HCFA and CO_2 Savings in Europe – Resources, Markets, Technologies

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KEYWORDS: calcareous fly ash, utilization of combustion by-products, impact of combustion by-products on CO_2 emission reduction

ABSTRACT

The upcoming years shall witness an increasing share of calcium type ash in the balance of combustion by-products representing an approximately 60% share in Europe. This increase stems from larger volumes of fired lignite and oil shale, the popularization of dry and semi-dry flue-gas desulphurization methods as well as from a considerable increase of fluidized beds.

Calcium type fly and bottom ash differ from other types of ash not only through a higher content of calcium compounds but also through a high hydraulic activity which decides of their usefulness for the production of construction materials and engineering works.

The utilization of calcium type combustion by-products is highly influenced by the involvement of its producers (power plants) which ensure the possibility of its selective delivery and possible treatment (mix with other components). A decisive role in the utilization of ash is played by the designed and implemented methods of utilization and the created markets.

In Europe, calcareous ash is used for the production of cement and non-cement binders, mass concrete, stabilization of engineering constructions, preparation of road asphalt, for fertilization and reclamation of soil, etc. The use of calcareous ash not only impacts the reduction of the use of natural resources and traditional materials but also contributes to the reduction of CO_2 emissions to the atmosphere. As a result of a reduced use of traditional resources including construction materials and the optimizing of their production technology, a considerable reduction of CO_2 emissions is achieved and competitive technologies appear.

The optimizing of the utilization of ash is possible through research, verification of the hitherto requirements and the preparation and implementation of new legislation and technologies in an international dimension.

1. Types of combustion by-products of the calcium type

In Europe, approximately 50% of electricity is generated through the firing of solid fuel, mainly hard coal and lignite and, to a lesser extent also through the combustion of oil shale. The consequence of this fact is the production of more than 160 Tg of combustion by-products of which approximately 100 Tg can be attributed to the 27 states of the European Union, as presented in table 1.

An analysis of combustion by-products proves a high diversity of their physicochemical properties depending on the type of fuel that is fired, the mineral component of the fuel, the combustion technology and the output method of slag, bottom and fly ash. The most frequently applied classification consists of a division of combustion by-products into those that are produced from the combustion of hard coal and lignite. At present there are no universal and international methods for the classification and evaluation of solid fuel combustion by-products [1, 2], which in global economy conditions becomes not only an important but also and urgent venture. From the utilization perspective, the division of combustion by-products is of major importance due to the content of silicon, aluminum, calcium and sulfur compounds and the granulation.

The combustion by-products of the **calcium type** characterized by a higher content of calcium compounds (above 3% CaO) as compared to siliceous and aluminous type ash, are of particular importance due to their high share of circa 60% in the European balances of combustion by-products and a forecast for further increase in the upcoming years.

Combustion by-products of the calcium type are composed of fly and bottom ash from the firing of:

- lignite containing calcium compounds (limestone, chalk, gypsum) fired in pulverized-fuel boilers;
- hard coal or lignite fired in fluidized bed boilers;
- hard coal fired in pulverized-fuel boilers with a system of dry and semi-dry flue-gas desulphurization;
- oil shale.

Due to its origin and thermal processes and methods of its production, the specified fly-ash of the calcium type differs considerably in both the content and type of calcium compounds present. Habitually fly and bottom ash from fluidized beds and fly ash from dry flue-gas desulphurization (SDA) not only contain high contents of calcium compounds but also sulfur compounds. Knowledge of the physicochemical properties decides of the directions and possibilities of rational utilization of these combustion by-products.

2. Directions and possibilities of utilizing combustion by-products of the calcium type

Insofar as fly and bottom ash as well as slag melted from the combustion of hard coal are widely used in the production of construction materials, engineering works and prophylaxis in mines, a major part of the calcium type combustion by-products comes upon serious difficulties in finding mass use possibilities [3]. Therefore, it is important to popularize the experiences shared by the individual countries in order to create conditions for the mass utilization of such by-products, with particular emphasis on directions enabling the reduction of CO_2 emissions to the atmosphere.

