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## Chemical characteristics of dust from cement kilns

### Introduction

The cement industry is a significant emitter of mineral dusts (Duszak et al. 2015), while the main sources of dust emissions in the cement production process are: rotary kilns, raw mills, clinker coolers, and cement mills (Best... 2013).

Cement dust and by-pass cement dust are classified as wastes from group 10 – Wastes from thermal processes, subgroups 10 and 13 – wastes from the manufacture of cement, lime and plaster and articles and products made from them. Cement kiln dust (CKD) is categorized as waste in the European Waste Catalogue under 10 13 06 – particulates and dust (except 10 13 12 and 10 13 13) (Nicholls et al. 2007), while Cement By-pass Dust (BPD) under 10 13 13 – solid wastes from gas treatment other than those mentioned in 10 13 12 (Whiteley et al. 2015).

Thanks to the activities of the cement industry, the emission was significantly reduced from 5 kg/t of cement to 0.131 kg per one ton of produced cement (<http://www.polskicement.pl/emisje-83>). The use of modern de-dusting equipment has resulted in a reduction of dust emissions, and thus an increase in the amount of waste to be managed (Duszak et al. 2015).

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Dust from cement kilns is waste that can primarily be used in the cement manufacturing process (a closed-cycle process) (Bulletin... 2012–2018; Osmanovic et al. 2018) (Table 1). The amounts of CKD and BPD waste used in the cement production process in the years 2011–2014 have been reduced and it was only in 2015 that they increased (Table 1).

Table 1. The use of CKD and BPD dust in the cement industry in Poland, Mg (Bulletin... 2012–2018)

Tabela 1. Wykorzystanie pyłów CKD i BPD w przemyśle cementowym w Polsce, Mg

Year	The amount used
2011	24,817.2
2012	12,938.0
2013	11,343.0
2014	9,015.0
2015	13,978.1

However, due to the high content of chlorides (7.5–21.9%) (Jøns et al. 2008; Lanzertorfer 2016), dusts from cement kilns may not always be used in the cement production process, as this could lead to excessive chloride concentrations in cement (Heikal et al. 2002).

Dust from cement kilns can be used as an additive to improve the geotechnical properties of poor soils (Miller and Azad 2000; Sreekrishnavilasam et al. 2000, 2007; Al-Homidy et al. 2017; Rimal et al. 2019), and their suitability for soil stabilization depends on the content of free lime (Sreekrishnavilasam et al. 2007).

The analysis carried out by Miller and Azad (Miller and Azad 2000) has shown that the addition of CKD increases the compressive strength significantly after 7–14 days after compaction. The increase of the compressive strength of soils with the addition of dust was also found by Sreekrishnavilasam et al. (Sreekrishnavilasam et al. 2000). Salahudeen et al. (Salahudeen et al. 2014) have found the usefulness of CKD to improve the soil properties during the construction of roads; however, it should be noted that this does not apply to the dusts with high ignition losses, which confirms the obtained results (Sreekrishnavilasam et al. 2007).

It was also suggested to use dusts from cement kilns to reduce Zn content in soils (Moon et al. 2010).

Another direction is the production of bricks, in which they can replace up to 50% of the raw material (El-Attar et al. 2017; Ahmed et al. 2018).

Dusts from cement kilns can also be used to remove lead (Salem and Velayi 2012), magnesium, iron, and nickel ions from wastewater (Salem et al. 2015). In addition, due to the

content of calcium oxide (CaO), they can replace lime in neutralizing acid mine drainage (ARD) (Mackie et al. 2010). Mackie and Walsh (Mackie and Walsh 2015) proposed the use of dust from cement kilns for the purification of acid mine water.

The production of concretes and mortars (Maslehuddin et al. 2008; Kunal et al. 2012; Najim et al 2014) has been postulated as a potential cement kiln dust recovery system for many years. Studies have shown that mortars and concrete mixes with 5–10% CKD have similar compression, bending, and tensile strength compared to the control mixture (Maslehuddin et al. 2008; Kunal et al. 2012; Najim et al 2014).

Cement kiln dust is a waste of variable composition, which makes it a difficult material to recover; this particularly applies to dust with high chlorine and sulfate concentrations (Siddique 2008). For this reason, there are ongoing efforts aimed at developing new recovery technologies.

