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TECHNOLOGICAL AND ENVIRONMENTAL ASPECTS OF CO-FIRING OF SCRAP TIRES WITH STEAM COAL

TECHNOLOGICZNE I EKOLOGICZNE ASPEKTY WSPÓŁSPALANIA ODPADOWYCH OPON Z WĘGLEM

A b s t r a c t

The article presents results of the industrial scale experiment which consisted in utilization of scrap tires by co-firing them with steam coal in a 5 MW boiler. Emission of selected trace elements: Zn, Pb, Cd, Ni and Hg to the environment has been determined during this process. It seems that the examined process may be a real solution to the problem of scrap tires on a local scale.

Keywords: scrap tires utilization, co-firing of coal and tires

S t r e s z c z e n i e

W artykule przedstawiono wyniki przeprowadzonego w skali przemysłowej eksperymentu utylizacji zużytych opon samochodowych na drodze ich współspalania z węglem w kotle o mocy 5 MW. Określono w tym procesie emisje do otoczenia wybranych pierwiastków śladowych: Zn, Pb, Cd, Ni i Hg. Wydaje się, że będący przedmiotem badań proces może stanowić realny sposób rozwiązania problemu zużytych opon samochodowych w skali lokalnej.

Słowa kluczowe: utylizacja opon samochodowych, współspalanie węgla i opon

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1. Introduction

Legal regulations in Poland impose the obligation to achieve an appropriate level of collected used tires on the producers and importers of car tires. These regulations are given in the different legal acts [1–3]. The final level is set at 75% of the weight of the tires sold in Poland (in force since 2007). At the same time storing used tires (whole or granulated) on waste dumps is forbidden. Additionally, another rule sets the minimal level of recycled tires at 15% [3]. It is assessed that currently the amount of tires which should be utilized reaches over 150 thousand tonnes per year [4, 5].

Firing tires with the retrieval of energy in a rotary cement kiln is a basic form of scrap tires disposal in Poland. It is connected with their high calorific value which amounts to about 30 MJ/kg and exceeds the calorific value of steam coal (about 25 MJ/kg) [6–8]. There are four cement plants in Poland that use scrap tires: Górażdże Cement S.A., Lafarge Cement Polska S.A. (Cement plants Małogoszcz and Kujawy) oraz Cementownia Nowiny S.A. It is worth noting that scrap tires may be used as fuel not only in cement kilns. Coal – rubber fuel has also been used since 2002 in stoker boiler of WR-25 type in Przedsiębiorstwo Energetyki Cieplnej S.A. in Wałbrzych. This fuel is a mixture of small coal and about 17% w/w of scrap tires granulated to the size of about 20 mm [9–12]. Although co-firing of coal and rubber brings positive ecological and economical effects, it is, up to now, the only heat generating plant of this type operating in Poland. A wider application of this solution, especially in smaller, local heat generating plants with stoker boilers of WR-5-25 types, might result in lowering the costs of rubber waste utilization (transport costs) and in the reduction of coal use. One of the barriers hindering the development of this method of scrap tires utilization is the necessity of possessing a very efficient system for flue gas cleaning in a heat generating plant, especially for SO_2 [13–15].

The aim of this research was to assess the emission of selected trace elements existing in rubber and coal (Zn, Pb, Cd, Ni and Hg) during their co-firing in small stoker fired boiler of WLM-5 II type. The addition of rubber to the small coal influences considerably its characteristics including the content of some elements (e.g. Zn). Interaction between rubber and coal components might also be expected.

2. Experimental

The experimental part of the work encompassed a 24 hour industrial trial during which the steam small coal (basic boiler fuel) and 12 Mg of mixture of this coal and about 21% w/w granulated scrap tires were fired. A proximate and ultimate analysis was made for both kinds of fuel. Selected trace elements (Zn, Pb, Cd, Ni and Hg) in fuels and solid products of firing (using FAAS method) were determined.

2.1. Raw materials analysis

Steam small coal used in the industrial trial was a low-sulfur coal (sulfur content less than 0.5%) coming from one of the Silesian mines. Tires used as an additive were granulated (size of pieces about 20 mm, chips shape) and came from the installation for rubber granulation operating in Przedsiębiorstwo Energetyki Cieplnej S.A. in Wałbrzych. Additionally, they were cleaned from any steal elements.

