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Chemical Recycling of Ash and Industrial Wastes at Coal-Fired Power Plants with CO₂ Utilization

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Abstract

The utilization of ash and slag from coal-fired power plants to ensure their environmental safety was considered. A comprehensive technology is proposed to utilize wastes of solid fuel combustion from thermal power plants and regional industrial wastes along with CO₂ emissions produced at thermal power plants, which is relevant under the Paris Climate Agreement signed by Russia. A low-waste process of energy generation and the production of substituents of natural materials for various purposes may be arranged by combining the production of free calcium and magnesium oxides from the mineral part of fuel burnt in the steam boiler, dry ash removal from the boiler and electrostatic precipitators, chemical saturation of the oxides with carbon dioxide from coal combustion products leading to the formation of thermodynamically stable carbonates. Integrated carbonation of basic components of ashes from the power plant during the mineralization of CO₂ emissions enhances the consumer properties of ash and slag and provides the reduction of CO₂ emission by 3–5 %, which is equivalent to an increase in power plant efficiency by 1.5–2 %. Involvement of regional resources (power plant ash and slag and other facilities, construction waste from housing renovation programs, etc.) in the chemical recycling process can increase the degree of power plant wastelessness up to 70–90% without turning to expensive technologies of carbon capture and storage (CCS). The possibility to solve the multifactor utilization task for solid and gaseous products of different kinds within a single technological process ensures the commercial attractiveness of this proposal.

Keywords: coal-fired power plant, CO₂ utilization, ash and slag wastes, mineralization, carbonation, chemical recycling

INTRODUCTION

Stern targeting for ecologization in the operation of coal thermal power plants (TPP) in the world leads to substantial structural shifts. In the countries with the developed coal economics, a principally new direction of the utilization of ash and slag wastes (ASW) is emerging in direct connection with the measures aimed at a decrease in anthropogenic emission of CO₂ and with the search for the forms to provide long-term retention of technogenic carbon in a thermodynamically stable form with low energy content. One of these methods is the use of solid wastes of power engineering, industry and communal facilities for mineralization of technogenic CO₂.

According to the data of the International Energy Agency (IEA) [1], an integrated approach to the problem of mineralization of CO₂ emissions due to carbonation of ASW from TPP is one of the most promising approaches to solve the global ecological problems of power engineering in the developed and developing economies. The application of this approach may lead to a substantial decrease in the load on the geological storage of CO₂ and hold back the accumulation of industrial wastes.

Implementation of the processes of CO₂ emission mineralization through carbonation of ASW and technogenic wastes by transforming them from a chemically active form into thermodynamically stable one will promote the transition to closed industrial cycles with the minimal ac-

cumulation of solid wastes and minimal release of greenhouse gases.

The problem of TPP emissions has not been considered in the science of our country in this formulation before [2].

RECYCLING METHODS

Mechanical and chemical methods of recycling as the basic routes of TPP waste utilization and the general necessity of the development of technologies to provide carbon capturing, using and storing (Carbon Capture Utilization and Storage, CCUS) occupy an important position in the Energy Strategy of Russia till 2035.

Choice of recycling method depends on the type of chemical activity exhibited by ash: pozzolanic, hydraulic, carbonate.

In turn, the type of chemical activity is determined by the basicity factor and the presence of free CaO (fr.) and MgO (fr.).

Basicity modulus used in construction industry (M_o) coincides at a good accuracy with the reciprocal modified energy acidity index (k_0) [3]: $M_o = \Sigma O / (\Sigma K - TiO_2) \approx \Sigma O / \Sigma K = 1/k_0$ (1) where ΣO , ΣK – are the sums of the content of basic and acidic oxides, respectively, mass %: $\Sigma O = CaO + MgO + K_2O + Na_2O$; $\Sigma K = SiO_2 + Al_2O_3 + TiO_2$.

The coincidence is due to the TiO_2 content which is usually low (<1 mass %) in the ash of energy coals.

