# Partial ozonation of activated sludge to reduce excess sludge, improve denitrification and control scumming and bulking

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**Abstract.** Disposal of sewage sludge is forbidden and agricultural use of stabilized sludge will be banned in 2005 in Switzerland. The sludge has to be dewatered, dried, incinerated and the ashes disposed in landfills. These processes are cost intensive and lead also to the loss of valuable phosphate resources incorporated in the sludge ash. The implementation of processes that could reduce excess sludge production and recycle phosphate is therefore recommended. Partial ozonation of the return sludge of an activated sludge system reduces significantly excess sludge production, improves settling properties of the sludge and reduces bulking and scumming. The solubilized COD will also improve denitrification if the treated sludge is recycled to the anoxic zone. But ozonation will partly inhibit and kill nitrifiers and might therefore lead to a decrease of the effective solid retention time of the nitrifier, which reduces the safety of the nitrification. This paper discusses the effect of ozonation on sludge reduction, the operation stability of nitrification, improvement of denitrification and gives also an energy and cost evaluation.
**Key words**: ozonation, activated sludge, nitrification, denitrification, bulking, disintegration

## Introduction

Agricultural use of stabilized sewage sludge will be banned in Switzerland in 2005 due to eco-toxicological considerations (heavy metals and trace pollutants). Because disposal in landfills is already forbidden in Switzerland, sewage sludge has to be dewatered, dried, incinerated and the ashes disposed in landfills. These processes are cost intensive lead also to the loss of valuable phosphate resources incorporated in the sludge ash. The implementation of processes that could reduce excess sludge production and recycle phosphate is therefore recommended.

Most of the disintegration processes are based on a physical treatment of the activated sludge and are operated in front of sewage sludge digestion to improve biogas production and reduce digested sludge (ATV, 2000 and ATV, 2001). The disintegration of activated sludge with ozone leads to a significant reduction of the excess sludge production (Yasui et al, 1994 and 1998; Sakai et al., 1997; Ried et al., 2002). An overview of previous ozonation studies are given in Liu (2003).

Partial ozonation of a fraction of the return sludge leads to an increased solubilization and improved mineralization of the organic solids. This paper will give an overview and discuss the consequences of the partial ozonation of a fraction of the return sludge for the activated sludge system. Results from batch experiments, e.g. TS reduction, COD solubilization, inhibition of nitrification, improvement of denitrification and sludge conditions will be described. Based on the energy balance and the evaluation of the economic efficiency the cost benefit analysis of partial ozonation for treatment plants with different sizes will be discussed.

## Material and methods

### Batch reactors for nitrification tests

In two laboratory scale glass reactors (3 l, diameter 12 cm, height 30 cm), one with partially ozonated activated sludge and the other as control, nitrification rate was investigated (Figure 1). Both fully mixed reactors were operated under the same temperature (20±0.5 °C) and pH conditions (pH = 7.8-8.0). A diffuser was used to supply air and ozone, respectively. The oxygen concentration was controlled between 2.5 and 3.5 $mgO_2\ l^{-1}$ and the oxygen consumption was continuously measured with a respirometer.

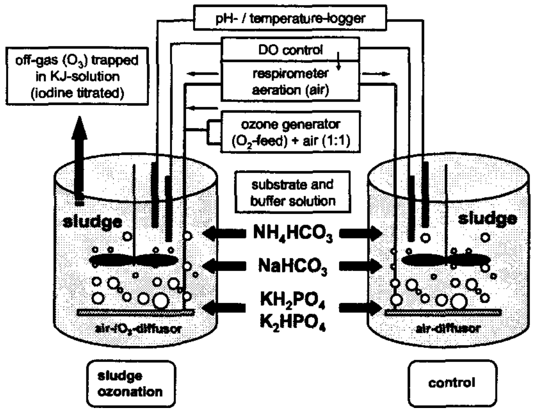


**Figure 1.** Schematic scheme of the experimental system

The ozonated sludge was taken from the return sludge flow of the activated sludge pilot plant of EAWAG (SRT = 20 d, 150 p.e.) that is fed with primary settled wastewater of the city of Duebendorf). The suspended solids concentration (SS) in the batch reactors was about 4.5 and 5.0 g $l^{-1}$ with a VSS/SS and a COD/SS ratio of about 0.65 and 1.1, respectively.

