CO_2 CONTENT OF GREEK LIGNITE: THE CASE OF PROASTIO LIGNITE DEPOSIT IN PTOLEMAIS BASIN, NORTHERN GREECE

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Abstract

Lignite is an important energy source for Greece, which severely relies on this fossil fuel for electricity generation over the years. The lignite combustion, however, releases a significant amount of carbon dioxide to the atmosphere per unit of energy generated, more than does the combustion of other fossil fuels. On the other hand, there is a growing concern over the possible consequences of global warming due to the increase of carbon dioxide in the atmosphere (a major greenhouse gas). Additionally, there is also a need for accurate estimates of carbon dioxide emissions.

There are many factors resulting in the increase of CO_2 content in lignite such as their formation and depositional environment, the possible presence of fossils, and their rank.

In the present paper the CO_2 content of the Proastio lignite deposit, Ptolemais Basin, is studied, in relation to the depositional palaeo-environment. An interpretation of CO_2 variation with depth, age and surrounding rocks is also attempted.

 CO_2 content of Proastio deposit is compared with this of other lignite deposits in the Ptolemais Basin, of various types and ages. Finally, the effect of CO_2 content in the combustion of lignite is studied, while the possibility of the geological storage of the emitted carbon dioxide is explored after its capture from the Thermal Power Plants (CCS technology).

Key words: lignite, carbon dioxide, Proastio, Ptolemais, NW Greece, carbon storage.

1. Introduction

There are a number of adverse environmental effects of coal mining and burning, especially in power stations. These effects include release of carbon dioxide, a greenhouse gas, which causes - according to the IPCC [Intergovernmental Panel on Climate Change] - climate change and global warming. Coal combustion is the largest contributor to the human-derived CO_2 in the air.

In Greece, approximately 38% of the annual CO_2 emissions, i.e. 53 t of a total of 140 t, derive from lignite combustion for the production of electric power. From P.P.C. data's it knows that for each pro-



Fig. 1: (a): Map of Florina-Ptolemais Kozani and Sarantaporo basins; (b): Map of Graben with ridges.

duced MW/h in the Thermal Power Plants, 1.2-1.3 t CO₂ are emitted in the atmosphere. To meet the enhancement of the annual energy demand that is expected to increase significantly until the year 2030, the use of fossil fuels (lignite, hydrocarbons) is necessary apart from the use of Renewable Energy Sources (R.E.S.), a fact resulting in an increase of CO₂ emission from 18 Gt in 1980 to 40 Gt in 2030. The Hellenic lignite, constituting the main electric power generation source in the country, contains varying CO₂ amounts depending mostly on the age of deposition, the depositional environment and the lignite features. The elevated CO2 content of the Proastio lignite and the Upper Pliocene lignite in general, is mainly due to the great amount of fossils, the CaCO₃ saturations and the thin intercalated marl layers. Carbon dioxide, a greenhouse colourless, inorganic gas is generated as a by-product of the combustion of fossil fuels or the burning of vegetable matter, among other chemical processes. Small amounts of carbon dioxide are emitted from volcanoes and other geothermal processes such as hot springs and geysers and by the dissolution of carbonates in crystal rocks. The Pliocene lignite deposits hosted in the Ptolemais Basin display high CO₂ contents (Metaxas et al., 2007) resulting in the emission into the atmosphere of $0.6-0.7 \pm CO_2$ per ton of lignite burned in the thermal power plants. A representative deposit of this age is that of Proastio, which, in terms of total reserves, is the second one after the Southern Field deposit.

2. Geological setting

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The Ptolemais Basin is located in the North-Western Greece and constitutes part of the Monastir-Ptolemais-Kozani-Servia tectonic trench (Fig.1a). It is a discontinued geological unit due to occurrence of recent tectonic disturbances of great scale, which were activated in Neogene and Quaternary times. The elongated and deep basins (Metaxas et al., 2007) of Ptolemais-Ardasa-Vegoritida, etc. as well as the tectonic ridges of Xyno Nero, Bordo-Filota, etc., disrupted the continuity of various lignite-bearing regions (Fig. 1b).



Fig. 2: Synthetic stratigraphic column of the Florina, Ptolemais-Amynteon, Kozani, Sarantaporo Graben.