Pozzolanic activity is understood as the ability to bind calcium hydroxide from an external source at usual temperatures and to form insoluble calcium – silicon and calcium – magnesium hydrates [4]:



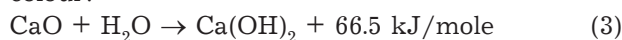
Their accumulation involves the hydraulic hardening of the binders composed of a mixture of lime and Portland cement with ash or slag [5].

Pozzolanic properties are exhibited by ash with $(CaO + MgO) \leq 10-12$ mass % and insignificant content of CaO (fr.) and MgO (fr.) [6], as a rule, unable to interact with water. Depending on the level of pozzolanic activity, acid ashes are divided into inert – $M_o < 0.1$ ($k_0 > 10$) and cryptoactive – $M_o > 0.1$ ($k_0 < 10$). The first ones are used in mechanical recycling as technogenic fillers and ground, while the latter species are used in chemical recycling as active mineral additives [6].

Concentration limitations on CaO and MgO are determined by the technological requirements to provide the uniform change of the volume of

products (concrete, grout) during solidification. The composition of acid ash in construction is limited according to GOST 25818–2017 by mass content: CaO < 10 %, $(SiO_2 + Al_2O_3 + Fe_2O_3) > 70$ % and humidity 1 %. The ash of this kind is related to silicic ash in the European Community [4]. Additional requirements according to GOST 25818–91 and GOST 25592–91 provide standards for the content of other oxides: MgO < 5 %, $SO_3 < 3-6$ % – to meet the requirement of sulphate stability, $(Na_2O + K_2O) < 1.5-3$ % – to avoid deformations during the interaction with fillers, the loss of the mass of mechanical underburning during annealing (a. l.) < 3–25 %.

Hydraulic activity is understood as the ability of the active components of ash (CaO (fr.), MgO (fr.)) to interact with water with the formation of finely dispersed ($d \sim 1 \mu m$) solid phase of white colour:



Ash with the mass content CaO 5–20 %, CaO (fr.) < 2 %, $M_o < 0.5$; $k_0 > 2$, obtained after the combustion of coal from Raichikhinsk, Bogoslovskiy mining district, Kharanorskiy ope pit, Cheremkhovo, Khakassiya and some others, relates to the cryptoactive kind. Thermal treatment with activizers is necessary for their solidification [6]. Brown-coal ash with CaO > 10 %, CaO (fr.) < 2–5 % (for three types of products of four applied in construction according to GOST 25818–2017) is close to this group, too.

Ashes with basic composition with $(CaO + MgO) \geq 20$ % ($M_o = 0.5-2.8$; $k_0 = 2.000-0.357$) and noticeable content of hydraulically active components (CaO (fr.) up to 30 %) manifest themselves as self-hardening binding materials.

The group of active materials includes ASW of shale rocks from the Volga region, coal from the Kansk-Achinsk coal basin, some kinds of peat and municipal solid wastes (MSW). The total content of CaO is 20–60 %, CaO (fr.) – 2–30 %. According to the European terminology, they relate to high-calcium ash [7–9].

The tendency of basic ash to be hydrated does not allow wet ash and slag withdrawal at TPP [3].

The pozzolanic and hydraulic types of activity are in the basis of the traditional practice of the application of ASW in the construction industry.

Carbonate activity is understood as the ability of the active components of ash (Ca, Mg) to interact with carbon dioxide with the formation of thermodynamically stable calcium or magnesium carbonate according to overall reactions, for the dry process:

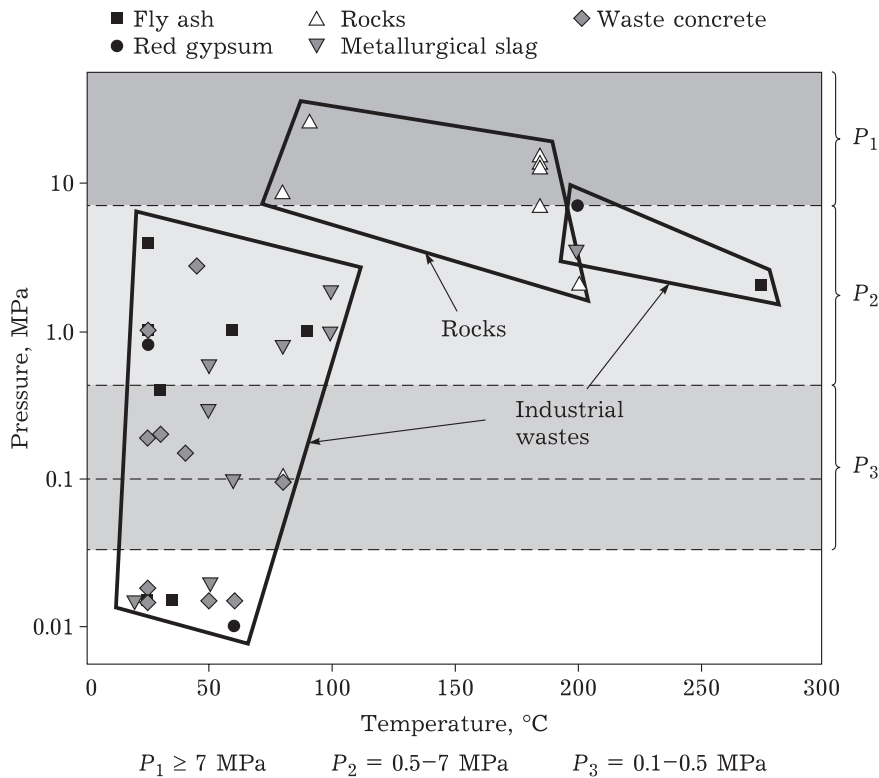
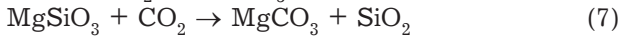
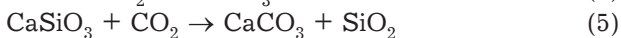


Fig. 1. Conditions of carbonation reactions for different materials [10].



For a faster wet process, the overall reaction takes into account the presence of water:



A substantial part of Ca and Mg in natural minerals with basic composition is in the inactive state in the form of silicates and aluminosilicates – chemical compounds with SiO_2 and Al_2O_3 . Another part of Ca and Mg, not bound in the structure of the tetrahedral silicon dioxide network, is free and reactive. After the isolation from the mineral mass, this part of Ca and Mg is ready to enter the reaction with CO_2 with the formation of solid $\text{CaCO}_3/\text{MgCO}_3$. However, as a rule, high temperature and pressure are necessary for the isolation of reagents (Fig. 1) [10].

Artificial materials are obtained at high temperatures (1200–1600 °C) of fuel combustion, for natural minerals to be thus subjected to high-temperature thermal treatment followed by quenching.

Mineral components dissociate or melt in the flame kernel [11]. The minerals of authigenic origin (carbonates, sulphides) dissociate (get decarbonized and desulphurized) with the formation of primary oxides (CaO , MgO , Fe_2O_3 , Fe_3O_4 , CO_2 ,

SO_2), which is followed by the interaction of calcium and sulphur oxides with the formation of calcium sulphate.

Some fraction of the products of primary thermal dissociation of authigenic and terrigenous minerals enter secondary synthesis with the formation of multiphase multicomponent systems [12].

Another fraction of primary oxides (CaO/MgO) remains in the free state and is able to enter chemical interaction with low-concentrated CO_2 flow at atmospheric pressure and low without any use of the Pre-Combustion system and compression. Depending on the availability of fluid, the time of carbonation (CaO/MgO) varies. Some oxides (CaO/MgO) get encapsulated during the melting of clay minerals and form vitreous globules hindering reagent input to the grains (CaO/MgO). This arising spatial non-uniformity of reaction will reduce the total process intensity and may lead to internal strain and destroying deformations.

To enhance the access of fluid to the reagents, intense mixing or additional grinding is used [13, 14]. Additional grinding has a positive effect on the mass exchange, similarly to mechanical activation of coal dust before burning [13, 15].

