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ALEKSANDAR JOVOVIĆ[1]
ZORAN KOVAČEVIĆ[2]
DEJAN RADIĆ[1]
DRAGOSLAVA STOJILJKOVIĆ[1]
MARKO OBRADOVIĆ[1]
DUŠAN TODOROVIĆ[1]
MIROSLAV STANOJEVIĆ[1]

[1]University of Belgrade, Faculty of Mechanical Engineering, Belgrade, Serbia
[2]Metroalfa, d.o.o, LME - Laboratory of Emission Measurements, Zagreb, Croatia

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THE EMISSION OF PARTICULATE MATTERS AND HEAVY METALS FROM CEMENT KILNS – CASE STUDY: CO-INCINERATION OF TIRES IN SERBIA*

Co-incineration of wastes started more than 20 years ago. In the last 10 years, the use of alternative fuels in the cement industry is continuously increasing. The use of solid wastes in cement kilns is one of the best technologies for a complete and safe destruction of these wastes, due to the fact that there is a simultaneous benefit of destroying wastes and getting the energy. However, particulate matters (PM) and gaseous chemicals emitted from a source into the environment could be directly transmitted to humans through air inhalation. Therefore, for accurate health risk estimation, the emission of pollutants must be determined. In this work, the analysis of the emission of different pollutants when replacing partially the fuel type used in a cement kiln is done. PM, PM_{10}, heavy metals and inorganic pollutants are analyzed. The methods used for sampling and analysis are the standard methods suggested by the EU regulations for stack analysis. Experimental results have shown the encouraging results: in particular clinker characteristics were unmodified, and stack emissions (NO_x, SO_2 and CO mainly) were in the case of tires, slightly incremented but remaining almost always below the law imposed limits, and in some cases were even decreased.

Key words: co-incineration; cement plants; waste; stack; emission.

Cement is an important binding agent for the construction industry and is produced world-wide in large amounts (app. 300-400 million tons in Europe). A central process step during the manufacturing of cement is the production of the intermediate product clinker. For this production, inorganic raw materials are calcinated at temperatures in the range of 1000–1500 °C [1]. In order to reduce the costs of this energy-intensive process, regular fuels like coal and petroleum coke are increasingly substituted by different types of waste. In the last 10 years, the use of alternative fuels has been continuously increasing. The share of secondary fuels in the total use of fuels in cement plants is expected to increase further. On the other hand, the accumulation of millions of worn automotive tires is a considerable environmental problem. On average, approximately one scrap tire per person per year is accumulated in industrialized countries. The use of solid wastes as a supplementary fuel or raw material substitutes in cement kilns is one of the best technologies for a complete and safe destruction of these wastes, due to the fact that there is a simultaneous benefit of destroying wastes and getting the energy [2]. Nevertheless, some wastes, such as those containing an important amount of Hg, should be carefully treated in the kiln. At the same time, the substitution of primary fossil fuels has environmental and economic advantages. In an incineration process, some chemicals are emitted as a consequence of the combustion process and these chemicals could be directly transmitted to humans through air inhalation.

One of the major hazards in the alternative fuel flue gas composition is the heavy metal (HM) content. Not all heavy metals are toxic and not all toxic heavy metals have the same toxicity. Therefore many countries differentiate between different toxicity classes:

- Class I: Cd, Hg, Tl;
- Class II: As, Co, Ni, Se, Te;
- Class III: Pb, Cr, Cu, Pt, V, Sn, Pd, Sb, Mn, Rh.

The HM in class I are the most toxic and harmful, the HM in class III the least ones. The main sour-

Correspondening author: A. Jovović, University of Belgrade, Faculty of Mechanical Engineering, Kraljice Marije 16, Belgrade, Serbia.
E-mail: ajovovic@mas.bg.ac.rs
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ces of HM emissions from cement kiln stacks are either raw materials or fuels containing heavy metals.

The present work has the main purpose of checking the amounts of pollutants emitted by a cement kiln in different situations. Tires were used as alternative fuels in clinker kilns of two different cement plants (A and B).

Heavy metals entering the kiln (with fuels and with raw materials) have three different ways to exit the system: they can exit with the cement clinker emitted through the stack and can also be found in the filter dust cement.

