

NEPTUNE

New sustainable concepts and processes for
optimization and upgrading municipal wastewater
and sludge treatment

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STRATEGIES FOR A SUSTAINABLE AND SAFE SLUDGE MANAGEMENT

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1. SUMMARY

The Neptune project was addressed to study new strategies of sludge treatment and new processes allowing:

- a) to sustain agricultural utilization by producing a very clean and stabilized sludge;
- b) to set up new inertization processes that may allow to overcome the problems linked to dioxins and furans formation during the conventional incineration;
- c) to develop a new approach to conventional incineration aimed to minimize the exhaust gas production and fuel consumption and allow of better energy and nutrients recovery;
- d) to evaluate the mass and energy balance of the different scenarios of sludge processing.

Separation of treatment between primary and secondary sludge was the first idea which was developed regarding sludge management. In fact secondary sludge was expected to be poorer in pollutants and richer in nitrogen and phosphorus than primary sludge. It should be therefore segregated and treated separately from primary sludge to increase chances of secondary sludge utilisation in agriculture. Separation of primary and secondary sludge treatment could also be advantageous from a technological point of view considering that primary and secondary sludge properties are so different that unit processing operations could be specifically designed for each type of sludge.

The first activity carried out in Neptune project was therefore “sludge triage” i.e. assessment of characteristics of primary and secondary sludge, using already available data and performing sampling on two wastewater treatment plants in the region of Rome.

Extensive data collected from two German plants show that there is not a constant enrichment of contaminants in primary or in secondary sludge. However, for TCP and TBEP (organophosphate contaminants), DBP and BBzP (Phtalates) and Bisphenol A it may be observed that primary sludge is always richer than secondary sludge, in both of the two monitored plants. For the other contaminants it is not possible to assess a predominant enrichment in one of the two sludges: only for tin organics a slight enrichment in secondary sludge is observed.

Extractable organic halogens (EOX), total hydrocarbons and methyl blue active substances (MBAS) were analyzed in three campaigns on two WW treatment plants in Italy. Enrichment of the above contaminants in primary sludge with respect to secondary one increases in the order hydrocarbons, EOX, MBAS. Heavy metals, whose presence in the sludges was detected at very low concentration, did not display any enrichment in primary or secondary sludge.

These results, therefore, do not confirm completely that secondary sludge is less polluted than primary sludge but this is certainly true with respect to many contaminants. A deeper knowledge of speciation of contaminants according to their chemical-physical properties (principally K_{Ow}), and the other status conditions (pH, temperature, oxygen concentration, interactions with other ions) would allow to understand when it is expected that such contaminants may enrich in primary or secondary sludge.

The presence of nitrogen and phosphorus in secondary sludge was determined to be 1.8 – 2.0 times than that in primary sludge. This means that agricultural use of secondary sludge, according to nutrient requirement by crops, would take lower amount of contaminants to land with respect to mixed sludge.

Incineration laboratory tests were carried out using these Italian sludge samples with the aim to assess whether different gaseous emissions might be expected from incineration of primary sludge with respect to mixed sludge. These laboratory tests were conducted with a specifically equipped apparatus, called system for thermal diagnostic studies (STDS), including four interconnected sub-assemblies thus enabling to carry out experiments in

flameless conditions. Exhaust gases are continuously monitored without any requirement of their sampling. Results show that when 130% of the theoretical stoichiometric O₂ was used a much higher temperature is required in order to get a negligible amount of organic micropollutants in the resulting emissions. This demonstrates that incineration temperature plays a major role in minimizing the formation of organics in the emissions. When incineration is carried out with a higher oxygen concentration (260% of the theoretical stoichiometric O₂) a minimization of the amount of PAHs in the emissions is achieved. With such conditions there is no noticeable difference between incineration of primary and mixed digested sludge in terms of amount of compounds present in the emissions.