The carbonate activity of ASW is used for the development of new technologies of carbonation and mineralization.

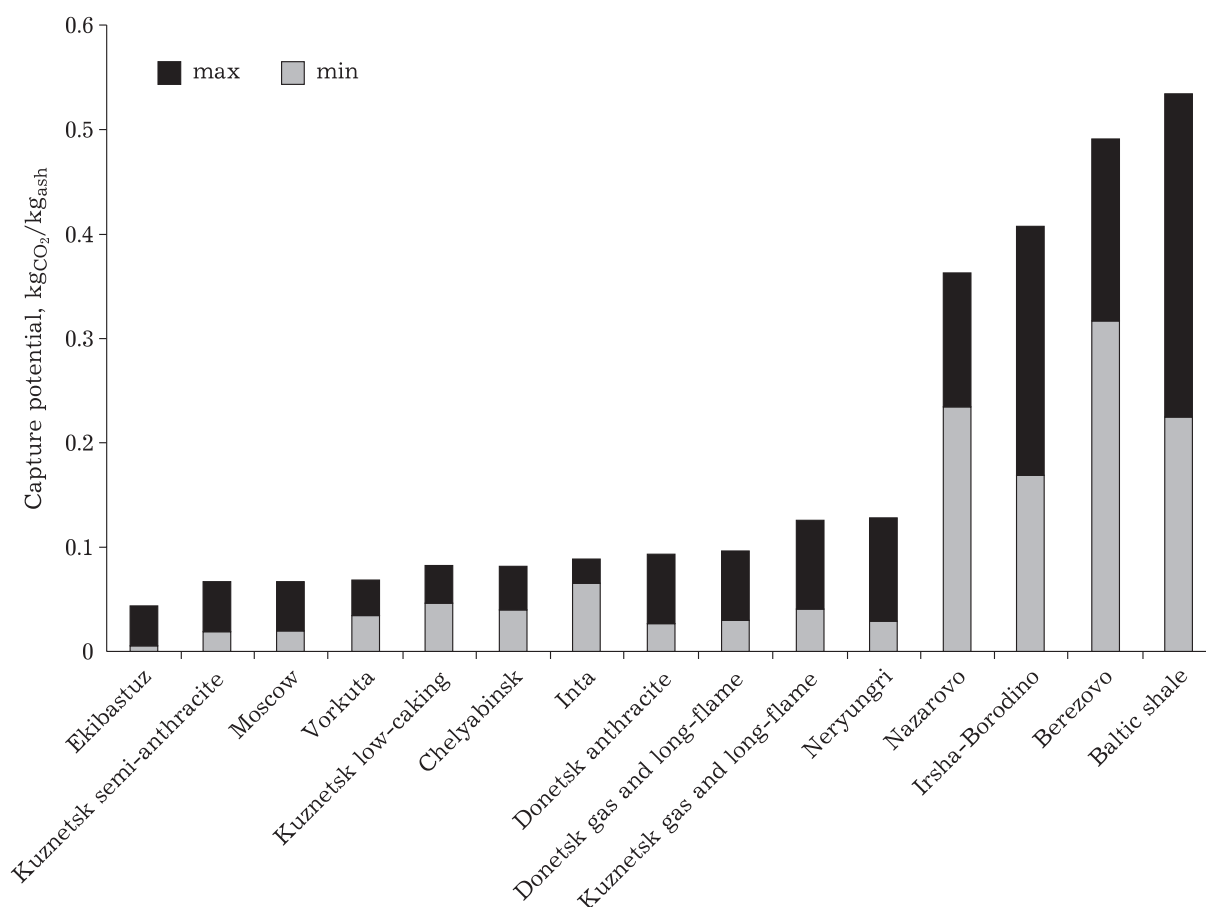


Fig. 2. Potential of CO₂ capture during carbonation of fly ash of coal from different deposits.

