Poly-Generation of Thermal Energy, Electricity and Anthropogenic Products

Tomasz SZCZYGIELSKI[1], Jan J. HYCNAR[2]

[1] Warsaw University of Technology, IBS, CIMA
[2] Ecocoal Consulting Center Katowice

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Abstract

This is the first in the series of engineering papers presenting new possibilities of coal-based power engineering, where the energy producing boiler is seen as a chemical reactor, which in the poly-generation process should be outputting only products, no waste. This is to help meeting the Circular Economy (CE) goals by the power sector.

Rich chemical composition of flyash and conditions in which they arise, high temperatures and flue gas control systems, many times suggest to purposefully combine the processes of combustion of fuels with the processes of their energy-and-technological processing. Taking into account the huge interest in extracting aluminum compounds (alumina) from flyash, theoretical considerations were made in terms of possibilities of combing the combustion of coals rich in alumina compounds with the process of their extraction. Out of a very rich list of techniques for producing alumina, in the context of ashes the most interesting are the alkali-sintering methods. Of particular potential is the sintering-disintegrating method by Prof J. Grzymek, which has been already verified in industrial conditions in the cement sector, while in this paper it is analyzed from the angle of coal combustion and sintering of calcium-oxide containing ash.

Keywords: high alumina fly ash (HAFA), extraction of alumina from ash, extraction of alumina in coal combustion process

Introduction

Modern boilers firing liquid and solid fuels use the chemical energy in fuels for creating the thermal energy. The chemical energy of the fuels is transformed unidirectionally into the thermal energy in defined spatial conditions (of the furnace chamber and the flue gas path), guaranteeing an appropriate increase/distribution of temperatures.

In these conditions the processes of heating up water and generation of water steam are to/may be treated as permanent consumers of the thermal energy from the ongoing chemical processes.

Viewing the power boiler as a high-temperature reactor we may notice, that depending on the required temperature parameters of steam/water and the temperatures achieved in furnaces, we are dealing with considerable differences deciding on the dynamics of heat transfer between the exothermic reactions and the heated media – Table 1. All these processes of heat exchange between the media in modern boilers/reactors and flue gas paths are balanced in a way ensuring the possibly fullest utilization of heat. Temperature distribution in the coal-fired power boilers is illustrated in Fig. 1 and 2.

In such power systems we may consider the furnaces/reactors as sources of high temperatures and gases/shielding atmospheres for additional chemical reactions and the structural transformations of series of materials/products.

Possible utilization of such a source of heat/high temperatures for additional endothermic processes would require some additional sources of heat/fuel, whereas in case of exothermic processes it would involve reducing the amount of fuel or utilization of excess heat.

Considering the thermal conditions of fuel combustion, we may view a number of mineral constituents forming bottom and fly ash as the substrata of series of chemical reactions. Power sector has a significant experience in controlling the series of chemical reactions in combustion chambers, which so far are aimed only at solving the numerous operational problems in boilers/reactors, such as:

- desulfurization of flue gas in the process of burning sulfur-laden coal, by adding calcium compounds to the combusted coal;
- countering the slagging of waterwall tubes of boilers and gasifying reactors, by supplying calcium compounds onto their surfaces;
- countering the high-temperature corrosion by adding a.o. vanadium compounds;
- increasing coal combustion efficiency by adding vanadium compounds;
- increasing fuel combustion efficiency by re routing into the combustion chamber the high LOI ashes and coal concentrates extracted by flyash decarbonization;
- reducing NO_x emissions in flue gases by dosing ammonia/urea;
- reducing CO_2 emissions by co-combustion of biomass.

Tab. 1. Example parameters of furnaces and sinter production acc. to J. Grzymek

Tab. 1. Przykładowe parametry pieców i spiekalni wg. Prof. J. Grzymka

Ref.	Parameters	unit	Type of furnace					**Production of alumina acc. to Grzymek**
			Stoker	Pulverized fuel	Fluidized bed station.	Fluidized bed circ.	Gasifying reactor	
1.	Temperatures:	°C	1,200 –	1,600 –	800 –	750 –	1,800 –	
1.1.	- coal combustion		1,600	1,800	900	950	2,000	-
1.2.	- sintering	°C	-	-	-	-	-	1,300
1.3.	- self-disintegration of sinter	°C	-	-	-	-	-	< 530
2.	Reaction time:							
2.1.	- combustion reaction	sec	120 – 180	1 – 6	150 – 180	240 – 330	-	-
2.2.	- sintering reaction	sec	-	-	-	-	-	?
2.3.	- time of self-disintegration	sec	-	-	-	-	-	20

