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CCGT unit with a carbonation system for CO2 capture

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Abstract. The paper considers the issues of creating energy-efficient and environmentally friendly resource-saving energy generation technologies based on fossil fuels, solid waste and materials. A natural gas CCGT with a MSW ash carbonation unit was chosen as the research object. The prototype of the CCGT unit is the CCGT “Akademicheskaya” with an installed capacity of 230 MW. For the carbonation of MSW ash, a direct semi-dry route is used. In the calculation of the CCGT, the power and efficiency of the cycle are determined, as well as the parameters of the flue gas, which are transferred to the calculation of carbonation. As a result of calculations, it was found that this specific CO2 emissions from the power plant using carbonation can be reduced by almost 20% from 403 to 329 g kWh-1, however, a large amount of required MSW (2.6-6.7 kg per kg of flue gases) causes certain difficulties for the implementation of the project.

Introduction
The problems of tightening the standards of emissions of harmful substances and the assumed obligations to reduce greenhouse gas emissions require the development of environmentally and economically viable technologies for capturing CO2 with subsequent utilization [1, 2]. According to global environmental programs, the scenario of reducing CO2 emissions will inevitably be realized for all industries, but only the energy industry needs to switch to emission-free low-carbon technologies in 2050-2060 with a reduction in CO2 emissions by 80-95% in relation to 1990, and emissions of others harmful substances by 100% [3].

One of the options for solving this problem is the CCS method (Carbon Capture and Storage) [4], including the capturing CO2 from industrial and energy source flue gases, its transportation to the storage and long-term isolation from the atmosphere. A more promising method is CO2 mineralization by carbonation of materials with an increased content of basic oxides: rocks, ash and slag waste (ASW), construction industry wastes, etc. For the first time, the idea of carbonation of minerals for the sequestration of CO2 in a stable solid phase was expressed in 1990 in the work [5].

Currently, the one-stage process of ex-situ carbonation of solid materials with CO2 capture, called direct accelerated mineral carbonation – AMC, is recognized as the most effective [6, 7]. The main problem of direct accelerated carbonation is the need to intensify reactions and rational use of heat release (thermal effects) [8]. The direct method means that CO2 is fed into dry or humidified chemically untreated alkaline waste such as fly ash or aqueous fly ash slurry. In this process, fly ash cations such as Ca2+ and Mg2+ are leached into solution and then precipitated as carbonates on the surface of the solids. Direct carbonation products are suitable, for example, for use as cement additives.

To start solving this problem, it is necessary to consider the technological options for the implementation of the chemical problem. In the review [4] the process of accelerated direct carbonation
is considered in three ways by liquid to solid ratio: (1) L/S=0 – dry process; (2) L/S=0.03-1 – semi-dry process; (3) L/S>0 – aqueous process.

Studies of the mineral carbonation of CO₂ using fly ash have focused primarily on the direct aqueous route, which involves the direct reaction of fly ash with CO₂ in a single reactor with water as the reaction medium. Direct carbonation can also be carried out in a semi-dry manner. The low water content makes the product easier to dry. This semi-dry processing route also allows control of the grain size and chemical composition of the carbonated material produced, which will help find applications for these materials, for example, in the construction industry. The third option for direct carbonation is the dry route. Dananjayan compared dry and aqueous carbonation and showed that dry is a slower process than wet carbonation with water. [9].

This paper considers the issues of creating energy-efficient and environmentally friendly resource-saving energy generation technologies based on fossil fuels, solid waste, and materials. A natural gas CCGT with a MSW ash carbonation unit was chosen as the research object. The prototype of the CCGT unit is the CCGT “Akademicheskaya” with an installed capacity of 230 MW. The direct semi-dry route described in [7] is used for the carbonation of MSW ash.

When calculating the CCGT, the power and efficiency of the cycle are determined, as well as the parameters of the flue gas, which are transferred to the calculation of carbonation. The purpose of calculating the carbonation plant is to assess the size of MSW ash consumption and the impact on the efficiency of the entire power plant.