Since combustion processes generate gaseous pollutants and solid waste materials which must be disposed of or reused as secondary raw materials, it is important to characterize these combustion products in order to assess the environmental impacts of the energy recovery from whole tires.

National legislation does not consider the emission level value (ELV) for co-incineration of waste [4]. For this reason we consider EU directive 2000/76/EC [5] and a very strong national ELV for the incineration of waste [4].

EXPERIMENTAL

The cement factories (Plants A and B) are located in Serbia with the current production of 2000 and 4000 t cement clinker per day, respectively. Plants are equipped with state-of-art bag filters [3].

Our tests in the cement kilns were performed through more than five years. Several series of runs were carried out, with different mass flows rate of coal, petrol coke and tires.

The characterization of the coals, petrol cokes and tires was carried out (Table 1).

The fuel analyses were carried out according to the appropriate standards for investigating a fuel. For ultimate analysis the instrument Vario EL III was used. The proximate analysis of a tire was done according to technical specifications for solid recovered fuels:

- Calorific value: CEN/TS 15400;
- volatile matter content: CEN/TS 15402;
- moisture content: CEN/TS 15414-1;

and for coal and petrol coke the following standards were used:

- moisture content: SRPS B.H8.311;
- ash content: SRPS B.H8.312;
- volatile matter content: SRPS B.H8.317;
- heating value: SRPS B.H8.318.

The methods used for sampling and analyses are the standard methods suggested by the EU and national regulations for stack analysis:

- heavy metals: EPA, UNICHEM and UNI 10169; EN 14385;
- HCl/HF: EN 1911-1 to 3 VDI 2470, Bl.1;
- particulate matters (dust): ISO 9096, EPA, UNICHEM and UNI 10169;
- NO/NO_2: EN 14792;
- SO_2: ISO 10396 and ISO 7935;
- CO: EN 15058;
- CO_2 and O_2: ISO 12039.

What almost all these methods have in common is the necessity to get an isokinetic regime for gas sampling. The isokinetic sampling equipment was a Zambelli 6000 Isoplus, according to ISO 9096:2003. The same standard used for the selection of measurement points. All measurement points are on main stack after the bag filters.

In addition, in all the samplings some parameters were continuously monitored at the same measurement plane with the equipment for continuously monitoring in both plants: O_2, SO_2, NO_2, NO, CO_2, CO, PM and gas temperature.

Table 1. Characteristics of the fuels used in the experiments (analytical mass, mean values)

Property	Plant A - coal + petrol coke (pulverised)	Plant B - coal (pulverised)	Plant B - petrol coke (pulverised)	Tire without metal
Moisture, W, %	1.24	0.74	0.45	0.32
Combustible, %	81.91	80.06	92.36	98.07
Ash, A, %	16.85	19.20	7.19	1.61
Volatile, %	21.00	18.57	13.19	61.55
Coke residue, %	77.76	80.69	86.36	38.13
Cfix, %	60.91	61.49	79.17	36.52
High heating value, HHV, kJ/kg	28440	27181	33767	44528
Low heating value, HV, kJ/kg	27741	26293	32979	43112
Carbon, C, %	70.81	65.11	81.86	88.14
Hydrogen, H, %	2.97	4.23	3.77	6.26
Nitrogen+Oxygen, N+O, %	5.01	10.59	4.16	1.42
Sulphur, %	3.12	0.13	2.57	2.25

RESULTS AND DISCUSSION

Tables 2 and 3 present the results on the emission of emitted gases from both cement kilns (all results are presented at 273K, 101,3kPa and 10% O_2 in dry gas).

The data shown in Figure 1 apparently indicate that the emission of some metals increased when using the increasing amounts of waste tires. Also, data show a very similar increase of the emission of Pb and Cr in both kilns when feeding tires.