Physical and chemical properties of coal and rubber were analyzed according to the Polish Standards:

– moisture content (W_{ex}^r and W^a) was marked in driers or weighing-drying machines according to the PN-G-04511:1980 – Solid fuels. Determination of moisture,
– ash content (A^d) was determined using the firing-in-air method according to the PN-G-04512:1980 – Solid fuels. Determination of ash by gravimetric method,
– gross calorific value (Q_s^a) and net calorific value (Q_i^r) were determined in automatic calorimeter KL-10 on the basis of the PN-ISO-1928:2002 – Solid mineral fuels. Determination of gross calorific value by bomb calorimetric method, and calculation of net calorific value,
– content of coal, hydrogen and nitrogen was determined in automatic analyzer PERKIN ELMER Model 2400 following the PN-G-04571:1998 – Solid fuels. Determination of carbon, hydrogen and nitrogen contents using the automatic analyzers. Macro method,
– total sulfur content was determined on the basis of the PN-G–04514:1981 – Solid fuels. Determination of total sulfur by the high temperature combustion method alkalimetric titration.

The results of proximate and ultimate analysis of components used in the trial are presented in Table 1.

Table 1

Chemical and physical properties of tire shreds and coal for industrial scale experiment

Sample	$\rho^{*)}$	W_{ex}^r	W^a	A^d	S_t	C^a	H^a	N^a	Q_s^a	Q_i^r
	[g/cm^3]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[MJ/kg]	[MJ/kg]
Rubber from scrap tires (R)	1.15	8.9	–	11.6	1.11	70.25	5.89	1.06	31.96	30.81
Coal (C)	1.41	4.3	1.4	21.2	0.46	64.70	4.16	1.11	22.39	21.56

[*] ρ – true relative density.

The analysis shows that the components of coal-rubber blend differ considerably from one another in terms of physical and chemical properties. Most significant differences concern ash and sulfur content and net calorific value.

2.2. Industrial trial

The 12-hour trial of co-firing granulated car tires (chips) with coal was conducted in stoker fired boiler of WLM 5 II type with power of 5 MW. 12 Mg (10 Mg of steam smalls coal and 2 Mg of chips from scrap tires) of coal-rubber fuel was prepared for the trial. It contained on average 21% w/w of scrap tires. This material was mixed using bulldozer--loader. The finished blend was entered into an empty coal bunker from which it was automatically dosed into the stoker. Basic fuel (steam small coal) was also fired under the same conditions (12 hours) for comparison. Figure 1 presents the schematic diagram of the boiler in which the industrial trial was conducted.

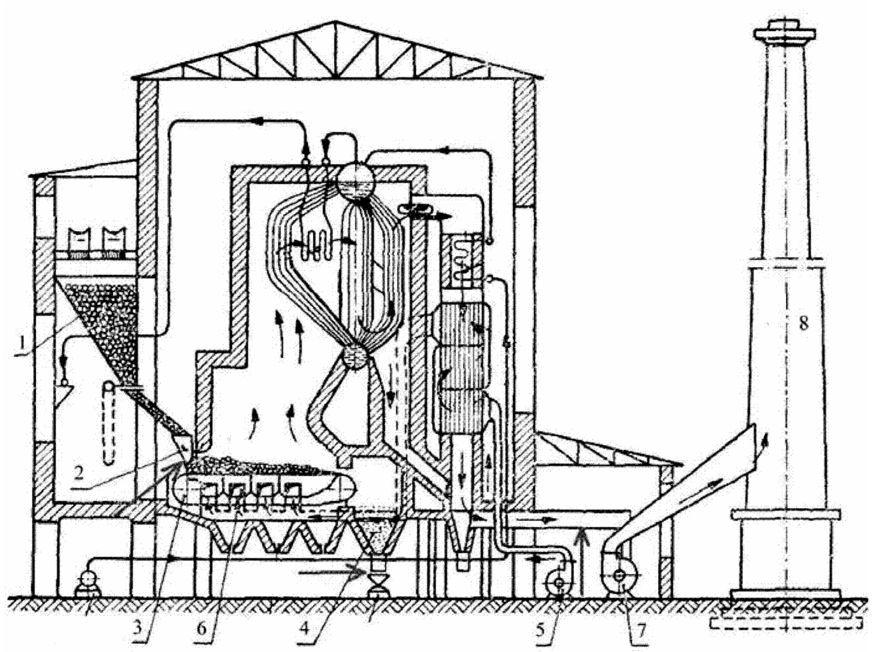


Fig. 1. Main parts of stoker fired boiler: 1 – coal bunker, 2 – charging hopper, 3 – stoker, 4 – chute of slag, 5 – air blower, 6 – blow zones, 7 – exhauster, 8 – chimney

