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REMOVING OF HARMFUL SUBSTANCES FROM WASTE GASES FROM THE NPK PRODUCTION[1]

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SUMMARY

This contribution deals with the reduction of emission from production of NPK fertilizer plant in Synthezia, Pardubice, Czech Republic. The production capacity of NPK fertilizer is 30 t/hr. The production did not conform with the emission limits required by the Czech Republic laws. The wet process did not meet the requirements. Emission concentration of ammonia, nitrogen oxides and fluorine compounds were exceeded.

The Research Institute of Inorganic Chemistry in Ústí Nad Labem worked on the solution of this problem. Three basic variations were suggested for elimination of harmful substances from waste gases of the wet-process. Absorption of mixed acid and alkaline waste gases was chosen for future efforts.

Designer: *The Research Institute of Inorganic Chemistry, Ústí Nad Labem*
Builder: *Sindat, Pardubice*
Investor: *Synthezia, Pardubice*

Apparatus for emissions reduction from NPK production started to work in September 1996.

RESUME

Cet exposé traite de la réduction d'émission dans la production d'engrais NPK à Synthesia, Pardubice, en République Tchèque. La capacité de production d'engrais NPK est de 30 t/h. La production n'était pas conforme aux limites d'émission imposées par les autorités de la République Tchèque. Le procédé humide ne satisfaisait pas les exigences. Les concentrations des émissions d'ammoniac, d'oxydes d'azote et des composés fluorés étaient trop élevées.

L'Institut de Recherche de Chimique Inorganique à Usti Nad Labem a travaillé pour chercher une solution à ce problème. Trois variations de base ont été proposées pour l'élimination des substances nocives dans les gaz résiduels du procédé humide. L'absorption de l'acide mixte et de déchets de gaz alcalin a été choisie pour les efforts futurs.

Concepteur :   L'Institut de Recherche de Chimie Inorganique, Usti Nad Labem
Constructeur : Sindat, Pardubice
Investisseur :   Synthezia, Pardubice

Les appareils de réduction des émissions de la production NPK ont commencé à fonctionner en septembre 1996.

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Introduction

The production of NPK fertilizer in a single phase is divided into wet and dry process. In the wet-process the production is under three steps:

- Acidulation of phosphate rock. Sulphuric acid is added during the nitric acid acidulation step, which converts part of the calcium nitrate to calcium sulphate.
- Ammoniation. The joint effect of sulphuric acid addition and subsequent ammoniation converts virtually all of calcium nitrate to less hygroscopic compounds.

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[1] *Elimination de substances nuisibles à partir de gaz résiduaires de la production d'engrais NPK*

- Evaporation of slurry. The salt of potassium is added into the slurry. Waste gas from every step is exhausted, partly cleaned and emitted into atmosphere.

Dry-process (granulation, drying, screening and cooling) has separate cleansing of waste gases.

Originally U-reactors of acidulation, neutralization and evaporation were exhausted separately. Emission limits for fluorine compounds and nitrogen oxides were exceeded in the waste gas from acidulation. Emission limits for fluorine compounds and ammonia were exceeded in waste gases from neutralization and evaporation. Three basic variations were proposed for harmful substances elimination from waste gases of wet-process to conform to the limits for NO_X, NH_3 and HF.

Absorption of mixed acid and alkaline waste gases was chosen for the next phase and implementation. Waste gases from 5 U-reactors of acidulation, 12 U-reactors of neutralization and evaporation and 1 U-reactor, where salt of potassium is added will be sucked off together. The rest of 5 U-reactors of evaporation and tank of melt will be cleaned in the same way until now through condenser of the water vapour.

Project of reduction nitrogen oxides, ammonia and fluorine acid emissions from wet-process of NPK fertilizer production.

Emissions from NPK production

Table 1 shows the emission concentrations of specific processes of NPK production. Emission concentrations are given in milligrammes of component in per m^3_n of wet gas under normal conditions (0°C, 101 325 Pa).

