Short Communication

Research of the Efficiency of a Secondary Catalyst for Nitrous Oxide Emission Reduction at a Nitric Acid Plant

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Abstract

Installing a secondary decomposing catalyst is an effective method for nitrous oxide emission reduction at a nitric acid production facility. Before the installation of a decomposing catalyst at a nitric acid plant in Devnya, Bulgaria, the N_2O concentration in the tail gas was 1,754 mg/Nm^3 while after the installation the N_2O concentration was 212 mg/Nm^3, which is almost 8.3 times lower. For the entire monitoring period a total N_2O emission reduction of 7,021 Mg was achieved. Research of the catalyst's behavior during the production campaign has been done, proving that the achieved reduction level depends on the catalyst's functional activity and the technological process conditions. Planning the duration of the decomposing catalyst's efficient operation throughout N_2O monitoring data analysis provides effective emission reduction.

Keywords: greenhouse gas, nitrous oxide emissions, production campaign, reduction potential, secondary decomposing catalyst

Introduction

Nitrous oxide N_2O is a greenhouse gas under the Kyoto Protocol [1], with a global warming potential 310 times exceeding that of carbon dioxide, thus becoming one of the main reasons for global warming effect [2-4]. Nitric acid production is a major industrial source of N_2O emissions [5]. From 1 January 2013 onwards N_2O emissions from nitric acid production are included in the scope of the European Union Emission Trading Scheme [6]. Different types of measurements for N_2O emission reduction are applied at nitric acid plants. Primary measurements affect the formation of N_2O during the catalytic oxidization of ammonia. Modifying the geometry of the platinum catalysts is a primary measurement that can lead to a higher conversion of ammonia to NO and/or 30-50% reductions in the formation of N_2O [7, 8]. Secondary measures are taken with regard to the process gas stream, produced in the process from the oxidization catalyst to the absorption tower. Some secondary measurements like homogeneous decomposition and high temperature catalytic decomposition can lead to 80-90% N_2O emission reduction [8-20]. Tertiary measures can be taken in the process that takes place between the absorption tower and the expansion turbine. Low temperature catalytic decomposition, selective catalytic reduction with hydrocarbons, and non-selective catalytic reduction of NOx with simultaneous N_2O reduction are tertiary measurements that can reduce N_2O emission up to 98-99% [7, 9]. Sequential (End-of-Pipe) measurements include some of the techniques described as tertiary, which can also be placed behind the expansion turbine (selective catalytic reduction, catalytic decomposition). End-of-pipe measurements can perform 80-97% N_2O emission reduction [7-9].

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High temperature catalytic decomposition is a secondary measurement that is based on the decomposition of N_2O right after its formation to oxygen and nitrogen at high temperature (1,073-1,223 K) throughout installing a suitable decomposing catalyst in the reactor chamber, where an oxidation of ammonia to NO takes place and N_2O and nitrogen are formed as undesired by-products of the reaction [21-24]. Studies upon the performance of different N_2O decomposing catalysts under various conditions have been done in order to achieve a significant improvement of the catalytic activity and more effective N_2O decomposition [10-20]. The objective of the present research is to explore the impact of the catalyst's functional activity and the technological process conditions upon the level of N_2O emission reduction.

Experimental Procedures

A method for N_2O emission reduction through installing a secondary non-platinum decomposing catalyst was applied at a nitric acid plant in Devnya, Bulgaria, in September 2005. The decomposing catalyst was installed right under the platinum gauze pack as an equally disturbed layer on top of the support grid of the reactors separated on top and bottom by steel screens [25]. The N_2O reducing catalyst is made of precious metal-coated ceramic pellets. Each pellet consists of 20% CuO, 16% ZnO, and Al_2O_3, plus promoters. The thickness of the catalytic layer is approximately 28 mm.

Continuous monitoring of N_2O emissions was done after the installation of the decomposing catalyst throughout online measurement of the tail gas parameters (N_2O concentration, flow rate, temperature, absolute pressure, and oxygen content). Within this research a study upon the decomposing catalyst's behavior during the production campaign was done by analyzing N_2O emission monitoring results from the moment of installing the secondary decomposing catalyst. A production campaign is the period of time beginning from the installation of a new platinum gauze pack until the subsequent plant shut down for its replacement [26]. Research results provide a reasonable conclusion about the subordination among the achieved catalytic reduction level, the duration of the production campaign, and technological parameters of the production process.

