Climate-Adaptive Materials Engineering

Journal Homepage: https://journals.explorerpress.com/came

Research Article

The Use of Coal Mining Rocks in Construction Industry

Elina Khobotova*, V. Datsenko

Kharkiv National Automobile and Highway University, Kharkiv, Ukraine

KEYWORDS

coal mining unburned rocks
mineral and oxide composition
hydraulic activity
modular classification
cement clinker production
physical and mechanical properties

ABSTRACT

Background: Resource-saving developments using industrial waste as a man-made raw material for the production of binders allow for the expansion of the raw material base and improve the environmental situation in regions through the recycling of large-scale industrial waste, including coal mining waste. The dump coal mining unburned rocks of the Khmelnitskaya mine and the Sverdlov mine of Ukraine have been studied in the work. **Methods:** The mineral composition of the rocks was determined by X-ray phase analysis, the oxide composition and micrographs of the surface of cement clinker particles were determined by electron probe microanalysis using scanning electron microscope. Results: Clinochlore and muscovite have been detected in coal mining waste rock. These minerals are typically present in clays used in the production of Portland cement clinker. High adsorption and hydraulic activity of coal mining waste rock has been established. **Conclusions:** The use of unburned coal mining rock in the raw mix, instead of the clay component (5.8−10.2%), was demonstrated in the production of Portland cement clinker. The resulting cement clinker matches Portland cement in terms of its oxide and mineralogical composition and physical and mechanical properties. **Significanc:** The applied direction of using industrial waste as a man-made raw material for the production of binders has received further development.

*CORRESPONDING AUTHOR

Elina Khobotova, Kharkiv National Automobile and Highway University, Kharkiv, Ukraine; Email: elinahobotova@gmail.com

ARTICLE INFO

Received: 29 October 2025 | Revised: 13 November 2025 | Accepted: 14 November 2025 | Published Online: 18 November 2025

DOI: https://doi.org/10.65773/came.1.1.51

1. Introduction

In the modern industry the concept of sustainable development is expressively relevant. Natural minerals are used to improve the ecological condition of soils, their hydrophysical and agrochemical characteristics [1]. The addition of aluminosilicate clays to the soil, along with mineral fertilizers, creates the preconditions for improving soil fertility by influencing available phosphorus [2]. Minerals contained in industrial waste acquire sorption properties during their oxidation and modification of surface properties [3]. Producing fuel and energy from both renewable sources and various types of waste are prospective directions for development [3]. It is necessary to optimize territorial loads and expand the volumes of recycling of associated rocks and their processing into materials with excellent technical characteristics and consumer appeal [5].

In the construction industry, there is a new trend of replacing primary materials with alternative raw materials. The authors of [6] offer to refuse storing the waste which is to be recycled, but to use it as a raw material for recirculation in accordance with the trend of the circular economy. The mining and coal industries produce a large amount of waste in the form of enclosing and overburden rocks that form the dumps [7,8]. The overburden rocks of coal mining should be used in the construction of temporary quarries and technological roads. The effective granulometric composition of aggregate with a high static modulus of elasticity and shear resistance is substantiated [9]. The use of various wastes from the mining and coal industries in brick production has been substantiated, which is considered an environmentally friendly method of waste disposal [10]. In some cases, this even implies improving the properties of the brick. The efficiency of using coal mining waste as a raw material component in cement technology has been theoretically proven [11].

Coal mining waste consists mainly of minerals and 20–30% of organic matter. The material classified as "mineral substance" includes crystalline minerals, as well as inorganic elements in the non-crystalline form. Oxidation of organic matter can cause self-heating and spontaneous combustion, resulting in the transformation of organic and mineral substances. The degree of change depends on the rank of the organic matter, the duration, the rate, the final temperature of heating and the degree of air access [12,13]. The prospects for using man-made deposits from mine dumps in the Eastern Donbass are shown: rock dumps, coal enrichment waste in the form of argillite-like clays, argillites, shales, siltstones in the production of wall ceramics [14]. Bricks with very good physical and mechanical properties were obtained from argillites. For the production of hydraulic lime, the coal washing wastes with the inclusion of coal and clay mineral residues and dolomite sifting in 1:1–1:2 ratios were used [15]. Some inert wastes of coal mining and their processing can be used as alternative sources of future environmentally efficient pozzolanic cements [16]. A comprehensive study of the properties of various coal mining wastes will help develop recommendations on their practical use in technologies of producing binding materials.

It is necessary to study the chemical composition and technically useful properties of industrial waste in order to determine the area of its use. We have suggested a method to determine the resource value of industrial waste aiming at their reclamation as technical materials [17]. The method optimizes consistency, increases the efficiency and completeness of the research. The choice of the research methods is based on the relevancy of studying the mineral, elemental and radionuclide compositions of industrial wastes, the structure of their surface, sorption and hydraulic activity, the behavior of minerals when heated.

The purpose of the research is to substantiate the resource value of coal mining rocks.

The research objectives are determining the mineral and oxide composition of coal mining waste in order to identify the presence of amorphous structures; studying the behavior of raw coal mining minerals during heating; studing the possibility of utilizing unburned coal mining rocks as clay raw materials for the production of cement clinker.

