsorbent's strengths and weaknesses in the context of a practical adsorption process for effective CO₂ separation [66] [67]. For that absorbent materials are ready for market implementation in 2020-2030, they must outperform current commercially viable amine-based scrubbing. So, the important specifications for adsorbent materials for market implementation in 2020-2030 are:

⁶⁵ F. Rezaei, P. Webley, 'Structured adsorbents in gas separation processes', Separation and Purification Technology 70 243–256, 2010.

⁶⁶ C. W. Jones et al.; 'Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources', ChemSusChem 2, 796 – 854, 2009.

⁶⁷ R.P. Lively, Ronald R. Chance and William J. Koros, 'Enabling Low-Cost CO₂ Capture via Heat Integration', Ind. Eng. Chem. Res. 49, 7550–7562, 2010.

- CO₂ Capacity as high as possible , eg.>5 mol/kg
- Fast adsorption/desorption kinetics; eg a working capacity of >3 mol/ kg in a one minute cycle
- Regenerability, taking cost of regeneration into account.
- Stability over a high number of adsorption/desorption cycles.
- Resistant to poisoning by common flue gas components and contaminants, eg. H₂O, Hg, SO_x, and NO_x.
- Low pressure drop for solid adsorbents in order to fit in with either pressure, temperature, vacuum and electric swing adsorption (PSA, TSA, VSA and ESA)
- Service life and economic material (eg. <0,1 Euro/mol CO₂), taken into account cost for eventual environmental and safety measures
- Overall low temperatures process
- Low energy penalty. Smaller than 6%

In 2020 adsorbent materials should be expected to be mature materials and are also projected for implementation in 2020-2030. In order that they will outperform the liquid amine scrubbing, it is projected that mainly cost, including safety and environmental costs, and (related) service life will have to meet the higher demands for market implementation beyond 2030.

3. Oxygen carriers for Chemical Looping technologies.

A number of factors describe the performance of oxygen carriers in Chemical Looping. In general, fast oxidation and reduction kinetics, large oxygen exchange capacity, infinite stability, and a relatively wide yet tunable range of operating conditions, low cost, non-toxic and environmental safe define an ideal, hypothetical O-carrier [68]. In practical circumstance however all O-carriers have trade-offs. Important parameters include rate of redox kinetics, oxygen capacity, stability on life, resistance to specific fuel components and impurities [69]. It should be noted that in reality no single ideal O-carrier is likely to be developed. Therefore O-carrier materials must be considered in the context of application in a practical CL-process. Consequently, the properties and specification are very likely to be different for Chemical Looping Combustion (CLC), Chemical Looping reforming (CLR) and Chemical Looping Oxygen Uncoupling (CLOU). On the other hand, whether the oxygen carrier will be applied in either CFB-reactors or in packed bed reactor or whether gaseous fuel (natural gas) or solid fuel (coal) is to be converted, makes it very likely that the materials will need to have different characteristics. The important requirements for oxygen carrier materials for market implementation of CL-technologies in 2020-2030 are:

- Thermo-mechanical stability for O-carrier packed beds
- Thermal conductivity for O-carrier in PB, in order to avoid hot spots
- Heat transfer supporting flow and structures
- Reactivity and fast conversion rate of fuel
- Fluidizability for CFB O-particles; particles should not agglomerate in order to enable continued circulation between the fuel and air reactor
- Pressure drop for PB material
- High resistance to deactivation and poisoning by fuel components and contaminants
- High service life, e.g. >10.000hours. This is related with mechanical integrity on life, ie attrition resistance for particles that circulate in CFB-reactors can be expressed as a minimum crushing strength, of eg 1 Newton

⁶⁸ Hossain, M, and de Lasa, H., 'Chemical looping combustion (CLC) for inherent CO₂ separations – a review', *Chem Eng Science* **63**, 2008, 4433- 4451.

⁶⁹ Lyngfelt, 'Oxygen carriers for chemical-looping combustion - 4000h of operational experience Oil & Gas Science and Technology - Rev. IFP.

- Economic, low cost: amongst other determined by reactivity, ie. composition and the solids inventory of the reactor, including costs for environmental and safety measures

For CFB, the solids inventory of the reactor can vary from 200 to 2000kg/MWatt, depending on the reactivity [70]. As a consequence, there is a trade off between the reactivity ie the MeO/Me-pair considered and the solids content of the reactor, determining the final cost in terms of size of reactors and materials cost.

Chemical Looping combustion is projected for industrial implementation in 2020-2030, for natural gas and other gaseous fuels. As such, it is expected that beyond 2030 oxygen carriers will have to meet stronger requirements on cost (including environmental and safety costs) and related service life are concerned. Further, beyond 2030, oxygen carriers will have to meet the more severe demands that are posed on the materials for being capable for use in CL-processes using other fossil fuels, eg oil and coal. This mainly concerns an increased resistance to deactivation and poisoning by fuel components and contaminants, but also cost will have to decrease.

4. Membranes for gas separation technologies.

Membranes are considered for all 3 post-, pre- and oxy-combustion routes. In every of the 3 routes, different separations are needed. For post-combustion CO₂/flue gas (mainly N₂) separation is required; oxy-combustion requires the production of O₂ in sufficient quantities via separation of O₂ air, and for pre-combustion again O₂/N₂-separation is needed, but also separation of H₂ from CO₂. Since not one single membrane will be able do the job, it is necessary to consider membrane materials in a specific gas separation process with its practical boundary conditions.

The performance of membranes is described by many factors: high permeation combined with good selectivity, stability in view of the operating conditions and economically feasible. In practice however all membrane materials have trade-offs that need balancing in order to make the optimal choice for the technology. To this end several types of membrane materials in a variety of configurations are considered. They rely on different physical principles for separation ao. selective adsorption by membrane contactors, sieve operation by porous (sol gel or zeolite) layers, and ion conduction by dense ceramics [71]. For O-separating MIEC-membranes it is aimed at a flux of >10 Nml/min.cm² [72]. For H₂-separation, mixed proton electron conductor materials should be considered, but also hydrogen permeable metal membranes, eg. Pd or Pd-alloys [73]. Except for the membrane materials systems, sealing materials are needed that enable that membranes can be gastight connected to reactor module components.

Specification targets* for polymer gas separation membranes and materials for market implementation in 2020-2030 are:

- Permeation rates (flux) from 1 to over 100 Barrers for micro-porous membranes (molecular sieve carbon and polymers)

⁷⁰ H. Leion, Capture of CO₂ from solid fuels with CLC and CLOU, PhD-thesis, Chalmers University of Technology, ISBN 0346-718X , 2008

⁷¹ M. Czaperek, P. Zapp, H.J.M. Bouwmeester, M. Modigell, K. Ebert, I. Voigt, W.A. Meulenberg, L. Singheiser, D. Stöver, Gas separation membranes for zero-emission fossil power plants: MEM-BRAIN, Journal of Membrane Science, 359, 1-2, 149-159, 2010.

⁷² Ciattaglia et Tautz, Public summary report of ENCAP deliverable D5.1.3: Economic evaluation of components and sub-systems costs for process selection to proceed to the next step. Available from Internet: www.encapco2.org

⁷³ S. Tosti, Overview of Pd-based membranes for producing pure hydrogen and state-of-art at ENEA laboratories, Journal of Hydrogen Energy, 35, 22, 12650-12659, 2010.

- Hydrogen permeation fluxes for supported Pd-(alloy) membranes, eg. $>100\text{m}^3/\text{m}^2\cdot\text{h}$ at temperatures $>550^\circ\text{C}$ and a H_2 pressure difference >10 bar
- Capable of operation at near to or at (flue) gas temperatures and compositions.
- Selectivity, eg >10 for O_2/N_2 –selectivity.
- Cost, including environmental and safety costs.

In [74], the trade off between O_2/N_2 selectivity and permeability is described. With commercial interesting O_2 -permeabilities in between 1 and 10 Barrers, the O_2/N_2 selectivity will be between 10 and 6, limited by the so-called Robeson's 1991 upper limit. Further, the higher the permeation flux and the higher the membrane operating temperature capability, the lower the amount of membrane surface area will be required, and the more economic membrane separation will be.

By 2020-2030, membranes considered for the post-combustion route, separating CO_2 from flue gas, will have to outperform liquid absorbent scrubbing and solid adsorbents. As such, the properties of these membranes will have to keep track with tighter performance specifications. For the pre- and oxy-combustion route, other separations are needed. Nowadays, pure oxygen is produced by cryogenic distillation and leads to an overall efficiency drop of the power plant of up to 10%-points. However, if the separation of oxygen from air could be integrated into the high temperature combustion process, the efficiency drop could be limited to around 5%-points [75] [76] [77].

