Journal of
Composites Science

Article

Production of Composite Cement Clinker Based on Industrial Waste

Aknur Kuandykova [1], Bakhitzhan Taimasov [1], Ekaterina Potapova [2], Bakhitzhan Sarsenbaev [3,*], Alexandr Kolesnikov [4,*], Meiram Begentayev [5], Erzhan Kuldeyev [5,*], Mukhtar Dauletiyarov [3], Nurgali Zhanikulov [6], Baurzhan Amiraliyev [1] and Aidana Abdullin [1]

[1] Department of Silicate Technology and Metallurgy, M. Auezov South Kazakhstan University, Shymkent 160012, Kazakhstan; aknur.01.07.94@mail.ru (A.K.); taimasovukgu@mail.ru (B.T.); badam777@inbox.ru (B.A.); aidana_gkz@mail.ru (A.A.)
[2] Department of Chemical Technology of Composite and Binding Materials, D. I. Mendeleev Russian University of Chemical-Technological, Moscow 125480, Russia; 55pen@mail.ru
[3] Scientific Research Laboratory «Building Materials, Construction and Architecture», M. Auezov South Kazakhstan University, Shymkent 160012, Kazakhstan; muhtar-66@mail.ru
[4] Department of Life Safety and Environmental Protection, M. Auezov South Kazakhstan University, Shymkent 160012, Kazakhstan
[5] K.I. Satpayev Kazakh National Research Technical University, Almaty 050013, Kazakhstan; m.begentayev@satbayev.university
[6] Department of Inorganic and Technical Chemistry, E.A. Buketov Karaganda University, Karaganda 100028, Kazakhstan; nurgali.zhanikulov@mail.ru
* Correspondence: stroitelstvo_ukgu@mail.ru (B.S.); kas164@yandex.kz (A.K.); e.kuldeyev@satbayev.university (E.K.); Tel.: +7-701-890-17-94 (A.K.)

Abstract: The possibility of producing cement clinker using low-energy, resource-saving technologies is studied. The composition of industrial waste for low-energy-intensive production of Portland cement clinker at factories in Southern Kazakhstan is analyzed. The possibility of replacing the deficient iron-containing corrective additive with "Waelz clinker for zinc ores" is shown. "Waeltz clinker from zinc ores" as part of the raw material charge performs several tasks: it is a ferrous corrective additive, works as a mineralizer for clinker formation processes, introduces coal into the charge and allows one to reduce the consumption of natural fuel. The processes of burning raw mixtures, wholly or partially consisting of industrial waste, are completed at 1350 °C. This reduces the consumption of main burner fuel for clinker burning and reduces CO_2 emissions into the atmosphere. High-quality cement clinker is obtained based on raw material mixtures with Waeltz clinker from zinc ores from the Achisai Metallurgical Plant, phosphorus slag, coal mining waste from Lenger mines and sodium fluoride. The phase composition and microstructure of low-energy clinkers are revealed. Involving industrial waste in raw material circulation will reduce environmental pollution and improve the environment.

Keywords: Portland cement clinker; roasting; industrial waste; zinc ore; "Waeltz clinker from zinc ores"; fuel consumption; environmental engineering; composite materials

Citation: Kuandykova, A.; Taimasov, B.; Potapova, E.; Sarsenbaev, B.; Kolesnikov, A.; Begentayev, M.; Kuldeyev, E.; Dauletiyarov, M.; Zhanikulov, N.; Amiraliyev, B.; et al. Production of Composite Cement Clinker Based on Industrial Waste. *J. Compos. Sci.* **2024**, *8*, 257. https://doi.org/10.3390/jcs8070257

Academic Editor: Francesco Tornabene

Received: 15 May 2024
Revised: 21 June 2024
Accepted: 26 June 2024
Published: 3 July 2024

1. Introduction

Portland cement is an energy-intensive product, since the cement base—clinker—is fired at a high temperature of 1450 °C. Clinker burning is a complex multi-stage process. To produce 1 ton of Portland cement clinker using the wet method, approximately 1.6 tons of natural raw materials, 1 ton of water, 3 tons of air and 0.2 tons of fuel are consumed. In total, it is 5.8 t/t clinker. Using the dry method, 1.6 tons of raw materials, 2.3 tons of air and 0.1 tons of fuel are consumed, totaling 4 tons [1,2]. In the Republic of Kazakhstan, 12 plants produce clinker using the dry method and 3 plants produce clinker using the wet method.

Therefore, the issues of clinker burning processes and energy saving, especially with the wet method of producing clinker, remain important and relevant [1,3,4].

Today in the Republic of Kazakhstan, more and more attention is being paid to the problems of sustainable development and reducing anthropogenic impacts on the environment and the climate system, including reducing greenhouse gas emissions in key industries [5–8]. Cement production is an extremely material- and energy-intensive process that produces significant amounts of carbon dioxide.

Cement production is one of the leaders in greenhouse gas emissions into the atmosphere [9,10]. Each year, the global cement industry produces approximately 6% to 7% of global CO_2 emissions and 5 to 7% of anthropogenic greenhouse gas emissions [11–14]. At the same time, during the production of cement clinker, a large amount of greenhouse gas CO2 is formed, which is released during the decarbonization of carbonate-containing raw materials (process CO_2) and during the combustion of fuel (energy CO_2) [15]. The share of costs for fuel and energy resources in the cement industry is about 40% of the cost of the produced product [16,17]. In fact, during the production of 1 ton of clinker, 840–900 kg of CO_2 is released into the environment [18].

Global cement producers believe that it is necessary to switch to eco-sustainable production methods. According to scientists' forecasts, emissions of carbon dioxide alone from cement production may reach 2.34 billion tons/year by 2050. By reducing carbon dioxide emissions from the production of cement and concrete, significant progress can be made in overcoming the global climate crisis. Decarbonization is consistent with international agreements and goals, such as the Paris Agreement, which aim to limit global temperature rise and combat the adverse effects of climate change [19–21].

The concept of carbon neutrality in the cement and concrete industry has been developed—the "Climate Ambition 2050" initiative [22]. For a successful transition to the production of "carbon-neutral" concrete, the cement industry needs to eliminate direct CO_2 emissions; reduce and eliminate indirect CO_2 emissions; introduce the use of new decarbonization technologies in production on an industrial scale; reduce both the clinker content in cement and the cement content in concrete; recycle construction scrap for reuse as aggregate in concrete production; improve the ability of concrete to absorb CO_2 throughout its life cycle; and increase the energy efficiency of finished products, which will reduce heating costs for buildings built from such concrete.

This goal can only be achieved by implementing carbon capture, utilization and storage (CCUS) concepts. But, today, the problem with all technologies is high operating and investment costs, which significantly affect the cost of cement production.

Some of these emissions reductions will be achieved through the introduction of disruptive technologies, but, crucially, CO_2 savings can also be achieved with limited technology investments [22].

In fact, a number of technologies, policies and operational changes will be required throughout the life cycle, from clinker production to concrete recarbonization and recycling. The degree of market readiness of many technologies is still insufficient. The most advanced technologies are to increase energy efficiency when using alternative fuels and raw materials [23–26].

Other groups of measures rely on technologies that have just begun to penetrate the market or have not yet left the laboratory. CO_2 emissions are indirectly reduced by replacing clinker with so-called secondary cementitious materials, such as fly ash or granulated blast kiln slag. However, with ambitious climate policies, the availability of such materials is decreasing [8].

New binders are being developed, such as low-carbon cements to replace conventional Portland cement, which include belite–yelemit–ferrite cement, Celitement, Solidia, Novacem, geopolymers, etc. [27–34].

In recent years, new binders based on calcined clays and limestone fillers, which are promising substitutes for raw materials, have been developed. Such materials are available during any cement production. Research results indicate a high mitigation potential, i.e., these compositions can replace up to 50% of Portland cement clinker, and therefore reduce CO_2 emissions by 50% [35].

For further improvement of clinker burning technology, waste disposal, the reduction of fuel consumption and CO_2 emissions, and emission quotas have been established for Kazakhstan cement plants, which amount to 7.893 million tons of CO_2 in 2022; 7.774 in 2023; 7.658 in 2024; and 7.524 million tons in 2025 [36].

Of course, it is not possible to reach a zero level of CO_2 emissions using various primary methods. However, increasing the resource efficiency of production and introducing approaches to the circular economy is a step in solving this problem.

Therefore, it is very relevant to use waste, natural or industrial, in the production of clinker and cement and develop low-energy resource-saving technologies to solve environmental problems, reducing both fuel consumption for clinker firing and CO_2 greenhouse gas emissions.

Taking into account the above, the Republic of Kazakhstan, following Western Europe and the Russian Federation, in 2021–2022 developed a "Handbook of the best available techniques for the production of cement and lime" (BAT Handbook) [17]. The Handbook outlines and recommends the best cement production technologies for cement enterprises with the lowest energy consumption, reduced CO_2 emissions into the atmosphere, the possibility of replacing natural raw materials with industrial waste and ways to increase the energy efficiency of grinding and baking equipment in cement plants.

At the cement factories in the Republic of Kazakhstan, the recycling of industrial waste has not yet found proper development. We tried to fill this gap. In this study, we developed and investigated firing processes for new efficient raw material mixture compositions to produce cement clinker. The waste completely or partially replaced the carbonate, aluminosilicate (clayey) component and the deficient iron corrective additive. In addition, the proposed waste had a mineralizing effect on the process of clinker formation and introduced combustible mass into the raw material mixture, reducing the firing temperature and specific fuel consumption in the kiln.

