

RECURRENT WATER FROM SLAG AND FLY ASH DISPOSAL PONDS AS A MEDIUM FOR CARBON CAPTURE AND STORAGE

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: Due to the increased use of fossil fuels and industrial production, the concentration of carbon dioxide in the atmosphere increases, causing greenhouse effect and, consequently, climate change. Stationary CO₂ sources like coal power plants produce the bulk of the world's CO₂ emissions. Electricity and heat plants and other fuel transformation activities account for 40% of total global CO₂ emissions. Therefore, great interest in the possibilities of CCS systems to reduce CO₂ emission is evident, either through removal or reduction measures. The experimental part of this paper deals with the determination of the potential of alternative media for use in CCS technologies, describing the lab-scale investigation. The role of alternative media in that context has been assigned to recurrent water from fly ash and slag disposal pond Jezero II of Power Plant Tuzla. When choosing an alternative medium for CCS applications, the following features were considered: that the medium currently has a negative impact on the environment; that the medium is available in sufficient quantities; that the medium has a low price and that its final disposal causes costs. Hence, the ability of the selected media (recurrent water) for CO₂ capture has been confirmed and its capacity in that context roughly determined.

KEYWORDS: carbon dioxide, CCS technologies, recurrent water, power plant.

INTRODUCTION

CCS is a process that consists of separating CO₂ from industrial and energy sources, transporting to a storage location and long-term extraction from the atmosphere¹. Spectrum of measures that need to be urgently implemented to mitigate climate change can play a decisive role because it can contribute to a 20% reduction of CO₂ that is considered necessary by 2050. According to LoS², carbon dioxide capture, extraction and storage technologies make a promising option that can significantly reduce emissions.

However, CCS systems will be difficult to apply as long as the policy that legally limits greenhouse gas emissions in the atmosphere does not change. Such political changes would lead to all new industrial fossil fuel plants being designed so that some of the CCS technologies can be used³.

Simplified, CCS processes consist of three main components: capture, transport and storage (disposal)⁴. However, some technologies can be rather expensive and there are no reliable estimates of the total cost as well as the individual costs of the links in the technology chain, but it is considered that the major part of cost are related to CO₂ separation processes. Nevertheless, the wider application would be considered to lead to a reduction in separation costs, which would make the generating of electricity from

fossil fuels still more cost-effective than the production from alternative, clean sources of energy.

CCS technologies are also needed in Bosnia and Herzegovina, but there is also the need for legal and regulatory framework regulating CCS. Development of ability to adopt new technology, additional efforts in order to solve transport, storage, location choices, monitoring, leakage responsibilities, property rights, environmental issues and public perceptions are the issues that require time and finance, which are mostly missing, so the technology implementation process is significantly slowed down. It has been shown that the necessary investments in the CCS will come only if there are adequate financial incentives and regulatory mandates⁵.

The development of CCS technology can potentially provide developing countries, as well as Bosnia and Herzegovina, a shift away from fossil fuels energy and the gradual abolition of the same. Determining the potential of alternative media that represents an environmental load, which is available in sufficient quantities, with a low price, for whose disposal is currently paid, as a carbon extraction medium in CCS technologies, could be of great importance in this respect. Such an approach can also be helpful in terms of the environmental performance of the emitters, but also provide the basis for improving the implementation of CCS technology, and additionally

purchase the time needed to switch to other materials and technologies with low carbon contents.

The idea of using recurrent water from slag and fly ash disposal pond Jezero II of Thermal Power Plant Tuzla, as an alternative medium for capturing CO₂ has been imposed on itself, knowing the above stated desirable properties that such a medium should hold and which correspond to the properties of recurrent water.

MATERIALS

(1) Recurrent water was supplied from disposal pond Jezero II of Power Plant Tuzla. The samples were taken 2017, March 28.

Power Plant Tuzla uses water for various purposes. A very significant quantity of water, from 1200 to 1500 m³/h is used as a transport fluid for the hydraulic transport of slag and ash from the thermal power plant to the disposal pond Jezero II. Waste water is largely free of suspended matter, it is relatively clear however, regular water analyses show:

- significant alkalinity expressed as CaCO₃ content (460-1900 mg/L),
- very high pH value from 10.5 to 13,
- pronounced toxicity.

This waste water is not in accordance with the criteria specified by the legal regulations, i.e. by the applicable ordinance⁶. Power Plant Tuzla has therefore started closing the circle of this water into recycle, so now water is not released into surface water in normal operation, and therefore does not represent a waste stream. However, under certain circumstances (especially in the case of high precipitation), recurrent water flows into the drainage to the surface water, so that its parameters become important from the environmental point of view. Additionally, the recurrent water is treated with additives in order to prevent the creation of fouling in the pipeline, so that the reduction in the content of the substances causing the fouling would be highly desirable from an economic point of view.