Specification targets* for gas separation membranes and materials for market implementation beyond 2030 would be:

- Permeation rates (flux) for either O_2 (pre- and oxy-combustion) and H_2 (pre-combustion) eg a flux of >20 $\text{Nml}/\text{min}\cdot\text{cm}^2$ for O_2 -separating MIEC-membranes, a flux of eg >5 $\text{Nml}/\text{min}\cdot\text{cm}^2$ for H_2 -separating MIEC membranes at operating temperatures $>750^\circ\text{C}$, and a flux of eg. $>100\text{m}^3/\text{m}^2\cdot\text{h}$ at a temperature $>550^\circ\text{C}$ and H_2 pressure difference >3 bar for supported Pd-(alloy) membranes.
- Selectivity: preferably as high as possible: ie (near to) 100%. For gastight MIEC membranes this condition is fulfilled, for micro-porous (polymer, zeolite, sol gel) membranes eg 25 for H_2/CO_2 –selectivity.
- Thermo-mechanical stability to allow a lifetime of eg. > 10000 hours
- Mechanical strength (to cope with ΔP operating capability of eg. >40 bars)
- Chemical stability in surrounding conditions of gas atmosphere and temperature, ie resistant to presence of sulphur, water, CO_2 and further compounds in either flue gas, air, syngas,... depending on where the separation is to be performed.
- Compatible with module and reactor component materials enabling gas tight connections. In this respect not only the coefficient of thermal and chemical expansion (in $^\circ\text{C}^{-1}$) are of importance but also a smart sealing strategy and process need being developed.
- Cost, including environmental and safety costs.

⁷⁴ W.J. Koros, Rajiv Mahajan, Pushing the limits on possibilities for large scale gas separation: which strategies? , Journal of Membrane Science, 175, 181-196, 2000.

⁷⁵ C.A. Scholes, K.H. Smith, S.E. Kentish and G.W. Stevens, CO_2 capture from pre-combustion processes – Strategies for membrane gas separation, Int. J. Greenhouse Gas Control, 4, 739-755, 2010.

⁷⁶ Eckl et al. Public summary report of ENCAP deliverable D5.3.11: Developments of the high temperature oxygen generation technology outside ENCAP in EU and USA. Available from Internet: www.encapco2.org :

⁷⁷ H. Stadler, F. Beggel, M. Habermehl, B. Persigehl, R. Kneer, M. Modigell, P. Jeschke, Oxyfuel coal combustion by efficient integration of oxygen transport membranes, Int. J. Greenhouse Gas Control (2010), doi:10.1016/j.ijggc.2010.03.004

**Figures are indicative: the materials target specifications for implementation depends strongly on application scenario, eg. Technology where the material is used, integration in power plant ,eg. Temperature and composition of flue gas, trade offs*

5. Catalyst materials

Conversion of fossil fuel, eg partial oxidation of methane, reforming to syngas and the production of hydrogen can be supported by using processes that are catalytic in nature [78] [79]. Catalysts are commercially available. But an optimization of their activity and selectivity could have an significant effects in the fossil fuel use. Generation of syngas rich in carbon monoxide and hydrogen are aided by high temperatures . The search for catalysts that improve the kinetic of the partial oxidation of the fuel to carbon monoxide and hydrogen could increase the yield of gasification [80]. The following properties for catalyst materials for market implementation of CCS-technology in 2020-2030 must be considered:

- High activity trough high and assessable surface area
- High selectivity for the reaction envisaged
- Resistant to poisoning agents that can occur during operation
- Structural integrity, for good multi-cycle performance and long service life
- Cost, including environmental and safety costs.

4.1.2. Structural materials

One of the ways of contributing to demonstrate the commercial viability of CCS technologies in coal fired power plants by 2020-2030 is to develop more efficient and cost competitive conventional power plants to compensate the penalty imposed by CO₂ capture. The target is to progressively increase the net efficiency of coal power plants up to reach efficiencies higher than 50% without CO₂ capture by 2020/2030 [81]. The increase of efficiency relies on the availability of suitable materials to support the more and more demanding working conditions imposed by the operation at higher temperatures. The steps to have structural materials with the required properties to be used for the construction of high temperatures/ high stresses components can be summarised as follow [82] [83].

- Qualification of existing, or development of new materials /coatings with optimised service properties.
- Development of adapted or/and new manufacturing technologies
- Implementation of advanced fabrication technologies
- Optimization of design methods, design by Analysis versus design by Formula, to fully exploit the material potential resulting in a cost reduction
- Development of residual life time concepts

⁷⁸ J.D. Holladay, J. Hu, D.L. King and Y. Wang, ‘An overview of hydrogen production technologies’, Catalysis Today 139, 244-260, 2009.

⁷⁹ S.C. Reyes, J.H. Sinfelt, J.S. Feeley: Evolution of processes for synthesis gas production: Recent developments in an old technology. Ind. Eng. Chem. Res. 42 (2003), 1588.

⁸⁰ J. Baxter, Z. Bian, G. Chen, D. Danielson, M. S. Dresselhaus, A. G. Fedorov, T. S. Fisher, C. W. Jones, E. Maginn, U. Kortshagen, A. Manthiram, A. Nozik, D. R. Rolison, T. Sands, L. Shi, D. Sholl and Y. Wu: Nanoscale design to enable the revolution in renewable energy. Energy Environ. Sci. 2 (2009), 559

⁸¹ A technology roadmap for the Communication on Investing in the development of Low Carbon Technologies (SET-Plan), 7-10-2009, pp 37

⁸² T. Ulf Kern, Materials Research and Development Challenges for Low CO₂, high efficient Steam Turbines with Advanced Technology, COOROTEC-Meeting, Enertec 2005.

⁸³ M. Speicher et al., Investigations on advanced Materials for 700°C steam power plant components, 3rd Symposium on Heat Resistant Steels and Alloys for High Efficiency USC Power Plants 2009, NIMS).

1. Ultra-supercritical coal power plants (USC)

The target for USC power plant boilers is to progressively increase the net efficiency of coal power plants up to reach an efficiency higher than 50% for operating temperature of 700°C by 2020/2025. The main materials/coatings requirements for boiler and steam turbines for USC power plants operating at temperatures of 700/720°C are high temperature strength for base and weld metal materials as well as corrosion and oxidation resistance.

- The creep strength after 100,000 hours is targeted in 100MPa for main steam pipe at 700°C, for super-heater tubing at 750°C as well as for re-heater tubing for which the metal temperature may exceed over 750°C and reach up to 800°C [84].
- Thermal fatigue and creep fatigue properties for high strength alloys with poor ductility and toughness are also important for thick wall pipes and in particular for turbines.
- From the corrosion point of view, fire side corrosion (ash deposits from the flue gas) and steam oxidation are also critical issues for advanced high temperature materials.
- Weldability, reparability and manufacturability in site are critical issues to be taken into consideration, as well as inspection, quality assurance (QA) programme and cost.

Nickel base alloys and coated systems are the candidate materials, as in the case of ADS 700 [83]. However if F/M steels could be developed for use at 650°C, significant improvements in efficiency would be gained at a fraction of the cost needed to build a 700°C power plant using austenitic steels and Ni-based super-alloys [85].

For advanced steam turbines, the production and verification of large components such as shaft and casing, as well as the performance of dissimilar welded joints between nickel base alloys and steels are critical issues to be resolved on time.

By 2020 and beyond, it could be considered technically feasible to increase the steam conditions up to 800°C by the use of improved nickel base alloys. The target is to exploit a potential efficiency of more than 60%. New approaches should be pursued for the development of advanced materials with optimised composition, taking advantage of the development of materials models [86].

2. Integrated Gasification Combined Cycle (IGCC)

By utilizing gas and steam processes, IGCC plants achieve higher efficiency than conventional steam power plant, more than 50%. This technology also permits the generation of synthesis gases for fuel, methanol, H₂ and SNG production. Coal fired power plants based on IGCC technology are also able to effectively separate CO₂. For this type of plants the target is the development of robust, efficient and low- cost technology on a commercial scale by 2020. Particular concerns for IGCC plants are the availability of gasifiers with the target of reaching the reliability of classical power plants, and the adaptation of gas turbines to hydrogen rich fuel gases with the aim of getting efficient H₂ combustion systems

For the different gasification processes, temperatures in the gasifiers can reach values lower (dry ash removal) or higher (liquid slag removal) than 1300°C. Materials/coatings resistant to oxidation and corrosion in the hot gas path with altered working fluids are needed, as could be the case of the

⁸⁴ M.Igarashi et al, Advances in Materials Technology for A-USC Power Plants Boiler, 3rd Symposium on Heat Resistant Steels and Alloys for High Efficiency USC Power Plants 2009, NIMS).

⁸⁵ C.J. Cowen et al. , New-high temperature iron-based alloys, 24th Annual Conference on Fossil Energy Materials, 2010.

⁸⁶ COORETEC Lighthouse Concept, research report 266, published in April 2008

formation of alkalis and vanadium in the IGCC plants operated with synthesis gas or the high steam partial pressure in the flue gas from combustible in IGCC processes with CO₂ separation. The working fluid for gas turbines integrated into coal based IGCC can be syngas, hydrogen and natural gas. The goals for the development of advanced gas turbines for these conditions are to increase the combined cycle efficiency, to reduce the cost and to reduce emissions. Temperatures of around 1500-1700°C are foreseen for the future turbines. The estimated thermal loading or heat flux imposed on a turbine airfoil would be about 10 times the level of the current state of the art turbines [87]. Structural integrity of turbine components requires high temperature creep resistant metal substrates, durable thermal barrier coatings (TBCs), effective and reliable bond coats and effective cooling techniques.