#### Experimental procedure for batch tests - substrate and buffer solution

Before starting the respiration experiments a phosphate puffer ($KH_2PO_4/K_2HPO_4 = 1$) was added to a maximum concentration of 20 mg P $l^{-1}$ to stabilize the pH during ozonation ($CO_2$ stripping effects pH). Then an equal molar amount of $NH_4HCO_3$ and $NaHCO_3$ was added for the nitrification experiments with an initial concentration of about 25 mg $NH_4$-N $l^{-1}$ in all batch tests (Table 1).

**Table 1.** Chronological experimental procedure of the nitrification tests

| Experimental procedure | reactor | time |
|---|---|---|
| $1^{st}$ determination of nitrification rate and oxygen consumption, COD and SS conc. | 1 and 2 | ~ 3h |
| sludge ozonation, determination of COD, SS conc. and ozone consumption | 1 | 0.15-0.6 h, depending on $O_3$ dosage |
| $2^{nd}$ determination of nitrification rate and oxygen consumption | 1 and 2 | ~ 3 – 5h |
| sludge aeration after addition of additional $NH_4HCO_3$ + $NaHCO_3$ (pH 7.8-8.0) | 1 and 2 | ~ 8 – 10h |
| $3^{rd}$ determination of nitrifying rate and oxygen consumption, COD and SS conc. | 1 and 2 | ~ 3 – 5h |

#### Ozone generation, ozone balance and analytical methods

Ozone was generated with an ozone generator fed with liquid oxygen. Ozone concentration in feed-gas (84 mg $O_3$ L¯3) was measured by an UV-photometer (ANSEROS OZOMAT GM, Tübingen, D). Ozone dosage (mass of ozone consumed per unit mass SS) was controlled by changing ozonation time. Off-gas was conducted through two washing flasks in series and the remaining ozone was determined using potassium iodine traps described in method 2350E of Standard Methods. The ozonated pure oxygen gas leaving the ozone generator was mixed with air (ratio 1:1) to keep the dissolved oxygen concentration in the reactor during ozonation smaller than 20 mg $l^{-1}$, which prevents inhibition of nitrifiers by pure oxygen. Sludge samples were analyzed for total and dissolved COD (Dr. Lange, with test tube), total solids (103°C, 24h) and ash content (550°C, 2h). Ammonia and Nitrite were measured colorimetrically with a flow injection analyzer (ASIA, ICMATEC AG, CH-Glattbrugg) after filtration of the sludge sample. Nitrate was analysed with an ion chromatograph (Dionex DX300, Dionex Corporation, Sunnyvale, CA, USA).

## Results and discussions

***Sludge reduction by a optimized ozone dosage***

Sludge solubilization and reduction depends strongly on the ozone dosage (Yasui et al., 1994; Déléris et al., 2000; Camacho et al., 2002; Ried et al., 2002). The ozone disrupts the cell, the cell content is released to the bulk solution and the ozone partly oxidizes the solubilized organics. Figure 1 shows a nearly linear increase of the sludge reduction with increasing ozone dosage up to an optimal dosage of 0.05 $gO_3$ $gSS^{-1}$, where 25-35% sludge reduction is reached. Above that level ozone efficiency decreases. The ozonation of activated sludge of treatment plants with real wastewater leads to lower sludge reductions than for the one grown on synthetic wastewater, which is probably due to lower organic content of the former one. The sludge reduction detected in this study includes the reduction due to normal endogenous respiration.

