

Alumina and Silica Produced by Chlorination of Power Plant Fly Ash Treatment

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Abstract.

We describe a process of chlorination of fly ash with either chlorine gas or calcium chloride, which successfully decomposes mullite and permits the extraction of a number of industrially useful, acid-soluble compounds. As a guide for determining optimal input molar ratios and temperatures, the Gibbs energies for three groups of reactions of major fly ash components between 973–1473 K were calculated: 1- chlorination with chlorine gas; 2- chlorination with chlorine gas in the presence of coal; 3- chlorination with calcium chloride. Laboratory-scale measurements with fly ash from six coal combustion power plants in Kazakhstan show that chlorination with either calcium chloride or chlorine gas allows efficient extraction of alumina (α -Al₂O₃) and silica with both high yield and purity.

Keywords: Fly ash, Power plants, Chlorine gas, Calcium chloride, Alumina, Silica.

Introduction.

Coal-fired power plants in developed countries annually produce large volumes of fly ash, of which more than half is disposed of in dry landfills : India – 112 million tons, China – 100 million tons; USA - 75 million tons; Germany - 40 million tons ; and Great Britain - 15 million tons [1]. In the Russian Federation, there are more than 170 coal-fired power plants, in which 300 million tons of fly ash and slag are produced each year. Over 20000 km² of land is currently used for storage of 1.3–1.5 billion tons of fly ash and slag waste from Russian power plants [2]. Such storage of fly ash and slag waste presents serious environmental, health and economic problems: fly ash contains hazardous trace elements, including As, B, Cr, Mo, Ni, Se, Sr and V, which can contaminate the environment due to leaching by rain and groundwater [3]. The problem of fly ash accumulation and storage is of particular relevance for Kazakhstan, where the development of electricity production in coal-fired power plants is an urgent governmental priority. To date, the total fly ash output from coal burning in this Republic is ~ 19 million tons per year and the amount of fly ash accumulated in landfills exceeds 300 million tons [4].

Fly ash from coal-fired power plants is potentially a valuable material for the manufacture of construction materials such as blended cement, fly ash bricks, mosaic tiles and hollow blocks. It also has other, high volume applications and can be used

for paving roads, building embankments, and mine fills [5]. Fly ash particles are fine, amorphous, and spherically shaped as a result of the high-temperature, pulverizing combustion of solid organic fuels [6]. They have an average size of 20 microns with a bulk density of 0.54–0.86 g/cm³ and a specific surface area of 0.3–0.5 m²/g. Untreated fly ash may also occasionally include aggregated glass-containing particles. The size of these aggregates ranges from 80 to 150 microns. The quantity of fly ash accounts for 85-95 % of the total waste and the remaining 5-15 % is unreacted coal with a particle size ranging from 40 to 200 microns.

The chemical composition of fly ash includes SiO₂, Al₂O₃, Fe₂O₃, CaO with minor impurities of MgO, as well as alkali oxides Na₂O and K₂O, sulfur, particles of carbides of metals and coke, and unburned particles of coal. As a rule, fly ash contains (mass%): SiO₂ - 50–58; Al₂O₃ - 18–25; Fe₂O₃ - 11–17; K₂O - 2.3-4.1; Na₂O - 0.5-1.35; TiO₂ - 0.9-1.1; CaO - 1.5-3.7; MgO - 1.7-3.1; P₂O₅ - 0.09-1.70; S - 0.6-0.5; Cl - 0.01-0.11. [7]. Aluminum is predominantly present in fly ash in the form of mullite (Al₂SiO₅) [8], which is a very stable alumina/silicate compound.

Metal recovery from fly ash also represents a conservation of natural resources. Since in coal there are elevated concentrations of a number of valuable metals - gallium, germanium, vanadium, tungsten, niobium, titanium, zirconium and some others. For example, up to 40–67% of titanium, 45–77% of beryllium, 70–87% of copper, 50–81% of manganese, 74%–84% of arsenic, 48–60% of vanadium and 62–83% gallium are extracted from brown coal fly ash [9]. Using the standard easiest and the most economical Bayer process for ash is not possible. Ash contains approximately 1.5-2 times less aluminum oxide than common aluminum raw materials (20-35% Al₂O₃ in ash as compared to 50-62% Al₂O₃ in bauxite). The high level of silica in ashes (40-65% SiO₂) makes it impossible to process them by the Bayer method and by the other methods of direct alkaline alumina extraction. Therefore for ash processing other methods are studied: acid (sulfuric, hydrochloric, nitric, or hydrofluoric acids), thermal (sintering with limestone and soda ash), thermal reducing, electrothermal melting, and new alkaline methods (SiO₂ dissolution and with separation from Al₂O₃ in the mullite form) [10].

Recovery of alumina, silica and other rare metals from the fly ash will not totally eliminate the disposal problem, but will reduce the amount of waste material and will improve the economics of fly ash disposal.

Murtha and Burnet [11] were the originators of the use of high temperature chlorine gas to recover valuable materials from fly ash. However, this method, although effective, was apparently not widely adopted, likely because of the numerous permits required in the United States to work with high temperature chlorine gas. In addition, the yield of alumina was not high (55%), as the sintering temperature in their case did not exceed 900°C.

