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ANALYSING OF POSSIBILITIES TO USE ALTERNATIVE FUELS AS ENERGY SOURCES

BY

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Abstract. Cement production at the global level has grown at a dizzying pace in recent decades, and with it the consumption of thermal and electrical energy of the producing factories. As a result, the negative effects on the environment also increased, effects also blamed on cement producers. The classic sources of obtaining the necessary thermal energy are obtained from fossil fuels, and their replacement with less polluting sources is of great importance. The use of alternative fuel sources, namely combustible waste, is a viable solution, but applying a strategy to use them as the main source of thermal energy is a complex process with many variables. The most delicate criterion is that of obtaining a product of superior quality, in large quantities and at constant values. Therefore, by burning an alternative fuel, the product obtained must not be negatively influenced by its use. The use of alternative fuels brings both a competitive advantage and the reduction of polluting gas emissions.

Keywords: alternative fuels, characterization, heavy metals, tires.

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1. Introduction

The increase of worn tires, whose main raw material is rubber, is a result of the world's growing automobile population. This contributes to the problem of hard removal waste. Rubber is a raw material that has a unique set of physical characteristics, including high ductility, low hardness, and high elasticity (Abitha *et al*., 2019). To determine the necessary application qualities, control processing behavior, and lower material costs, a wide variety of additives are used. The most significant rubber fillers are dispersion additives (SiO_2, ZnO, Al_2O_3, $MgCO_3$) and active and inactive carbon (Urtekin *et al.*, 2023). Tire manufacturing accounts for the biggest portion of rubber use (35–45%). Their manufacturing process involves the use of natural rubber (NR), polyisoprene rubber (IR), butadiene-styrene rubber (SBR), and polybutadiene rubber (BR) (Čabalová *et al.*, 2021).

Cement production needed high energy consumption approximatively 3.3 GJ/ton of clinker, the cost of energy represents 30-40% from the total cement cost. In the Europe, cca. 25 million tons of traditional coals are used for cement production. The main fuel used is methane gas and petroleum coke, that are expensive, and producers trying to substitute these with alternative fuel. The cement producers demand studies to reduce of the production cost (Żygadło and Purgał, 2020) and environmental impact footprint. One way to achieve this is to use alternative fuels (Poudyal and Adhikari, 2021). A total of 2.5 million tons of coal are saved each year in fuel due to the use of alternative fuels in European kilns (Chen *et al.*, 2022). Austria used 35% of alternative fuels, Belgium 20%, Czech Republic 10.7%, France 51.4%, Germany 16%, Italy 5.1%, etc. (Sahoo and Kumar, 2022). The production of cement uses 7% of total industrial fuels (Zhang *et al.*, 2019). Thus, the alternative fuels will not only reduce energy consumption, but have a significant environmental effect (Kishan *et al*., 2021), by conserving resources, reducing the amount of waste disposal and decreasing emissions (Vasiliu *et al*., 2023a; Vasiliu *et al*., 2023b).

Tires, scrap rubber, plastic, sewage sludge, graphite waste, petroleum pellets, electrode coke, paper trash, household waste, agricultural waste, wood, sludge, etc. (Rosyid *et al.*, 2020) are the most commonly used waste-derived fuels in the cement industry. The cement industry is one of the largest industrial sources of CO_2 emissions in the world, accounting for 1.7 Gt/year in 2021, or more than 8% of global emissions from fossil fuel use. Over the years, the cement industry has substantially reduced CO_2 emissions per ton of cement by improving energy efficiency, replacing fossil fuels with waste that can sometimes be considered “carbon neutral” and increasing the use of additives in the cement product (Markl and Lackner, 2020). Any reduction in the required energy has a beneficial influence both on the viability of the cement plant and on the environment. Cement plants have great options for recycling/use of used tires.

Used tires are of interest to the cement industry due to their high constant calorific value, the possibility of recycling iron as iron oxide in the clinker process, and the possibility of minimizing nitrogen oxide emissions from chimneys. Resources are widely distributed, so collecting them is important. Both whole tires and shredded tires can be burned in cement plants. Collaborative processing is a logical first response to the tire disposal problem in countries with large processing capacity, as solutions can be implemented quickly. A cement plant with a precalciner or preheater achieves a heat exchange rate of 20%.