The purpose of this research was to develop low-energy resource-saving technologies for the production of clinker and cement with the complete or partial replacement of natural raw materials with large-tonnage industrial waste containing non-carbonate lime and coal, allowing us to reduce the sintering temperature of clinker, reduce fuel consumption, increase the productivity of kilns and solve environmental problems through the mass recycling of waste and the reduction of greenhouse gas CO_2 emissions.

Relevance of this work.

The clinker formation processes and specific heat consumption for clinker burning depend on many factors [3,37–39]. The main ones are the type and composition of the raw materials and charge, their saturation coefficient and modules, the burning method and temperature, and the mineral composition of the resulting product.

It is possible to speed up the burning of clinker and reduce fuel consumption through the use of mineralizers, utilizing various industrial wastes containing non-carbonate lime as raw materials: blast kiln, electrothermophosphorus, granulated or crystallized steelmaking slags and non-ferrous metallurgy slags. This waste is heat-treated in a previous process and does not contain calcium and magnesium carbonate.

In traditional cement production technology, about 1790 kJ/kg is spent on the decarbonization of $CaCO_3$. Therefore, those wastes that contain non-carbonate lime will be effective.

When using slag, the specific consumption of raw materials for the production of 1 ton of clinker is reduced by 10–20%. The humidity of the fired charge is reduced from 38 to 20–25% with additional feed of the kiln to granulated slag. The proportion of material requiring decarbonization is reduced from 75–77% to 50–60%. The clinker burning temperature is reduced by 50–100 °C. In general, these factors reduce heat costs by 300–400 kcal/kg of clinker [1,40].

In addition to the huge energy consumption when burning clinker (1450 °C), the cement industry uses a large amount of natural raw materials. Therefore, the production of Portland cement clinker based on industrial waste is an important task from the point of view of the efficient use of resources and reducing environmental load. This solution to the problem makes it possible not only to preserve natural resources and dispose of waste, but also to reduce CO_2 emissions. Many scientists have studied various types of waste and their effect on the burning process, the quality of the finished product and the optimization of production processes, taking into account the use of alternative raw materials. The economic feasibility of this approach must be taken into account, including the costs of modernizing production and the potential economic benefits of using waste.

When burning slag-containing raw material mixtures, kilns operate with increased productivity, heat consumption for clinker formation processes is minimized and heat consumption for the endothermic reaction of calcium carbonate decomposition is reduced.

Earlier, at the M. Auezov South Kazakhstan University (M. Auezov SKU), extensive research was conducted to improve the clinker burning process, increase the energy efficiency of the process and reduce fuel consumption; traditional natural raw materials were completely or partially replaced by industrial waste [41–53]. Issues regarding the complete or partial replacement of the carbonate and aluminosilicate component of the raw material charge (loess) with coal mining waste from the Lenger coal mines and igneous rock—Daubabinsky tephrite basalt and granulated lead slag—have been studied.

Replacing the clay- and iron-containing component with tephrite basalt and lead slag in the initial charge reduced the burning temperature by 100 °C. The specific consumption of raw materials was 1.481 t/t of clinker. This is 60–70 kg less than when using natural raw materials. The total content of non-traditional components was 24.69%. Tephritobasalts improved the processes of clinker formation, lowered the burning temperature and intensified the clinker burning process. Lead slag, introduced into the mixture in an amount of 5–8%, improved the structure of the clinker and accelerated the process of mineral formation, reducing the anthropogenic impact on the environment through the disposal of industrial waste. The strength of cement after 28 days of curing was 41.8 MPa [46].

Tephritobasalt contains 45–50% silica, 9–15% alumina, 8–12% iron oxides and 10–12% calcium oxide. Tephritobasalt can completely or largely cover the required amount of these oxides in the composition of the cement raw material mixture. Granulated lead slag from the Shymkent plant contains up to 40% iron oxides and replaces the traditional iron additive, i.e., pyrite or pyrite cinders. Non-carbonate lime slag does not require heat for the decarbonization of $CaCO_3$ [47]. Coal mining waste contains silica, alumina and 18–24% coal.

Granulated electrothermophosphorus slag according to the requirements of GOST 3476-2019 must contain at least 40% SiO_2; no less than 43% CaO; and no more than 2.5% P_2O_5.

The processes of clinker formation in the developed charges were completed at 1350–1400 °C, which was confirmed during pilot tests at Sastobe Technologies LLP, Standard Cement LLP [43,45,47,49,54].

Indian scientists used lime sludge from the paper and pulp industries as the carbonate component of the raw material mixture. With saturation factor (LSF) = 0.92 and 0.93, silica modulus (SM) = 2.19 and alumina modulus (AM) = 1.12, more alite phases were formed in clinker fired at 1450 °C (within 59%) and there was less free lime. The strength of cement prepared from this clinker after 28 days of curing was 50–62 MPa [55].

Russian scientists utilized waste from the Yuzhno-Uralsk mining and processing company as raw materials. Metallurgical slags can replace the clayey and partially carbonate components in their chemical composition. In experimental charges, exothermic processes of the formation of silicate phases occur at 1000 and 1200 °C. The melting of the material occurs at 1259 and 1308 °C. The main clinker melt is formed at 1327 °C. Metallurgical slag accelerates the formation of the belite phase during low-temperature burning stages. The features of the crystallization of clinker phases are also influenced by changes in the composition of the "liquid" phase, increasing its temperature and melt viscosity with increasing dosages of waste in the raw material charge [56].

2. Materials and Methods

Raw Materials and Research Methods

In this work, to obtain clinkers as an alternative raw material and corrective additives, waste from crushing limestone from the Sastobe deposit, «Waeltz clinker from zinc ores» from the Achisai Metallurgical Plant, electrothermophosphorus slag from the Novo-Dzhambul phosphorus plant in Taraz and coal mining waste from the Lenger mines (Turkestan region) were studied. All of these man-made raw materials are located in close proximity to three large cement plants in Southern Kazakhstan; these are Standard Cement LLP, Shymkentcement LLP and Sastobe Technologies LLP. Accordingly, logistics and transportation costs for the delivery of industrial waste to these enterprises was affordable.

In the last decade, due to a large shortage of cinders, many cement factories in Kazakhstan have switched to using iron ore and some industrial waste. In particular, the plants in Southern Kazakhstan use iron ore from the Abaiyl deposit, located in the Tyulkubas district of the Turkestan region. The transportation distance is short and is about 20–50 km. Gezhuba Shieli Cement Company LLP uses iron ore from the Shoiyntas deposit, located in the Karaganda region. The transportation distance is long. Therefore, the search for local iron-containing waste was important. Iron ore, the main and only raw material in ferrous metallurgy, will be preserved for future generations.

The studies were carried out with raw materials from 4 plants: Shymkent, Sastobe, Standard Cement LLP and Gezhuba Shieli Cement Company LLP.

To study the composition of raw materials, industrial waste and the resulting cement clinker, chemical analysis methods were used in accordance with GOST 5382-2019 Cements and materials for cement production. Methods of chemical analysis [57] included X-ray phase analysis of raw materials and clinkers, which was carried out on a DRON-3 derivatograph [58], an ENDEAVOR D8 diffractometer and an X-ray device (S8 Tiger) [59]; electron microscopic studies were performed on a JEOL JSM-6490 LV microscope [59]. The quality of clinker burning was assessed by the content of unassimilated CaO, which was determined by the ethyl–glycerate method [57].

Table 1 Analyses of raw materials and waste were carried out. The effectiveness of producing cement clinker based on them is shown.

Table 1. Chemical composition of natural, non-traditional raw materials and industrial waste.

Natural and Man-Made Raw Materials, Deposit	Chemical Composition, wt.%						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss on Ignition
Natural raw materials							
Limestone from the Kazygurt deposit	4.86	0.72	0.81	51.75	0.36	0.02	41.12
Limestone from the Kutau deposit	1.65	0.24	0.14	54.14	0.28	0.05	42.73
Loess from the Tekesu deposit	50.54	10.35	4.43	13.91	2.67	0.21	13.06
Clay from the Zhanakorgan deposit	46.73	12.91	5.24	12.84	2.98	0.06	14.68
Iron ore from Abaiyl	16.67	1.74	56.39	7.43	0.96	0.03	13.39
Shointas Iron Ore	7.9	1.32	53.88	17.07	1.13	0.04	18.66
Industrial waste that had been subjected to heat treatment							
Electrothermophosphorus slag (ETPS)	42.68	0.74	0.17	41.18	4.55	0.4	-
«Waeltz clinker from zinc ores» from the Achisai plant	27.55	5.74	33.5	17.33	6.07	1.31	6.5
Industrial waste that had not been subjected to heat treatment							
Sastobe limestone crushing waste	9.63	1.72	1.26	46.0	0.55	1.15	36.2
Coal mining waste from Lenger mines	55.50	10.60	2.01	3.21	0.70	0.79	24.08

In addition to the chemical composition of the raw material, its mineralogical composition is important, which affects the technological process, clinker burning and cement properties. Table 2 shows the mineralogical composition of waste from crushing Sastobe limestone and limestone from the Kutau and Kazygurt deposits.

Table 2. Mineral content of waste from crushing Sastobe limestone and limestone from the Kutau and Kazygurt deposits.