Table 1 - Emissions from NPK Production

Component	Acidulation		Neutralization		Evaporation		Dry-process	
	c_E (mg/m^3_n)	E (kg/hr)	c_E (mg/m^3_n)	E (kg/hr)	c_E (mg/m^3_n)	E (kg/hr)	c_E (mg/m^3_n)	E (kg/hr)
NO_2	1374	8,2					37	6,0
NH_3			4730	9,76	5100	43,8		
HF	231	1,4	1470	4,66	4,7	0,11	3,9	0,3
dust							47	3,76
SO_2							16	1,48

Emission limits for production of fertilizers in the Czech Republic are stated in the Table 2, where is:
E   mass flow of component - emission (kg/hr)
c_E emission concentration of component in wet gas under normal conditions 0°C, 101 325 Pa (mg/m^3_n)

Table 2 - Emission limits for production of fertilizer in the Czech Republic

Component	E	C_E
	(kg/hr)	(mg/m^3_n)
NO_X [a)]	10	500
NH_3	0,5	50
HF [b)]	0,1	10

[a)] Nitrogen oxides are expressed as nitrogen dioxide
[b)] Fluorine and its gaseous compounds are expressed as HF

The emission concentration has to be equal or lower than shown on Table 2.

From Tables 1 and 2; it is obvious that emissions from wet-process (emission of NO_2 from dry-process is 6 kg/hr and HF is 0,3 kg/hr) have to be:

$E\ (NO_2) < 4$ kg/hr. or $C_E(NO_2) < 500\ mg/m^3_n$

$E\ (NH_3) < 0,5$ kg/hr. or $C_E(NH_3) < 50\ mg/m^3_n$

$C_E(HF)\ < 10\ mg/m^3_n$

Technical Input Data for Project

Absorption of harmful substances from waste gas of wet-process of NPK production will be projected to accomplish given emission limits.

Maximum mass flows of components in mixed waste gases from wet-process (U-reactors number 1-18) are:

NO_2 60 kg/hr

NH_3 600 kg/hr

HF   5 kg/hr

Technology of Emissions Reduction Process

The project technology consists of 3 absorption columns and 1 filter for aerosols. The process is done continuously. Compounds of fluorine are absorbed in the 1st absorption column. Ammonia is absorbed in the 2nd and 3rd absorption column. Nitrogen oxides are absorbed in all absorption columns. Basic function of filter is to remove aerosol of ammonium nitrate, which is created in the 2nd absorption column. Waste gases from acidulation and neutralization (evaporation) are fed separately to the 1st absorption column to prevent formation of incrustations in pipeline. Figure 1 is the gas flow diagram of the emission reduction process.

Figure. 1 Simple gas flow diagram of the emission reduction
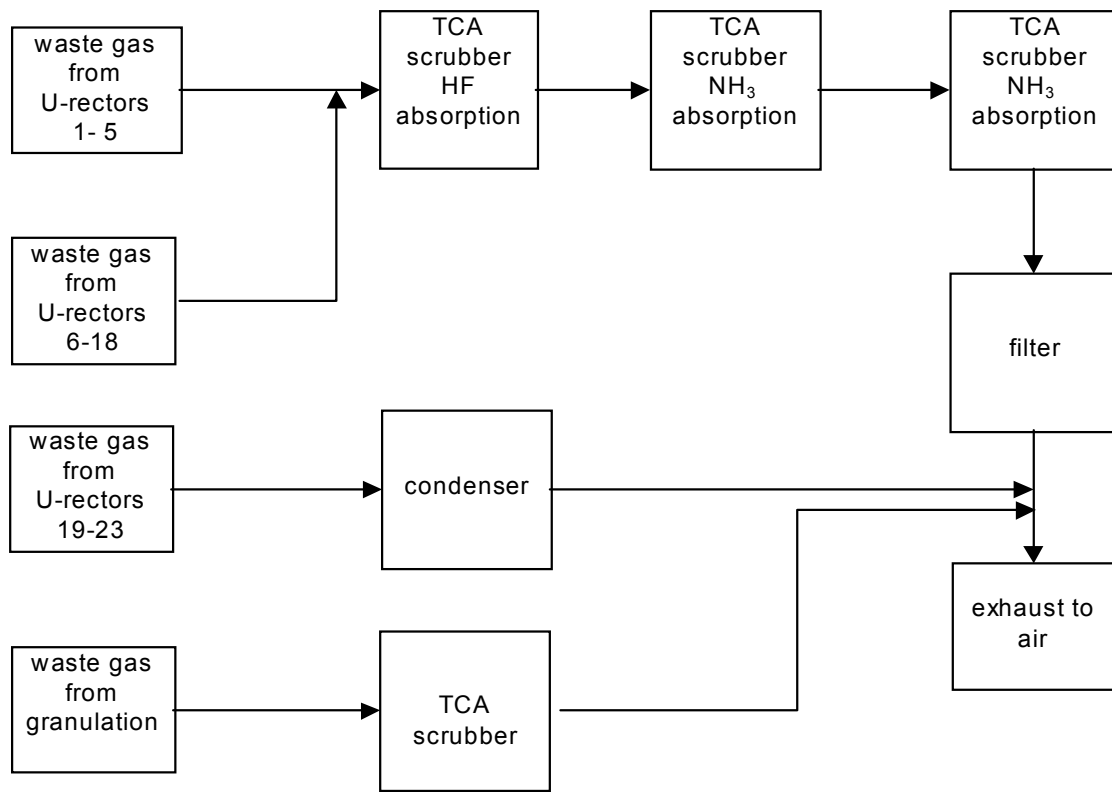
Scrubbing solutions

