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STUDY ON EMISSIONS OF POLLUTANTS COMING FROM THE RUBBER DEVULCANIZATION S.C. ARTEGO S.A. TG-JIU, USING AS A REGENERATION AGENT THE MEDIUM AROMATIC OIL

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ABSTRACT. Lignite SC ARTEGO SA, Rubber and Renewable Department and Power Station, following the processes or different technological operations, removes residual gaseous effluents, which contain pollutants: CO, NOx, SO_2, particulate matter, SO_2, H_2S, ammonia, mercaptani, acroleina and COV. After cycle devulcanization opening and autoclaves, hot gases are discharged through a tubing into the atmosphere after passage through scruber. Its role is to drop the gas temperature, the concentration decrease in emissions and to retain the fine particles of dust (pudreta rubber), involved with the gaseous pollutants. For rubber devulcanization, are used in frequently as an agent of regeneration, environmental aromatic oil (type Teleajen). To calculate the actual height of the sources of pollution and dispersion parameters were used formulas developed by Briggs in 1982. Applying the model and climatological dispersion were calculated on the maximum concentrations of environmental mediation (daily - 24 h) for NO_2, SO_2, H_2S, NH_3, acroleina. Emissions of pollutants SO_2, H_2S, NH_3, and COV acroleina determined to cart exhaust, the entry and exit of the scrubber initial and of the scrubber modernized by decreasing pressure comparison with CMA, are represented graphically.

ИЗУЧАВАНЕ НА ЗАМЪРСЯВАЩИТЕ ЕМИСИИ ОТ ОТДЕЛЕНИЕТО ЗА КАУЧУКОВО ДЕВУЛКАНИЗИРАНЕ S.C.ARTEGO S.A., **ТУРГУ ЖИЛ**, **ИЗПОЛЗВАЩО АРОМАТИЗИРАНО МАСЛО КАТО ВЪЗСТАНОВЯВАЩ АГЕНТ**

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РЕЗЮМЕ. Лигнитният SC ARTEGO SA, Каучуковото и обновено отделение и ТЕЦ в резултат на различни технологични процеси, отстраняват утаечните газообразни изпарения, съдържащи замърсителите: CO, NO, SO_2, частици, SO_2, H_2S, амоняк и COV. След цикъл на девулканизация и отваряне на клапите, горещите газове се изпускат в атмосферата. По този начин се намалява температурата на газа, концентрацията на емисиите и се задържат фините прахообразни частици, намиращи се в газовите замърсители. За каучуковата девулканизация като агент се използва ароматично масло (тип Телеагент). За изчисляване на действителните стойности на замърсителите и дисперсията са използвани формулите на Бригс (1982 г.). Прилагайки модела и климатоложката дисперсия бяха изчислени максималните концентрации на азотен двуокис, SO_2, H_2S, NH_3, за 24 часа. Емисиите на замърсителите SO_2, H_2S, NH_3, COV са представени с помощта на графики, като намаляването се извършва чрез CMA.

Introduction

The emission of pollutants in the atmosphere is removing pollutants solid, liquid or gaseous, point source or area (stationary sources fixed or mobile), discharging into the atmosphere, pollutants from different socio-economic activities.

S.C. ARTEGO S.A., Rubber and Renewable Department and Power Station, following the processes or different technological operations, removes residual gaseous effluents, which contain pollutants:

- CO, NOx, SO_2, particulate matter (from burning gas to fuel power station, waste gases are discharged through a chimney dispersion with height from the ground 20 m in diameter and 1,4 m peak)
- SO_2, H_2S, ammonia, mercaptani, acroleina, COV (Department of Rubber renewable exhaust emissions are routed through a tubing, which takes the waste gases from the scrubber gas washing plant; tubing has a section of 0,196 m² and a ground height of 12 m).

Thermal power of the central heating is 34,9 MW/boiler. Since Central operates with a single boiler (the second one is spare), a thermal power plant is less than 50 MW. In table 1 are given PA and PI for combustion installations, which use fuel gas and thermal power below 50 KW, and in table 2 are given PA and PI, for the pollutants resulted from technogical processes rubber-regeneration.