Aim of this paper. In this report, we describe the high temperature chlorination of fly ash with chlorine gas or calcium chloride to bring about the decomposition of insoluble mullite and amorphous silica and conversion of aluminum into acid-soluble compounds (calcium aluminum silicates).

Materials and methods

Materials. Fly ash from six coal combustion power plants in Kazakhstan was used as input material. The major components are presented in Table I, with average content of minor components as follows: Be - 30-50 ppm, Cr - 120-150 ppm, Cu - 20-40 ppm, Zr - 40-70 ppm, Co - 30-70 ppm, Ba - 2-4 ppm, Zn - 250-350 ppm, Ni - 60-90 ppm, Sr - 3-5 ppm, V - 130-150 ppm, K - 0.2-0.3 mass%, Na - 0.1-0.15 mass%, P₂O₅ - 0.9-1.2 mass%.

Quantitative phase analysis of X-ray diffraction patterns of powdered fly ash (Fig. 1a) showed that the mullite, quartz, amorphous SiO₂, and hematite are basic dominated phases (Figures 1a, 1b). The phase composition of all used fly ash practically does not differ from each other in the main components (Mullite, Quartz, Amorphous phase, and Hematite). Quantitative phase analysis of the fly ash phases as obtained from the XRD pattern in Figure 1a is presented in the Figure 1b.

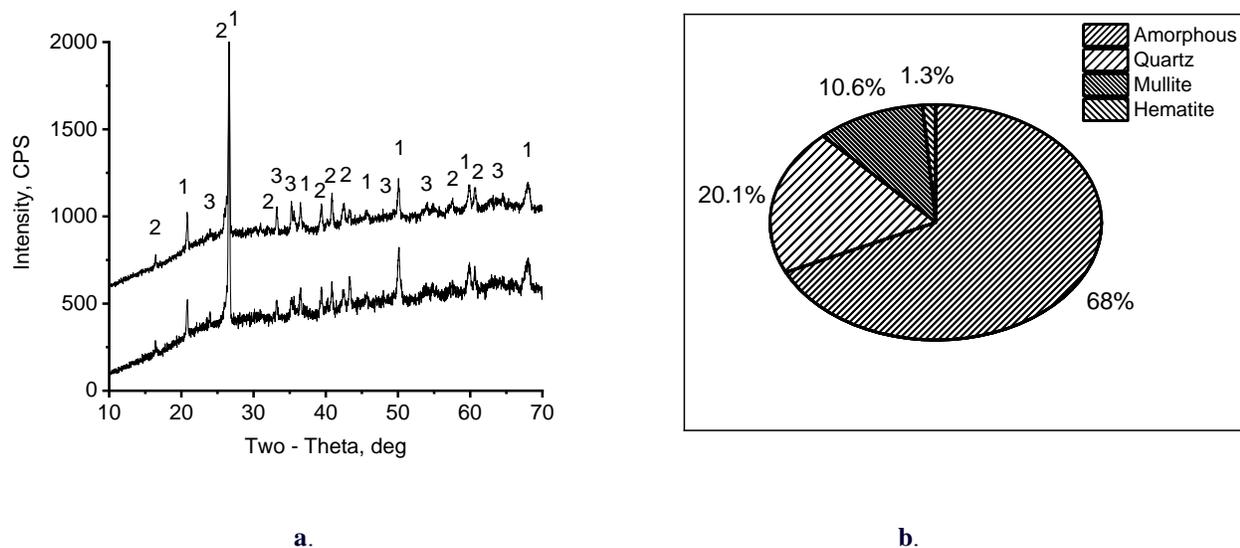


Figure 1

a. Powder X-ray diffraction (XRD) pattern of the fly ash samples

1 – Quartz, 2 – Millite, 3 – Hematite

b. Quantitative phase analysis of the fly ash phases as obtained from the XRD pattern in Figure 3a.

Table I. Major components of fly ash (in mass %) from Kazakh coal combustion power plants numbered (1-6) using atomic absorption spectrophotometry as described in Materials and Methods.

Fly ash	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	CaO	SiO ₂	Loss on ignition at 600°C
#1	29.50	4.00	1.80	1.80	8.40	35.30	6.6
#2	27.20	6.32	0.95	1.59	2.00	52.98	2.0
#3	26.71	5.26	2.38	1.08	7.70	44.55	4.3
#4	18.18	4.07	0.81	0.92	2.01	68.90	2.4
#5	21.25	7.60	1.33	0.98	4.28	58.80	1.3
#6	21.29	6.91	3.94	0.87	5.10	42.94	11.7

Analytical Methods. Preparation of the samples for chemical analysis was carried out as follows: 250 mg fly ash was mixed with 1.5 g. lithium tetraborate (Li₂B₄O₇) and fused at 1100°C in a platinum crucible. After cooling to room temperature, the melt was dissolved in 10 vol% hydrochloric acid and then analyzed.

Material composition was characterized using an atomic absorption spectrophotometer equipped with a graphite combustion chamber (Perkin Elmer 5100). Powder X-ray diffraction (XRD) was performed on an Ultima III diffractometer (Rigaku Corporation, Japan) with quantitative phase analysis accomplished using Jade_10 (MDI, Cal.) software and the ICSD database.

