

7 NITROCELLULOSE 2016

- Process of treating
- Results from operation
- Operational problems

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# Treatment of wastewater from nitrocellulose production



### Quality and Amount of Wastewater

| mg/L       | рН    | N-NO <sub>3</sub> - | SO <sub>4</sub> <sup>2-</sup> | COD      | TSS    |
|------------|-------|---------------------|-------------------------------|----------|--------|
| Wastewater | 1 - 2 | 100 - 400           | 1,000 – 2,000                 | 50 - 100 | 0 - 30 |

- Volume of wastewater is about 2,000,000 m³/year
- Temperature from 15 °C to 35°C
- It is necessary to adjust pH and remove nitrates



# Princip of treatment

**Neutralization** by sodium hydroxide

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$$
  
 $H_2SO_4 + 2 NaOH \rightarrow Na_2SO_4 + 2 H_2O$ 

**Denitrification** - bacteria use nitrate as electron-acceptor in the respiration chain instead of oxygen under anaerobic conditions:

$$12 \text{ NO}_3^- + 5 \text{ C}_2 \text{H}_5 \text{OH} \rightarrow 6 \text{ N}_2 + 10 \text{ CO}_2 + 12 \text{ OH}^- + 9 \text{ H}_2 \text{O}$$

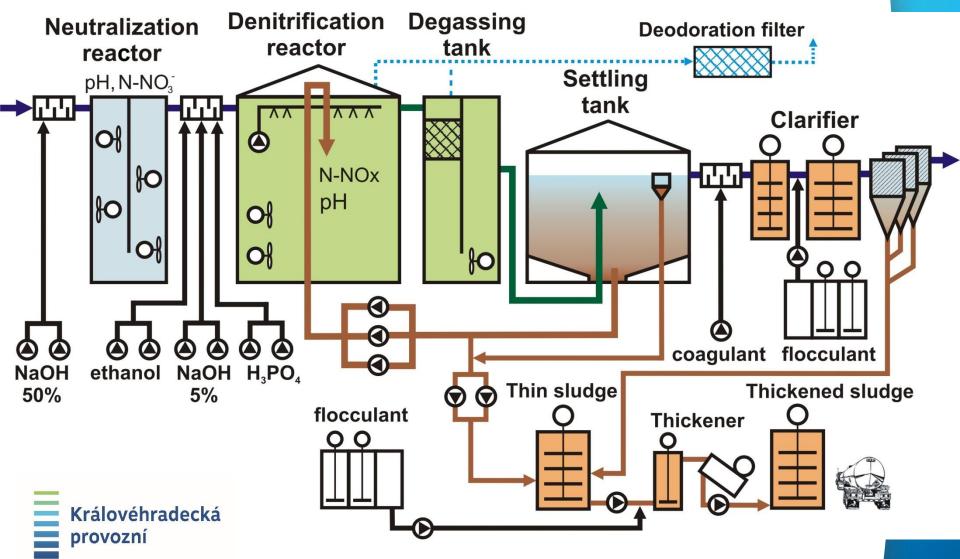
- 2.86 g COD are needed per gram of nitrate-nitrogen
- pH is increasing because hydroxide ions are produced

Complete denitrification pathway:

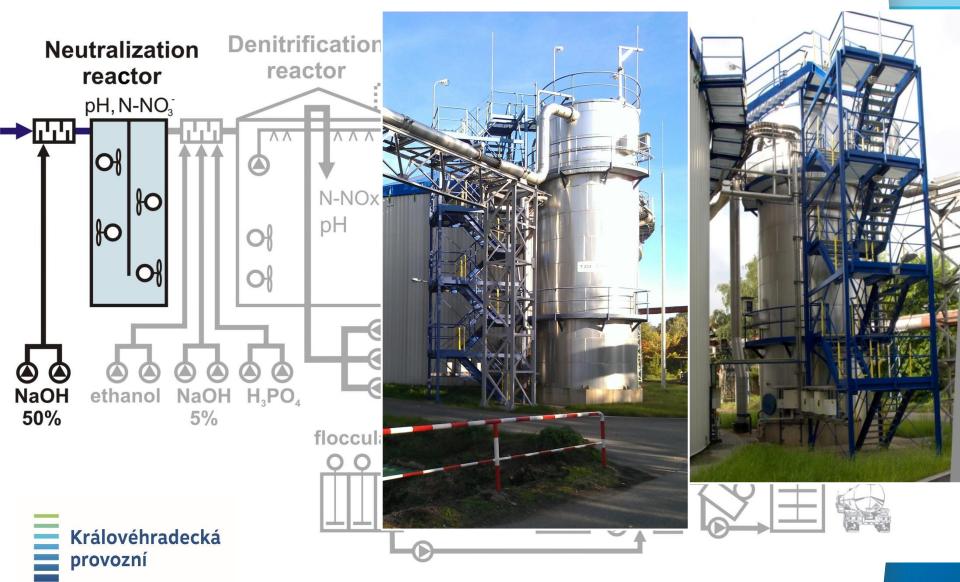
$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$