Rys. 1. Główne elementy kotła z rusztem przesuwnym: 1 – zasobnik węgla, 2 – kosz zsypowy, 3 – ruszt, 4 – odprowadzenie żużla, 5 – wentylator podmuchu, 6 – strefy podmuchowe, 7 – wentylator ciągu, 8 – komin

During the trial the following working parameters of the boiler were registered: water flow – $\dot{G}$, Mg/h; inlet temperature of water – t_{in}, °C; outlet temperature of water – t_{out}, °C; oxygen content in flue gas – O_2, %.

Average excess-air coefficient λ and power of the boiler P were calculated on the basis of the values taken from the measuring equipment. The formulas are as follows [16]

$$\lambda = \frac{21}{21 - O_2} \tag{1}$$

$$P = 0.0028 \cdot \dot{G} \cdot c_p \cdot \Delta t = 0.0028 \cdot \dot{G} \cdot c_p \cdot (t_{\text{out}} - t_{\text{in}}),\ \text{MW} \tag{2}$$

where:

c_p – specific heat,
c_p = 4,19 J/g·K

The average values of working parameters of stoker WML 5 II achieved during the industrial trial are presented in Tab. 2. Relatively low powers and very high values of excess-air coefficient λ that were achieved resulted from low heat demand, which followed from the high temperatures of the surroundings during the trial.

Table 2

Stoker parameters during experiments

Fuel	$\dot{G}$	Water temperature		O_2	λ *)	P
		t_{in}	t_{out}			
	Mg/h	°C	°C	%	[–]	MW
Blend	93	47	63	14.78	3.38	1.7
Coal	90	49	62	15.96	4.17	1.4

* Value of excess-air coefficient for nominal heat demand λ = 1.3–1.6.

During the trials of firing the coal-granulated car tires blend and basic fuel (steam small coal), according to the regulations of the Polish Standard PN-G-04502:1990, the following samples of materials were gathered for analysis:

– coal or coal-granulated car tires blend from charging hopper,
– solid remaining after firing (slag) from chute of slag,
– fly ash from cyclones.

Samples were gathered twice: after one hour and after four hours from achieving the stability of boiler parameters. Granulated car tires content varied between 19–23% i.e. on average 21% w/w.

2.3. Determination of selected trace elements content

In order to determine the content of Zn, Pb, Cd, Ni and Hg in fuels used in the experiment and in the solid products of their firing, the samples were mineralized and soluted. The mineralization was carried out in the microwave Uni-Clever mineralizer made by "PLAZMATRONIKA". This mineralizer is purposed to solute samples in a chemical way with wet method in a closed, Teflon container. All the analyzed materials were mineralized and soluted in one-stage procedures using appropriate mixtures of acids: HNO_3 65% (analytical reagent), HF 40% (analytical reagent), $HClO_4$ 70% (analytical reagent), H_2SO_4 96% (special pure reagent) and distilled water (special pure reagent).

The content of selected trace elements in coal, granulated car tires and solid products of their firing and co-firing was determined using atomic absorption spectrometry in a flame variant on AVANTA PM type device made by GBC Scientific Equipment Pty Ltd. and partially using ICP method in device ULTIMA 2000 Sequential ICP made by HORIBA Jobin Yvon Inc. Mercury was determined with the device MA-2000 made by Nippon Instruments Co. This analyzer works on the basis of atomic adsorption using the technique of cold pairs CVAAS.

Analytical curves for the determination of the selected elements were prepared on the basis of original, standard solutions. The efficiency of choosing appropriate mineralization conditions and the correctness of determining the selected elements using FAAS method were verified using the following reference materials:

– Standard Reference Material 1632c; Trace Elements in Coal (bituminous); U.S. Department of Commerce; National Institute of Standards and Technology, Gaithersburg, MD 20899.
– Certified Reference Material; CTA-FFA-1 (Fine Fly Ash), IchiTJ, Warszawa, Polska.