Experimental Procedures. Sintering of fly ash with chlorinators was carried out in a temperature controlled laboratory furnace (950°C to 1150°C): sintering time was 1 hour. The laboratory setup is described in Fig.2.

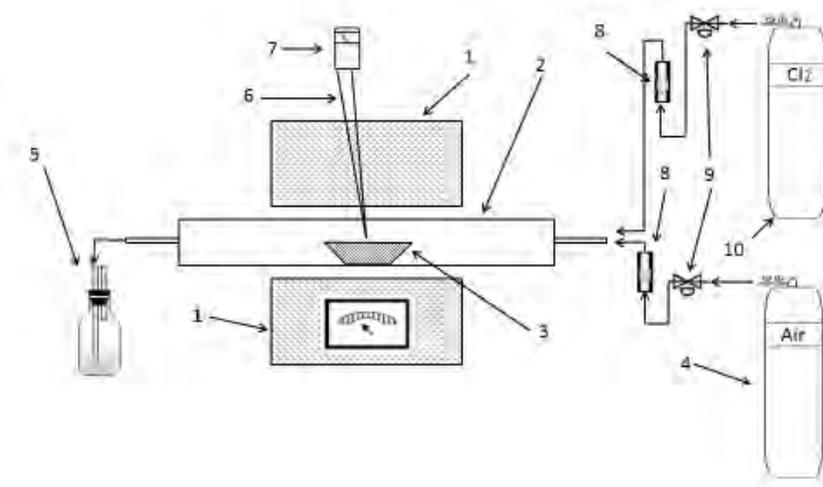


Figure 2. Laboratory setup. 1 – furnace with temperature controller; 2 – quartz reactor; 3 – alumina crucible with sample; 4 –air cylinder; 5 – gas absorption bottle; 6 – thermocouple type K; 7 – additional temperature monitor; 8 – flowmeter; 9 – valve; 10 – chlorine cylinder.

Sintering experiments with calcium chloride. Fly ash was mixed with calcium chloride at different mass ratios. The mixture was held in an alumina crucible inside the furnace, which was heated and then held at a given temperature under 100 ml/min air flow. Exhaust gases were transferred to a gas absorption bottle. After settling and cooling under air flow, the crucible was removed from the furnace and broken. The final product (clinker) was weighed and analyzed according to the methods described above.

Calculations were shown that for fly ash containing 15% Al_2O_3 , it is necessary to add 121 kg of calcium chloride per 100 kg of fly ash, and for fly ash containing 30% Al_2O_3 , it is necessary to add 139 kg of calcium chloride per 100 kg of fly ash (Fig. 3a). Calculation of the amount of calcium chloride is carried out for a given fly ash composition and for 100 kg of fly ash. In the calculations, it was assumed that 25-30% of all the aluminum present in the fly ash goes into clinker in the form of gellenite $2CaO \cdot Al_2O_3 \cdot SiO_2$, and the rest of the aluminum goes into clinker in the form of anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (data from Figure 4b). Silicon remaining after the alumocalciumsilicates (gellenite and anorthite) formation goes into pseudowollastonite $CaO \cdot SiO_2$. The formation of calcium ferrite $CaO \cdot Fe_2O_3$ and calcium titanate $CaO \cdot TiO_2$ was also taken into account for correct

calculate the total amount of calcium chloride. The calcium chloride excess in the calculations was equal to 10% of the stoichiometric amount to take into account the effect of the remaining minor elements.

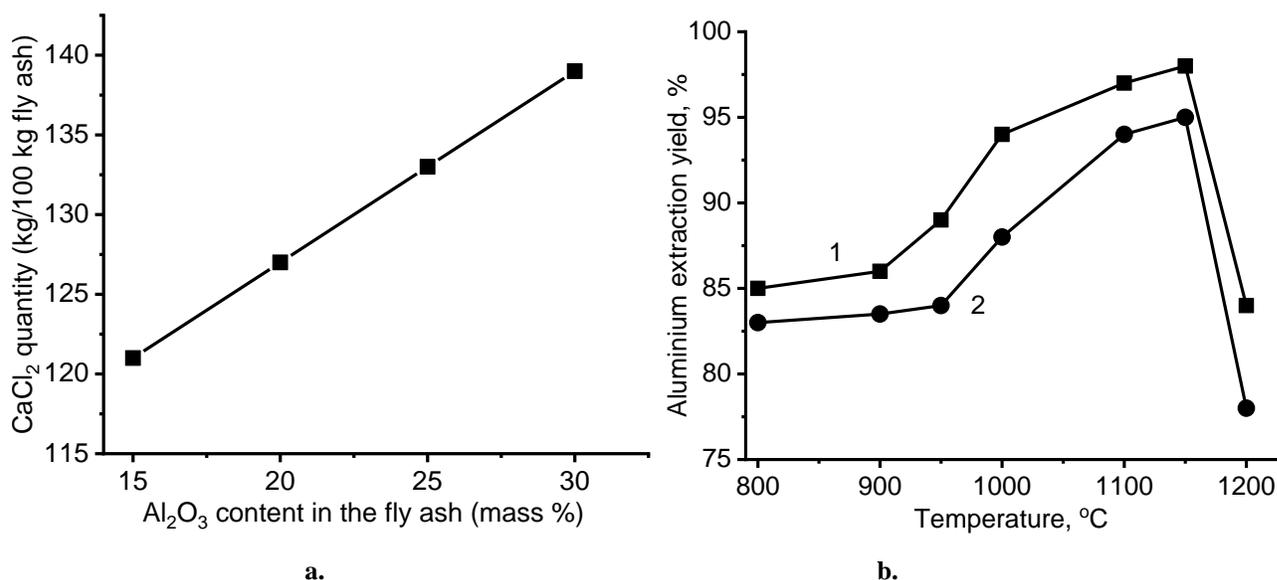


Figure 3.

