CO_2TRACCS meeting – 2 November 2012
International Workshop,
ISPE headquarter, Bucharest – Romania

Task 2.3: Corrosion risk

Potential Flue Gas Impurities in Carbon Dioxide Streams Separated from Coal-Fired Power Plants located in Black Sea region

Dimityr Popov

Technical University of Sofia, Bulgaria, e-mail: dpopov@tu-sofia.bg

Content

1. ***Overview of the work within Task 2.3 Corrosion risk;***
2. ***Deliverables/Milestones;***
3. ***Delivery D2.3: Determination of the CO_2 streams composition oriented to typical Black Sea region located lignite fired power plants. (M8);***
4. ***Tasks for the next 10 months***

Task 2.3. Corrosion risk: main sub-tasks

1. CO_2 streams composition evaluation related to carbon capture processes within Black Sea region power generation context;
2. Understanding the role of typical low grade coal induced impurities such as H_2S, SO_2, and NO_x as well O_2 on the corrosion behaviour of different pipeline construction materials. The analyses should be based on a set of corrosion experiments conducted in the autoclave corrosion test system.
3. Development of mitigation strategy for corrosion protection of CO_2 transport pipelines with CO_2 streams having high level of impurities by utilizing adequate carbon capture technology and/or new or improved pipeline construction materials and techniques.

Deliverables/Milestones related to Task 2.3. Corrosion risk

D2.3: Determination of the CO_2 streams composition oriented to typical Black Sea region located lignite fired power plants. (M8);

D2.4: Realization of corrosion test program with pipeline construction materials in supercritical CO_2-water environments in the presence of different impurities (M18)

D2.5: Development of mitigation strategy for corrosion protection of CO_2 transport pipelines accounting for the CCS induced impurities (M22)

Internal corrosion protection of CO_2 pipelines: state of the art

CO_2 transporting pipelines in USA

source: http://www.kindermorgan.com/business/co2/article_052001.pdf

Internal corrosion protection of CO_2 pipelines: state of the art

CO_2 transporting pipelines in USA and future CO_2 pipelines in Europe

1. ***In USA all existing 3900 miles of pipelines transporting CO_2 are designed and used for enhanced oil recovery (EOR) operations;***
2. ***In the US, the transported CO_2 in the most cases is produced out of natural reservoirs, as opposed to anthropogenic $CO_{2;}$***
3. ***These enhanced oil recovery (EOR) CO_2 pipelines mostly cover sparsely populated areas;***
4. ***The type of safety regulations applied in the US differ from those implemented already in some countries in Europe;***
5. ***Thus, the CO_2 specifications in the US should only act as a starting point for the discussion of impurity limits for anthropogenic CO_2 related to CCS.***

Internal corrosion protection of CO_2 pipelines: state of the art

Water content problem

1. ***All of the operational CO_2 transmission pipelines are manufactured from regular carbon steel which is essentially non-corrosive in pure CO_2;***

2. ***Trace water dissolved in the CO_2 stream is not a significant problem.***

3. ***However, in the presence of free water, highly corrosive carbonic acid is formed and it has been reported that carbon steel can corrode at rates of more than 10 mm/year in wet pure CO_2;***

4. ***The water content in the CO_2 stream should be low enough to ensure that no free water can be formed at any part of the pipeline;***

5. ***A minimum safety factor of two between the specified maximum allowable water content and the calculated minimum water content that may cause water drop within the operational envelope should be specified;***
6. ***Drying of captured CO_2 costs both money and energy and dependent on technology choice, can reduce flexibility in the CCS chain. Therefore a water concentration limit should not be more stringent than necessary!***

Internal corrosion protection of CO_2 pipelines: state of the art

Water content limits

Reference	ppm (by mol)
Kinder Morgan - US pipeline operations (Maximum)	640
Mohitpour et al (2003)	380-640
Odru et al (2006)	50
DYNAMIS	500

1. **The DYNAMIS (2007) project reports that water concentration in a CO_2 pipeline with a good safety margin for avoiding corrosion is 500 ppm;**
2. **The DYNAMIS figure of 500 ppm is an attempt at considering the role of impurities on the corrosion behaviour of CO_2 streams coming from different carbon capture processes as the allowable water content may need to be lower in the presence of other impurities, such as O_2, SO_x and NO_x, as they lower the solubility limit;**
3. **The corrosion protection within this water concentration limit is not proved to demonstration at laboratory scale;**