Obtained results confirmed the correctness of the used procedures.

3. Discussion

The comparison of physical and chemical parameters of coal and rubber from scrap tires shows that after blending them in the analyzed proportion there will be a significant change in the properties of fired fuel. Most significant differences concern ash and sulfur content and net calorific value (Tab. 1). Addition of rubber to coal causes a decrease in ash content in the fired blend and increases net calorific value and sulfur content at the same time.

Industrial trial that was conducted shows that the process of co-firing coal with the addition of 21% w/w of rubber from car tires runs without disturbances. Addition of granulated rubber improves the firing process by reducing by one third the content of flammable parts in the solid remaining after firing (in slag). The content of flammable parts in slag decreased from 18.7% to 13.4% (on average). The content of flammable parts (by 0.5%) and sulfur content (from 0.19% to 0.37%) increased subtly in fly ashes. It is in accordance with the expectations and this effect results from technical conditions of the industrial trial (air blow). Relatively big pieces of rubber added to coal cause an increase in the air permeability of the layer on the stoker. It leads to blowing out the smallest particles of fuel, which are later caught with fly ash.

This experiment also allowed for the assessment of behaviour of selected elements during the co-firing of coal and rubber from scrap tires. These were: zinc (Zn), mercury (Hg), lead (Pb), nickel (Ni) and cadmium (Cd) contained in analyzed fuels. The results of the analysis are presented in Table 3. The concentration of analyzed elements in the coal--rubber blend (C-R) was calculated assuming that it is the sum of contents of these elements in coal and in rubber, taking into consideration that the fired blend contained on average 21% w/w of rubber from car tires. Although this industrial trial allowed for taking samples, its range was not sufficient to carry out full and detailed mass balance of the process. It may be derived from the observations that slag accounted for about 20% of the mass of fired fuel and fly ash separated from the flue gas in the cyclone for about 10% of the mass.

Addition of 21% rubber from granulated scrap tires to the coal fired in the boiler causes a very significant increase in zinc content in fuel (almost sixty times). The reduction in Pb and Ni and increase in Cd is insignificant. Due to too low concentration it was not possible to determine the mercury content in the waste rubber. This content is considerably lower than in coal. It may be assumed that the coal-rubber blend contains less mercury than basic fuel (steam small coal).

Observing the distribution of the analyzed elements among solid products of firing (Tab. 3 and Figures 2, 3) it may be noted that mercury (Hg) has the highest volatility. Its concentration in fly ash is nearly one hundred times higher than in slag. It is worth noting that the content of mercury in fly ash and slag obtained by co-firing of coal-rubber blend is about 10% lower than in the case of firing basic fuel. This is a very positive effect for ecological reasons, which results from reduction in content of this element in fired fuel.

Zinc (Zn) is characterised by considerable volatility. Its concentration in fly ashes is nearly five times higher than in slag. It has to be noted that the increase in Zn content after the addition of rubber results in a considerable increase in its content in slag as well as in fly ash. Assuming that analyzed solid products of the firing process account for about 1/3 of the mass of fired fuel, only about 60% of the introduced zinc can be balanced. Therefore one may draw a conclusion that the remaining 40% of zinc escapes with flue gas from the chimney or is reduced and, similarly to the blast furnace process, circulates inside the boiler and settles down on the pipes and furnance lining. This effect should be checked after a longer usage of the boiler fuelled with coal-rubber from scrap tires blend.