The results of research conducted in the *Czech Republic* [4] prove that it would be reasonable to use an additive of fluidized ash to limestone and marl in the production of **clinker.** An additive of ash of a content of CaO 4.01 and 12.7 % in quantities adequate to obtain input with a calcium saturation indicator of 96 % with a siliceous module MS = 2.6 and ferroaluminous module MA = 1.6 will cause an increase of the clinker melting temperature and a reduction of the end temperature of decarbonization. The obtained clinker was characterized by a high alite content whereas the produced mortar was characterized by a durability analogous to and even frequently higher than mortar from reference cement.

The use of calcium ash for the production of **cement** as a regulator of the setting time has been known for decades and is implemented in many countries. For example in *Estonia* standard cement „KUKERMITE" is produced which is a mix of 18 to 28 % of small grain calcium ash from the combustion of oil shale with portland clinker [5]. The obtained concrete is characterized by smaller deformations and higher resistance to water and frost and enables the acquisition of concrete of required brands with cement savings of 50 to 100 kg/m^3.

Interesting research was conducted in *Germany* [6] consisting of a study of an additive of 10, 20 and 30% calcium ash (CaO from 2 to 52%, CaO_{free} from 0.1 to 25%) from the combustion of lignite to clinker, jointly milled. „Based on the analysis of results of studies on ferments and mortars produced from cements with an additive of fly ash, it can be concluded that calcium fly ash can be used as the main component of cement mixes despite the fact that it fails to comply with the norm EN DIN 197-1 requirements set for calcium fly ash." This provides for the necessity to legally enforce the obtained results and to popularize new norm solutions – especially in light of the fact that during the existence of the GDR cements were produced with a content of 20 to 40% of fly ash (PUZ 225, ZP 9/35 and PZ 9/40a).

In *Poland,* however, research was conducted on the use of calcium ash obtained from lignite combustion [10] and fluidized ash in the production of cement [11]. It was concluded that calcium ash W is useful in the production of multicomponent cement CEM II/A-M and CEM II/B-M and that, furthermore, such ash favorably impacts cement durability, water demand, texture and workability. By replacing siliceous fly ash and gypsum with fluidized-bed bottom ash, it was possible to obtain cement characterized with a fast durability growth and high final durability. The quantity of applied bottom ash, however, was limited by the restrictions of norm PN-EN 197-1, which did not allow for the exceeding of the calcium sulphate content limit of 3.5 % SO_3.

Particularly valuable experience with calcium ash was obtained in *Greece* which not only advanced such research but also prepared technologies of its adaptation to the effective requirements and introduced its mass use for the production of hydrotechnical **concrete** and construction elements [7-9]. By introducing a pre-selection process, it was possible to eliminate the use of ash with a CaO_{free} content exceeding 12% or high sulfur content as well as course-grained ash. By grinding course-grained ash, fine-grained ash was obtained with a leftover on a 45 μm sieve within the limits of 20 to 30% characterized by higher hydraulic activity and pozzolanic. Ash with an exceeded CaO_{free} content was deactivated by adding water so that after hydration its CaO_{free} content would not exceed 3%. Thus prepared ash was, among others, used in the construction of the Planatovryssi water dam. This dam is a great scientific and technical achievement as it represents the first use of calcium ash and RCC (roller compacted concrete) containing 50 kg/m^3 of standard portland cement (42.5) and 225 kg/m^3 of calcium ash, previously milled and deactivated through hydration. The aforementioned ash was also used to produce concrete bricks and to stabilize argillaceous and sandy soils thus increasing their carrying capacity, shear strength, etc.

The presented examples of obtained research results and calcium ash uses are, on one hand, proof of the high economic and ecological benefits and vast possibilities of their use and, on the other hand, witness to the existence of limitations in their mass use due to the fluctuation of the composition and properties of the created ash and need for a system of pre-selection and adaptation of ash to specific uses. Irrespective of the listed constraints, it remains crucial to draft international norms based on the obtained research results that would allow for a broader use of calcium ash for the production of cement, concrete, etc.