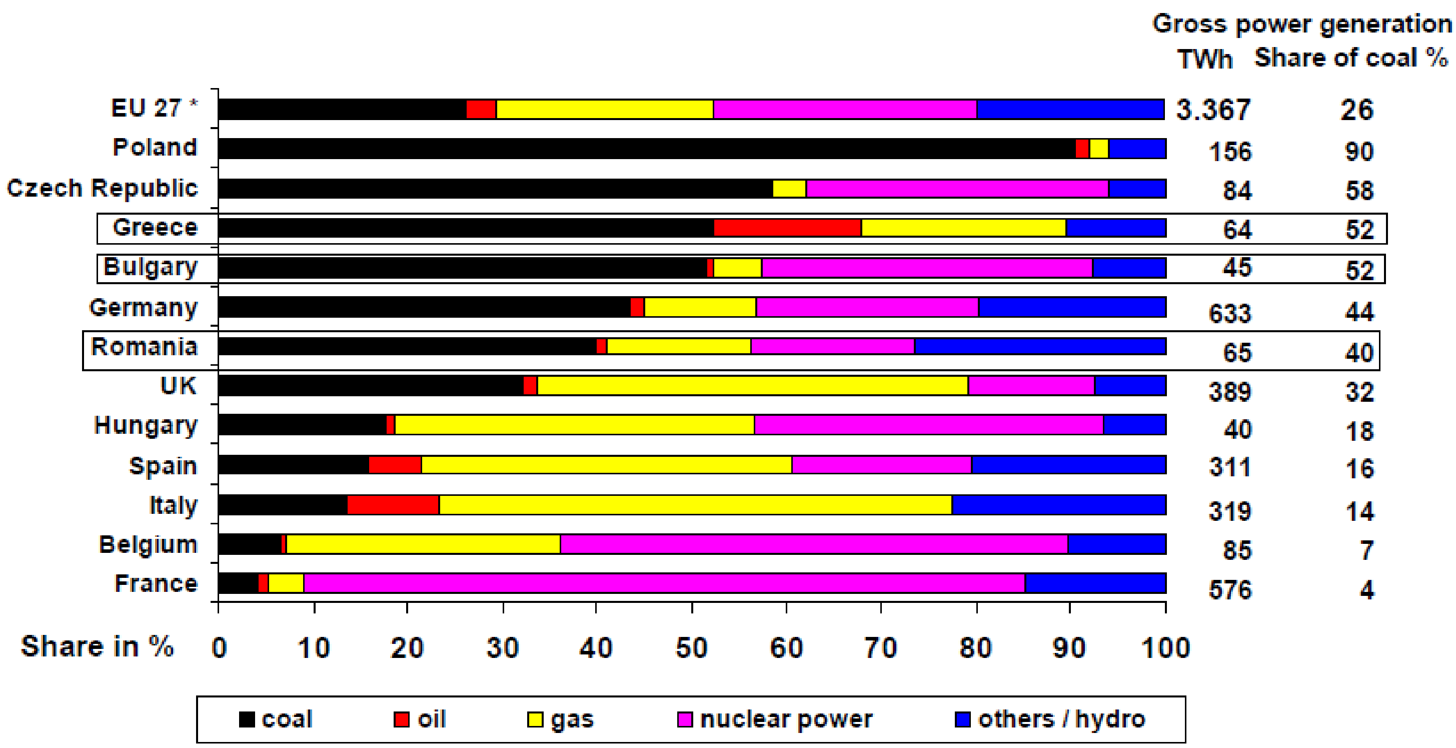
The allowable water content may need to be lower in the presence of other impurities, such as O_2, SO_x and NO_x!?

The presence of H_2S, SO_x and NO_x in CO_2 streams can vary due to:

1. ***The specific components in the fuel;***
2. ***The type of process that is used to convert the fuel into usable energy;***
3. ***The amounts and proportions of various impurities removed from a raw flue gas stream before CO_2 capture (e.g., through de-NOx and/or desulphurisation processes);***
4. ***The CO_2 capture process;***
5. ***CO_2 compression and purification at the outlet of the power plant.***

Fuel base in Black Sea Region

Structure of Power Generation in selected EU-Countries 2008



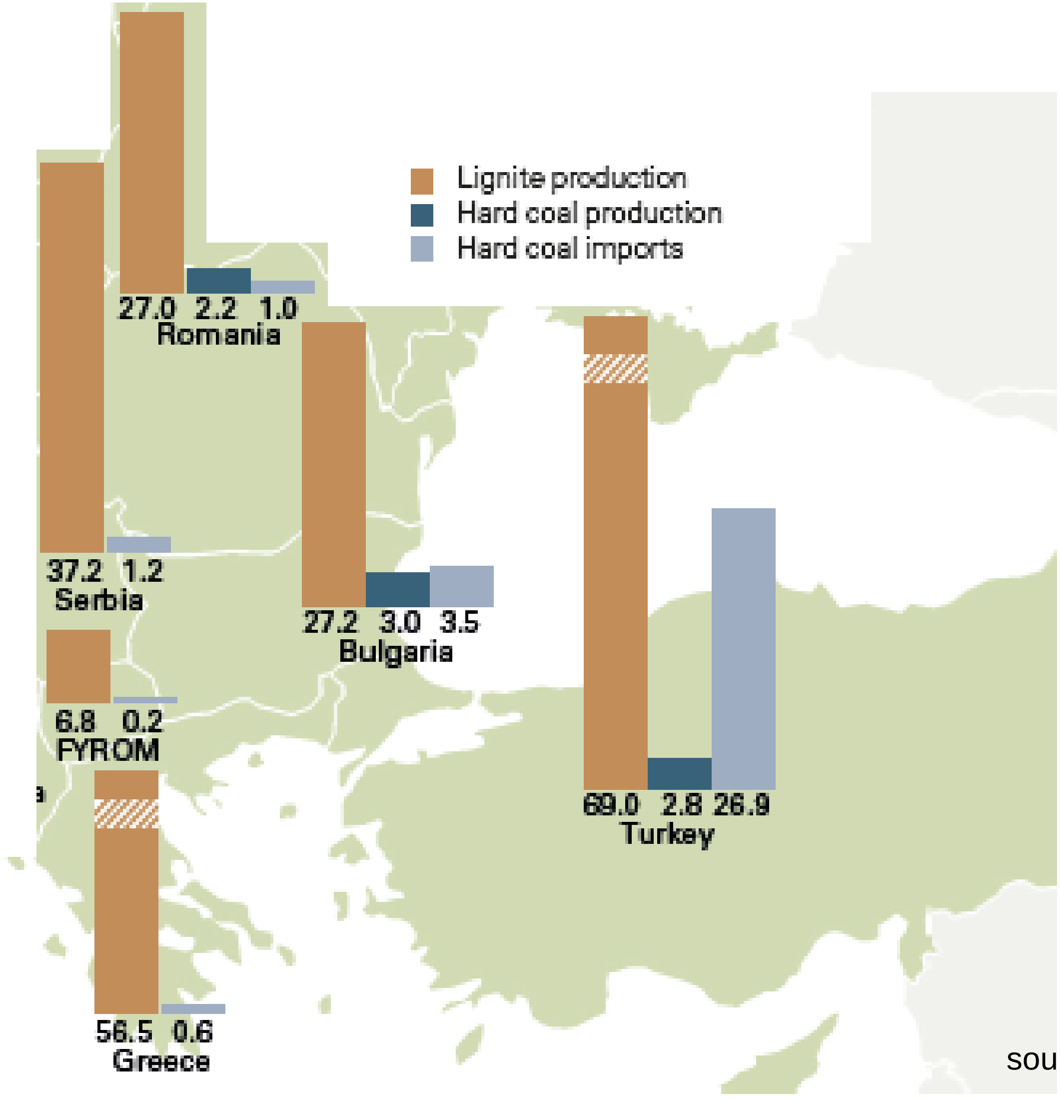
* Peat and oilshale included in Other/Hydro