Calculation methods

Modern technologies provide a wide range of software packages that can significantly reduce the time and improve the accuracy of mathematical calculations. Currently, there are many widely used commercial software such as "AspenPlus", which is used to simulate chemical and thermodynamic processes. Among open source software, the alternatives are “COCO Simulator” and “DWSIM”. The programs allow performing stationary thermodynamic calculations of technological schemes, determining phase equilibria of multicomponent media, and simulating chemical processes. Based on our own experience in these programs, we may say that "DWSIM" has a better solver that can handle complex circuits with many circular threads. The advantage of the "COCO Simulator" is a wide functionality for setting new substances that are absent in the standard library. However, these products are still inferior to "AspenPlus" in terms of substance bases, thermodynamic models, and functional elements.

To calculate the thermal scheme of the CCGT unit, the “DWSIM” package was chosen, and for the calculation of the carbonation unit – “COCO Simulator”. The property package based on the IAPWS-IF97 formulation is used to determine the thermodynamic properties of pure water flows. Gas streams (air, fuel, combustion products) are considered as real gases, and their enthalpy, entropy and heat capacity are calculated using Peng-Robinson equations of state for real gas [10].

CCGT calculation

The thermal schematic of the CCGT-230 “Akademicheskaya” power unit was taken as a prototype of the design scheme. The CCGT unit includes: one GT13E2 gas turbine (GT) with a rated electrical power (according to ISO conditions) of 166.6 MW and an efficiency of 36.5%, one P-86 heat recovery steam generator (HRSG) and one T-63-7.0 steam turbine (ST). The first three stages of GT have air cooling, which must be considered for a more correct calculation of the exhaust gas temperature. Detailed data on this system are closed by the manufacturer, so the approximate values were taken from [11] and corrected further, so 7% of the inlet air consumption goes to cooling the turbine, of which 72.4% falls on the 1st stage cooling (supplied to the combustion chamber element), 19, 7% and 7.9% – at the 2nd and 3rd steps, respectively. Double-circuit HRSG has heating installation for domestic hot water needs. The deaerator is fed with steam taken from the LP drum.

The calculation is carried out with the ambient parameters: temperature 15 °C, pressure 1.013 bar, humidity 60%, and the nominal operating mode of the CCGT equipment. The steam turbine is assumed
to operate in condensing mode. Other main assumptions and schematic for calculating the CCGT are presented in appendix.

To verify the calculation, the data on the operation of the CCGT unit at the "Akademicheskaya" are used. The verification data and the data obtained in the calculation are presented in table 1.

Table 1. Main results of the CCGT.

| Parameters                        | Measurement units | Calculated values | Verification values | Relative deviations, % |
|-----------------------------------|-------------------|-------------------|---------------------|------------------------|
| GT outlet temperature             | °C                | 505.8             | 507.8               | 0.39                   |
| Combustion products composition  | %                 |                   |                     |                        |
| N₂                                |                   | 75.0              | 75.0                | 0.00                   |
| O₂                                |                   | 14.15             | 14.06               | 0.64                   |
| H₂O                               |                   | 6.93              | 6.98                | 0.72                   |
| CO₂                               |                   | 3.02              | 3.07                | 1.63                   |
| Ar                                |                   | 0.89              | 0.89                | 0.00                   |
| HP steam capacity                 | kg s⁻¹            | 58.22             | 59.64               | 2.38                   |
| LP steam capacity                 | kg s⁻¹            | 13.4              | 13.06               | 2.60                   |
| HRSG flue gas temperature        | °C                | 91.3              | 91.9                | 0.65                   |
| GT electric power (gross)         | MW                | 163.87            | 166.6               | 1.64                   |
| ST electric power (gross)         | MW                | 67.51             | 65                  | 3.86                   |
| Fuel compressor electric power    | MW                | -2.39             | –                   | –                      |
| Pump electric power               | MW                | -0.97             | –                   | –                      |
| CCGT electric power (gross)       | MW                | 231.38            | –                   | –                      |
| CCGT electric power (net)         | MW                | 228.01            | –                   | –                      |
| Thermal input                     | MW                | 455.87            | –                   | –                      |
| GT efficiency (gross)             | %                 | 35.95             | –                   | –                      |
| HRSG efficiency                   | %                 | 72.63             | –                   | –                      |
| ST efficiency (gross)             | %                 | 27.2              | –                   | –                      |
| CCGT efficiency (gross)           | %                 | 50.76             | –                   | –                      |
| CCGT efficiency (net)             | %                 | 50.02             | –                   | –                      |
| Specific CO₂ emissions           | g kJWh⁻¹         | 403.7             | –                   | –                      |