2. Materials and Methods

The dump coal mining unburned rocks of the Khmelnitskaya mine and the Sverdlov mine of the Lugansk region of Ukraine have been studied. The dispersion of waste samples into granulometric fractions was performed using a set of grading screens. The following fractions were identified, mm: > 20, 10–20, 5–10, 2.5–5, 1.25–2.5, 0.63–1.25, <0.63.

An X-ray phase analysis, which is instrumental in determining the mineral composition of the crystalline part of the samples, is performed on a Siemens D500 powder diffractometer in copper radiation with a graphite monochromator. The full-profile diffractograms were measured in the angle range of $5° < 2\theta < (110–120°)$ with a step of 0.02° and an accumulation time of 15 s. The primary phase search was carried out using the PDF-1 card file [18], after which the X-ray diffraction was calculated by the Rietveld method using the FullProf program [19].

Derivatographic analysis was used to study unburned coal mine waste rock. This method is often used to record thermal transformations of minerals based on aluminum, silicon, and iron oxides [20]. The analysis was performed on an "MOM 1500" derivatograph with a 10 ºC/min heating rate of a sample weighing 449 mg to a final temperature of 1000 ºC. An isothermal curing time was 60 min at 1000 ºC in the air medium.

The sorption properties of coal mining rocks were determined under static conditions by changing the concentrations of the absorbed substance (sorbate) in the solution. Methylene blue (MB) was the sorbate. The initial concentration of MB solution was 0.01 g/l. The optical density of the solution was determined by the spectrophotometric method with a SPEKOL 11 instrument at λ = 620 nm relative to distilled water. The sorption capacity (*a*) of coal mining rocks was determined by the formula

$$a = \frac{(C_1 - C_2) \cdot V}{m}, \text{mg/g} \quad (1)$$

where C_1 is the initial concentration of the sorbate, mg/l; C_2 is the concentration of the sorbate after adsorption, mg/l; V is the volume of the sorbate solution during adsorption, l; m is the mass of the sorbent sample, g.

The hydraulic activity of coal mining rocks was estimated by the amount of absorbed lime CaO. The crushed lot of coal mining rock (10 g) was kept in a CaO solution with the initial concentration of 5.63% and density of 0.995 g/cm^3. In the process of interaction with the rock the concentration of CaO was controlled in time using the titrimetric method.

The elemental composition and micrographs of the surface of cement clinker particles are determined by means of the method of electron probe microanalysis by the JSM-6390 LV scanning electron microscope having the INCA microroentgen analysis system.

Sintering of the samples pressed from the raw mixtures was carried out in a cryptol furnace under the following conditions: the sample with waste from the Khmelnitskaya mine (sample no. 1) was sintered at 1460 °C, followed by rapid cooling after the onset of melting; the sample with waste from the Sverdlov mine (sample no. 2) was sintered at 1400 °C for 2 hours, followed by rapid cooling.

The strength of cement samples was determined using the P-5 press with three sensitivity scales, kN: 0–10; 0–25; 0–50. Pressing speed 3 mm/min.

3. Results and Discussion

3.1. The Mineral Composition of Coal Mining Rocks

It was shown that, as a significant amount of coal is present in the mine pile rocks of the Sverdlov mine, a wavy background can be seen on radiographs of dump rocks [21]. The distinct wavy background on the radiograph of the fraction >20 mm of the mine pile rock is associated with the presence of the amorphous phase.

Several minerals were found in the crystalline part of the dump rocks, their mass content and the average crystallite size are given in Table 1. Muscovite prevails by mass, then comes quartz and the least is clinochlore. Clinochlore and muscovite could have formed in the process of chilling hot waste pile rocks by atmospheric precipitation. The presence of these minerals is allowed in the composition of the clay rocks used in the production of Portland cement clinker.

The structures of clinochlorine and muscovite are laminated sandwich-type. Each "sandwich" consists of two flat layers of silicate tetrahedral with a layer of magnesium or aluminum octahedral between them. Such compounds are thermally unstable and, when heated, they split off water, which is confirmed by the destruction of both phases during calcination of the heap of rocks of the Khmelnitskaya mine (Table 1). Hematite is found as a decomposition product of clinochlorine and muscovite. If during thermolysis silicates or aluminates of potassium and/or sodium are formed, they can be amorphous.

If the rock stays long in the waste pile, it can be the reason for transformations of its minerals. The process of weathering of layered minerals involves their transition to clay minerals. Muscovite eventually turns into illites (hydromica), zeolites, and kaolin. One of the causes of weathering is leakage of groundwater. When mica contacts with acidic solutions, potassium is replaced by H_3O^+-ion. Rainwater can be the second reason for weathering, it always has a weak acid reaction (pH = 5.7) when CO_2 is dissolved. This process is very likely to occur in the waste slagheaps at acid rains, which is so characteristic of the industrial Lugansk region. Since the illites are marked by a higher water content than conventional micas and emit constitutional water more easily, then when the rock is heated, the appropriate endothermic effects should be observed. The derivatographic analysis was made to clarify this circumstance.

Table 1. The results of X-ray phase analysis of the samples of unburned dump rocks.