By 2020, the commercial viability of advanced gas turbines relies on TBCs and cooling techniques. Thermal barrier coatings (TBCs) are used to extend the life of metal components by creating a temperature drop across the coating, permitting the underlying metal to operate at a reduced temperature. Future gas turbines (GT) will use TBC technology to permit the simultaneous increase of turbine inlet temperature and the reduction of turbine cooling air, thereby increasing efficiency. New ceramic thermal barrier coatings and corrosion resistant adhesive layers, also able to work in extreme cyclic operation, must be developed for new operating conditions. Targets for TBCs would be:

- New thermal bond coat systems with a improvement of 30% -40% of failure time regarding the base metal [88].
- Industrial application of these advanced system for 2020 and beyond.
- Lifetime monitoring

By 2030 and beyond, alternative materials such as oxide fibre/oxide ceramic CMC and fibre reinforced materials could be an interesting alternative for hot gas components in gas turbines. Currently, experience is restricted to laboratories. Innovative materials such as open pored multilayer materials are an option [89].

- These new materials together with new design principles for the highly stresses components could allow to reach efficiency of 65% and more [86] by 2030.

Oxide Dispersion Strengthened (ODS) alloys outperform Ni-based superalloys in terms of creep and oxidation resistance at temperatures above 900°C and could be used up to 1200°C [90]. Potential applications are higher temperatures components such as fuel nozzles and combustor cans in hydrogen turbines, and HT heat exchangers. The target for this type of material would be

- To recuperate the fabrication capabilities in EU to be commercial by 2020.
- The implementation of new fabrications routes for ODS alloys to be cost competitive with the Ni base alloys [91].
- Non fusion joining techniques have to be developed and validated to fulfil the target of components fabrication for 2020/2030 [90].

3. Co-combustion (biomass)

⁸⁷ M.A. Alvin et al, *Materials and Components Development for Advanced Turbine Systems*, ASME Turbo Expo 2008, Berlin 2008

⁸⁸ T. Bradley, *Advanced H₂ Turbine Development*, ASME Turbo Expo 2009

⁸⁹ E.W. Kreutz, High- temperature Turbine Applications using Open Porous Metallic Foams with Thermal Barrier Coatings and Cooling Hole Arrays, ISCORMA-4, Calgary, Alberta, Canada 27-31, August 2007.

⁹⁰ S. Dryepontd et al, Qualification of New, Commercial Oxide Dispersion Strengthened (ODS) Alloys, 24th Annual Conference on Fossil Energy Materials, 2010.

⁹¹ I.E. Anderson et al., Atomization and Power Processing of High Temperature Ferritic Stainless Steels, 24th Annual Conference on Fossil Energy Materials, 2010.

Biomass combustion and biomass/coal co-firing, both in retrofit and new plants, are expected to expand in the next years. However, co-utilisation of biomass or wastes promotes operational problems such as slagging, fouling and corrosion of boiler materials. Due to the complexity and variability of flue gas from plant to plant, the transferability between lab and plants is not straightforward. Combined experimental laboratory and field test projects would be helpful. To improve the efficiency of cogeneration plants, the development of models focused on these degradation phenomena would allow to increase the reliability of the cogeneration plants and to increase the percentage of biomass used.

Torrefaction is an option to maintain energy conversion efficiency, which is usually reduced when adding biomass, and can be in principle be maintained using torrefied biomass/bio-coal.

4. *Oxy-combustion*

The oxyfuel process is one of the methods to separate CO₂ from the flue gases of coal-fired power plants. This process is being considered since the early 1980s. But there is still no reliable information on the optimum design and economic viability of this technology [86]. Pulverized coal firing is the preferred design for the oxyfuel process. Flue gases in an oxy-combustion coal plant are rich in CO₂ and steam water and have higher concentrations of NO_x and SO_x than in a conventional coal plant. High temperatures materials and coatings with required creep resistance, good response to oxidation/corrosion, and resistance against carburization in oxyfuel environment are needed.

The considerations made for steam turbines are applicable to steam turbine in oxy-combustion plants. For the case of oxy-fuel gas turbine with a mixture of CO₂/H₂O as working medium, an adaptation of the available technology for gas turbine and future developments must be available by 2020 [92].

5. *Cross-cutting activities for structural materials*

The following topics have been identified of application to the different technologies:

- Quantification of material microstructure in relation to its properties
- Robust modelling to describe material-component performance evolution during long-term service aimed at improving the efficiency of steam power plants.
- Computational simulation at different scale for optimization of materials design and elaboration of behaviour models: creep, creep-fatigue, oxidation,, including methodologies for validation of models.
- Monitoring methods including residual lifetime prediction models

4.1.3 Materials for storage

When dealing with CO₂ injection and storage operations a number of the key parameters are:

- Corrosion resistance (steel, composites, cements....)
- Very long longevity material and sensors in the subsurface (many decades)
- State of the art fluid management and control materials (tracers, leakage preventions compounds, dissolution and mineralisation catalysts, flow plugging agents, fraction fluids and propping agents).
- Robust numerical tools for modelling, and monitoring storage complexes.

⁹² K. Natesan et al., Corrosion Performance of structural Alloys for Oxy-Fuel Combustion Systems, 21 Annual Conference on Fossil Energy Materials, 2007.

In the near future a demand is expected for cheaper materials to replace chromium steel when recompleting offshore well completions and process piping/pumps and for the range of materials related to the drilling and completion of slim-hole full coring wells as a less costly alternative to large-bore conventional drilling.

Section 5: Synergies with other Technologies (Dolores Gómez-Briceño, Frans Snijkers)

5.1 Functional Materials

Sorbents and solvents technologies are common to many gas purification systems. Membranes are applied in many fields for separation processes in harsh environments. Separation in organic solvents and corrosive environments require membranes of inorganic nature. Further, high temperature ceramic ion conducting gas separation membranes are used in solid oxide fuel cells, where they have been developed in flat and tubular geometries, with appropriate sealing to module components [93]. For this reason, R&D in the field of high temperature ceramic membranes for gas separation in pre- and oxy-combustion route are expected to benefit from synergy with membrane technology for SOFC application. But with the same risk and unexpected success.

Both chemical looping technologies as well as membrane separation technology involve the use of reactor and boiler technology; in this respect both technologies will benefit from synergy emerging with reactor development for the chemical sector as well as with boiler development for the energy sector. Further, the chemical industry needs to continuously innovate in order to deliver ever more efficient, environmentally friendlier and increasingly intensified chemical processes. In this respect, catalysis is globally playing an increasingly vital role in the innovation of green chemistry and sustainable production of chemicals. So, it is expected that specific CCS-technologies will profit from synergy with catalyst research and development undertaken for the chemical industry in the light of process intensification [94]

5.2 Structural materials

High temperature materials are a common issue for high efficiency coal fired power plants and Gen IV innovative nuclear reactors. Most Gen IV systems are aimed at technology advances that enable high operating temperatures. The high temperature will allow the production of hydrogen and process heat, as well as electricity production with higher efficiency cycles [95]. Nickel based alloys are the material candidates for the heat exchanger in Gen IV systems. Common alloys for nuclear and coal fired cycles are being considered [96]. Both technologies can take advantage of the optimization of fabrication processes, materials qualification, weldability issues, NDE techniques, etc. On the other hand, concentrated solar power (CSP) based on central receiver technology also required high temperatures materials with good behaviour under low cycle fatigue conditions, such as alloy 625 LCF [97]. Nickel base alloys are extensively used by the aeronautic industry

⁹³ A.B. Stamboul and E. Traversa, Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy, *Renewable and Sustainable Energy Reviews*, 6, 5, 433-455, 2002.

⁹⁴ K. Li, Ceramic Membranes for Separation and Reactions, John Wiley & Sons Ltd, ISBN 978 0470014400

⁹⁵ A technology Roadmap for Generation IV Nuclear Energy Systems, GIF-002-00, December 2002

⁹⁶ Updated Generation IV Reactors. Integrated Materials Technology Program Plan. Revision 2, ORNL/TM-2003/244/R2, December 2005

⁹⁷ J.M. Lata et al. "High Flux Central Receivers of Molten Salts for the New Generation of Commercial Stand-Alone Solar Power Plants", *Journal of Solar Energy Engineering*, Volume 130, Issue 2, May 2008.

As mentioned in section 4, Oxide Dispersion Strengthened (ODS) alloys outperform Ni-based superalloys in terms of creep and oxidation resistance at temperatures above 900°C and could be used up to 1200°C [98]. ODS steels were developed for coal fired plants some decades ago. However, there are some issues to be resolved for practical application: joining techniques and better processing techniques to improve strength of tubes and to re-establish a viable ODS alloy manufacturing capability [99]. New fabrication methods are being investigated aimed at improving the materials properties and decreasing the cost [100]. As ODS are being considered as candidate materials for Gen IV nuclear reactors, both technologies nuclear and coal-fired would gain profit working in collaboration.