1st absorption column

solution of CaO (CaO concentration 0,5% wt.)

2nd absorption column

solution of NH_4NO_3 and HNO_3 (HNO_3 concentration 2,3% wt.).

3rd absorption column

solution of NH_4NO_3 and HNO_3 (HNO_3 concentration 0,34% wt.).

4th scrubbed filter

solution of NH_4NO_3 and HNO_3 (HNO_3 concentration 0,3% wt.).

Solution from filter is fed to recirculation tank of the 3rd absorption column.

Used scrubbing solution from the 3rd absorption column (solution of NH_4NO_3 and residue of HNO_3) is fed back to the slurry in the production of NPK and therefore, it is important, that this solution should contain as little as possible amount of water.

Chemical Processes during Absorption

Waste gases from acidulation (U-reactors 1-5).

Waste gases contain (except air and water vapour) nitrogen oxides and fluorine compounds, largely in the form of silicon fluoride SiF_4. This gas is acid.

Waste gases from neutralization and evaporation (U-reactors 6-18).

These gases are alkaline. Waste gases (except air and water vapour) contains big amount of ammonia.

Fluorine compounds present in this gas occur in the form aerosols of NH_4HF_2, NH_4F, $(NH_4)_2SiF_6$.

Mixing of Acid and Alkaline Waste Gases

There is large excess of ammonia created after the mixing of waste gases. Ammonia forms aerosol of ammonium nitrate and ammonium nitrite. Ammonium nitrite decomposes in wet environment and forms ammonium nitrate and nitrogen oxide. This process can be described with this equation:

$$3\ NO_2\ (g) + 2\ NH_3\ (g) + H_2O\ (g)\ \rightarrow\ 2\ NH_4NO_3\ (s) + NO\ (g) \qquad (1)$$
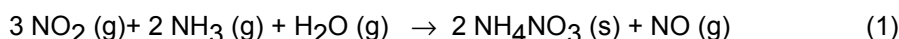
This process can run to the 2nd absorption column. It is estimated that 10% wt. NO_2 will react in this way.

The next reaction in the mixed gases is the reaction of ammonia with silicon fluoride. The reaction is:

$$SiF_4\ (g) + 2NH_3\ (g) + 2H_2O\ (g)\ \rightarrow\ 2\ NH_4HF_2\ (s) + SiO_2\ (s) \qquad (2)$$
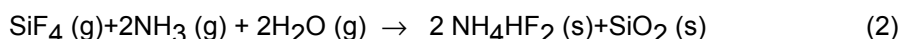
Considering the large excess of ammonia in mixed gases can probably run the complete conversion from SiF_4 to NH_4HF_2 aerosol. All aerosol absorbed in the 1st absorption column reacts with lime to evolve ammonia.