- a. Weight of calcium chloride required to treat fly ash, calculated as a function of the amount of Al₂O₃ present.
- b. Sintering temperature and calcium chloride amount dependence of the efficiency of aluminum extraction yield
 - 1 - 130 kg of calcium chloride per 100 kg of fly ash:
 - 2 - 110 kg of calcium chloride per 100 kg of fly ash.

Sintering experiments with gaseous chlorine. Fly ash was initially burned at 620°C under 100 ml/min air flow for 1 hour in order to eliminate residual coal particles (LOI at 600°C (residual coal) for fly ash samples ranged from 1.3 -11.7 mass%). Burned fly ash was placed in the furnace in an alumina crucible. Prior to heating, the reactor was cleaned under 100 ml/min nitrogen flow, following which the furnace was heated to a given temperature, again under 100 ml/min nitrogen flow. Chlorine gas was fed into the reactor after the latter had reached the designated temperature. For some tests, coal was added to the burned ash in amounts of 10% or 18% by weight of fly ash. After cooling under nitrogen flow, the crucible was removed from the furnace and broken. The final product (clinker) was weighed and analyzed according to the procedure described above.

Thermodynamic Calculations. Calculations of Gibbs energy were performed using a computer program developed by the authors and based on standard values for the pure substances [12]. The Gibbs energy (ΔG) in the temperature range 1073–1473 K for three groups of reactions of the major fly ash components is shown in Table II: Group 1- chlorination reactions with chlorine gas; Group 2 -chlorination reactions with chlorine gas in the presence of coal; Group 3- chlorination reactions with calcium chloride.

Table II. Gibbs energy (ΔG) calculated for high temperature treatment of fly ash.