Data as per: 06/2010

Source: EUROSTAT – Energy / Yearly statistics 2008

Power generation sector in Black Sea Region countries is dominated by the combustion of fossil fuels!

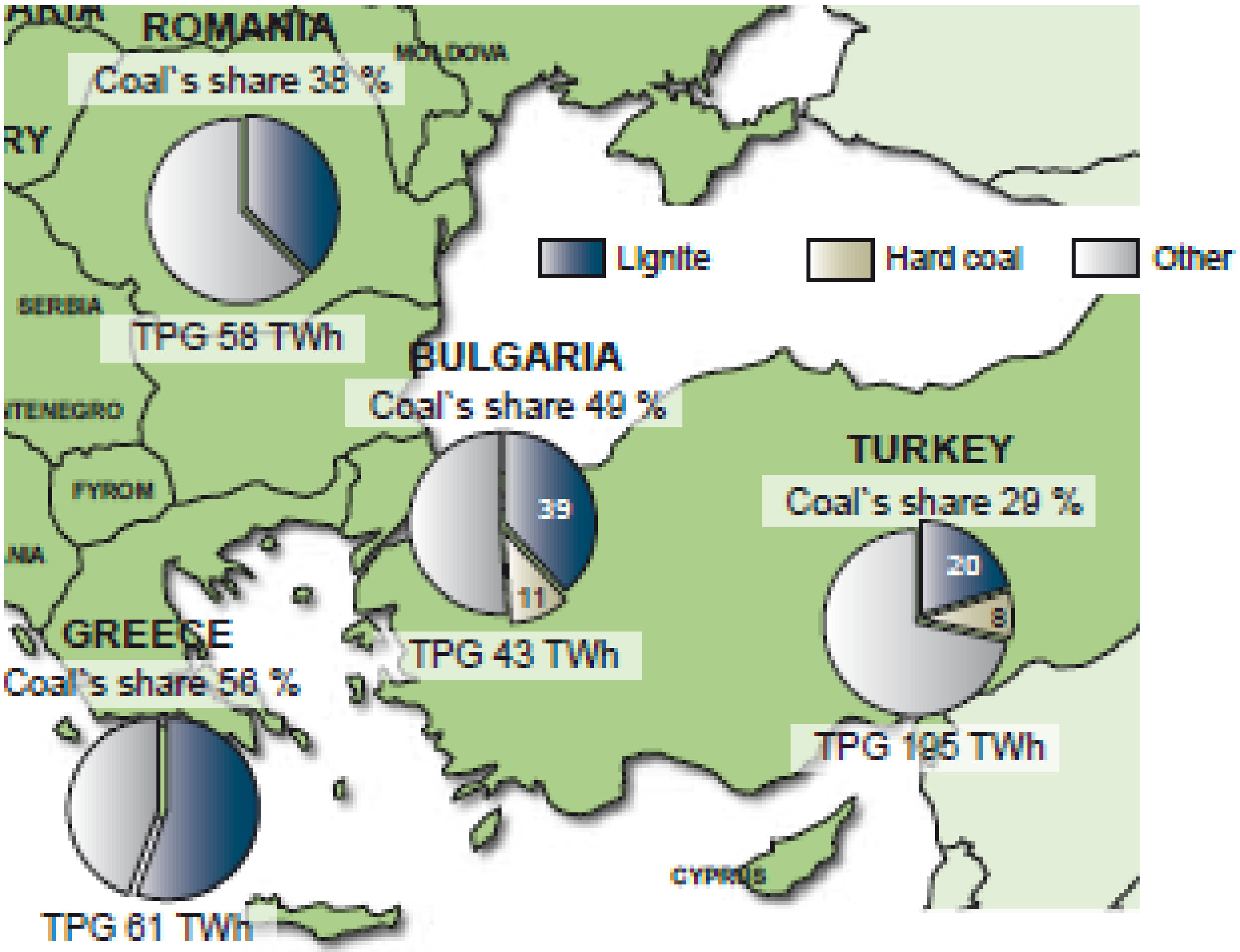
Coal in Black See Region Countries



source: http://www.euracoal.be

All Black Sea Region countries mine huge amount of lignite every year

The role of coal for power generation in Black See Region Countries



source: http://www.euracoal.be

Local lignite is the main power plants fuel in Romania, Bulgaria and Greece

Lignite in Black Sea Region

1. Large lignite production in Black Sea Region contributes significantly to the local energy self-sufficiency;
2. The only problem is that this fuel is usually with very bad quality.

