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Impact of the use of alternative fuels in cement production on emission of harmful pollutants

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Abstract: Cement industry is a huge energy consumer, and at the same time a huge greenhouse gases generator – approx. 7% seven percent of the total global CO_2 emission in 2010 (Deja, Uliasz-Bochenczyk and Mokrzycki, 2010). High fuel consumption weakens the economy of the process and the acceptance of cement’s market price, so many cement companies have turned to research to use alternative fuels in production in order to reduce both the production costs and greenhouse gas emissions. However, due to the fact that this process is basically a waste incineration, the cement industry is constantly under pressure from the general public and environmental associations, so the tests are constantly being carried out to determine emissions of harmful pollutants during the use of various alternative materials in the cement production process. This paper investigates the impact of the use of some alternative fuels (scrap tires, used oils, waste from the coal industry, waste from the tanneries and leather industry, waste from oil refining – filter cake and oily wipes & rags) in an amount of 10% (energy) on emission of harmful pollutants in cement production. The results obtained by these tests show that, although there are evident differences in the content of individual pollutants for different types of alternative fuels, total emissions stays within statutory limits.

INTRODUCTION

In today's world, cement factories are considered successful, if they have managed to get 70% energy needs from alternative sources. Some plants in the world in their plans already predict a one-hundred-percent replacement of fossil fuels by alternative fuels. FCL (Cement Factory Lukavac) has a relatively new production line that is designed so that it can use alternative fuels with continuous monitoring and control of all production and environmental parameters. The results of the previous measurements for selected pollutants, the emissions of which have been produced in the process of cement production and determined by strict EU standards, have shown values within the permitted limits and for some pollutants the obtained values have been lower than the prescribed ones. This kind of controlled combustion with continuous monitoring of conditions and product control can only be achieved with efficient plants – what's in the FCL embedded during the building a new furnace line and mills of raw meal, released in mid-2009.

Theory

The cement industry, due to alkaline environment, high temperature and long processing time, has the potential to adequately handle large amounts of fuels, including waste, by co-combustion (Rahman, Rasul, Khan and Sharma, 2013). Fuel incineration is carried out both in the primary air stream which carries fuel into the furnace and in the heated secondary air stream where the raw material is heated up to 1450°C, so the flue gas temperature reaches 2000°C. The gases are maintained at this temperature from5 to 7 seconds, that is enough to break all organic energy constituents while the inorganic residue of the incineration, or ashes, become part of the clinker. Along with the main components of ash (silicon oxide, aluminum, iron and calcium salts), heavy metals are also incorporated into clinker.

Thermal treatment of waste or its use as fuel in the Federation of Bosnia and Herzegovina must be carried out with full respect to emission limit values in accordance with the applicable ordinance (Pravilnik o uvjetima za rad postrojenja za spaljivanje otpada, 2005), that can be achieved by installation of equipment for control of the emission of flue gases. The use of alternative fuels in the cement industry began in the 1970s and since then, the number of cement factories in the world, using alternative fuels, is in constant growth.

From the production costs of cement, 30-40% goes to the energy consumption (Radwan, 2012). With the aim of lowering these energy costs, alternative fuels were introduced in the cement industry, so today more than 200 cement factories worldwide use alternative fuels. In Germany, according to Verein Deutscher Zementwerke (2017), the share of fossil fuels (particularly lignite and coal) has continuously dropped from 74.3% in 2000 to currently 35.2%. Heat energy requirements are today primarily covered using alternative fuels such as treated commercial and municipal waste, scrap tires, used oil or sewage sludge (64.8% in 2016), while the high energy efficiency of the cement production process was not affected by this substitution.

It has been shown that combustion of waste as alternative fuels in cement plants preserves natural resources and reduces emissions. In comparison of the environmental impact of this technique and the environmental impact of the landfill, the landfill has a much larger emission and impact on the greenhouse effect due to the conversion of the organic part of the waste to the gases. Approximately half of degradable organic waste turns into CO_2, and the remainder into methane – CH_4, whose potential impact on global warming for the one hundred- year time horizon is 28 (IPCC, 2013). If the organic material from the waste is used in the cement industry, indirect decrease of potential methane emissions from the landfill is achieved in the incineration process.