Section 6: Needs and Recommendation of Activities addressing Market Implementation in 2020/30 and beyond (Niklas Hedin, Marco Falzetti)

6.1. Needs for Market Implementation in 2020/2030

6.1.1. Capture technologies / materials aspects

In the short term, CCS would have to be focused on capturing carbon dioxide from large point sources [101] and to create public acceptance by successful demonstration of storage. Technically, it is possible to implement CCS today, but reducing the cost and energy intensity of the capture step will improve the competitiveness of the technology. There are two distinct classes of technologies for carbon capture. The first class concerns carbon dioxide capture from flue gas from existing power plants. In such post-combustion capture, the materials involved in the capture have to be adapted to the physical and chemical characteristics of flue gas. Flue gas has a relatively low partial pressure of carbon dioxide, especially from natural gas fired power plants, a high content of water, and traces of other components. This puts significant demands on the function of the materials that facilitates the capture. In the near or mid term, technologies for post combustion capture are expected to be deployed (of course depending on research advances, incentives for CCS, legislative action, etc) [80]. The focus of the activities relating to market implementation 2020/2030 should have a focus on materials that facilitate such post combustion technologies.

1. *Absorption based stripping* of carbon dioxide with amines in water (e.g. MEA), chilled ammonia are probably the first technologies to be deployed on a large scale for CCS. Full-scale demonstration units are currently being constructed. Other non-toxic absorption fluids or salts with reduced adsorption heat should be developed. Ionic liquids with amine functions could offer advantages, due to their very low vapour pressures. However, cryogenic separation of carbon dioxide is also well developed. Stripping technologies are costly both on the OPEX and on the CAPEX side. Materials that increase the contact area between the MEA or a low molecular weight polymeric amine and the flue gas could make the devices smaller and the CAPEX cost to be reduced. Such materials include porous oxides or porous carbons, as well as polymer membrane contactors. Important issues are reduced amine emissions, fast mass and heat transfer, and for the membrane contactors, significant hydrophobicity. Synthesis and screening of absorbents experimentally and theoretically, integration of the full process are important. Low cost and corrosion resistant materials for the strippers are important.

⁹⁸ S. Dryepontdt et al, Qualification of New, Commercial Oxide Dispersion Strengthened (ODS) Alloys, 24th Annual Conference on Fossil Energy Materials, 2010.

⁹⁹ F. M.Glaser, Workshop on Fe-Based ODS Alloys .Role and future applications, ODS 2010 Materials Workshop November 2010

[¹⁰⁰] J.R. Rieken, Simplified Power Processing and Microstructural control of Fe-based ODS alloys, ODS 2010 Materials Workshop, November 2010

¹⁰¹ Carbon Capture Sequestration and Storage, Eds. RE Hester and RM HARRISON, Issues Environ. Sci Technol., RSC publishing, 2010

2. *Adsorption based technologies* that operate with nano-porous materials at low or high temperatures have the possibilities to reduce the cost for carbon capture. These technologies operate with cyclic pressure or temperature variations. Standard processes are too slow for the large fluxes of flue gas, and rapid swing processes need to be developed. Kinetics (mass transport), capacity and selectivity for carbon dioxide, mechanical robustness, and thermal properties are all important to the efficiency and cost of capture. Heat of adsorption and robustness towards water are important. Rapid swing cycles demand robust or structured materials. A wide range adsorbents are being studied [102], e.g., zeolites, metal organic frameworks (MOFs), porous carbons, porous organics, hybrids, microporous aluminophosphates, and highly alkaline adsorbents. Further efforts in synthesis and screening of adsorbents experimentally and theoretically, integration of the full process are needed. Ranges of properties are important for the function of the adsorbents. It would be helpful if standardized targets for the properties could be defined.

3. *Membranes and membrane/adsorption hybrids* have possibilities to reduce the cost for capture of carbon dioxide [103]. The compact, modular, and rather simple constructs of polymer membrane separation units could possibly under certain circumstances be competitive to absorption in MEA. Hybrids between polymer membranes and solid adsorbents have shown to offer means for rapid temperature swing adsorption. Research needs relating to polymer membranes and membrane/adsorbents hybrids. Developing such with high stability, selectivity, and permeance; hybrids that could merge advantages of the adsorption and membrane technologies

6.1.2. Fossil fuel conversion technologies

Energy efficiency and a diverse range of other technological aspects relating to fossil fuel conversion technologies are relevant for market implantation 2020/2030. Highly efficient steam power plants have strong materials aspect related to them, involving metallic and non-metallic materials, as high alloy steels, Ni-based alloys, special coatings as well as advanced ceramics and refractory materials. For all these materials fundamental developments are still necessary to reach the targeted performances and in-service models to evaluate the performance are necessary to allow for a robust industrial application and long-term efficiency. As co-firing of coal with dry or wet biomass is getting increasingly more relevant, certain materials issues relating to slagging/corrosion/erosion, high temperature high pressure embrittlement phenomena become dramatically important (for both metallic and non metallic materials), for which no final neither sound industrial solutions are available today.

Efficient steam power plants, optimized co-firing technologies, and chemical looping technologies are fossil conversion technologies for market implementation in 2020/2030. Developments in bulk materials (alloy steels, Fe-Ni and Ni-based super alloys, ODS, and their welded joints, obtained through the application of innovative joining technologies) and protective-thermal barrier coatings (metallic and non metallic), in conjunction with diffused sensors and robust modelling to describe material-component performance evolution during long-term service, could allow for more efficient steam power plants. Protective coatings could allow for a more efficient co-firing with a wide range of dry and wet biomass.

Certain needs for materials are summarized in Table 1, both for technologies for CCS and fossil fuel conversion. For CCS, we suggest research activities relating to: the development of materials that increase the contact area for absorption; robust and highly selective low temperature and high temperature adsorbents with high capacities; membranes and combined membrane/adsorbents hybrid materials.

¹⁰² S. Choi et al. "Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources" ChemSusChem 2 (2009) 79.

¹⁰³ E. Favre: Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption? J. Membr. Sci., 294 (2007), 50

Table 1: Specific needs relating to materials to be utilized in capture technologies and fossil conversion technologies for market implementation in 2020/2030

| Post combustion CCS technologies/ materials aspects | Specific needs relating to materials |
|--|---|
| Absorption | |
| Functional materials | <i>Porous solid-polyamine hybrids</i> |
| | <i>Membrane contactors for liquid amines. Alternative absorption materials, fixed bed structures</i> |
| Structural materials | <i>Corrosion resistant materials or material systems, low cost</i> |
| Adsorption | |
| Functional materials | <i>Low temperature adsorbents high capacity, selectivity, hydrophobic, low cost etc.</i> |
| | <i>High-temperature sorbents such as CaO</i> |
| | <i>Adsorbents with optimized mass and heat transfer properties</i> |
| Structural materials | <i>Mechanically robust and structured adsorbents</i> |
| | <i>Materials for rotary (and other types) of valves for rapid swing adsorption</i> |
| Membranes | |
| Functional materials | <i>CO₂-separation membranes and membrane/adsorbent hybrids; Hydrogen and oxygen separating membranes</i> |
| | <i>High permeance and selectivity, operating temperature capability.</i> |
| Fossil fuel conversion technologies | |
| Structural materials | |
| | <i>Steels, Fe-Ni, Ni-based alloys and , Oxide Dispersed Steels, with optimized creep, creep-fatigue, corrosion/erosion/oxidation/HTHP embrittlement properties</i> |
| | <i>Fireside and steam-side protective coatings, to increase metallic components performance in highly aggressive environments</i> |
| | <i>Thermo-mechanical coatings, inter-metallic materials</i> |
| | <i>Fibre reinforced Oxide, Ceramics and refractory materials operating at pick temperature of 1800°C in variable (T, P) conditions and highly aggressive environments</i> |
| Functional materials | <i>Thermal junction, Seebach-based materials as typically used in thermal sensors, actuators and thermal-to-electricity conversion devices</i> |
| | <i>Oxygen carriers for CL-technologies</i> |

6.1.3 Storage materials technology

For storage, market implementation in 2020/2030 should be achieved of

- standard completion materials (cement, steel, elastomer) with adequate long-time behaviour when exposed to CO₂;
- new well materials (including composites) for better long-term resistance to CO₂, impurities and saline brine attacks;
- materials for better repair of leakages;
- materials for favouring dissolution of CO₂ and catalysts for in situ mineralisation.

