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THE INFLUENCE OF THE ADDITION OF ALTERNATIVE FUEL ON THE MINERALOGICAL COMPOSITION OF CLINKER AND THE COMPRESSIVE STRENGTH OF CEMENT CEM II/B-W 42.5N

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ABSTRACT
Traditional cement production depends largely on fossil fuels like coal, significantly contributing to CO_2 emissions and environmental degradation. In response, alternative fuels are being investigated to reduce the industry's ecological footprint. This study explores the use of refuse-derived fuel (RDF) in Portland cement production and its effect on clinker quality. Clinker was produced in an industrial rotary kiln with two fuel regimes: 100% coal (reference) and 90% coal with 10% RDF. X-ray diffraction (XRD) was conducted to quantify the content of principal phases. Cement samples were tested for compressive strength at 2, 7, and 28 days using standard testing procedures. The results showed that clinker produced solely with coal had a higher average alite content, while the RDF addition to fuel increased belite levels. The addition of RDF to the fuel had a negligible effect on the content of tricalcium aluminate and tetracalcium aluminoferrite. Additionally, compressive strength tests conducted at 28 days showed that cement produced from the RDF-blended fuel had approximately 11% lower strength than that from the coal-only process. While both cement types met industry standards, incorporating RDF into the fuel mix altered the clinker's mineral composition and reduced strength, emphasizing the need to optimize RDF processing for better combustion efficiency and cement performance.

1. INTRODUCTION

Materials that produce significant amounts of heat energy during combustion (oxidation) and are used for a variety of reasons are referred to as fuels. But not all substances that produce heat when exposed to oxygen are considered fuels; rather, they must fit specific criteria, such as having a high calorific value and gaseous combustion products, which allow for easier process control and the efficient use of combustion product heat.

Energy is needed to produce any substance, and cement is made using a variety of energy sources. Natural gas, coal, and petrolcoke are examples of fossil fuels that can supply the thermal energy required by the cement industry. Large volumes of greenhouse gases are released during the cement industry's use of fossil fuels to produce cement. Most of these gases are CO_2 emissions, which account for 5 % of all CO_2 emissions worldwide due to human activity, and have the greatest effect on climate change and global warming.

Burning limestone produces chemical pollutants that also release CO_2. Carbon dioxide (CO_2) is generated during the conversion of calcium carbonate ($CaCO_3$) to calcium oxide (CaO). When producing one ton of cement, one ton of CO_2 is released [1].
Due to this, the usage of alternative fuels is growing in the modern day; when these fuels are utilized to generate cement, "green cement" is created. Research is currently being conducted to create new cement production techniques that will lower the emissions of harmful compounds and gases that worsen the greenhouse effect. Thus, in addition to reducing harmful emissions into the atmosphere, plants that use coal as fuel also, whenever possible, use a part of waste materials that fit the criteria of alternative fuels. This practice also lessens the exploitation of natural cement raw materials. All waste materials, including plastics, tires, textiles, and other types of domestic garbage, have the potential to be utilized as alternative fuels provided they go through specific processing and adjustments. Since conserving non-renewable natural resources is the cement industry's biggest problem, it is strategically critical to maximize the use of natural resources, including natural fossil fuels, as their supplies are limited [2,3].

1.1. Alternative fuels from waste – RDF

Various waste kinds, including bulky garbage, mixed municipal waste, and other non-toxic waste types, can be treated in plants for mechanical biological waste processing, which can result in the production of fuel from waste, or RDF (refuse derived fuel). Waste that is produced during waste processing, such as shredding, metal, stone, PVC plastic, and so forth, is known as fuel from waste, or RDF. It is made up of several materials, including textiles, paper, cardboard, wood, plastic, and even inorganic components. RDF often contains a high concentration of metallic components and is a somewhat heterogeneous mixture. When it comes to thermal power, this kind of fuel is quite similar to fossil fuels like hard coal. It may be utilized safely and profitably in huge quantities throughout the cement production process. It is used as an alternative source of energy and meets the criteria prescribed by the European standards CEN TC Solid Recovered Fuels [3,4].
The thermal power of RDF is about 16 747 kJ/kg. The reason for such a high calorific value is due to the presence of plastic, cardboard and other materials in RDF. Municipal solid waste is first processed in a primary shredder followed by a magnetic separator. After that, it is sent to a device that works on the principle of separating waste by weight (ballistic separator), where it separates waste of low heat value. The rest of the waste material is screened to remove iron, inert fractions (glass) and wet fractions (food) before shredding the material. Fuel produced in this way from waste is called RDF.
Solid recovered fuel (Solid Recovered Fuel - SRF) is a mechanically shredded solid secondary raw material, i.e. waste that can be used as an alternative fuel and by its nature is qualified as non-hazardous waste. It is considered as a subtype of RDF, which means fuel that complies with the requirements of the norms of the technical committee CEN/TC 343 Standardization of solid recovered materials, including solid recovered fuels, from non-hazardous waste for the purpose of utilisation (recovery and recycling) in a following process). SRF consists of combustible segments of waste: paper, fabric, light fractions of artificial materials, wood, rope, etc. SRF is most often produced in plants (near landfills and municipal waste) where, after the separation of recyclable waste fractions, the remaining residue is fragmented, dried, stabilized and packaged [4].