The area of Proastio is located at a distance of about 5 km to the S-SE of Ptolemais city. It is not an independent geological unit and is attributed to the geological unit of Ptolemais basin.

The stratigraphic structure of the sedimentary series, the lithofacies analysis of the geological formations and the geological structure of the lignite deposits in general, were based on the data obtained from the study of borehole cores (Kotis et al., 2001).

The overview of the geological setting of the broad Ptolemais basin (Metaxas et al., 2007) is showing in the stratigraphic column (Fig. 2).

During Upper Miocene-Lower Pliocene, the Ptolemais Basin was supplied with materials from the North and West. The rocks in these basin margins are metamorphic, such as gneisses, schists, etc. This is one of the main reasons that calcium carbonate display low contents in these formations. Fossils occur rarely into these formations due to the small concentration of $CaCO_3$ during this period. The aforementioned feeding is due to the ascension of the basement of the Florina Basin during Mio-Pliocene, in relation to Ptolemais Basin, which is going on up to now. Moreover, it seems that the ascension of the western margins of Ptolemais Basin was quicker and higher compared to the eastern ones. The sediments deposited during this period are coarser in Florina Basin and the western margins of Ptolemais Basin (coarse-grained sands, conglomerates, etc.) compared to these deposited at the eastern margins (clays, silts, etc.). Lignite deposition of this type could not form in the West and North of the trench due to the aforementioned rea-

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Fig. 3: Correlation between CO₂ and moisture.

sons and in addition to the quick flow and great volume of transported materials. During Upper Pliocene, when lignite of Ptolemais type was deposited, the feeding of the Ptolemais Basin took place from the East. Further ascension of Florina Basin impeded deposition of Pliocene lignite in this basin as well as a quicker ascension of the eastern margins of Ptolemais Basin and subsidence of the central area and the western margins. Thus, this lignite type occurs in the central and the western parts of Ptolemais Basin. Given that the feeding took place from the eastern bedrock, where carbonate rocks such as limestone, semi-meta-morphic marble etc., occur, high concentrations of CaCO₃ and fossils are included into the sediments of this period resulting in, respectively, high CO₂ amounts released from the lignite of Ptolemais type. Another factor of CaCO₃ deposition is the environment of lignite formation of this type. Sediments of biochemical type with increased CaCO₃ are observed due to the smooth environment where the time required for creation and deposition of these sediments is ensured. Furthermore, capture of CO₂ by the plants through the solutions took place resulting in CaCO₃ deposition.

The lignite deposit of Proastio is remarkable and second in terms of total volume of deposit after the South Field. This deposit can be developed and exploited securing the supply of two units of 600 MW for 43 years.

The formations observed in the area (Kotis et al., 2001) are described in the stratigraphic column of Fig. 3. The maximal cumulative thickness of the lignite seam is 360 m and this of lignite 81 m. The average moisture of lignite is 45.8%, the ash yield [on dry basis] 29.7%, the volatile matter content 40.0%, while the fixed carbon [on dry basis] ranges from 31.4 to 35.1%. The average combustible sulphur is 0.63% and the total 1.19%. The elemental analysis of the fuel (d.b.) gave a Carbon content of 50.7%, Hydrogen content 4%, Nitrogen content 1.39%, Oxygen content 10.61%. The Gross calorific value (G.C.V.) is of 2485 kcal/kg while the net calorific value (N.C.V.) 2085 kcal/kg.

Geological reserves are estimated to 370 m. tn. and mineable reserves to 273 m. tn, with an average exploitability relation [(Overhead deadwood + Intermediate deadwood) / lignite, $(Y+E)/\Lambda=9,88:1$] and average ash content [on dry basis] 27.8%.

3. CO₂ Content In The Ash

The content in carbonate minerals constitutes a very important factor for the qualitative differentiation of the lignite beds. During lignite combustion into the steam power plants these minerals are split in carbon dioxide and oxide of the respective element, for example $CaCO_3 \rightarrow CaO + CO_2$ [↑].

The higher the CO₂ content, the worse the lignite quality, because a part of the power (425 kcal/kg)

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is absorbed for break down the carbonates (endothermic reaction) thereby reducing the amount of energy produced. Thus, determining the quantity of CO_2 released by the decay of carbonate minerals is essential for characterising the actual coal.