Raw Material	Mineralogical Composition, wt. %								
	Calcite	Dolomite	Quartz	Illite	Chlorite	Albite	K-Feld Spar	R_wp	CO_2
Sastobe limestone crushing waste	80.6	2.2	9.3	2.9	1.5	2.3	1.3	16.32	36.5
Limestone Kutau (Shieli)	92.6	0.8	2.2	1.3	0.4	2.4	0.3	9.54	41.1
Limestone Kazygurt	81.9	2.0	0.2	7.8	0.3	1.5	6.3	11.27	37.0

As can be seen from the data in Table 2, the limestones are quite pure, consisting mainly of calcite with small admixtures of quartz, dolomite and clay minerals. The purest is the limestone from the Kutau deposit, used by Gezhuba Shieli Cement Company LLP. The calcite content is 92.6%; that of dolomite is less than 1%. The limestone from the Kazygurt deposit (Shymkentcement LLP) is characterized by a high content of the clay mineral illite. The waste from crushing limestone from the Sastobe deposit contains an increased amount of quartz and clay minerals such as illite, chlorite and albite.

In Southern Kazakhstan, as well as in other regions of the Republic, there are large sources of technogenic raw materials from which cement clinker and cement can be produced. The dumps of this waste occupy vast territories, pollute the environment and cause irreparable damage to nature and public health. Significant funds are spent on maintaining dumps.

Industrial production waste is divided into two categories: the first is waste that was not subjected to heat treatment during the formation process; the second is waste that was subjected to heat treatment. The first includes waste from crushing limestone and waste from coal mining in Lenger. The second includes electrothermophosphorus, blast kiln, lead slag and «Waeltz clinker of zinc ores» from the Achisay Metallurgical Plant.

The first group of waste is of interest as resource-saving raw materials. When using them, the need to produce this or that material in quarries is eliminated, i.e., when producing clinker, there is no need to carry out drilling and blasting operations or crushing limestone or clay rock. Reserves of natural raw materials in the quarries will be preserved for future generations.

The second group of waste is of interest as resource-saving and energy-saving raw materials. They underwent heat treatment in the previous process, there is no calcium or magnesium carbonates in the waste; calcium oxide is in non-carbonate form, in the form of low-basic minerals such as belite, pseudowollastonite, etc.; and clay minerals are dehydrated and decomposed. When using them, the heat costs for decarbonization of the raw material charge, the total specific fuel consumption in the kiln and the consumption of raw materials for clinker production are significantly reduced, and the productivity of the kilns is increased.

According to scanning electron microscopic analysis, «Waeltz clinker of zinc ores» from the Achisai Metallurgical Plant has the following chemical composition, in percentages (%): SiO_2, 13.82; Al_2O_3, 3.23; Fe_2O_3, 24.1; CaO, 12.7; MgO, 3.76; SO_3, 1.5; K_2O, 0.37; TiO_2, 0.65; Mn_2O_3, 0.32; ZnO, 3.01; C, carbon, 23.15 (Figure 1).

Element	Weight, %	Oxidic, %
C	23.15	
O	36.54	
Mg	2.24	3.76
Al	1.71	3.23
Si	6.46	13.82
S	0.60	1.5
K	0.31	0.37
Ti	0.39	0.65
Mn	0.25	0.32
Fe	16.85	24.1
Zn	2.42	3.01
Total	100.00	

Comments: Waeltz clinker from

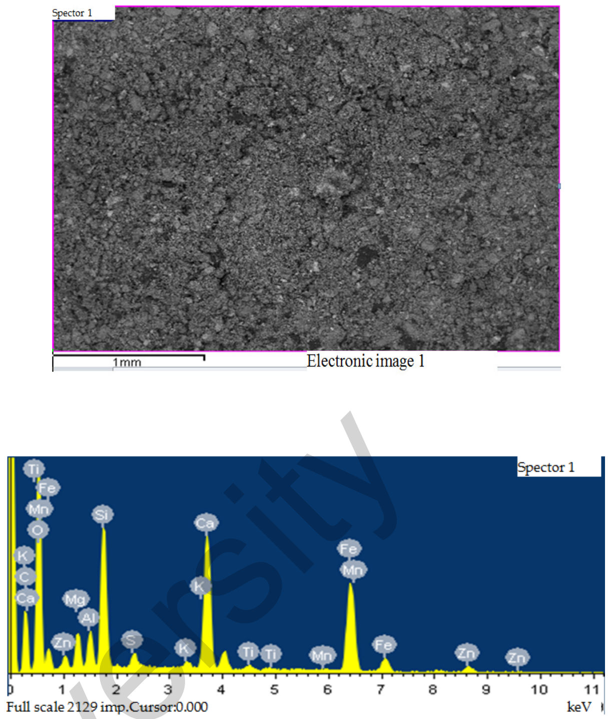


Figure 1. Composition of Waelz clinker from zinc ores at Achisai Metallurgical Plant (according to electron microscopic analysis).

"Waelz clinker" contains up to 15–20% coke (coal), which will reduce the consumption of nozzle coal when firing clinker. More than 4.6 million tons of "Waelz clinker of zinc ores" have been accumulated in the dumps of the Achisai Metallurgical Plant.

Waelz clinker from zinc ores at the Achisai Metallurgical Plant contains up to 24–33% iron oxides. In fact, this is a new ferrous additive to the raw material mixture for the production of Portland cement clinkers.

According to the results of the analysis of "Waelz clinker of zinc ores" from the Achisai plant, performed on an X-Rai device in the laboratory of Shymkentcement LLP, this waste contains, in addition to the main oxides of the raw material charge for clinker production, oxides of metals such as TiO_2 0.331%, Mn_3O_4 0.41%, Cr_2O_3 0.25%, BaO 1.731% and CuO 0.407%, which will have a modifying effect on the structure of clinker minerals. As a result, the structure of the clinker should improve and the activity of the clinker and cement should increase. In addition, zinc oxide, in an amount of 3.12%, will have a mineralizing effect on clinker burning and reduce the sintering temperature. When introducing "Weltz clinker of zinc ores" into the raw mixture in an amount of 3.5–5.1%, the content of zinc oxide in Portland cement clinker will not exceed 0.1–0.2%. This amount of zinc does not exceed the threshold values for this microelement [60–72]. As a result, the specific fuel consumption for burning will be reduced, the productivity of the rotary kiln will be increased and CO_2 emissions into the atmosphere will be minimized.

According to X-ray phase analysis, "Waelz clinker from zinc ores" consists of the following minerals (Figure 2): magnetite $FeFe_2O_4$ (d = 4.28; 2.99; 2.526; 2.43; 2.058; 1.694; 1.61; 1.48 Å); hematite (α-Fe_2O_3 d = 3.62; 2.704; 2.489; 2.431; 2.203; 1.857; 1.694; 1.482; 1.465 Å); β-quartz (d = 4.24; 3.34; 2.45; 2.30; 2.224; 2.137; 1.95; 1.81; 1.67; 1.54; 1.387 Å.

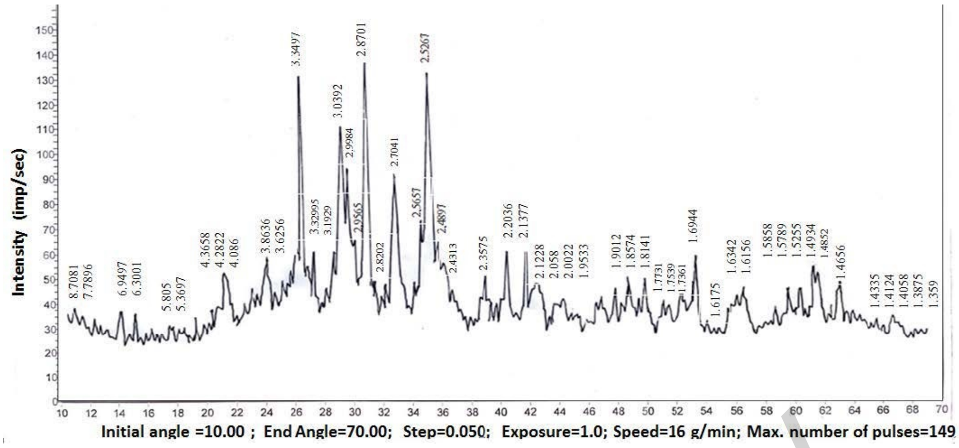


Figure 2. X-ray diffraction pattern of Waeltz clinker from zinc ores at the Achisai Metallurgical Plant.

There are low-intensity peaks, such as C_3A d = 2.7041, 1.9012 and 1.54 Å and C_4AF d = 2.76, 2.6649, 2.5657, 2.058 1.9012 and 1.8141 Å.

Waste from crushing limestone from the Sastobe deposit was formed during the period when the plant produced white cement. Limestone was enriched at the quarry. After the crusher, the limestone was screened and a fine fraction of up to 15–20 mm, enriched with clay impurities containing an increased amount of coloring iron oxides, and others were sifted out, which reduced the whiteness and grade of white clinker. During this time, several million tons of waste accumulated in the dump. In terms of chemical composition, crushing waste contains an increased amount of silicon oxide and a slightly smaller amount of CaO (see Table 1, Figure 3). Studies have shown the suitability of limestone crushing waste for producing clinker.