Table 1.
Alert thresholds and the thresholds for intervention outbreaks fueled with gaseous fuel for combustion plants with thermal power less 50 MW / t.

Indicators	U.M.	Fuel gas	
		PA	PI
- powders	mg/m³N	3,5	5
-sulfur oxides (SO_x)	mg/m³N	24,5	35
-nitrogen oxides (NO_x)	mg/m³N	245	350
-carbon monoxide (CO)	mg/m³N	70	100

Table 2.
Thresholds and alert thresholds for pollutants Intervention resulted from processes rubber-regeneration.

Indicators	U.M.	PA	PI
- powders	mg/m^{3}N	35	50
- H_2S	mg/m^{3}N	3,5	5
- sulfur oxides (SO_x)	mg/m^{3}N	350	500
- ammonia	mg/m^{3}N	21	30
- acroleina	mg/m^{3}N	14	20
- VOCs	mg/m^{3}N	100	150

2. Material and methods

Power station is equipped with 2 types Teruzzi boilers that produce steam required Rubber of the regeneration. Central heating power of 34,9 MW/boilers, each boiler has a burner, the fuel gas being used. Central functions with a single boiler (the second being the backup boiler) gas discharge being through two metal baskets, one for each boiler.

Were measured concentrations of pollutants discharged into the atmosphere by means of:
- automatic (burned gas)
- lab (for dust)
- spectrophotometric (for SO_2, H_2S, ammonia, acroleina).

For measurements of gas burned (performed Analyzer Testo 350) if the outcome measurements are expressed in ppm transformation in mg/Nm^3, is done by multiplying by appropriate factors (2,05, 2,93, 1,25 for NOx, SO_2 and CO, respectively), report the conditions of normal temperature and pressure (0°C and 1013 mbar).

Because the emission limit values (VLE) are reported at an oxygen content of the reference of 3% (volume), the fuel gas, the measurements should be related to the content using the formulas:

$$\mathrm{Noxa}_{[\mathrm{mg/Nm^3}]_{3\%O_2}} = \{\frac{(21-3)}{21-[\mathrm{O_2}]}\}\cdot[\mathrm{Noxa}] \quad [\mathrm{mg/Nm^3}] \quad (1)$$

where:
$\mathrm{Noxa}_{[\mathrm{mg/Nm^3}]_{3\%O_2}}$ = concentration noxa expressed under Order 462/1993 and 541/2003; 21 = volume of oxygen content in air;
3% = volume content of oxygen reference for gas combustibill;
O_2 = oxygen content by volume measured in effluent gas [%];
[noxa] = noxa concentration [mg/Nm^3].

Reporting to the volumetric flow is normal using the equation:

$$\frac{Q_v}{T} = \frac{Q_{v0}}{T_0} \quad (2)$$

where:
Q_v, Q_{v0} = volumetric flow corresponding temperatures;
T, T_0 = temperature [^{0}K]

Mass concentrations of pollutants associated gas combustion are reported in normal conditions (0°C and 1013 mbar), so are expressed in mg/Nm^3, the oxygen content of specific reference fuel used (Gamaneci et al., 2008).

After cycle devulcanization opening and autoclaves, hot gases are discharged through a tubing into the atmosphere after passage through scruber. Its role is to drop the gas temperature, the concentration decrease in emissions and to retain the fine particles of dust (pudreta rubber), involved with the gaseous pollutants. Effluent gas samples were taken from tubing entry pollutants in scrubber respectively output to be determined yield install. For rubber devulcanization, are used in frequently as an agent of regeneration, environmental aromatic oil (type Teleajen).

Calculating concentrations in the atmosphere were carried out with Gaussian dispersion model, focused on wind, which allows knowledge model concentrations at ground level at distances of different sources and for different weather situations.