Table 3

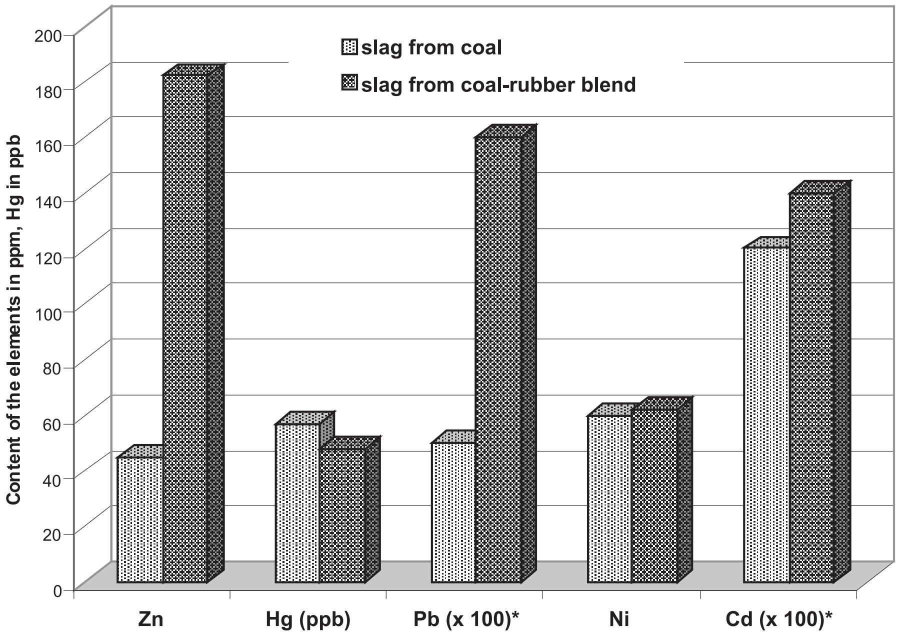
Comparison of the determined concentrations of the selected trace elements in raw materials and solid products of firing during the industrial trial

Symbol	Zn	Hg	Pb	Ni	Cd**
	ppm	ppb	ppm	ppm	ppm
R	15256.7 ± 98.5	N/D	2.5 ± 0.8	1.2 ± 0.1	2.5 ± 1.0
C	55.9 ± 5.2	238 ± 23	11.6 ± 0.8	18.9 ± 4.0	1.7 ± 0.5
C-R	3248.1	N/D	9	15.26	1.91
S0	44.9 ± 0.7	57 ± 3	0.5 ± 1.1	59.9 ± 4.0	1.2 ± 0.7
S1	182.2 ± 22.9	48 ± 2	1.6 ± 0.9	62.3 ± 5.0	1.4 ± 0.9
FA0	248.6 ± 16.8	5140 ± 46	39.2 ± 22.0	104.3 ± 5.8	2.7 ± 0.2
FA1	591.4 ± 22.7	4149 ± 41	37.7 ± 13.2	98.7 ± 4.7	5.4 ± 0.9

[*] Content of the element determined with CVAAS method.
[**] Content of the element determined with ICP method.
N/D – no data,
R – rubber from the used car tires used in industrial trial,
C – steam small coal used in industrial trial,
C-R – steam small coal-rubber blend (79% w/w of coal + 21% w/w rubber from scrap tires); content of elements calculated proportionally,
FA0 – fly ash from steam coal obtained in conditions of industrial trial,
FA1 – fly ash from coal-rubber blend obtained in conditions of industrial trial,
S0 – slag from steam coal obtained in conditions of industrial trial,
S1 – slag from coal-rubber blend obtained in conditions of industrial trial.

Lead (Pb) is also characterized by volatility. The data obtained indicate that the rubber additive, which contains less lead than coal causes a change in distribution of this element among solid products of the described process. The content of lead in slag increases (three times) and only weakly decreases in fly ash at the same time. Similar effects can be observed in the case of nickel (Ni). The decrease in the concentration of nickel in the fired blend (dilution effect) results also in an increase in its content in slag and a slight decrease in its content in fly ash. These effects may suggest interactions between components of coal and rubber during their co-firing.

Adding cadmium (Cd) to the fired fuel together with a rubber additive results in its increased content in the obtained fly ash (almost double increase in concentration). The content of cadmium in the obtained slag increases only slightly.



[*] Multiplier of real concentration of the element.