Phases	Khmelnitskaya mine rock				Sverdlov mine rock			
	Sample 1waste slagheap rock		Sample 2calcinated rock		Sample 3 < 5 mm fraction		Sample 4 > 20 mm fraction	
	mass content, %	size,nm	mass content, %	size,nm	mass content, %	size,m	mass content, %	size, nm
Quartz	44.1	> 200	73.5	140	40.3	140	7.7	120
Clinochlore $(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$	10.2	38	–	–	11.1	47	17.4	48
Muscovite $K_{0.94}Na_{0.06}Al_{1.83}Fe_{0.17}Mg_{0.03}(Al_{0.91}Si_{3.09}O_{10})(OH)_{1.65}O_{0.12}F_{0.23}$	45.7	32	21.2	35	48.0	45	74.9	25
Hematite Fe_2O_3	–	–	5.3	–	–	–	–	–
Gypsum $CaSO_4{\cdot}2H_2O$	–	–	–	–	0.7	–	–	–

3.2. The Behavior of Raw Coal Mining Minerals During Heating

The results of the derivatographic analysis are given for the dump rock of the Khmelnitskaya mine. On the thermal effect curve – *dTa* (Figure 1) the peaks which are characteristic of the detected minerals are noted. For clinochlore at a temperature of 475 ºC, a clear endothermic effect is observed, corresponding to the release of all constitutional water [22]. The intense endothermic reaction at 550–650 ºC [22], characteristic of clinochlore, is somewhat erased, as is the exothermic effect at 820 ºC [22], resulting from the interaction of active amorphous SiO_2 and MgO oxides in the solid state with the formation of magnesium orthosilicate. According to the literature data, two endothermic

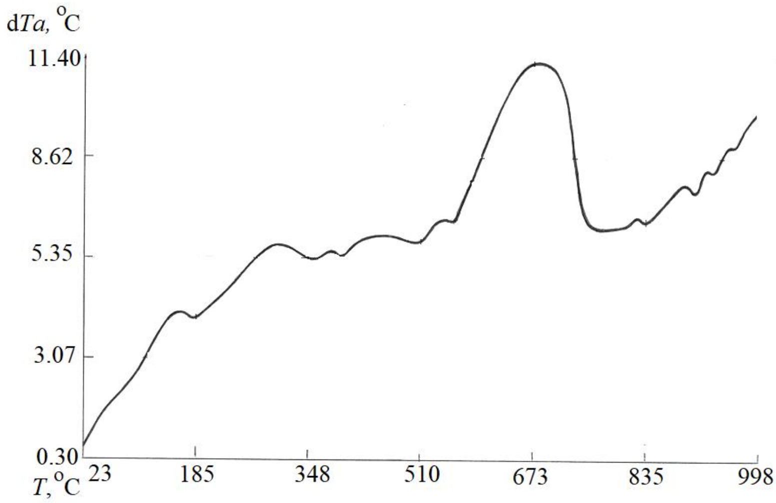


Figure 1. The thermogram of the dump rock of Khmelnitsky mine: d*Ta* is a heat effect

effects should be observed on the heating curves of muscovite: at temperatures 860 °C and 1200 °C [22]. The first effect, due to the release of structural water, is noted on the thermogram at 897 ºC. The second effect, associated with the destruction of the crystalline lattice, was not fixed in the experiment, since the heating was up to 1000 ºC.

The thermal behavior of clinochlore and muscovite largely depends on the degree of the samples grinding. The presence of a clear endoeffect at 185 ºC (Figure 1) indicates a high granularity of the samples, including muscovite [22].

Low-temperature endothermic effects of the heat effect curve (Figure 1) can belong only to the minerals that bind water loosely. For example, illite dehydration has several stages, therefore, several endothermic effects were recorded on the heat effects curve in the temperature range of 100–400 ºC.

In the temperature range from 185 to 510 ºC (Figure 1), endothermic effects associated with several processes are observed. First, volatile substances are released. This corresponds to a wide endothermic minimum, ending at 400 ºC. Secondly, the water of the illites, represented by OH^- ions, is removed. The loss of OH^--ions causes insignificant disturbances in the crystalline structure of the illites, which persists to the temperatures of about 750 °C [22]. Two small endothermic peaks at 928 and 967 ºC can be attributed to the destruction of the residual structure of the illite crystalline grid (850–950 ºC) with the appearance of spinel in this temperature range [22]. The exothermic effect at 670 ºC is associated with the combustion of carbonaceous matter.

Thus, as a result of derivatographic analysis, the initial transformation of the minerals of the waste piles rock was confirmed, and it was shown that the carbonaceous part of the rock can be burned.

3.3. The Hydraulic and Sorption Activity of of Coal Mining Rocks

The hydraulic activity of unburned waste rocks from coal mining, determined by the absorption of CaO over three days, is 360.7 mg/g for rocks from the Khmelnitskaya mine and 261.2 mg/g for rocks from the Ya. M. Sverdlova mine.

The presence of hydraulic activity of unburned waste rocks is indirectly confirmed by determining their adsorption activity when absorbing the MB dye. The presence of carbonaceous particles slightly increases the sorption capacity of rocks. According to the sorption capacity, the studied rocks can be classified as adsorbents characterized by high adsorption activity (Figure 2).