6.2. Needs for Market Implementation beyond 2030

The second class of carbon capture is fundamentally different from post combustion capture. This class will be implemented on new types of power plants; plants that have been specially designed to make the capture of carbon dioxide more economically or energetically favourable [80]. This latter class includes techniques for pre-combustion capture, oxy-combustion, circulating fluidized-bed-combustion, OTM Power Cycle, and chemical looping. In a long-term perspective, we expect such power plants to replace those with traditional designs. Hence, the needs and recommendations for research with market implementation beyond 2030 should be focused on other functional and structural materials. These techniques are closely connected to the development of new fossil fuel conversion technologies for which structural materials research is crucial. It is possible that different gasification technologies, oxyfuel technologies, and chemical looping technologies could be mature for large-scale market implementation already in the later part of the 2020/2030 period. However, due to the uncertainty for their market introduction, they are discussed in this section. Specific needs for structural materials research and the functional materials for the CCS technologies are presented in Table 3₂ and discussed below

In the *integrated gasification combined cycle* (IGCC) coal or other fuels are gasified into gas and synthesis gas (syngas) in an optimized manner of the combined cycle for the plant. The capital cost for IGCC is today very large. Separation of oxygen from air is a part of IGCC and is performed cryogenically or with Lithium-exchanged zeolitic adsorbents. Adsorbents, membranes, or hybrids thereof are expected to be more economical than cryogenic separation by 2030 if appropriate research and development efforts are made. Note that pressure swing technologies were expected to already have replaced cryogenic processes for oxygen production; however, this has not yet happened. The search for catalysts that facilitate partial oxidation of the fuel to carbon monoxide and hydrogen could lower the temperature needed for gasification [103]. For the carbon capture step in IGCC, and related processes, the development of solid adsorbents or membranes that allow separation of carbon dioxide from hydrogen should be supported, robustness towards impurities may become an issue. Materials for low temperature and high temperature processes for the CO₂ capture from H₂ should be investigated. One expects that very different kinds of biomass, waste and fossil fuel will be gasified. This diversity puts demands on materials design.

Oxy combustion in pulverised coal, oxy-fuel, offers the advantage that carbon dioxide may be captured rather inexpensively by condensing water from the flue gas that mainly consists of carbon dioxide and water. As for many gasification processes the processes needs pure oxygen and economical separation of oxygen from air is a prerequisite. Adsorption, micro porous membranes, or dense membranes operating with oxygen diffusion, have possibilities to reduce the cost for oxygen enrichment. *Chemical looping combustion* is researched and pilot scale units are being built. The configuration oxidizes the fuel without air in the fuel reactor, oxygen transfer agents are either metal

oxides or carbonates. The metal oxides or carbonates are transformed to metals or oxides and circulated to the air reactor where they are transformed.

Table 2. Specific needs relating to materials to be utilized in capture technologies and fossil conversion technologies for market implementation beyond 2030

| <i>CCS technologies/ materials aspects</i> | <i>Specific needs relating to materials</i> |
|--|--|
| Pre-combustion capture | |
| Functional materials for O ₂ /N ₂ separation | <i>Adsorbents, membranes, or hybrids</i> |
| Functional materials for H ₂ /CO ₂ -separation | <i>Adsorbents, inorganic and polymeric membranes</i> |
| | <i>Robust membranes or adsorbents</i> |
| Structural materials: Fossil fuel conversion technologies | <i>Corrosion resistant high temperature steels, Fe-Ni and Ni-based alloys, ODS, intermetallics, protective-thermal barrier coatings (both metallic and non metallic)</i> |
| Oxy-fuel combustion | |
| Functional materials for O ₂ /N ₂ separation | <i>Adsorbents, membranes, or hybrids</i> |
| Structural materials: Fossil fuel conversion technologies | <i>Corrosion and carburization resistant high temperature steels, Fe-Ni and Ni-based alloys, ODS, intermetallics, protective-thermal barrier coatings (both metallic and non metallic)</i> |
| Functional materials for fuel conversion | <i>Further development (on economy) of carbonate/oxide and metal oxide/ metal pairs</i> |
| Structural materials: Fossil fuel conversion technologies | <i>Corrosion and carburization resistant high temperature steels, Fe-Ni and Ni-based alloys, ODS, intermetallics, protective-thermal barrier coatings (both metallic and non metallic)</i> |

6.3.Recommendations for activities for Market Implementation in 2020/2030 and beyond

The proposed activities classified in different types of research actions are presented in Table 3. In this table; the time for implementation of the proposed research actions is also indicated. Note that some technologies with envisaged implementation beyond 2030 also lead to activities in the timeframe 2010-2020. Special efforts should be made to bring together engineering and chemistry/physics communities, as well as companies of different sizes together in research activities.

Table 3. Proposed activities relating to materials to be utilized in CCS technologies and fossil conversion technologies for market implementation in 2020/2030 and beyond

| <i>Topic</i> | <i>0 to 3 years</i> | <i>3 to 6 years</i> | <i>6 to 10 years</i> |
|---|---|--|----------------------|
| Research programme on functional materials for post-combustion capture | | | |
| Research actions on adsorbents | <i>Applied research on adsorbents (liquids)(e.g.: various amines) for CO₂-over-N₂ separation from</i> | <i>Basic research on non-conventional adsorbents (liquids) (e.g.: ionic liquids, salts ...) for CO₂-over-N₂ separation from flue gas with the aim to reduce the energy requirement for capture ...</i> | |

| | | | |
|---|--|---|---|
| | <i>flue gas with the aim to reduce the energy for capture ...</i> | | |
| Research actions on adsorbents | Basic/applied research⁽¹⁰⁴⁾ on adsorbents (e.g. salts zeolites, microporous carbons, and amine modified nanoporous sorbents) for CO ₂ -over-N ₂ separation from flue gas with the aim to reduce the energy requirement for capture. Also carbonate looping | | Basic research on non-conventional adsorbents (e.g. microporous molecular organics, metal or covalent organic frameworks) for CO ₂ -over-N ₂ separation from flue gas with the aim to reduce the energy requirement for capture ... |
| Research actions on membranes | Basic/applied research on polymeric and inorganic membranes (e.g.: microporous inorganics and regular type of polymer membranes) for CO ₂ -over-N ₂ separation from flue gas with the aim to reduce the energy requirement for capture <i>Demonstration or proof of lifetime >30.000hours</i> | | Basic research on non-conventional polymeric and inorganic membranes (e.g.: metal organic frameworks and microporous polymers) for CO ₂ -over-N ₂ separation from flue gas with the aim to reduce the energy requirement for capture ... |
| Pilot actions on absorbents and post-combustion membranes | <i>Testing already proven absorbents and post-combustion membranes in industrial/operational setting) on pilot scale: performance, cyclability, capacity, economics ,lifetime, etc</i> | | <i>Scale-up absorbents or post-combustion membranes: performance, cyclability, capacity, economics, etc</i> |
| Pilot actions on adsorbents | | | <i>Scale-up test of adsorbents for rapid cycle technologies</i> |
| Research programme on functional materials for oxyfuel and pre-combustion technologies | | | |
| Research actions on oxygen carriers | Applied research on oxygen carriers for CL-technologies with the aim to reach upscalability and improved/optimal CL-performance. Concentration on kinetic limits | | |
| Pilot and demonstration actions on oxygen carriers | Pilot: <i>Scale up and integration of oxygen carriers in CLC-plant, ~MW-scale: performance, economics,(¹⁰⁵)</i> | Demonstration: <i>Scale up and integration of oxygen carriers in CLC-plant, ~100MW-scale, performance, economic, ...</i> | Demonstration: <i>Scaled up oxygen carriers for full-scale power plant: economics, ...</i> |

¹⁰⁴ When it is referred as Basic/Applied it means that some fundamental knowledge exist on the matter and materials options are available on the market for justifying an applied research, but the overall mechanisms of the material behavior are not totally explained and controlled.

¹⁰⁵ Up-scaling should be feasible with specific O-carrier developed in 6FP CLC Gas Power, of course there is always room for improvement so a need for research

| | | | |
|--|---|---|---|
| Sorbent technologies for CO ₂ separation and sorption-enhanced water-gas-shift | Basic research CO ₂ sorbents for CO ₂ /H ₂ S separation from syngas and on PSA cycle design. | Pilot: 10 MW pilot for sorption-enhanced water-gas-shift | Demonstration: > 100 MW demo-plant for SEWGS |
| Research actions on oxygen separation membranes | Basic research on oxygen separating membrane materials with the aim to reach the rate of oxygen flows needed and integrity against steam and SO ₂ at working conditions(Oxygen flow, temperature and pressure) | | Basic and applied research on oxygen separation membranes with the aim to integrate in practical operation |
| Pilot action on oxygen separation membranes | | | Pilot: Integration of oxygen separating membranes in small-scale oxyfuel and pre-combustion power plant concept: performance, economics, |
| Research actions on hydrogen separation membranes | Basic research on hydrogen separating membranes materials with the aim to reach the rate of hydrogen flows needed | | Basic and applied research on hydrogen separating membranes with the aim to integrate in practical operation conditions |
| Pilot action on hydrogen separation membranes | | Pilot: Integration of hydrogen separating membranes in small-scale oxyfuel and pre-combustion power plant concept: performance, economics, | |
| Cross-disciplinary research action for functional materials for CCS | | | |
| Cross-disciplinary research action for functional materials for CCS | Bringing physics/ chemistry and engineering communities closer, and experiments and theory (e.g. ITNs and other training actions).Modelling of reaction kinetic, modelling of materials, ab-initio modelling of surface conditions. | | |
| Research programme on structural materials related to fossil fuel conversion technologies | | | |
| Research actions on structural materials: USC boilers | | Applied research on optimization of F/M steels up to 650 °C; Protective coating system | Applied research on Advanced martensitic steels (up to 17-20%Cr) to be used up to 670°C |
| Research actions on structural materials: USC boiler, pipe work, and steam turbines | Development of test methodologies at operating conditions to improve the testing capabilities (procedures and equipments) of the structural material characteristics; | Applied research on improved (better creep resistance and corrosion) nickel base alloys, optimized processing routes for easy fabrication. | |