Regarding scrap tires, or TDF (tire-derived fuel, which is composed of shredded scrap tires), numerous studies (e.g. Reisman, 1997; Baird, Horrocks, Kirton and Woodbridge, 2008; Cheema and Badshah, 2013 or The Pembina Institute and Environmental Defence, 2014) have shown that their use as an alternative fuels in cement kilns either reduces or does not significantly affect emission of most pollutants. For example, one extensive survey involving thirty-one cement plants (Richards, Goshaw, Speer and Holder, 2008) demonstrated that "Dioxin-furan emission test results indicated that kilns firing TDF had emissions approximately one-third of those kilns firing conventional fuels – this difference was statistically significant. Emissions of particulate matter (PM) from TDF-firing kilns were 35% less than the levels reported for kilns firing conventional fuels (not statistically significant due to the low PM emissions reported for essentially all cement kilns). Nitrogen oxides, most metals, and sulfur dioxide emissions from TDF-firing kilns also exhibited lower levels than those from conventional fuel kilns. The emission values for carbon monoxide and total hydrocarbons were slightly higher in TDF versus non-TDF firing kilns. However, none of the differences in the emission data sets between TDF versus non-TDF firing kilns for sulfur dioxide, nitrogen oxides, total hydrocarbons, carbon monoxide, and metals were statistically significant", which mostly confirms mentioned results of earlier research, however, it should be noted that the emissions are highly dependent on the technological process of a particular cement plant, which was a main motive for detailed research on a specific process: production of cement in FCL (Cement Factory Lukavac).

EXPERIMENTAL

In the FCL, for the production of heat and clinkering of meal various fuels are used: heavy fuel oil – SNS (with sulfur content up to 1%), domestic brown coal (with sulfur content of 2-3%) and brown coal imported from the Czech Republic (with sulfur content up to 1%). At present, a combination of domestic coal and imported coal is used in the ratio of 30:70 due to the reduction of SO_2 emissions during combustion in a rotating kiln. In the absence of imported brown coal, medium fuel oil with sulfur content below 1% (FCL, 2007) is used in the combination of fuels. The first attempts to use alternative fuels in the FCL started in 2010 when the first trial run was carried out, and since then several tests have been conducted alongside activities related to obtaining approval from relevant institutions for the use of alternative fuels in the cement production process. Therefore, it can be said that today FCL is capable of using various alternative fuels in the production process: scrap tires, used oils, waste from the leather and textile industry, filter cakes and oily waste. For conducting the testing of the impact of the use of alternative fuels on pollutants emissions in the period of 5 days, measurements of the pollutant concentration in flue gas from the rotary kiln in the Lukavac cement factory were performed.

During the first series of measurements, the rotary kiln worked with a normal working regime, i.e. with the only coal used as a fuel. Subsequently, in the rotary kiln, alternative fuels (scrap tires, used oils, waste from the leather industry, waste from the textile industry, waste from oil refinery – filter cake and oily wipes & rags) were used in a percentage of 10% (energy) of coal. Waste from the leather and textile industry was acquired from the company Prevent-Visoko, and used oil and oily wipes & rags was collected by the Kemokop from Tuzla, the company authorized to manage such types of waste, while the filter cake was purchased from the Oil Refinery Modriča.

The calorific values of liquid fuels were determined according to the ASTM D240-09, using the IKA C 5000 bomb calorimeter. For solid fuels, calorific values were determined according to the BAS ISO 1928:2010, using the same bomb calorimeter.

Since it was necessary to measure the mean concentration of flue gas, the sampling was carried out in several points per cross-section of the flue duct. Sampling was performed isokinetically, using Tecora G4 isokinetic automatic sampler, according to BAS ISO 9096, BAS EN 13284-

1:2006, BAS EN 1948-1 and BAS EN 1911:2011. The sampling site was on the chimney of the rotary kiln (Figure 1).

Figure 1: Sampling site at the chimney

Determination of dust concentration was performed according to BAS EN 13284-1:2006. Using the Horiba Model PG-250 multi-gas portable analyzer, the concentration of SO_2, CO and NOx were determined, according to BAS ISO 7935:2000, BAS EN 15058:2008 and BAS EN 14792:2007. Concentrations of HCl and HF were determined using Varian Cary 50 UV-Vis spectrophotometer, according to BAS EN 1911:2011 and BAS ISO 15713:2008. AA240FS fast sequential atomic absorption spectrometer was used for determination of Hg and other heavy metals, according to APHA Standard Methods 3111B and 3112 and also to BAS EN ISO 15586:2005.