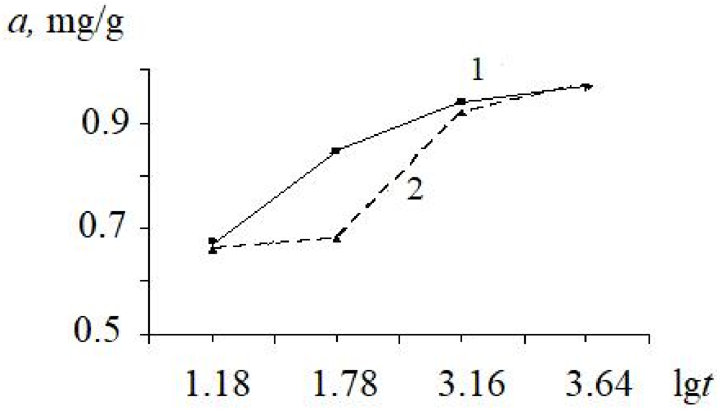


Figure 2. Dependence of the sorption capacity (*a*) of coal mining waste rocks when absorbing the MB dye on time (*t*): 1 for unburnt rock of the Khmelnitskaya mine; 2 for unburnt rock of the Sverdlov mine

The value of the efficiency of sorption purification of the MV solution for 15 minutes is 67.5%, and in 3 days it reaches the maximum value of 99%.

The calculated oxide compositions of the non-carbon part of unburned waste rocks of the Sverdlov and Khmelnitskaya mines after sintering and the modular classification are given in Table 2. Low content of basic oxides CaO and MgO and high content of acidic oxides SiO_2 and Al_2O_3 indicate the ultra-acidic nature of sintered waste rocks.

Table 2. Relative content of oxides in the non-carbon part of unburned waste rocks after sintering and the values of the modules

Oxide	Content of oxides (% mass)	
	Sverdlov mine rock	Khmelnitskaya mine rock
Na_2O	1.10	0.67
K_2O	3.06	3.56
MgO	1.10	2.54
CaO	2.21	–
SiO_2	42.74	66.88
Al_2O_3	39.56	21.78
TiO_2	0.60	0.70
Fe_2O_3	9.63	3.87
Module	Value of modules	
Activity module $M_a = Al_2O_3/SiO_2$	0.93	0.33
Silicate module $M_s = SiO_2/Al_2O_3$	1.08	3.03
Clay-iron module $M_{c.i.} = \frac{Al_2O_3 + Fe_2O_3}{SiO_2}$	1.15	0.38

The hydraulic activity of the rocks was characterized using a system of modules. According to the M_a value, the Sverdlov mine rock belongs to the first grade of acidic slags ($M_a \geq 0.4$); the Khmelnitskaya mine rock belongs to the second grade of acidic slags ($M_a \geq 0.33$).

Classification of samples as ferruginous rocks shows that all samples are highly active, with $M_{c.i} > 0.45$. Presumably, the most active is the sintered rock of the Sverdlov mine.

High concentrations of oxides Al_2O_3 and Fe_2O_3, sufficient values of $M_{c.i}$ and high hydraulic and adsorption activity make it possible to use coal mining unburned rocks in the production of Portland cement clinker in the raw mix instead of the clay component, aluminous cement, as corrective or active additives to Portland cement clinker or in the production of lime-slag binder.

3.4. Utilization of Unburned Coal Waste as Clay Raw Material for Cement Clinker Production

The varying carbonaceous particle content of coal waste determines how they can be used in the production of binders to reduce their accumulation. Unburned coal waste can be used as raw material in cement production instead of clay. The key factor is the similarity of the oxides formed during high-temperature decomposition of the waste to those formed in the rotary kiln used for cement clinker production during the decomposition of kaolinite clays.

3.4.1. Calculation of Raw Mix for Producing Portland Cement

Correct calculation of the raw mix is an important condition for ensuring the normal course and complete completion of the clinker formation processes during firing and obtaining clinker of a given mineralogical composition. The composition of the raw mix was calculated in accordance with [25] based on the results of chemical analysis of raw materials (Table 2), limestone, sand, pyrite cinders (Table 3) and the specified characteristics of the predicted clinker composition (saturation coefficient CS = 0.91; silicate module Ms = 2.5; alumina module Mal = 1.3). Composition No. 1 of the cement clinker raw mix was calculated based on coal mining waste from the Khmelnitskaya mine, and composition No. 2 was calculated based on waste from the Sverdlov mine. The quantitative ratios of the initial raw components and the calculated chemical composition of the Portland cement clinker are presented in Table 4.

Compliance with the composition of Portland cement clinker is determined by the content of the clinker's constituent oxides; the values of the CS and modules; and the content of the main clinker minerals.

Table 3. Chemical composition of the initial components.

Component	Mass fraction of the component, %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	loss on ignition	other	∑
limestone	0.95	1.68	0.24	52.25	42.45	2.43	100
sand	97	–	–	–	0.41	2.59	100
pyrite cinders	13.621	4.34	61.67	3.85	12.09	4.429	100

Table 4. Composition of the raw mix and the calculated chemical composition of clinker using coal mining waste.

Component	Mass fraction of the component, %	
	Composition No. 1	Composition No. 2
limestone	77.58	80.25
coal mining waste	10.17	5.78
sand	9.16	10.36
pyrite cinders	3.09	3.61
Calculated chemical composition of clinker		
SiO_2	21.70	21.67
Al_2O_3	4.91	4.90
Fe_2O_3	3.77	3.77
CaO	64.72	64.61
MgO	0.17	0.17

The calculated chemical composition of cement clinker with coal mining waste (Table 4) falls within the specified ranges of the content of the main oxides in Portland cement clinker, % by weight: CaO – (62−67); SiO_2 – (20−24); Al_2O_3 – (4−7); Fe_2O_3 – (2−5); MgO, SO_3, etc. – (1.5−4.0) [26].