Element	Weight, %	Oxidic, %
C	12.20	
O	47.45	
Mg	0.33	0.55
Al	0.91	1.71
Si	4.50	9.62
S	0.46	1.15
K	0.39	1.59
Ca	32.88	46.0
Fe	0.88	1.26
Total	100.00	

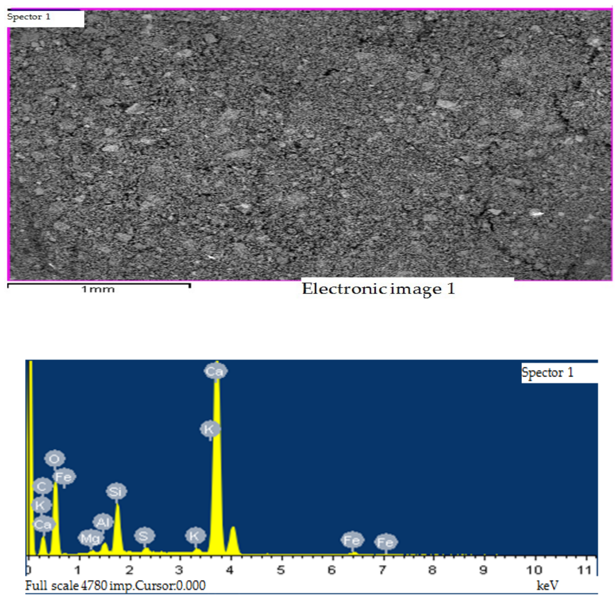


Figure 3. Composition of waste from crushing limestone from the Sastobe deposit according to electron microscopic analysis.

Electrothermophosphorus and lead slags are granular materials with a grain size of up to 2–5 mm, are transportable, easy to dose and their disposal for cement production does not present technological difficulties.

The compositions of low-energy-intensive charges have been calculated for the production of general construction cement, sulfate-resistant cement and cements for road construction.

Calculations were carried out according to Bogue R.H. formulas [73,74] using natural and waste limestones and technogenic raw materials. From the prepared raw material mixtures, tablets with a Ø30 mm and a height of 20–25 mm were molded at a pressure of 20 MPa. The tablets were fired in a high-temperature laboratory kiln at 1350 and 1400 °C. Raising the temperature to maximum occurred over 2 h; isothermal holding occurred over 30 min. Then, the clinker was sharply cooled in air.

The following are studies of the production of low-energy clinkers based on substandard raw materials and production waste

3. Results and Discussion

3.1. Production of Clinker with Limestone Waste from the Sastobe Deposit

To study the processes of burning raw mixtures consisting entirely of industrial waste, "Sastobe limestone waste + phosphorus slag + «Waeltz clinker of zinc ores» from the Achisai plant (hereinafter referred to as Achisai clinker)", four raw mixtures were compiled (Table 3) with saturation coefficient (SC) from 0.90 to 0.92.

Table 3. Influence of the compositions of mixtures with Sastobe limestone waste on the process of CaO binding in resource-energy-saving clinkers.

Mixtures	Components of Raw Mixtures, %			SC	Modules		Content of CaO_{free}, %		Amount of Liquid Phase, L%, at 1400 °C
	Sastobe Limestone Waste	Phosphorus Slag	Achisai Clinker		n	p	1350 °C	1400 °C	
1	78.90	15.93	5.15	0.90	3.5	0.64	1.4	0.2	26.10
2	78.82	17.34	3.84	0.90	4.0	0.73	1.9	0.3	24.45
3	79.90	15.21	4.89	0.92	3.5	0.66	1.5	0.2	25.83
4	79.83	16.58	3.59	0.92	4.0	0.76	2.0	0.4	24.20

As can be seen from the data in Table 3, when burning raw mixtures at 1350 °C, the content of free CaO does not exceed 2%, and at 1400 °C it is 0.2–0.4%. Phosphorus slag containing CaF_2 and Achisai clinker have a significant mineralizing effect on the burning process of the raw material mixture, which makes it possible to reduce the burning temperature by 100 °C and obtain high-quality Portland cement clinker (Figure 4).

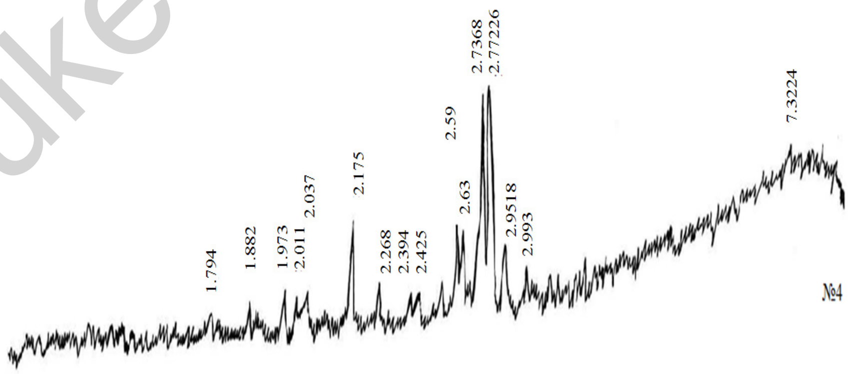


Figure 4. X-ray diffraction pattern of clinker No. 4 from the raw material mixture "Limestone waste + electrothermophosphorus slag + Achisai clinker", burned at 1350 °C.

According to X-ray phase analysis, the following minerals were formed in clinker synthesized at 1350 °C: alite (d = 3.05; 2.7726; 2.595; 2.33; 2.172; 1.973; 1.757; 1.484 Å); belite (d = 2.78; 2.758; 2.595; 2.425; 2.268; 2.172; 2.037; 1.973; 1.882 Å); and C_4AF (d = 7.3224; 2.772; 2.678; 2.63 Å). Due to the fairly low aluminum content in the charge, diffraction reflections characteristic of C_3A were not detected in the X-ray diffraction pattern.

The microphotograph of clinker No. 4 shows hexagonal and pentagonal alite crystals, rounded belite crystals and an intermediate phase (Figure 5). Crystallization of the clinker minerals is clear and good. The sizes of alite crystals are from 20–30 to 50–60 microns. The microphotograph also shows clinker pores. Spectrum 3 shows a point analysis of the composition of tetracalcium aluminoferrite in the clinker.

Element	Weight, %	Compound, %	Formula
Na	0.88	1.19	Na_2O
Mg	1.17	1.95	MgO
Al	7.95	15.02	Al_2O_3
Si	5.50	11.77	SiO_2
S	0.20	0.50	SO_3
K	0.12	0.14	K_2O
Ca	40.95	57.29	CaO
Ti	0.74	1.23	TiO_2
Mn	0.36	0.47	MnO
Fe	8.12	10.44	Fe_2O_3
Total	34.01		

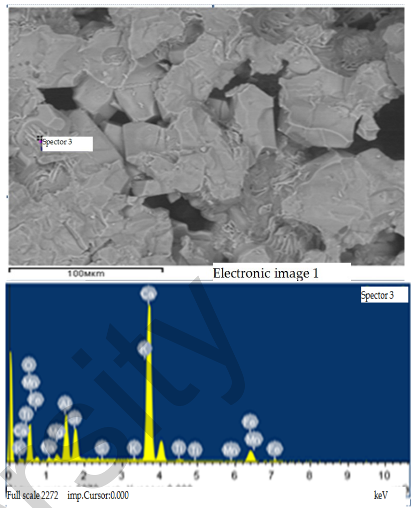


Figure 5. Structure of clinker No. 4, fired at 1350 °C, and composition of C_4AF according to electron microscopic analysis.

Thus, the results obtained show that when fired already at 1350 °C, high-quality clinker is formed from a raw material mixture based on Sastobe limestone waste, phosphorus slag and Achisai clinker. Using waste instead of natural components saves energy resources and preserves limestone and loess quarries. Expensive drilling and blasting operations at a limestone quarry are eliminated from the technological process.

The synthesis of clinker minerals ends 50–100 °C lower than when producing Portland cement clinker from natural materials. Up to 10–15% of non-carbonate lime and magnesium is added to the raw material charges. At the same time, fuel consumption for clinker firing is reduced and, consequently, emissions of CO_2 and NOx into the atmosphere are reduced [16,17].

3.2. Production of Clinker with Limestone from the Kazygurt Deposit, Loess and «Achisai Clinker»

The processes of clinker burning in raw mixtures with Kazygurt limestone, Tekesu deposit loess and Achisai clinker were studied. In energy- and resource-saving charges with SC 0.9 and 0.92, the silicate module was changed from 2.0 to 2.5 (Table 4). Clinker burning was carried out at temperatures of 1350 and 1400 °C with exposure at these temperatures for 0.5 h.

Table 4. Influence of the compositions of resource- and energy-saving mixtures with Kazygurt limestone and Achisai clinker on clinker burning processes.