In this paper is presented a compressive characterization of tires, for establishing the possibilities to use as alternative fuel and determining the content in heavy metals from tires ash, that can influence the cement quality.

2. Materials and method

For heavy metals determination was determined by atomic absorption spectrometry according to SR EN 13211:2003 and SR EN 14385:2004. The determinations were realized with a graphite oven atomic absorption spectrometry, and a NovAA 400 hydride generator. IKA type C5000/C6000 calorimeter was used to determine the calorific value. Oxides components of raw materials were determined with by XRF OASIS 9900, ARL producer. Calcination lost was determined with Nabertherm LE4/11 oven. The chlorine content was determined by wet chemistry. All determinations were realized in triplicate. The chemicals used were purchased from Sigma Aldrich.

3. Characteristics of alternative fuels

The energy value of combustible waste is given by their physico-chemical characteristics. The main characteristic of waste when talking about its use as alternative fuels is its calorific value, Table 1.

Table 1
Energy characteristics of various fuel categories

Primary fuels	**Calorific value (kJ/kg)**
Coal	25,000 – 27,000
Lignite	20,000 – 23,000
Petroleum coke	28,000 – 34,000
Natural gas	25,000 – 40,000
Alternative fuels (secondary, combustible waste)	**Calorific value (kJ/kg)**
Used tires/shredded rubber	25,000 – 34,000
Plastic waste	36,000 – 42,000
Various substitute materials	13,000 – 15,000
Sewage sludge	11,000 – 28,000
Wood waste	14,000 – 18,000
Used oils	36,000 – 40,000
Solvents	25,000 – 44,000
Gases recovered from landfills	10,000 – 20,000

It can be seen that the higher the ash and moisture content, the lower the calorific value. Low O_2 and low ash fuels have a calorific value close to that of coal. Also, depending on the calorific value, the place to feed the combustible waste to the furnace is chosen. A waste with a high calorific value will feed to the main burner of the kiln (if sufficiently shredded or powdery) or if it is a liquid waste (used oil).

Chemical composition of different type of combustible waste is presented in Table 2.

Table 2

Physico-chemical characteristics of some combustible waste

Components	Used tires	Plastic waste	Sewage sludge	Wood waste
C	70.0 - 85.0	38.7 - 73.8	51.0 - 65.0	40.5 - 51.9
H	6.0 - 10.0	5.2 - 10.9	7.0 - 8.0	4.5 - 5.5
O	3.0 - 8.0	1.4 - 15.6	30.0 - 34.0	31.4 - 37.5
N	0.3 - 0.4	0.3 - 0.8	7.0 - 8.0	0.2 - 9.7
S	1.0 - 1.7	0.1 - 0.2	< 1.5	0.0 - 0.2
Cl	0.1 - 0.2	0.9 - 1.8	< 0.6	0.0 - 0.5
Ash	-	1.6 - 22.3	44.0 - 48.0	0.1 - 0.3
Humidity	< 0.5	10.0 - 16.0	6.0 - 8.0	10.0 - 15.0
Volatile	-	-	-	-

It can be seen from the data presented that some combustible waste has a high chlorine content with negative implications on the operation of the kiln. Also, the humidity of some categories of secondary fuels shows an increased level. Table 3 shows the heavy metal concentration of refuse-derived fuel (RDF) waste compared to conventional fuel (Reza *et al*., 2013).

Table 3

Average coal/RDF heavy metal content

Chemical element	Fuel type	
	Coal mg/kg	RDF mg/kg
Cadmium	0.1	3.0
Thallium	<0.1	0.05
Mercury	<0.1	0.20
Antimony	0.2	100
Arsenium	1.1	1.3
Lead	18.2	214
Chomium	4.9	112
Cobalt	0.8	6.6
Copper	11	315
Manganese	308	117
Nickel	0.8	26
Vanadium	8	4.2

As for the concentration of heavy metals in combustible waste, it varies from case to case. Depending on the content of heavy metals in the combustible waste, it must be limited at the entrance to the kiln, because heavy metals with high volatility are found in the form of emissions at the kiln chimney (in the case of Hg), and those with low volatility are embedded in the clinker.