Digestion performance of secondary sludge is quite unsatisfactory (VS destruction in the range 35-40%) and therefore the strategy of separation in sludge processing entails that some pre-treatments are needed to increase digestibility and therefore suitability of processed sludge to be recovered for agricultural use. In fact secondary sludge is very difficult to digest due to the rate-limiting cell lysis. In the last years a renewed interest for the anaerobic digestion of sludge raised from the possibility of a significant gain in solids degradation and energy recovery by applying an appropriate sludge pre-treatment that leads to the breakage of flocs, cell walls, and bacteria membranes enhancing the hydrolysis of sludge volatile solids. A comparison of thermal and ultrasound (mechanical) disintegration was carried out on the base of already available data.

Cambi process, carried out at 170°C and 0.85 MPa, for a typical residence time of 20 min, was considered as reference process for thermal disintegration. The typical performances of secondary sludge anaerobic digestion after the Cambi process, derived from two full-scale plants in Europe, may be so summarized:

- ⇒ VS destruction and biogas production can both increase in the range of 40 to 50% in comparison with the typical performance with no pre-treated sludge so that VS destruction is typically higher than 60%;
- ⇒ significant improvement in sludge dewaterability, so that cake concentration after dewatering can be in the range of 30-50%;
- ⇒ increased digester performance, considering that feed sludge concentrations may reach 10% solids: it is estimated that only 50% of the digester volume is required, compared with conventional digestion;
- ⇒ the high dry solids (DS) concentration hydrolysis results in increased ammonia concentrations requiring a dilution of digester content to limit the NH₄-N concentration to the maximum value of 2.400 to 2.600 mg/L. Dilution can be performed either with water or with the effluent from WW treatment plant;
- ⇒ thermal hydrolysis shortens the retention times in the digestion to 10 - 12 days;
- ⇒ this process has been certified by Norwegian authorities to fulfil the requirements for sludge pasteurisation and its subsequent use in agriculture.

Pilot tests carried out by Aquafin with three parallel anaerobic digesters, one of these fed by pre-treated sludge by Cambi at 150°C, 0.6 MPa and 20 min residence time, evidenced that VS destruction increased from 24 (reference digester) to 35% (digester fed with thermal disintegrated sludge by Cambi). Performance was not considered satisfactory in these pilot tests due to the loss of volatile fatty acids which were stripped when sludge was taken from the Cambi reactor.

Ultrasound equipment typically consists of an ultrasound generator, which changes the frequency of the applied electric current from 50 Hz to the typical frequency of 20 kHz used for sludge disintegration.

Regarding mechanical disintegration by ultrasounds, the study evidenced that the technology is continuously upgraded and it allows improving performance by decreasing energy input by ultrasounds. It is not clear at the moment whether a balance of the energy can be reached

i.e. whether the energy input by ultrasounds can be compensated by the increase of biogas production from digestion. To reach this balance, energy input by ultrasound should be lower than 0.25-0.30 kWh/kg dry solid. Normally, only for overloaded digesters or if operation problem occur, e.g. foaming sludge, mechanical disintegration will be of advantage. The process on full-scale plants is generally performed by sonicating only a fraction of secondary sludge (generally not higher than 30%), the amount which is considered sufficient for liberating the easily degradable material, directly responsible for the activation of methanogenic process, from the flocs.

Typical performance data of secondary sludge sonication (with an electrical energy input of 0.5-1.0 kWh/kg DS) followed by anaerobic digestion show an increase in biogas production and VS destruction of 20-30% with respect to the digestion of not disintegrated sludge. Thermal balance evidenced that sonicating sludge at ~10% disintegration degree the biogas produced is enough to provide the heat required for sludge and digester heating (Braguglia et al., 2008).

Studies on sludge management have included the disposal processes as well (inertisation processes), specifically addressed to secure the final destination of sludge which is not suitable for utilization, through transformation/oxidation of organic matter into soluble matter or gases. These processes are finalized to obtain an inert material (waste) which can be disposed without any environmental problem. An added benefit of some of the above processes is that the final form of phosphorus might be suitable for recovery.