Mixtures	Components of Raw Mixtures, %			SC	Modules		Content of CaO_{free}, %	
	Limestone Kazygurt	Loess Tekesu	Achisai Clinker		n	p	1350 °C	1400 °C
5	74.42	16.25	9.32	0.90	2.0	0.62	1.2	0.1
6	75.12	17.58	7.30	0.90	2.2	0.72	1.35	0.16
7	75.98	19.21	4.81	0.90	2.5	0.91	1.6	0.85
8	74.94	15.88	9.19	0.92	2.0	0.62	1.96	0.1
9	75.63	17.18	7.19	0.92	2.2	0.72	1.92	0.16
10	76.48	18.78	4.74	0.92	2.5	0.91	2.24	0.74

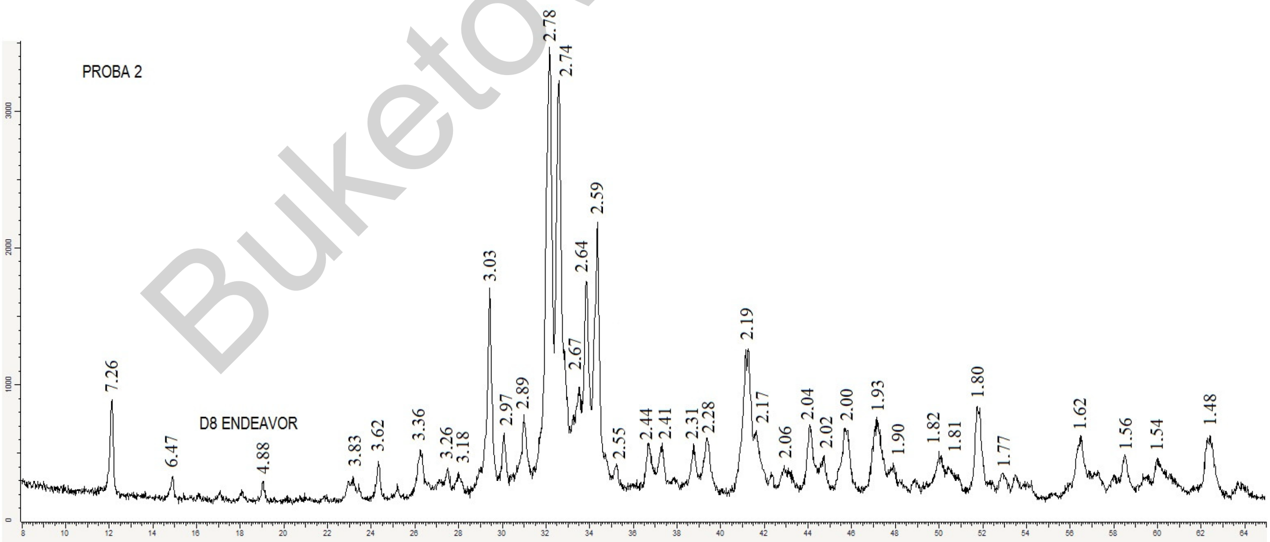
The content of free calcium oxide in clinker, determined in the laboratory of Standard Cement LLP on an X-ray device (S8 Tiger), after burning at a temperature of 1350 °C was 1.35–1.92%, and when the temperature increased to 1400 °C it decreased by 0.16–0.17%. The synthesized clinkers passed standard tests on the Le Chatelier apparatus. The chemical and mineralogical composition of fired cakes No. 6 and No. 9 are shown in Table 5.

Table 5. Calculated and actual chemical and mineralogical compositions of clinkers according to X-ray data (S8 Tiger).

Clinker	**Chemical Composition, %**					**SC**	**Modules**		**Mineralogical Composition of Minerals, %**			
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**		**n**	**p**	**C_3S**	**C_2S**	**C_3A**	**C_4AF**
Actual chemical and mineralogical composition of clinkers according to X-ray (S8 Tiger)												
6	23.5	4.29	5.72	62.57	0.8	0.90	2.35	0.75	59.1	17.9	1.70	17.4
9	24.17	4.18	5.78	62.25	0.9	0.92	2.43	0.72	63.3	14.2	1.3	17.6
Calculated chemical and mineralogical composition of clinkers												
6	21.77	4.16	5.74	63.74	1.77	0.90	2.2	0.72	57.91	18.72	1.27	17.44
9	21.51	4.10	5.67	64.17	1.75	0.92	2.2	0.72	62.13	14.80	1.23	17.25

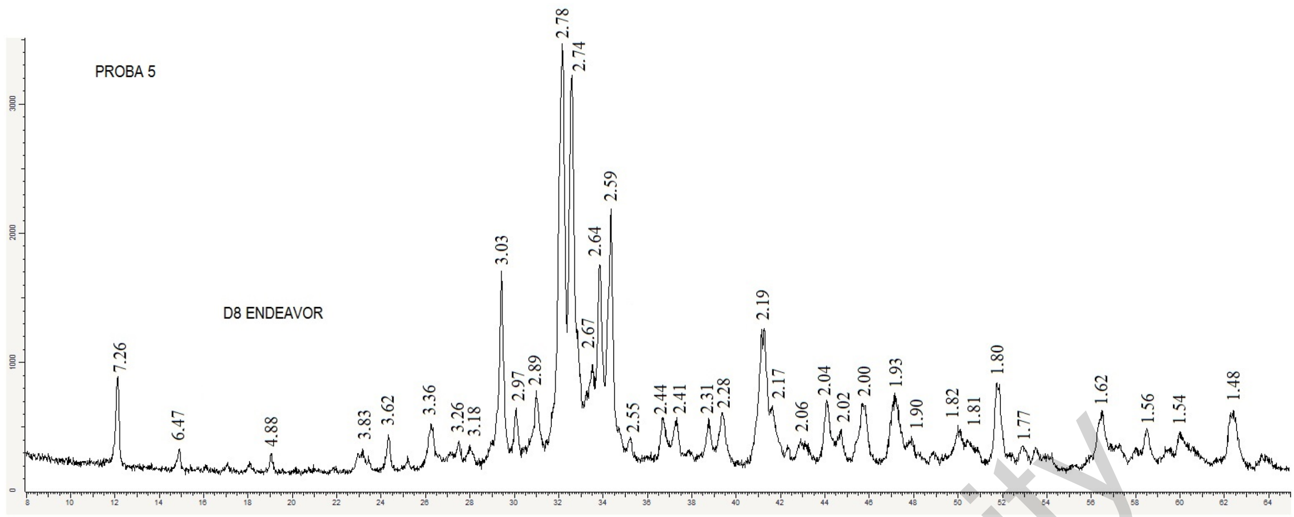
According to Table 5, the calculated and actual analysis of low-energy clinkers generally coincide. From the developed raw materials, sulfate-resistant clinkers were obtained that comply with GOST 22266-2013 [56,75] with a C_3A content of 1.3–1.7%, satisfying the requirements for the mineralogical composition of this special cement.

X-ray phase studies of low-energy clinkers (Figure 6), performed on an ENDEAVOR D8 diffractometer, showed the presence of alite (d = 3.03; 2.97; 2.78; 2.74; 2.59; 2.44; 2.31; 2.19; 1.93; 1.82; 1.77; 1.62 Å); belita (d = 3.83; 3.26; 3.18; 2.89; 2.77; 2.59; 2.41; 2.28; 2.19; 2.04; 2.02; 1, 93; 1.48 Å); C_3A (d = 2.78; 2.59; 2.55; 2.17; 1.90; 1.55 Å); and C_4AF (d = 3.62; 2.76; 2.67; 2.04; 1.93; 1.82 Å). No diffraction reflections characteristic of free CaO were detected.



(**a**)

Figure 6. *Cont.*



(**b**)

Figure 6. X-ray patterns of low-energy clinkers No. 6 (**a**) and No. 9 (**b**) based on limestone–loess raw material mixture with Achisai clinker.

3.3. Production of Clinker from Raw Materials of Gezhuba Shieli Cement LLP with Additions of Waelz Clinkers

For Gezhuba Shieli Cement LLP, the iron-containing component—Shoiyntas iron ore—was replaced in the raw material mixture with Achisai clinker (Table 6). Raw mixtures with SC = 0.90 and 0.95 were fired at low temperatures of 1350 and 1400 °C.

Table 6. Synthesis of clinkers in factory and energy-saving raw material layers of Gezhuba Shieli Cement LLP.

Mixtures	Components of Raw Mixtures, %					SC	Modules		Content of CaO_{free}, %		Amount of Liquid Phase, L%, at 1400 °C
	Kutau Limestone	ZhanaKorgan Clay	Iron Ore Shoiyntas	Quartz Sand	Achisai Clinker		n	p	1350 °C	1400 °C	
Factory raw material mixture											
10	70.83	26.49	2.62	0.06	-	0.90	2.0	1.12	1.87	0.54	29.23
11	71.90	25.55	2.53	0.02	-	0.95	2.0	1.12	1.94	1.26	28.40
Energy-resource-saving raw material mixture											
12	72.40	14.82	-	-	12.78	0.90	2.0	0.79	0.96	0.35	28.61
13	73.47	14.12	-	-	13.41	0.95	2.0	0.79	1.16	0.58	27.77

According to Table 6, the introduction of Achisai clinker in quantities of 12–13% makes it possible to completely replace iron ore from the Shoiyntas deposit in the raw material mixture. The transportation distance of this corrective additive for the Shieli plant is more than 1500 km. The Achisai clinker dumps are located 200 km from the cement plant, which will reduce the cost of transporting the corrective additive.

Calculations showed that the amount of clinker melt, depending on the saturation coefficient, was 28–29%. Therefore, the processes of clinker formation in the developed raw materials were completed at a low temperature of 1350 °C. The content of unassimilated CaO in clinkers at a burning temperature of 1350 °C was 0.96–1.16%, and at a temperature of 1400 °C it was 0.1–0.3%. In factory clinkers, the amount of free CaO was significantly higher, even despite the larger amount of liquid phase. Apparently, the decrease in the amount of clinker melt was compensated by an improvement in its properties due to the presence in the "Achisai clinker" of modifying impurities of titanium, manganese, zinc, barium, etc., leading to a decrease in the viscosity of the clinker melt, which intensified the processes of mineral and clinker formation [37,38].