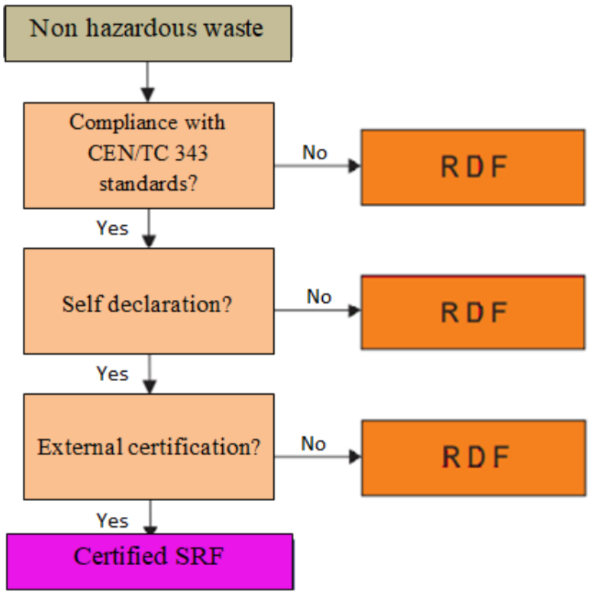

Figure 1. Difference between SRF and RDF

1.2. Cement production and mineralogical composition of clinker

The production of Portland cement is a complex technological process in which the raw materials, limestone and clay, are significantly changed and transformed by heat treatment in a rotary kiln, creating cement clinker which, after grinding with gypsum, represents the final product - Portland cement. Clinker, as the main ingredient of Portland cement, is obtained by firing raw materials containing oxides of calcium, silicon, aluminum and iron. By sintering at a temperature of about 1450 °C, clinker minerals are formed, on which the final properties of cement depend, such as compressive and flexural strength, hydration, chemical resistance, etc. Four main clinker minerals are formed in Portland cement clinker: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminate - ferrite (C_4AF).

The main minerals formed in cement clinker can be shown as listed in Table 1 [5,6]:

Table 1. "Clinker phases" or clinker minerals [6]

Clinker minerals	Chemical formula	Abbreviation in cement chemistry	Mineralogical term
Tricalcium silicate	$3CaO \cdot SiO_2$	C_3S	Alite
Dicalcium silicate	$2CaO \cdot SiO_2$	C_2S	Belite
Tricalcium aluminate	$3CaO \cdot Al_2O$	C_3A	Aluminate
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	Ferrite

1.3. Requirements of standard EN 197-1 for CEMII/B-W 42.5N

- Standard strength

The standard strength of cement is the compressive strength, determined in accordance with the EN 196-1 standard after 28 days and should meet the requirements of table 2 where 3 classes of standard strength are shown: class 32.5, class 42.5 and class 52.5.

- Initial strength

The initial strength of the cement is the compressive strength, determined in accordance with the EN 196-1 standard after 2 or 7 days and should meet the requirements in table 2.

For each of the standard strength classes, two initial strengths are included, a class with an ordinary initial strength, marked with the letter N, and a class with a high initial strength, marked with the letter R.