The paper presents the results of the analysis on the chemical composition, phase composition, and leaching of pollutants (considered as one of the basic properties affecting the choice of waste recovery method) of the three dusts from cement kilns.

## 1. The materials used for testing

Three dusts (Figs. 1–3) from dry cement kilns were used in the tests:

- ◆ cement by-pass dust – BPD 1,
- ◆ cement by-pass dust – BPD 2,
- ◆ cement kiln dust – CKD 1.

CKD is a gray to brown fine powder of a relatively uniform grain size – particle size (Kunal et al. 2012), which is confirmed by photographs of the analyzed waste (Fig. 1).

## 2. Research methodology

### Chemical composition

The analysis of cement dust included the determination of the elemental composition using a MobiLab X5000 X-ray spectrometer.

### Phase composition

XRD measurements were made using a Philips X'Pert Pro MPD diffractometer.

DTA (Differential thermal analysis) measurements and TG (Thermogravimetry) were carried out using a Netzsch STA 449F3 Jupiter thermal analyzer.

### Leaching

The content of chlorides in the leachates was determined argentometrically, by means of the Volhard method (back titration). The content of sulfates (VI) was determined by weight.



Fig. 1. The analyzed dusts

Rys. 1. Analizowane pyły

The content of heavy metals: As, Co, Cd, Cr, Cu, Hg, Ni, Pb, Mn, and Ti was determined by inductively coupled plasma mass spectrometry (ICP MS). The content of Ba, Zn, P, K, Na, and Sr was determined by means of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

### 3. Research results

Dust from cement kilns is a waste of variable composition, which results from a number of factors such as (Whiteley et al. 2015):

- ◆ type of kiln,
- ◆ existing dust extraction systems and by-pass systems,
- ◆ temperature changes in the kiln,
- ◆ input materials (including waste),
- ◆ fuel type.

The latter factor is increasingly taken into account due to the increasing number of alternative fuels from waste used in cement plants (Graur and Gawlicki 2016).

### 3.1. Chemical composition

The analyzed waste was characterized by a high content of chlorine, calcium, and potassium (Table 2), which is confirmed by the results of other authors (Duchesne et al. 1998; Najim et al. 2014; El-Attar et al. 2017; Sultan et al. 2018). Particularly high concentrations of chlorine and potassium have been found in BDP 1 and BPD 2 dusts, which is characteristic of this type of waste (Duszek et al 2015).

Table 2. The chemical composition of dust from cement kilns, %

Tabela 2. Skład chemiczny pyłów z instalacji pieców cementowych, %

Component	BPD 1	BDP 2	CKD 1
Si	1.66	1.3459	2.24
S	0.1761	0.7392	0.3015
Cl	12.1814	23.3800	5.3306
K	10.1437	24.5556	6.1497
Ca	37.6251	24.7657	48.2550
Ti	0.1211	0.1229	0.1537
V	–	0.0469	–
Cr	0.0259	0.0212	0.0332
Mn	0.0421	0.0357	–
Fe	1.0702	0.8351	2.0347
Ni	0.0067	0.0086	–
Cu	0.0038	0.0063	–
Zn	0.0096	0.1632	0.0535
Zr	0.0034	0.0025	0.0066
Pb	0.0128	0.1284	0.0251
Bi	0.0041	0.0138	0.0048
LE	36.91	23.83	35.41