Equation for calculating the dispersion is:

$$C(X,Y) = \left(\frac{Q}{2\pi\cdot\sigma_y\cdot\sigma_x\cdot U}\right)\cdot\exp\left(-0{,}5\cdot\frac{Y^2}{\sigma_{y^2}}\right)\cdot\exp\left(-0{,}5\cdot\frac{H^2}{\sigma_{X^2}}\right) \quad (3)$$

where:
C (X,Y) = pollutant concentration in the point x, y;
Q = mass flow rate;
H = effective height of the source of pollution, according to the basket height, diameter at the top of its speed and temperature of exhaust gas air stratification;
σ_X, σ_Y = dispersion parameters depending on source-receiver distance, stratification of air in which instead pollutant dispersion (urban-rural);
U = wind speed at source height.

To calculate the actual height of the sources of pollution and dispersion parameters were used formulas developed by Briggs in 1982 (Popa et al., 2008). For the calculation was considered an area of 2000 x 2000 m, with step of 200 m, the unit being placed in zone line. Applying the model and climatological dispersion were calculated on the maximum concentrations of environmental mediation (daily - 24 h) for NO_2, SO_2, H_2S, NH_3, acroleina [1].

3. Results and discussion

Determinations of burned gas and powders have been made to cart dispersion of a boiler Teruzzi; the results are presented in table 3:

Table 3. *Results of dust and gas burned determinations at Power station*

Source emission	Pollutant	UM	Concentration					Emission limit value /Order 462/93
			Det. 1	Det. 2	Det. 3	Det. 4	Media	
Cart dispersion	powders	mg/Nm³	0	0	0	0	0	-
		mg/Nm³	0	0	0	0	0	5
	CO	ppm	1	0	1	0	-	-
		mg/Nm³	1,58	0,00	1,52	0,00	0,77	100
	NOx	ppm	142	145	149	148	-	-
		mg/Nm³	367,71	363,73	370,99	367,51	367,48	350
	SO_2	ppm	0	0	0	0	-	-
		mg/Nm³	0	0	0	0	0	35
	O_2	%	6,75	6,29	6,18	6,14	6,34	-

From the results presented in the table as shown in the effluent gaseous waste resulting from the power station, NO_2 concentrations exceed the threshold and alert threshold for intervention, which corresponds to a significant pollution of the order I. In consequence, it is recommended to optimize combustion by mounting a burner with low NOx.

To determine the level of emissions routed, generated by stationary source of Regenerated Rubber, measurements were made of emissions after devulcanization cycle for each of the four autoclaves of the plant, the results being presented in table 4:

Table 4. *Emissions of pollutants, using as a regeneration agent a medium aromatic oil (initial scrubber)*

Source emission	Pollutant	UM	Concentration					Emission limit value/ Order 462/93
			Det.1	Det.2	Det.3	Det. 4	Media	
Exhaust Cart scrubber before water curtain)	SO_2	mg/Nm³	493,2	510,02	515,5	543,76	515,62	500
	H_2S	mg/Nm³	5,98	6,23	7,30	8,33	6,96	5
	NH_3	mg/Nm³	29,86	30,23	32,25	40,66	33,25	30
	Acroleina	mg/Nm³	19,7	18,89	22,98	24,83	21,60	20
	COV	mg/Nm³	6500	6580	6920	6670	6667,5	150
Exhaust Cart (scrubber after water curtain)	SO_2	mg/Nm³	411,2	420,8	421,06	431,98	421,26	500
	H_2S	mg/Nm³	4,80	4,96	4,24	5,92	5,23	5
	NH_3	mg/Nm³	19,8	20,25	20,67	22,56	20,82	30
	Acroleina	mg/Nm³	16,9	17,25	17,05	17,68	17,22	20
	COV	mg/Nm³	5820	5850	6030	5910	5902,5	150

Emissions of pollutants SO_2, H_2S, NH_3, and COV acroleina determined to cart exhaust, the entry and exit of the scrubber and initial comparison with CMA, are represented graphically in figures 1,2,3,4 and 5.