Waste gas from neutralization with moisture content 50% vol. is cooled by mixing of waste gases and by prevailing endothermic reaction. Part of water vapour will condense. Mixture will pass through the 1st absorption column.

1st absorption column

In the 1st absorption column are mainly absorbed fluorine compounds (NH_4HF_2). In addition, aerosols of ammonium nitrate and nitrogen oxides are absorbed in this column. Solution of lime 0,5% wt. is used for scrubbing. Such solution is diluted for ease of manipulation. TCA scrubber was chosen for absorption (turbulent contact absorber). TCA scrubbers have good efficiencies for absorption of aerosols and restrict formation of incrustation. Formation of incrustation is possible when solution of lime is used for scrubbing. Aerosol of NH_4HF_2 is absorbed in TCA scrubber by the following reaction:

$$NH_4HF_2\ (s) + Ca(OH)_2\ (aq) \rightarrow\ CaF_2\ (s) + NH_3\ (g) + 2\ H_2O\ (l) \qquad (3)$$
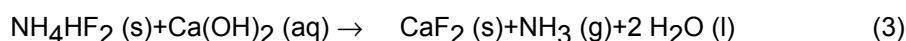
Absorption of nitrogen oxides proceed by the following reaction:

$$NO_2\ (g) + NO\ (g) + Ca(OH)_2\ (aq) \rightarrow Ca(NO_2)_2\ (aq) + H_2O\ (l) \qquad (4)$$
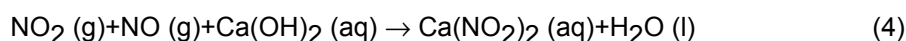
It is estimated that about 35% wt. nitrogen oxides will react in this way. Efficiency of the absorption was estimated on the basis of the test of NOx absorption from waste gas from NPK production on model of TCA scrubber with two stages. (velocity of gas in the scrubber v = 3 m/sec.)

Ammonia will not be absorbed in the 1st absorption column when scrubbing solution is not used.

The big leakage of drops of alkaline scrubbing solution from the 1st absorption column (TCA scrubber) is not acceptable. For this reason there is a mist eliminator fitted in the head of the column.

Part of water vapour will be condensed in the 1st absorption column, because there is a little heat of reaction in comparison with heat losses of column. Heat is needed in the new scrubbing solution.
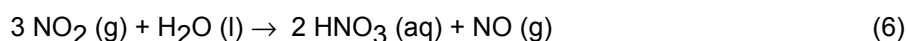
2nd absorption column

Waste gases from the top of the 1st absorption column are introduced into the bottom of the 2nd absorption column. Because waste gases still contain aerosol NH_4HF_2, TCA scrubber was designed as the 2nd absorption column. Advantage of this scrubber is high overall mass transfer coefficient and therefore a dimension of this scrubber can be smaller in comparison with a dimension of a spray tower scrubber. Disadvantage is higher pressure drop.

The 2nd absorption column is scrubbed by ammonium nitrate solution, which contains 2,3% wt. of nitric acid. This acid solution absorbs ammonia with efficiency 97%. The reaction is:

$$NH_3 \text{ (g)} + HNO_3 \text{ (aq)} \rightarrow \quad NH_4NO_3 \text{ (aq)} \tag{5}$$
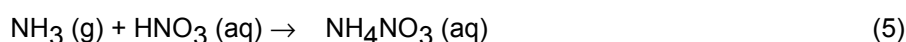
Next scrubbing solution absorbs nitrogen oxides according to the equation:

$$3 \, NO_2 \text{ (g)} + H_2O \text{ (l)} \rightarrow 2 \, HNO_3 \text{ (aq)} + NO \text{ (g)} \tag{6}$$

Efficiency of nitrogen oxides absorption is approx. 26%. The next absorbed substances in this column are NH_4F aerosol (efficiency about 50%) and leakage of drops from the 1st TCA scrubber.

The heat of neutralization in the 2nd absorption column will be compensating the heat losses of the column including recirculation tank. The heat of neutralization heats up the new scrubbing solution and water will be evaporated from solution.