Until around 1980, there was no need to calculate the CO_2 content in the evaluation of the deposits. For this reason no measurements and information exist before this date. After 1980 the CO_2 content is taken into account in the calculations referred to in the evaluation of each deposit, based on the ash (Kolovos et al., 2002; 2002; 2002; 2003, Sotiropoulos et al., 2005).

The ash yield of each sample is due to the presence of various fossils shells, apart from the inorganic materials comprised into lignite and the thin barren layers (clay, marls, etc.) collected with lignite during sampling.

The only concern previously considered during the sampling of lignite layers was the thickness of the barren layer, if consisting of clay, not to exceed 5% of the length of the core - sample.

The other criterion in the evaluation of the deposits was the relatively low ash yield on dry basis (35%) in the mineable bed. But today, after implementation of chemical analyses it was proved that in many layers, where ash is less than the above limit, adding CO₂, exceeds 45 to 50% and the exploitable reserve decreases down to the 1/3 of the initially calculated reserve without the CO₂.

As a result, several operational problems are created, even black out of the station, depending on the specifications of the lignite combustion unit. Furthermore, problems are created in the exploitation and the overall design of a mine as well as in the use, transportation, combustion, etc.

Re-evaluation of several lignite deposits is suggested, mainly of those assessed before 1980, using new datasets, taking into consideration the CO_2 and the specifications of the combustion plants to be fed by the specific lignite deposit. If for example a station can use lignite having thermal capacity up to 1280 kcal/kg, the N.C.V. of the mineable lignite seams should be taken into account for the evaluation.

The ash yield on an as-received basis varies widely due not only to the different content in inorganic matter, but also to the different moisture of the samples. Moisture varies even for lignite samples of the same composition. Thus, in order to compare the values of ash yield and therefore of CO_2 , it is appropriate to refer them to a fixed percentage of moisture or to a dry and ash free basis. Figure 3 shows that as the moisture increases, the CO_2 decreases on an as-received basis.

4. Origin of CO₂

During the exploration of the Proastio deposit, a specific sampling of lignite was carried out, depending on the reaction to the hydrochloric acid (HCl, density 1:10), as well as on the fossils contained and the thin marl or clay layers included.

The samples of the pure or clayey lignite are not reacting to the hydrochloric acid (no bubbling) and their average CO_2 content ranges on an as-received basis is about 1.5% (Fig. 4). This amount of CO_2 is mainly due to CaCO₃ dissolved from the surrounding carbonate rocks by surface and karstic waters feeding the palaeomires.

Only the fossils included in the lignite samples react to the HCl (strong bubbling) and the average CO_2 values are c. 7%. These values vary from sample to sample, depending on the fossils content. In this category, the CaCO₃ reaches values up to 40%.

Samples with thin marl or clay layers are classified to the third category. They display very strong reaction to the HCl (very strong bubbling); the average CO_2 value is about 9%, while $CaCO_3$ exceeds 45% (Fig. 5).



Fig. 4: Correlation between pure CO₂ and depth.



Fig. 5: Correlation between CaO content in lignite ash and CO₂ content (on dry basis).

The marl layers hosted into the lignite beds are mainly due to changes of the depositional environment, the feeding from the surrounding rocks and the vegetation type (abstraction of CO_2 from the plants for the photosynthesis resulting to CaCO₃ precipitation).

In Proastio area and beneath a depth of 210 m, the CO_2 content decreases drastically in all categories of lignite samples, as well as the CaCO₃ content below 11% (Fig. 6).

One of the main reasons is the feeding environment. During the deposition period of the deeper lignite beds (Miocene/Pliocene boundary), the feeding took place from North and West where the surrounding rocks are metamorphic (gneiss, schist). Almost stable relation of CO_2 is observed in the lignite free from saturations, marl layers and fossils, compared to the combustible (Fig. 7) and fixed carbon (Fig. 8), with however a small decrease when CO_2 increases. Conversely, a great decrease in lignite beds with fossils and marl layers is observed. The greater decrease of the permanent carbon is mainly observed in the lignite with $CaCO_3$ saturations. Almost stable relation between O_2 and CO_2 is observed in the lignite samples including fossils or thin marl layers, with a small increase of O_2 when CO_2 increases. On the contrary, in samples not reacting to HCl or with $CaCO_3$ saturations,



Fig. 6: Correlation between CaO, CaO+CO₂ and depth.