The relative deviations of the calculated values from the verified ones are less than 4%. Thus, the computational model of the CCGT-230 thermal scheme can be considered complete and satisfactory. At the next stage, the flue gas parameters is used for calculating the carbonation of MSW ash.

Calculation of carbonation

1. Verification

The AMC (Accelerated Mineral Carbonation) process proposed in [7] was chosen as the design scheme and includes dryer, blower fan, humidifier, heater, and fluidized bed reactor (FBR) (figure 1). The flue gas is removed from the funnel and fed to the dryer. Condensed moisture is trapped to protect the blower. The humidifier and heater allow to control the humidity and temperature of the flue gases.

The upper inlet of the reactor is connected to the ash hopper to supply the required amount of fresh material to the reactor. The fly ash particles are fluidized by the flue gas stream, thereby ensuring proper mixing and good contact between the particles and the gas. Solid lines 1-8, 18, 31 represent material flows. Dotted lines 21, 22, 33, 34 are information streams providing the adjustment of ash and water supply.

According to the conditions [7], the flue gas consists of CO₂ – 13%, H₂O – 10%, N₂ – 66%, O₂ – 11%, its consumption is 10.38 kg min⁻¹. The composition of fresh ash is presented in table 2. The pressure in the reactor is 115.1 kPa. The isentropic efficiency of the compressor is 75.0%. Before
entering the reactor, the gas is humidified to a water content of 16%. The gas temperature in front of the reactor is 60 °C.

![Figure 1. The AMC process diagram for the direct capture of CO\(_2\) from flue gases.](image)

### Table 2. Elemental composition (in terms of oxides) of fresh ash for verification (% wt.) [7].

| Element      | Fresh Ash Composition (%) |
|--------------|---------------------------|
| SiO\(_2\)    | 58.61                     |
| Al\(_2\)O    | 19.06                     |
| Fe\(_2\)O\(_3\)| 5.37                      |
| CaO          | 7.5                       |
| MgO          | 3.85                      |
| Na\(_2\)O    | 0.7                       |
| K\(_2\)O     | 0.94                      |
| CaCO\(_3\)   | <0.1                      |
| Water        | 0.042                     |

The calculation considers the following four reactions of interaction of CO\(_2\) with metal oxides:

- \(\text{CaO} + \text{CO}_2 = \text{CaCO}_3\);
- \(\text{MgO} + \text{CO}_2 = \text{MgCO}_3\);
- \(\text{K}_2\text{O} + \text{CO}_2 = \text{K}_2\text{CO}_3\);
- \(\text{Na}_2\text{O} + \text{CO}_2 = \text{Na}_2\text{CO}_3\).

The author does not give the value of the carbonation efficiency; therefore, the completeness of the reactions was taken as 30% as for a semi-dry process in [9]. Verification is carried out by the concentration of CO\(_2\) in the gases after the reactor and by the content of CaCO\(_3\) in the carbonized ash. The results of the verification of the calculation according to the data [7] are presented in table 3, it speaks about the adequacy of the model.

### Table 3. AMC model verification.

| Flue gases (% mol.) | Ash (% wt) |
|---------------------|------------|
| Component Before carbonation [7] | Component Before carbonation [7] |
| Component After carbonization [7] | After carbonization Calculation |
| Component Before carbonation [7] | Component After carbonization Calculation |
| CO\(_2\) 13 | CaCO\(_3\) 0.10 |
| 9.6 | 3.5-4 |
| 9.6 | 3.98 |

The calculation results show that the degree of CO\(_2\) conversion is 22.6% and 0.033 kg of CO\(_2\) per kg of ash is captured.