3. Calcium type ash – a method to reduce CO_2 emissions to the atmosphere

The use of combustion by-products as substitutes for traditional mineral resources and a source of new products has been known for many years and popularized in many countries. The basis of these actions consisted and consists of the requirements to rationalize the use of natural resources and, in many cases, to simplify the production technology of products and to eliminate the negative impact of waste on the environment. All these arguments become real and permanent in the function of time if they bring economic benefits including benefits from the use of combustion by-products.

As the Kyoto protocol provisions on CO_2 emission reductions became the key direction of global civilization growth and became a part of the development of the economies of individual states, all possibilities in this respect are being seriously considered.

The hitherto experiences clearly prove that combustion by-products may adopt a new function i.e. a **function of CO_2 emission reduction,** through the following, among others:

- replacement of traditional resources subject to decarbonization and, therefore, emitting CO_2 to the atmosphere, with combustion by-products in the scope of clinker, cement and lime production and, furthermore, in flue-gas desulphurization;
- reduction of fuel use in the process of clinker burning;
- replacement of traditional mineral binders with low-cement and cement-free binders based on combustion by-products;
- replacement of products requiring high pulverization;
- replacement of calcium fertilizers with selected ash and ash mixes.

The capacity to limit CO_2 emission reduction through the use of combustion by-products stems from the processes of its creation. As a result of the impact of high temperatures (800 to 1600^oC), mineral components contained in fired fuel undergo processes of dehydration and decarbonization and, consequently, disintegration and synthesis of new compounds of Si, Al and Ca. As a result of thermal treatment, dehydrated aluminum silicates acquire pozzolanic properties. However, in the aforementioned conditions, calcium carbonates contained in fired coal and added limestone and dolomites undergo decarbonization and partial reactions with sulphoxides as illustrated by the present reactions, among others:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (I)$$
$$CaO + SO_2 + 0{,}5\ O_2 \rightarrow CaSO_4 \qquad (II)$$

The obtained calcium compounds are responsible for the hydraulic binding properties of fly and bottom ash obtained from the combustion of hard coal and lignite as well as oil shale.

The aforementioned facts are of particular importance for the cement and power industries due to the imposed CO_2 emission restrictions. In many cases production will be limited and/or product generation costs will be increased. Particularly high possibilities of limiting the emission of CO_2 to the atmosphere through the use of combustion by-products of the calcium type are found in the cement industry, which has been documented with numerous analyses and research results [12-15].

The cement industry, besides the power industry, is the largest source of CO_2 emissions (representing 5% of global emissions). The cement industry of European Union states in 2003 emitted an average of 750 kg CO_2/Mg of cement. In Poland, the said emission in 2002 amounted to 694 kg CO_2/Mg of cement. A source analysis proves that the highest level of CO_2 emissions originates from the decarbonization process (reaction I) and represents 50 to 60% followed by the burning of clinker connected with the firing of fuel (40 to 30%). The remaining 10% of emissions is attributable to the transport of resources, electricity, etc.

Satisfying the Kyoto obligation, the cement industry undertook a series of actions aiming at the reduction of CO_2 emissions which, depending on their scope, may achieve a value of 50%. Depending on the quantity and quality of the applied fly ash and, optionally, slag in the process of clinker production and as a result of eliminating resources requiring decarbonization, the reduction of CO_2 emissions may range from 1 to 35% of total emissions.

The amount of applied additives depends on the produced types of cement with the highest quantities added to mixed cements. Such possibilities are well seen through the German experiences presented on drawing 1. On their basis, it can be clearly concluded that the reduction of clinker content and the increase of additive content (including ash) in mixed cements linearly reduces the emission of CO_2 to the atmosphere.

Normative requirements imposed on cements regulate and permit the use of not only siliceous type ash but also calcium type ash whose quantity depends on the type of cement and may fluctuate between 5 to 50% - see table 2.