| | | | |
|---|--|---|---|
| | <i>Qualification of nickel base alloys and coated systems</i> | | |
| Research actions on structural materials: Advanced steam turbines | | <i>Advanced Fe-Ni alloys (Ni less than 40%) Gradient materials including processing routes for fabrication Coating for steam turbines</i> | |
| Research actions on structural materials: Gas turbine | <i>Development of test methodologies at operating conditions to improve the testing capabilities (procedures and equipments) of the structural material characteristics;</i> | Basic research on improved intermetallic materials; Thermal barrier coatings; production processes for critical turbine components | Basic research on development of oxide fibre/oxide ceramic (CMC) and fibre reinforced materials |
| Research actions on structural materials: Co-combustion | | Basic/applied research: Kinetic and thermodynamic models development for fouling/slagging/corrosion in co-combustion | |
| Research actions on structural materials: Oxy-combustion | | Basic/applied research on refractory materials for peak temperature up to 1800°C | |
| Research actions on structural materials: ODS | Basic research on optimized ODS alloys Applied research on optimization of non-fusion joining techniques | Applied research to develop industrially feasible fabrication routes for ODS | Applied research on qualification of ODS alloys in simulated industrial/operational environment |
| Research actions on structural materials | | Applied research on Life time prediction and assessments of critical components. Models on bases of field data and laboratory work | |
| Pilot actions on structural materials | | Pilot: Protective coating systems under new operating conditions (USC, Gas turbines, Co- and oxy combustion). Cycling conditions | Pilot: Long-term assessment of components and systems for testing durability and reliability of significant plant parts/components based on advanced materials Pilot: Refractory materials developed for |

| | | | |
|---|---|--|--|
| | | | <i>new operating conditions (Oxy combustion)</i> |
| | | <i>Pilot: Production and verification of large components and welded joints (Advanced steam turbine, USC) of currently state of art materials. Cycling conditions</i> | <i>Pilot: Re-qualification of commercial production of ODS alloys for achieving consolidated material production processes and affordable commercial products</i> |
| Research programme on storage technologies | | | |
| Research into standard completions materials (cement, steel, elastomer) | <i>Basic research on standard completions materials (cement, steel, elastomer) with adequate long-time behaviour when exposed to CO2</i> | <i>Pilot to validate materials in real-life conditions and enable further upscaling</i> | |
| Research into new well materials (including composites) | <i>Basic research on new well materials (including composites) for better long-term resistance to CO2, impurities and saline brine attacks</i> | <i>Pilot to validate materials in real-life conditions and enable further upscaling</i> | |
| Research into materials for leakage repair | <i>Basic research on materials for better repair of leakages;</i> | <i>Pilot to validate materials in real-life conditions and enable further upscaling</i> | |
| Materials for favouring dissolution of CO2 and catalysts for in situ mineralisation | <i>Basic research on materials for favouring dissolution of CO2 and catalysts for in situ mineralisation</i> | <i>Pilot to validate materials in real-life conditions and enable further upscaling</i> | |
| Reference test facilities | | | |
| EU test facility, standardization of materials* | | | |
| A virtual centre that validates outcomes from pilot scale project/ demonstrators | | | |
| International cooperation | | | |
| Outside EU | <i>US, China, Canada</i> | <i>US, China, Canada (India?),</i> | <i>US, China, Canada, (India?)</i> |

*The EU test facility should not necessarily be established physically. One can imagine a network between existing EU test facilities and existing national test facilities within the European Countries including selected international partners.

Research activities relating to materials to be utilized in CCS technologies and fossil conversion technologies for market implementation beyond 2030 should be focussed in developing tailored materials with the required specifications by using computational tools for materials design, linked with multi-scales simulation of materials behaviour understanding. Computational approach should be

supported by exhaustive micro/nano structure characterization taking advantage of the foreseen huge development of equipment for materials characterization.

APPENDICES SECTIONS 1 AND 3 – FUNCTIONAL MATERIALS

APPENDIX 1 – Principal CCS technologies and example functional materials

Table 1. Processes and example functional materials for CCS

| CCS Technology | Process | Notes / Example materials |
|-------------------------|-------------------|--|
| Pre-combustion capture | Physical Solvents | Rectisol, Selexol, Purisol. |
| | Solid Sorbents | Low temperature – activated carbons, zeolites, other porous solids |
| | | High temperature – SEWS type materials |
| | Membranes | Metal and ceramic types for CO ₂ – H ₂ separation WGS membranes |
| Post-Combustion Capture | Chemical Solvents | Alkanol amine based materials, hindered and advanced solvent systems |
| | Solid Sorbents | Low temperature - zeolites, MOFs, activated carbons, supported amines (silica, polymer etc supports) hydrotalcites |
| | | High temperature – CaO, etc |
| | Membranes | Functional, separation membranes Contact membranes – for novel solvent contact systems |
| Ionic Liquids | | |
| Oxyfuel-combustion | Membranes | OTM / ITM power cycle |
| | | Gas separation (air separation) |
| | Chemical looping | Metal oxides. |

APPENDIX 2 – Main Challenges for current CCS materials and technologies, influence of gas composition and process conditions.

The environment in which the functional materials are placed will greatly impact on their stability and lifetime. From the combustion of fossil fuels, especially coal which will contain a wide range of heteroatoms and inorganic components. This gas composition will vary depending on the location of the capture unit in the power plant, for example before or after flue gas desulphurisation. Example composition and physical conditions of a post combustion flue gases from coal combustion before and after flue gas desulphurisation treatment, as well as from natural gas combustion are presented in Table 1. Similar gas compositions can be produced from industrial processes for example iron and steel production. Gas composition is generally more variable and a function of the plant and process involved. However, the separation technologies being developed for CCS could find application in these processes, although plant integration will require careful design. For post-combustion capture, water and oxygen will be always present in the flue gases irrespective of the fuel or pre-treatment. Functional materials for carbon capture will have to be stable with these gas components present as their removal prior to the capture process will involve a significant energy penalty. Typical gas compositions and example temperatures of operation are presented in Table 2. CO₂ concentration in the flue gas can reach values of around 92% in oxy-fuel plants. Trace gas components in the flue gas also lead to significant challenges for materials. SO₂ is more acidic than CO₂ and will likely react aggressively with any basic surface sites, especially amines. Cos may also be present in gas streams and react to cause degradation of functional materials. While the concentration of these components in the gas stream are low after treatment to levels required for amine capture (Table 2), they will still

present challenges for materials with respect to their degradation and long term lifetime in the capture systems where the materials are to be cycled numerous times.

Table 2. Typical flue gas composition and potential conditions from coal and gas combustion.

| Component | Post-combustion Capture | | Pre-combustion Capture | |
|------------------|-----------------------------|--------------------------------|---------------------------|-----------|
| | Coal (no FGD) ⁴¹ | Coal (after FGD) ⁴¹ | Natural Gas ⁴² | |
| N ₂ | 75-80% | 75-80% | 75% | 0.25 |
| CO ₂ | 12-15% | 12-15% | 3% | 35.5 |
| H ₂ | 0 | 0 | 0 | 61.5 |
| SO ₂ | 1800 ppm | 60 - 10 ppm ¹ | <10ppm | - |
| NO _x | 500 ppm | 50 ppm ¹ | 50ppm | - |
| H ₂ O | 5-7% | 5-7% | 7% | 0.2% |
| O ₂ | 3-4% | 3-4% | 13-15% | - |
| H ₂ S | 0 | 0 | 0 | 1.1% |
| CO | <100 ppm occasionally | <100 ppm occasionally | <5ppm | 1.1% |
| Hg / As | 5000ppm ppb | 5000ppm ppb | 0 | trace |
| Particulates | 10 mg/Nm ³ | 10mg/Nm ³ | not present | |
| Pressure (MPa) | 0.1 | 0.1 | 0.1 | 4.0 – 5.0 |

Based on the performance and key technical issues associated with current capture technologies, Table 3 summarises the key potential mechanisms of degradation and loss of functional materials based on those experienced in solvent capture systems [106]. As well as loss and degradation associated with composition of the gas streams, degradation and sintering can also result from the cycling of materials, for example temperature and pressure swing as well as physically moving materials resulting in attrition and materials loss.