Table 2. Requirements regarding physical and mechanical properties according to EN 197-1 [7]

Strength class	**Compressive strength [MPa]**				Binding start [min]	Volume constancy [mm]
	Initial strength		**Standard strength**			
	2 days	**7 days**	**28 days**			
32,5 N	-	≥ 16,0	≥ 32,5	≤ 52,5	≥ 75	≤ 10
32,5 R	≥ 10,0	-				
42,5 N	≥ 10,0	-	≥ 42,5	≤ 62,5	≥ 60	
42,5 R	≥ 20,0	-				
52,5 N	≥ 20,0	-	≥ 52,5	-	≥ 45	
52,5 R	≥ 30,0	-				

2. MATERIALS AND METHODS

The practical part of this work was done in the company Heidelberg Materials Cement BiH d.d. Kakanj in Bosnia and Herzegovina where 2 types of fuel were used for testing, fossil fuel that is coal and coal with addition of alternative fuel – RDF (10 %).

2.1. Materials

2.1.1. Clinker

The clinker that was tested, was produced in a rotary kiln by burning 100% coal in the first case, and by burning 90% coal + 10% RDF in the second case. The first type of fuel – coal was added from a fine coal dust silos, while the second type of fuel – RDF was added via a conveyor system to the main burner of the rotary kiln.

2.1.2. Cement

To determine the quality parameters of CEM II/B-W 42.5N cement, cement samples obtained by mixing the following components in the proportions as indicated were taken: clinker 68%, gypsum 4.5% and fly ash 27.5%.

2.2.2. Coal and RDF

Compositions of coal and RDF that were used for testing are given in table 3 and 4.

Table 3. Composition of used coal

Sample	**Moisture 105°C**	**C [%]**	**H [%]**	**N [%]**	**Cl [%]**	**Hg [ppm]**	**Ash [%]**	**Combustile materials [%]**
C1	2,02	61,4	4,19	1,88	0,041	0,24	20,57	77,41
C2	3,04	60,4	4,29	2,13	0,042	0,216	19,63	77,33
C3	3,11	62,4	4,06	1,8	0,04	0,22	19,75	77,14
C4	3,11	62,4	4,06	1,8	0,04	0,22	19,75	77,14
C5	3,02	62,4	4,09	1,85	0,047	0,223	19,85	77,13
C6	3,72	61,5	4,18	1,92	0,046	0,218	19,44	76,84
C7	3,71	60,4	4,24	1,86	0,041	0,243	19,59	76,7
C8	5,98	59,4	4,34	2,05	0,05	0,229	19,05	74,97
C9	2,64	61,9	4,28	1,88	0,043	0,203	19,11	78,25
C10	3,64	59,6	4,25	1,93	0,044	0,23	18,91	77,45
Average	**3,39**	**61,18**	**4,20**	**1,91**	**0,043**	**0,224**	**19,56**	**77,04**

Table 4. Composition of used RDF

Sample	Moisture 105°C	C [%]	H [%]	N [%]	Cl [%]	Hg [ppm]	Ash [%]	Combustile materials [%]
RDF1	42,7	61,5	7,54	0,4	0,32	0,319	13,43	43,87
RDF2	22,5	58,1	10,18	2,06	0,393	0,098	12,4	65,1
RDF3	20,1	58,8	9,57	0,51	0,247	0,243	13,7	66,2
RDF4	14,9	52,1	7,02	0,41	0,28	0,174	17,06	68,04
RDF5	11,2	58	9,2	0,72	0,457	0,155	10,98	77,82
RDF6	24,5	55,8	9,02	0,4	5,217	0,09	10,25	65,25
RDF7	13	64,1	9,42	0,35	1,067	0,184	20,35	66,65
RDF8	14,1	45,4	6,81	0,7	0,633	0,185	51,1	34,8
RDF9	16,7	52,3	7,9	0,97	0,497	0,23	17,32	65,98
RDF10	14	42,2	6,1	1,29	0,486	0,294	19,13	66,87
Average	**19,37**	**54,83**	**8,28**	**0,781**	**0,959**	**0,197**	**18,57**	**62,06**

2.2. Methods

X-ray diffractometry – XRD

The test was conducted on 10 samples of clinker produced in rotary kiln with 100 % of coal, and then on 10 samples of clinker produced with 90 % coal + 10 % RDF.

Clinker samples for testing must be ground to a certain granulation, and after the grinding process it is necessary to put them in a press where they are held under a pressure of 150 kN for about 10 seconds. After that, the samples are ready for mineralogical analysis. The X-ray diffraction (XRD) method is used for the mineralogical analysis of clinker.