There are no uniform opinions as to the quantity of usable combustion by-products whereas one can also find minimalist „programs” in print. In Poland, ash obtained from coal combustion is used in the production of cement in two stages:

1) clinker production where it is added to the batch in an amount of approximately 12% of the obtained clinker,
2) clinker milling where it represents an additive in an amount ranging from 20% to 25% of the obtained cement.

This means that 1 Mg of cement contains:

- 200 to 250 kg of fly ash, as a direct additive to cement,
- 90 to 100 kg of an ash-slag mix or fly ash as a charge to the clinker furnace,
- a total 90 to 350 kg of fly ash.

Assuming that 40% of the produced clinker will be used for cement production with a 25% additive of fly ash, an estimate of the maximum demand for fly ash was drawn at 1603 thousand Mg/year. What has been just recently assumed to be hypothetical values was then corrected by reality and the consumption of fly ash in Poland exceeded 1800 thousand Mg/year with a tendency towards 2000 Mg/year.

Further reduction of CO_2 emissions in the cement industry is possible and is being performed in many countries through an increase of the share of fly and bottom ash in the batch used to produce clinker as well as through the reduction of clinker production and its share in produced cements.

The increase of the share of combustion by-products in clinker production, while maintaining the required modules such as calcium saturation, shall not only reduce CO_2 emissions thanks to limiting limestone quantities subject to decarbonization but also thanks to reduced fuel consumption for conducting a highly endothermic decarbonization reaction (I). In the case of high shares of calcium ash as the source of CaO there can also occur an increase of the efficiency of existing furnaces due to a reduction of the batch mass subject to clinkerization (mass ration of CaO to $CaCO_3$ is 1:1.78).

The main tendency in CO_2 emission reductions in the cement industry, besides the diversification and rationalizing of fuel, shall most probably consist of reducing the share of clinker and the production of mixed cements. In this respect, the plans of the European Union states (UE 15) assumed an improvement of the average clinker/cement ratio from 0.81 in 1990 to 0.77 in 2010. In Poland this indicator of approximately 0.77 was already achieved in 2001.

In the **power industry** as well there exist possibilities of reducing CO_2 to the atmosphere which have already been partially realized through the return of fly and bottom ash to fluidized bed burners and flue-gas desulphurization circuits in both the dry and semi-dry methods. Studies of the discussed combustion by-products prove that in a majority of cases the overreaction degree of calcium compounds with sulphoxides does not exceed 50%. Through their mechanical or hydrothermal activation and return to circuits, the overreaction degree of calcium compounds may achieve 80%. This represents a reduction of approximately 30% of CO_2 emissions to the atmosphere as a result of reducing the quantity of applied limestone.

4. Conclusion

In the upcoming years, it will be possible to observe an increase of the share of calcium type ash in the balances of combustion by-products as a result of increasing the quantity of fired lignite and oil shale, popularizing methods of flue-gas desulphurization and increasing the amount fluidized bed burners.

Fly and bottom ash of the calcium type are characterized by an increased content of calcium compounds and a high hydraulic activity.

The use of calcium type ash not only affects the reduction of natural resource exploitation but also contributes to the reduction of CO_2 emissions to the atmosphere.

Calcium type ash acquires a new function namely the **function of CO_2 emission reduction,** through the following, among others:

- replacement of resources requiring decarbonization in clinker, cement and lime production and, furthermore, in flue-gas desulphurization;
- reduction of fuel use in the process of clinker burning;
- replacement of traditional mineral binders with low-cement and cement-free binders based on combustion by-products;
- replacement of products requiring high pulverization;
- replacement of calcium fertilizers with selected ash and ash mixes

Satisfying the Kyoto obligation, the cement industry undertook a series of actions aiming at the reduction of CO_2 emissions which may achieve a value of 50%. Depending on the applied additives, including fly ash, in the process of clinker and cement production, the reduction of CO_2 emissions may range from 1 to 35% of total emissions.

The increase and optimizing of the use of calcium type ash is possible through the conducting of joint research, the verification of requirements and the preparation and implementation of new international norms and legislation.