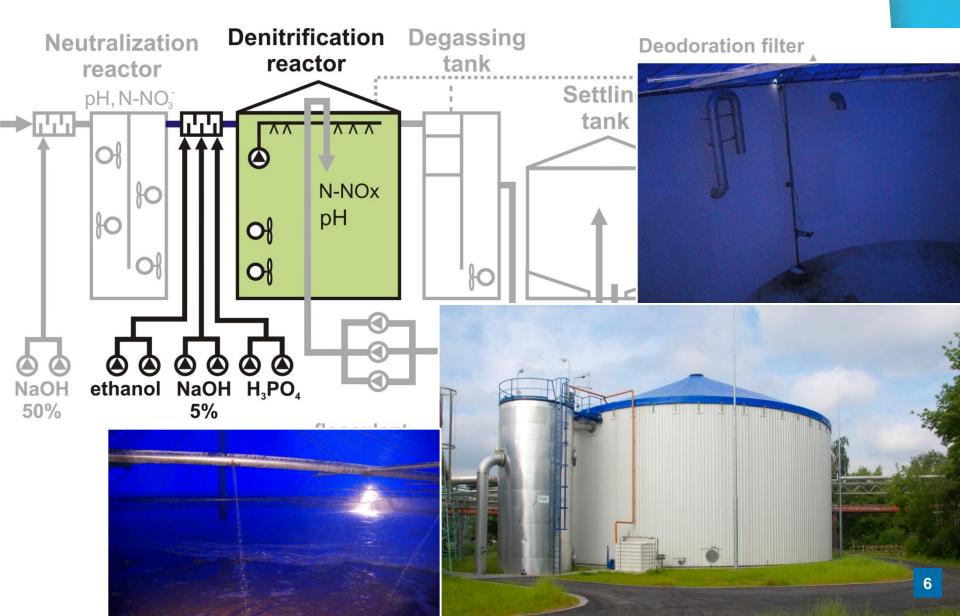
### Process flow scheme



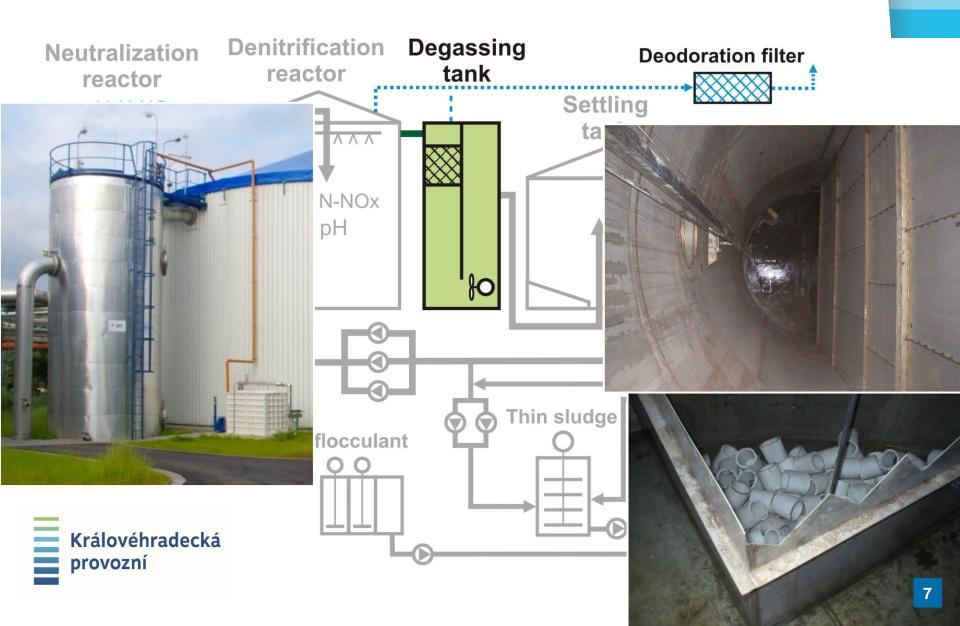
### **Neutralization**



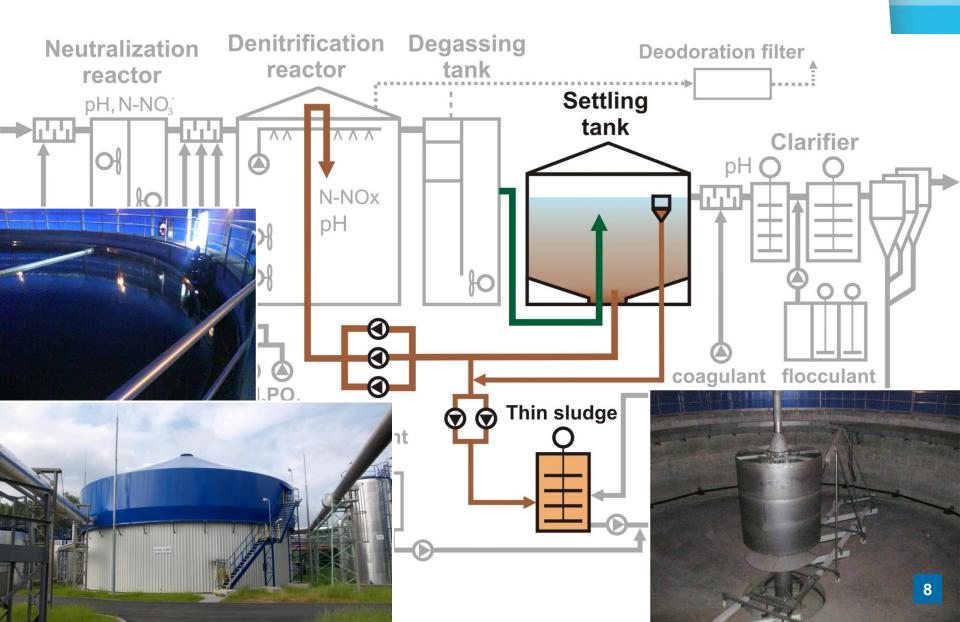
### Denitrification



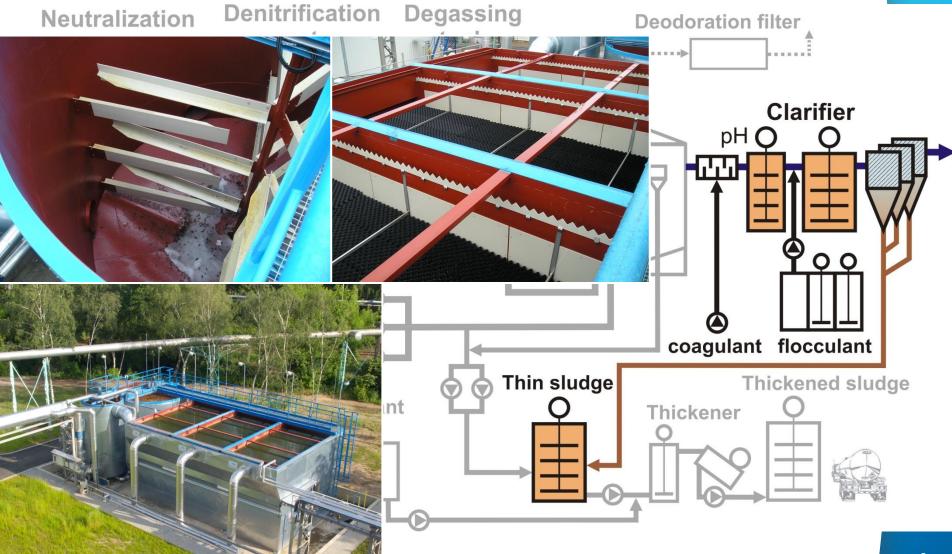
# Degassing



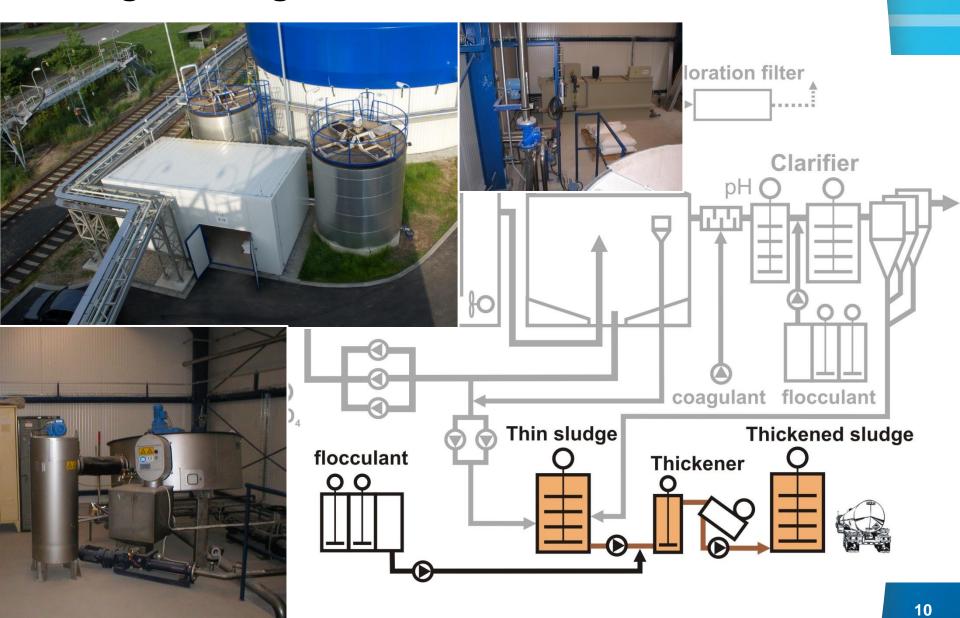
# Separation of Sludge



### **Tertiary Treatment**



# Sludge Management



# Hydraulic and mass loading

| Volume of wastewater   |                       |
|------------------------|-----------------------|
| 5200 m <sup>3</sup> /d | 60 L/s (40 – 100 L/s) |

| Acidity |                      | NaOH     |        | ratio                |
|---------|----------------------|----------|--------|----------------------|
| kmol/d  | m <sup>3</sup> 50%/d | t 100%/d | kmol/d | mol NaOH/mol acidity |
| 176     | 8,0                  | 6,0      | 150    | 0,80                 |

20% of acidity is neutralized by hydroxide ions produced in denitrification.

| $\Delta$ N-NO $_3^-$ | ethanol | Total consumed COD |        | ratio     |
|----------------------|---------|--------------------|--------|-----------|
| t/d                  | $m^3/d$ | t/d                | PE     | t COD/t N |
| 1.1                  | 2.4     | 3.8                | 32,000 | 3.6       |



### **Technological Parameters**

| Sludge concentration (MLSS)    | 2 - 3  | g/L      |
|--------------------------------|--------|----------|
| Organic part of sludge (VMLSS) | 80     | %        |
| Excess sludge production       | 0,9    | T SS/day |
| Return sludge flow             | 50     | L/s      |
| Hydraulic retention time       | 6 – 8  | hours    |
| Sludge retention time          | 8 - 12 | days     |

- Concentration of sludge is slightly lower then in classical activated sludge system.
- The organic part of the sludge is larger due to absence of suspended solids in the influent.