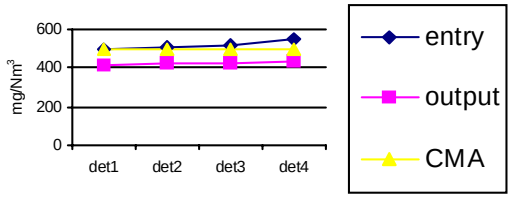

Fig.1. Emissions of SO_2 at entry / exit, scrubber initial

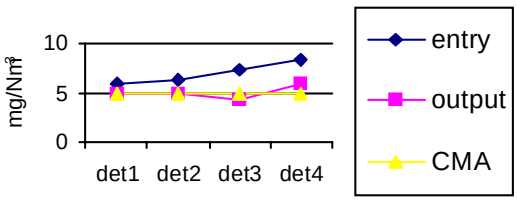

Fig.2. Emissions of H_2S at entry / exit, scrubber initial

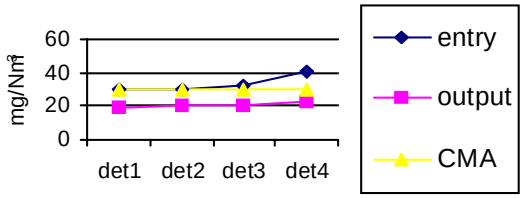

Fig.3. Emissions of NH_3 at entry / exit, scrubber initial

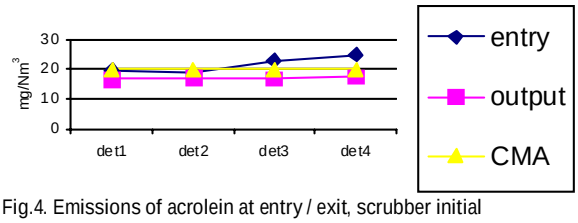

Fig.4. Emissions of acrolein at entry / exit, scrubber initial

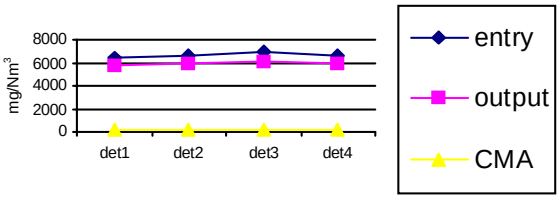

Fig.5. Emissions of COV at entry / exit, scrubber initial

After passing through the wash, it is found that the emission limit value, the threshold for intervention (PI), the indicators SO_2, NH_3, and overcoming acroleina alert threshold (PA) for SO_2, and ammonia acroleina at one sample analyzed. For H_2S and VOC is exceeded and alert thresholds and thresholds for intervention, which proves the efficiency low scrubber is the recommended replacement. Increasing capacity for retention of existing scrubber and increase its efficiency, has been replaced with other modernized, more efficient [2].

After the cycle devulcanization opening and autoclaves, hot gases are discharged with a pressure of about 30 atm. Since this pressure is relatively low absorption capacity of the plant washing, pressure drop is needed gas before discharge in tubes. The only viable solution is that, after devulcanizare gases to be discharged into a second autoclave not working (empty), the pressure decreasing to half (approximately 15 atm.)

After installation of new equipment washing and taking measure to decrease the gas pressure, were again made determinations on the route of the exhaust gas effluent (before and after the scrubber), using in the recipe, as an agent of regeneration, environmental aromatic oil, type Teleajen. Results are presented in table 5.

Emissions of pollutants SO_2, H_2S, NH_3, and VOC acroleina determined to Cart exhaust, the entry and exit of the scrubber modernized by decreasing pressure and comparing with the CMA, are represented graphically in figures 6,7,8,9 and 10.