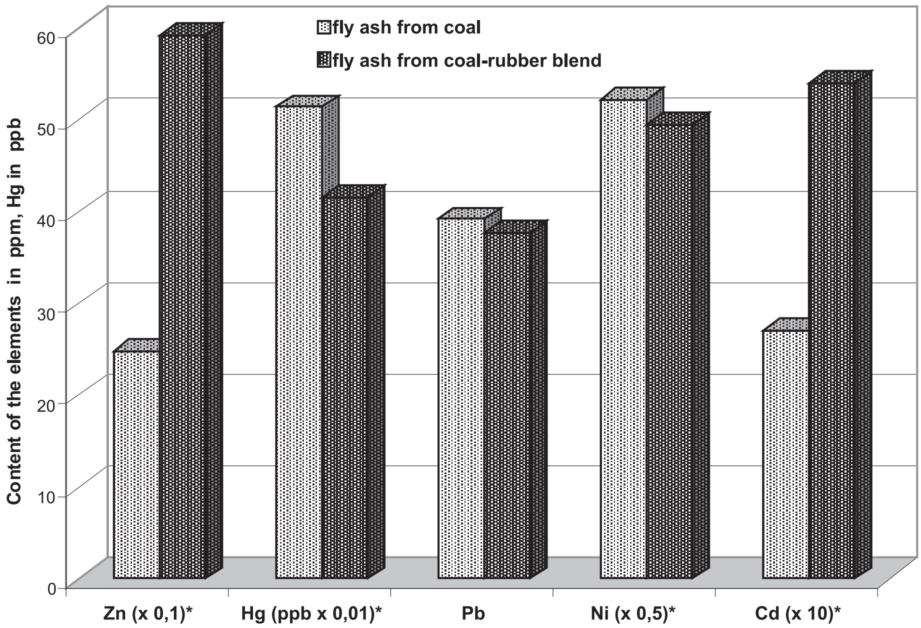
Fig. 2. Content of analyzed elements in slag from coal and coal-rubber blend

Rys. 2. Zawartość analizowanych pierwiastków w żużlu z węgla i mieszanki węgiel-guma

The analysis of the results concerning the distribution of zinc (Zn), mercury (Hg), lead (Pb), nickel (Ni) and cadmium (Cd) among the solid products obtained during the firing process of coal and its blend with rubber indicates that one of the main problems which has to be considered is a significant increase in zinc content in fired fuel. Its behaviour in the furnace and heater areas may lead after some time to technical problems with operation of the boiler. In case of lack of appropriate flue gas cleaning devices one must additionally consider an increased and harmful emission of this element to the environment. The range of concentrations of the remaining elements and their distribution among the firing products in the analyzed process does not differ significantly from the one for firing basic fuel. The observed reduction in mercury emission to the environment is very positive and results from its very low content in the rubber which is added to the coal. It causes a decrease in total mercury content in the fired blend.

4. Conclusions

1. Addition of about 21% w/w of granulated used car tires to the fired steam small coal did not cause additional technical problems in operating stoker boiler WLM-5 II. It can be found that the firing conditions are getting better, which results in a decrease by one third in flammable parts content in slag.



* Multiplier of real concentration of the element.

Fig. 3. Content of the analyzed elements in fly ash from coal and coal-rubber blend

Rys. 3. Zawartość analizowanych pierwiastków w popiele lotnym z węgla i mieszanki węgiel-guma

2. Coal-rubber blends are characterised by a reduced ash content (by about 9%) and a higher net calorific value (by about 11%) in comparison to coal. Addition of granulated scrap tires leads to the increase in sulfur content in fired blend (by about 13%).
3. Researches concerning the behaviour of trace elements like: zinc (Zn), mercury (Hg), lead (Pb), nickel (Ni) and cadmium (Cd) during the co-fireing process of coal-rubber blend indicate that this behaviour is differentiated. The highest volatility characterises mercury. Nevertheless, its low content in scrap tires leads to a decrease in its emission to the environment. The volatility of other elements is lower and therefore their content in slag increases.
4. A very significant increase in zinc content in the fired blend creates a serious problem in the case of co-firing coal with car tires. This increase is caused by a high content of that element in added tires. As a result the concentration of zinc in fly ash and slag increases significantly. There is also a possibility of circulation of metallic zinc in the furnace and boiler area. Therefore, periodic examinations of furnace walls and its pipes should be recommended.
5. The industrial trial of co-firing of small coal and granulated car tires confirmed that it is advisable to use such fuels for firing stoker boilers. Application of such fuel allows for effective utilization of waste tires and is an alternative solution to firing tires in cement kilns. However, one must remember to equip heat generating plants fuelled with coal--rubber blend with an effective flue gas cleaning system, especially in the case of SO_2.

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