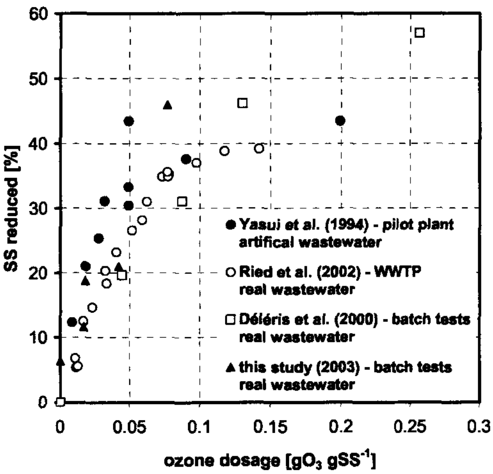


**Figure 2.** Reduction of excess sludge due to mineralization and solubilization of the sludge by ozonation

If the ozonated sludge is recycled to the activated sludge system new biomass will grow on the solubilized degradable organic fraction. But also an inert soluble organic fraction is produced that accumulate in the batch tests (Figure 6). A basic model that describes the processes, which lead to sludge reduction due to ozonation, is found in Kamiya et al. (1998) and in Yasui et al. (1994).

Yasui et al. (1994 and 1998) found a linear reduction of the excess sludge production in a pilot plant fed with synthetic wastewater (yeast extract and peptone) by daily treating 10, 20 and 30% of the reactor sludge with an optimal ozone dosage of 0.05 $gO_3$ $gSS^{-1}$ (Figure 3). The laboratory plant was operated with a solid retention time (SRT) of 10 days, a suspended solids concentration of 4000 gSS $m^{-3}$ and a BOD load of 1000 gBOD $m^{-3}$ $d^{-1}$. The biomass yield without ozone application was 0.4 gSS $g_{BOD}^{-1}$, (0.25 gSS $g_{COD}^{-1}$, assuming a COD/BOD ratio of 1.6) corresponding to 400 gSS $m^{-3}$ $d^{-1}$. By treating daily 30% of the activated sludge no excess sludge was produced. This corresponds to an ozone application of $4000 \cdot 0.3 \cdot 0.05/400 = 0.15$ $gO_3$ $gSS^{-1}$ initial excess sludge (without ozone treatment) or 0.06 $gO_3$ $gBOD_{inlet}^{-1}$.

Ried et al. (2002) describe a two-lane full-scale activated sludge plant treating the wastewater of 16’000 p.e. with a solid retention time of 15 days. In one lane a portion of the return flow was ozonated. They measured a nearly 30% reduction of the excess sludge production in the ozonated lane by treating daily 10% of the activated sludge with an ozone dosage of 0.052 $gO_3$ $gSS^{-1}$. This corresponds to an ozone dosage of about 0.08 $gO_3$ $gSS^{-1}$ initial excess sludge (Figure 3). The result with real wastewater is similar to the above described laboratory plant.

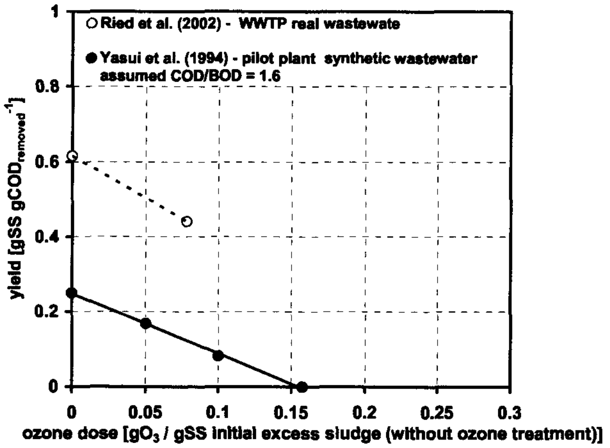


**Figure 3.** Decreasing yield in activated sludge systems with partial ozonation.

**Ozonation reduces the effective sludge retention time of nitrification**

If the excess sludge is taken from the reactor the solid retention time (SRT) is calculated by dividing the reactor volume with the daily excess sludge flow:

$$SRT = \frac{V_{reactor} \cdot X_{reactor}}{Q_{excess\ sludge} \cdot X_{excess\ sludge}} = \frac{V_{reactor}}{Q_{excess\ sludge}} \quad \text{if } X_{reactor} = X_{excess\ sludge} \qquad (1)$$

With increasing ozone treatment excess sludge production is reduced. This would lead to an apparent higher SRT if the suspended solids concentration in the reactor was kept constant.