4. Results and discussion

As alternative fuels were analyzed different types of tires. The energy content of tires varies considerably depending on their physical characteristics. While car tires have a content of up to 5% metal insert, those of trucks and buses can reach up to 25%, which implies changes in their energy content. The water content of stored used car tires can also influence the lower calorific value. Used car tires used in the cement industry have a lower calorific value between 6448 Kcal/kg (26998Kj/kg) - 7165 kcal/kg (29999.9 Kj/kg). Table 4 shows compositions of used car tires used for burning in cement plants.

Table 4
Compositions of waste tires used for combustion in cement plants, %

Nr.	Characteristic	Type 1	Type 2	Type 3
1	Rubber	76-90	-	
2	C	89.2	78.2	71.3
3	H	7.3	7.0	5.9
4	S	1.8	1.4	1.5
5	0	-	5.0	2.6
6	N	0.2	0.2	0.26
7	ZnO	-	1.1	1.4
8	Ash	1.5	-	6.6*
9	Steel	5-20	3	12
10	Cl	-	-	0.13
11	Metallic cord	cca.4	-	-
12	Low calorific value	-	7980 kcal/kg 33412Kj/kg	7382kcal/kg 30908Kj/kg

According to other authors, the tires are made up of approx. 88% of carbon, hydrogen and oxygen, and the lower calorific value is approx. 7493kcal/kg (31371 Kj/kg) - 8325 kcal/kg (34854Kj/kg). The variation of calorific power is a function of the proportion of metal insert in the tires, their type and degree of aging. Tables 2 and 3 summarize the environmental and process implications of car tire use according to literature data.

Remarks

- low value of sulphur content. Minimal impact on kiln operation and NOx emissions.
- high values of the content of volatile substances.
- high lower calorific value. Values comparable to those specified in the specialized literature.

Elemental analysis of tires waste is presented in Table 5.

Table 5

Elemental analysis of used tires

Tire sample characteristics	Unit	Values	
		With metal insertion	Without metal insertion
Moisture content	%	0.44	0.67
Volatile matter content	%	58.37	65.18
Ash content + metal	%	19.94	1.86
Elementary analysis			
C	%	72.5	78.93
H	%	5.35	7.27
N	%	0.34	0.34
O	%	0.55	8.24
S	%	0.93	1.27
Cl	%	0.54	1.32
Lower calorific value	kcal/kg Kj/kg	7250 (30354)	8493 (35558)

For a more complete characterization of the tires, calculations were made of the potential elemental composition and the lower calorific value based on the analysis of the tire without a metal insert and considering different degrees of wear, going up to a value of approx. 25%, considered maximum following practical determinations, variable proportion of metal insert (according to Romanian standards for different types of tires-3-20%).

The results of the calculations are presented synthetically in table 6. The variation of the lower calorific power is presented depending on the degree of wear and the content of metal inserts.

Remarks: the lower calorific value varies in the range of 6370 Kcal/Kg (26669Kj/kg) – 8211Kcal (34377Kj/Kg), depending on the percentage of metal insertion and the degree of wear. The obtained values are comparable to those presented in the specialized literature.

Table 6
Variation of the lower calorific value according to the degree of wear and the content in metal insert

Initial composition (without insertion)	Degree of wear 10%			Degree of wear 15%			Degree of wear 20%			Degree of wear 25%		
	3%	15%	20 %	3 %	15%	20%	3%	15%	20%	3%	15%	20%
8493	8211	7101	6647	8195	7033	6563	8177	6959	6471	8157	6875	6370

Chemical analysis of the ash resulted from car tires

The chemical analyses of the ash on two tire samples of different types, carried out the lab and are presented in Table 7.