Fig. 7: Correlation between combustible carbon and CO₂ on dry basis.

the O_2 decreases when CO_2 increases with greater decrease in the saturations (Fig. 9).

The above described situation is the same in all Pliocene lignite deposits of Ptolemais Basin. In the Proastio deposit the average CO_2 value on dry basis of the mineable lignite is 3.8%, while the geological lignite ranges from 1.3 to 14.4%, with an average value 4.5%.

Conversely, the respective CO_2 in the Miocene xylite-rich lignite deposits of Ptolemais and Florina Basins is from 0.8% to 2.2% (Anatoliko-Karyohori).

Based on all the aforementioned, and taking into consideration the fact that lignite constitutes the main resource for electric power generation in Greece, it is obvious that the CO_2 capture and storage (CCS) technology should be applied in the near future.

5. Current Situation of the CCS Technology

The CCS technology began developing in the 1990's, when the first large-scale storage of CO_2 started in the underwater reservoir of Sleipner, Norway (North Sea). Other large-scale (industrial) projects were carried out in Weyburn, Canada, and in Salah, Algeria. In all these cases, either there

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Fig. 8: Correlation between fixed carbon and CO₂ on dry basis.



Fig. 9: Correlation between O_2 and CO_2 on dry basis.

is no cost for pure CO_2 from other gases, or there is economic benefit from the improved extraction of hydrocarbons. The Intergovernmental Panel on Climate Change suggested in 2005 that CCS could achieve 55 per cent of the global mitigation effort while reducing costs by 30 per cent or more compared with a non-CCS solution. The European Commission found in 2008 that the costs of meeting its climate change commitments to 2030 will be 40 per cent higher, at \in 60 billion (\$95 billion), if CCS is not included. The Pew Center on Climate Change, concluded in 2007 that building 30 CCS demonstration projects for \$30 billion would save the US \$80 to \$100 billion in subsequent mitigation costs. This tranche of CCS demonstration projects will be expensive, but in the medium term they will bring considerable savings to society (Aarnes et al., 2008).

The CCS technology in electric power stations or other industries, which require the capture of CO_2 , is currently at the stage of pilot applications, such as in the Schwarze Pumpe (Berlin) and Ketzin, Germany, where capture and storage technologies are tested in units of 30 MWe with lignite fuel. In the Schwarze Pumpe the capture of CO_2 takes place before combustion using the Oxyfuel technology. According to the officers of VATTENFALL, which is responsible for the unit, the technology for "clean lignite stations" with capture and storage of CO_2 will be rentable in a decade at a cost

equivalent of the CO2 emissions rights market.

Interdisciplinary research groups examine the role of coal in a world where constraints on carbon dioxide emissions are adopted to mitigate global climate change. The future of coal in a carbonconstrained world, will evaluate the technologies and costs associated with the generation of electricity from coal along with those associated with the capture and sequestration of the carbon dioxide produced coal-based power generation. Growing electricity demand in Greece and in the world will require increases in all generation options (renewable, coal, and nuclear) in addition to increased efficiency and conservation in its use. Coal will continue to play a significant role in power generation and as such carbon dioxide management from it will become increasingly important. A study, which examines all interrelated technical, economic, environmental and political challenges, must be undertaken the soonest possible. The final report, addressed to the Hellenic Government, but also to the industry and the academic leaders, will help to meet this urgent scientific challenge. Additionally, an aggressive R&D effort in the relatively near term will yield significant dividends down the road, and should be undertaken immediately. A significant charge on carbon emissions is needed to increase the economic attractiveness of new technologies that avoid carbon emissions and specifically to lead to large-scale CCS in the coming decades. A large-scale demonstration project of the technical, economic and environmental performance of an integrated CCS system is needed in Greece over the next decade with government support. This is important for establishing public confidence for a large-scale sequestration program anticipated in the future.

Cost constitutes the great problem in the implementation of the CCS, followed by the monitoring and authorization. CCS technology should reduce costs by 2 to 4 times $(30-15 \in /t \text{ CO}_2)$ to be economically viable. Improving and standardizing the relevant technology can address this challenge. Something similar was also observed in the case of the flue-gas desulphurization plants of the thermal power stations, in which the cut down of cost was remarkable.