### Wastewater quality

| mg/L     | N-NO <sub>3</sub> - | N-NH <sub>4</sub> <sup>+</sup> | COD | BOD | TSS | рН    |
|----------|---------------------|--------------------------------|-----|-----|-----|-------|
| Influent | 240                 | 0.4                            | 100 | 25  | 20  | 1.5   |
| Effluent | 10                  | 0.2                            | 50  | 10  | 30  | 6 - 8 |

- Removal of nitrates and adjustment of pH
- High operation costs







### Operational problems

### 1) Severe inhibition of denitrification process

- Loss of ability to reduce nitrates
- Stopping the wastewater flow into WWTP
- Inhibitions lasted 8 48 hours

### 2) Poor sedimentation properties of sludge

- Problems with separation of the sludge in the settling tank
- Restriction of wastewater volume



### Inhibition of denitrification

Nitrous gases above the surface of the denitrification reactor.

Possible causation: Nitric oxide

- Denitrification intermediate
- Free radical
- Toxic to bacteria





# Theory of formation of nitric oxide

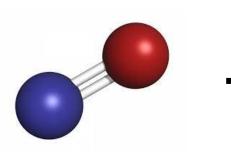
High nitrates loading, low pH → accumulation of NO

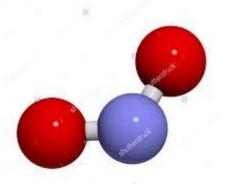
$$NO_3^- >>> NO_2^- >>> NO (aq) > N_2O > N_2$$

After reaching solubility limit

$$NO (aq) \rightarrow NO (g)$$

$$NO(g) + \frac{1}{2}O_2 \rightarrow NO_2(g)$$





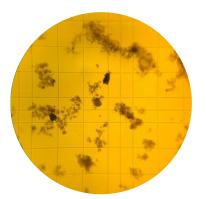




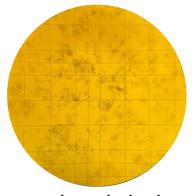
# Poor sedimentation properties of sludge

Zoogloeal bulking = excessive amount of extracellular polymers. Polymers retain large amount of water and prevent the sludge flocs approaching to each other closely.

- slow sedimentation velocity
- poor dewatering



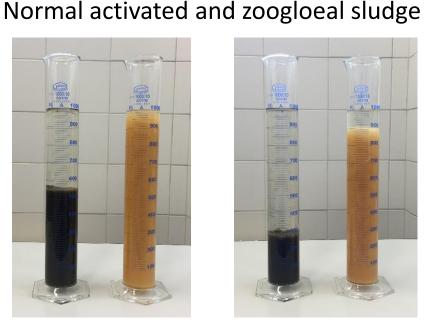
Normal sludge



Zoogloeal sludge



After 30 minutes



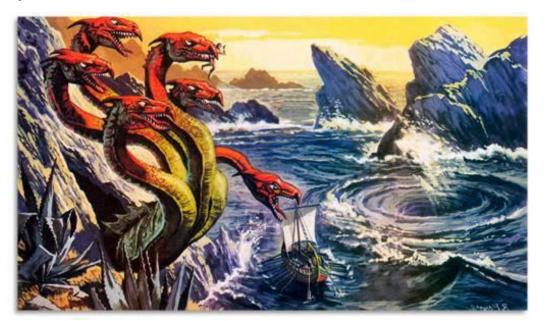
After 2 hours



### Solution attempts

- Dosing of weighting material (milled limestone)
- Dosing of coagulant (Ferric Sulphate) and flocculant
- Partial change of substrate (Brenntaplus VP1)
- Dosing of micronutrients (Vithane)
- Decrease of sludge concentration in reactor

poor sedimentation vs. inhibition





# Thank you for your attention