Remarks

- in the chemical composition, the main oxidic constituents of the raw meal are found, but in smaller proportions.

Table 7
Chemical analyses of ash resulting from burning tires

Chemical composition	**Unit**	**Values**	
		Sample 1	Sample 2
SiO_2	%	81.48	15.12
AI_2O_3	%	0.43	1.93
Fe_2O_3	%	0.17	9.03
MgO	%	0.28	0.51
Na_2O	%	0.94	3.18
K_2O	%	0.15	0.95
TiO_2	%	0.04	0.08
MnO	%	0.01	0.07
P_2O_5	%	0.31	0.55
SO_3	%	0.35	0.98

In Table 8 is presented content in heavy metals of ash.

Remarks

- the heavy metals present in the ash of tire samples, in descending order of content, are: Zn, Pb, Mn, Ni, Cd;
- the metal with the highest weight is Zn - This represents about 99% of the total heavy metal content of tire ash;

- the content of Zn introduced into the system with the furnace feed flour and fuel must not exceed the limit recommended by the specialized literature (<4000 ppm) in order not to influence the setting time of the cement.

Table 8
Analysis of heavy metals, ash, used tires

Chemical composition	Unit	Values	
		Sample 1	Sample 2
Cd	ppm	4.3	
TI	ppm	**0.1**	
Hg	ppm	0.0044	**0.0046**
As	ppm	**19**	38
Co	ppm	2.2	3.1
Cr	ppm	3	45
Cu	ppm	3	59
Zn	ppm	25300	194200
Mn	ppm	85	594
Ni	ppm	7.3	35,2
Pb	ppm	54	204
Sb	ppm	0.5	1,9
V	ppm	51	78
Sn	ppm	6	17
Total	ppm	**25536**	**195283**

5. Conclusions

Decades of experience using waste as an alternative source of energy needed in the cement manufacturing process have demonstrated a solution that is not only economically beneficial but also ecologically justifiable. The energy consumption to produce a single ton of cement is about 3.3 GJ, an amount that corresponds to the use of about 120 kg of coal with a calorific value of 27.5 MJ/kg. The costs attributed to the energy requirement of cement manufacturing are found at a value of 30-40% of the total cost, a very high percentage, and these costs can be reduced by substituting classic fossil fuels with alternative fuel sources.

For cement factories that use waste as an energy source, replacing fossil fuels with alternative fuels represents a competitive advantage, both by reducing production costs and by reducing polluting gas emissions. The burning conditions found in the clinker kiln ensure a total destruction of many polluting elements as well as the recycling of non-combustible matter from the burning of alternative fuels. The use of waste as an alternative source of energy represents an ecological solution and an efficient method of waste management, by eliminating the need to build specialized incineration facilities, as well as reducing the use of landfills, a fact that translates into benefits for society, and may have its support.

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ANALIZA POSIBILITĂȚILOR DE UTILIZARE A COMBUSTIBILILOR ALTERNATIVI CA SURSE DE ENERGIE

(Rezumat)

Producția de ciment la nivel global a crescut în ritm vertiginos în ultimele decenii, iar odată cu aceasta şi consumul de energie termică şi electrică al fabricilor producătoare. Ca urmare au crescut și efectele negative asupra mediului, efecte puse şi pe seama producătorilor de ciment. Sursele clasice de obținere a energiei termice necesare sunt obținute din combustibili fosili, iar înlocuirea acestora cu surse mai puțin poluante este de mare importanță. Utilizarea surselor de combustibili alternativi, respectiv a deșeurilor combustibile, reprezintă o soluție viabilă, însă aplicarea unei strategii de utilizare a acestora ca şi sursă principală de energie termică este un proces complex, cu foarte multe variabile. Cel mai delicat criteriu este cel de obținere a unui produs de o calitate superioară, în cantităţi mari şi la valori constante. Aşadar, prin arderea unui combustibil alternativ, produsul obținut nu trebuie să fie influențat negativ de utilizarea acestuia. Utilizarea combustibililor alternativi aduce atât un avantaj competitiv cât și reducerea emisiilor de gaze poluante.