Figure 2. Bruker D8 Endeavor XRD device

2.2.2. The compressive strength of cement

Cement strength was also tested on 10 cement samples obtained with previously mentioned clinker produced with 100 % coal and 10 cement samples obtained with clinker produced with 90 % coal + 10 % RDF.

In the company Heidelberg Materials Cement BiH d.d. Kakanj for compressive and flexural strength testing uses a Toni Technik digital press that displays the test results directly. The load speed is adjusted and in the compressive strength test the load is increased at a rate of

2400 ± 200 N/s until failure, and in the flexural strength test the load is increased at a rate of 50 ± 10 N/s.
The samples (cement prisms) prepared according to the procedure are placed in a thermostatic pool with distilled water where they remain until the end of the test, that is, 2, 7 and 28 days. For compressive strength testing, the compressive and flexural strength testing press shown in Figure 4 is used. During the test, half of the prism is used, which is centered according to the standard, and the load is evenly distributed until the fracture occurs, and then the value of the compressive strength is read. According to the EN standard [196-1], the compressive strength test result is expressed as the arithmetic mean of six compressive strengths determined for a series of 3 prisms.

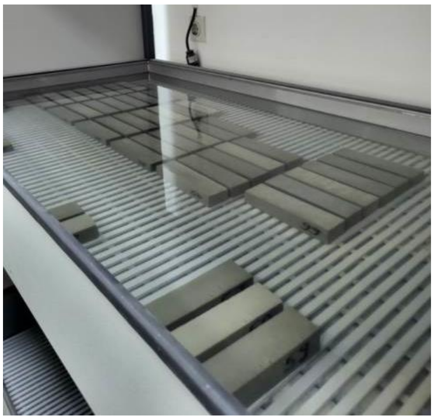

Figure 3. Thermostatic pool with cement prisms

Figure 4. Press for testing compressive and flexural strength

2. RESULTS AND ANALYSIS

Tables 5 and 6 show the mineralogical composition of clinker produced with 100 % coal and clinker produced with 90 % coal + 10 % RDF, and figure 5 graphically shows the results of testing the mineralogical composition of clinker.

Table 5. Mineralogical composition of clinker produced with 100 % coal

Sample	**Alite [%]**	**Belite [%]**	**C_3A [%]**	**C_4AF [%]**
C1	67,21	11,77	7,31	10,95
C2	69,17	10,45	7,55	11,16
C3	68,81	11,07	6,9	12,02
C4	62	17,17	7,62	10,88
C5	64,46	15,38	7,3	11,59
C6	63,71	15,83	7,11	11,59
C7	62,92	14,55	7,52	11
C8	63,83	14,67	7,71	10,62
C9	61,57	16,77	7,37	10,8
C10	66,69	12,81	7,1	10,96
Average	**65,037**	**14,047**	**7,349**	**11,157**

Table 6. Mineralogical composition of clinker produced with 90 % coal + 10 % RDF

Sample	**Alite [%]**	**Belite [%]**	**C_3A [%]**	**C_4AF [%]**
RDF1	59,45	19,84	7,36	10,96
RDF2	56,19	21,85	7,58	11,16
RDF3	56,42	22,54	7,29	10,74
RDF4	58,28	20,72	6,39	11,8
RDF5	58,77	20,33	6,78	11,86
RDF6	59,71	19,1	7,62	11,29
RDF7	59,26	18,16	9,82	9,72
RDF8	58,55	19,29	9,53	9,47
RDF9	58,36	21,5	7,6	10,75
RDF10	55,46	21,67	7,77	10,22
Average	**58,045**	**20,5**	**7,774**	**10,797**

Alite, C_3S, is the main mineral of Portland cement clinker on which the strength of the cement depends the most. It is responsible for cement strength at 7 and 28 days and its content in clinker is typically from 50 % to 70 %. Figure 5 shows that both tested clinkers meet that parameter, but also that clinker produced with 100 % coal in all samples has a higher alite content, which is reflected in higher strength. The average content of alite in coal is 65.04 %, and in RDF 58.05 %.

Belite (C_2S) is formed in the sintering process and usually occupies from 10 to 20 % of the total mass of clinker. It shows great shrinkage during hydration and in larger amounts in cement has a negative effect, which is why its content in cement is limited. In Figure 5, it can be seen that the samples with used RDF fuel contain in all samples a greater amount of belite compared to the coal samples and the average value of the belite content in those samples is 20.5 %, while it is 14.05 % in coal. It can be assumed that the quality of clinker will be better with the use of coal as an energy source compared to clinker with the addition of RDF.