Procedure of determination of dioxins and furans was performed according to BAS EN 1948-2:2007 and BAS EN 1948-3:2007. Total organic carbon content was determined according to BS EN 12619:2013. The analysis were performed in cooperation with the laboratory of the company Dvokut from Sarajevo, accredited according to BAS EN ISO/IEC 17025:2006.

Results and Discussion

In order to determine the mixing ratio (90% of coal with 10% of alternative fuel, in an energetic sense), the calorific values of coal and alternative fuels were determined. These values are presented in Table 1.

Table 1: Calorific values of fuels

Fuel	**Calorific value [kJ/kg]**
Coal	23.330
Scrap tires	24.000
Waste from tanneries/leather industry	11.688
Waste from textile industry	22.000
Used oil	40.000
Waste from oil refinery – filter cake	23.000
Oily wipes & rags	22.000

Based on determined calorific values, the amounts of individual fuels were calculated and the operating modes, during the measurement is set, as shown in Table 2

Table 2: The amount of individual fuels in the mixture

Fuel	**15.07. 12:30-13:30**	**15.07. 14:00-15:00**	**18.07. 9:30-11:00**	**18.07. 12:00-13:30**	**18.07. 14:00-15:00**	**19.07. 9:00-11:00**	**19.07. 11:00-12:45**
				[kg/h]			
Coal	11500	10000	10000	10000	10000	10000	10000
Scrap tires		1050					
Waste from tanneries/leather industry				1950			
Waste from textile industry					900		
Used oil			585				
Waste from oil refinery – filter cake						1000	
Oily wipes & rags							950

The results of measurements given in the Table 3 are treated as the average values of all measured values of emissions in the period of measurement. All emission measurement results are presented in the form of measured values corrected to normal conditions and dry gas and reference content $O_{2\ REF}$ = 10%.

Comparing emission results regarding the use of coal fuels and a mixture of 90% coal and 10% (energy) of alternative fuels, it can be stated that concentrations of pollutants generated by the incineration of all alternative fuels used in these tests lie below the limit values prescribed by the applicable ordinance (Pravilnik o uvjetima za rad postrojenja za spaljivanje otpada, 2005 and 2012).

NO_x concentration while waste is used as an alternative fuel is reduced, except in the case of waste from the leather industry. CO emission is increasing, with the largest increase of 300% seen when waste textile and oily wipes & rags are used as fuel, that could be attributable to the fact that this waste has a non-homogeneous composition and consists of different types of textiles (natural fibers, cotton, silk, etc., synthetic fibers, polyesters, viscose, etc.) and require different conditions for full combustion. The emission of dioxins and furans is rather low regardless of used fuel or fuel mixture, most probably due to high temperature and retention time of several seconds.

Table 3: The emission of pollutants and comparison with emission limit values (ELV)

Parameter	ELV [mg/m³]	The results normalized to dry gas, normal conditions and $O_{2,REF}$ [mg/Nm³]						
		Coal	Coal + tires	Coal + used oil	Coal + leather waste	Coal + textile waste	Coal + filter cake	Coal + oily rags
Dust, total	30*	3.2	6.1	7.0	5.8	6.6	10.8	10.9
SO_2**	50*	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO	-***	60.2	71.6	74.8	82.4	106.5	106.5	212.6
NO_X	500*	420.0	408.1	394.3	464	344.6	361.7	377.6
HCl	10*	2.9	1.8	2.5	2.4	1.6	3.8	4.2
HF	1*	-	-	-	-			
Cd +Tl	0.05*	$12.6\cdot10^{-4}$	$11.9\cdot10^{-4}$	$6.9\cdot10^{-4}$	$10.3\cdot10^{-4}$	$7.8\cdot10^{-4}$	$21.5\cdot10^{-4}$	$36.0\cdot10^{-4}$
Hg	0.05*	$7.10\cdot10^{-5}$	$4.32\cdot10^{-5}$	$7.7\cdot10^{-5}$	$5.05\cdot10^{-5}$	$5.86\cdot10^{-5}$	$7.33\cdot10^{-5}$	$9.59\cdot10^{-5}$
Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V	0.5*	$6.3\cdot10^{-4}$	$12.3\cdot10^{-4}$	$11.0\cdot10^{-4}$	$14.7\cdot10^{-4}$	$16.4\cdot10^{-4}$	$20.2\cdot10^{-4}$	$28.9\cdot10^{-4}$
Dioxins and furans	0.1*	0.019	0.011	0.017	0.0148	0.0628	0.0093	0.01
TOC	10*	4.81	5.71	4.79	6.60	4.68	9.37	8.14

* ELVs according to applicable ordinance (Pravilnik o uvjetima za rad postrojenja za spaljivanje otpada, 2005 and 2012)

** SO_2 was measured, and results were negative, which means that the SO_2 has been present in samples, but the lower calibration point of the instrument lied higher than measured value.

