

CO₂ Capture and Storage (CCS) by means of Coal Combustion Products of Fluidised-Bed Boilers

Petr BURYAN¹⁾, Pavel DONÁT²⁾, Šimon BURYAN³⁾

¹⁾ Prof., Ing., Dr.Sc.; University of Chemical Technology, Faculty of Chemical Technology, 5 Technická, 166 28 Prague 6, Czech Republic; email: buryanp@vscht.cz

²⁾ Ing.; ČEZ Energetické produkty, s.r.o.

³⁾ Bc.; University of Economics, Faculty of International Relations, 4 Churchilla, 130 67 Praha 3, Czech Republic

Summary

Through a one-year monitoring of the coal combustion products (CCP) coming from the Tisová Power Plant, using lime for the desulphurisation of the combustion gases from fluidised-bed boilers burning lignite from Sokolovská uhelná, a.s., it was conclusively proved that these coal combustion products significantly absorb carbon dioxide from the atmosphere during free deposition. Nevertheless, this irreversible sorption of carbon dioxide is not included in monitoring plans for reporting CO₂ emissions of any power plant, or in the plans for CO₂ stratification.

Keywords: fluidised-bed boilers, carbon dioxide, storage, coal combustion products

Introduction

CCP are subject to various law regulation. In the European Union (EU) REACH-Regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals) belongs to most significant ones. REACH entered on the 1st June 2007 into force. By this, each producer or importer of coal combustion products (CCPs) has to register the marketed or imported substances at the European Chemicals Agency. The regulation places requirements on safety of the products regarding chemical, physical, toxicological and ecotoxicological features of the products [1].

The current ratified international agreements between the individual states aimed at the regulation of greenhouse-gas emissions within the UN Framework Convention on Climate Change and the related protocols build on the assumption that the inventory will be conducted in a unified and controllable way by the agreed methodology [2-4].

An inseparable part of these methods is the evaluation of the so-called lifecycles, where in compliance with the sense of ISO 10040 the term 'lifecycle assessment' refers to an 'inventory' of the input and output streams and potential impacts on the environment of the whole system of production during its entire cycle, i.e. of the entire group of process units, which are interconnected by the flow of materials or energy and fulfil one or more defined functions.

In practice, the assessment is performed by the inventory analysis and the related calculation (lifecycle impact assessment). In the case evaluated, it has so far been an aggregation of data connected with coal com-

bustion and lime (CaCO₃) calcination with CO₂ as the product.

A new determination, unanticipated by the national inventarisation systems, is the ability described in the report of carbon dioxide sorption by deposited energy by-products from fluidised-bed combustion (FBC) boilers containing free calcium oxide during deposition in the landfills reacting with carbon dioxide from the air, which significantly contributes also to its stratification.

Another important finding is the fact that the CCPs delivered now contain carbonates, which is not anticipated by the Plan of monitoring either.

CO₂ Emissions Connected with the Desulphurisation of Fluidised-Bed Boilers

The amount of CO₂ created in coal combustion in FBC boilers with the addition of limes as means of desulphurisation is determined on the basis of the balance calculation that arises from the composition of the reactants, i.e. of the relevant coal and limes (carbonates), or in some cases also of the biomass. The reaction equations applied capture primarily the initial and final state of the ongoing reactions, hence which materials and in which mutual ratio react to one another and which reaction products are created. They always proceed from specifically defined chemical elements, which mean that with coal the equations of all of the combustible compounds are considered. With limes, which during combustion in boiler are subjected to calcination, mainly decompositions of carbonates are considered, with the amount of car-

Tab. 1. CO₂ content after 3, 6, 9 and 12 months of model 'deposition' – in wt. % (LP – FBC bottom-ash, FL – FBC fly-ash)

Tab. 1. Zawartość CO₂ po 3, 6, 9 oraz 12 miesiącach modelowego 'osadzania' – wyrażone w wag. %
(LP – FBC popiół denny, FL – FBC popiół lotny)

| Sample | Content of CO ₂ bound as CaCO ₃ |
|------------------------|--|
| LP/0 – FBC bottom-ash | 4.73 |
| FP/0 – FBC fly-ash | 0.56 |
| LP/3 – FBC bottom-ash | 8.73 |
| FP/3 – FBC fly-ash | 5.51 |
| LP/6 – FBC bottom-ash | 9.79 |
| FP/6 – FBC fly-ash | 7.65 |
| LP/9 – FBC bottom-ash | 9.65 |
| FP/9 – FBC fly-ash | 8.22 |
| LP/12 – FBC bottom-ash | 9.31 |
| FP/12 – FBC fly-ash | 7.35 |

bon dioxide emissions being assessed on the basis of the balance data of their consumption or on the basis of the proved amount of the gypsum created.