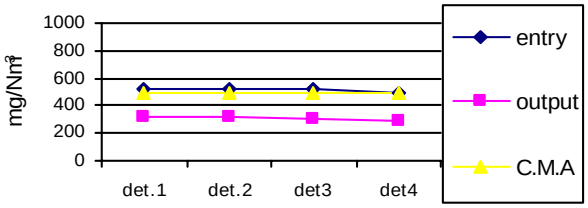

Fig.6. Emissions of SO_2 at entry/exit, scrubber modernized

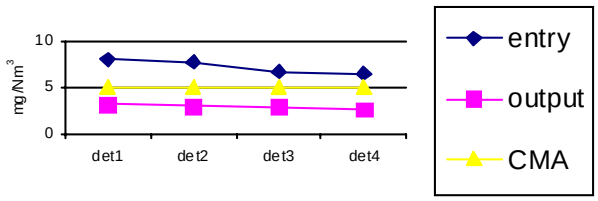

Fig.7. Emissions of H_2S at entry/exit, scrubber modernized

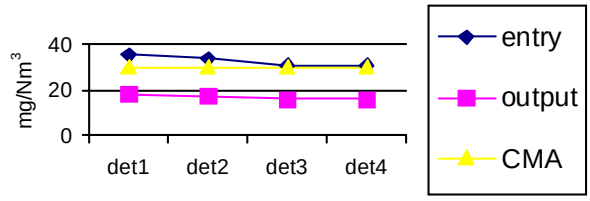

Fig.8. Emissions of NH_3 at entry/exit, scrubber modernized

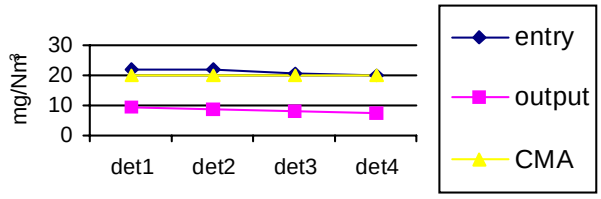

Fig.9. Emissions of acroleina at entry / exit, scrubber modernize

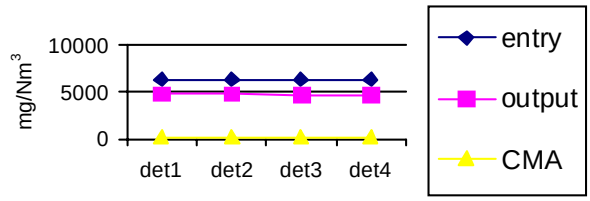

Fig.10. Emissions of COV at entry / exit, scrubber modernized

Comparing values obtained with the emission limit values, is observed a drastic decrease in concentrations of pollutants after passage through the wash, they are framing in the VLE, and even in the alert threshold, except for volatile organic compounds, whose concentration has major overruns.

Table 5. *Emissions of pollutants, using as a regeneration agent a medium aromatic oil (imodernized scrubber)*

Source emission	Pollutant	UM	Concentration					Emission limit value /Order 462/93
			Det.1	Det.2	Det.3	Det 4	Media	
Exhaust Cart (scrubber before water curtain)	SO_2	mg/Nm3	525,03	522,06	515,33	498,06	515,12	500
	H_2S	mg/Nm3	78,96	7,65	6,62	6,41	7,16	5
	NH_3	mg/Nm3	35,63	33,98	31,22	31,09	32,98	30
	Acroleina	mg/Nm3	22,23	21,96	20,97	20,12	21,32	20
	COV	mg/Nm3	6420	6410	6380	6350	6390	150
Exhaust Cart (scrubber after water curtain)	SO_2	mg/Nm3	323,23	315,02	311,32	295,43	311,25	500
	H_2S	mg/Nm3	3,23	3,01	2,95	2,65	2,96	5
	NH_3	mg/Nm3	18,56	17,53	16,10	16,01	17,05	30
	Acroleina	mg/Nm3	9,65	8,36	7,72	7,39	8,28	20
	COV	mg/Nm3	4850	4830	4690	4700	4767,5	150

In conclusion, the new plant is more efficient than the first, but not entirely, considering the large amounts of COV.

Analyzing the results of dispersion modeling from izoconcentrations curves (fig. 11, 12.13, 14, 15, 16, 17, 18), it was found that for all analyzed pollutants (NO_2, SO_2, H_2S, NH_3, acroleina) concentrations lies well below the limit values time limit for daily mediation.