Table 3. Key routes to materials degradation

| Process | Potential and Impact |
|---|--|
| Chemical degradation / alteration | A potential problem for chemically active functional materials where repeat cycles can lead to degradation. For example carbonate polymerisation for 1° or 2° amines as observed in amine solvents above 100 °C ¹ . |
| Thermal Degradation | Thermal breakdown of materials during capture and regeneration cycles. For some high temperature materials this can result from agglomeration and sintering reactions. |
| Oxygen | Oxidative degradation reported to be main degradation processes for solvent systems ³ . Will have a potential impact on all materials in post combustion operation |
| Interaction with other gases (SO₂, NO₂, HCl, H₂S, HCN, COS) | Other acid gases reacting irreversible with CO ₂ reactive sites. Resulting in loss of capacity and eventual breakdown of materials. |
| Particulates | Fly ash not removed from combustion process in the case of coal. Causing clogging of porous materials, associated systems. |
| Water | Reduction in CO ₂ capture capacity (competition for pores), hydrolysis, swelling, pore blocking, dissolution, corrosion and hydrolysis reactions. |
| Attrition | Break down of particles / pellets of solid materials in the capture system and subsequent loss. |

¹⁰⁶ R. M. Davidson, 2007. Post-combustion carbon capture – solid sorbents and membranes.

APPENDIX 3 – Development routes for Ionic Liquids

Development of ILs for CCS involves the modification of their chemistry for specific applications. ILs can be classified into 2 broad types, physical ILs which act as physical solvent and task specific ILs that contain functional groups to enhance their performance for a certain application, for example amines in application to CCS. The two different types of IL have found application in pre and post combustion capture respectively. Physical solubility is attractive due to the process having a low regeneration energy and is attractive for pre-combustion capture where high pressure CO₂ is present. However, for post combustion capture the resultant CO₂ capacity is too low resulting in a research focus to increase capacity by adding amine chemical functionality [107, 108, 109]. A wide range of ILs have been developed and tested with the aims of maximising capture capacity. Research is focussed on determining the performance of the ILs as well as their impact on corrosion, feasibility of process designs, thermodynamics, synthesis, and molecule design.

APPENDIX 4. Development of Membranes for CCS application.

In general, for application for post-combustion capture current membranes generally do not have the selectivity needed to be competitive with amine based systems. This has prompted materials development to incorporate amine functional groups, for example by the modification of inorganic silica membrane [110, 111, 112]. Different membranes have been developed for higher temperature operation, for example zeolite based membranes which operate at around 400 °C. Polymeric membranes have also demonstrated promise in this application (MTR USA). Key challenges still exist for membranes in terms of their limited temperature range of operation, depending on the membrane type a low tolerance to flue gas impurities and for the process a parasitic load to create the pressure gradient across the membrane. An alternative use for membranes for post combustion capture is to use them as essentially a gas – liquid contactor by using gas permeable membranes to contact flue gas with amine solvents. This has potential benefits in increased contact efficiency and reduction of combustion impurities (ie SO_x and NO_x) contacting the solvent [113]. As previously the selectivity and permeability of the membranes are key properties and the subject of research.

For application in pre-combustion capture, H₂ separation membranes have been developed using various materials, for example palladium and its alloys, alumina and silica. The most appropriate membrane types for pre-combustion capture applications, based on temperature range and hydrogen selectivity are dense metallic and porous ceramic membranes [114]. Silica membranes have been synthesised by a range of techniques, for example sol-gel synthesis and chemical vapour deposition / infiltration using a range of precursors. Research has also focussed on chemical modification of separation layers, for example through the modification with MgO CaO and Nickel. Metal based membranes, specifically Palladium based have demonstrated high hydrogen selectivity and permeability and are possibly the most promising route for hydrogen separation [115]. However, due to their high costs and reactivity towards H₂S, recent research has focussed on reducing the amount of palladium whilst using a substrate to improve performance, for example through lowering the film

¹⁰⁷ J. H. Davis, Abstr Pap Am Chem S, 2003, 225, U952-U953.

¹⁰⁸ E. J. Maginn, J. L. Anderson, J. Dixon, W. Shi, E. Mindrup, W. Schneider and J. F. Brennecke, Abstr Pap Am Chem S, 2008, 235, -1053.

¹⁰⁹ C. M. Wang, H. M. Luo, D. E. Jiang, H. R. Li and S. Dai, *Angew Chem Int Edit*, 2010, **49**, 5978-5981.

¹¹⁰ J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, *Int J Greenh Gas Con*, 2008, 2, 9-20.

¹¹¹ R. P. Singh, J. D. Way and S. F. Dec, *J Membrane Sci*, 2005, **259**, 34-46.

¹¹² R. P. Singh, J. D. Way and K. C. McCarley, *Ind Eng Chem Res*, 2004, 43, 3033-3040.

¹¹³ M. Teramoto, N. Ohnishi, N. Takeuchi, S. Kitada, H. Matsuyama, N. Matsumiya and H. Mano, *Sep Purif Technol*, 2003, **30**, 215-227.

¹¹⁴ S. C. A. Kluiters, 2004. Status review on membrane systems for hydrogen separation. Intermediate Report of EU project MIGREYD MNE5-2001-670.

thickness to save costs and increase hydrogen flux. Additionally palladium alloys, for example with copper have been explored to improve resistance to poisoning by H₂S, increase H₂ permeability and reduce embrittlement [115]. Metal based membranes also have a potential application in enhanced water gas shift reaction, where membranes can be employed to continuously remove CO₂. Typically these will be palladium-based hydrogen permeable membranes. One challenge in this technology is that a membrane may be subject to poisoning or any other reduced functionality because of substances, like sulphur compounds and heavy metals, in the syngas.

APPENDIX 5. Key EU research activities

The principal academic and research groups in the EU are part of the EERA CCS Joint Programme, which involves over 30 members from 12 countries. To meet the principal aims of EERA project partners have who have committed more than 270 person years /year to carry out joint R&D activities. The following table gives the key program members and a brief summary of materials developments at each institution.

Functional Materials

| Institute | Country | Solvents | Membranes | Solid Sorbents | Chemical Looping Combustion | Enhanced Water Gas Shift |
|--|-------------|----------|-----------|----------------|-----------------------------|--------------------------|
| IFP | France | x | | | x | |
| SINTEF | Norway | x | x | x | | x |
| ECN | Netherlands | | x | x | x | x |
| TNO | Netherlands | x | | | x | |
| RSE | Italy | | x | x | | x |
| IFE | Norway | | | x | | |
| ENEA/CNR | Italy | x | | x | x | |
| LNEG | Portugal | x | x | | | |
| UKCCSC- University of Nottingham | UK | | | x | x | |
| UKCCSC- Imperial College | UK | x | | x | x | |
| UKCCSC – SCCS | UK | x | x | x | | |
| VTT | Finland | | | | x | |
| VITO | Belgium | | x | | x | |
| CSIC | Spain | | | x | | |
| GKSS | Germany | | x | | | |
| Chalmers UT | Sweden | | | | x | |
| FZJ | Germany | | x | | | |
| Fraunhofer | Germany | | x | | | |
| POLIMI | Italy | | x | x | | x |

¹¹⁵ H. D. Tong, J. W. E. Berenschot, M. J. De Boer, J. G. E. Gardeniers, H. Wensink, H. V. Jansen, W. Nijdam, M. C. Elwenspock, E. C. Gielens and C. J. M. van Rijn, *Journal of Microelectromechanical Systems*, 2003, **12**, 622-629.

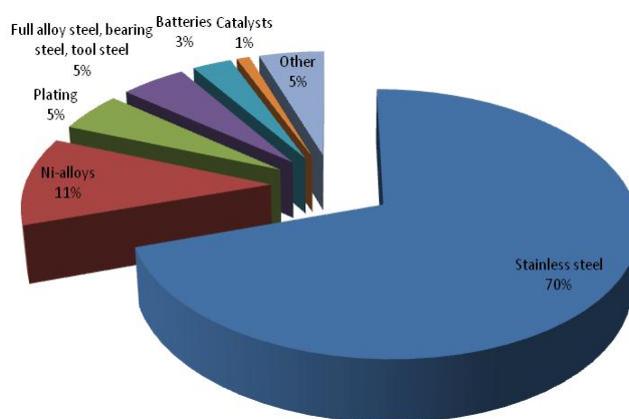
APPENDIX 6. Brief information about the principal minerals/elements with supply risks

Nickel

The vast majority of reserves are found outside of the European Union, most notably in Oceania (Australia and New Caledonia), Russia and the Americas (Canada, Cuba, Brazil). More than 10% of the reserves are located in New Caledonia, which is part of the French territory. As a result, mine production mainly takes place outside the EU whose mine output (in New Caledonia, Greece, Spain and Finland) represents only 8.6% of world total.

Nickel demand in the EU is quite important: five out of the top 10 nickel-using markets are located in the European Union. Germany is the fourth most important nickel-using market. Other countries with high nickel demand are Italy, Belgium, Spain, and Finland. Nickel use in these markets is essentially linked to production of stainless steel - the main downstream use of nickel.