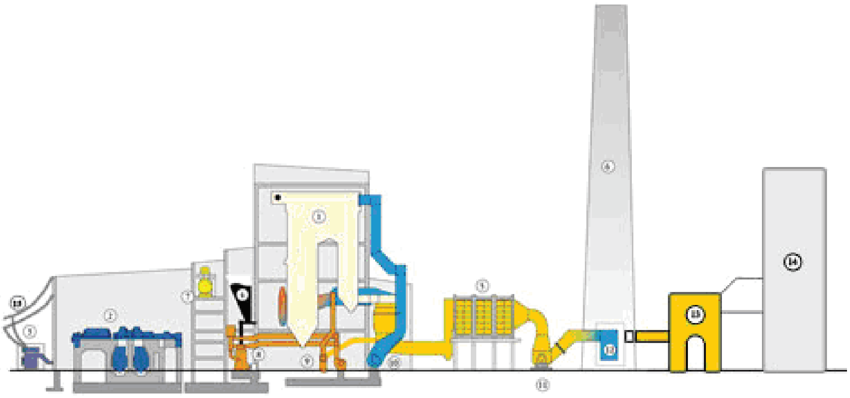


Fig. 1. Diagram of the combustion pass and flue gas path with emission control system of a 200 MW$_e$ Unit: Furnace ; 1400 – 1800°C, Convection path 550 – 200°C, Flue gas path 200 – 110°C

Rys. 1. Schemat przejścia spalin z układem sterowania dla kotła 200 MWe:; 1400 – 1800°C, Ścieżka konwekcyjna 550 – 200°C, Ścieżka spalin 200 – 110°C

All this practical experience suggests/confirms the expediency of considering power processes and mineral constituents included in flue gases as a source of additional products/materials, bu controlling/regulating the composition of substrata, as well as temperatures and times of mutual interactions of these factors.

Concepts

Long-standing testing of flyashes from hard coal and lignite demonstrate the significant differences in their chemical composition and in many cases inspire the purposefulness of their use instead of/in addition to numerous natural mineral materials. Local unavailability/lack of many mineral resources and their high costs stimulate developments of such trends, which is accompanied by increased volumes of deposited flyashes. In this respect, many impressive and prospective works may be noted on the comprehensive utilization of coal combustion products [1, 2, 3, 4], supporting thereby the implementation of Circular Economy [5].

There are very few publications on the direct use of the conditions of coal combustion for intended creation of end products, and they are limited to attempts of producing binders [12] and deactivation of free CaO [10].

Concepts of alumina recovery

Of particular relevance is the development of research and technical trials involving the use of flyash for producing aluminum oxides. The content of aluminum compounds in HAFA flyash (High-Alumina Fly Ash) in China is 38–50%, in Kazakhstan 35–37%, in Poland up to 34%, and i Republic of South Africa amounts to 30% with total absence of boxites.

Developed since more than 80 years technologies of aluminum oxide recovery have been dwelling on processing of flyash outside of power plants, and the majority of them is based on alkaline-sintering process or leaching of aluminum compounds using alkalies/acids. Published reports [1, 6, 13, 14] present a rich overview of methods of producing alumina (Al_2O_3) from flyash.

Technologies of solubilization/leaching/extraction of ashes with acids (hydrochloric, nitric, sulphuric, oxalic, etc.) or strong hydroxides (potassium, sodium, etc.) allow for precipitating iron and calcium compounds from