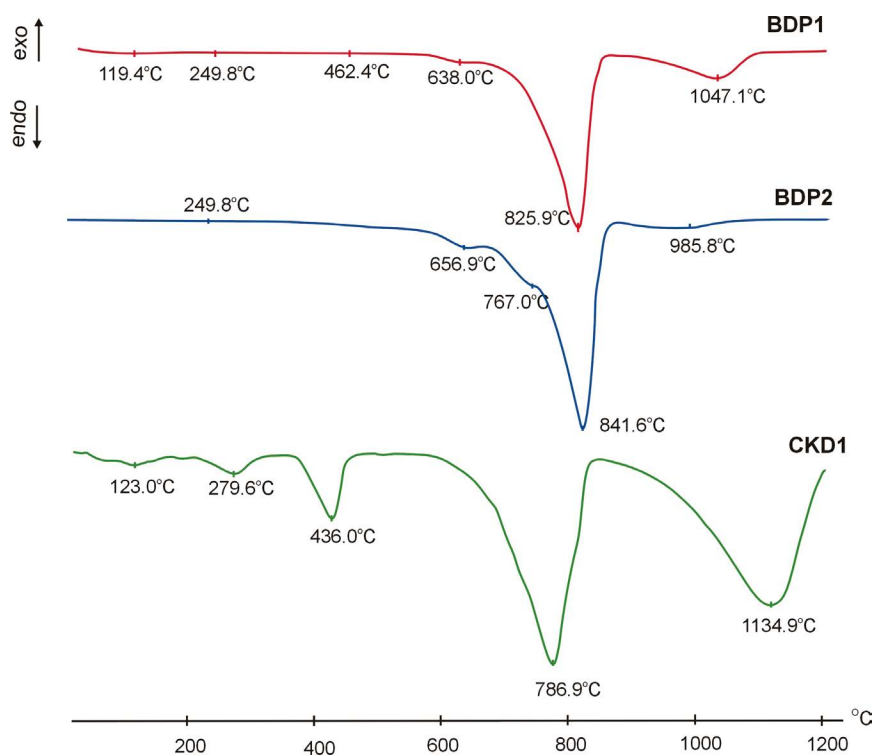


Fig. 3. DTG curves of the dusts analyzed

Rys. 3. Krzywe DTG analizowanych pyłów

- ◆ clinker phases (alite, belite),
- ◆ hydrates formed as a result of air exposure (Portland clinker phase hydrates, portlandite).

BDP dusts contain more cement phases compared to CKD (Limbatchiya et al. 2015), which is confirmed by the obtained results (Fig. 2, Table 3).

Based on the XRD analysis, the contents of calcite and aragonite, which, under normal conditions, is unstable and transforms into calcite, in the BDP1 sample (51 and 21%, respectively) have been determined. In addition, the sample contains belite (13%), sylvine (10%), and quartz (5%) (Fig. 2).

The results of the differential thermal analysis and thermogravimetry (Fig. 3), have confirmed the presence of: calcite (endothermic effect with a maximum at 825.9°C) and dolomite (endothermic effect with a maximum at 638°C). The endotherm effect with a maximum at 123°C corresponds to the process of evaporation of adsorbed water.

Two small endotherms, with a maximum at temperatures of 279.6°C and 436°C, are associated with the dehydration of hydrates present in the sample. The effect with a maximum

Table 3. Phase compositions of dusts from cement kilns  
 Tabela 3. Składy fazowe pyłów z instalacji pieców cementowych

Portlandite (Ca(OH) <sub>2</sub> )	-	CKD1	+	BDP1	+	BDP2	+	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
Syngenite (K <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O)	-	-	-	-	-	-	-	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
Quartz (SiO <sub>2</sub> )	+	+	+	+	+	+	+	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
Sylvite (KCl)	-	-	+	+	+	+	+	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
Calcite (CaCO <sub>3</sub> )	+	+	+	+	+	+	+	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
Aragonite (CaCO <sub>3</sub> )	-	-	+	+	+	+	+	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
Halite (NaCl)	-	-	-	-	-	-	-	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
Lime (CaO)	-	-	-	-	-	-	-	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
Anhydrite (CaSO <sub>4</sub> )	-	-	-	-	-	-	+	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>	-	-	-	-	-	-	-	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub>	-	-	-	-	+	-	-	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998
Lamite (Ca <sub>2</sub> (SiO <sub>4</sub> )	-	-	-	-	-	-	-	Heikal et al. 2002	Ali et al. 2011	El-Attar et al. 2017	Bondar and Coakley 2014	Sadek et al. 2017	Sreekrishnavilasam et al. 2006	Mackie and Walsh 2015	Salem et al. 2015	Chaunsali and Pethamparan 2015	Duchesne and Reardon 1998





at 279.6°C is probably related to the presence of cement phase hydration products such as: monosulfate, etringite and/or C-S-H. In turn, the one with a maximum temperature at 436°C is associated with portlandite.