	Reaction	Temperature, K				
		1073	1173	1273	1373	1473
		ΔG, kJ/mole				
Group 1						
1	$\text{Al}_2\text{SiO}_5 (\text{s}) + 3\text{Cl}_2 (\text{g}) = 2\text{AlCl}_3 (\text{g}) + \text{SiO}_2 (\text{s}) + 1.5\text{O}_2 (\text{g})$	457.3	453.8	449.8	445.4	440.5
2	$\text{TiO}_2 (\text{s}) + 2\text{Cl}_2 (\text{g}) = \text{TiCl}_4 (\text{g}) + \text{O}_2 (\text{g})$	115.8	110.1	104.6	99.0	93.6
3	$\text{Fe}_3\text{O}_4 (\text{s}) + 4.5\text{Cl}_2 (\text{g}) = 3\text{FeCl}_3 (\text{g}) + 2\text{O}_2 (\text{g})$	115.3	116.7	117.3	117.1	116.2
4	$\text{FeO} (\text{s}) + 1.5\text{Cl}_2 (\text{g}) = \text{FeCl}_3 (\text{g}) + 0.5\text{O}_2 (\text{g})$	-24.3	-20.5	-17.0	-13.7	-10.6
5	$\text{Fe}_2\text{O}_3 (\text{s}) + 3\text{Cl}_2 (\text{g}) = 2\text{FeCl}_3 (\text{g}) + 1.5\text{O}_2 (\text{g})$	104.1	100.1	95.6	90.6	85.2
Group 2						
6	$\text{Al}_2\text{SiO}_5 (\text{s}) + 3\text{Cl}_2 (\text{g}) + 1.5\text{C} (\text{s}) = 2\text{AlCl}_3 (\text{g}) + \text{SiO}_2 (\text{s}) + 1.5\text{CO}_2 (\text{g})$	-136.7	-140.2	-144.3	-148.9	-153.9
7	$\text{TiO}_2 (\text{s}) + 2\text{Cl}_2 (\text{g}) + \text{C} (\text{s}) = \text{TiCl}_4 (\text{g}) + \text{CO}_2 (\text{g})$	-280.1	-285.9	-291.6	-297.1	-302.6
8	$\text{Fe}_3\text{O}_4 (\text{s}) + 4.5\text{Cl}_2 (\text{g}) + 2\text{C} (\text{s}) = 3\text{FeCl}_3 (\text{g}) + 2\text{CO}_2 (\text{g})$	-676.6	-675.4	-675.0	-675.3	-676.2
9	$\text{FeO} (\text{s}) + 1.5\text{Cl}_2 (\text{g}) + 0.5\text{C} (\text{s}) = \text{FeCl}_3 (\text{g}) + 0.5\text{CO}_2 (\text{g})$	-222.2	-218.5	-215.0	-211.8	-208.7
10	$\text{Fe}_2\text{O}_3 (\text{s}) + 3\text{Cl}_2 (\text{g}) + 1.5\text{C} (\text{s}) = 2\text{FeCl}_3 (\text{g}) + 1.5\text{CO}_2 (\text{g})$	-489.8	-494.0	-498.6	-503.7	-509.2
Group 3						
11	$\text{Al}_2\text{SiO}_5 (\text{s}) + 2\text{CaCl}_2 (\text{l}) + \text{O}_2 (\text{g}) = \text{Ca}_2\text{Al}_2\text{SiO}_7 (\text{s}) + 2\text{Cl}_2 (\text{g})$	-298.9	-412.8	-534.4	-663.2	-798.7
12	$\text{Al}_2\text{SiO}_5 (\text{s}) + 2\text{CaCl}_2 (\text{l}) + 2\text{H}_2\text{O} (\text{g}) = \text{Ca}_2\text{Al}_2\text{SiO}_7 (\text{s}) + 4\text{HCl} (\text{g})$	-326.9	-454.4	-589.7	-732.2	-881.4
13	$\text{Al}_2\text{SiO}_5 (\text{s}) + \text{SiO}_2 (\text{s}) + \text{CaCl}_2 (\text{l}) + 0.5\text{O}_2 (\text{g}) = \text{CaAl}_2\text{Si}_2\text{O}_8 (\text{s}) + \text{Cl}_2 (\text{g})$	94.3	92.9	91.8	90.7	89.8
14	$\text{Al}_2\text{SiO}_5 (\text{s}) + \text{SiO}_2 (\text{s}) + \text{CaCl}_2 (\text{l}) + \text{H}_2\text{O} (\text{g}) = \text{CaAl}_2\text{Si}_2\text{O}_8 (\text{s}) + 2\text{HCl} (\text{g})$	80.3	72.1	64.1	56.3	48.5
15	$\text{SiO}_2 (\text{s}) + \text{Al}_2\text{O}_3 (\text{s}) + 2\text{CaCl}_2 (\text{l}) + \text{O}_2 (\text{g}) = \text{Ca}_2\text{Al}_2\text{SiO}_7 (\text{s}) + 2\text{Cl}_2 (\text{g})$	-411.9	-526.6	-649.0	-778.6	-914.9
16	$2\text{SiO}_2 (\text{s}) + \text{Al}_2\text{O}_3 (\text{s}) + \text{CaCl}_2 (\text{l}) + 0.5\text{O}_2 (\text{g}) = \text{CaAl}_2\text{Si}_2\text{O}_8 (\text{s}) + \text{Cl}_2 (\text{g})$	-18.7	-20.9	-22.8	-24.6	-26.3
17	$2\text{TiO}_2 (\text{s}) + 3\text{CaCl}_2 (\text{l}) + 1.5\text{O}_2 (\text{g}) = \text{Ca}_3\text{Ti}_2\text{O}_7 (\text{s}) + 3\text{Cl}_2 (\text{g})$	158.7	153.5	149.1	145.4	142.2
18	$\text{TiO}_2 (\text{s}) + \text{CaCl}_2 (\text{l}) + 0.5\text{O}_2 (\text{g}) = \text{CaTiO}_3 (\text{s}) + \text{Cl}_2 (\text{g})$	25.7	24.1	22.7	21.6	20.6
19	$\text{Fe}_3\text{O}_4 (\text{s}) + \text{CaCl}_2 (\text{l}) + 0.5\text{O}_2 (\text{g}) = \text{CaFe}_3\text{O}_5 (\text{s}) + \text{Cl}_2 (\text{g})$	179.3	204.7	234.7	267.1	301.6
20	$3\text{Fe}_2\text{O}_3 (\text{s}) + 2\text{CaCl}_2 (\text{l}) + 0.5\text{O}_2 (\text{g}) = 2\text{CaFe}_3\text{O}_5 (\text{s}) + 2\text{Cl}_2 (\text{g})$	491.3	536.4	586.4	640.9	699.5

(s) – solid, (l) – liquid, (g) – gas.

Under sintering conditions, the Gibbs energy of the reactions in Group 1 is strongly positive (100–450 kJ/mole), with the exception of reaction (4): thermodynamic calculations predict that the reaction of iron (II) oxide from fly ash with chlorine gas can result in the formation of iron (III) chloride within a wide temperature range, including the range of interest 1173–1473 K. Group 2 includes chlorination reactions between fly ash components and pure chlorine gas in the presence of carbon particles.

The likelihood of reactions (6) – (10) is ensured over the entire temperature range of interest, with the most negative value being $\Delta G = -676$ kJ/mole for reaction (8). In practice, the disruption of mullite (Al_2SiO_5) described by reaction 6 is essential. The Gibbs energy of this reaction in the presence of coal is -150 kJ/mole, thereby predicting rapid decomposition of mullite from the fly ash upon chlorination. Aluminum acquires soluble chloride form accompanied by the transfer of silicon into the filtrate cake. Titanium and iron from fly ash take on the chloride form with Gibbs energy of reactions (7) - (10) both being very negative (< -300 kJ/mole) (Table II). Thus, the highest probability of reactions (6) – (10) can be expected immediately after injection of the chlorine gas. The third group of reactions in Table II includes the reaction between fly ash components and calcium chloride. The Gibbs energy of reactions (11) - (12) from mullite to gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and reaction (15) from alumina and silica to gehlenite under sintering conditions is strongly negative (≈ -800 kJ/mole). The Gibbs energy of reactions (13) – (14) from mullite to anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) under sintering conditions is positive ($50-90$ kJ/mole), but reaction (16) from separated alumina and silica to anorthite under sintering conditions is negative (approx. -20 kJ/mole). The Gibbs energy of reactions for titanium and iron (17) - (20) under sintering conditions is highly positive. The presence of water vapor slightly increases the thermodynamic probability of mullite decomposition reactions (reactions (11) – (12) and (13) – (14)). Therefore, when calcium chloride is added, mullite should completely transform into acid-soluble gehlenite. However, the formation of calcium titanates and calcium ferrites is thermodynamically unlikely.

