Pretreatment of chemical wastewater containing explosives and solvents

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PROJECT A. REMOVAL OF SOLID EXPLOSIVES AND SOLVENT FROM EFFLUENT OUT OF A PETN/RDX AND HMX PLANT.

PROJECT SCOPE.

The purpose of this project is to minimize the environmental impact to the soil and groundwater, reducing contaminants coming from the manufacture of PETN-RDX, and HMX wastewater.

The goal is to achieve this by a pretreatment of residual water. The first objective is to reduce solids by mechanical filtering in a cavern at the first stage and a complementary sedimentation chamber for the sedimentation of remaining fine solid (explosive) particles. The second objective is to reduce C.O.D. levels by dragging volatiles organic components (acetone) in a round chamber with a fine bubble aeration system (air spray from the bottom). All installations are manufactured from stainless steel.

It is identified that the analysis of parameters of the so cleaned effluent shows an evolutionary tendency.

At this first stage, the pretreatment confirms that it is a basic step in an integrated project for the improvement of wastewater quality of this kind of production plants.

In the previous process the wastewater was sent to a lagoon after filtering, but the now sedimented fine (explosive) particles remained in the effluent. In a next step the lagoon will be cleaned up also using the introduced sedimentation technology. Previously used collecting chambers out of concrete with tile covered walls will be remediated.

INTRODUCTION.

Liquid effluents generated at the facilities of PETN - RDX and HMX (acids, solids and high organic content of acetone) flow gravitationally to the new pretreatment plant after passing a cavern containing a cloth filter basket for pre-segregating solid particles from each plant. The solids retained in these filters are collected for further use or disposal.

The objective of pretreatment is to strip off the remaining solid (explosive) particles that could become a future explosive recovery issue.

The effluent is therefore directed to a sedimentation basin for settling. Finally, the liquid free of settleable solids is entering an aeration chamber where the acetone is stripped by a continuous stream of fine (dispersed) air bubbles, and then finally discharged into the lagoon.

The described process is hence to improve the quality of discharges into the lagoon in terms of suspended solids and C.O.D., currently provided mainly by acetone.

MATERIALS AND METHODS.

The Wastewater Pretreatment Plant is composed of the following elements, order of appearance along the route to meet the fluids in the process (Appendix 1 Layout):

F1: filter bag. It is a filter basket located in the plant effluent RDX and PETN stream prior to the decanter. Basket contains a polyester filter cloth bag.

F2: F1 idem. This case corresponds to the effluent HMX plant.

R1: decanter. Container made from stainless steel. The outlet is directed to the pretreatment plant.

R2: R1 idem. This case corresponds to the HMX plant effluent.

C1 C2 C3: Drainpipe (stainless steel). Guides the liquid effluent from the clarifiers to the pretreatment plant.

Z1 to Z5: Inspection chambers (stainless steel).

E5: API settler (stainless steel, fully buried) (Appendix 2 Equipment). The settler has four main areas, namely:

a) the input chamber,
b) the adjustable outlet chamber to control the flow to the aeration chamber and to check for clear liquid free from solid particles,
c) the sedimentation unit with a steep declining bottom to allow solid particles to slide into the sludge pit by gravity,
d) the sludge pit where the solids settle.

The sludge pit is emptied by an "air lift". This is composed of a pipe boom gooseneck (stainless steel) with its lower end 0.10 m above the bottom of the sludge pit. Compressed air lead through this pipe creates a sensation of the sludge that is sucked off through a second pipe of larger diameter with a vacuum pump to a lateral chamber. From there the sludge is collected for final disposal (burning).

E6: Chamber of aeration (stainless steel vessel, fully buried). (Appendix 2 Equipment). The bottom of this chamber has a grid distributor fed by to lines of compressed air (from compressor S1) to provide a continuous flow of small air bubbles to evaporate the acetone from the liquid effluent.

The outlet of the aerated liquid is controlled by an overflow weir that sets the high level overflow. The aerated liquid is then discharged into the lagoon by gravity.

S1: Multifunction Roots compressor. The Roots-type compressor is suitable for generating an air flow Q = 150 m^3 a pressure of 800 mBar.

RESULTS.

Sampling points for monitoring can be seen in the drawing in Appendix 3.

The sampling points were selected to evaluate the entry and exit of the pretreatment plant, in addition to monitor the effluent discharged to the lagoon.