*** According to above mentioned Ordinance (Annex II, point 1.3), also according to the □Directive 2010/75/EU (Annex VI, Part II, point 2.4), "The competent authority may set emission limit values for CO", but still it wasn't.

Emissions are even lower when the mixtures of coal and alternative fuels are used, which is something that may be the subject of further research, but such a phenomenon could be the consequence of slight lowering the temperature during the combustion of the alternative fuels, as lower temperatures are believed to prevent the post combustion catalytic formation of dioxins and furans (Karstensen, 2006). An exception is the waste from the textile industry where increased concentration of dioxin (0.0628 mg/Nm³) was recorded, which is attributable to the composition of the fabric and the fact that many of them contain plastic compounds.

The metal emission is increased but it is necessary to point out that all values lie below the emission limit value of 0.5 mg/Nm³. Used alternative fuels contain metals in its composition so such an increase was expected. HCl and Cd + Tl emissions are reduced when alternative fuels are used. The exception is waste from the oil industry and the oily wipes & rags, which can be attributed to the character of this waste and the fact that it comes from the environment in which it could come into contact with the compounds (chlorine, heavy metals) which can cause the rise of emission of these compounds in the rotating kiln. Hg emission is reduced by the use of wastes from textile, leather and used oil while an increase has been recorded when scrap tires, waste from oil refining - filter cake and oily wipes & rags are used, what is expected with regard to the chemical composition of given alternative fuels.

The TOC concentration increases, except when scrap tires and waste from the textile industry are used as alternative fuels, where the emissions are approximately equal to emissions when using solely conventional fuel - coal. Total dust emissions are increasing

CONCLUSION

The basic requirement for co-combusting alternative fuels in the cement industry is that this process has no adverse impact on the environment or on the quality and properties of the main product.

The aim of the research described in this paper was to determine the emission level when burning alternative fuels in a rotary kiln in comparison to rotary kiln operation when only coal is used as fuel.

The results of the measurement showed that the values of all pollutants observed during the use of various alternative fuels in an amount of 10% (energy) were lower than the emission limit values, while the operator at the same time achieved economic benefits in terms of reducing the fuel costs.

REFERENCES

APHA Standard Method 3111 (1999) (Editorial revisions, 2011). *Metals by Flame Atomic Absorption Spectrometry*.

APHA Standard Method 3112 (2009) (Editorial revisions, 2011). *Metals by Cold-Vapor Atomic Absorption Spectrometry*.

ASTM D240-09 (2009). *Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter*.

Baird, D., Horrocks, S., Kirton, J., Woodbridge, R. (2008). *Science Report – The use of substitute fuels in the UK cement and lime industries*. Environment Agency, Bristol, UK.

Cheema, K.M., Badshah, S. (2013). Cement Industry, Alternate Fuel and Environmental Benefits. *International Journal of Engineering Research & Technology (IJERT), 2013, 2 (10)*, 1571-1581.

BAS EN 13284-1:2006 (2006). *Stationary source emissions - Determination of low range mass concentration of dust - Part 1: Manual gravimetric method*.

BAS EN ISO 15586:2005 (2005). *Water quality - Determination of trace elements by atomic absorption spectrometry with graphite furnace*.

BAS EN 14792:2007 (2007). *Stationary source emissions - Determination of mass concentration of nitrogen oxides (NOx) - Reference method: Chemiluminescence*

BAS EN 15058:2008 (2008). *Stationary source emissions - Determination of the mass concentration of carbon monoxide (CO) - Reference method: Non-dispersive infrared spectrometry*.

BAS EN 1911:2011 (2011). *Stationary source emissions - Determination of mass concentration of gaseous chlorides expressed as HCl - Standard reference method*.

BAS EN 1948-1:2007 (2007). *Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 1: Sampling of PCDDs/PCDFs*.

BAS EN 1948-2:2007 (2007). *Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 2: Extraction and clean-up of PCDDs/PCDFs*.