The role of tricalcium aluminate, C_3A, in clinker is to determine the setting time and hardening characteristics of the cement if the sulfate concentration is the same. There is an inverse relationship between aluminate and ferrite. When the content of C_3A decreases, the content of C_4AF increases and vice versa. Aluminate reacts very quickly with water, and although it does not have hydraulic characteristics, it is useful because thanks to it early cement strengths are achieved. From the diagram shown in Figure 5, it can be seen that the aluminate content is very similar in clinker produced with coal, with an average value of 7.35 %, and with RDF, where the average value is 7.77 %.

Tetracalcium alumo-ferrite, C_4AF, affects the chemical resistance of cement and, to a lesser extent, increases its strength. As in the case of aluminate, in all clinker samples, both with RDF and only with coal, the content of alumino-ferrite is very slightly higher in clinker produced with 100 % coal. The average content of this phase in clinker with 100 % coal is 11.15 %, while in clinker with 10 % RDF, the average is 10.8 %.

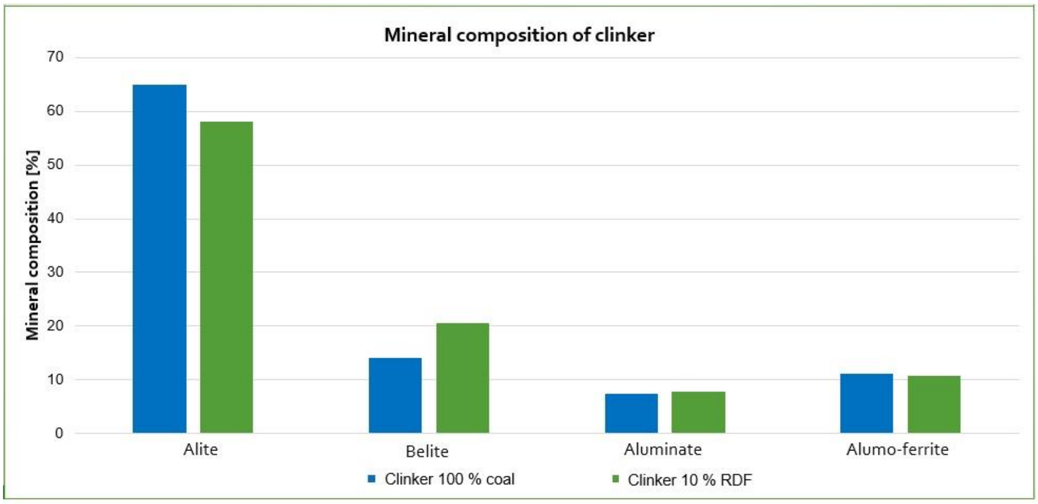

Figure 5. Mineral composition of clinker

To determine the quality parameters of cement CEM II/B-W 42.5N, cement samples obtained by mixing the following components in the proportions as stated: clinker 68 %, gypsum 4.5 % and fly ash 27.5 % were taken.

The results of testing the compressive strength of cement, as well as the average values, are presented in tables 6 and 7.

Table 7. Compressive strength of cement produced with 100 % coal

Sample	**Compressive strenght 2d [MPa]**	**Compressive strenght 7d [MPa]**	**Compressive strenght 28d [MPa]**
C1	23	37,7	56,8
C2	23,5	38	57,2
C3	22,4	35,2	52,7
C4	21,2	34,6	53,4
C5	21	33,6	51,9
C6	21,1	33,3	51,5
C7	21,5	34	52
C8	21	34,3	53
C9	20,8	34,7	53,3
C10	22,3	35	54,6
Average	**21,78**	**35,04**	**53,64**

Table 8. Compressive strength of cement produced with 90 % coal + 10 % RDF

Sample	**Compressive strenght 2d [MPa]**	**Compressive strenght 7d [MPa]**	**Compressive strenght 28d [MPa]**
RDF1	17,8	32,7	48,3
RDF2	18	33,5	49,1
RDF3	17,4	31	47,5
RDF4	16,7	29,1	47,8
RDF5	16,5	28,8	47,4

RDF6	16,1	28,5	47
RDF7	17	31,3	47,4
RDF8	16,5	31,7	47,6
RDF9	16,1	28,5	47,1
RDF10	18,2	31,8	48,1
Average	**17,03**	**30,69**	**47,73**

Figure 6 shows the compressive strength values of the cement after 2, 7 and 28 days. The values of cement samples produced with clinker with 100 % coal are higher compared to cement produced with 90 % coal + 10 % RDF. Thus, the average value of compressive strength after 2 days for cement produced with 100 % coal is 21.78 MPa, and for the other case 17.03 MPa.