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Table 1. Production and utilisation of CCP

No.	Region or Country	Year	**C** - Coal **HC**- Hard coal **L**-Lignite **C=HC+L**	CCP production, Gg **Total**	Fly ash **FA**	Bottom ash **BA**	FBC Ash **FBC-A**	FGD product **FDG**	**Others**	**Utilisation rat, %**
1.	World	2003 2030	**C** **C**	480.000 950.000						
2.	USA	2007	**C**	131.128	71.700	18.100	7.366	12.300	21.662	42,7
3.	Europa		**C** **L**[1]	≈160.000 ≈71.000						
4.	UE									
4.1	EU-15	1997	**C**	63.000	44.000	9.450	1.269	6.930	630	65
	EU-15	2000	**C**	59.001	38.959	7.928	1.015	10.639	460	53,5
	EU-15	2001	**C**	59.587	39.947	8.080	1.060	9.767	733	89
	EU-15	2003 2003 2003	**C** **HC** **L**	 63.913	44.230 20.630 23.600					48 78 18
	EU-15	2005	**C**		42.751	6.130	955	11.541	2.536	89,0
4.2	EU-27	2007	**C**	≈100.000	-	-	-	-	-	-
5.	Germany	2006 2006 2006	**C** **HC** **L**	26.130 9.360 16.770	13.300 4.400 8.900	2.560 620 1.940	710 350 360	7.490 1.920 5.570	2.070 2.070 0	99,0 99,0 100.0
6.	Polska	1989	**C**	22.978	19.758	3.220				19,5
	Polska	1995	**C**	14.556	12.763	1.793				54,0
	Polska	2000 2000 2000	**C** **HC** **L**	15.229 9.437 5.792	13.365 7.718 5.647	1.864 1.719 145		1.155		75,1
	Polska	2004 2004 2004	**C** **HC** **L**		13.457 7.141 6.316	2.238 2.073 165				97,3
	Polska	2005	**C** **HCFA**[3]	14.766	12.710	2.056	 2.168			82,9
	Polska	2006 2006 2006	**C** **HC** **L**	15.627 9.282 6.345	13.313 7.156 6.157	2.314 2.126 188				79,4
7.	Greece	2004	**L**	11.500						10
8.	Romania	2000	**L**	10.050						
9.	Bułgaria	2000	**L**	8.200						
10.	Serbia	2000	**L**	7.000						
11.	Czech Rep.	2000 2005	**L** **C**	5.500			 1.180			 66,3
12.	Estonia	2000	**L**[2]	5.000						2
13.	Spain	2000	**L**	2.900						
14.	Hangary	2000	**L**	2.300						
15.	Macedonia	2000	**L**	1.400						
16.	Bosnia-H	2000	**L**	1.400						
17.	Slovenia	2000	**L**	1.000						
18.	Slovakia	2000	**L**	900						
19.	Austria	2000	**L**	300						

[1] Only 14 country [6]: [2] Oil shale; [3] High Calcium Fly Ash

Tabela 2. The permissible content of additives for cements, including fly-ash.

Types of cement for concrete BS EN 197-1	**Percentage minimum limits are derived from BSEN 197-1 : 2000**
CEM I Portland cement	Comprising Portland cement and up to 5 % of minor additional consitituents
CEM II Portland-composite cement	***a. Portland fly ash cement (siliceous or calcareous)*** **I. CEM II / A-M**: Minimum 15% combined blastfurnace slag and fly ash of the total mass of the final product **II. CEM II / B-M**: Minimum 30% combined blastfurnace slag and fly ash of the total mass of the final produkt **or** **III. CEM II / A-W**: minimum qualifying content of 20% calcareous fly ash of the total mass of the final product **IV. CEM II / B-W**: minimum qualifying content of 27% calcareous fly ash of the total mass of the final produkt ***b. Cement from a combination of blastfurnace slag and fly ash*** **I. CEM II / A-M**: Minimum 15% combined blastfurnace slag and fly ash of the total mass of the final product **II. CEM II / B-M:** Minimum 30% combined blastfurnace slag and fly ash of the total mass of the final product
CEM III Blastfurnace cement	Comprising Portland cement and higher percentages blastfurnace slag
CEM IV Pozzolanic cement	Comprising Portland cement and higher percentages of pozzolana
CEM V Composite cement	**I. CEM V / A**: minimum qualifying content of 25% of the total mass from a combination of siliceous and/or calcareous content derived from fly ash. Total combined content must not accede 30% of the total mass of the final product. **II. CEM V / B**: minimum qualifying content of 35% of the total mass from a combination of siliceous and/or calcareous content derived from fly ash. Total combined content must not accede 50% of the total mass of the final product.