The different inertisation processes are commercially developed at different level. The incineration process by fluidised bed furnace is applied in several full-scale plants in Europe, in the United States and in the Far East, including Japan. Fluidised bed incineration, both by bubbling and circulating furnaces, is at present the most used sludge incineration technology in the world. In spite of the bad reputation of municipal waste incineration, sludge incineration appears to have much lower emissions especially if coupled with indirect drying thus performing an integrating process with internal thermal recovery. In fact the steam which can be produced in a recovery boiler downstream the fluidised bed furnace using the sensible heat of the exhaust gas leaving the furnace at approximately 850°C is generally overabundant with respect to the steam required for sludge drying to increase the solid concentration to the minimum target value required for self-sustaining combustion. This mode of operation allows minimization of the exhaust gas production, which for a quite big plant serving 500.000 p.e. is lower than 7.000 Nm³/h (< 8 Nm³/kg dry solids treated by the furnace). Such a plant might be therefore considered a pilot plant rather than a full-scale plant.

Moreover, it is worth mentioning that chlorine concentration of sewage sludge is so low, unless sludge is dewatered using FeCl₃ as conditioner, that formation of PCDD/F and other chlorinated toxic compounds is quite unlikely. Generally, the heat recovery in the boiler can be stopped when exhaust gas reaches a temperature of 350-400°C which is sufficient to guarantee the steam production required for sludge drying. This option is an intrinsic security to avoid any formation of PCDD/F for the de-novo synthesis.

Among the other inertisation processes presented in this report, currently wet air oxidation seems to be the technology with the major full-scale applications. The process is carried out in liquid phase by injecting pure oxygen into a reactor where the temperature increases up to 250-300 °C and the pressure correspondingly to 6-10 MPa. Typical residence time is 0.5-1.0 h. The advantage of this process, considering that it is conducted in the liquid phase, is that the sludge does not need to be previously dried. The problems are generally connected with the sludge-sludge heat exchanger which is used to recover the heat from treated sludge. It generally experienced clogging problem and the performance reduction due to deposits and incrustations. These problems can be overcome by using steam for sludge heating avoiding the use of sludge-sludge heat exchanger. Obviously, this type of process entails higher energy consumption. The degree of mineralization is not completed (25% of organic substance not completely oxidized still remains at the end of the process) but in spite of this

the organic content of treated sludge might be very low (< 3%). This can be explained by the great proportion of the organic matter which is solubilised and has to be recycled with liquid side-stream (of 9-10 m³/t dry solid dewatered to 70-120 kg COD/m³ digested sludge) to the sludge digester for additional biogas production. Literature data show that consumption of electric energy and pure oxygen account for about 350 kWh/t dry solid and 875 kg pure O₂/t dry solid, respectively. Production of effluent gas to be vented to the atmosphere is under 1 Nm³/kg dry solid which is really negligible, only 10% of that from incineration.

Supercritical wet air oxidation is similar to the above process but in this case it is conducted above the critical point of water (374°C and 22 MPa). Consumption of oxygen and electric energy are similar to those of wet oxidation, but in the supercritical conditions a complete mineralization of organic matter occurs in less than 1 minute. A big advantage of such a process is that heavy metals are transformed into insoluble oxides. Therefore the residue appears practically inert without producing harmful emission.

Sludge pyrolysis at high temperature (> 1,000°C) seems a promising technology which can reduce considerably the production of effluent gas, in comparison with both conventional incineration and wet air oxidation. The process carried out in total absence of oxygen takes to the production of a syngas, constituted by 85% of CO and H₂, to be used for energy production. Currently, very few plants are in operation, most of them on a pilot scale, which implies that this technology still has to be improved. One of this, with a capacity of 25 t/d of sludge at concentration of 70-90% solids (7,000 t/year), was in operation for about 3 years in two locations of Germany. Electric energy consumption was about 100 kWh/t dry solid and therefore less than 1/3 of that of wet air oxidation. Sludge was completely transformed into inert material (250 kg/t dry solid). Investment cost for such a plant were estimated in about 1,800 €/t/year of dry solid to be treated) i.e. 16-20 million € for a plant serving 500,000 p.e. The sludge has to be previously dried; this cost is not included in the above data, however the required heat can be balanced by the heat from the reactor.