None of these methods assumes that free CaO from the process of desulphurisation which is contained in the deposited CCPs in the course of storage reacts with CO₂ from the air while producing new carbonates, particularly calcium carbonate. Because of the reactivity of CaO and the thermodynamic conditions at landfills, the reaction producing CaCO₃ always takes place, namely until the free calcium oxide (hydroxide) or other oxides capable of reacting with CO₂ from the air are fully depleted. The balance calculations used so far also assume that 100% calcination of the carbonates in the furnace always occurs and the expelled coal combustion products do not contain carbonates, which does not correspond to technological practice.

The residue in the expelled slag, filter or FBC fly-ash ascertained in many cases in the laboratory as the decrease of the mass at 850°C in the presence of air includes besides the actual burnt residue also the calcined decomposition of the carbonate. This incorrectness is then transformed into the carbon dioxide balances.

Sample Creation

Within the aims of this work, the samples of fluidised-bed and filter ash were studied. They had been collected during typical operation in the Tisová Power Plant (2 × 350 tons of steam/hour), which combusts lignite from Sokolovská uhelná, a.s., and wood chips and uses limes from the localities of Čertovy schody and Štramberg for the desulphurisation of the combustion gas.

Model Deposition

The collected samples of FBC fly-ash and bot-

tom-ash were deposited in the laboratory in open specimen tubes to provide them with free access of air. In order to capture weather conditions and the influence of precipitation on the waste substrate, the samples were sprinkled with distilled water always once in three months during the year. This made it possible to capture in a model way the reactions of snow and rain precipitation transferring free calcium oxide to hydroxide.

At the beginning of the modelling and every three months, the CO₂ content was determined in the observed samples [4], when the homogenised sample was applied with 17% hydrochloric acid and the CO₂ released was captured in absorption containers, which were weighed. To the acid, we added copper bichloride, which captured also the sulphane being released.

The data obtained are summarised in Table 1 and are evaluated graphically in Figures 1 and 2.

Through a quantification of the values of Table 1 in terms of weight after a year's chemisorbtion of carbon dioxide in the landfill for the Tisová Power Plant a.s., we attain the following values:

FBC bottom ash

1. Average amount of produced FBC bottom ash per year → 115,000 t
2. CO₂ content after 12 months → 9.31% mass
3. CO₂ amount captured in deposited FBC ash → 11,000 t

FBC fly ash

1. Average amount of produced FBC fly ash per year → 175,000 t
2. CO₂ content after 12 months → 8.22% hm.
3. CO₂ amount captured in deposited FBC fly ash → 13,000 t