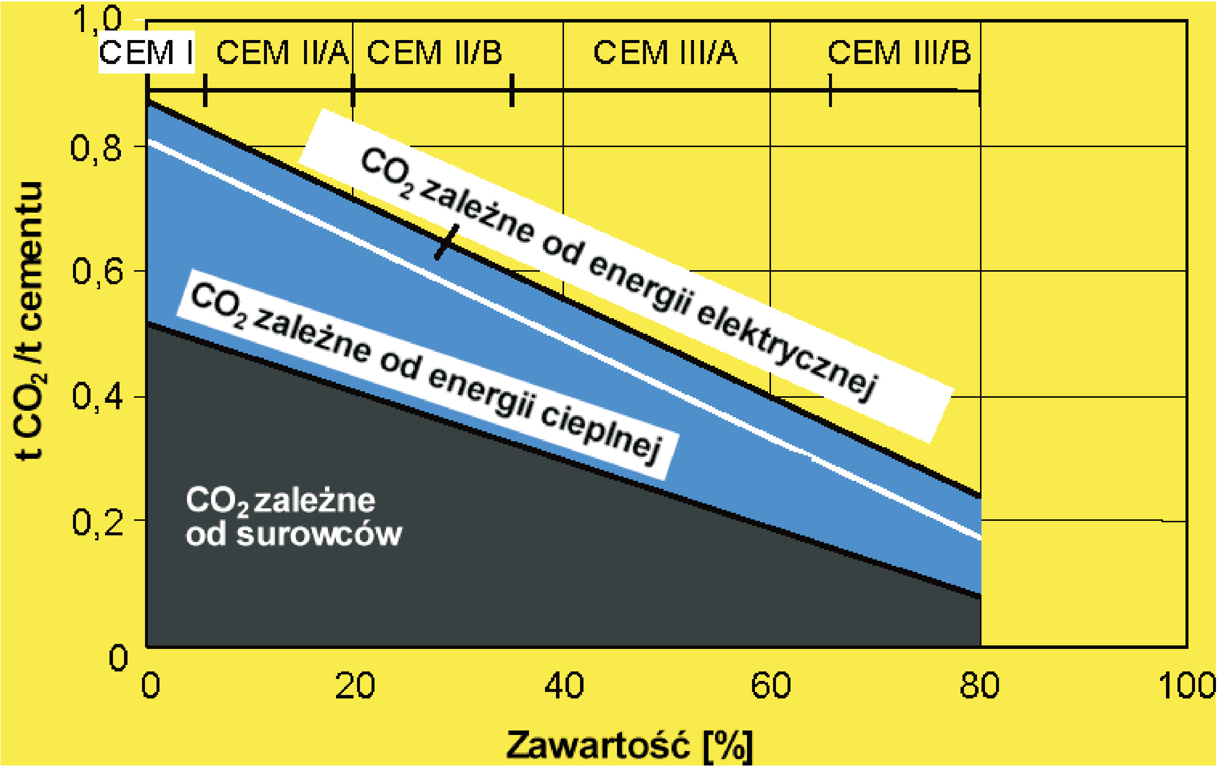

Fig. 1. **CO_2 emissions from the production of blended cements in Germany in function of main constituents content apart from clinker [13]**