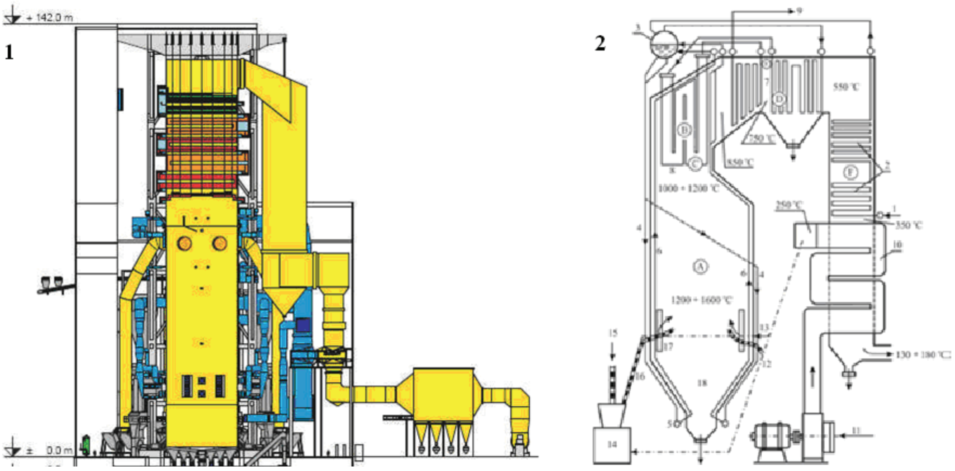


Fig. 2. Diagram of BB-2400 single pass supercritical steam boiler of a 858 MWe Unit (1), and temperature distribution in a two-pass boiler (2)

Rys. 2. Schemat jednokanałowego kotła parowego BB-2400 z jednostki 858 MWe (1) i rozkładu temperatury w kotle dwuprzebiegowym (2)

reaction product mass and for separating/leaching metals' concentrations from residual solutions, using chelates, selective solvents, ion-exchangers, sintering, etc.

The solubilization methods are preferred, a.o. due to a possibility of recovering of all contained elements, including rare earth metals. In Poland, a similar approach was developed by Prof Breitsznajder for processing flyash from Turów Power Plant [7].

Much promising for a wider implementation of flyash solubilization method is a new technology of producing sulphuric and nitric acid in the process of flue gas treatment and its application in ash processing (NeuStream method). NeuMetals Inc. is erecting a pilot plant processing several tons of ash per day at Ray Nixon Power Plant in Fountain, Colorado [8].

Sintering and sinter disintegration technologies

Among very numerous methods of sintering and sinter disintegration of flyash with limestone known around the world, only the method of Prof. J. Grzymek was practically verified in experimental-industrial scale at Groszowice Cement Plant [9, 15, 16]. In a rich overview of methods of extraction of alumina from flyash from coal combustion, particular attention was devoted to Prof J. Grzymek method not only due to being the only one industrially implemented method of production of aluminum oxide from ash, but also as a prospective method [1].

In the case of Prof Grzymek technology, ash/coal slate is sintered with limestone at 1300°C, forming calcium ortosilicate and calcium aluminates. Due to cooling down below 530°C, the sinter disintegrates (ca. 95%) in approximately 30 minutes, forming gamma $2CaO.SiO_2$ and dust with grain size of ca. 20 µm. Arising dust is subjected to leaching with water solution of calcium carbonate. Post-extraction solution contains 20–35 kg/m^3 of aluminum oxide and is further processed (silica removal, carbonization) as illustrated in Fig. 3 [9].

In the said technology the following process nodes may be distinguished:

- sintering node (ca. 1300°C) and sinter disintegration (below 530°C), where the main constituents are calcium ortosilicate $2CaO.SiO_2$ and aluminum-calcium minerals $12CaO.7Al_2O_3$ and $CaO.Al_2O_3$, which, during cooling down, disintegrate into a fine dust;
- leaching/extraction node of dust with soda solution for separating calcium aluminates, which after cleaning are subjected to silica removal, carbonization with CO_2; calcination of aluminum hydroxide and uptake of aluminumoxide;
- cement production node consisting in mixing the post-extraction mud with limestone and burning of the mixture in rotary kilns into the high-alite Portland clinker.

Considerations on combining combustion process with sintering process

While analyzing the conditions of alumina producing, only the sintering node has the temperature profile approximating the pulverized fuel furnace boilers, while in the flue gas path a potential auto-disintegration of sinters might be located – Fig. 1.

Considering the temperature distribution in the kiln used for producing clinker (in similar conditions Al_2O_3 was produced), we notice a systematic increase of temperatures up to 2000°C (flue gas), whereas sintering in temperatures 1250 to 1450°C takes place in merely approx. 13% share during processing of feed in the rotary kiln, as illustrated in Fig. 4.

