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Deep Catalytic Treatment of Waste Gas from Sulfur Dioxide, Nitrogen Oxides and Carbon Monoxide at Processing Products of Detoxication of Toxic Substances

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Abstract—The Russian Federation in January 1993 signed the Parisian "Convention about the prohibition of development, production, accumulation and application of chemical weaponry and about its destruction." In 1996 Federal target program "The destruction of the reserves of chemical weaponry in the Russian Federation" that has status of presidential was approuved for purposes of the realization of the Convention. The convention came into force on April 29, 1997.

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The Perm branch of Russian Sci. Center "Applied Chemistry" was practically immediately involved into the works on chemical disarmament. In particular, a work on the destruction of the chemical weaponry of 2nd class, phosgene, was carried out on the mobile plant developed according to technology that was suggested by Perm branch, in 2001–2002. Phosgene was recalibrated from 3844 artillery ammunition into the 40-liter balloons and utilized in the experimental production of the Permian branch of Russian Sci. Center "Applied Chemistry."

In the context of State Contract since 2003 in the Permian branch were carried out studies on the development of the alternative technology of the processing the products of the detoxication of the organophosphorus toxic substances (POS]), reaction masses (RM), by a technique of low-temperature oxidation by calcium nitrate. The technology that consisted in the oxidation of RM at 300–450°C by calcium nitrate in a reactor with the aerated bed was suggested [1, 2].

A solid slime and a waste gas containing SO_2, NO, NO_2, CO are the main products of processing RM. The solid slime from the processing RM-sarin or RM-soman according to the data of X-ray diffraction analysis is the analog of natural mineral francolite (carbonatehydroxyfluoroapatit]) of the general formula $Ca_5(PO_4)_3CO_3(OH)F$, fluoride, nitrate and calcium oxide present as the admixtures. The content of francolite in the slime reaches 80%. During processing RM-Vx the slime contains mainly calcium sulfite and calcium sulfate, calcium nitrate and calcium oxide.

The neutralization of the waste gas is attained firstly by a wet alkaline cleaning in a nozzle scrubber then by the final treatment of gases in two bulk filters [2, 3]. The first filter (on the motion of gas) is equipped with chemisorbent MDS, and the second filter is filled with activated carbon of grade SKT-6 impregnated with urea.

The nozzle scrubber is sprinkled by 6–9% NaOH solution and intended for the recovery of a basic amount of SO_2 from the gas. An efficiency of the treatment is 95%. The deep treatment of the gas from SO_2 is conducted with the aid of the bulk filter equipped with the chemisorbent MDC, and from NOX, with the aid of a filter with the activated carbon SCT-6.

Drawbacks in this scheme of purification are:

– the necessity of the presence of a unit for recovery of the spent scrubber liquid produced in the course of regeneration of a hard realized dump of calcium sulfite.

– the necessity of conducting the operations of the regeneration of worked out chemisorbents MDS and coal SKT-6 directly in the filters themselves that requires additional apparatuses in the plant of the gas purification.

Furthermore, the regeneration is accompanied by the periodic formation of drains and additional gas emissions (from the stage of drying);

– the high material, power and operational expenditures at the stage of gas purification and at the stages of the regeneration of the worked out chemisorbents;

– a removal of carbon monoxide from gases by the used chemisorbents is not possible. Therefore a highly effective technology of the treatment of the waste gas should be developed from nitrogen oxides, carbon monoxide and sulfur dioxide. We solved this problem with the help of catalysts of selective action.