Because the optimum ozone dosage is low (0.05 $gO_3$ $gSS^{-1}$) at least 10% of all activated sludge have to be treated daily to significantly reduce excess sludge production. The effective SRT of the nitrifiers could therefore be strongly reduced due to partial inactivation or dead of the nitrifiers by ozone treatment (equation 2, Figure 4).

$$SRT_{nitrifier} = \frac{V_{reactor}}{Q_{excess\ sludge} + Q_{ozonated} \cdot \eta_{nitrifier}} \quad \text{with } \eta_{nitrifier} = \text{fraction of nitrifiers inactivated or killed (-)} \qquad (2)$$

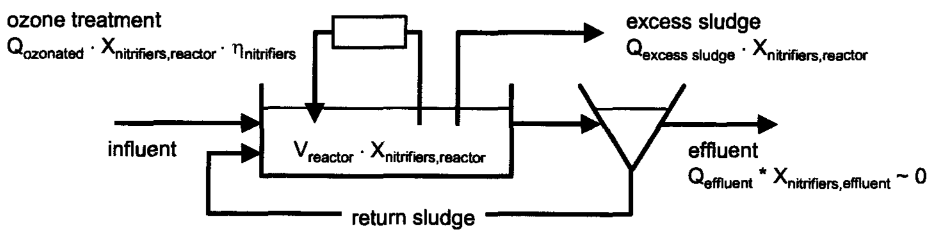


**Figure 4.** Schematic flow scheme of an activated sludge system with ozone treatment.

Nitrifiers are overgrown by the faster growing heterotrophs and might therefore be partly protected in the sludge floc and not as much exposed to the ozone than the heterotrophs. The knowledge of the effective SRT of the nitrifiers is important to estimate the safety of nitrification towards ammonium overload. The detected reduction of the nitrification capacity after partial ozonation is described in Table 2, it is similar to the sludge reduction. The reduction of the SRT of the nitrifiers due to ozonation (equation 2) is therefore about compensated by the increased apparent SRT due to the lower excess sludge production.

**Table 2.** Disintegration of sludge and inactivation of nitrifiers by ozone treatment

| run | ozone dosage | reactor | nitrification rate $r_{nit}$ [mgN $gSS^{-1}$ $h^{-1}$] in first, second and third experiment | | | loss of nitrification capacity $\eta$ | sludge reduction $100\% \cdot (X_{initial} - X_{final})/X_{initial}$ |
|---|---|---|---|---|---|---|---|
| | $gO_3$ $gSS^{-1}$ | | first | second | third | % | % |
| 1 | | control | 1.27 | 1.48 | 1.49 | | |
| | 0.077 | ozonated | 1.32 | 0.71 | 0.83 | 46 | 46 |
| 2 | | control | 1.18 | 1.28 | 1.57 | | |
| | 0.042 | ozonated | 1.45 | 1.09 | 1.18 | 25 | 21 |
| 3 | | control | 1.34 | 1.39 | 1.59 | | |
| | 0.018 | ozonated | 1.35 | 1.01 | 1.24 | 25 | 19 |
| 4 | | control | 1.29 | 1.27 | 1.72 | | |
| | 0.017 | ozonated | 1.45 | 1.23 | 1.63 | 15 | 15 |