2. **Calculation of MSW ash carbonation**

Own calculation of the MSW ash carbonation is made for two ash compositions, the composition of which is taken from [12]. In the work, the author investigated the solid residues that are formed during the thermal processing of MSW using the two most common combustion technologies – combustion grate (CG) and a swirl fluidized bed (SFB) furnace. The composition of these ashes is given in table 4.

![Diagram of MSW ash carbonation process.](image)
The carbonation parameters obtained at the verification stage and included in the main calculation are as follows: the degree of conversion of carbonated oxides is 30%, the degree of CO₂ conversion is 22.6%. The flue gas of the CCGT unit consists of CO₂ – 3.02%, H₂O – 6.93%, N₂ – 75.0%, O₂ – 14.14%, its consumption is 547.6 kg s⁻¹. The calculation results for two evils are presented in table 5.

**Table 4.** Elemental composition (in terms of oxides) of MSW ashes from two incineration plants, % (by weight) [12].

| Oxide  | CG ash min | CG ash max | CG ash average | taken in calculation | SFB ash min | SFB ash max | SFB ash average | taken in calculation |
|--------|------------|------------|----------------|---------------------|-------------|-------------|------------------|---------------------|
| SiO₂   | 29         | 43.2       | 36.1           | 45.1                | 54.9        | 77          | 65.95            | 68.15               |
| TiO₂   | 0.9        | 2.6        | 1.75           | 0                   | 0.6         | 0.8         | 0.7              | 0                   |
| Al₂O₃  | 7.2        | 13.6       | 10.4           | 10.4                | 4.5         | 11.1        | 7.8              | 7.8                 |
| Fe₂O₃  | 1.5        | 5.9        | 3.7            | 3.7                 | 0.7         | 2.4         | 1.55             | 1.55                |
| CaO    | 13.8       | 37         | 25.4           | 25.4                | 10.8        | 19          | 14.9             | 14.9                |
| MgO    | 1.5        | 2.5        | 2              | 2                   | 0.5         | 1.3         | 0.9              | 0.9                 |
| K₂O    | 0.5        | 4.5        | 2.5            | 2.5                 | 0.9         | 1.4         | 1.15             | 1.15                |
| Na₂O   | 2.2        | 6.5        | 4.35           | 4.35                | 1.3         | 2.1         | 1.7              | 1.7                 |
| SO₃    | 4.5        | 8.6        | 6.55           | 6.55                | 1.2         | 6.5         | 3.85             | 3.85                |
| P₂O₅   | 2.1        | 6.5        | 4.3            | 0                   | 0.5         | 2.1         | 1.3              | 0                   |
| Cl     | 0.8        | 2.7        | 1.75           | 0                   | 0.3         | 1.4         | 0.85             | 0                   |

**Table 5.** Results of calculating the MSW ash carbonation.

| Parameter                                      | Measurement units | CG ash | SFB ash |
|-----------------------------------------------|-------------------|--------|---------|
| Ash consumption                               | kg s⁻¹            | 73.0   | 133.6   |
| Specific ash consumption                      | kg kg⁻¹ of flue gas | 0.133  | 0.207   |
| Specific yield of fly ash [12]                | kg kg⁻¹ of MSW    | 0.02   | 0.08    |
| The amount of MSW consumed                    | kg kg⁻¹ of flue gas | 6.65   | 2.59    |
| CO₂ concentration in exhaust gas              | % mol.            |        | 2.11    |
| Concentration of carbonates in finished ash   | % wt.             |        |         |
| CaCO₃                                         |                   | 9.21   | 7.94    |
| MgCO₃                                         |                   | 1.01   | 0.56    |
| K₂CO₃                                         |                   | 0.54   | 0.50    |
| Na₂CO₃                                        |                   | 1.43   | 0.87    |
| Flue gas compression power required           | MW                | 10.04  |         |

As a result of the calculation, we find that for capturing 22.6% of CO₂ from flue gases of the natural gas CCGT 0.1-0.2 kg of MSW ash per kg of flue gases will be required. Energy consumption for the injection of flue gases into the carbonization unit reduces the net efficiency of the power unit from 50.02% to 47.81%. At the same time, the specific CO₂ emissions of the entire power plant will decrease by almost 20% from 403 to 329 g kWh⁻¹. However, in this work, the system of humidification and heating of flue gas in the installation has not yet been thought out, therefore, the heat costs of the carbonization unit are not estimated.