Table 2. Characteristics of the emissions from plant A (without and with tires content)

No. of measurement, tires content as % of total input heat	I 0%	II 5%	III 6.6%	IV 11.35%
O_2, vol%	6.7	8.8	7.07	8.99
Flue gas flow rate, m_N^3/h	120841	154232	155492	168974
Temperature, °C	161	167	171	167
PM, mg/m_N^3	0.7	1.2	9.9	56.4
NO_2, mg/m_N^3	968	1385	1272	493
SO_2, mg/m_N^3	954	1018	58	182
CO, mg/m_N^3	1075	1228	1589	1674
HCl, mg/m_N^3	3.27	8.74	2.62	2.46
HF, mg/m_N^3	0.382	0.461	0.32	0.63
NH_3, mg/m_N^3	1.56	1.83	18.07	43.9

Emission of PM_{10} from plant A is 34 mg/m_N^3.

Figures 1a and 1b present the comparison of the emissions of heavy metals.

The gaseous emission data measured for given fuels mostly show good reproducibility between the runs. For example, the volume percentages of O_2 and CO_2 (combustion quality indicators) during the runs were similar, between 6.7 and 8.99% (plant A) and 11.6 and 13.51% (plant B) for O_2, and 11.4 and 15.3% for CO_2.

It is of particular note that the NO_x emissions generally did not decrease with the addition of tires. This observation is in contrast to other studies, some of which reported that adding tires typically leads to a reduction of NO_x emissions [6]. SO_x emissions decreased with the addition of tires, because the content of sulfur in the fuel mixture decreased.

Nevertheless, all results are under ELV [5] and indicate that the conditions of the furnace (very high temperature, good mixing and excess of oxygen) make the cement kiln factory an ideal place to get a very good combustion. Some paper reported that the amount of organic matter in the cement raw material seems to be responsible for the possible changes in emission [8,9].

CONCLUSION

Experimental results have shown encouraging results: in a particular clinker characteristics were unmodified, and stack emissions (NO_x, SO_2 and CO mainly) were in the case of tires, slightly incremented, but remaining almost always below the law imposed limits, and in some cases they were even decreased.

Table 3. Characteristics of the emissions from plant B (without and with tires content)

No. of measurement, tires content as % of total input heat	I 0%	IV 0%	II 3.3%	III 6%	V 6%	VI 9.1%	VII 9.9%	IX 12%	VIII 15.3%
O_2, vol%	11.88	13.51	12.53	11.6	12.5	11.66	11.65	12.6	11.92
CO_2, vol%	14.64	11.4	12.72	14.89	12.7	14.17	14.04	15.3	13.84
Flue gas flow rate, m_N^3/h	438773	507247	436938	427450	465807	424402	429923	487716	446205
Temperature, °C	140	134	166	140	136	138	146	148	140
PM, mg/m_N^3	7	10.1	7.8	7.4	5.1	8.1	7.9	1.4	7.9
NO_2, mg/m_N^3	511	699	385	387	779	383	418	892	566
SO_2, mg/m_N^3	300	441	170	379	351	330	244	179	297
CO, mg/m_N^3	1508	977	1133	1143	968	1128	1233	736	1673
HCl, mg/m_N^3	2.99	3.38	2.31	3.68	5.76	3.36	3.6	1.92	3.57
HF, mg/m_N^3	0.32	0.75	0.95	0.26	0.64	0.33	0.34	0.45	0.32