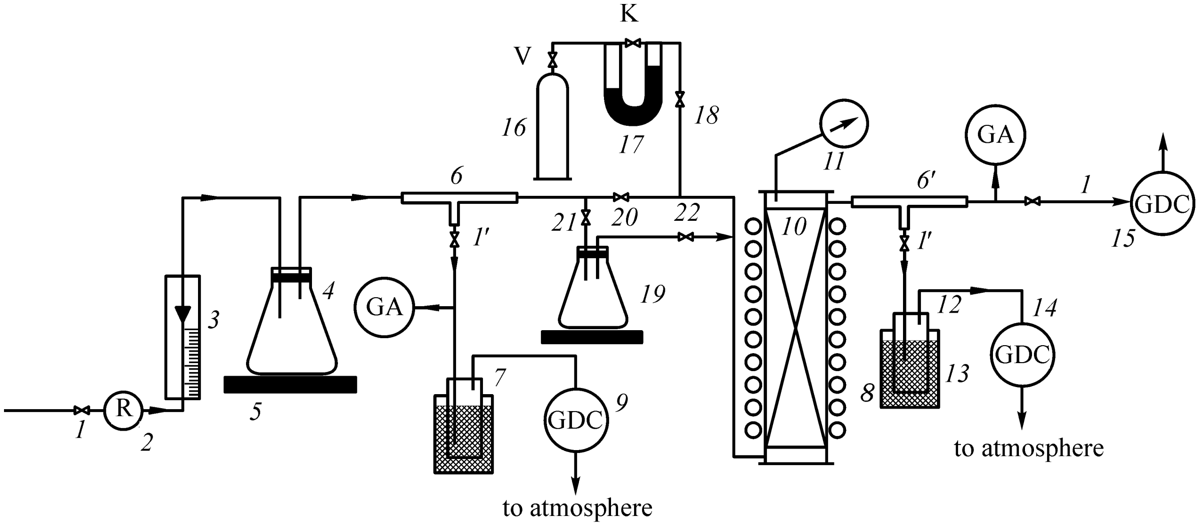
EXPERIMENTAL

Varios catalysts were considered for the gas treatment. We selected alumovanadium [AOK] 78-55, cupromangamese catalyst AOK 63-22, alumocuprochromium IKT 12-8 and carried out studies of the chemical activity of these catalysts in the course of removal of the toxic admixtures from air. The scheme of laboratory setup is presented in the figure.

The compressed air from the main gas pipe is fed with the given speed through reducer (*2*) and rotameter (*3*) into the generator of vapors of NO_2, CO and SO_2 that is a sealed heated Erlenmeyer flask (*4*) with a dropping funnel intended for dosing liquid reagents. The generation of the toxic admixtures indicated is produced due to the realization in the flask of chemical reactions according to the procedures described in [4, 5].

Gas–air mixture (GAM) from flask (*4*) enters tee tube (*6*) where it is divided into two flows: small (3–5% of total flow) and large fed to column (*10*) with the external electric radiator filled with the catalyst ($V_{\text{nozzles}} = 525\ \text{cm}^3$) being investigated. The adjustment of the small flow is produced with the aid of the needle-shaped teflon gate (*1'*). A destination of the flow is measurement of the initial concentration of the toxic admixture in GAM with the aid of the universal gas analyzer "Kaskad", and also constant gas probing for the chemical analysis to determine an average concentration of the admixture in the gas before the column. Necessary condition is a constant (during the experiment) feed rate GAM into the Drechsel vessel (*7*) filled with absorbing solution. For maintaining room temperature in the absorbing solution the Drechsel vessel is placed into the water thermostat (beaker with water). The volume of air which passed in experiment through Drechsel vessel, is recorded with gas counter (*9*).

The introduction of ammonia and water vapors in



Scheme of the laboratory setup for the study of chemical catalyst activity. Designations: (*1, 18, 20, 21, 22,* G) shutoff valves (G, *18, 20, 21, 22* are teflon stop cocks); (*2*) air reducer; (*3*) air rotameter (to 1000 dm h^{-1}); (*4*) generator of vapors NO_x, CO. SO_2; (*5*) the sand bath, the magnetic mixer with the electric heating; (*6, s'*) teflon (quartz) tees; (*7*) Drechsel's vessel with the absorbing solution (determination of the initial concentration of the admixture); (*8, 13*) cooling vessels; (*9, 14, 15*) gas drum counters; (*10*) column with the external electric heating filled with the catalyst; (*11*) thermocouple (control of the temperature in the catalyst bed); (*12*) the system of the probing the treated gas for the chemical analysis (determination of residual impurity content); (*16*) balloon with ammonia; (*17*) U-shaped manometer; (*19*) generator of ammonia and water vapors; (V) the needle-shaped gate; (K) capillary; (GA) universal gas analyzer "Kaskad."