3rd absorption column

The 3rd absorption column is another TCA scrubber too. The 3rd absorption column is used to achieve the emission limit of ammonia. There are the same reactions as in the 2nd absorption column. Efficiencies of absorption in this column are approx. 96% for ammonia, about 16% for nitrogen oxides and about 29% for aerosol of NH_4F. The TCA scrubber is scrubbed by solution of ammonium nitrate, which contains 0,33% wt. HNO_3. Part of scrubbing solution is returned to the production of NPK.

Filter

Waste gas with leakage of drops from the top of the 3rd absorption column is being diverted to the bottom of the scrubbed fibrous filter. Scrubbing solution is sprayed into waste gas in front of the filter by nozzles.

The same reactions like in the 2nd absorption column proceed in this filter. Efficiencies of absorption in the filter will be different in comparison with efficiencies in absorption column.

Efficiencies for ammonia absorption in this filter are approximately 40% for nitrogen oxides, 10% for aerosol of NH_4HF_2, 70% for aerosol of NH_4NO_3, 90% to 100% for leakage drops.

Absorption efficiency of ammonia (40%) is due to a large surface filter area. Absorption efficiency of nitrogen oxides (only 10%) is caused by very short time of contact and low concentration of NOx in the filter. Filtration efficiency of NH_4HF_2 aerosol, (70 %) is given by its low concentration. By reason of high concentration of NH_4NO_3 aerosol, the efficiency of filtration is related to the filter. Filtration efficiency of drops leakage (100%) is due to large drops, from which is leakage created.

Waste gas from filter (volume flow of wet waste gas under normal conditions is 20220 m^3_n/h) is led to the stack, where it is fed with waste gas from:

- Condenser of water vapour (exhaust of U-reactors 19-23)
  Volume flow of wet waste gas under normal conditions is 12150 m^3_n/h)

- TCA scrubber (cleaning of waste gas from granulation) and work environment around U-reactors (Volume flow of wet waste gas under normal conditions is 13500 m^3_n/h)

The mixing of waste gases from NPK production (volume flow of wet waste gas under normal conditions 45870 m^3_n/h, moisture content is 17,8% vol.) makes the reduction of the number stacks possible. To the stack are fed all wet-process exhalations from NPK production. It allows the monitoring of substance concentrations regularly in one stack.

The expected emission concentrations of monitored substances in waste gas after cleaning are shown in Table 3. Emission concentrations were computed from mass balance of the absorption process on the basis supposed efficiencies of absorption for monitored substances. Mass balance was calculated from maximum possible mass flows of components in waste gases.

Table 3 - Mass Flow and Calculated Emission Concentrations in Outlet Waste Gas from Apparatus for Emissions Reduction

Component	Mass flow of component	Mass flow of component	Emission concentration	Efficiency of absorption
	inlet	outlet	outlet	
	kg/hr	kg/hr	mg/m^3_n	%
NO_X (g)	60	21,52	469	64,1
NH_3 (g)	600	2,15	47	99,6
HF (g)	5	0,135	3	97,3

Emission concentrations are given in milligrams of component in l m^3_n of wet gas under normal conditions (0°C, 101 325 Pa).

Product from Absorption of Ammonia

The solution of ammonium nitrate

Composition component: % wt.

H_2O	32,9
NH_4NO_3	66,6
HNO_3	0,4
NH_4HF_2, CaF_2, $Ca(NO_3)_2$	0,1

Design of a Reduction Emission Apparatus

Aerosol is created during the process of harmful substances absorption. Therefore, apparatus for emission reduction has to absorb gaseous components of aerosol as well. Further, the apparatus has to turn absorption into suspension. For example, TCA and Venturi scrubbers are useful for these purposes. Both of them are used for waste gases cleaning from fertilizers production.