6. Conclusions

The CO_2 emissions from lignite combustion to generate electric energy contribute 38% to the greenhouse effect since for each MW/h 1.2-1.3 t of CO_2 is emitted.

The CO_2 lignite content varies and depends on the age, the deposition environment and the lignite type in general.

The Pliocene lignite deposits display higher CO₂ contents compared to the Miocene ones.

The CO_2 content in the Upper Pliocene lignite in Ptolemais Basin, for example in the Proastio deposit, is mainly due to the great amount of fossils and the CaCO₃ saturation.

The Proastio lignite deposit is noteworthy and can feed two units of 600MW for 43 years.

It was observed that with increasing CO_2 the fuel elements of lignite are reduced such as the permanent and combustible coal, the O_2 etc.

The amounts of CO₂ emissions during lignite combustion must be determined.

Re-evaluation of the lignite deposits assessed before 1980 is necessitated since CO_2 contents were not taken into account. As it was proven, several lignite beds with TEX \leq 35% were considered exploitable, while adding CO_2 they became non-exploitable given that ash exceeded 50% and thus the estimated deposit was reduced to 1/3 causing problems in the exploitation planning, transportation, combustion, production. CCS is the critical enabling technology because it allows significant reduction in CO₂ emissions while allowing lignite to meet future energy needs. Taking into consideration that lignite will be for the next few decades the main resource for electric power generation in Greece, it is clear that the CCS technology should be applied, which to be economically viable has to reduce the cost of capture 2 to 4 times (30-15 \in /t of CO₂).

7. References

- Aarnes, J., et al. 2008. Guidelines for geological storage of CO2: selection and qualification of sites and projects. 9th International Conference on Greenhouse Gas Control Technologies, Washington DC, USA.
- Kolovos, N., Georgakopoulos, A., Filippidis, A., Kavouridis, C. 2002. Environmental Effects of Lignite and Intermediate Steriles Coexcavation in the Southern Lignite Field Mine of Ptolemais, Northern Greece. *Energy Sources*, 24(6): 561-573.
- Kolovos, N., Georgakopoulos, A., Filippidis, A., Kavouridis, C. 2002. The Effects on the Mined Lignite Quality Characteristics by the Intercalated Thin Layers of Carbonates in Ptolemais Mines, Northern Greece. *Energy Sources*, 24(8): 761-772.
- Kolovos, N., Georgakopoulos, A., Filippidis, A., Kavouridis, C. 2002. Utilization of lignite reserves and simultaneous improvement of dust emissions and operation efficiency of a Power Plant by controlling the calcium (total and free) content of the fed lignite. Application on the Agios Dimitrios Power Plant, Ptolemais, Greece. *Energy & Fuels*, American Chemical Society, 16: 1516-1522.
- Kolovos, N., Sotiropoulos, D., Georgakopoulos, A. 2003. Lignite Recovery in Multi-Seam Open-pit Mining Operations in Northern Greece. In: Proceedings IIIrd International Scientific Conference on Modern Management of Mine Producing, Geology and Environmental Protection "Surveying Geology-Ecology-Management" SGEM 2003, Section II: Technology and Technical Equipment for the Open-pit Mining of Mineral Resources. June 2003, Varna city, Bulgaria, p. 59-65.
- Kotis, Th., Ploumidis, M. and Dimitriou, D., 2001. Geological and Mineral Deposit Research of Lignite in the area of Proastion Ptolemais Basin. I.G.M.E. p. 1-68, Athens (in Greek).
- Metaxas, A., Kotis, Th., G. Varvarousis, Ploumidis, M., Karageorgiou, D. E., Papanikolaou, G. 2007. Geological Evolution – Stratigraphy of Florina, Ptolemais, Kozani and Saradaporo Graben. 11th I.C.G.S.G. Vol.XXXX/1 pp. 161-172 Athens.
- Sotiropoulos, D., Georgakopoulos, A., Kolovos, N. 2005. Impact of free-calcium oxide content of the fly ash on dust and sulfur oxide emissions in a lignite-fired Power Plant. *Journal of the Air and Waste Management Association*, 55: 1042-1049.