Greek Lignite 2 – Ultimate analysis

	Basic	Worst 1	Worst 2	Best 1	Best 2
Hu (kJ/kg)	5443	4438	4438	6908	6908
Hu (kcal/kg)	1300	1060	1060	1650	1650
Moisture	53.2	50.13	60	51.37	48.5
Ash	16	20	12.78	11	14.19
Volatiles	17	15.8	14.5	19	19.8
Fixed carbon (incl. CO2)	13.8	10.07	12.47	18.32	17.17
Carbon	17.82	14.8	15.4	21.1	21
Hydrogen	1.44	1.28	1.36	1.98	1.92
Sulphur	0.45	0.4	0.42	0.6	0.6
Nitrogen	0.6	0.6	0.6	0.6	0.6
Oxygen	8.29	7	7.34	10.55	10.39
Carbon Dioxide	2.2	2	2.1	2.8	2.8

General data for the local lignite used in Romania

No.	Indicator	MU	Minimum	Maximum
1.	Lower heating value,	kJ/kg	6,700	÷ 8,790
2.	Total humidity content, Wti	%	38.30	45.90
2.	Ash, at origin A'	%	16.90	30.50
4.	Carbon content at origin C'	%	19.00	25.00
5.	Hydrogen content at origin H'	%	1.89	2.53
6.	Nitrogen content at origin N'	%	0.50	0.80
7.	Sulphur content at origin S'	%	0.69	1.11
8.	Oxygen content at origin O	%	8.00	10.00

General data for the local lignite used in Bulgaria

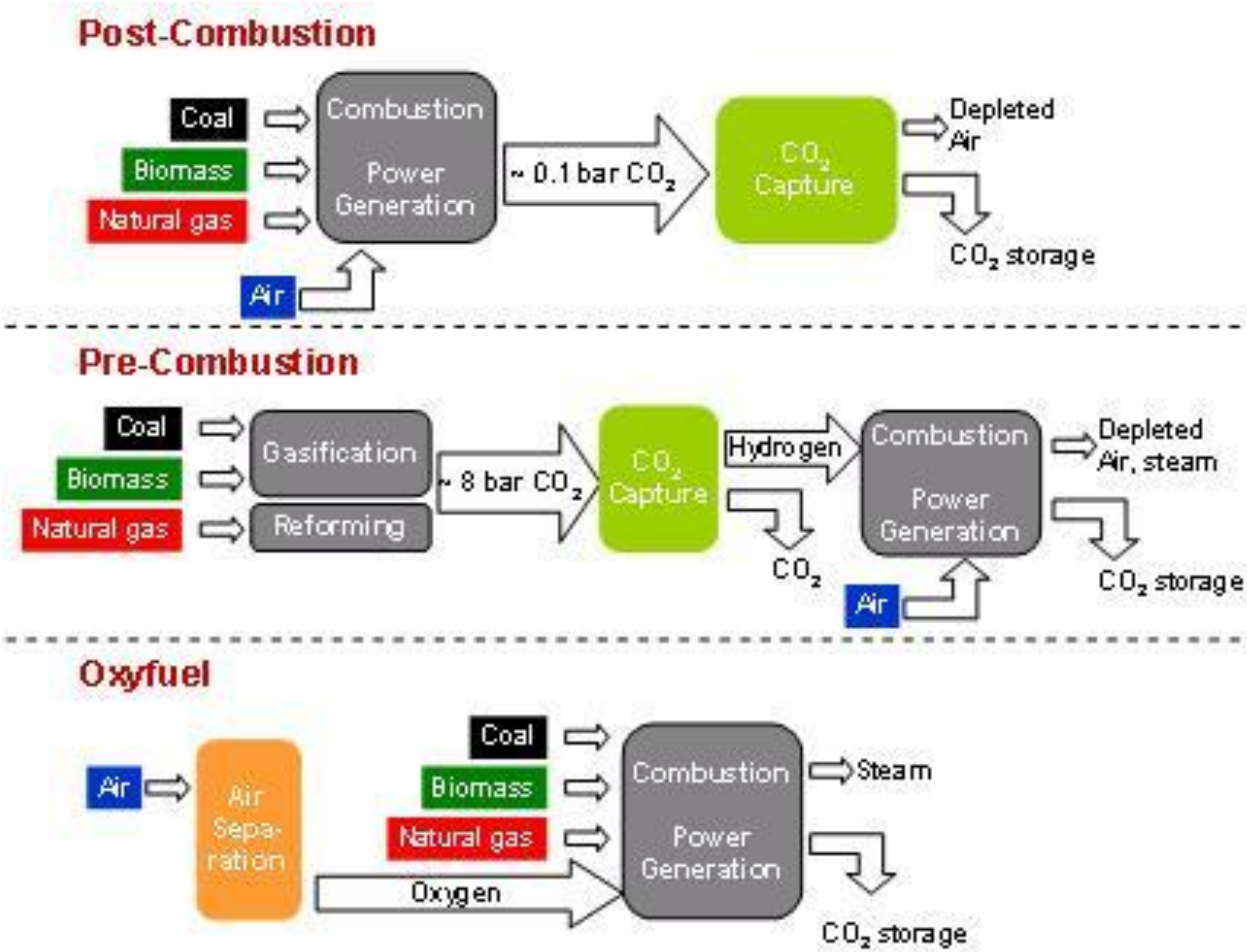
No.	Indicator	MU	Minimum	Maximum
1.	Lower heating value	kJ/kg	5652	7746
2.	Total moisture content, a.r.	%	50	60
3.	Ash content, a.r.	%	17	45
4.	Carbon content a.r.	%	15	23
5.	Hydrogen content a.r.	%	1.8	2.3
6.	Nitrogen content a.r.	%	1.1	1.3
7.	Sulphur content, a.r.	%	2.2	2.8
8.	Oxygen content a.r.	%	6.0	7.5