3.4.2. Composition and Properties of Cement Clinker

The oxide composition of the cement clinker formed after sintering was calculated based on the elemental composition determined by electron probe microanalysis. The content of the main clinker oxides involved in subsequent mineral formation was approximately the same in both samples (Table 5).

The clinker sample containing coal mining waste from the Sverdlov mine is sulfur-free, which is beneficial for subsequent hardening and concrete stability. A comparison of the calculated oxide composition of the clinker and the results of X-ray microanalysis of the sintered samples shows that the latter are characterized by lower SiO_2 and Al_2O_3 contents (up to 1.2 times) and higher CaO, Fe_2O_3 (1.3–1.8 times) and MgO (11.4–14.8 times) contents.

Table 5. Results of X-ray microanalysis of cement clinker samples using coal mining waste.

Cement clinker with coal mining waste from the Khmelnitskaya mine				Cement clinker with coal mining waste from the Sverdlov mine			
Element	Mass fraction of the element, %	Oxide	Mass fraction of the oxide %	Element	Mass fraction of the element, %	Oxide	Mass fraction of the oxide %
Ca	48.505	CaO	67.869	Ca	49.603	CaO	69.404
Si	8.248	SiO_2	17.644	Si	8.273	SiO_2	17.698
Al	2.329	Al_2O_3	4.401	Al	2.138	Al_2O_3	4.04
Mg	1.163	MgO	1.929	Mg	1.520	MgO	2.521
Fe	4.651	Fe_2O_3	6.650	Fe	3.503	Fe_2O_3	5.009
Cr	0.323	Cr_2O_3	0.472	Cr	0.375	Cr_2O_3	0.548
Ti	0.370	TiO_2	0.618	Ti	0.468	TiO_2	0.78
S	0.167	SO_3	0.418	O	34.120		
O	34.243						
Total	100.0		100.0		100.0		100.0

The oxide composition of cement clinker samples allows us to characterize them from the perspective of their use in the production of binders. Table 6 presents the results of calculating individual modules as quantitative indicators of oxide composition. According to the calculated

Table 6. Evaluation of cement clinker with coal mining waste according to modular classification.

Indicator	The value of indicators for clinker with waste rocks from coal mines	
	Khmelnitskaya	Sverdlov
Basicity module [28] $M_b = \dfrac{CaO + MgO}{SiO_2 + Al_2O_3 + Fe_2O_3}$	2.43	2.69
M_s [181]	1.59	1.96
Hydraulic module [27] $M_{hyd} = \dfrac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3}$	2.37	2.59
Clay-iron module $M_{c.i.}$[24]	0,63	0.51
Quality factor [29] $QF = \dfrac{CaO + MgO + Al_2O_3}{SiO_2 + MnO}$	4.21	4.29
Alumina module [27] $M_{al} = \dfrac{Al_2O_3}{Fe_2O_3}$	0.66	0.81
Saturation coefficient [25] $CS = \dfrac{CaO - (1.65Al_2O_3 + 0.35Fe_2O_3)}{2.8SiO_2}$	1.18	1.23
CS according to Lee-Parker [27]	115.2	120.5

$CS = \frac{100CaO}{2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3}$		
CS according to Kindu-Jang [27] $CS = \frac{CaO - (1.65Al_2O_3 + 0.35Fe_2O_3 + 0.7SiO_2)}{2.8SiO_2}$	0.93	0.98

data, the clinker samples are basic ($M_b > 1$). The M_{al} values are below the specified optimal range for materials used in the production of Portland cement (1.5–2.5) [27]. Other quantitative indicators correspond to those of materials used in the production of binders: the quality factor corresponds to the active group of materials (QF > 1.65; the value of M_s practically fits into the range of values for Portland cement clinker 1.8–3.75 [25].

Cement clinker samples with coal mining waste rock are characterized by high hydraulic properties. The hydraulic module M_{hyd} is quite high for both samples (1.7–2.4 [27]). High CS values were calculated without taking into account corrections for the amount of CaO associated with SO_3 and for the content of free lime and silicic acid, which can only be determined during the production process. The CS values according to Lee-Parker (85–100 [27]) and Kindu-Jang (0.92–0.95 [27]) are also high.

The calculation of the mineralogical composition of Portland cement clinker with complete equilibrium crystallization during clinker cooling was carried out using the Kind method [30] According to this method, the content of the main minerals of clinker (alite – C_3S, belite – C_2S, tricalcium aluminate – C_3A and cellite – C_4AF) can be calculated based on the oxide composition using the following formulas

$$C_3S = 4.07C – 7.6S – 6.72A – 1.42F \quad (2)$$

$$C_2S = 8.6S + 5.07A + 1.07F – 3.07C \quad (3)$$

$$C_3A = 2.65A – 1.70F \quad (4)$$

$$C_4AF = 3.04F, \quad (5)$$

where C, S, A and F are the percentage content in clinker, respectively, of CaO, SiO_2, Al_2O_3 and Fe_2O_3.
The results of calculating the mineralogical composition of clinker based on the calculated chemical composition (Table 4) are presented in Table 7.

Table 7. Calculated mineralogical composition of cement clinker.