Based on the XRD analysis, it can be stated that the dominant component is alite (55%), while the presence of calcite (26%), sylvine (7%), quartz (7%), portlandite (3%), and dolomite (2%) and  $K_3Na(SO_4)_2$  (below 1%) has also been confirmed in BDP2 (Fig. 2).

The results of differential thermal analysis and thermogravimetry (Fig. 3) also indicate the presence of portlandite (about 5%) (endothermic peak with a maximum at 462.4°C) and, possibly, monosulfate, etringite and/or C-S-H (endothermic peak with maximum at 249.8°C). In addition, the presence of carbonates: calcite (endothermic effect with a maximum at 825.9°C) and dolomite (endothermic effect with a maximum at 638°C), which constitute about 55% of the sample, has also been found. The presence of sylvine confirms the endotherm effect at 1047°C. The endotherm effect with a maximum at 119.4°C indicates the process of evaporation of adsorbed water.

The CKD1 sample consists mainly of calcite (74%) and quartz (23%) (Fig. 3). The dust sample No. 3 consists mainly of carbonates (about 70–75% share). There are three endothermic effects on the DTG curve with a maximum at: 656.9°C, 767.0°C and 841.6°C. which are related to the presence of carbonates in the sample. The endotherm effect with a maximum at 656.9°C indicates the presence of dolomite, which, in turn, with a maximum at about 767.0°C is associated with the decarbonization of complexes with carbonates and precedes the larger effect with a maximum at approximately 841.6°C indicating the decomposition of calcium carbonate (Ubbriaco and Calabrese 2000). The endotherm effect with a maximum at 1134.9°C probably indicates the presence of sylvine (Duszak et al. 2015).

The obtained results are confirmed by analyses made by other authors (Table 3).

### 3.3. Leaching of pollutants

CKD consists of a set of oxidized, anhydrous phases which include: oxides, aluminosilicates, sulfates, and chlorides. Many of these phases including: calcium oxide (CaO), arcanite ( $K_2SO_4$ ), and sylvine (KCl) are unstable or highly soluble. After the contact of dust with water, these phases can completely dissolve, followed with the precipitation of more or less stable phases (Siddique 2008).

Dust leachates from by-pass dust and dust from electrostatic precipitators are characterized by high concentrations of chlorides and potassium (Table 4), which confirms the results of other authors (Duchesne and Reardon 1998). This may limit the use of this type of waste. Table 4 compares the results of dust analysis with the requirements of the PN-G-11011 standard Materials for Backfilling and Caulking of Cavings – Requirements and Tests (PN-G-11011: 1998). Exceedances of limits are visible in the case of chlorides (all analyzed dusts), sulfates (dusts: BDP1 and CKD), Pb (BDP1) and pH (BDP1 and BDP2). The remaining values are compliant with the standard.

Table 4. The leaching of pollutants from the analyzed dusts and pH, mg/dm<sup>3</sup>Tabela 4. Wymywalność zanieczyszczeń z analizowanych pyłów i pH, mg/dm<sup>3</sup>

Type of pollution/pH	Leaching of pollutants			
	BPD 1	BDP2	CKD	the requirements of the PN-G-11011
Chlorides	8,021.0	3,811.0	1,448.0	1,000.0
Sulfate	4,310.0	120.0	1,502.0	500.0
As	0.0284	0.0233	0.0188	0.1
Ba	0.38	0.52	0.07	–
Co	0.00056	0.00064	0.00072	–
Cd	0.00025	0.00009	0.00092	0.02
Cr	0.094	0,136	0.013	0.5
Cu	0.0018	0.002	0.0016	0.5
Ni	0.0015	2.6	2.6	–
Pb	2.00	0.012	0.0005	0.5
Zn	2.093	0.061	0.0818	–
P	3.7	2.8	2.4	–
K	7862	4185	1832	–
Na	206	97	62	–
Mn	0.024	0.018	0.092	–
Ti	0.044	<	0.063	–
Sr	3.1	1.9	2.4	–
Hg*	–	–	–	0.05
pH	12.2	12,3	10.5	6.0–12.0

\* Hg – below the detection level.