Results and Discussion

The nitric acid plant in Devnya, Bulgaria, is operating continuously and the duration of one production campaign usually varies between 8 and 10 months (30-40 weeks), followed by 2 to 4 months of outage for replacing the platinum gauze pack in order to recover the platinum loss that occurred during operation at high temperature in the reactor chamber. The effectiveness of N_2O catalytic reduction has been estimated by analyzing the monitoring data collected during seven production campaigns – from September 2005 when the secondary decomposing catalyst was installed until the last replacement of the platinum gauze pack, which took place in July 2012. For this period of time only one replacement of the secondary decomposing catalyst was done in November 2009. Nitrous oxide emission levels have been measured as kg N_2O emitted into the atmosphere per week for every production campaign during the monitoring period. Monitoring data representing the N_2O emission levels (kg per week) for the entire monitoring period is charted on Fig. 1.

Separate production campaigns have different duration – approximately 32-35 weeks. The briefest production campaign 2006-07 lasts 22 weeks due to the long-lasting maintenance of the plant technological equipment and the most prolonged production campaign (2007-08) lasts 45 weeks. It is a common feature of all production campaigns that N_2O emission levels are increasing gradually as time goes by due to platinum evaporation during the ammonia oxidation at high temperature in the reactor chamber. Platinum loss causes less effective catalytic operation of the platinum gauzes and increased levels of N_2O formation during the production campaign. The increased formation of N_2O during the ammonia oxidation reaction leads to higher concentrations of this pollutant in the tail gas, even if a secondary decomposing catalyst is installed. N_2O emission levels are increasing gradually along production cam-

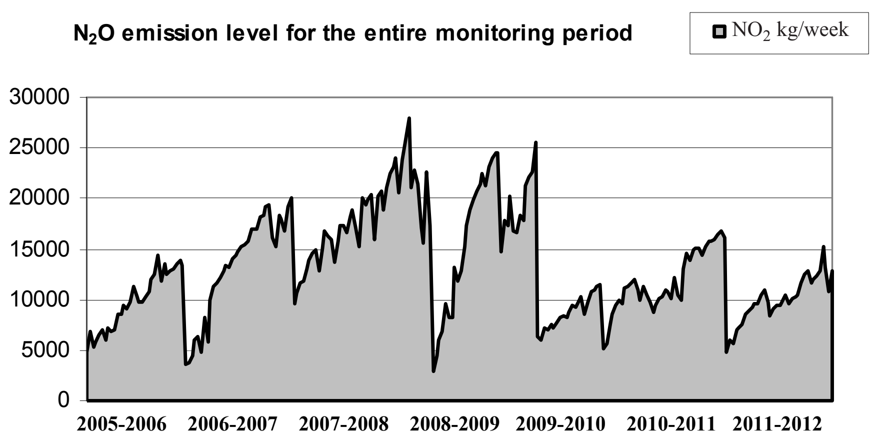

Fig. 1. N_2O emission level for the entire monitoring period.

paigns, which proves the exhaustion of the secondary catalyst's reduction potential.

During the first production campaign 2005-06 from the monitoring period N_2O emission levels start at 4,769 kg per 1st week and increase gradually to 13,937 kg per 31st week and 13,398 kg per 32nd week. The highest measured value is 14,360 kg per 24th week.

The second production campaign 2006-07 starts at even lower emission levels – 3,572 kg per 1st week and 3,719 kg per 2nd week, but in the 17th week a value of 14,396 kg is measured, which exceeds the highest emission level of the first production campaign. The second production campaign lasts 35 weeks and a peak value of 20,123 kg per the last week is measured, which is 1.4 times higher than the peak value of the first production campaign.

The third production campaign 2007-08 is the most prolonged one (45 weeks duration). High emission levels of N_2O are measured at the very beginning – 9,575 kg per 1st week. Emission levels are increasing gradually as the value of 20,483 kg per 26th week is exceeding the peak value of the second production campaign. The highest emission level for this campaign is 27,942 kg per 38th week. The third production campaign ends with a slight emission level decrease due to reduced production capacity of the nitric acid plant – 17,327 kg per 45th week.

The fourth production campaign (2008-09) is the briefest one (22 weeks duration). It starts at very low emission levels – 2,880 kg per 1st week and 4,442 kg per 2nd week, but a progressive increase is registered at the end of the campaign as a peak value of 24,527 kg is measured in the last week.

The fifth production campaign 2009-10 starts at high N_2O emission levels – 14,673 kg per 1st week. A trend of emission level increase is registered as a value of 25,620 kg per 12th week. A replacement of the secondary decomposing catalyst has been done in November 2009, which is almost in the middle of the production campaign. A significant reduction of N_2O emissions is registered right after the replacement of the catalyst – 6,352 kg per 13th week. The production campaign lasts 33 weeks and an emission level of 11,464 kg per last week is measured, which is the peak value after the replacement of the catalyst and yet is more than twice lower than the peak value for the entire production campaign – 25,620 kg per 12th week.