Results and discussion

Experiments with calcium chloride (Group 3 reactions). We found that sintering fly ash in the presence of calcium chloride completely decomposes mullite within the temperature range $950-1150^\circ\text{C}$ with the formation of gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), and pseudowollastonite (CaSiO_3), depending, in part, on the amount of calcium chloride used. Thermodynamic calculations predicted that in this temperature range, the formation of gehlenite should be most likely. Laboratory scale measurements showed complete conversion of aluminum to calcium aluminosilicates (gehlenite or anorthite).

Quantitative phase analysis of X-ray diffraction patterns of powdered clinker (Fig. 4a) showed that three crystalline alumina-silicate phases were obtained with anorthite being dominant (Fig. 4b). The phase composition of all obtained clinkers practically does not differ from each other in the main components (Gehlenite, Anorthite, Pseudowollastonite).

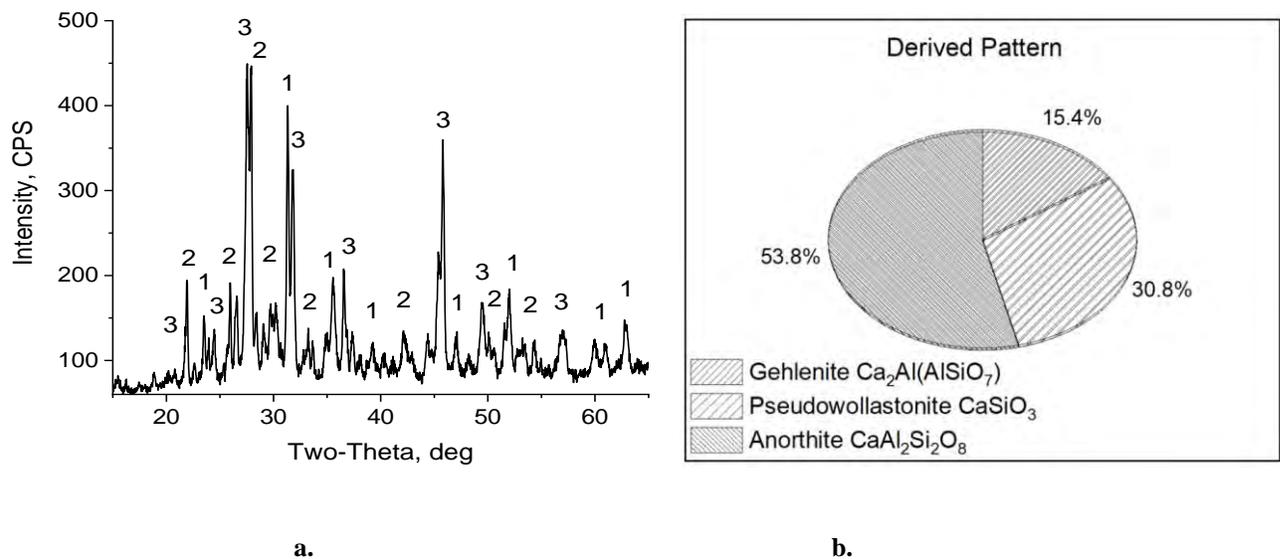


Figure 4.

a. Powder X-ray diffraction (XRD) pattern of the fly ash samples number 2 following high temperature treatment (1000°C) with calcium chloride. Weight ratio calcium chloride/clinker was 1.35 : 1.00.

1 – Gehlenite, 2 – Anorthite, 3 – Pseudowollastonite.

b. Quantitative phase analysis of the crystalline alumina-silicates as obtained from the XRD pattern in Figure 4a. No amorphous material was detected.

To assess the maximum degree of extraction yield of aluminum and silicon from fly ash, the burned clinker, consisting of alumina-silicates and oxides of other metals, was leached with a 30% hydrochloric acid solution. The experiments were carried out with a 200-300% excess of hydrochloric acid, only to assess the maximum degree of conversion of aluminum from mullite to acid-soluble compounds.

Real leaching tests.