## Conclusions

Dusts from cement kilns are wastes with diverse chemical and phase compositions, which is due to the use of various raw materials and fuels.

The analyzed dusts were characterized by significant concentrations of: chlorine, calcium, and potassium. The content of: Si, S, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Zr, Pb, and Bi has also been confirmed.

The phase compositions are dominated by carbonates (calcite, dolomite, and aragonite) obtained from the raw meal. The presence of phases from clinker and alkali condensation products have also been found.

The leaching studies have shown high concentrations of chlorides and sulfates (except for BDP2) in leachates which were characterized by an alkaline reaction.

These dusts, due to their composition and, above all, the significant concentration of chlorides, could be problematic to recover.

Factors affecting chemical and phase compositions of dust from cement kilns are the reason why each waste should be analyzed individually.

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#### CHEMICAL CHARACTERISTICS OF DUST FROM CEMENT KILNS

##### Key words

cement kiln dust, by-pass dust, chemical composition,  
phase composition, leaching of pollutants

##### Abstract

The cement production process is associated with the emission of dust. These are mainly CKD (cement kiln dust) and BPD (by-pass dust), classified as wastes from group 10 – Wastes from thermal processes, subgroups 10 and 13 – wastes from manufacture of cement, lime and plaster and articles and products made from them. Cement kiln dust is a waste of variable composition and properties, which makes it a difficult material to recover. The main directions of recovery presented in the world literature indicate the use of dust from cement kilns in cement, mortar and concrete production, the production of bricks and in order to improve soil quality and wastewater treatment. Factors affecting chemical and phase compositions of dust from cement kilns are the reason why each waste should be analyzed individually. The paper presents the results of the analysis of the cement kiln dust after dedusting cement kilns and two bypass dusts. Analysis of the chemical composition has shown significant concentrations of chlorine, potassium and calcium in all wastes. The content of: Si, S, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Zr, Pb, and Bi has also been confirmed. The analyzed dusts were characterized by the presence of carbonates (calcite, dolomite, and arcanite), quartz, alite, belite, sylvine, anhydrite, and portlandite in their phase composition. The leachates which were characterized by an alkaline reaction. In terms of leachability, high concentrations of chlorine ions in the analyzed dust leachates were confirmed, which significantly limits their use.

## CHARAKTERYSTYKA CHEMICZNA PYŁÓW Z INSTALACJI PIECÓW CEMENTOWYCH

## Słowa kluczowe

pyły z instalacji pieców cementowych, skład chemiczny,  
skład fazowy, wymywalność zanieczyszczeń

## Streszczenie

Proces produkcji cementu związany jest z emisją pyłów. Są to przede wszystkim pyły z instalacji pieców cementowych (CKD i BDP) klasyfikowane w grupie 10 – *Odpady z procesów termicznych*, podgrupy 10 13 – *Odpady z produkcji spoiw mineralnych (w tym cementu, wapna i tynku) oraz z wytworzonych z nich wyrobów*. Pyły z pieców cementowych są odpadem o zróżnicowanym składzie i właściwościach, co powoduje, że są materiałem trudnym do odzysku. Badania przedstawione w literaturze światowej jako główne kierunki odzysku wskazują wykorzystanie pyłów z instalacji pieców cementowych w procesie produkcji cementu, zapraw, betonów; do poprawy jakości gleb i oczyszczania ścieków. Czynniki wpływające na składy chemiczne i fazowe pyłów z instalacji pieców cementowych powodują, że każdy odpad należy analizować indywidualnie. W artykule przedstawiono wyniki badań pyłu z odpylania z instalacji pieca cementowego oraz 2 pyłów z bypassów. Analiza składu chemicznego wykazała znaczącą zawartość: Cl, K, Ca we wszystkich odpadach. Stwierdzono również obecność: Si, S, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Zr, Pb, Bi. Analizowane pyły charakteryzowały się obecnością w składzie fazowym: węglanów (kalcytu, dolomitu, arkanitu), kwarcu, alitu, belitu, sylwinu, anhydrytu i portlandytu. W zakresie wymywalności stwierdzono wysokie stężenia jonów chloru w odciekach z analizowanych pyłów, co znacząco ogranicza możliwości ich wykorzystania.