The sixth production campaign (2010-11) lasts 40 weeks. It starts at 5,165 kg N_2O per 1st week which is even lower than the emission level measured immediately after replacing the secondary catalyst in week 13 of the previous production campaign. N_2O emission levels increase gradually and a peak value of 16,813 kg is measured in week 39. The production campaign ends at 16,036 kg N_2O per the last week.

The last production campaign (2011-12) from the monitoring period lasts 35 weeks. It starts at very low N_2O emission levels – 4,838 kg per week 1. A peak value of 15,269 kg N_2O is measured in week 32 and a slight emission reduction is registered at the very end of the campaign – 12,875 kg per the last week.

From the beginning of the production campaign (2005-06) till the end of production campaign (2011-12) the total amount of N_2O emissions is $3{,}321\times10^3$ kg (3,321 Mg), while the supposed value of N_2O emissions for the same period without the catalyst being installed would have been $10{,}342\times10^3$ kg (10,342 Mg) [25, 27]. This means that a total N_2O emission reduction of 7021×10^3 kg (7,021 Mg) has been achieved for the monitoring period.

N_2O emission levels during each production campaign from the monitoring period is increasing gradually. Also, N_2O emission levels at the end of each campaign are higher than the emission levels at the end of the previous campaign. The secondary catalyst's replacement takes place in the middle of the production campaign (2009-10) when a significant reduction of the N_2O emission level is distinguished. Although low emission levels are typical for every campaign start, a solid trend for reducing the emission levels at the end of the campaign (including the peak values) is observed after the replacement of the secondary catalyst compared to those before the replacement took part. During the week before the catalyst replacement the N_2O concentration is measured to be almost equal to the concentration at the end of every production campaign before the implementation of the decomposing catalyst. At the end of the production campaign (2004-05) the N_2O concentration is 1,754 mg/Nm^3 while before the secondary catalyst replacement the average daily concentration is 1,050 mg/Nm^3, which proves the exhaustion of the catalyst's reduction potential.

Statistic data about N_2O emission mean value (kg) in every production campaign and standard deviation is presented in Fig. 2.

Results indicate that at the beginning of the research (production campaign 2005-06) N_2O emission mean value is 9,828 kg and it increases significantly during the next campaign 2006-07, up to 13,345 kg as the difference is of strong statistical significance ($P<0.001$). The increase is more significant during the next production campaign 2007-08, when the N_2O emission mean value is 18,000 kg ($P<0.001$). During the production campaign 2008-09 high levels of N_2O emission are still registered – up to 17,551 kg, indicating the necessity of replacing the secondary catalyst. During the next campaign (2009-10) the decomposing catalyst is replaced and the N_2O emission mean value drops considerably to 8,774 kg as the decrease is of strong statistical significance ($P<0.001$). The N_2O emission mean value during the next two production campaigns stays lower than the value before the replacement of the catalyst ($P<0.001$), which proves the effect of the decomposing catalyst's functional activity upon its emission reduction potential.

The N_2O daily average concentration (mg/Nm^3) as a function of time during each production campaign from the monitoring period is charted in Fig. 3.

A trend for a gradual increase of this pollutant's concentration is observed as higher N_2O concentrations are measured at the end of each production campaign compared to those measured at the end of the previous campaign.

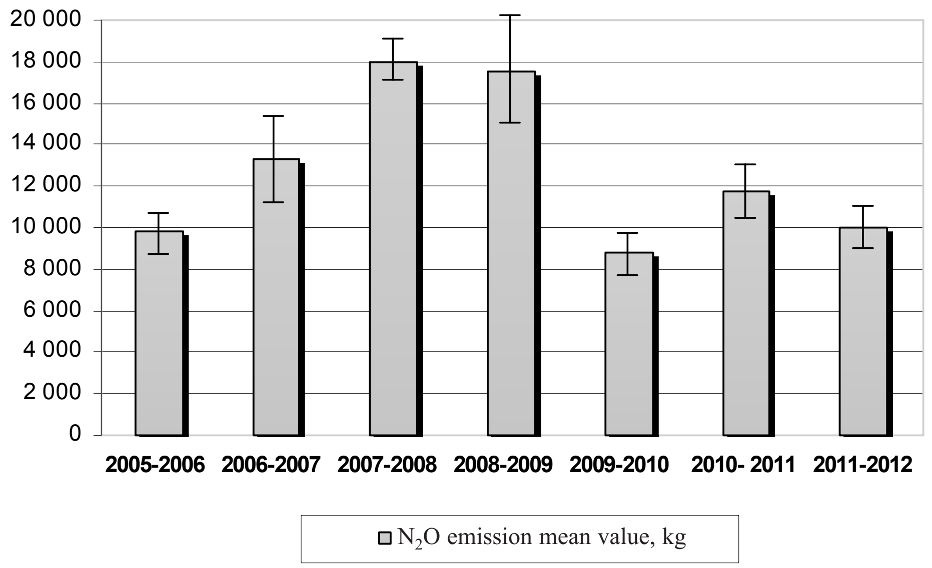

Fig. 2. Statistics on N_2O emission mean value and standard deviation.