Hence, by hydraulic transport, suspension of slag, ash and water arrives to the disposal pond Jezero II, where the slag and ash are deposited with natural decantation, and the discharged water from the pond drainage system and the drainage channel (drain E3) in regular operation returns to the Thermal Power Plant and is reused for the same purpose; or it is discharged into the natural recipient – the River Jala⁷ (in the event of an excessive amount, mainly due to high precipitation).

(2) Carbon dioxide was supplied from MESSER Ltd Tehnoplina (Schl. Nr. ELN 13891L10 Typ TG 400 Nr 11133 ND2 MM – 530) – 5 kg tank.

EXPERIMENTAL

The apparatus was assembled from:

- Glass beaker 3 L;
- Magnetic stirrer (Tehnica Železniki);
- pH-meter (WTW InoLab 720) with SenTix[®]41 electrode;
- Rotameter (MLW/ WEB MLW PRUFGERATE – WERK MEDINBGEN/SITZ FREITAL 1 GDR) 3 L/h;
- Glass aspirator (Intos Boral Pula);
- Two diffusers (airstones).

The picture of apparatus is given in the Figure 1.



Figure 1. Assembled apparatus

A glass beaker with a sample of recurrent water, in an amount of 2 L was placed on a magnetic stirrer. In the same beaker, the immersed electrode was previously kept in 3 mol/L KCl, and washed with distilled water. From the CO₂ tank, gradually and very slowly moving the valve, gas was released, and through the rubber hose was passed through a glass aspirator, which actually serves as a buffer tank for preventing the flow fluctuation. The aspirator was connected to the rotameter with a rubber hose, and owing to its scale, the gas flow was monitored, read, and continuously maintained at 1 L/h. The rubber

hose, through which CO₂ flowed from the rotameter, was placed in the glass beaker containing the recurrent water. At the end of the hose that plunged into water, a Y-shaped extension was attached with two diffusers (airstones) on its two ends. The diffusers serve to form smaller bubbles of CO₂ as much as possible, thereby increasing the surface of the gas in contact with the aqueous medium, for the purpose of better gas dissolution in water, and at the same time prolonging its retention. A magnetic stir bar was also placed in the glass cup.

Three series of experiments were performed, with different setups:

- Series 1 - without installed gas diffusers;
- Series 2 - with installed gas diffusers;
- Series 3 - with installed gas diffusers, for shorter time.

Each series of measurement consisted of three consecutive measurements, with identical parameters.

The average values of experimental results are shown graphically.

RESULTS AND DISCUSSION

SERIES 1

During the measurements, pH and temperature values were monitored for every 60 and then 30 seconds. The initial pH value was 12.93, temperature 21.5°C with a volume flow of 1 L/h. At the end of the measurement, monitored pH value was 6.25 and temperature 22.4°C. A rise in temperature of 0.9°C corresponded to a decrease in pH to a value of 6.68. The pH was kept constant, until a sudden decrease of pH value below 7 at about 19 minute of experiment. Measured pH values were incorporated into formulas for expressing the concentration of [H]⁺/[OH]⁻ ions in order to graphically display the dependency of average concentrations of [OH]⁻ ions from time *t*. In this regard, a shortened time scale is given, with the aim of a clearer representation of the important 'moment' of the measurement series, when a significant decrease in the pH value occurred.

Starting from the onset of the experiment, the initial concentration of [OH]⁻ ions, 0.085 mol/dm³, was decreasing for about 19 minute, after which the pH of the solution went to 'acidic' values, and it is to assume that from this moment, part of the formed residue was dissolved, which can be concluded from the fact that from that moment the solution began to clarify.

SERIES 2

Measurements were done, with monitored pH and temperature values, for every 60 seconds. The

initial pH value was 12.86, temperature 21.5°C with a volume flow of 1 L/h. At the end of the measurement series, pH was 6.02 and temperature 23.5°C. While the temperature increased by 2°C, the pH value decreased by 6.84. The pH value was kept relatively constant, with a slight decrease until about the 9th minute, when the significant decrease in pH happened, leading to a 'drop' of pH below 7, after which pH was kept relative constant to about 6, and thus until the experiment was completed. pH values were translated to the concentration of [OH]⁻ ions whose dependency of the average values of time *t* is shown graphically with a shortened time scale for the same reason as in the series 1, for a clearer view of the 'moment' of the measurement series when a significant 'drop' in pH values occurred.

From the very beginning of the experiment implementation, the initial concentration of [OH]⁻ ions, 0.07 mol/dm³, was decreasing until about the 11th minute of experiment, after which pH of the solution went into 'acidic' values. A part of the formed residue was dissolved, and the solution was slowly beginning to clarify.