GAM (for the purpose of the determination of their influence on the efficiency of purification) is performed as follows:

– NH_3 flow (mg h^{-1}) regulated by gate *V* is given from balloon (*16*) through the capillary (K) and maintained on the adjusted level with the aid of calibrated U-shaped manometer (*17*);

– a supply of NH_3 and H_2O in GAM occurs due to the tension of aqueous ammonia vapors of known composition placed into the same flask. Concentration of NH_3 and H_2O in GAM is calculated on the losses of the weight of the aqueous ammonia in the flask and by data on the vapor tension of the components of the aqueous ammonia at the various temperatures;

– the supply of the water vapors in GAM is executed by the evaporation of pure water. The concentration of the water vapors is determined also by the losses of the weight of the liquid phase in the flask. Reagents are heated in flask (*19*) by electroheating of magnetic stirer (*5*). The gas probing after column (10) is produced analogously with one for determining the initial concentration of the admixture in the gas. For this GAM after column is directed to tee (*6*’) and we get two flows, one of which is probed for the chemical analysis (*12*), and another flow is supplied to the gas analyzer (GA).

The universal gas analyzer “Kaskad” which made it possible to practically instantly measure the concentrations NO, NO_2, CO, and SO_2 at the points of the probing was the basic means of the monitoring of the content of the toxic admixtures in GAM in the course of the studies on the laboratory setup.

Production of GAM with NO_2

In order to get NO_2 vapors cerium nitrate (trihydrate or anhydrous) or lead nitrate is added into three neck flask (*4*). The flask with nitrate is immersed in the heated sand bath and connected to a system of air feed–outlet. The temperature of the sand bath must be in the range of 150–250°C at the use of cerium nitrate, and in the range of 500–550°C in the case of lead nitrate. The required air flow is maintained with the aid of reducer (*2*) and rotameter (*3*), then 3–5% gas bleeding into the Drechsel vessel (*7*) and a supply of a basic amount of the gas to the catalytic treatment into column (*10*) are established. Concentration NO_2 in GAM varies by the temperature of sand bath (*5*). The formation of NO_2 can be described by a reaction

$$2Ce(NO_3)_3 \xrightarrow{150\text{–}250°C} 6NO_2\uparrow + CeO_3 + 1.5O_2$$

Production of GAM with CO

In order to get CO vapors 100 ml of concentrated sulfuric acid (d = 1.84) is added into three neck flask (*4*). The flask is connected to a system of air feed–outlet. The dropping funnel that contains 25–50 ml of 85% formic acid is hermetically fixed in the upper (vertical) neck. Then the flask is placed in the sand bath and heated up to 100°C. The air movement in the system of the gas treating is then tuned. Then into the vapor generator (*4*) from the dropping funnel formic acid is added at a rate of 1 drop in 3–5 minutes. The concentration of CO in GAM varies by the rate of adding formic acid. The formation of CO can be described by a reaction

$$HCOOH + H_2SO_4 \rightarrow CO\uparrow + H_2SO_4 \cdot H_2O$$

Production of GAM with SO_2

In order to get SO_2 vapors the saturated solution of sodium sulfite (or solid sodium pyrosulfite $Na_2S_2O_5$) is added into three-neck flask (*4*). The flask is connected to a system of air feed–outlet. The dropping funnel that contains 20–30 ml of concentrated sulfuric acid (d = 1.84) is hermetically fixed in the upper (vertical) neck. The air movement in the system of the gas treating is tuned. Then into the flask (*4*) from the dropping funnel sulfuric acid is added at a rate of 1 drop in 3–5 minutes. The concentration of SO_2 in GAM varies by the rate of adding sulfuric acid. The formation of SO_2 can be described by a reaction

$$Na_2SO_3 + H_2SO_4 \rightarrow SO_2\uparrow + Na_2SO_4 + H_2O$$

RESULTS AND DISCUSSIONS

Studies were carried out at different regimes of the gas treating to determine an influence of the most important technological parameters on the efficiency of the catalytic processes: the temperature of catalysis, time of the contact of the phases gas–solid, additives in GAM before the catalytic treating vapors of ammonia and water, the initial concentration of the toxic admixture in the gas.

The results of studies of the chemical activity of the selective catalysts at the air treatment from nitrogen oxides, carbon monoxide, and sulfur dioxide on the laboratory setup are presented in the table. The analysis of experimental data has revealed the features of proceeding of the catalytic processes at different regimes of the gas treating which is described below for each catalyst.