Maximum concentration on the average mediation (daily) to determine the pollutants from the Department of regenerated rubber, of using the agent of regeneration medium aromatic type Teleajen, variant of initial scrubber and the modernized scrubber and are presented in tables 6 and 7.

Table 6.
Daily maximum concentration of pollutants/scrubber initial + aromatic oil

Pollutant	Maximum concentration			Observations
	C_{max} [µg/m³]	Alert threshold (PA) [µg/m³]	Limit value (VL) threshold for intervention [µg/m³]	
SO_2	46,1	-	125	< VL
H_2S	0,55	-	8	< VL
NH_3	1,8	-	100	< VL
Acroleina	1,8	-	10	< VL

Table 7.
Daily maximum concentration of pollutants/scrubber modernized + aromatic oil

Pollutant	Maximum concentration			Observations
	C_{max} [µg/m³]	Alert threshold (PA) [µg/m³]	Limit value (VL) threshold for intervention [µg/m³]	
SO_2	32,2	-	125	< VL
H_2S	0,3	-	8	< VL
NH_3	1,76	-	100	< VL
Acroleina	0,86	-	10	< VL

Daily average concentrations of SO_2, H_2S, NH_3, acroleina (µg/m³) from the regeneration section of rubber, using as a regeneration agent the medium aromatic oil, type Teleajen, for the situation of initial scrubber, are shown in figures 11, 12, 13 and 14.

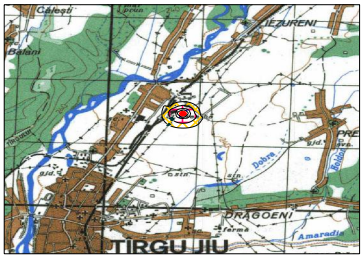

Fig.11. Daily average concentrations of SO_2 initial scrubber

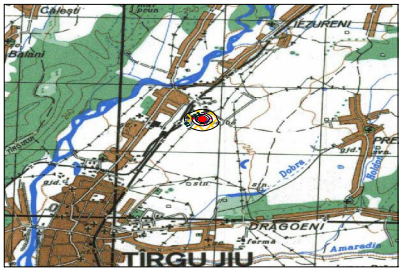

Fig.12. Daily average concentrations of H_2S initial scrubber

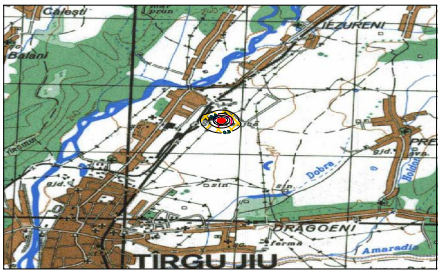

Fig.13. Daily average concentrations of NH_3 initial scrubber

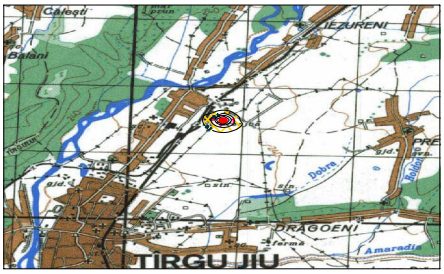

Fig.14. Daily average concentrations of acroleina initial scrubber

Daily average concentrations of SO_2, H_2S, NH_3, acroleina (µg/m³) from the regeneration section of rubber, using as a regeneration agent the medium aromatic oil, type Teleajen, for the situation of modernized scrubber, are shown in figures 15,16,17 and 18.