Mineral	Mass fraction of mineral, %	
	Composition No. 1	Composition No. 2
C_3S	60.12	60.02
C_2S	16.88	16.85
C_3A	6.59	6.58
C_4AF	11.48	11.45

The content of the main clinker minerals in Portland cement clinker, according to [30], varies within the range of % by weight for C_3S – (40–60), C_2S – (15–35, C_3A – (4–14), C_4AF – (10–18).

Using X-ray phase analysis, the following mineral phases were found in a clinker sample with rocks from the Khmelnitskaya mine (sample No. 1): $54CaO·16SiO_2·Al_2O_3·MgO$, Ca_2SiO_4 lamite, $Ca_2(Al,Fe)_2O_5$ brownmillerite, Ca_3SiO_5, $Ca_{14}Mg_2(SiO_4)_8$ bredigite, $Ca_2Al(Al,Si)_2O_7$ helenite, $Ca_3Al_2O_6$; in a clinker sample with rocks from the Sverdlov mine (sample No. 2): $54CaO·16SiO_2·Al_2O_3·MgO$, $Ca_3Al_2O_6$, $Ca_2(Al,Fe)_2O_5$, Ca_3SiO_5, Al_2O_3, $CaAl_2(Si_2Al_2)O_{10}(OH)_2$ margarite, Ca_2SiO_4. The phases are listed in order of decreasing content, i.e. the main phase in both samples is $54CaO·16SiO_2·Al_2O_3·MgO$.

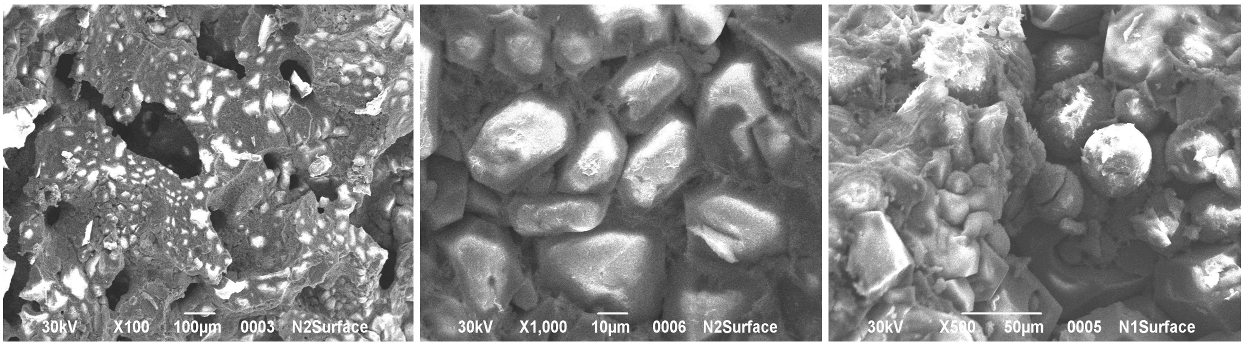
Several minerals are important for cement clinker production technology. The minerals larnite and bredigitite are the β- and α'-forms of dicalcium silicate. They are part of belite, which is thermodynamically unstable at normal temperatures. This explains its hydraulic activity [31]. Rapid cooling of the clinker and the use of slag raw materials facilitated the production of metastable high-temperature C_2S modifications. In the case of pure raw materials, the β- and α'-form minerals expand upon cooling, forming the γ-modification C_2S lattice, which is more stable at low temperatures [26].

The compound $3CaO{\cdot}SiO_2$ (C_3S) formed in cement clinker is alite. The most common composition of alite is $54CaO{\cdot}16SiO_2{\cdot}Al_2O_3{\cdot}MgO$. Under normal conditions, alite is in a supercooled state and has high hydraulic activity, which increases with the number of structural defects arising from the presence of impurities in the material [26]. A similar situation is observed when using production waste.

Brownmillerite and tricalcium aluminate of Portland cement clinker possess binding properties. Gehlenite and margarite minerals do not exhibit hydraulic properties, but they constitute a smaller proportion of the clinker by weight.

Micrographs of the surface of cement clinker particles show that the sintered particles consist of fragments of varying degrees of roundness, even spherical ones (Figure 3). After a short sintering time, granular conglomerates are formed. The absence of a large, dense glassy mass facilitates clinker grinding. The main type of pores are complex voids measuring 300−500 μm, formed as a result of loose particle packing during the aggregation and evaporation of water droplets (Figure 3a). Slit-shaped pores are observed at the contact areas, i.e., the interfaces between adherent grains.

The viscosity of the liquid phase largely determines the aggregation of the bulk powder raw material mixture. The viscosity of liquid clinker masses depends linearly on the alumina modulus M_{al} in the temperature range 1350−1500 ºC [26]. Raw material mixtures with a low M_{al} value of 0.64−1.5 are characterized by high particle adhesion at low sintering temperatures of 1300 ºC, which leads to the formation of large clinker grains. The value of the silicate modulus M_s also determines the adhesion of clinker grains. The adhesion increases sharply at M_s=1.5−2.1



a b c

Figure 3. Micrographs of the surface of cement clinker particles with unburned coal mining rocks from the Sverdlov mine (a, b) and the Khmelnitskaya mine (c) at magnifications of a – 100, b – 1000, c – 500

[26], and large clinker grains with an insufficiently fired middle part are formed. Based on their tendency to aggregate, raw mixes are divided into two groups, the first of which includes both samples of cement clinker. Namely, with $M_s < 2$ and $M_{al} < 1.5$, the mixture intensively aggregates at 1300−1400 °C. In the experiment the temperature did not rise above 1460 °C. Regardless of the chemical composition, adhesion also increases with increasing temperature in the range of 1300−1500 ºC, which is associated with an increase in the amount of melt. The shape of clinker conglomerates determines the predominant pattern of their formation: the adhesion of individual granules due to the appearance of a melt on their surface, followed by compaction and an increase in the contact surface area.