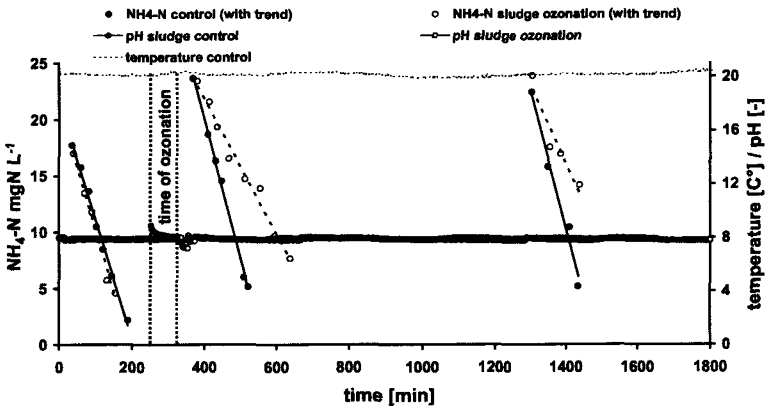


**Figure 5.** Comparison of nitrification rate in ozonated sludge (0.077 $gO_3$ $gSS^{-1}$) and control of run 1.

**Solubilized carbon from sludge reduction increases inert COD and improves denitrification**

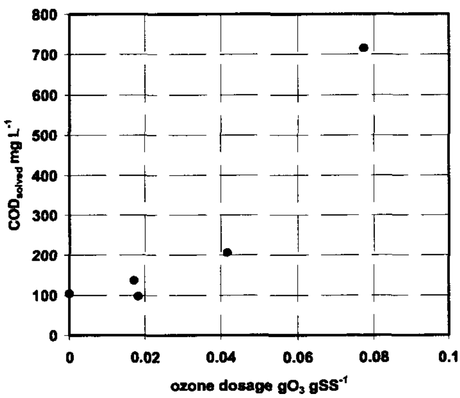


**Figure 6.** Accumulated inert dissolved COD after third determination of nitrification ($SS_{batch}$ = 4.5-5 g $l^{-1}$)

During ozonation inert dissolved and colloidal COD is released to the bulk solution similar as during a long term stabilization of activated sludge. This effect leads to an increase of the inert soluble COD in the effluent of the plant (Yasui et al., 1996, Sakai et al., 1997, Kamiya et al., 1998; Ried et al., 2002, Vranitzky et al., 2002). Depending on ozone dosage the increase of inert COD in our batch experiments was about 0.05 to 0.15 gCOD $gSS^{-1}$ (Figure 6), which is 0.15±0.1 gCOD gSS$^{-1}$ reduced (compare with Table 2) and would lead to an increase of about 20% of the effluent COD for a plant with 30% sludge reduction.

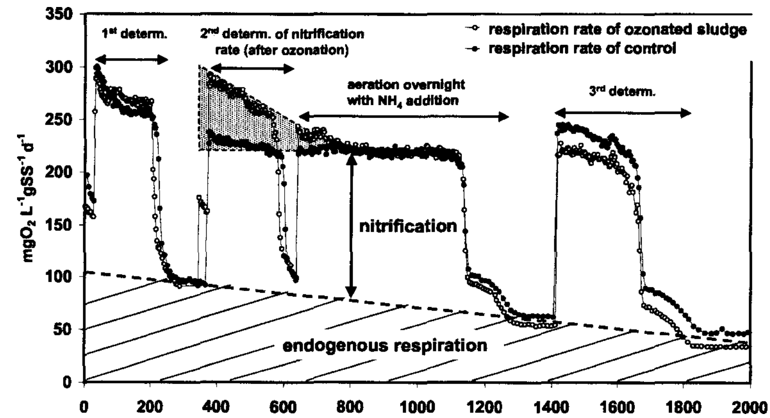


**Figure 7.** Heterothrophic respiration (grey area) on solubilized COD after ozonation (0.017 $gO_3$ $gSS^{-1}$)

Denitrification is often limited by the carbon source in the inlet of the plant. The solubilized degradable organic compounds from sludge ozonation could therefore improve denitrification capacity if the ozonated sludge is recycled to the anoxic zone. The grey area in Figure 7 indicates the increased respiration rate due to heterotrophic growth on the dissolved degradable COD.