BAS EN 1948-3:2007 (2007). *Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 3: Identification and quantification of PCDDs/PCDFs*.

BAS ISO 15713:2008 (2008). *Stationary source emissions - Sampling and determination of gaseous fluoride content*.

BAS ISO 1928:2010 (2010). *Solid mineral fuels - Determination of gross calorific value by the bomb calorimetric method and calculation of net calorific value*.

BAS ISO 7935:2000 (2000). *Stationary source emissions - Determination of the mass concentration of sulfur dioxide - Performance characteristics of automated measuring methods*.

BAS ISO 9096/Cor 1:2008 (2008). *Stationary source emissions - Manual determination of mass concentration of particulate matter; Technical Corrigendum 1*.

BS EN 12619:2013 (2013). *Stationary source emissions. Determination of the mass concentration of total gaseous organic carbon. Continuous flame ionisation detector method*.

Deja, J., Uliasz-Bochenczyk, A. Mokrzycki, E. (2010). CO_2 emissions from Polish cement industry. *International Journal of Greenhouse Gas Control, 2010, 4 (4)*, 583-588.

Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control): Recast (2010) OJ L 334/17-119.

FCL-Fabrika cementa Lukavac (2007) *Plan aktivnosti za izdavanje okolinske saglasnosti*, broj izvještaja 068 d – III/07, Fabrika cementa Lukavac dd. Lukavac.

IPCC (2013). *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

Karstensen, K.H. (2006). *Formation and Release of POPs in the Cement Industry: Second edition*. World Business Council for Sustainable Development, Geneve, CH.

The Pembina Institute, Environmental Defence (2014). *Alternative Fuel Use in Cement Manufacturing: Implications, opportunities and barriers in Ontario*. Available online: http://www.pembina.org/pub/alternative-fuel-use-in-cement-manufacturing. Accessed 18/10/2017.

Pravilnik o uvjetima za rad postrojenja za spaljivanje otpada, Službene novine Federacije BiH, 12/05 and 102/12.

Radwan, A.M. (2012). Different Possible Ways for Energy in the Cement Production. *Advances in Applied Science Research, 2012, 3 (2)*,1162-1174.

Rahman, A., Rasul, M.G., Khan, M.M.K., Sharma, S. (2013). Impact of Alternative Fuels on the Cement Manufacturing Plant Performance: An Overview. *Procedia Engineering, 2013 (56)*, 393-400.

Reisman, J.I. (1997). *Air Emissions from Scrap Tire Combustion: Project Summary*. United States Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH, USA.

Richards, John; Goshaw, David; Speer, Danny, and Holder, Tom (2008) *Air Emissions Data Summary for Portland Cement Pyroprocessing Operations Firing Tire-Derived Fuels*, SN3050, Portland Cement Association, Skokie, Illinois, USA, 32 pp.

Verein Deutscher Zementwerke e.V. (2017) *Environmental data of the German cement industry 2016*, VDZ, Duesseldorf.

Summary/Sažetak

Cementna industrija je veliki potrošač energije i u isto vrijeme veliki generator stakleničkih plinova – oko 7% ukupne globalne CO_2 emisije u 2010 (Deja, Uliasz-Bochenczyk i Mokrzycki, 2010). Velika potrošnja goriva slabi ekonomiku procesa i cjenovnu prihvatljivost cementa na tržištu, tako da su se mnoge cementare okrenule istraživanjima sa ciljem upotrebe alternativnih goriva u proizvodnji kako bi se pojeftinio proizvodni proces i smanjila emisija stakleničkih plinova. Ipak, zbog činjenice da se u osnovi radi o spaljivanju otpada, cementare su stalno pod pritiskom javnosti i ekoloških udruga, stalno se rade ispitivanja sa ciljem određivanja emisije štetnih polutanata pri korištenju različitih alternativnih materijala u procesu proizvodnje cementa. U ovom radu je vršeno ispitivanje utjecaja korištenja nekih alternativnih goriva (auto gume, rabljena ulja, otpad iz kožarske industrije, otpad iz tekstilne industrije, otpad iz prerade nafte – filter kolač i zauljene krpe) u količini od 10% (energetski) na emisiju štetnih polutanata pri proizvodnji cementa. Rezultati dobijeni ovim ispitivanjima pokazuju da, iako postoje evidentne razlike u sadržaju pojedinih polutanata za različite vrste alternativnih goriva, ukupne emisije ostaju unutar zakonom dozvoljenih vrijednosti.