The major advantages of firing lignite are that;

- it is relatively abundant (especially in Turkey, Greece and Bulgaria);
- relatively low in cost since it is surface mined;
- in some case low in sulphur content which can reduce the need for post-combustion sulphur emission control devices

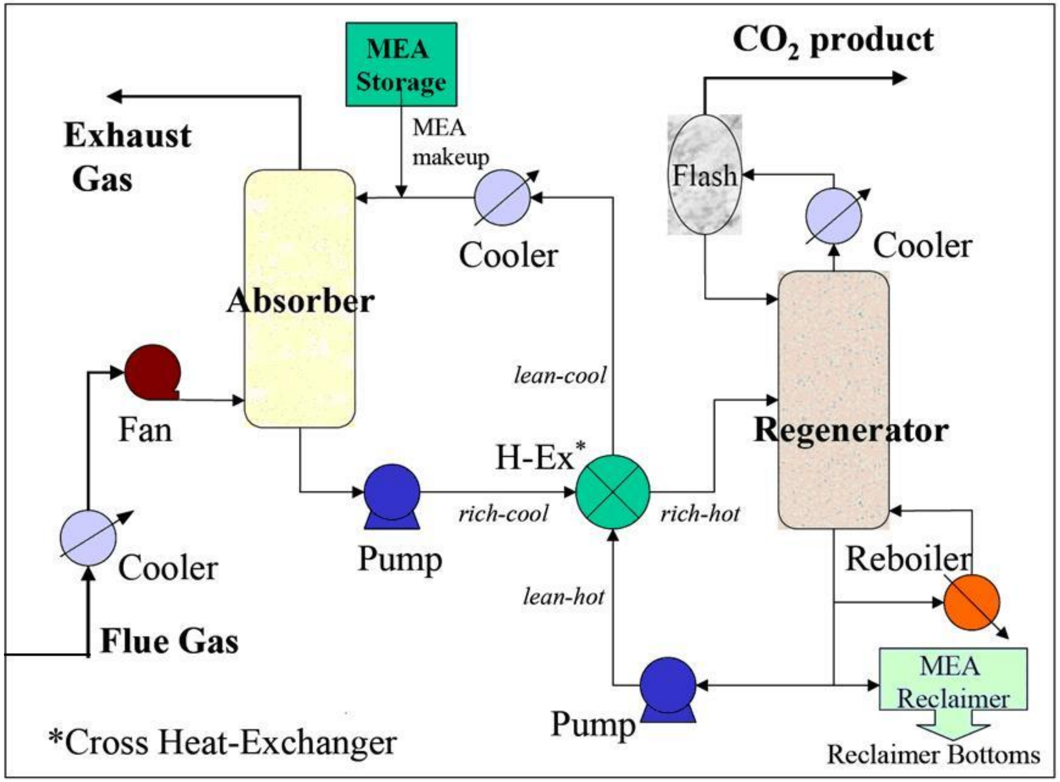
The main problem is that due to high moisture content, more fuel must be burnt and as a result pollutants generated from traditional lignite-fired plants are generally much higher than for comparable black-coal plants!

CO_2 capture technologies



source: http://www.ecn.nl/units/bkm/co2-capture/

Process flow diagram of MEA based post-combustion CO_2 capture



Source:

Ziegler, W. H., NISC,

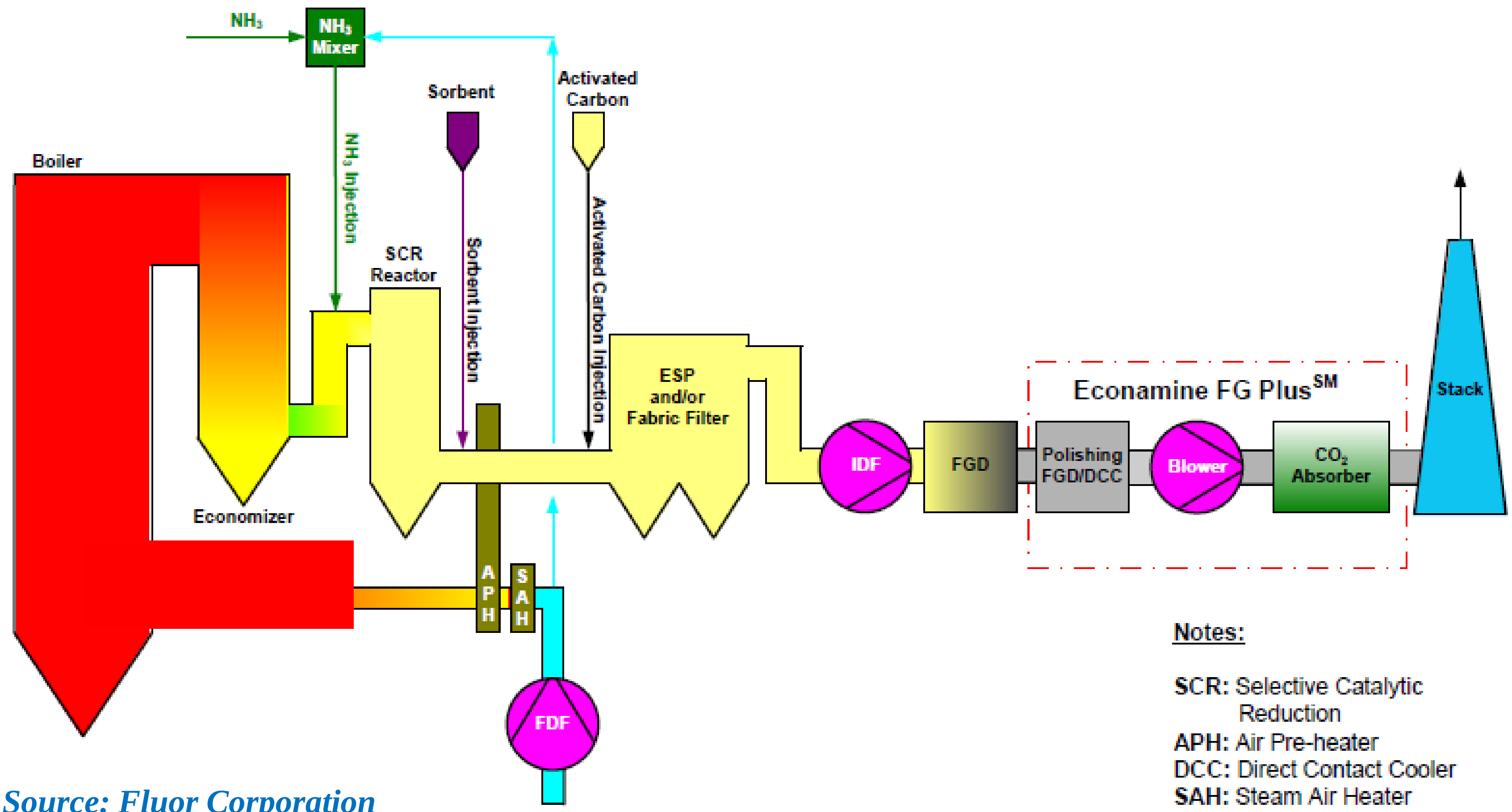
Post-combustion capture of CO_2 involves separation of CO_2 from the flue gas stream after combustion of the fuel with air through chemical absorption, and the subsequent release of the captured CO_2 into a concentrated CO_2 stream by applying heat;

Alkanolamines are the most widely used solvents, and new solvents are under study and development to selectively capture and separate CO_2 from coal-fired flue gas streams more energy efficiently and effectively

The influence of the post-combustion CO_2 capture on the composition of the CO_2 stream:

1. The flue gases coming from direct combustion of coal will contain nitrogen (N_2), oxygen (O_2), water (H_2O), sulphur oxides (SO_X), nitrogen oxides (NO_X), particulates, and chemical compounds containing chlorine (Cl), fluorine (F), mercury, other metals and other trace organic and inorganic chemicals;
2. Typical post-combustion process applies ***chemical absorption*** using solvents (most commonly alkanolamines like MEA) to form weakly bonded intermediate compounds, which are subsequently recovered through the application of heat.
3. ***Many of the components of flue gas (particularly SO_x and NO_x)) react with MEA, causing its irreversible degeneration with the precipitation of stable salts. This suggests that there are economical benefits to purifying the gas prior to CO_2 absorption***!

Post-combustion CO_2 capture process – intensive flue gas cleaning prior CO_2 absorber



Source: Fluor Corporation

Notes:

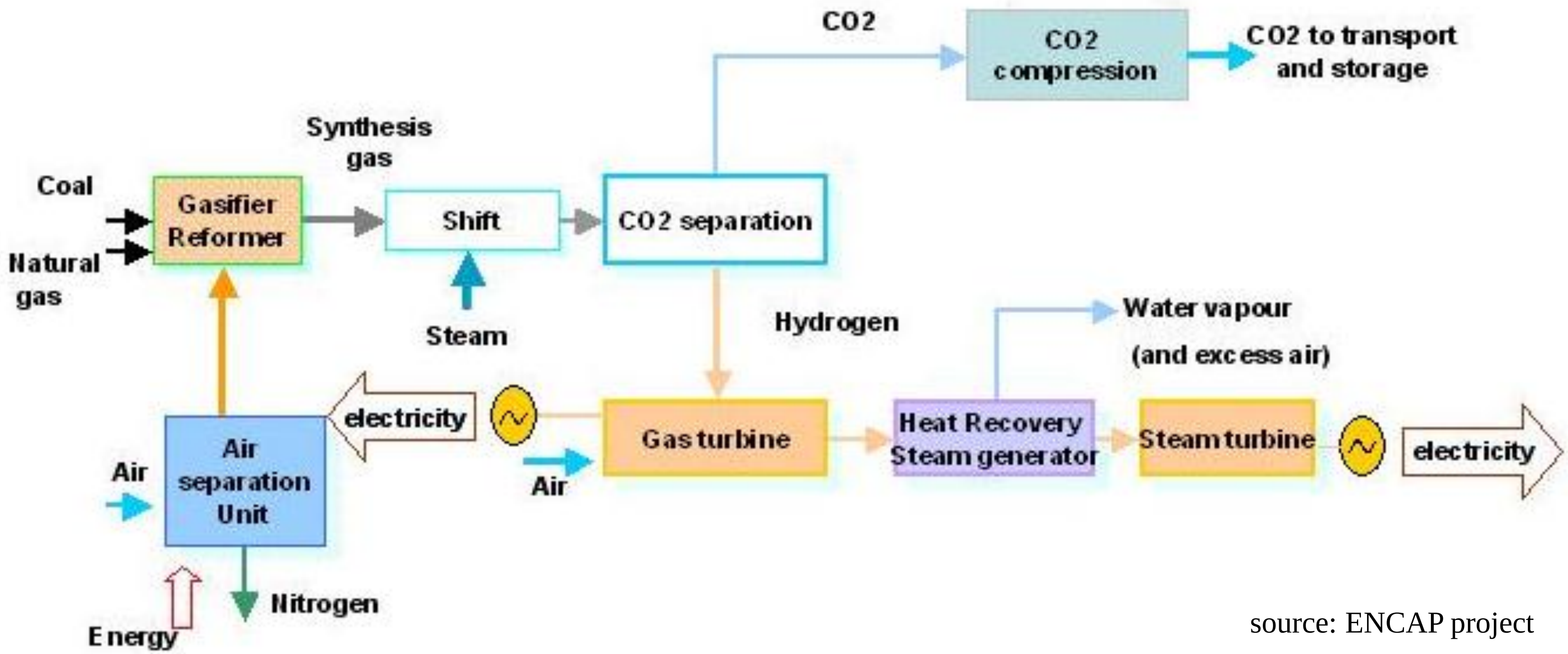
SCR: Selective Catalytic Reduction
APH: Air Pre-heater
DCC: Direct Contact Cooler
SAH: Steam Air Heater
FDF: Forced Draft Fan
IDF: Induced Draft Fan
ESP: Electrostatic Precipitator
FGD: Flue Gas Desulphurization

Commercial MEA processes set a maximum of 10 ppmv of SO_2 as a feed specification to keep solvent consumption and make-up costs at reasonable values

The influence of the post-combustion CO_2 capture on the composition of the CO_2 stream:

1. ***The composition of CO_2 stream will nearly be the same regardless of the fossil fuel feedstock used;***
2. ***Post-capture processes will result in streams that are overwhelmingly carbon dioxide;***
3. ***The 'pure' CO_2 stream after the CO_2 capture process will contain small amounts of nitrogen, oxygen, argon, water and, in some cases, very small amounts of ash, trace metals, SO_2 and NO_x;***
4. ***The corrosion risk seems to be minimal when the post-combustion CO_2 capture is implemented .***

Process flow diagram of pre-combustion CO_2 capture:



source: ENCAP project

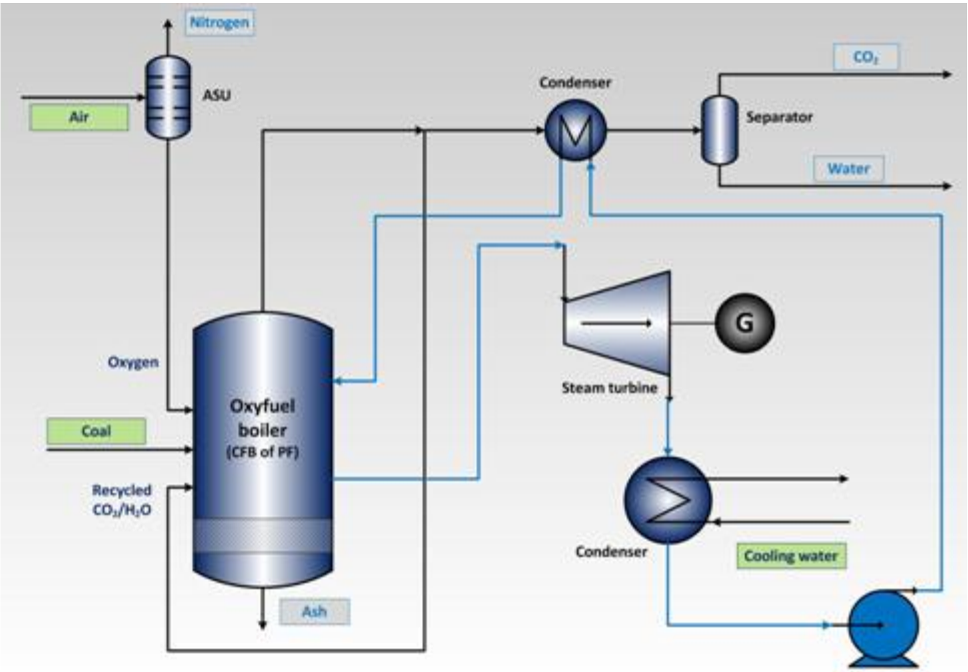
•In pre-combustion capture, CO_2 is removed from a gasification stream before combustion;

• the gasification process produces a synthetic gas containing mostly CO and H_2, which can then be converted to CO_2 using a water-shift reactor;

• In the reducing atmospheres of pre-combustion processes, the sulphur in the fuel mainly yields hydrogen sulphide (H_2S), although some other compounds such as carbonyl sulphide (COS) are also formed.