An estimation of the additional denitrification capacity due to sludge solubilization gives equation (3). It has to be mentioned that only a fraction of the released degradable COD improves denitrification. A fraction is consumed for biomass production (yield = Y) and a fraction is used up by the oxygen input from ozonation (about 25 $mgO_2$ $l^{-1}$).

$$\frac{NO_3 - N_{denitrified}}{SS_{reduced}} = \frac{(COD_{released} - COD_{inert}) \cdot (1 - Y) - S_{O2}}{2.86 * SS_{reduced}} = \frac{(i_{COD} - 0.15) \cdot (1 - Y) - S_{O2} / SS_{reduced}}{2.86} \quad (3)$$

with $COD_{released} = SS_{reduced} \cdot i_{COD}$, $i_{COD} = 1.4$ gCOD gSS$^{-1}$, $COD_{inert} = 0.15 \cdot SS_{reduced}$ (Fig. 6), $Y = 0.4$ $gCOD_{BM}$ gCOD$^{-1}$

If activated sludge with 3000g SS m$^{-3}$ is treated and 30% reduced:

$$\frac{NO_3 - N_{denitrified}}{SS_{reduced}} = \frac{(1.4 - 0.15) \cdot (1 - 0.4) - 25/(3000 \cdot 0.3)}{2.86} = 0.25\, g\, N_{denitrified}\, g\, SS_{reduced}^{-1}$$

For an average sludge production of 100gSS m$^{-3}$ wastewater and 30% sludge reduction, denitrification increases by 7 gN m$^{-3}$. This effect is partly reduced due to the additional ammonium (1 gN m$^{-3}$) released during sludge ozonation.

**Influence of ozonation on sludge settling properties and dewatering conditions**

Sludge disintegration produces smaller flocs and a turbid supernatant. Recirculation of the ozonated sludge leads to an equalization of the particle size distribution, which improves sludge settling. Ozone dosage has a direct influence on the sludge volume index (SVI) in the ozonation experiments of Kamiya et al. (1998), Ahn et al. (2002), and Déléris et al. (2002). Ried et al. (2002) described in his full-scale studies a significant decrease of SVI at an ozone dosage of 0.04 $gO_3$ $gSS^{-1}$ (Figure 8, phase II). Microscopic investigations showed a clear reduction of the filamentous organisms in the ozonated lane.

Sludge ozonation decreases dewatering conditions and deteriorates filtration resistance and CST (Ried et al., 2003; Ahn et al., 2002). In the full scale experiments of Ried et al. (2002) the ozonated sludge was mixed with the return sludge that led to an improvement of the CST-value.

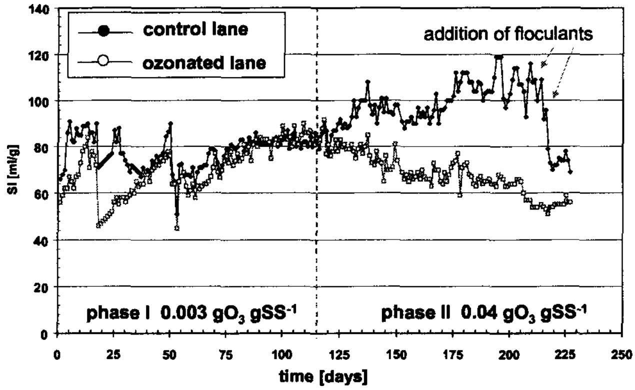


**Figure 8.** SVI in activated sludge system with and without ozone treatment (Ried et al. 2002)

**Costs of ozone treatment and energy consumption**

The economic efficiency and the energy balance are important tools to evaluate the cost benefit analysis of the partial ozonation process (Boehler and Siegrist, 2002). The cost calculations are based on three treatment plant sizes (300`000, 100`000 and 50`000 p.e.), practical experience and information from suppliers and plant operators and a daily treatment of 10% of the activated sludge with an ozone dosage of 0.05 $gO_3$ $gSS^{-1}$. The economic efficiency calculation comprises investment, operation and maintenance costs as well as additional cost due to biogas reduction and cost reduction due to the 30% sludge reduction for sludge treatment (conditioning, dewatering, drying, incineration, disposal). With an effluent fee on nitrogen overall cost is additionally reduced.