GAM treatment from sulfur dioxide with catalyst AOK-63-22 demonstrates:

– For insuring the high efficiency of sulfur dioxide removal at elevated temperatures (250°C) a preliminary treatment of gases consisting in the addition of the ammonia gas before the reactor in a quantity no less than 0.6–0.8 g m^{-3}GAM should be carried out. As the source of NH_3 vapors it is possible to use ammonia, aqueous ammonia or crystalline carbonate of ammonium heated to the temperature of 30–40°C.

– The presence in GAM of water vapors increases the efficiency of catalytic removal of SO_2 from gases, in the absence of NH_3 vapors the process of purification proceeds unstably, and the degree of SO_2 removal varies in the range of 0 of 70%.

– A decrease in the temperature of the catalytic treatment of gases (10–50°C) ensures the high efficiency of removal GAM of SO_2 without the preliminary processing the treated gases by vapors of ammonia and in this case the degree of purification practically does not depend on the moisture content of the treated gases.

– It is noted that the high degree of SO_2 removal for the short time after a stop of the ammonium vapor supply to GAM (run 10). This is probably due to the accumulation in the catalyst bed of ammonium sulfite forming because of the excessive NH_3 supply to the gas. Obviously at a temperature 250°C ammonium sulfite dissociates according to the scheme $(NH_4)_2SO_3 \rightarrow NH_3^{+}\uparrow + NH_4HSO_3$ creating an alkaline medium of gases both in the reactor itself, and after it. The isolation of NH_3 ceases upon complete transition of sulfite to bisulfite. The removal of SO_2 drastically deteriorates, and the gas medium after the reactor becomes neutral or slightly acid (run 11). The contact time of the phases gas–solid equal to 1 s ensures the deep neutralization of SO_2-containing gas in the case of its preliminary processing by means of ammonia vapors.

GAM treatment from nitrogen dioxides with catalyst AOK-78-55 demonstrates:

– The neutralization of gas occurs insufficiently effectively without the preliminary processing GAM or the catalyst by ammonia gas, in this case with an increase in the temperature in the catalyst bed up to 50°, 150°, and 250°C the degree of NO_2 and NO removal substantially decreases varying in the ranges of 86.7–78%, 57–37.5% and 29.1–3.6% (runs 26–28). It was revealed that with the high concentrations of NO_2 (> 840 mg m^{-3}) the catalytic treating of GAM at 250°C occurred not at all or was very insignificant.

– Moistening GAM that contains the relatively moderate concentrations of the nitrogen oxides (<840 mg m^{-3}) lead to the reduction in the degree of removal of NO, NO_2 at temperature in the reactor 50° and 150°C (runs 26, 27, and 29, 30).

– For ensuring the high degree of removal of nitrogen oxides in the range of temperatures of 50°, 150°, 250°C ammonia gas in the amount >0.175 g m^{-3} should be added in GAM before the reactor (runs 21–23). As in the case of the neutralization of the SO_2 containing gas ammonia, aqueous ammonia or crystalline ammonium carbonate of ammonium can be used as the generator of NH_3 vapors.

– Moistening GAM containing ammonia practically does not lead to reduction in the efficiency in catalytic removal of nitrogen oxides in the range of temperatures of 50°, 150°, 250°C (runs 25, 33–35).

– The contact time of the phases gas–solid equal to 1 s ensures deep neutralization of GAM which contains the nitrogen oxides at the investigated temperature range in the case of preliminary processing GAM before the reactor by means of ammonia vapors.

GAM treatment from carbon monoxide with catalyst IKT-12-8 demonstrates:

– The temperature in the catalyst bed is the determining parameter which ensures the high degree of removal of carbon monoxide. In the range of 50–250°C the temperature 250°C is optimum at which are reached 99% degree of gas treating (runs 26–28).

– Moistening GAM or feeding it with ammonia vapors before the reactor practically does not exert a substantial influence on the efficiency of the neutralization of the CO containing gas (runs 38–41). At a temperature in the reactor 50°C the process of the catalytic treating of wet GAM from CO obeys the law of chemical kinetics. It was shown that an increase in the degree of gas cleaning proceeds with an increase in the initial concentration of the carbon oxide in GAM from 210 to 1990 mg m^{-3} at a temperature 50°C (run 42) from 14 to 28%, and at the temperature in the catalyst bed 150°C (runs 42–44), from 53 to 65%.