The analysis of temperature distribution in boilers fired with pulverized coal, presented in Fig. 1, 2 and 5 shows similar temperature zones as those present in minerals clinkering processes. Fundamental differen-

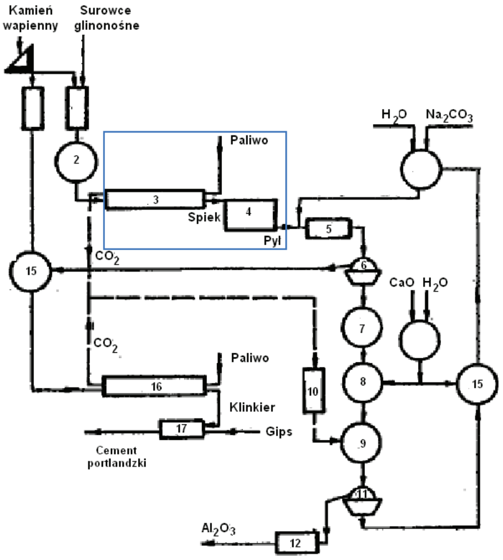


Fig. 3. Diagram of sintering-disintegrating technique of producing aluminum oxide acc. to Prof J. Grzymek [9]: 2 – Feed bunker, 3 – Rotary cement kiln, 4 – Cooler, 5 – Extractors, 6 – Rotary vacuum kiln, 7 – Decanter, 8 – Silica-removal tank, 9 – Carbonization tank, 18 – Quenchers, 10 – Water scrubber, 11 – Rotary vacuum filter, 12 – Rotary kiln, 13 – Tank, 16 – Rotary kiln, 17 – Ball Mill

Ryc. 3. Schemat spiekania i techniki wytwarzania tlenku aluminium wg. prof. J. Grzymka [9]: 2 - Bunkier zasilający, 3 - Piec obrotowy cementowy, 4 - cooler, 5 - Ekstraktory, 6 - Piec obrotowy próżniowy, 7 - Dekanter, 8 - Zbiornik do usuwania krzemionki, 9 - Zbiornik do karbonizacji, 18 - Wygaszacze, 10 - Skruber wodny, 11 - Obrotowy filtr próżniowy, 12 - Piec obrotowy, 13 - Zbiornik, 16 - Piec obrotowy, 17 - Młyn kulowy

ces are found in the environment of chemical reactions, where in the combustion process the oxidation reactions take place in the air aerosol, whereas in the sintering process the chemical reactions occur between a mix of solid (or slightly melted) constituents.

By comparing the thermal parameters of the sintering node with temperatures of combustion of coals and dust removal from flue gas, a suggestion appears on the possibilities of combining these processes in a common volume (the combustion chamber). In these conditions two different energy processes and different chemical reactions would need to be occurring at the same time (presented in a simplified way):

- exothermic reactions of coal combustion and releasing of mineral constituents, e.g.:

Coal (C,S,A) + $O_2 \rightarrow CO_2 + SO_2 + (Al_2O_3)_x.(CaO)_y.(SiO_2)z$ (1200–1600°C)

(C,S,A coal; A – mineral constituents in coal)

- endothermic reactions, disintegration of carbonate, and forming and disintegration of sinters;
- disintegration of calcium carbonate:

$CaCO_3 \rightarrow CaO + CO_2$
(ca. 1000°C)

- forming of sinter calcium and aluminum-calcium ortosilicate:

$(Al_2O_3)_x.(CaO)_y.(SiO_2)_z + CaO \rightarrow 2CaO.SiO_2 + 12CaO.7Al_2O_3 + CaO.Al_2O_3$
(1200 – 1400°C)

- sinter disintegration:

$2CaO.SiO_2 + 12CaO.7Al_2O_3 + CaO.Al_2O_3$
(< 530°C).

If we analyze the occurring chemical reactions it means, that if they would be happening in the combustion chamber, then the amount of calcium oxide additionally supplied into the boiler would be respectively:

- proportionately to the released Al_2O_3:

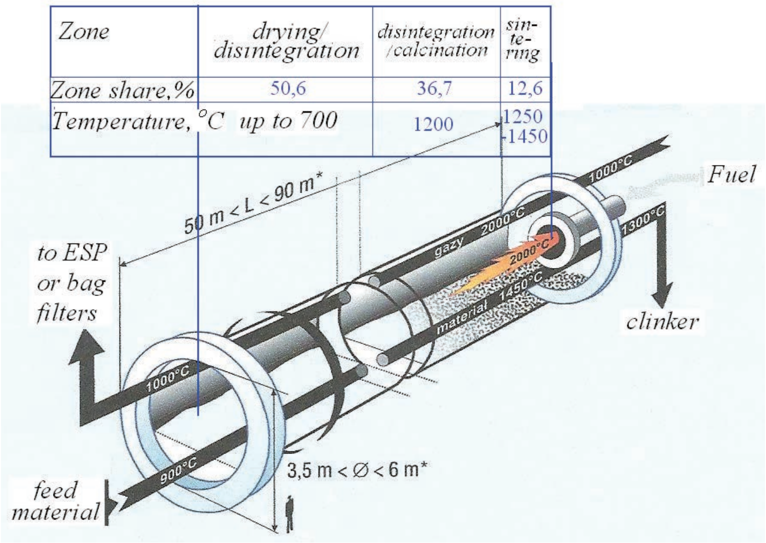
$8Al_2O_3 + 13CaO \rightarrow 12CaO.7Al_2O_3 + CaO.Al_2O_3$
($x = 8$)

$Al_2O_3 + 1.6CaO \rightarrow 0.75CaO.0{,}87Al_2O_3 + 0.12CaO.0.12Al_2O_3$
($x = 1$)

- proportionately to the released SiO_2:

$SiO_2 + 2CaO \rightarrow 2CaO.SiO_2$

Considering the chemical composition of sinters of flyash with CaO, the amount of CaO necessary for the occurrence of the above reaction is respectively:



Zone	drying/ disintegration	disintegration /calcination	sin-te-ring
Zone share,%	50,6	36,7	12,6
Temperature, °C	up to 700	1200	1250 -1450

Fig. 4. Example of gas temperature distribution in Unax type cement kiln [17]

Rys. 4. Przykładowy rozkład temperatury gazu w piecu typu Unax [17]

- *for Al_2O_3 in compound $CaO.Al_2O_3$ the share of CaO amounts to 0.52*

for 0.48 (2x26,98 + 3x16) = 51,82 kg Al_2O_3 falls 0.52 (40,08 + 16) = 29.16 kg CaO
mass increase amounts to 51.82 + 29.16 = 80.98 kg, which represents 1,56 fold increase in mass

- *for Al_2O_3 in compound $12CaO.7Al_2O_3$ the share of CaO amounts to 0.47*

for 7(2x26.98 + 3x16) = 755.72 kg Al_2O_3 falls 12 (40.08 + 16) = 672.96 kg CaO
mass increase amounts to 755.72 + 672.96 = 1428.68 kg, which represents 1.89 fold increase in mass

- *for SiO_2 in compound $2CaO.SiO_2$ the share of CaO amounts to 0.65*

for 28.09 + 2x16 = 60.09 kg SiO_2 falls 2(40.08 + 16) = 112.16 kg CaO
mass increase amounts to 60.09 + 112.16 = 172.25 kg, which represents 2.87 fold increase in mass.

Moreover, the additional loading of the combustion chamber is to be considered due to using limestone, which usually contains ca. 55% CaO. Chemically pure calcium carbonate has the molecular mass of 106 kg, while containing 56 kg of calcium oxide, i.e. 1.89 fold mass increase.

Considering, for example, the 10% ash content in the combusted coal, resulting in arising of flyash with chemical composition: SiO_2 40 % i Al_2O_3 % 30 %, for creating the conditions for occurrence of the described chemical reactions, and sintering and disintegration of reaction products, it is going to be necessary to add the following amounts of CaO to the combusted coal:

- due to the included Al_2O_3:

30x (0.125x1.56 + 0.875x1.89) = 30(0.95 + 1.65) = 30x2.60 = 78.11
content of aluminum compounds in ashes shall increase 2.60 times;