The shape of the intergrowths of crystals in the inner part of the grains (Figure 4b, c) determines their belonging to certain minerals. Belite crystallizes well in a kiln at temperatures above 1500 °C, forming aggregates of prismatic and needle-shaped crystals. Brownmillerite crystals also have a prismatic shape. No such formations were detected in micrographs. The intergrowths of hexagonal crystals (Figure 4b) are alite and are formed during prolonged exposure of the raw mixture to the high temperature zone of the firing kiln. Large crystalline structures usually appear during prolonged firing of clinker [29]. At the same time, rapid cooling of clinker grains also caused the correct crystallization of minerals.

The amount of melt also contributes to the correct crystallization of alite. It is estimated by the value of M_{al}. A decrease in the value of M_{al} from 1.28 to 0.32−0.64 [29] leads to the appearance of fairly regular hexagonal crystals in the sinters. In the cases under consideration $M_{al} \leq 0{,}81$. The presence of a ferrous liquid phase leads to the formation of round alite crystals (Figure 4c).

The research results formed the basis for the production of a pilot batch of cement clinker using unburned coal mining rock from the Khmelnitskaya and Sverdlov mines (compositions 1 and 2, Table 4). An environmentally friendly technology with dry raw mix preparation was employed. The results of the physical and mechanical testing of the cement clinker are presented in Table 8.

Table 8. Physical and mechanical properties of cement clinker samples

Sample	Compressive strength over time, MPa	
	2 days	28 days
Composition No. 1	17.5	43.1
Composition No. 2	16.0	41.2

Studies of the chemical composition and physical and mechanical properties of the developed cement clinker, carried out in pilot industrial conditions, confirmed the clinker's compliance with the requirements for Portland cement clinker.

4. Conclusions

Crystalline coal mining waste rock minerals have been identified and the presence of amorphous compounds has been confirmed. The presence of minerals in waste rock that have technical value in the production of binders has been proven. The possibility of thermal transformation of minerals in unburned waste rock during heating and the ability of the carbonaceous part of the rock to burn have been shown. The use of unburned waste rock from the Khmelnitskaya and the Sverdlov mines in the production of Portland cement clinker, instead of a clay component, is feasible. This is confirmed by the chemical composition, modulus properties, physical and mechanical properties of the cement clinker.

Further research will be aimed at justifying the increase in the content of coal mining waste rocks in the production of cement clinker with high activity and physical and mechanical properties.

Author's Contributions

E. Khobotova's individual contribution includes conducting research on the mineralogical and elemental composition of coal mining rocks, determining their hydraulic activity, and conducting sintering of raw mixtures, as well as writing the Results and Discussion and Conclusions sections.
V. Datsenko's individual contribution includes conducting derivatographic analysis and determining the sorption properties of coal mining rocks, as well as writing the Introduction, Results and Discussion and Conclusions sections.

Funding

This research received no external funding.

Data Availability

The data supporting the findings of this published article are available from the authors [HFK] upon request.

Conflict of Interest

The authors declare no conflict of interest.

References

[1] Agayeva, Z.R., Mammadova, B.G., Naseri, Sh.A., Jabbarov, E.E., Mammadova, S.G., Shabanova, Ch.M., Rafiyeva, Kh.L., Aliyev, E.M. (2021). Study of the mutual effect of phosphorus-containing fertilizers and clay minerals of aluminosilicate type on the productivity of agricultural products and the ecological condition of brownbrown soils. Azerbaijan Chemical Journal, 2, 54–58. https://doi.org/10.32737/0005-2531-2021-2-54-58

[2] Agayeva, Z.R., Mammadova, B.G., Kazimova, E.M., Talibli, I.A., Efendiyeva, S.G., Shabanova, Ch.M. (2020). Influence of alyumosilicate clays on ecological condition of Apsheron lands. Azerbaijan Chemical Journal, 1, 82–86. https://doi.org/10.32737/0005-2531-2020-1-82-85

[3] Gulieva, A.A.(2019). Study of the surface properties of minerals in the composition of tails of Dashkesan iron ores. Azerbaijan Chemical Journal, 4, 48–53. https://doi.org/10.32737/0005-2531-2019-4-48-53

[4] Savinykh, P.A., Kipriyanov, F.A., Palitsyn, A.V., Zubakin, A.S., Korotkov, A.N. (2020). A new device for energy recovery from carbon-containing waste and plant biomass. Petroleum and Coal, 62, 516–524.

[5] Korolev, N., Korolev, I., Gribanova, G. (2016). Possibilities of rational use of by-products and coal industry wastes. High technology development and use of mineral resources, 3, 512–515.