The sampling sequence was established weekly. The parameters for physicochemical analysis report were: temperature, pH, chloride, nitrate, settleable solids and C.O.D. (chemical oxygen demand) (Appendix 4 Analysis results)

The acetone content was determined by gas chromatography using a HP 5890 series II chromatograph with FID detector (Appendix 5 Determination of acetone).

DISCUSSION.

The analysis of the settleable solids parameter shows that the new Bag Filter / Decanter / Sediment system ensures satisfactory removal of explosive materials or byproducts in the effluent stream prior to entering the lagoon (waste water collecting basin).
The amount of settleable (explosive) solids could be reduced by more than 90%.
The efficiency of the aeration chamber is clearly seen as about 60% of acetone is stripped by a physical process with natural air.

It is expected that in the months of higher temperatures evaporation of remaining acetone in the lagoon is higher than during the coldest months of the year.

As a final result it can be concluded that the pretreatment of wastewater from plants of PETN and HMX meets the objective of improving the quality of liquid effluents by reducing the amount of suspended solids and C.O.D. (chemical oxygen demand).

ACKNOLEDGEMENTS.

Ing. Carlos Mayol – Environmental assessment
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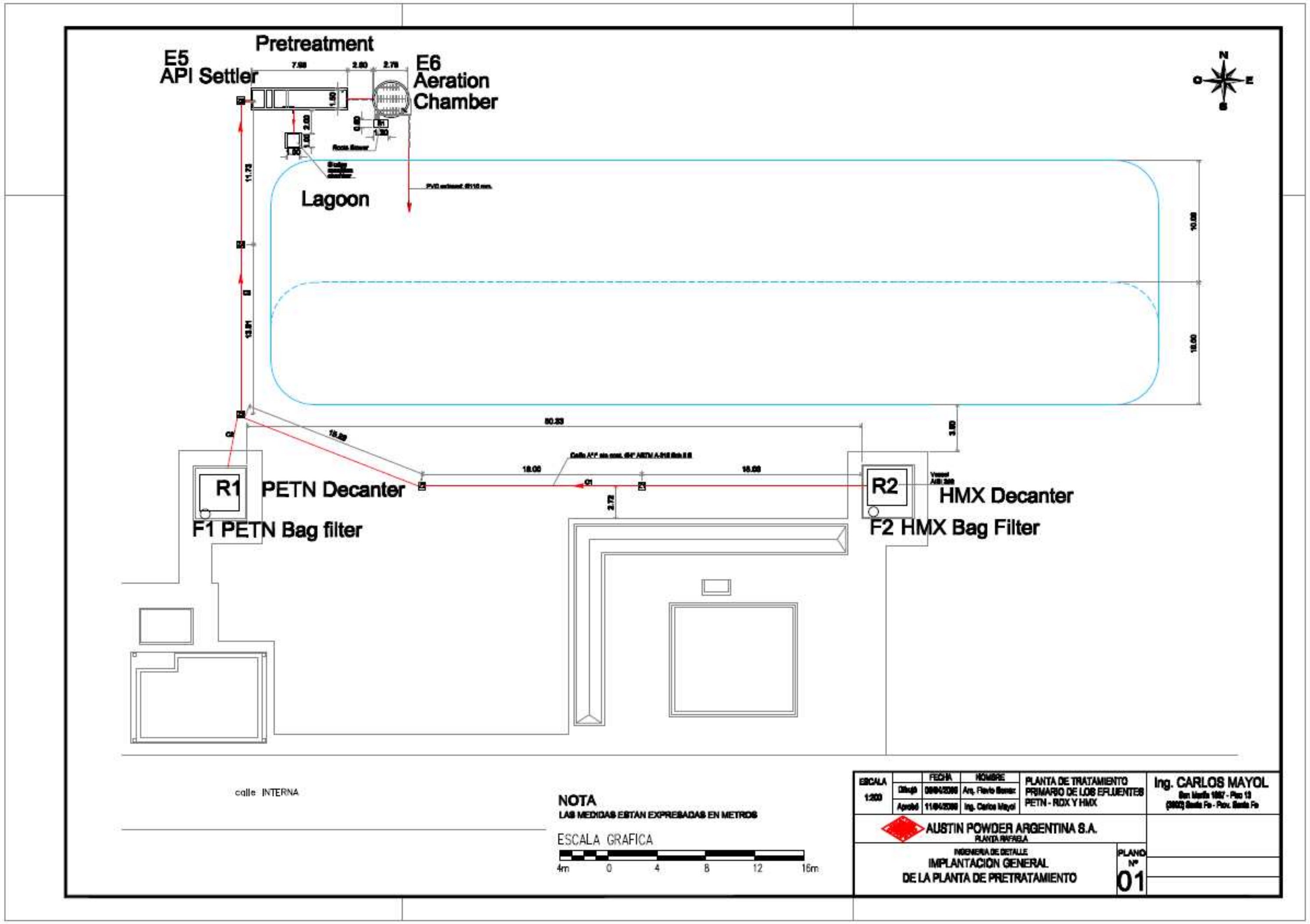
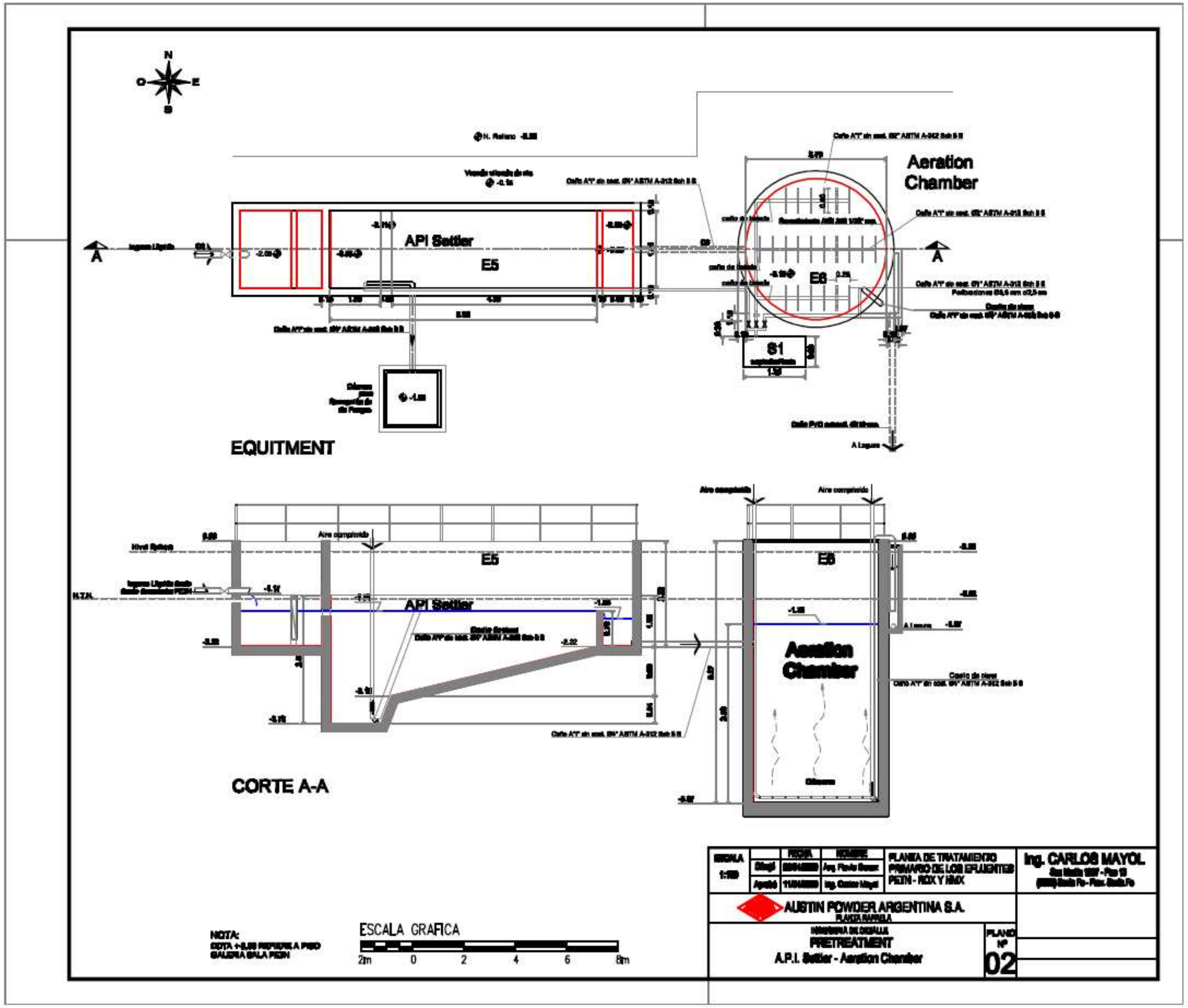
And to everyone who participated in this project.