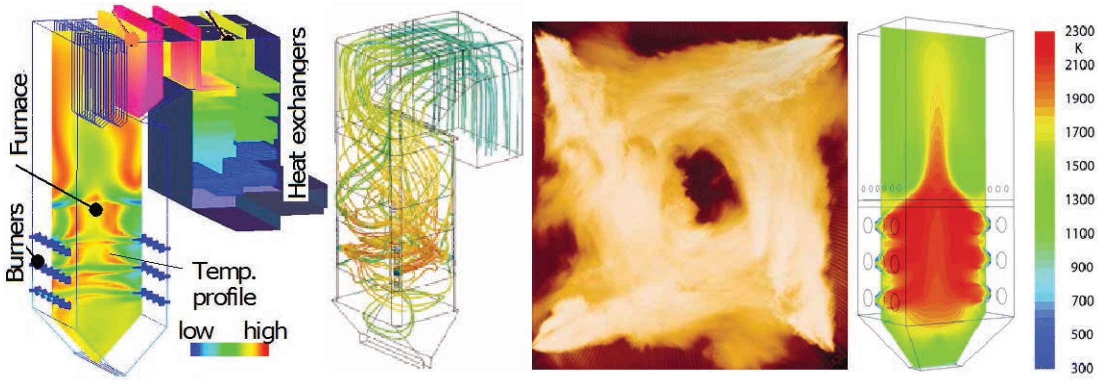
- due to the included SiO_2

increase in mass of silicate compounds 2.87 times to value 114.8

For the discussed example (SiO_2 40% and Al_2O_3 30%), the increase of ash amount will be 2.75 times, which means the increase of ash content in the combusted coal from 10% to 17.6% Nearly twofold increase in the amount of mineral constituents in coal should not constitute an obstacle in implementing of trials, if we consider the rich experience of power sector with burning coals with high ash content.

The amount of combusted coal also needs to be corrected, on the one hand because increased ash content in coal, and on the other due to the necessity of providing energy for carrying out the endothermic sintering reactions.

A number of elements of the proposed process, a.o. conditions for occurrence of sintering in the aerosol environment, temperatures and time of forming of sinters, if they coincide with the time of combustion and flue gas flow, etc. require explanation. These subjects require very serious analyzes not only in terms of times and temperatures of reactions, but also for making a thermal and material balance, ensuring the possibilities of up taking the self-disintegrating sinter in the co-



Temperature, °C	1600 -1200	1200 -1000	850	750	550 - 350	250 130
Share,%	22,0	23,0	9,6	8,9	14,5	21,3

Fig. 5. Example of gas temperature distribution in boilers fired with pulverized coal [Internet]

Rys. 5. Przykładowy rozkład temperatury gazu w kotłach opalanych pyłem węglowym [Internet]

nvection pass and dust removal from flue gas, as well as further processing of the aluminum concentrate.

Undertaking research and tests in this scope should allow for developing new techniques of combustion and sintering of ashes in the processes of combined production. Solving of method of combusting-with--sintering would contribute to the rational use of flyash and reducing the costs of production of alumina and cement.

Poly-generation is the future of power sector

An idea of directly linking the manufacturing of products requiring high temperatures with processes of producing thermal-electric energy is increasingly being discussed. In this respect, by now, a steel making facility was commissioned in Brazil two years ago combined with power generation.

Poly-generation, in which the thermal energy, electricity and anthropogenic products are arising in the same process, charts a new development perspective for the power sector. It provides an opportunity for reducing the costs and risks for mining and power sectors, and coal becoming such fuel, whose power-related combustion needs not to generate any solid waste.

At the same time the anthropogenic products will have a low environmental footprint and would be competitive on the market of construction and metallurgical products. Such an approach should stimulate processes of optimization and innovation in the power sector. Goals of the Circular Economy (CE) for the mining and power sectors can be achieved.