In addition, zinc oxide, present in Achisai clinker in an amount of 3%, has a strong mineralizing effect. Therefore, clinker formation processes in energy-resource-saving raw material mixtures were completed at temperatures 50–100 °C lower than in the factory mixture.

The determination of the actual mineralogical composition (Table 7) in experimental clinkers showed that with almost the same amount of alite, clinker contains half as much tricalcium aluminate (2.32–2.46%). This will make it possible to obtain sulfate-resistant cements, such as CEM I SR, CEM II SR, CEM III SR [75] and others, based on them.

Table 7. Actual mineralogical composition of clinkers obtained from factory and energy-saving raw materials of Gezhuba Shieli Cement LLP.

Clinkers	Mineralogical Composition, wt.%						SC	Modules	
	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	MgO		n	p
Clinkers from factory raw material mixture									
Clinker—10	55.56	18.03	6.29	15.01	0.13	1.57	0.90	2.0	1.12
Clinker—11	65.53	8.78	6.11	14.57	0.13	1.53	0.95	2.0	1.12
Clinkers from energy-resource-saving raw material mixture									
Clinker—12	56.14	18.22	2.46	17.89	0.33	1.33	0.90	2.0	0.79
Clinker—13	66.20	8.87	2.32	17.42	0.33	1.30	0.95	2.0	0.79

To analyze the physical and mechanical properties of clinkers No. 10–13, cements were ground in a laboratory ball mill with the addition of 5% gypsum to a residue of 9–10% on sieve No. 008 (Table 8).

Table 8. Portland cement stone test results.

Clinker Cements	Residue on Sieve No. 008, %	Specific Surface Area, S, cm^2/g	Average Particle Size, Microns	Water–Cement Ratio W/C	Strength of Samples 2 × 2 × 2 cm, MPa, Over	
					3 Days	28 Days
10	9.8	3220	6.6	0.26	23.0	44.2
11	10.2	3210	6.6	0.26	25.1	48.5
12	9.7	3200	6.7	0.26	23.2	44.6
13	10.1	3188	6.6	0.26	25.3	48.8

According to the results in Table 8, cements from experimental clinkers have a strength of 44–48 MPa after 28 days. The strength of the experimental cement samples increases in accordance with the age of the samples. Hydration reactions of clinker minerals lead to the formation of new hydrate compounds that compact the structure of the cement stone and increase its mechanical strength to 48.5–48.8 MPa.

3.4. Processes of Burning Raw Materials, including Limestone, Coal Mining Waste and Achisai Clinker

The processes of new raw materials from industrial waste were studied [76]. The effect of adding sodium fluoride mineralizer on clinker formation processes is shown (Table 9). In this case, NaF was a production waste from the sodium fluoride production workshop at the Taraz mineral fertilizer plant of Kazphosphate LLP. Products that did not meet the requirements for sodium fluoride content were considered defective and disposed of. Currently, the workshop is not operating, but there is a large amount of this waste in the dumps.

Table 9. Compositions of raw mixtures and the results of their testing.

Mixtures	Raw Material Mixture Compositions, %				SC	Modules		Content of CaO_{free}, %		Specific Heat Consumption, kJ/kg Clinker	Specific Fuel Consumption for Burning, kg/t Clinker
	Limestone	Coal Mining Waste	NaF	Achisai Clinker		n	p	1350 °C	1400 °C		
14	73.04	17.73	0.7	8.27	0.88	2.3	0.69	0.3	0	3870	132.5
15	73.73	18.6	1.0	6.77	0.88	2.5	0.79	0.5	0.2	3919	134.2
16	73.49	17.5	0.5	8.26	0.9	2.3	0.68	2.0	0.6	3957	135.5
17	74.0	18.26	0.7	6.78	0.9	2.5	0.78	2.5	0.9	3983	136.4
18	74.02	17.18	0.4	8.15	0.92	2.3	0.68	3.2	1.2	4032	138.1
19	74.54	16.62	0.6	7.98	0.93	2.3	0.67	3.5	1.6	4065	139.2

From raw materials charges No. 14, 15 and 16, high-quality clinker was obtained at 1350 °C; from raw materials charges No. 17, 18 and 19, it was obtained at a temperature of 1400 °C.

The content of unassimilated CaO in clinkers did not exceed 1–2%; the samples passed the test on the Le Chatelier device.

During the firing process, sodium fluoride and Waelz clinker of zinc ores from the Achisai Metallurgical Plant had a mineralizing effect; sufficient absorption of CaO into clinker minerals was completed at temperatures 50–100 °C lower than in traditional Portland cement clinker. The clinker sintering coefficient improved. The specific heat consumption was 3870–3957 kJ/kg, which is close to the dry method of production.

4. Conclusions

The possibility of producing cement clinker using low-energy resource-saving technologies has been shown. It has been established that the chemical and mineralogical composition of the studied industrial waste allows it to be used for the production of low-energy Portland cement clinkers.

New effective compositions of raw materials have been developed for the production of Portland cement clinker with full or partial replacement of natural raw materials with large-tonnage industrial waste.

The prospects of replacing the scarce iron-containing corrective additive with “Waeltz clinker for zinc ores” for cement plants in Southern Kazakhstan are shown. Waelz clinker as part of the raw material charge performs several tasks: it is a ferrous corrective additive, acts as a burning mineralizer, introduces coal into the charge and allows us to save fuel.

The burning of raw material mixtures, consisting entirely of industrial waste—Sastobe limestone waste, phosphorus slag and Waeltz clinker of zinc ores from the Achisai plant—is completely completed at 1350 °C. Producing Portland cement clinker at low temperatures will help reduce natural fuel consumption and reduce carbon dioxide emissions into the air.

When firing the raw material mixtures developed by us, the sintering temperature of the clinker is reduced by 50–100 °C; up to 10–15% of non-carbonate lime and magnesium are introduced into the raw material mixtures. Taken together, this will lead to a reduction in CO_2 and NOx emissions into the atmosphere and an improvement in the environmental situation.

From the developed raw material charges, including industrial waste, it is possible to obtain both general construction cements and sulfate-resistant cements that comply with GOST 22266-2013 with a C_3A content of 1.3–1.7%.

Low-energy-intensive, resource-saving raw material mixtures were developed with Waeltz clinker from zinc ores from the Achisai Metallurgical Plant, phosphorus slag, coal mining waste from the Lenger mines and sodium fluoride mineralizer. The determination of the mineralogy and microstructure of clinker allows us to conclude that high-quality clinker was synthesized at a temperature of 1350 °C, while the content of unassimilated CaO did not exceed 2%.

Thus, the use of Waeltz clinker from zinc ores as part of the raw material mixtures of various cement enterprises makes it possible to obtain high-quality clinker at 1350–1400 °C, which is 50–100 °C lower than when producing Portland cement clinker from natural materials. This allows us to reduce fuel consumption for burning, increase kiln productivity and reduce CO_2 and NO_x emissions into the atmosphere. The recycling of large-scale industrial waste will improve the environmental situation in the region and outline the path to a circular economy.

Author Contributions: Conceptualization, A.K. (Aknur Kuandykova), B.T., B.S., A.K. (Alexandr Kolesnikov) and E.K.; Methodology, A.K. (Aknur Kuandykova) and M.B.; Validation, B.T.; Formal analysis, E.P.; Resources, A.A.; Data curation, M.B., M.D., B.A. and A.A.; Writing—original draft, A.A.; Writing—review & editing, A.K. (Aknur Kuandykova), B.T., A.K. (Alexandr Kolesnikov), N.Z. and B.A.; Visualization, M.B. and N.Z.; Supervision, E.P., A.K. (Alexandr Kolesnikov), M.D. and B.A.; Project administration, B.S., E.K. and B.A.; Funding acquisition, B.T., B.S. and E.K. All authors have read and agreed to the published version of the manuscript.

Funding: Research carried out according to the Program. This research was funded by the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. BR21882292—"Integrated development of sustainable construction industries: innovative technologies, optimization of production, effective use of resources and creation of technological park").