- **Stainless Steel:** Nickel is used in steel to increase strength. For instance, nickel-containing alloys are essential in many applications (e.g. turbines, jet engines). Nickel alloys are also resistant to corrosion.
- **Non-ferrous Alloys:** about 11% of Nickel is used as an alloy with non-ferrous metals in various applications.
- **Plating:** Nickel is used in plating to increase corrosion resistance, especially in medical equipment, construction materials and household cutlery/fittings. Plating is also used in CD/DVD manufacture.



Given its unique characteristics, nickel is difficult to substitute for the production of alloys – any reduction in use results in a reduction in performance. In other applications, such as the hot parts of jet engines and land turbines, there may be currently no suitable alternative to a nickel containing material.

On the supply side - The operation of the nickel industry in Europe is challenged by high operating costs related amongst other factors to a strict regulatory framework especially in the field of EHS legislation. Moreover, supply of concentrates and intermediates containing nickel is challenged by inappropriate classifications, affecting transport as well as storage and processing. All these factors will lead to, as a consequence, that nickel production is shifted to countries outside EU, resulting in higher dependency on import and competitive advantages for uses in downstream industries in regions outside EU.

On the demand side, nickel finds application in a number of downstream uses, which are highly critical for the future of the EU. Most of the technologies and practices, which are playing a central role in mitigating the climate change will rely on use of nickel and nickel containing alloys.

Chromium

Around 94% of global chromite production is destined for use in the metallurgical industry, for the production of ferro-chrome, with the remainder produced for use in the foundry, chemical and refractory sectors. World mine production of chromite therefore follows the pattern of world ferro-

chrome production. Around 70% of global chromite production is consumed domestically in ferro-chrome production in the country of origin. Supply situation of ferro-chrome is of strategic importance for steel production.

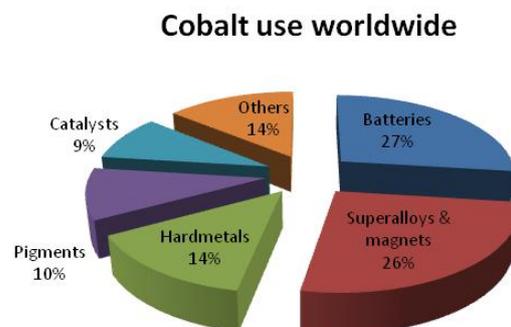
Finland and Turkey are the only countries in Europe with significant chromium production, which amounted to 9% of world production. Relating to the fact that 70% of worldwide chromite production is used in the country of origin to produce ferrochrome, Europe is considered to be import dependent on chromite ore as well as on ferro-chrome.

Cobalt

Among other uses, cobalt is a fundamental element in superalloys/wear resistant alloys: historically the major end-use of cobalt, which is alloyed with other metals (mostly nickel, but also iron), was to provide superior thermal, corrosion and wear resistance.

There is no mine production of cobalt in Europe. In view of the EU industry fabric, however, the distribution of cobalt consumption in the EU significantly differs from its worldwide distribution.

In particular, there is no production of rechargeable batteries and only a small production of Co catalyst within the EU. However, the EU cobalt industry is a major world supplier of cobalt chemicals for both these applications.



The growth of its use in various sectors in Asia will shift market demand for cobalt products towards these regions (e.g. rechargeable batteries production is already concentrated in Asia) and will therefore require high export competitiveness from the EU cobalt industry.

The growth of chemical applications will result in an increased demand for cobalt chemicals, in particular for Co-based catalysts (e.g. for gas-to-liquid technology for the processing of natural gas into synthetic diesel fuel), and for rechargeable batteries whose fast growth of production is likely to offset some substitution of cobalt by other metals (manganese and nickel).

Both trends will require the EU cobalt industry to continuously improved competitiveness on export. Export outlets will become even more important for the EU cobalt enterprises than they are now. Competitiveness and levelled playing-field in access to raw materials will in this respect remain a key factor to secure such competitiveness on export.

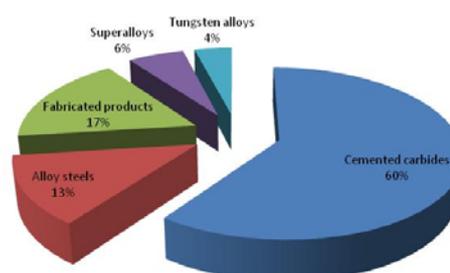
Tungsten

Almost 78% of world's production of tungsten comes from China. However, China only exports tungsten in value added forms meaning that the main tungsten raw materials available for export are APT (ammonium paratungstate) and oxide. Europe imports about 26% of World's production. Overall the EU is import dependent.

On the supply side, the main concern relates to competition with China for both access to raw materials and the sale of products.

On the demand side, the EU tungsten industry has historically developed a world leadership as top ranking suppliers on the global market. The EU market is the industry's natural outlet but the European tungsten resources are not sufficient to cover the demand of the European tungsten downstream industry.

According to the ITIA, recycling is an important factor in the world's tungsten supply, and the tungsten processing industry is able to treat almost every kind of tungsten-containing scrap and waste to recover



tungsten, and, if present, other valuable constituents. Tungsten scrap, due to its high tungsten content in comparison to ore, is a valuable raw material.

Rhenium

Rhenium is a critical component in nickel-based “superalloys,” (about 70% of rhenium is used for such use) which are capable of functioning under very high stress. These superalloys are used in the jet engines of military aircraft and some of the world’s most energy-efficient gas turbines. In recent years its price has increased sharply due to its use in turbine blades.

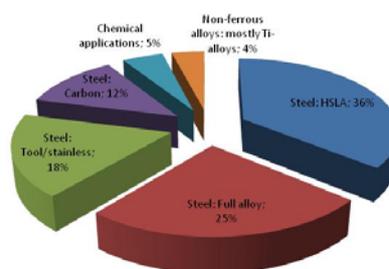
Chile is the world's largest rhenium producer, being responsible for half of the world production (more according to other estimates), being followed by the USA. Some attempts have been launched to develop alternative superalloys that use less rhenium.

Vanadium

China and South Africa are together responsible for more than 70% of the world production. In the third place is Russia with approximately 26% of the total world production. South Korea is the largest exporter to the EU market, with a share of over 90%.

According to information from the USGS the recycling rate of vanadium is low. Vanadium can be recycled from certain tools and catalysts, but the rate is only a few percents. The bulk of vanadium used in special alloys is distributed in the dross during re-melting.

Regarding substitution, steel containing various combinations of other alloying elements can be substituted for steels containing vanadium. Certain metals, such as manganese, molybdenum, niobium (columbium), titanium, and tungsten, are to some degree interchangeable with vanadium as alloying elements in steel.



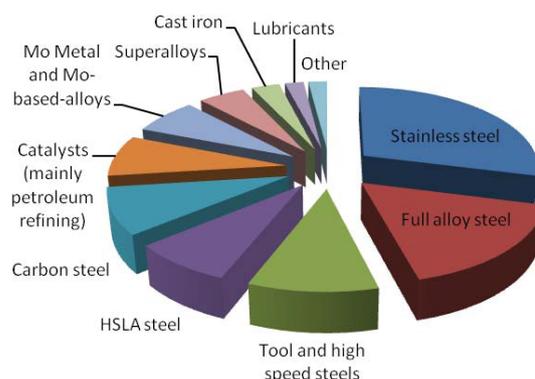
Molybdenum

Molybdenum forms alloys with many other metals such as aluminum, tungsten, lead, niobium, chromium, manganese and iron. In many of these alloys a small share of molybdenum increases the hardenability, strength, toughness and corrosion resistance, which explains its importance in the iron, steel and superalloy industry.

The biggest deposit of molybdenum in Europe is situated in Norway, though there is no molybdenum production within the EU at the moment. As a consequence the EU’s molybdenum consumption is covered by imports, mainly from the United States and from Chile. World resources are adequate for projected demands in the foreseeable future.

On the supply side, the EU molybdenum industry is sourcing all primary feed of raw material from outside the EU, with a strong reliance on Chinese producers as regards ores, concentrates, oxides and molybdates.

On the demand side, the EU molybdenum industry has historically developed a world leadership as top ranking suppliers on the global market for mill products. The EU market is the industry’s natural outlet but many industry consuming molybdenum based products are located in the USA and Asia. These markets are increasingly important markets



for the EU molybdenum industry.

Niobium

Niobium has an important impact as an alloying element in nickel base superalloys. Niobium alloys have become increasingly important in industrial applications, where superior heat and corrosion resistance are required. These properties are required for applications such as in land based turbines and aircraft turbine engines, petrochemical industry, on and off shore oil and gas production, power generation, thermal processing, Typical types of superalloys contain up to 5% niobium.

The bigger world producers is Brazil with about 75% of production followed by Canada with a about 7%.

The amount of niobium recycled is not available, but it may be as much as 20% of primary niobium. On the supply side, the EU niobium industry is sourcing its entire primary niobium feed from outside the Community as Europe is not endowed with any niobium resources. The main raw materials imported by the EU niobium industry are ores and concentrates. As the main resources and the main producer is located in Brazil the EU niobium industry is facing as quasi monopolistic situation on the supply side with indeed presents a certain risk.

On the demand side, the EU niobium industry has historically developed amongst the top ranking suppliers on the global market.

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