The potential of capturing CO₂ by ash (CO₂ mineralization) is calculated using the stoichiometric Stenoir's equation [16] and corresponds to the maximal possible capturing ability of ash:

$$\text{CO}_2 \text{ (mass. \%)} = 0.785(1 \% \text{ CaO} - 0.7 \% \text{ SO}_3) + 1.09 \% \text{ MgO} + 0.71 \% \text{ Na}_2\text{O} + 0.468 \% \text{ K}_2\text{O} \quad (9)$$

Where the mass content of oxides (%) in ash is given in the right-hand part of the equation.

It is assumed that the whole amount of CaO (except that bound in CaSO₄) and other oxides will react giving rise to corresponding carbonates. If bicarbonates are formed instead of Na and K carbonates, the coefficients at Na₂O and K₂O are to be multiplied by 2 [17].

If we assume that all available oxides enter the reaction leading to the formation of carbonates, then the capturing ability of volatile ash from Russian coal will vary, according to equation (10), from several per cent (for acid ash) to ~40 % (for high-calcium basic ash) (Fig. 2).

The actual carbonation efficiency (CE) is calculated using equation

$$\text{CE} = G_{\text{CO}_2} / G_{\text{CaO}} \quad (10)$$

where G_{CO_2} is the amount of mineralized CO₂, kg; G_{CaO} is the amount of carbonized CaO in the ash, kg. Taking into account kinetic limitations, CE ~ 10–50 %, or 0.1–0.5 kgCO₂/kgCaO. To determine the carbonation efficiency, it is necessary to carry out the corresponding experiments or calculations [17, 18].

INTEGRATED TECHNOLOGY OF CHEMICAL RECYCLING

Chemical recycling will be understood in the narrow sense as the recovery of consumer properties of worked out materials (wastes) through chemical interaction with carbon dioxide captured from combustion products.

A combination of the process of obtaining active calcium and magnesium oxides from the mineral part of fuel in a steam boiler, dry ash withdrawal from the boiler and electric filters, and saturation with carbon dioxide from the products of coal combustion, leading to the formation of thermodynamically stable carbonates, allows one to arrange a low-waste process of the

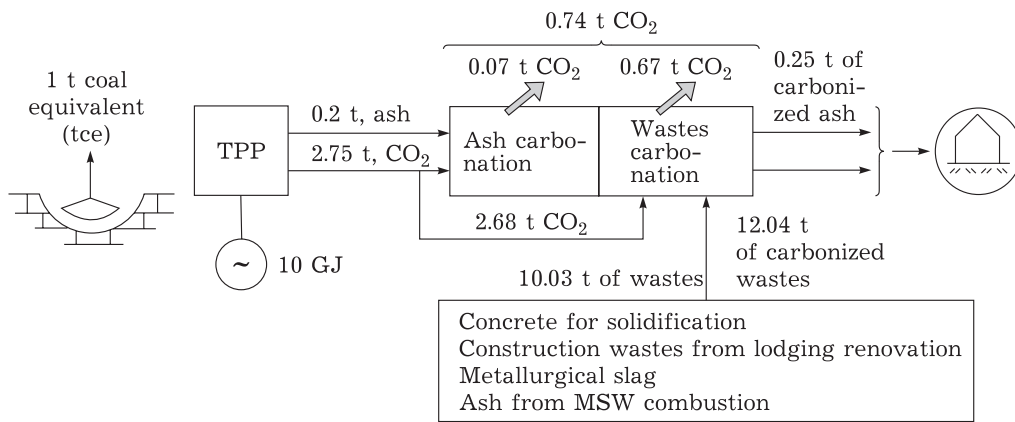


Fig. 3. Mass balance for CO₂ in coal-based energy producing complex.