Data Availability Statement: The data used to support the findings of this study are included within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Taimasov, B.T.; Klassen, V.K. *Chemical Technology of Binding Materials*; Additional; BSTU Publishing House: Belgorod, Russia, 2017; 448p.
2. Klassen, V.K.; Borisov, I.N.; Manuilov, V.E. *Technogenic Materials in Cement Production, Monograph*; Publishing House of BSTU: Belgorod, Russia, 2008.
3. Taylor, H.F.W. *Cement Chemistry*; Thomas Telford Publishing, Thomas Telford Services Ltd.: London, UK, 1997; p. 457.
4. Pavel, K. *Compressive Strength of Concrete*; IntechOpen: London, UK, 2020. Available online: https://dlib.hust.edu.vn/bitstream/HUST/20480/1/OER000001759.pdf (accessed on 14 May 2024).
5. Hjort, M.; Skobelev, D.; Almgren, R.; Guseva, T.; Koh, T. Best Available Techniques and Sustainable Development Goals. In Proceedings of the 19th International Multidisciplinary Scientific GeoConference SGEM, Albena, Bulgaria, 28 June–7 July 2019; pp. 185–189.
6. Potapova, E.N.; Guseva, T.V.; Tolstykh, T.O.; Bubnov, A.G. Technological, technical, organizational and managerial solutions for the sustainable development and decarbonization of cement sector. *Tech. Technol. Silic.* **2023**, *30*, 104–115.
7. Bashmakov, I.A.; Potapova, E.N.; Borisov, K.B.; Lebedev, O.V.; Guseva, T.V. Cement Sector Decarbonization and Development of Environmental and Energy Management Systems. *Stroit. Mater.* **2023**, 4–12. [CrossRef]
8. Barbhuiya, S.; Kanavaris, F.; Das, B.D.; Idrees, M. Decarbonising cement and concrete production: Strategies, challenges and pathways for sustainable development. *J. Build. Eng.* **2024**, *86*, 108861. [CrossRef]
9. Kleib, J.; Aouad, G.; Abriak, N.; Benzerzour, M. Production of Portland cement clinker from French Municipal Solid Waste Incineration Bottom Ash. *Case Stud. Constr. Mater.* **2021**, *15*, e00629. [CrossRef]
10. Moudar, J.; Agourrame, H.; Fami, N.E.; Diouri, A.; Taibi, M. Stabilization and characterization of dicalcium silicate belite phase by metallic zinc. *Mater. Today Proc.* **2022**, *58*, 1442–1446. [CrossRef]
11. Gartner, E.; Hirao, H. A review of alternative approaches to the reduction of CO_2 emissions associated with the manufacture of the binder phase in concrete. *Cem. Concr. Res.* **2015**, *78*, 126–142. [CrossRef]
12. Technology Roadmap-Low-Carbon Transition in the Cement Industry 2014. Electronic Resource. Available online: https://webstoreleaorg/technology-roadmap-low-carbon-transition-in-the-cement-industry (accessed on 23 March 2020).
13. Leitan, F. A look ahead: What will the cement plant look like in the near future. Vzglyad vpered: Kakim budet tsementnyy zavod v blizhayshem budushchem. *Cem. Its Appl. Tsement Yego Primen.* **2020**, *1*, 124–128.
14. Concrete Is More Than a Material. It's About Life/Global Cement and Concrete Association (GCCA) of 03.02.2021. Available online: https://gccassociation.org/ (accessed on 14 May 2024).
15. *Environmental Regulations of Enterprises: Best Available Technologies, Increasing Energy Efficiency and Greenhouse Gas Emissions*; International Experience and Russian Approaches; Infotropik Media: Moscow, Russia, 2017; p. 104.
16. Best Available Techniques (BAT) Reference Document for the Production of Cement, Lime and Magnesium Oxide. Available online: https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/CLM_Published_def_0.pdf (accessed on 26 March 2013).
17. Guide of the Best Available Techniques for Cement and Lime Production. No. 941. Available online: https://adilet.zan.kz/rus/docs/P2300000941 (accessed on 24 October 2023).

18. Scrivener, K.L.; John, V.M.; Gartner, E.M. Eco-efficient cements: Potential economically viable solutions for a low-CO_2 cement-based materials industry. *Cem. Concr. Res.* **2018**, *114*, 2–26. [CrossRef]
19. Watari, T.; Cao, Z.; Hata, S.; Nansai, K. Efficient use of cement and concrete to reduce reliance on supply-side technologies for net-zero emissions. *Nat. Commun.* **2022**, *13*, 4158. [CrossRef]
20. Griffiths, S.; Sovacool, K.; Rio, D.D.F.D.; Foley, A.M.; Bazilian, M.D.; Kim, J.; Uratani, J.M. Decarbonizing the cement and concrete industry: A systematic review of socio-technical systems, technological innovations, and policy options. *Renew. Sustain. Energy Rev.* **2023**, *180*, 113291. [CrossRef]
21. Brecha, R.J.; Ganti, G.; Lamboll, R.D.; Nicholls, Z.; Hare, B.; Lewis, J.; Meinshausen, M.; Schaeffer, M.; Smith, C.J.; Gidden, M.J. Institutional decarbonization scenarios evaluated against the Paris Agreement 1.5 °C goal. *Nat. Commun.* **2022**, *13*, 4304. [CrossRef] [PubMed]
22. Cement and Concrete Companies Reveal '2050 Climate Ambition'. World Cement. Available online: https://www.worldcement.com/europe-cis/02092020/cement-and-concrete-companies-reveal-2050-climate-ambition/ (accessed on 2 September 2020).
23. Shah, I.H.; Miller, S.A.; Jiang, D.; Myers, R.J. Cement substitution with secondary materials can reduce annual global CO_2 emissions by up to 1.3 gigatons. *Nat. Commun.* **2022**, *13*, 5758. [CrossRef] [PubMed]
24. Juenger, M.C.G.; Winnefeld, F.; Provis, J.L.; Ideker, J.H. Advances in alternative cementitious binders. *Cement Concr. Res.* **2011**, *41*, 1232–1243. [CrossRef]
25. Marsh, A.T.; Velenturf, A.P.; Bernal, S.A. Circular Economy strategies for concrete: Implementation and integration. *J. Clean. Prod.* **2022**, *362*, 132486. [CrossRef]
26. Martínez-García, R.; Jagadesh, P.; Fraile-Fernández, F.J.; Morán-del Pozo, J.M.; Juan-Valdés, A. Influence of design parameters on fresh properties of self-compacting concrete with recycled aggregate—A review. *Materials* **2020**, *13*, 5749. [CrossRef]
27. An, S.; Wang, B.; Chen, W.; Yu, Z.; Fan, C. Preparation of geopolymer based on municipal solid waste incineration fly ash-phosphorus slag and its function for solidification of heavy metals. *Waste Manag.* **2024**, *178*, 186–198. [CrossRef]
28. Ameri, F.; Shoaei, P.; Zareei, S.A.; Behforouz, B. Geopolymers vs. alkali-activated materials (AAMs): A comparative study on durability, microstructure, and resistance to elevated temperatures of lightweight mortars. *Constr. Build. Mater.* **2019**, *222*, 49–63. [CrossRef]
29. Provis, J.L. Alkali-activated materials. *Cement Concr. Res.* **2017**, *114*, 40–48. [CrossRef]
30. Collins, F.G.; Sanjayan, J.G. Workability and mechanical properties of alkali activated slag concrete. *Cement Concr. Res.* **1999**, *29*, 455–458. [CrossRef]
31. Ding, Y.; Dai, J.G.; Shi, C.J. Mechanical properties of alkali-activated concrete: A state-of-the-art review. *Construct. Build. Mater.* **2016**, *127*, 68–79. [CrossRef]
32. Winnefeld, F.; Martin, L.H.; Müller, C.J.; Lothenbach, B. Using gypsum to control hydration kinetics of CSA cements. *Construct. Build. Mater.* **2017**, *155*, 154–163. [CrossRef]
33. Gartner, E.; Quillin, K. Low-CO2 cements based on calcium sulfoaluminates. *Sustain. Cem. Concr. Ind. Nor. Cem. Assoc.* **2007**, *16*, 95–105.
34. Tao, Y.; Rahul, A.V.; Mohan, M.K.; Schutter, G.D.; Tittelboom, K.V. Recent progress and technical challenges in using calcium sulfoaluminate (CSA) cement. *Cement Concr. Compos.* **2022**, *137*, 104908. [CrossRef]
35. Sharma, M.; Bishnoi, S.; Martirena, F.; Scrivener, K. Limestone calcined clay cement and concrete: A state-of-the-art review. *Cement Concr. Res.* **2021**, *149*, 106564. [CrossRef]
36. National Carbon Quota Plan of the Republic of Kazakhstan for 2022–2025. Astana. 2022. Available online: https://legalacts.egov.kz/npa/view?id=13760465 (accessed on 14 May 2024).
37. Butt, Y.M.; Timashev, V.V.; Osokin, A.P. The Mechanism of Clinker Formation Processes and the Modification of Its Structure. VI International. Congress on Cement Chemistry. Moscow. September. 1974. Available online: https://www.muctr.ru/upload/university/departments/cis/znamenitye-mendeleevtsy/1002.pdf (accessed on 14 May 2024).
38. Timashev, V.V. The Kinetics of Clinker formation the structure and composition of clinker and its phases. In Proceedings of the 7th International Congress on Chemistry of Cement, Paris, France, 30 June 30–4 July 1980.
39. Ludwig, H.-M.; Zhang, W. Research review of cement clinker chemistry. *Cem. Concr. Res.* **2015**, *78*, 24–37. [CrossRef]
40. Taimasov, B.T.; Sarsenbayev, B.K.; Khydyakova, T.M.; Kolesnikov, A.S.; Zhanikulov, N.N. Development and Testing of Low-Energy-Intensive Technology of Receiving Sulphate-Resistant and Road Portlandcement. *Eurasian Chem.-Technol. J.* **2017**, *19*, 347–355. [CrossRef]
41. Taimasov, B.T.; Khudyakova, T.M.; Zhanikulov, N.N. *Integrated Use of Natural and Technogenic Raw Materials in the Production of Low-Energy Cements*; Auezov SKSU: Shymkent, Kazakhstan, 2017.
42. Taimasov, B.T.; Khudyakova, T.M.; Alzhanova, A.Z. Synthesis of clinkers from non-standard raw materials. *Cem. Its Appl.* **2014**, 138–141.
43. Zhanikulov, N.N.; Khudyakova, T.M.; Taimasov, B.T.; Sarsenbayev, B.K.; Dauletiarov, M.S.; Kolesnikov, A.S.; Karshygaev, R.O. Receving portland cement from technogenic raw materials of South Kazakhstan. *Eurasian Chem.-Technol. J.* **2019**, *21*, 333–340. [CrossRef]
44. Taimasov, B.T.; Saduakasov, T.M.; Alzhanova, A.Z.; Khudyakova, T.M.; Dauletiyarov, M.S.; Sidorenko, V.G.; Abekov, K.O.; Zhanikulov, N.N.; Kaltai, A.; Bekmurzina, A.; et al. Raw Mixture for the Production of Portland Cement Clinker. Eurasian Patent No. 033588, 7 November 2019. p. 4.