LEGEND OF FIGURES.

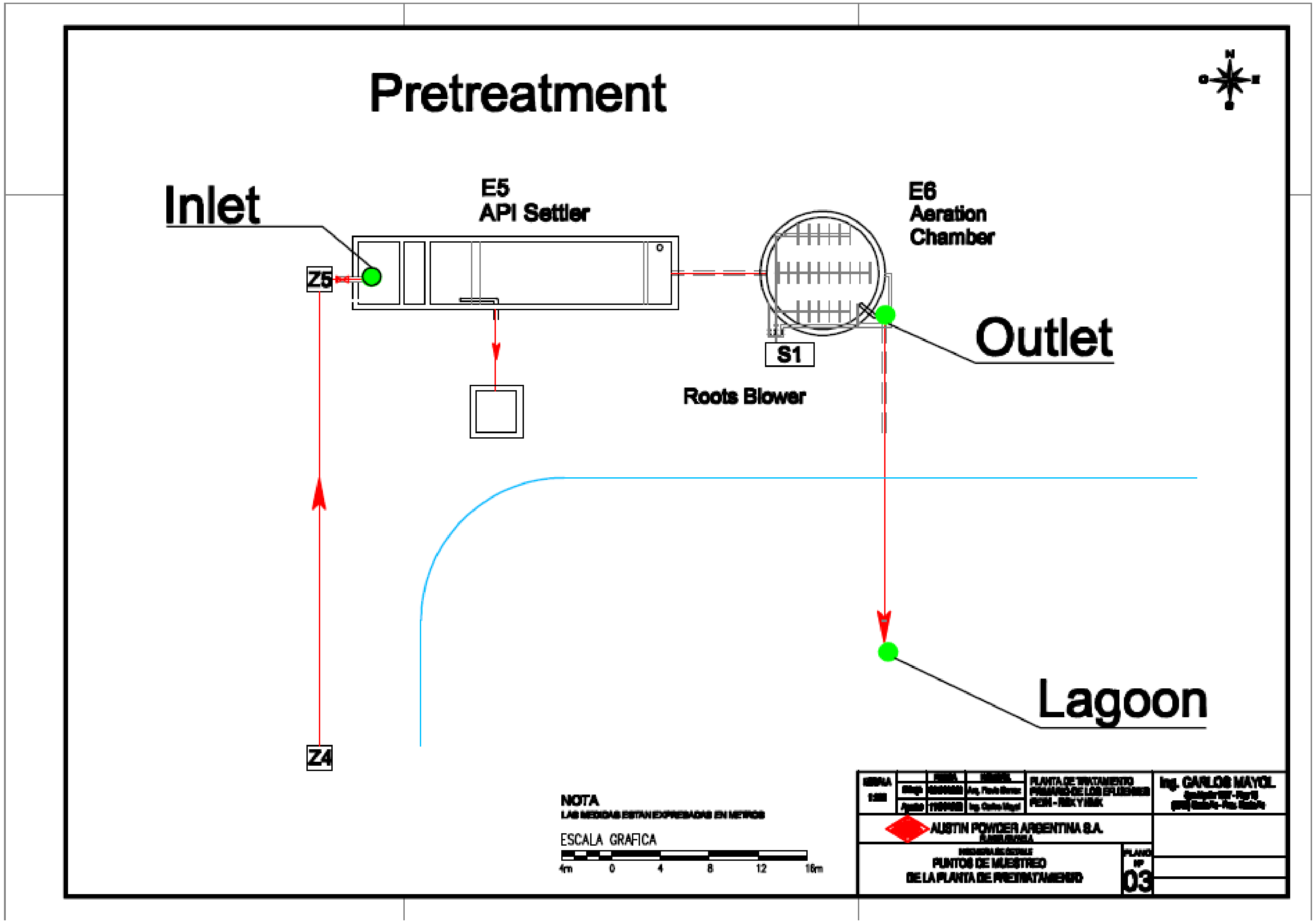
Appendix 1: Layout



Appendix 2: Equipment



Appendix 3: Sampling points



Appendix 4: Analysis results

INLET

Parameters	27-May-10	11-Jun-10	18-Jun-10	25-Jun-10	02-Jul-10	07-Jul-10
Temperature	27	26	31	46	46	41
pH	1,41	3,99	1,13	2,21	1.92	3,34
Chloride (mg / l Cl-)	730,7	564,5	579,7	421,6	449,7	449,7
Nitrate (mg / l NO3-)	12111		18598	6187	5368	7889
Settleable solids 10 min (ml/l)	0,6	0,1	0,1	< 0,1	< 0,1	0,1
Settleable solids 2 hours (ml/l)	0,5	1,5	0,1	< 0,1	< 0,1	0,4
O.Q.D. (mg/l O2)	6367	12900	3941	4095	7066	9696