After 7 days, cement produced with 100 % coal clinker has the highest compressive strength. The average value of compressive strength after 7 days for cement samples produced with 100 % coal is 35.04 MPa. For the case of cement produced with clinker with 90 % coal + 10 % RDF, the average compressive strength value after 7 days is 30.69 MPa.

As for the previous two cases, the compressive strength of cement after 28 days is higher in all 10 samples of cement produced from clinker with 100 % coal with an average value of 53.64 MPa, while the average value of compressive strength of cement with RDF after 28 days is 47.73 MPa, which can be seen from Figure 6.

Based on the compressive strength values shown, it can be concluded that all samples produced with 100 % coal in all three cases have higher compressive strength values and this is because the clinker used for cement production has a higher alite content, which is the most responsible for strength.

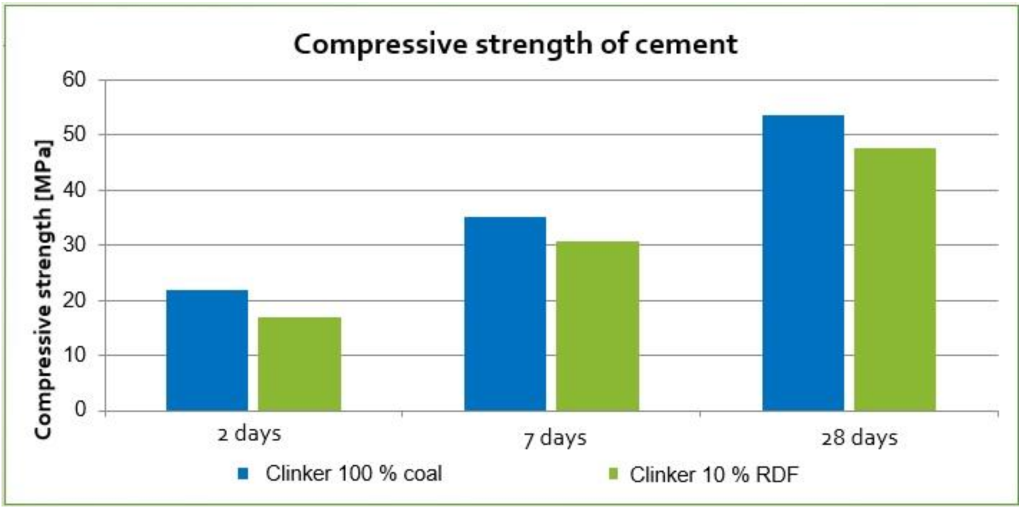

Figure 6. Compressive strength of cement

5. CONCLUSION

Based on research carried out in laboratory and industrial conditions and the obtained results, it can be concluded that the mineralogical composition of clinker alite, belite, aluminates and ferrite in both types of fuel meets the required values.

The compressive strength after 2, 7 and 28 days of setting is higher for fuel with 100 % coal due to the higher content of alite in the clinker. The average compressive strength of cement with fuel of 90 % coal + 10 % RDF after 28 days is 47.73 MPa, while for cement with 100 % coal the average value of compressive strength is 53.64 MPa. From the obtained results, it

can be concluded that cement produced with fuel from 100 % coal, as well as fuel with 90 % coal + 10 % RDF meets the requirements of the EN 197-1 standard in terms of physical and mechanical properties.
However, according to all test parameters, it is clear that the use of 100 % coal shows significantly better results compared to the used fuel with the addition of 10 % RDF. The different composition of RDF, the presence of a larger amount of moisture in this fuel, lower heat power are the main reasons why the results of clinker and cement are worse when using an alternative fuel compared to the used 100 % coal.
Although both types of cement met industry standards, the addition of RDF to the fuel noticeably altered the mineral composition of the clinker and reduced overall strength. These findings highlight the importance of optimizing RDF processing to enhance its combustion efficiency and, ultimately, the performance of the cement.

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