The first production campaign (2005-06) from the monitoring period starts at 212 mg/Nm^3 N_2O daily average concentration, which is 8.3 times lower than the N_2O concentration measured at the end of the 2004-05 production campaign before the secondary catalyst's installation. At the end of the 2005-06 campaign the N_2O concentration is 677.5 mg/Nm^3 and the peak value for this campaign is 745 mg/Nm^3 measured during the last week of the campaign (Fig. 3a). The lowest N_2O concentration during the second production campaign 2006-07 is 130.7 mg/Nm^3 measured during the first week of the campaign while the peak value is 879.5 mg/Nm^3 measured during the next to the last week (Fig. 3b). The third production campaign 2007-08 starts at 410.1 mg/Nm^3 N_2O concentration but extreme peak value of 1,185.2 mg/Nm^3 is measured during week 38 of the campaign followed by a slight N_2O concentration decrease due to reduced production capacity of the nitric acid plant (Fig. 3c). The fourth production campaign 2008-09 starts at a very low N_2O daily average concentration of 106.9 mg/Nm3 measured during the first week of the campaign, while the peak value is 1,054 mg/Nm^3 measured during the last week (Fig. 3d). The 2009-10 production campaign starts at an extremely high N_2O concentration of 1,131.6 mg/Nm^3 measured during the first day of the campaign, which is the peak value for the entire campaign. Every daily average N_2O concentration measured during week 12 of this campaign exceeds 1,000 mg/Nm^3, which is almost equal to the concentration of this pollutant in the tail gas without a secondary decomposing catalyst being installed in the reactor chamber, and proves that the reduction potential of the catalyst has been exhausted. The replacement of the decomposing catalyst during week 13 of this production campaign leads to a significant N_2O concentration decrease – 278.3 mg/Nm^3 is measured right after the replacement, which is 4 times lower than the highest N_2O concentration within this campaign, and 471.7 mg/Nm^3 is measured during the last day of the campaign (Fig. 3e).

The sixth production campaign (2010-11) starts at N_2O concentration of 288.3 mg/Nm^3, which is almost equal to the N_2O daily average concentration measured right after the replacement of the decomposing catalyst in the middle of the previous campaign and ends at N_2O concentration of 711.5 mg/Nm^3, which is near the peak value of 720.9 mg/Nm^3 measured during week 38 of the campaign (Fig. 3f). The last production campaign (2011-12) from the monitoring period is quite like the previous one – the campaign starts at N_2O concentration of 235.2 mg/Nm^3 and ends at N_2O concentration of 725.6 mg/Nm^3, which is the peak value for this campaign (Fig. 3g). A solid trend for a gradual increase of the measured daily average N_2O concentration during the production campaign is registered and higher N_2O concentrations are measured at the end of each production campaign compared to those measured at the end of the previous campaign, which means that the decomposing catalyst's reduction potential is exhausted over time.

Conclusions

From 1 January 2013 onwards, N_2O emissions from nitric acid production are included in the scope of the European Union Emission Trading Scheme, thus obliging all the European nitric acid plant operators to apply measurements for reducing N_2O emissions in compliance with the European Community's commitment to reduce overall greenhouse gas emissions by at least 20% below 1990 levels by 2020 [6]. A study upon the achieved levels of N_2O emission reduction proves that the high reduction potential of the secondary decomposing catalyst as an actual reduction of 73% of the N_2O emissions at the nitric acid plant in Devnya, Bulgaria is achieved [27]. According to the results of research upon the behavior of the decomposing catalyst, its reduction potential depends on the duration of the secondary catalyst's functional activity and the specific technological conditions of the production process. The exhaustion of the secondary catalyst due to inactivation of the precious metal active layer upon the ceramic pellets after prolonged operation leads to decreased reduction potential of the catalyst. N_2O concentration in the tail gas exceeding 1,000 mg/Nm^3 is typical for nitric acid production, where no emission abatement technique is applied and proves the exhaustion of the decomposing catalyst. As the average duration of the production campaign varies between 30 and 40 weeks, the exhaustion of the secondary catalyst's reduction potential takes place after operation during 3 production campaigns. Technological parameters of the production process also affect the functional activity of the decomposing catalyst. Reducing the production capacity of the