Clinkers for leaching tests was prepared from mixture with ratio CaCl_2 –fly ash = 1.35:1.0 in laboratory furnace at temperature 1150°C. Chemical composition of used clinker: 19% Al_2O_3 , 39% CaO , 0.7% Fe_2O_3 , 26% SiO_2 , 0.7% TiO_2 . Leaching tests were carried out in laboratory leaching equipment at boiling temperature. Volume of the initial HCl acid (32%) was equal 1000 ml. All materials (HCl acid and clinker) were fed continuously. HCl acid consumption was equal 4 liter/hour. Clinker consumption was equal 0.8 kg/hour. Suspension after leaching was continuously discharged from the reactor through overflow to the laboratory Batch filter. Precipitation cake after filtration was washed on the filter with water to pH 5–7. AlCl_3 content in the filtrate was equal 12-14%, CaCl_2 – 10%, FeCl_3 – 0.4%, TiCl_4 – 0.3%. Composition of the silica precipitation cake: Al_2O_3 – 0.04%, CaO – 0.15%, Fe_2O_3 – 0.05%, TiO_2 – 0.2%, Na_2O – 0.18%. Whiteness was equal 92%, Surface area – 165 m^2/gr , Oil absorption (linseed oil) – 140 gr/100 gr.

Aluminum and other metals went into solution. Aluminum extraction yield into an acid-soluble form depends on the sintering temperature and the amount of added calcium chloride. With an increase in temperature from 950°C to 1150°C, aluminum extraction yield increased from 89% to 98%. With further increase in temperature, some fusible components of the mixture melted and the extraction yield of aluminum into acid-soluble form decreased sharply. With reduction in the amount of

added calcium chloride, aluminum extraction yield decreased to 95% at a temperature of 1150°C. Aluminum extraction yield changes with temperature and calcium chloride amount is presented on Figure 3b for fly ash #1.

Silica remained in the filter cake.

All next stages of the process: aluminum chloride extraction from filtrate after leaching, aluminum chloride thermal decomposition for alumina production, refining of the calcium chloride solution from iron and recirculation of the pure calcium chloride solution, were described earlier in our paper [13].

The iron extraction process from clinker during fly ash sintering with calcium chloride was accomplished after gaseous hydrogen chloride mixed with air was supplied to the furnace. The amount of hydrogen chloride was twice the stoichiometric quantity required for iron compound chlorination. Iron was completely (96-99%) chlorinated and passed into sublimates. Other elements were not chlorinated and sublimated under such conditions.

Chlorination with calcium chloride allows the extraction of pure aluminum oxide (α -Al₂O₃) and pure silica from the fly ash. Aluminum extraction yield from fly ash was equal 98% and silicon extraction yield – 98.5%. Al₂O₃ content in the alumina powder was equal 99.1 mass % and was received silica cake with 99.1 mass % of the silica. Comparative analysis of technological indicators of CaCl₂*2H₂O sintering technology with known Bayer process technology and Na₂CO₃ sintering technology is presented in the Table III. The main properties of the obtained alumina and silica are presented in the Table III.

Table III. Comparative analysis of technological indicators of CaCl₂*2H₂O sintering technology with known Bayer process technology and Na₂CO₃ sintering technology and main properties of the obtained alumina and silica.

	Bayer Process (NaOH leaching)	Sintering with Na ₂ CO ₃	Sintering with CaCl ₂ *2H ₂ O
Raw Material	Bauxite	Bauxite	Fly ash
Reactant	NaOH	Na ₂ CO ₃	HCl
Intermediate material	Al(OH) ₃	Na ₂ O·Al ₂ O ₃	AlCl ₃ · 6H ₂ O
Sodium concentration in the alumina	0.2 – 0.4	0.2 – 0.4	< 0.03
By-product	None	None	Pure silica, Iron oxide

Table IV. Main properties of the obtained alumina and silica.

	Alumina Properties
Al ₂ O ₃	99.8%
SiO ₂	0.02 – 0.03%
CaO	0.01 - 0.02%
Na ₂ O	0.03 - 0.04%
Fe ₃ O ₄	0.010 – 0.015%
Surface area	5 - 15 m ² /gr

	Silica Properties
SiO ₂	> 99%
Al ₂ O ₃	0.1 – 0.2%
CaO	0.1 - 0.2%
Fe ₃ O ₄	< 0.05%
TiO ₂	0.3 – 0.4%
Na ₂ O	0.15 - 0.25%
Whiteness	92 - 95
Surface area	150 – 170 m ² /gr
Oil absorption (linseed oil)	150 - 170gr/100gr

Experiments with chlorine gas. We used chlorine gas in the presence of coal particles for the decomposition of mullite. We observed that at 1100°C this combination completely breaks down mullite from fly ash with the formation of aluminum (III) chloride. The content of components in the clinker are listed in Table V.

Table V. Components of the clinker following treatment with chlorine gas at 1100°C in the presence of added coal.

Fly ash	Coal (% by weight of fly ash)	Major components of the clinker (% mass)				
		Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	CaO
#1	0	27.12	0.11	1.14	0.86	10.45
	10	25.60	0.09	0.78	0.72	10.37
	18	8.85	0.12	0.53	0.36	7.13
#2	0	29.73	0.64	0.53	1.07	3.21
	10	29.26	0.57	0.37	1.22	2.84
	18	7.90	0.64	0.21	0.75	1.62
#3	0	23.21	0.10	0.89	0.37	8.24
	10	21.59	0.08	0.74	0.24	8.02
	18	7.49	0.25	0.03	0.15	6.42
#4	0	16.07	0.18	0.43	0.41	2.89
	10	13.70	0.13	0.27	0.35	2.56