**Conclusions**

Simulation of the scheme of natural gas CCGT unit with the installation of MSW ash carbonation has been carried out. The prototype of the CCGT unit is the CCGT “Akademicheskyaya” with an installed capacity of 230 MW. The direct semi-dry route described in [7] is used for the carbonation.
The calculation of the CCGT was carried out in the open software for modeling chemical processes “DWSIM”. The relative deviations of the calculated values from the declared ones are less than 4%. Calculation of the carbonization process of MSW ash of two compositions (CaO content is 25.4–14.9% wt.) was carried out in the free software package "COCO Simulator". The carbonization parameters obtained at the verification stage and included in the main calculation are as follows: the degree of conversion of carbonated oxides is 30%, the degree of conversion of CO_2 is 22.6%.

As a result of the calculation, we find that to capture a given amount of CO_2 from the flue gases of a CCGT fired with natural gas 0.1-0.2 kg of MSW ash per kg of flue gases will be required. Energy consumption for the injection of flue gases into the carbonization unit reduces the net efficiency of the power unit by 2.2% absolute. At the same time, the specific CO_2 emissions of the entire power plant will decrease by almost 20% from 403 to 329 g kWh\(^{-1}\). However, in this work, the system of humidification and heating of flue gas in the installation has not yet been thought out, therefore, the heat costs of the carbonization unit are not estimated. A large amount of required MSW (2.6-6.7 kg per kg of flue gases) causes certain difficulties for the implementation of the project.

### Appendix

![Figure 2. Schematic of gas turbine part.](image)

![Figure 3. Schematic of steam turbine part.](image)
Table 6. Main assumptions for the calculations of CCGT.

| Parameter                                                      | Dimension | Value                  |
|----------------------------------------------------------------|-----------|------------------------|
| Fuel composition: CH₄, C₂H₆, C₃H₈, N₂                          | %         | 97.69, 0.82, 0.33, 1.16 |
| Air/fuel compressor pressure ratio                             |           | 16.9/3.9               |
| Isentropic efficiency of compressors/turbine                  | %         | 92.0/84.0              |
| Turbine inlet temperature                                      | °C        | 1095                   |
| Flue gas mass flow rate                                        | kg s⁻¹    | 547.6                  |
| Heat loss at combustor                                         | % of fuel LHV | 0.9                  |
| Pressure loss at combustor                                     | %         | 3                      |
| Mechanical efficiency of the gas turbine/compressors           | %         | 99.8                   |
| HRSG gas side pressure loss                                    | kPa       | 3                      |
| Live steam temperature (HP/LP)                                | °C        | 483.6/276.7            |
| Live steam pressure (HP / LP)                                 | bar       | 79.8/11.9              |
| Deaerator pressure                                             | bar       | 6                      |
| Condenser pressure                                             | kPa       | 5                      |
| Condensate temperature before LTE                              | °C        | 60                     |
| Thermal power of WWHE                                          | Gcal h⁻¹  | 22.9                   |
| HRSG heat losses from ambient cooling                          | %         | 0.7                    |
| Pinch point (HP / LP)                                          | °C        | 10                     |
| Condensate underheating to saturation temperature at the deaerator | °C     | 7                      |
| Feed water underheating to saturation temperature in drums     | °C        | 5                      |
| Hydraulic losses in HPSH/LPSH/live steam lines/stop valves     | %         | 5/5/8.5/3              |
| Isentropic efficiency of HPT/LPT/pumps                         | %         | 83.0/78.0/75.0         |
| Mechanical efficiency of the steam turbine                     | %         | 99.5                   |
| Generator efficiency                                           | %         | 98.7                   |

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