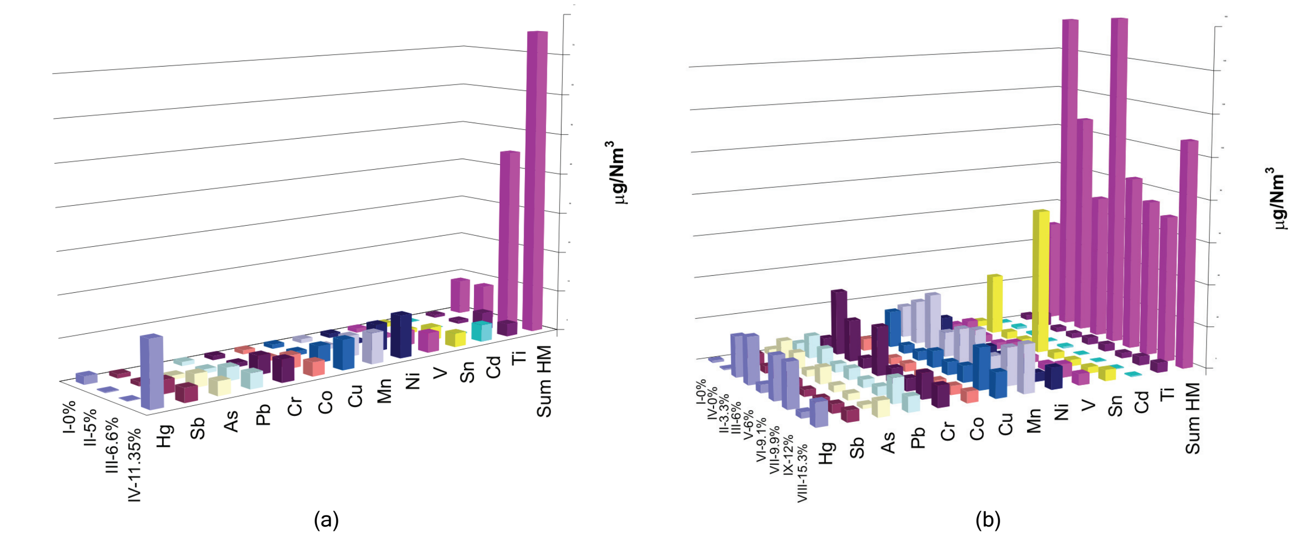

Figure 1. Emission of HMs in Plants A (a) and B (b).

In general terms, it can be concluded that the incremental risk, due to the emissions of the cement plant, is comparatively very small, not only with respect to human health effects, due to the emission of criteria contaminants, but also in relation to toxicological and cancer risks produced by exposure to pollutants such as metals emitted by the facility. Further investigations should also include other waste and also long-range transport and detailed evaluation of health risks.

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ALEKSANDAR JOVOVIĆ[1]
ZORAN KOVAČEVIĆ[2]
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MARKO OBRADOVIĆ[1]
DUŠAN TODOROVIĆ[1]
MIROSLAV STANOJEVIĆ[1]

[1]Univerzitet u Beogradu, Mašinski fakultet, Kraljice Marije 16, 11000 Beograd, Srbija
[2]Metroalfa, d.o.o, LME - Laboratory of Emission Measurements, Zagreb, Croatia

NAUČNI RAD

EMISIJA ČVRSTIH ČESTICA I TEŠKIH METALA PRI KO-SAGOREVANJU GUMA – PRIMER CEMENTNIH PEĆI U REPUBLICI SRBIJI

Ko-sagorevanje otpada se već duže vremena koristi u različitim industrijskim oblastima: industriji cementa, termoelektranama i toplanama, industriji prerade celuloze i papirnoj industriji, proizvodnji gvožđa i čelika, industriji nemetala i hemijskoj industriji. Poslednjih desetak godina, korišćenje čvrstog otpada u pećima za pečenje cementnog klinkera, tj. proizvodnju cementa, značajno raste. Korišćenje otpada u cementnim pećima predstavlja jedan od najefikasnijih tehnoloških procesa za potpunu razgradnju otpadnih materija uz iskorišćenje dobijene toplotne energije. Medjutim, emitovane čvrste čestice i gasovite zagadjujuće komponente u životnu sredinu inhalacijom mogu dospeti i u ljudske organizme. Iz tog razloga, a u cilju odredjivanja rizika po zdravlje ljudi, neophodno je izršiti odgovarajuća merenja emisije ovih komponenta iz izvora emisije. Podaci prikazani u ovom radu predstavljaju rezultate merenja emisije čvrstih čestica, teških metala i neorganskih gasovitih komponenata prilikom ko-sagorevanja guma sa fosilnim gorivom (ugljem) u cementim pećima dva domaća proizvodjača cementa. Korišćene metode uzorkovanja i analize su u skladu sa EU standardima koji se odnose na merenja emisije iz izvora zagadjenja. Rezultati ukazuju da emisije merenih komponenata zadovoljavaju nacionalne i medjunarodne propise, kao i da je kvalitet cemantnog klinkera ostao nepromenjen.

Ključne reči: ko-sagorevanje; cementna peć; otpad; dimnjak; emisija.