Results of the investigation of the chemical catalyst activity at treatment of GAM from nitrogen oxides, carbon oxide, and sulfur dioxide

Run no.	Characteristic of GAM before the gas treatment					Time of experiments, min	Parameters attained as a result of the treatment in the reactor			
	GAM flow, l h^{-1}	toxic admixture (TA)	concentration of TA in GAM	content (g m^{-3}) in GAM of NH_3	H_2O		temperature in the catalyst bed, °C	contact time for the phase gas–solid, s	concentration of TA in GAM after the reactor, mg m^{-3}	removal degree, %
Removal of SO_2 from GAM										
1	570	SO_2	120–290	0	0	150	250	1.71	140–300	0
2	570	SO_2	70–500	0	17.5	240	250	1.71	20–140	71.7
3	570	SO_2	440–600	0	0	300	250	1.71	430–730	0
4	570	SO_2	210	0	0	30	250	1.71	200	4.8
5	570	SO_2	110–210	12.7	0	210	250	1.71	from 90 to 0 (in the end of the experiment)	18.2–100
6	570	SO_2	440–700	14.0	0	75	250	1.71	0–10	98.6–100
7	570	SO_2	250–490	0.754	0	300	250	1.71	0–10	98–100
8	570	SO_2	210–290	1.72	0.26	240	250	1.71	0	100
9	570	SO_2	180–220	0.80	1.78	210	250	1.71	0	100
10	570	SO_2	660–830	0	0	135	250	1.71	0–10	98.8–100
11	570	SO_2	300–600	0	0	180	250	1.71	190–300	36.7–50.0
12	570	SO_2	270–300	0.60	0.35	120	250	1.71	0–10	96.7–100
13	570	SO_2	300–460	0	0	90	250	1.71	250	16.7–45.7
14	975	SO_2	220–230	0	0	105	250	1	80–90	60.9–63.6
15	975	SO_2	120–240	1.22	0.71	90	250	1	0	100
16	975	SO_2	130–230	0	14.5	210	250	1	from 0 to 100 (in the end of the experiment)	from 100 to 56.5 (in the end of the experiment)
17	975	SO_2	320–540	0	0	135	250	1	260–330	18.7–38.9
18	975	SO_2	140–330	0	19.4	180	250	1	60–140	57–58
19	975	SO_2	1020 930 570	000	6.6	90	50	1	2000	98–100
20	975	SO_2	1150 1050 940 600 480	0	0	300	10	1	20 10 10 0 0	98.3–100

Table (Contd.)

Run no.	Characteristic of GAM before the gas treatment					Time of experiments, min	Parameters attained as a result of the treatment in the reactor			
	GAM flow, l h^{-1}	toxic admixture (TA)	concentration of TA in GAM	content ($g\ m^{-3}$) inGAM of			temperature in the catalyst bed, °C	contact time for the phase gas–solid, s	concentration of TA in GAM after the reactor, mg m^{-3}	removal degree, %
				NH_3	H_2O					
Removal of NO_2, and NO from GAM										
21	570	NO_2, NO	265	1.228	0	60	250	1.71	1–20	99.2–100
22	975	NO_2, NO	240	0.368	0	60	250	1	0–20	99.2–100
23	570	NO_2, NO	435	0.175	0	60	250	1.71	00	100
24	975	NO_2, NO	90	0.051 0.102	0	60	250	1	3–0	96.7–100
25	570	NO_2, NO	290–300	0.088 0.175	35.087	105	250	1.71	1–2 0	99.3–100
26	975	NO_2	30	0	0	120	50	1	4	86.7
			50						10	80
			80						17	78.8
			100						22	78
27	975	NO_2	80	0	0	75	150	1	50	37.5
			110						61	44.5
			150						74	50.7
			200						86	57.0
28	975	NO_2, NO	172	0	0	235	250	1	122	29.1
			320						285	10.9
			450						434	3.6
			640						590	7.8
29	975	NO_2, NO	320	0	21.65	180	50	1	151	52.8
			595						330	44.5
			790						560	29.1
			840						720	14.3
30	975	NO_2	310	0	19.91	180	150	1	280	9.7
			363						328	9.6
			520						480	7.7
			800						750	6.3
31	975	NO_2	200	0	15.453	180	250	1	170	15.0
			410						380	7.3
			520						410	21.1
			640						580	9.4
32	975	NO_2	68	0.912	0.533	150	50	1	2	97.1
			98						3	96.9
			155						22	85.8
			320						68	78.7

Table (Contd.)