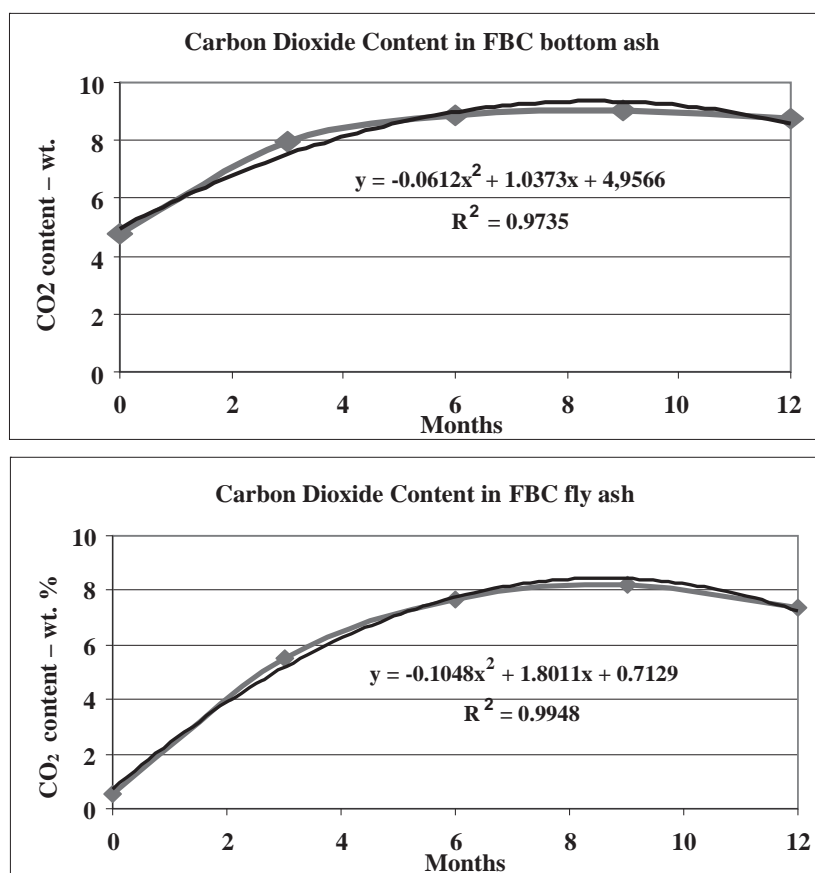


Figure 1 and Figure 2

Figura 1 i Figura 2,

It is clear from Figures 1 and 2 that the adsorption capacity of the observed samples for CO₂ capture was substantially utilised already after six months, which for technological practice means that this finding can be advantageously applied in the organisation of the deposition of FBC ash in landfills, i.e. that already after half a year the deposited FBC ash can be further covered by another.

Conclusions

From the conducted model study dealing with the chemisorption of carbon dioxide as an observed greenhouse gas, it clearly arises that FBC bottom ash as well as FBC fly ash from the operation of the FBC boilers combusting lignite and using limes as a desulphurisation medium of the combustion gases during their deposition at landfills captures from the free air a significant amount of carbon dioxide with the creation of carbonates.

Within the model balance data of all of the FBC boilers of ČEZ, a.s. company during the production of app. 450,000 t FBC fly ash and 300,000 t FBC bottom ash, we acquire in the CR on the basis of the above-mentioned data a mass of irre-

versibly captured CO₂ from the free air during the year equalling app. 60–70,000 t [8].

The estimate for the entire Czech Republic at such a total efficiency of FBC boilers in the transformation of data dealing with the proved chemisorption is app. 200,000 t CO₂ per year. This amount of captured carbon dioxide corresponds to the amount of the created, deposited oxide, which is produced by combustion from ca 130,000 tonnes of typical lignite in electric power plants.

The proved reactivity of the CCPs should therefore be also considered in the annual balance emissions of the carbon dioxide of all of the sources utilising FBC boilers, which has so far not been respected. This as-yet not respected experience should be respected also in the assessment of the methods of the stratification of carbon dioxide studied today.

The same is true also for the content of carbonates in the CCPs expelled, which are not deposited in landfills but are also used as landscaping material, building material, etc.

Acknowledgements

A part of the results of this work was gained with

the financial support the authors obtained in the framework of resolving Research Plan of the Ministry of Education, Youth and Sports MŠM ČR 604 613 7304 and research grant of University of Economics in Prague F2/7/2014 "New Di-

rections governance in light of the financial and debt crisis".

Received May 19, 2014; reviewed; accepted January 23, 2015.

Literatura - References

1. Feuerborn, H. J.: *Coal combustion products in Europe—An update on production and utilization, standardisation and regulation*, World Coal Ash Conference, May. 2011. p. 9–12.
2. *Revised 1966 IPCC Guidelines for National Greenhouse Gas Inventories*, Vol. 1–3, IPCC
3. 1997 (<http://ipcc-nggip.iges.or.jp>)
4. *Good Practice Guidance for Land Use, Land Use Change and Forestry*, IPCC 2000
5. <http://ipcc-nggip.iges.or.jp>
6. *Good Practice Guidance and Uncertainty Management in National GHG Inventories*, IPCC
7. 2000 (<http://ipcc-nggip.iges.or.jp>)
8. ČSN 44 13 57.
9. ISO 925.
10. *Reaction mass of Residues, calcium sulfate-contg., flue gas wet desulfurization neutralization and Slags, coal*. EC number 916-663-2. ECHA 2015.
11. Buryan P, Donát P, Ederová J., Sokol P: *Most recent scientific data on chemisorption of CO₂ by coal combustion products from energy sector*, *Proceedings of the 17th International Conference Ashes from Power Industry*, 24–26 October 2010, p. 139–149, Warszawa, ISBN 978-83-60050-17-0.

Pozyskiwanie i przechowywanie CO₂ (CCS) przy użyciu produktów spalania węgla w kotle ze złożem fluidalnym

Po roku obserwacji produktów spalania węgla pochodzącego z elektrowni Tisová, używając wapna do odsiarczania gazów spalania lignitu, w kotle ze złożem fluidalnym, który pochodził z Sokolovskáuhelná, a.s., ostatecznie udowodniono, że te produkty spalania węgla znacząco wchłaniają dwutlenek węgla z atmosfery w trakcie swobodnego osadzania. Niemniej jednak, ta nieodwracalna sorpcja dwutlenku węgla nie została zawarta w planach obserwacyjnych zawiadomienia o poziomie emisji CO₂ w żadnej z elektrowni, lub w planach stratyfikacji CO₂.

Słowa kluczowe: kocioł ze złożem fluidalnym, dwutlenek węgla, przechowywanie, produkty spalania węgla