OUTLET

Parameters	27-May-10	11-Jun-10	18-Jun-10	25-Jun-10	02-Jul-10	07-Jul-10
Temperature	21	25	24	31	36	33
pH	1,75	1,87	1,15	2,01	1,62	3,36
Chloride (mg / l Cl-)	1405,2	548,3	667,5	414,5	449,7	463,7
Nitrate (mg / l NO3-)	6942		12613	7258	6943	6565
Settleable solids 10 min (ml/l)	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
Settleable solids 2 hours (ml/l)	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
O.Q.D. (mg/l O2)	4574	9100	2414	2762	3946	7878

LAGOON

Parameters	27-May-10	11-Jun-10	18-Jun-10	25-Jun-10	02-Jul-10	07-Jul-10
Temperature	16	10	11	12	16	19
pH	1,38	1,83	1,62	2,01	1,78	3,51
Chloride (mg / l Cl-)	632,4	1387	1598,5	1616	1356,3	1342
Nitrate (mg / l NO3-)	10431		5431	5242	5248	5120
Settleable solids 10 min (ml/l)	0,1	< 0,1	0,3	0,1	< 0,1	< 0,1
Settleable solids 2 hours (ml/l)	0,5	0,1	0,4	0,2	< 0,1	< 0,1
O.Q.D. (mg/l O2)	3049	3350	2019	3175	2569	2357

Appendix 5: Determination of acetone

DETERMINATION OF ACETONE		
	qualitative result (%)	quantitative result (g/l)
INLET	100	8,2
OUTLET	41,6	3,41
LAGOON	6,4	0,52

Appendix 6: Comparison between past and present situation

OULET	**Before**	**After**
Parameters	**30-Nov-05**	**Average 2010**
Temperature	34	28
pH	2,74	1,96
Chloride (mg / l Cl-)	369,8	658
Nitrate (mg / l NO3-)	2835	8064
Settleable solids 10 min (ml/l)	0,7	< 0,1
Settleable solids 2 hours (ml/l)	0,9	< 0,1
Q.O.D. (mg/l O2)	15263	5112

PROJECT B. NEW TECHNIQUE OF PRIMARY EXPLOSIVES DECOMPOSITION IN WASTEWATER.

INTRODUCTION.

Austin Detonator s.r.o. (AD) annually manufactures more than 5 tons of primary explosives (PE) including Lead Azide (LA), Lead Picraminate (LP) and Lead Styphnate (LS).

The production processes generate an average amount of wastewater of 1,700 liters per day.

The old decomposition process for PE had several disadvantages not only from an occupational health, but also from an environmental perspective. These were increasing with a growing production and amount of wastewater requiring treatment.

Therefore, AD implemented, in cooperation with the Faculty of Chemical Technology, Institute of Chemical Technology Prague (ICTP) and the company AQUACOMP HARD s.r.o., a new and progressive technology which uses a new technique of primary explosives decomposition in wastewater.

This technology is patented and was awarded as ‘Best Available Technology (BAT)’ by the European Union and is a recommended industrial standard for wastewater treatment of PE manufacturing processes.

PREVIOUS TECHNOLOGY.

The previous technology applied the following (chemical) processes for the decomposition of PE:

LA decomposition:

$Pb(N_3)_2 + 2\,NaNO_2 + 4\,HNO_3 \rightarrow Pb(NO_3)_2 + 2\,NaNO_3 + 2N_2O + 2N_2 + 2H_2O$

$Pb(NO_3)_2 + Ca(OH)_2 + 2\,Na_2S \rightarrow PbS + 2\,NaNO_3 + Ca(OH)_2 + Na_2S$

LP and LS decomposition:

1. Na_2CO_3 treatment (lead precipitation)

2. Fe - HCl treatment (reduction of –NO_2 groups to –NH_2 groups)
3. $Ca(OH)_2$ treatment (pH value from 7 to 9)
4. Sediment taken to the waste dump, water solution emitted into the chemical sewer

Disadvantages.