	18	5.49	0.16	0.02	0.27	1.94	
#5	0	20.34	0.21	0.74	0.23	4.64	
	10	18.18	0.11	0.53	0.15	4.31	
	18	7.44	0.14	0.05	0.25	3.31	
#6	0	14.49	0.10	0.92	0.19	8.64	
	10	6.47	0.06	0.76	0.14	8.01	
	18	2.82	0.09	0.06	0.09	8.54	
Fly ash	Coal (% by weight of fly ash)	Minor elemental components of the clinker (ppm)					
		Be	Cr	Cu	Zr	Co	Ba
#1	10	0.02	0.07	0.03	2.3	–	3.5
	18	0.02	0.05	0.03	2.05	–	3.1
#2	10	0.02	0.08	0.04	0.29	–	2.4
	18	0.01	0.07	0.02	0.22	–	1.9
#3	10	0.02	0.02	0.05	0.15	–	3.3
	18	0.01	0.02	0.03	0.13	–	3.1
#4	10	0.03	0.02	0.04	0.55	–	1.5
	18	0.01	0.01	0.04	0.51	–	1.2
#5	10	0.02	0.04	0.09	0.31	–	2.1
	18	0.01	0.03	0.06	0.28	–	1.8
#6	10	0.01	0.04	0.07	0.55	0.03	3.8
	18	0.01	0.02	0.05	0.49	0.03	3.2
Fly ash	Coal (% by weight of fly ash)	Minor components of the clinker including oxides (ppm)					
		Zn	Ni	Sr	V	K ₂ O % mass	Na ₂ O % mass
#1	10	0.02	0.03	4.3	0.01	0.18	0.07
	18	0.02	0.02	3.9	0.01	0.16	0.06

#2	10	0.03	–	2.1	0.07	0.06	–
	18	0.02	–	1.6	0.05	0.03	–
#3	10	0.02	–	3.8	0.02	0.13	0.05
	18	0.02	–	3.6	0.01	0.12	0.05
#4	10	0.01	–	1.3	0.03	0.05	–
	18	0.02	–	1.2	0.03	0.04	–
#5	10	0.02	0.03	1.6	0.03	0.12	0.06
	18	0.02	0.02	1.2	0.04	0.10	0.05
#6	10	0.03	0.03	3.5	0.02	0.22	0.10
	18	0.02	0.04	3.5	0.01	0.22	0.12

Sublimation yield of the major components (Table VI) was calculated taking into account loss of weight during sintering. Average loss of weight was 10 % without coal addition, 34 % with 10 mass% added coal, and 54 % with 18 mass% added coal. Adding coal to the mixture did not influence iron removal. Silicon sublimation did not occur during the chlorination process, while aluminum, titanium and calcium sublimation practically did not occur in the absence of coal. While magnesium sublimation was small, iron sublimation from fly ash was almost complete.

Table VI. Sublimation yield of major elements following treatment of the fly ash with chlorine gas at 1100°C in the presence of different amounts of added coal.

Fly ash	Coal quantity (% by weight of fly ash)	Sublimation yield (%)				
		Al	Fe	Mg	Ti	Ca
#1	0	0	90	10	0	0
	10	31	98	66	68	2
	18	86	98	83	89	52
#2	0	0	91	28	0	0
	10	10	92	67	35	0
	18	90	93	84	65	41
#3	0	0	92	15	0	0

	10	40	99	77	84	23
	18	86	98	99	89	57
#4	0	0	91	18	0	0
	10	44	98	75	72	6
	18	85	98	98	82	41
#5	0	0	92	15	0	0
	10	34	99	69	88	22
	18	84	99	98	76	51
#6	0	0	93	20	0	0
	10	86	100	91	92	25
	18	96	100	100	97	47

^a Sublimation yield (%) was calculated taking into account the average weight loss during sintering : 10% in the absence of coal, 34% with 10wt% added coal and 54% with 18wt% added coal .

After sintering with chlorine gas and coal addition, a mixture of sublimated metal chlorides in the form of sublimates and clinker containing silica and some calcium chloride were obtained. The mixture of metal chlorides can be captured with a standard tower or electrostatic filter and then separated by known methods [14, 15]. The clinker was washed with hot water to completely dissolve the calcium compounds. After washing with water, pure silica was obtained from the filter cake.

Conclusions.

Chlorination of fly ash with either chlorine gas or calcium chloride is clearly suitable for mullite decomposition and conversion of aluminum and silicon into valuable compounds. Although each process would succeed in reducing environmental contamination with toxic landfill, it is clear that the advantages of the chloride far outweigh those of the gas. We have shown that chlorine gas separates elements of fly ash in one stage and most metal chlorides are converted to dust. Only silica and some calcium chloride remain in the clinker. Furthermore, acid leaching is not required, while hot water treatment can be used for pure silica cake production. On the other hand, chlorine gas at high temperature is very corrosive, requiring special materials and permits for its use. By contrast, calcium chloride treatment of fly ash is environmentally friendly: both hydrochloric acid and HCl gas are recycled and reused. The possibility of obtaining special-grade aluminum oxide, pure silica, iron pigment and rare earth element concentrate in the form of valuable products increases its economic significance. A comparative analysis of our

technology with known methods for producing alumina by the Bayer process or by the Na_2CO_3 sintering process shows its significant superiority for expanding the range of commercial products from fly ash.

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