45. Zhanikulov, N.N. Creation of Energy- and Resource-Saving Technologies for Portland Cement and Wall Ceramics Using Coal Mining Waste and Technogenic Raw Materials. Ph.D. Thesis, Al-Farabi KazNU, Almaty, Kazakhstan, 2020; p. 145.
46. Zhanikulov, N.; Sapargaliyeva, B.; Agabekova, A.; Alfereva, Y.; Baidibekova, A.; Syrlybekkyzy, S.; Nurshakhanova, L.; Nurbayeva, F.; Sabyrbaeva, G.; Zhatkanbayev, Y. Studies of Utilization of Technogenic Raw Materials in the Synthesis of Cement Clinker from It and Further Production of Portland Cement. *J. Compos. Sci.* **2023**, *7*, 226. [CrossRef]
47. Taimasov, B.T.; Zhanikulov, N.N.; Borisov, I.N.; Dzhanmuldaeva, Z.; Dauletiarov, M.S. Research on the obtaining of low energy cements from technogenic raw materials. *J. Chem. Technol. Metall.* **2020**, *55*, 814–823.
48. *GOST 3476-2019*; Granulated Blast Kiln and Electrothermophosphorus Slags. Technical Conditions. Publishing House Standard-Inform: Moscow, Russia, 2019.
49. Zhanikulov, N.N.; Taimasov, B.T.; Borisov, I.N.; Dauletiyarov, M.S.; Aitureev, M.Z.; Dzhanmuldaeva, Z.K. Preparation low-energy content cement from technogenic raw materials. *Refract. Ind. Ceram.* **2020**, *61*, 2020. [CrossRef]
50. Otarbaev, N.S.; Kapustin, V.M.; Nadirov, K.S.; Bimbetova, G.Z.; Zhantaso, M.K.; Nadirov, R.K. New potential demulsifiers obtained by processing gossypol resin. *Indones. J. Chem.* **2019**, *19*, 959–966. [CrossRef]
51. Gapparov, J.; Syrlybekkyzy, S.; Filin, A.; Kolesnikov, A.; Zhatkanbayev, Y. Overview of techniques and methods of processing the waste of stale clinkers of zinc production. *MIAB Min. Informational Anal. Bull.* **2024**, *4*, 44–55.
52. Nadirov, R.K.; Nadirov, K.S.; Esimova, A.M.; Nadirova, Z.K. Electrochemical synthesis of biflavonoids. *Chem. Nat. Compd.* **2013**, *49*, 108–109. [CrossRef]
53. Urakaev, F.K.; Khan, N.V.; Shalabaev, Z.S.; Tatykaev, B.B.; Nadirov, R.K.; Burkitbaev, M.M. Synthesis and photocatalytic properties of silver chloride/silver composite colloidal particles. *Colloid J.* **2020**, *82*, 76–80. [CrossRef]
54. Zhangabay, N.; Suleimenov, U.; Utelbayeva, A.; Buganova, S. Experimental research of the stress-strain state of prestressed cylindrical shells taking into account temperature effects. *Case Stud. Constr. Mater.* **2022**, *18*, e01776. [CrossRef]
55. Dikshit, A.K.; Gupta, S.; Chaturvedi, S.K.; Singh, L.P. Usage of lime sludge waste from paper industry for production of Portland cement Clinker: Sustainable expansion of Indian cement industry. *Case Stud. Chem. Environ. Eng.* **2024**, *9*, 100557. [CrossRef]
56. Konovalov, V.; Fedorov, A.; Goncharov, A. Use of slags in the production of Portland cement clinker. In Proceedings of the 14th International Congress for Applied Mineralogy, Belgorod, Russia, 23–27 September 2019; pp. 327–330.
57. *GOST 5382-2019*; Cements and Materials for Cement Production. Methods of Chemical Analysis. Publishing House Standard-inform: Moscow, Russia, 2019.
58. Gorshkov, V.S.; Timashev, V.V.; Savelyev, V.G. Methods of physical and chemical analysis of binders. In *Textbook*; Moscow Higher School: Moscow, Russia, 1981; p. 335.
59. Myrzakozha, D.; Mirzakhodzhayev, A.A. Modern Research Methods. Almaty. 2006. p. 302. ISBN 9965-700-62-1. Available online: http://elib.kstu.kz/lib/document/IBIS/E7C49A47-C0E0-44DD-AF64-87CBBCD8A9AE/ (accessed on 14 May 2024).
60. Gineys, N.; Aouad, G.; Sorrentino, F.; Damidot, D. Effect of the clinker composition on the threshold limits for Cu, Sn or Zn. *Cem. Concr. Compos.* **2011**, *42*, 1088–1093. [CrossRef]
61. Gineys, N.; Aouad, G.; Damidot, D. Managing trace elements in Portland cement—Part II: Comparison of two methods to incorporate Zn in a cement. *Cem. Concr. Compos.* **2011**, *33*, 629–636. [CrossRef]
62. Li, J.; Cheng, G.; Huang, S.; Lian, P. Effect of ZnO on the whiteness of white Portland cement clinker. *Cem. Concr. Res.* **2021**, *143*, 106372. [CrossRef]
63. Yang, Y.; Yong Lai, Y.; Xu, L.; Wang, W.; Fang, J.; Yuan, Q.; Wu, K.; Yang, Z. Effect of ZnO on the clinkerization and carbonation behavior of γ-C2S. *Sustain. Mater. Technol.* **2024**, *40*, e00945. [CrossRef]
64. Andrade, F.R.D.; Maringolo, V.; Kihara, Y. Incorporation of V, Zn and Pb into the crystalline phases of Portland clinker. *Cem. Concr. Res.* **2003**, *33*, 63–71. [CrossRef]
65. Yuan, Z.; Cai, G.; Gao, L.; Wu, M.; Kong, L.; Bai, J.; Bai, Z.; Li, H.; Li, W. The physical encapsulation and chemical fixation of Zn during thermal treatment process of municipal solid waste incineration (MSWI) fly ash. *Waste Manag.* **2023**, *166*, 203–210. [CrossRef]
66. Amin, M.; Birawidha, D.C.; Muttaqii, M.A.; Isnugroho, K.; Hendronursito, Y. The effect of combustion temperature on the characteristic of clinker. *AIP Conf. Proc.* **2020**, *2232*, 040010. [CrossRef]
67. Chatterjee, A.K. *Cement Production Technology: Principles and Practice*; CRC Press: Boca Raton, FL, USA, 2018.
68. Bedov, A.I.; Gabitov, A.I.; Domarova, E.V.; Kolesnikov, A.S. Investigation of the stress-strain state of domical masonry vaults. *Constr. Mater. Prod.* **2023**, *6*, 6.
69. Fediuk, R.S.; Lesovik, V.S.; Vavrenyuk, S.V.; Zaiakhanov, M.Y.; Bituyev, A.V.; Klyuev, S.V.; Yu, K.; Lesovik, Y.R.; Bakatov, K.A. Composite cement materials for structures foundation strengthening. *Mag. Civ. Eng.* **2024**, *17*, 12701.
70. Muratov, B.; Shapalov, S.; Syrlybekkyzy, S.; Volokitina, I.; Zhunisbekova, D.; Takibayeva, G.; Nurbaeva, F.; Aubakirova, T.; Nurshakhanova, L.; Koishina, A. Physico-Chemical Study of the Possibility of Utilization of Coal Ash by Processing as Secondary Raw Materials to Obtain a Composite Cement Clinker. *J. Compos. Sci.* **2023**, *7*, 234. [CrossRef]
71. Kolesnikov, A.S. Thermodynamic simulation of silicon and iron reduction and zinc and lead distillation in zincoligonite ore-carbon systems. *Russ. J. Non-Ferrous Metals* **2014**, *55*, 513–518. [CrossRef]
72. Panarin, I.I.; Fediuk, R.S.; Vykhodtsev, I.A.; Vavrenyuk, S.V.; Klyuev, A.V. Injection mortars based on composite cements for soil fixation. *Constr. Mater. Prod.* **2023**, *6*, 15–29.

73. Besedin, P.V.; Trubaev, P.A. *Research and Optimization of Processes in Cement Clinker Technology*; Besedin, P.V., Ed.; Publishing House BelGTASM, BIEI: Belgorod, Russia, 2004; 420p.
74. Bogue, R.H. *The Chemistry of Portland Cement*; Reinholdl Pub. Corp.: New York, NY, USA, 1950; 326p.
75. *GOST 22266-2013*; Sulfate-Resistant Cements. Technical Conditions. Publishing House Standardinform: Moscow, Russia, 2014.
76. Patent of the Republic of Kazakhstan 36495 for the Invention According to Application 2022/0538.1. Raw Mixture for the Production of Portland Cement Clinker. 8 December 2023. Available online: https://patents.google.com/patent/RU2032634C1/ru (accessed on 14 May 2024).