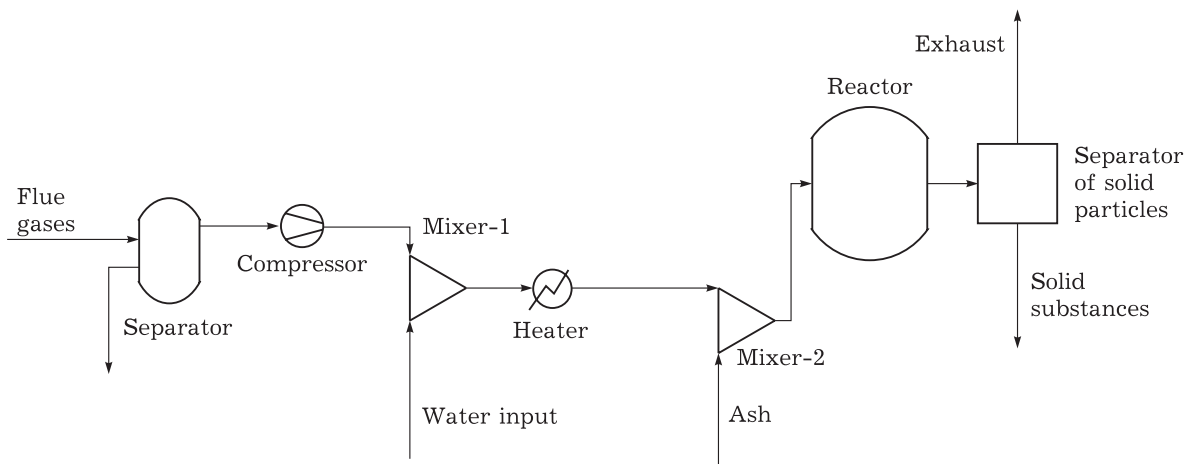


Fig. 4. Calculation scheme for ash carbonation.

production of electric and thermal energy and substituents for natural materials for different purposes (Fig. 3).

Calculation of carbonation is carried out using a COCO Simulator software. The calculation scheme for the dry ash carbonation compiled in agreement with the scheme of the test of the pilot plant [17] is presented in Fig. 4.

Results of verification over the data [17], shown in Table 1, provide evidence that the model is adequate.

The carbonation efficiency for the dry process is accepted to be equal to 33 %, calculation was

carried out per 1 kg of ash. Before supplying into the reactor, gas was humidified to 16 %. The degree of CO₂ conversion was 22.6 %, and 0.034 kg_{CO₂}/kg_{ash} was captured.

CONCLUSION

An integrated process of carbonation of the basic components of ash from TPP taking place during mineralization of emitted CO₂ allows one to enhance the consumer properties of active basic ash and slag with a decrease in CO₂ emission by 3–5 %, which is equivalent to an increase in the

TABLE 1
Verification of calculation scheme

Flue gases, mol. %				Ash, mass %			
Composition	Before carbonation [17]	After carbonation [17] Calculation		Composition	Before carbonation [17]	After carbonation [17] Calculation	
CO ₂	13	9.6	9.6	CaCO ₃	0.10	3.5–4	4.36

coefficient of efficiency of TPP by 1.5–2 %, and additional carbonation of the wastes of other plants allows a decrease in CO₂ emission by 70–80 %.

Stabilization of ASW achieved through carbonation allows using these wastes in the construction industry instead of natural minerals and for recultivation of affected land, for making an isolating layer at MSW grounds, for preventing wash-out of microelements (arsenic, cadmium, lead, selenium, etc.) into surface, soil and underground waters, which generally improves the ecological safety of the environment during utilization of the products of solid fuel combustion.

Involvement of regional resources (ash and slag from other plants, construction wastes from lodging renovation programmes, etc.) into chemical recycling may improve the degree of TPP low-waste performance with respect to CO₂ emission up to 70–90 %.

The possibility to solve a multifactor problem of the utilization of solid and gaseous products of different types within one technological process ensures the commercial attractiveness of the present proposal.

Development of technological solutions of the proposed process is carried out at the Ural Energy Institute of the Ural Federal University (Ekaterinburg). Intermediate results were discussed at the XXXVI Siberian Thermophysical Seminar, V All-Russian Scientific Conference “Thermophysics and Physical Hydrodynamics”. Proposals concerning the integrated use of the carbonate activity of ash have been submitted to the Ministry of Energy of the Russian Federation.

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