1st absorption column

Absorption of fluorine substances by suspension of lime. Solution of lime (1% wt. concentration) is dosed to recirculation tank. Lime concentration in recirculation tank is 0,5 % wt.

type of absorber	TCA (transport contact absorber with fluid bed)
working temperature	72-74°C
volume flow of gas	27 000 m^3/h
diameter of absorber	1800 mm
height of absorber	6500 mm
number of stages	2
distance of stages	1200 mm
intensity of scrubbing	40 m^3/m^2h

filling: plastic spheres with diameter 40 mm
material of column: polypropylene.
mist eliminator in the top of column

2nd and 3rd absorption column

Absorption of ammonia into nitric acid. Solution of nitric acid with concentration 52% wt. is dosed to recirculation tank. Quantity of dosed nitric acid is controlled by measuring the scrubbing solution pH.

type of absorber	TCA (transport contact absorber with fluid bed)
working temperature	79-82°C
volume flow of gas	28 500 - 29 500 m^3/h
diameter of absorber	1800 mm
height of absorber	6500 mm
number of stages	2
distance of stages	1500 mm
intensity of scrubbing	50 m^3/m^2h

filling: plastic spheres with diameter 40 mm

material of column: polypropylene.

Gas filtration

The filtration on fibrous material with scrubbing of waste gas in front of the filter was designed for reduction of aerosols in waste gas.

Designed parameters of filter:

operation temperature	80-82°C
volume flow of gas	29 500 m^3/h
filtration surface	30 m^2
velocity of gas (linear) through filtration material	0,2 m/s

material: polypropylene

Apparatus to test emissions reduction

Apparatus was tested for 72 hours. Determination of emissions from apparatus was measured at the same time. Determined emission concentrations had to be less than emission limits given in Table 2. Test was carried out after test run period: 28-30.11.1996.

Conditions of test:

1. Apparatus will be able to operate stably and continually
2. The fertilizer Synferta P11/12/12 will be produced during this test. This type of NPK fertilizer is produced from Kola phosphate.
3. Production capacity will not exceed 30 t/hr.
4. Mass flows of harmful substances in waste gases from U-reactors number 1-18 feeding into apparatus will not exceed the following values:

    for NO_2 max. 60 kg/hr.   a)

    for NH_3 max. 600 kg/hr.

    for HF   max.   5 kg/hr.   b)
    a) Nitrogen oxides are expressed as nitrogen dioxide
    b) Fluorine and its gaseous compounds are expressed as HF

Comment: Emissions will be measured in stack. To the stack are fed all exhalations from wet-process of NPK production.

    mixed acid and alkaline waste gases from (U-reactors 1-18)
    waste gas from condenser of water vapour (U-reactors 19-23)
    waste gas from granulation and from work environment around U-reactors

Parameters of technology (wet-process) during the test

Test was carried out during production of Synferta P fertilizer

production:	100% of capacity, 30 t/hr
average dosing of phosphate:	10 t/hr
used acids:	nitric acid max. 54%
	sulphuric acid max. 76%
temperatures of acidulation:	UR 1, UR 2 max. 80°C;
	UR 3 max. 90°C;
	UR 4 and UR 5 max. 85°C
dosing of ammonium nitrate solution:	2,25-2,5 m^3/h, (density: 1210 kg/m^3, concentration: 55% wt.)

Parameters of apparatus for emissions reduction

<u>Pressures in exhaust pipelines</u>

Reduced pressure in exhaust pipelines of U-reactors was necessary to maintain on minimal 1000 Pa for sufficient exhaust of U-reactors. Optimum velocity through absorbers is necessary to achieve expected efficiencies under these conditions.

Scrubbing of absorbers:

1st absorber:	75 m^3/h
2nd absorber:	95 m^3/h
3rd absorber:	95 m^3/h
scrubbing of filter	0,35 m^3/h

<u>pH of scrubbing solutions</u>

A set values of pH in particular absorbers must be maintained to achieve the expected efficiencies of apparatus.

<u>1st absorber</u>

pH of scrubbing solution was maintained at minimal value 12.

<u>2nd and 3rd absorbers</u>

Average pH in the 2nd absorber was 0,1
Average pH in the 3rd absorber was 0,4

Results of the Test

Average determined volume flows of waste gases during the test (list of determined volume flows of gases is given in the Table 4).