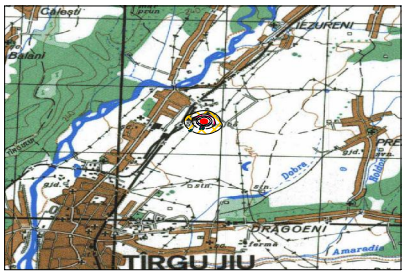

Fig.15. Daily average concentrations of SO_2 modernized scrubber

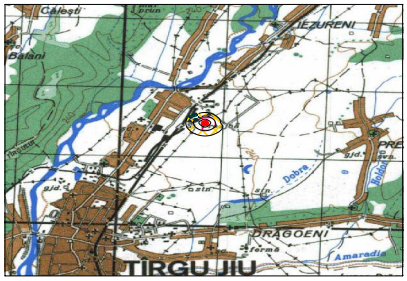

Fig.16. Daily average concentrations of H_2S modernized scrubber

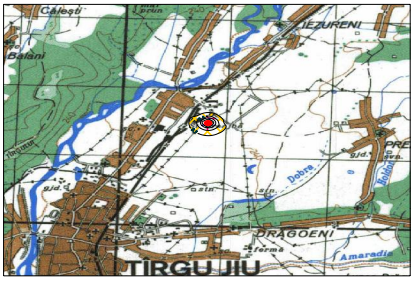

Fig.17. Daily average concentrations of NH_3 modernized scrubber

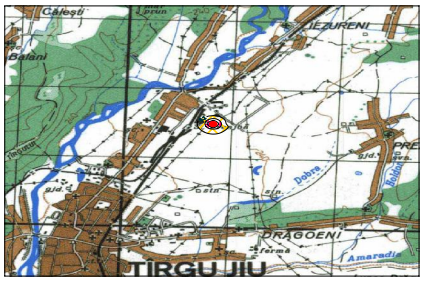

Fig.18. Daily average concentrations of acrolein modernized scrubber

4 Conclusion

- SC ARTEGO SA Tg-Jiu, Department Regenerated Rubber and power station, following different processes or technology operations, remove residual gaseous effluents, which contain pollutants CO, NOx, SO_2, dust, H2S, ammonia, mercaptani, acroleina, COV.

- Central heating is fitted with 2 type Teruzzi boilers that produce steam required by Rubber Regeneration Plant, and the thermal power of the power station is 34,9 MW/boiler. Central functions with a single bobiler (the second being the backup boiler), gas discharge being through two metal baskets, one for each boiler.

- For rubber devulcanization, there has been used the medium aromatic oil as a regeneration agent (type Teleajen).

- After ending the devulcanization cycle and the autoclave opening, hot gases are discharged through a tubing into the atmosphere, after passing through the scrubber, which is to drop the gas temperature, to decrease the concentration in emissions and to retain the fine particles of dust, together with gaseous pollutants.

- Effluent gas samples were taken from entry tubing entry of pollutants in scrubber, respectively output, to be determined the yield of washing plant.

- To determine the level of emissions routed generated stationary source of regenerated rubber, measurements were made of emissions after devulcanizare cycle for each of the four autoclaves of the plant. After passing through the wash, it is noted that the limit value of pollutant emission of SO_2, NH_3, acroleina. For H_2S and COV is exceeded and alert thresholds and thresholds for intervention, which proves the low efficiency of scrubber, its replacement being recommended. In order to increase capacity for retention of existing scrubber and increase its efficiency, it has been replaced with other modernized, more efficient.

- After installation of new equipment washing and taking measure to decrease the gas pressure, there were again made determinations on the route of the exhaust gas effluent (before and after the scrubber).

- Comparing values obtained with the emission limit values, it is observed a drastic decrease in concentrations of pollutants after passage through the wash, they are framing in the VLE, and even in the alert threshold, except for volatile organic compounds, whose concentration has major overruns. In conclusion, the new plant is more efficient than the first, but not entirely, considering the large amounts of COV.

- Calculating concentrations in the atmosphere, was performed with Gaussian dispersion model. Applying the model and climatological dispersion were calculated on the maximum concentrations of environmental mediation (daily) for NO_2, SO_2, H_2S, NH_3, acroleina. Analyzed the results of dispersion modeling izoconcentratii curves, as was found for all pollutants analyzed, the concentrations lies well below the limit values for daily mediation time.

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