SERIES 3

The third series of measurements was carried out for the purpose of indicating the potential of recurrent water for capturing CO₂. Measurements were carried out to the point of noticeable pH change, with an average time of 19 minutes, monitoring pH and temperature values every 60 seconds (the first 10 measurements), and then for 30 seconds until the end of the experiment. The initial pH value was 12.76, temperature 22.6°C, with a volume flow of 1 L/h. At the end of the measurement series, the pH was 7.9 and temperature 23.4°C. The increase in temperature of 1.8°C corresponded to a pH reduction of 4.86. The pH value was kept relatively constant, until about the 18th minute of the experiment, when a significant decrease was observed, and the pH dropped below 8, after which the experiment was stopped (after 19 minutes), in order to avoid the re-dissolution of the residue. At that moment, a total of 0.32 L CO₂ was transmitted. The pH values on the same principle as in the series 1 and 2 were translated to the concentration of [OH]⁻ ions, for the same reason. The initial concentration of [OH]⁻ ions, slightly less than 0.06 mol/dm³, from the beginning of the experiment, decreased until about the 18th minute of experiment progression, when pH value of the solution went to the 'acidic' values.

After completion of the third series of measurements (shortest one), the resulting residue was filtered, dried, and weighed. The characterization of the

formed residue was not performed, but it was assumed that this 3.566 g of residue was mainly composed of calcium carbonate. If so, it could be concluded that the 2 L of recurrent water captured cca 1.57 g CO₂, which could be roughly taken as the minimal potential for CO₂ capture.

Carbon dioxide within the solution reacted with the molecules of the medium, but only a small part, so carbonic acid was formed in a small concentration. Water containing a lot of carbon dioxide has a low pH, 6-7. In relation to this, and according to the graphic presentation (Figure 2) where the pH dropped between 6 and 7, the used medium "captured" the maximum possible amount of CO₂, which would represent a breakthrough capacity for capturing CO₂.

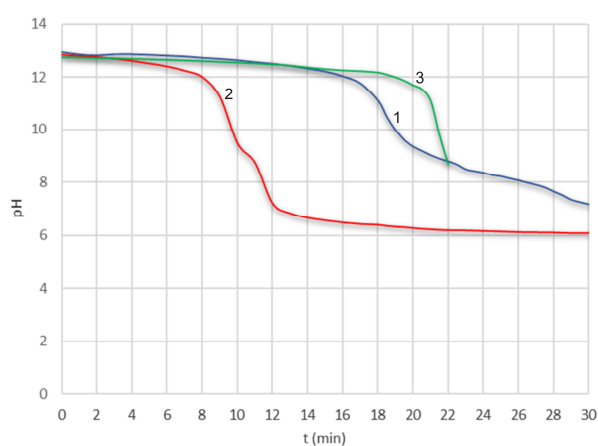


Figure 2. pH vs time for all three series together

Based on the determined concentrations of [OH⁻] ions, which decreased during all three series of measurements (Figure 3), it can also be determined that the used medium or wastewater shows a certain ability to capture CO₂.

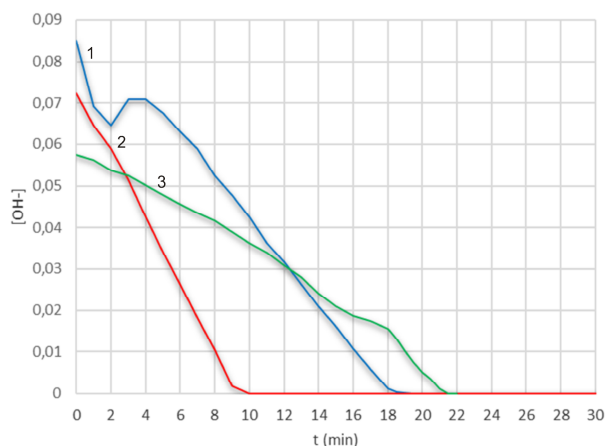


Figure 3. [OH⁻] vs time for all three series together

CONCLUSIONS

During all three series of measurements, with minor deviations, the recurrent water showed similar properties in contact with CO₂ gas. Therefore, it was possible to determine the capacity to capture carbon dioxide in all measurement series. Also, the recurrent water from the disposal pond Jezero II has shown satisfactory results in terms of application in CCS technologies, and has become a good candidate for consideration when it comes to wider application in the environment, perhaps not as an independent medium, but certainly in combination with other media, especially if CCS is combined with flue gas desulfurization by wet process.

Hence, recurrent water has a composition that is not in accordance with the legislation; certainly represents the load for the ecosystem; it is available in an ample amount without any costs; its disposal into the environment causes the costs and, according to the results of this research, it has a potential for capturing the CO₂. Taking all these facts into account, it could be concluded that the recurrent water from slag and fly ash disposal ponds of Power Plant Tuzla could be a convenient medium for use in CCS technologies.

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