Neutralization

Average volume flow of dry waste gas from neutralization during the test was 9362 m^3/hr under normal conditions. Average volume flow of wet waste gas under real conditions was 8434 m^3/hr. Average gas moisture was 33% vol.

Acidulation

Average volume flow of dry waste gas from acidulation during the test was 4527 m^3/hr under normal conditions. Average volume flow of wet waste gas under real conditions was 5441 m^3/hr. Average gas moisture was 4,2% vol.

Condenser of water vapour

Average volume flow of dry waste gas from condenser of water vapour during the test was 12272 m^3/hr under normal conditions. Concentration of water vapour was 2,4% vol.

Mixed waste gases in the stack

Average volume flow of dry mixed waste gases emitted into air during the test was 38845 m^3/hr under normal conditions. Average volume flow of wet waste gas under real conditions was 55525 m^3/hr. Average gas moisture was 14,2% vol.

Table 4 - List of determined volume flows of gases

Volume flows of gases	Neutralization	Acidulation	Condenser	Mixed waste gases
dry gas (0°C and 101 325 Pa) (m^3_n/hr)	9362	4527	12272	38845
wet gas (0°C and 101 325 Pa) (m^3_n/hr.)	13973	4725	12574	45274
wet gas (m^3/hr)	18436	5441		55525
H_2O (% vol.)	33,0	4,2	2,4	14,2

Ammonia

Sources of ammonia are waste gases from neutralisation and from the condenser of water vapour. Only ammonia from the neutralisation is removed in the apparatus for emission reduction. The average emission of ammonia from the neutralisation during stable trouble-free operation of absorption was 623 kg/hr.

The average emission from the stack during stable trouble-free operation was 0,226 kg/hr and the average emission concentration was 5,0 mg/m^3 in wet waste gas. Most of determined values of concentration was under limit of determination.

The average efficiency of ammonia absorption during stable operation was 99,96%.

Determined average concentrations of harmful substances during the test are given in the Table 5.

Fluorine compounds of expressed as fluorine acid

The average emission of fluorine acid from the decomposition (acidulation) of a phosphate rock was 1,293 kg/hr.
The average emission of fluorine acid from the neutralisation was 0,463 kg/hr.
The average emission of fluorine acid from the stack was 0,35 kg/hr.
The average emission concentration of fluorine acid was 8 mg/m^3 in wet gas.
The average absorption efficiency of fluorine compounds was 80,1 %.

Nitrogen oxides

The average inlet mass flow of nitrogen oxides into the apparatus was 36,2 kg/hr.
The average outlet mass flow of nitrogen oxides from the equipment was 36,2 kg/hr.
The average emission concentration was 430 mg/m^3 in wet gas.
The average absorption efficiency of nitrogen oxides was 46,4%.

Table 5 - Determined mass flows values and emission concentration during the test

Component	Mass flow of component inlet	Mass flow of component outlet	Emission concentration outlet	Efficiency of absorption
	kg/hr	kg/hr	mg/m^3_n	%
NO$_X$ (g)	36,2	19,40	430	46,4
NH$_3$ (g)	623,0	0,23	5	99,96
HF (g)	1,8	0,35	8	80,1

Evaluation of determined values

The test accomplished all required parameters of the emission reduction apparatus and the production apparatus.

The test lowered emission concentrations for fluorine compounds and for nitrogen oxides without problems. It kept the technology parameters (temperatures of slurry in U-reactors, concentrations of acids used for acidulation of phosphate rock) to achieve the limits of inlet mass flows of harmful substances into apparatus.

The emission concentration of ammonia was achieved when all operation parameters of the apparatus (for example scrubbing of absorbers and filter) were maintained. After nitric acid dosing correction into the 2nd absorber was carried out, the emission limit of ammonia, even in cases of the inlet mass flow of ammonia into the apparatus, was exceeded.

Conclusion

The test demonstrated the successful utilization of the emission reduction apparatus. The apparatus is able to reduce the emission concentrations for all monitored harmful substances (ammonia, nitrogen oxides and compounds of fluorine) within the parameters required by regulations.