Run no.	Characteristic of GAM before the gas treatment					Time of experiments, min	Parameters attained as a result of the treatment in the reactor			
	GAM flow, l h^{-1}	toxic admixture (TA)	concentration of TA in GAM	content (g m^{-3}) inGAM of			temperature in the catalyst bed, °C	contact time for the phase gas–solid, s	concentration of TA in GAM after the reactor, mg m^{-3}	removal degree, %
				NH_3	H_2O					
33	975	NO_2, NO	60	0.734	0.428	180	50	1	1	98.3
			75						0	100
			110						2	98.2
			165						0	100
			235						0	100
			250						1	99.6
34	975	NO_2, NO	68	0.700	0.407	225	150	1	0	100
			237						1	99.6
			290						1	99.7
			722						0	100
			1436						0	100
35	975	NO_2	120	0.719	0.419	120	250	1	0	100
			200						0	100
			380						1	99.7
			400						0	100
36	975	NO_2, NO	65	0.456	0	135	250	1	0	100
			119						0	100
			185						0	100
			254						0	100
			400						0–1	99.8–100
37	975	NO_2, NO	320	0.645	0	105	150	1	0	100
			420						0	100
			480						0	100
38	975	NO_2, NO	117.5	0.492	0	120	50	1	0	100
			200						0	100
			380						0	100
Removal of CO from GAM										
39	570	CO	800–18030	0	0	60	250	1.71	0–20	99.9–100
40	975	CO	610–15300	0	0	120	250	1	0–20	99.9–100
41	975	CO	1010–3600	0	0	60	300	1	0–20	99.4–100
42	975	CO	980–6110	0	40.35	60	250	1.71	0–250	95.9–100
43	975	CO	1560–19920	0	5.60	120	250	1	0–60	99.7–100
44	975	CO	170–15420	0.77	0.45	180	250	1	0–50	99.7–100
45	975	CO	210	0	3.09	180	50	1	180	14.3
			380						320	15.8
			700						540	22.9
			860						650	24.4
			1990						1440	27.6

Table (Contd.)

Run no.	Characteristic of GAM before the gas treatment					Time of experiments, min	Parameters attained as a result of the treatment in the reactor			
	GAM flow, $l\ h^{-1}$	toxic admixture (TA)	concentration of TA in GAM	content ($g\ m^{-3}$) in GAM of			temperature in the catalyst bed, °C	contact time for the phase gas–solid, s	concentration of TA in GAM after the reactor, $mg\ m^{-3}$	removal degree, %
				NH_3	H_2O					
46	975	CO	2540	0	3.67	120	150	1	1200	52.80
			5090						2400	52.85
			7070						3100	56.15
			15600						7260	56.34
47	975	CO	140	4.06	2.37	90	150	1	50	53.30
			400						140	65.00
			4250						1600	62.35
			1300						600	54.85
48	975	CO	150	0	3.23	180	250	1	0	100.0
			300						0	100.0
			410						0	100.0
			1100						0	100.0
			2500						10	99.6
			2870						0	100.0

– The influence of the concentration (i.e. changes in the initial concentration of CO in the gas) on the rate of the CO removal at $T = 150$°C practically is not manifested.

– The contact time of the phases gas–solid equal to 1 s ensures the deep neutralization of the CO containing gas at a temperature in the catalyst bed 250°C. Preliminary treating GAM by means of ammonia vapors before the reactor does not required.

CONCLUSIONS

On the basis of the studies taking into account the nature of the selective catalysts the treatment of the gases which simultaneously contain the sulfur dioxide, nitrogen oxides, and carbon monoxide should be performed in three connected in series filled filters: the first filter is equipped with the catalyst of SO_2 removal, the second one, with the catalyst of removal of nitrogen oxides, the third, with the catalyst of CO removal.

The optimum conditions which ensure the 99–100% degree of removal of the toxic admixtures from GAM for each catalyst are determined. So removal of SO_2 and NO_x requires additional processing GAM by means of ammonia gas. The temperature of catalytic removal of all toxic gases must be maintained about 250°C, and the contact time must be not less than 1 s.

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