•Pre-combustion process is not likely to be implemented for large scale carbon capture in Black Sea Region due to complexity of the technology and specifics of the local fuels.

Process flow diagram of oxy-fuel combustion for CO_2 removal



source:
http://www.nebb.com/oxyfuel-coal

•Nearly-pure oxygen is used as the oxidant, instead of air;

•Flue gas recirculation is needed to keep temperatures on the flue gas side and the water/steam side below slagging and material constraints, making the raw flue gas stream from oxy-fuel combustion predominantly CO_2 and water;

•The amount of incidental substances present in the CO_2 stream is primarily dependent on the type of fossil fuel used in the combustion process

The influence of the oxy-fuel CO_2 capture on the composition of the CO_2 stream:

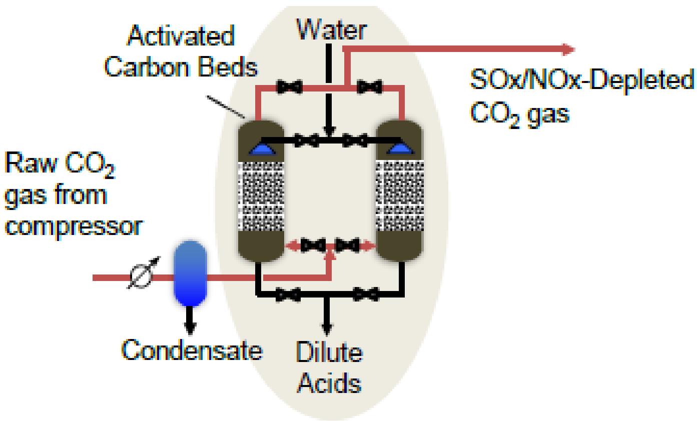
1. The incidental substances include SOx, NOx, HCl and Hg derived from the fuel, and nitrogen, argon and oxygen, derived from the oxygen feed or air leakage into the system.
2. The concentrations of incidental substances in the raw wet flue gas from oxy-fuel combustion are at least 3 to 4 times higher than in conventional air combustion since the combustion products flow volume is 3 to 4 times lower due to the lack of nitrogen.
3. Depending on the sulphur content in coal, a flue gas desulphurisation (FGD) is used to meet air emission requirements.
4. There can be significant amounts of nitrogen, argon and oxygen (3.7 - 10% dry volume in total) present in the CO_2 stream.
5. Moisture is another critical component of the stream – prior to drying, water can account for more than 30% of the flue gas volume
6. ***CO_2 purification unit is needed*** at the outlet of the plant!

CO_2 purification technology is a critical issue in oxy-fuel CO_2 capture

- *Very fast developments in the recent years;*
- *All major gas processing companies have projects in this field*:
  - *Air Liquide;*
  - *Air Products;*
  - *Linde;*
  - *Praxair*

Praxair CPU project results

Activated Carbon Process



$$SO_2 + 1/2O_2 \rightarrow SO_3$$
$$NO + 1/2O_2 \rightarrow NO_2$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

- SO_2 and NO are oxidized and retained on activated carbon
- Carbon is regenerated by water wash followed by drying
- Dilute acid stream is produced

	Inlet ppm		Average Outlet ppm		Removal eff. %	
	SOx	NOx	SOx	NOx	SOx	NOx
Low Sulfur Coal	450	200	2.3	13.0	99.8	93.9
Intermediate S Coal	2000	750	1.6	17.1	>99.9	98.2
High Sulfur Coal	4000	400	1.5	22.8	>99.9	95.2

In despite of the excellent simultaneous SOx/NOx removal achieved, NO_x content is still high.

Conclusions - 1

- Local low grade lignite coals are and will be one of the main energy sources in the Black Sea Region;
- Post-combustion and Oxy-fuel CO_2 capture processes are more likely to be implemented for large scale carbon capture.
- Post-capture processes will generally result in streams that are entirely carbon dioxide; this 'pure' CO_2 stream will still contain small amounts of nitrogen, oxygen, argon, water and, in some cases, very small amounts of ash, trace metals, SO_2 and NO_x. The specific amount of these impurities is dependent on the degree of compression and the number of condensation stages installed;
- The oxy-fuel process may generate a CO_2 stream containing significant amount of impurities like SO_X, NO_X, HCl and Hg derived from the fuel, and nitrogen, argon and oxygen, derived from the oxygen feed or air leakage into the system;
- Internal corrosion of pipelines can be a major failure mechanism if moisture or oxygen is not sufficiently reduced in the CO_2 stream.
- In the presence of water, incidental substances, as well as CO_2 itself, can form acids that can corrode pipelines

Conclusions - 2

- Acidity and corrosiveness from flue gas components originating from post-combustion capture and especially from oxy-fuel processes (SO_2, SO_3, NO_X, and HCl) may lead to the situation when further drying below the current limits is needed;
- The allowable water content may need to be lower also in the presence of other impurities, such as H_2S, O_2 and N_2, as they lower the solubility limit.
- Implementation of oxy-fuel carbon capture in Black Sea Region will create challenging conditions for CO_2 transportation infrastructure;
- Corrosion tests assumed CO_2 stream containing O_2, S and N-bearing compounds above the current implemented levels (USA standards) and within the advanced CPU technology limits have to be performed along with the new lower water content threshold of 500 ppm

Tasks for the next 10 months

- Engineering, procurement and installation of autoclave corrosion test system;
- Accomplishing a set of corrosion experiments with carbon steels
- Contribution to the preparation of the first year report