The disadvantages of these processes can be summarized as follows:

- Releasing of NO_2 as a result of the side reaction between $NaNO_2$ (sodium nitrite) and HNO_3 (nitric acid) during the process of LA decomposition
- $NaNO_2 + 2\ HNO_3 \rightarrow 2\ NO_2 + NaNO_3 + H_2O$
- Releasing of azoimide (HN_3) to the surroundings during the process of LA decomposition, especially when LA waste water stirring is made by air and reaction vessels with waste water are uncovered
- Operating crew has to work using a breathing apparatus
- Use of many different chemicals in decomposition processes of LA, LP and LS - (nitric acid, sodium nitrite, sodium sulfide, sodium carbonate, hydrochloric acid, scrap iron, calcium hydroxide etc.)
- If the process of PE decomposition is not automated, then it requires longer presence of operating crew in toxic and dangerous environment and their increased attention while dosing chemicals manually (with an emphasis on sequence and quantity).
- During the process of LP and LS decomposition only toxic lead is precipitated and nitrogroups are reduced to aminogroups, but the benzene ring itself is still intact.
- The process of LP and LS decomposition is slow, it takes about 48 hours

NEW TECHNOLOGY.

The new technology applied since 2006 comprises the following basic principle: PE in wastewater are oxidized by potassium permanganate ($KMnO_4$) in the presence of nitric acid (HNO_3, pH = 1). The reaction schemes are as follows:

LA decomposition:

$5\ Pb(N_3)_2 + 4\ KMnO_4 + 22\ HNO_3 \rightarrow$

$5\ N_2O + 10\ N_2 + 11\ H_2O + 4\ Mn(NO_3)_2 + 5\ Pb(NO_3)_2 + 4\ KNO_3$

LP decomposition:

$5\ (C_6H_4O_5N_3)2Pb + 62\ KMnO_4 + 196\ HNO_3 \rightarrow$

$60\ CO_2 + 30\ NO_2 + 5\ Pb(NO_3)_2 + 62\ Mn(NO_3)_2 + 62\ KNO_3 + 118\ H_2O$

LS decomposition:

$5\ (C_6HN_3O_8)Pb + 23\ KMnO_4 + 79\ HNO_3 \rightarrow$

$30\ CO_2 + 15\ NO_2 + 5\ Pb(NO_3)_2 + 23\ KNO_3 + 23\ Mn(NO_3)_2 + 42\ H_2O$

Characteristics:

- No NO_2 is released during the decomposition of LA
- LA decomposition is carried out in a closed reaction vessel and HN_3 released during acidification of waste water is drifted away with stirring air to the absorption tower which is filled with NaOH solution and where the following chemical reaction occurs:
    - $HN_3 + NaOH \rightarrow NaN_3 + H_2O$
- NaOH solution from absorption tower is once a month replaced by a new one and the „old“ NaOH solution with NaN_3 content is disposed in the same process as LA.
- Clarified air from the absorption tower consequently passes through an active carbon filter and is then released into the atmosphere.
- Measurements made by external company confirmed that the level of possible dangerous and toxic gases in the air outgoing from the system is below the legal emission limit.
- CO_2 and NO_2 from the decomposition process of LP and LS can be captured in the same way (absorption with NaOH solution) if needed.

Advantages.

The advantages from this new process can be summarized as follows:

- Modern and automated technology including the absorption of HN_3, CO_2 and NO_2
- Trouble-free system (according to 4-year recent experience)
- Only one oxidizing agent needed ➔ simplification and unification of PE decomposition process, less chemicals needed
- Benzene ring disposal during the decomposition process
- Faster decomposition of LP and LS in waste water (48h ➔ 8h)
- End of decomposition process in the reaction vessel is very simply determined by redox potential measurement and also visually (redundant $KMnO_4$ reacts with Mn^{2+} cations, MnO_2 is formed and the reaction solution turns brown)

Automated operations after LA, LP and LS decomposition process.

- Waste water mixing in a common reservoir
- NaOH addition (water with pH value of 7)
- Flocculant dosing (precipitation of $PbCO_3 \times 2\ Pb(OH)_2$, $MnCO_3$)
- Sedimentation
- Salt solution (above the sediment) is pumped and stored in a separate reservoir from which it is gradually moved into the evaporator where it is concentrated. The outgoing water from the evaporator is finally emitted to the sewer system and the salt concentrate is disposed of by specialized firm.
- The sediment is pumped to the filter press, the water from the filter press is pumped to the water reservoir from which the evaporator takes the water.

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