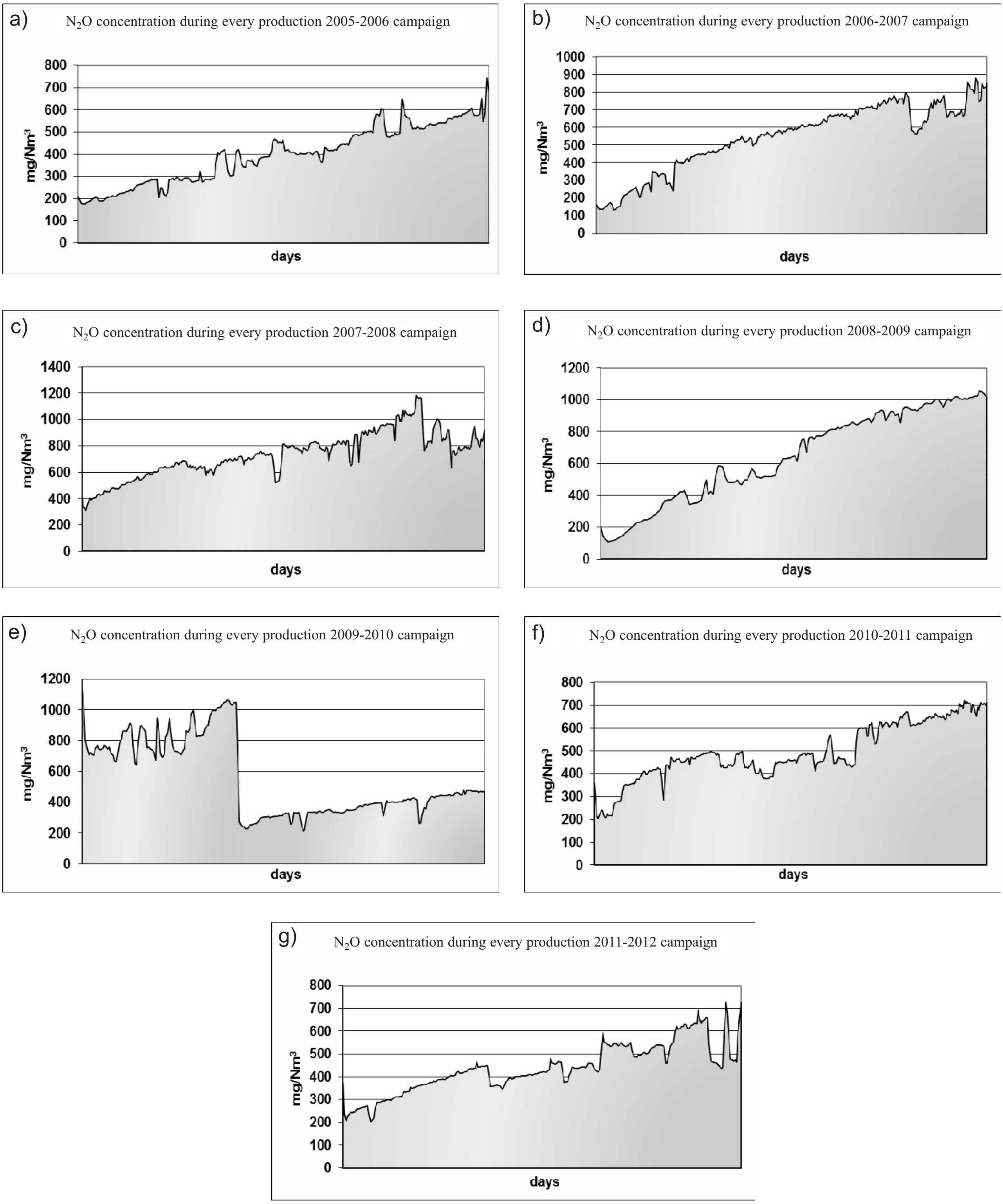

Fig. 3. N_2O concentrations during every production campaign from the monitoring period.

nitric acid plant leads to slower exhaustion of the secondary catalyst's reduction potential. A research of N_2O monitoring data provides the possibility for planning the effective lifetime of the secondary decomposing catalyst and its replacement necessity. Nitric acid plant operation with a secondary catalyst kept at high reduction, potential guarantees effective N_2O emission reduction which is a step toward global warming prevention.

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