Literatura

1. Yao Z.T., Xia M.S., Sarker P.K., Chen T.: A review of the alumina recovery from coal fly ash, with a focus in China. Fuel, Vol. 120 (2014).
2. Joshi P.B., A low-cost rare earth elements recovery technology. WOCA 2-13Ch
3. Mayfield D., Levis A.: Coalash: A resource for rare earth and strategic elements. Ash At Work 2013, !riCh
4. Hycnar J.J., Tora B., Szczygielski T., Kadlec D.: Discussion on the possibility and relevance of recovery of rare earth and trace metals concentrations from coal combustion products. 22 International Conference "Ashes from Power Generation" Krynica Zdrój 21-23 October, 2015
5. Szczygielski T.,: Anthropogenic minerals from power sector and Circular Economy. 22 International Conference "Ashes from Power Generation" Krynica Zdrój 21-23 October, 2015
6. Matjie R.H., Bunt J.R., Van Heerden J.H.P.: Extraction of alumina from coal fly ash generated from a selected low rank bituminous South African coal. Minerale Engineering 2005 nr 18
7. Kowocki W.: Prospects of utilizing ash from Turoszów Power Plant for producing aluminum oxide by acid method. Ogólnokrajowa Konferencja Turoszów 1971
8. Myfield D., Lewis A.: Coal Ash Recycling: A Rare Opportunity. Waste Mnagement Word 2015, no 5; Metal z …popiołów. Energia Gigawat 2013, nr 12
9. Kosacka E., Rajczyk K.: Sintering-disintegration method by J. Grzymek for producing aluminum oxide and cement from national resources. Przegląd Geologiczny 1974, nr 5
10. Szczygielski T., Hycnar J.J.: Deactivation of CaO in fly ash from combustion of lime-rich lignite. Warszawa – Katowice 2016
11. Hycnar J.J.: Factors influencing the physical-chemical properties and usability of solid products from combustion of fuels in fluidized bed furnaces. Wyd. Górnicze. Katowice 2006
12. Groppo J.: A combustion perspective for processing coal ash into products.XXIV Międzynarodowa Konferencja "Popioły z Energetyki". Sopot 25-27 października 2017
13. Baudet G.: A documentary study on alumina extraction proesses. Bureau de Recherché et Minieres Mission Arabic Saoudite. Departement mineralurgie. Orleans Cedex Fevriev 1977
14. Sun Pei-meil, Guang –min, Tong –wul, XU Hong-yan, Zhao Zhel.: Study on sintering process of Raw Materials In extracting alumina from fly ash of coal industry Power plate. Journal of China Coal Society 2007, 07
15. Grzymek J., Derdacka A., Konik Z., Grzymek W.: Sposób otrzymywania tlenku glinu i cementu według patentów 43444 i 44998. Cement Wapno Gips 1980, nr 8-9
16. Konik Z., Weryński B., Komorowski E.: Spiekalność surowców stosownych w produkcji tlenku glinu. Cement Wapno Gips 1984, nr 5
17. Polski Cement: Piece cementowe.
18. A. FARZANEGAN, E. SEPAHVAND, Z.S. MIRZAEI, 2016 – Optymalizacja układu mielenia klinkieru w prasach HPRG w zakładzie Abyek Cement Plant za pomocą programu Steady-State Process Simulations, Inżynieria Mineralna z. 2(38), Wyd. Polskiego Towarzystwa Przeróbki Kopalin, Kraków, s. 255–260
19. Bradło D., Żukowski W., Czupryński P., Jura K., 2015 – Potencjał odzysku metalu z produktów spalania węgla. Część I: Opis właściwości fizykochemicznych, Inżynieria Mineralna z. 1(35), Wyd. Polskiego Towarzystwa Przeróbki Kopalin, Kraków, s. 157–162.

Poligeneracja energii cieplnej, energii elektrycznej i produktów antropogenicznych

Jest to pierwsza z serii prac inżynieryjnych prezentujących nowe możliwości energetyki węglowej, w której kocioł energetyczny jest postrzegany jako reaktor chemiczny, który w procesie poligeneracji powinien wytwarzać tylko produkty, bez odpadów.
Ma to pomóc w osiągnięciu celów gospodarki o obiegu zamkniętym (Circular EconomyE) przez sektor energetyczny.
Bogaty skład chemiczny popiołów lotnych i warunki, w których powstają, wysokie temperatury i systemy kontroli spalin, sugerują celowe łączenie procesów spalania paliw z procesami przetwarzania powstających odpadów i produktów ubocznych.
Biorąc pod uwagę ogromne zainteresowanie wydobyciem związków glinowych (tlenku glinu) z popiołów lotnych, przeprowadzono analizę możliwości adaptacji procesów spalania węgli bogatych w związki glinu do zwiększenia odzysku związków glinu.
Z bardzo bogatej literatury dotyczącej technik wytwarzania tlenku glinu na bazie popiołów najciekawsze są metody spiekania alkalicznego. Szczególny potencjał stanowi metoda spiekania i dezintegracji wg Prof. J. Grzymka, która została już zweryfikowany w warunkach przemysłowych w sektorze produkcji cementu, natomiast w niniejszym opracowaniu przeprowadzono analizę spalania węgla i spiekania popiołu zawierającego tlenek wapnia.

Słowa kluczowe: popioły lotne z wysoką zawartością tlenku glinu (HAFA), ekstrakcja tlenku glinu z popiołu, ekstrakcja tlenku glinu w procesie spalania węgla