**Table 1.** Specific cost for three WWTP sizes based on a sludge reduction of 3 kgSS p.e.$^{-1}$y$^{-1}$ and an ozone consumption of 5 $kgO_3$ p.e.$^{-1}$y$^{-1}$ (0.05 $gO_3$ $gSS^{-1}$, Figure 3).

| | 300'000 | 100'000 | 50'000 | p.e.$^{-1}$ year$^{-1}$ |
|---|---|---|---|---|
| investment (annuity) | 0.43 | 0.48 | 0.77 | € p.e.$^{-1}$ year$^{-1}$ |
| operating (energy, personal, maintenance) | 0.52 | 0.53 | 0.62 | € p.e.$^{-1}$ year$^{-1}$ |
| loss of energy (reduction of digester gas) | 0.20 | 0.20 | 0.20 | € p.e.$^{-1}$ year$^{-1}$ |
| reduced effluent fee for nitrogen | -0.44 | -0.44 | -0.44 | € p.e.$^{-1}$ year$^{-1}$ |
| sludge treatment | -2.77 | -2.77 | -2.77 | € p.e.$^{-1}$ year$^{-1}$ |
| total cost for ozone treatment (reduction of expense) | -1.62 | -1.55 | -1.17 | € p.e.$^{-1}$ year$^{-1}$ |

Cost for operation and investment of sludge ozonation is compensated by the decreasing operation cost for sludge treatment and disposal. The pay off period of sludge ozonation is strongly reduced if an enlargement of an activated sludge plant could be delayed or prevented due to the lower sludge production (Boehler and Siegrist, 2002).

**Table 2.** Specific energy consumption based on a sludge reduction of 3 kgSS p.e.$^{-1}$y$^{-1}$ and an ozone consumption of 0.5 $kgO_3$ p.e.$^{-1}$y$^{-1}$ (0.05 $gO_3$ $gSS^{-1}$, Figure 3).

| | | |
|---|---|---|
| ozone production (air fed) and ozone transfer | 20 kWh $kgO_3$ | 10 kWh p.e.$^{-1}$ year$^{-1}$ |
| COD loss for biogas production (50% of SS reduction) | 4 kWh kgCOD$^{-1}$·1.5 kg p.e.$^{-1}$y$^{-1}$ | |
| electrical efficiency | 35% | 2.1 kWh p.e.$^{-1}$ year$^{-1}$ |
| reduction of energy consumption for sludge treatment | 0.1 kWh $kgSS_{reduced}$ | -0.3 kWh p.e.$^{-1}$ year$^{-1}$ |
| total electrical energy consumption for ozone treatment | ~12 kWh p.e.$^{-1}$ year$^{-1}$ | |

Based on a nitrifying-denitrifying plant with an average SRT of 15 days, energy consumption was estimated (Boehler and Siegrist, 2002). Ozonation needs energy for ozone production and transfer into the sludge. The energy calculations are based on ozone production from air (air fed).

Energy consumption for partial ozonation of the return sludge with an excess sludge reduction of 30% amounts to about 15% of the total electrical energy consumption of a municipal WWTP.

## Conclusions

Partial ozonation of activated sludge decreases excess sludge production proportional to the amount of sludge ozonated if the ozone dosage does not surpass 0.05 $gO_3\ gSS^{-1}$ significantly. With an ozone dosage of 0.05 $gO_3\ gSS^{-1}$ of and a daily treatment of 10% of the activated sludge, sludge reduction amounts to 30%. The decrease of the nitrification capacity due to ozonation is similar to the sludge reduction. The effective SRT of nitrification is therefore not significantly reduced if the SS concentration in the reactor is kept constant (increase of the apparent SRT partly compensates decrease of nitirifiers). Denitrification could be improved if ozonated sludge is added to the anoxic zone due to the production of soluble degradable COD during ozone treatment. But also inert COD in the effluent is increased. Ozonation improves settling properties but decreases dewatering conditions. Cost for operation and investment of sludge ozonation is compensated by the decreasing operation cost for sludge treatment and disposal. The pay off period of sludge ozonation is strongly reduced if an enlargement of an activated sludge plant could be delayed or prevented due to the lower sludge production. But a sludge reduction of 30% increases total electrical energy consumption of the WWTP by about 15%. With increasing sludge solubilization phosphate incorporated in the sludge is released and post precipitation might be an interesting option to introduce phosphate recycling.

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