[6] Wo´zniak, Ju., Pactwa, K. (2018). Overview of Polish Mining Wastes with Circular Economy Model and Its Comparison with Other Wastes. Sustainability, 10, 3994. https://doi.org/10.3390/su10113994

[7] Kharionovsky, A., Kalushev, A., Vaseva, V., Simanova, E. (2018). Ecology of the coal industry: state, problems, solutions. Bulletin of the Coal Safety Research Center, 2, 70–81 (in Russian).

[8] Myaskov, A. (2018). Ecological safety: ways to reduce the negative impacts of mining enterprises on natural ecosystems. Bulletin of the Coal Safety Research Center, 3, 39–43 (in Russian).

[9] Shalamanov, V., Pershin, V., Shabaev, S., Boiko, D. (2017). Justification of the optimal granulometric composition of crushed rocks for open-pit mine road surfacing. Paper presented at the E3S web of conferences. The 1st scientific practical conference “International innovative mining symposium”, 15, 01006. https://doi.org/10.1051/e3sconf/20171501006

[10] Zhang, L. (2013). Production of bricks from waste materials. A review. Construction and Building materials, 47, 643–655. https://doi.org/10.1016/j.conbuildmat.2013.05.043

[11] Klassen, V., Borisov, I., Manuilov, V., Khodykin, E. (2017). Theoretical substantiation and efficiency of the use of coal waste as a raw material component in cement technology. Construction Materials, 8, 20–21 (in Ukrainian).

[12] Misz-Kennan, M., Fabiańska, M. (2011). Application of organic petrology and geochemistry to coal waste studies. Intern. J. Coal Geology. 2011, 88, 1–23. https://doi.org/10.1016/j.coal.2011.07.001

[13] Gong, D. Song, Y., Wei, Y., Liu, C., Wu, Yi., Zhang, L., CuI, H. (2019). Geochemical characteristics of Carboniferous coaly source rocks and natural gases in the Southeastern Junggar Basin, NW China: Implications for new hydrocarbon explorations. Intern. J. Coal Geology, 202, 171–189. https://doi.org/10.1016/j.coal.2018.12.006

[14] Kotlyar, V.D.,Yavruian, Kh. S.(2017). Wall ceramic products based on finely dispersed waste heap products. Construction Materials, 4, 38-41 (in Russian). https://doi.org/10.31659/0585-430X-2017-747-4-38-41

[15] Shpirko, N., Bondarenko, S. (2017). Construction materials using waste coal. Construction, Materials Science, Engineering, 9, 213–217 (in Ukrainian).

[16] Giménez-García, R., de la Villa Mencía, R., Rubio, V., Fría,s M. (2016). The transformation of coal-mining waste minerals in the pozzolanic reactions of cements. Minerals, 6, P. 64–74. https://doi.org/10.3390/min6030064

[17] The method of determination of useful properties of industrial waste for the purpose of their utilization as technical materials. Author’s license No 34221 UA.

[18] JCPDS PDF-1 File. ICDD: The International Centre for Diffraction Data, release 1994. PA. USA. Acces mode: http://www.icdd.com

[19] Rodriguez-Carvajal, Ju., Roisnel, T. FullProf. 98 and WinPLOTR New Windows 95/NT Applications for Diffraction. Extended software/methods development: International Union of Crystallography. Newsletter No. 20. Summer 1998. P. 35–36. Acces mode: http://www.fkf.mpg.de/xray/CPD_Newsletter/cpd20.pdf

[20] Talibli, I.A., Samedzade, G.M., Alieva, J.M., Mammadov, A.N., Gamidov, R.G., Gasimova, A.M., Shadlinskaya, G.V. (2022). Sludge-free production of pure alumina from rocks containing iron oxides and silica. Azerbaijan Chemical Journal, 1, 69–72. https://doi.org/10.32737/0005-2531-2022-1-68-72

[21] Khobotova, E., Ukhaneva, M. (2010). Chemical evaluation of coal waste. Bulletin of Kharkov University, 18, 260–268 (in Russian).

[22] Encyclopedia of inorganic materials (1977). V. 2. Kiev, Main editors of the Ukrainian Soviet Encyclopedia. (in Russian).
[23] Alyokhin, V., Migulya, P., Proskurnya, Yu. (1998). Mineralogical, petrographic and ecological-geochemical features of the rocks of the Donbass heaps (on the example of the Donetsk-Makeevka industrial region). Collection of Scientific Works of the National Mining Academy of Ukraine, 5, 35–39 (in Russian).
[24] Knigina, G.N. (1966). Building materials from burnt rocks. Moscow, Building Publishing House. (in Russian).
[25] Kholin, I.I. (1963). Handbook of cement production. Moscow, State Building Publishing House. (in Russian).
[26] Butt, Yu.M., Timashev, V.V. (1967). Portland cement clinker. Moscow, Stroyizdat. (in Russian).
[27] Kuzhvart, M. (1986). Non-metallic minerals. Moscow, Mir. (in Russian).
[28] Perepelitsyn, V.A. (1987). Fundamentals of technical mineralogy and petrography. Moscow, Nedra. (in Russian).
[29] Budnikov, P.P., Znachko-Yavorsky, I.L. (1953). Granulated blast-furnace slags and slag cements. Moscow, Promstroyizdat. (in Russian).
[30] Butt, Yu.M., Timashev, V.V. (1973). Workshop on chemical technology of binders. Moscow, Higher School. (in Russian).
[31] Pashchenko, A.A. (1986). Physical chemistry of silicates. Moscow, Higher School. (in Russian).