Sludge gasification is generally carried out at the temperature of incineration (850°C) or even higher. Gasification is an incomplete combustion of the organics in order to breakdown the molecules into a syngas by carefully controlling the amount of oxygen. The core of gasification process is that the oxygen (about 1/3 of the stoichiometric value) reacts with carbon to produce CO₂ which further reacts with un-combusted C to give production of CO. Hydrogen in the organic matter is converted to H₂ gas instead to H₂O as in incineration. It is well known that gasification of coal and char was used during the Second World War to produce the so-called town gas, i.e. the mixture of CO + H₂. On a pilot plant treating 170 kg/h of sludge the following data were obtained: electric energy consumption 350 kWh/t dry solid, air consumption 0.9 Nm³/kg dry solid, exhaust gas production 1.8 Nm³/kg dry solid.

One of the advantages of gasification and pyrolysis is that they offer more chances for recovering products from waste than incineration. When waste is burnt in an incinerator only energy can be produced by means of a steam turbine. Pyrolysis and gasification can be used in conjunction with gas engines, gas turbines or coupled gas/steam turbines (integrated gasification combined cycle, IGCC) to obtain higher conversion efficiency. Moreover, the syngas can not only be used as a fuel but they may be used as a feedstock (secondary raw materials) for the petrochemical industry and other applications provided that it is purified.

Other advantages of wet oxidation, pyrolysis and gasification are linked with the possibility to recover phosphorus from the ashes, due to its better solubility in comparison with incineration ash.

Strategies for a sustainable and safe sludge management should be based on the preliminary assessment on the available disposal routes. The conventional options for sewage sludge outlets, i.e. agricultural utilisation, landfilling and incineration, have to be critically revised according to the European and national legislation and to the specific local perceptions and opportunities. No rigid rules can be fixed but each case has to be studied and the final choices, on territorial level (district, province, prefecture), should privilege flexible solutions which minimize environmental impact (emissions, fuel and energy

consumptions, chemicals). Other general aspects to be considered are the robustness of the solutions (where they already applied on full plants with consolidated results?) and of course the costs (capital and operating). From the environmental point of view, assessment is carried out by LCA, where all the variables are weighted to transform and normalize all the emissions to a single parameter. Taking into account the above general consideration some reference scenarios were defined in this study to try and establish a common comparison (LCA) and therefore to design strategies for sustainable and safe sludge management.

A first scenario is based on conventional treatment of mixed sludge (primary + secondary one) including gravity thickening, anaerobic digestion, mechanical dewatering by centrifuge and on-site incineration by the integrated process described in Figure 6.5 (pag. 67). In alternative to on-site incineration, on-site drying and off-site co-incineration (power plants or cement factories) or off-site incineration (together with MSW) were considered.

A second scenario is based on the separate processing of primary and secondary sludge. For primary sludge the treatment chain is the same as for the first scenario. For secondary sludge the treatment chain includes dynamic thickening, ultrasound or thermal (Cambi) disintegration, anaerobic digestion and mechanical dewatering by centrifuge. The secondary sludge was considered suitable for agricultural utilization. In alternative to disintegration and digestion, a sub-scenario considered short aerobic thermophilic treatment.

Total mass of a) mixed sludge (1st scenario) is reduced from 16.2 (before gravity thickening) to 0.72 (after dewatering) kg/m³ WW, of b) primary sludge (2nd scenario) from 4.0 (before gravity thickening) to 0.363 (after dewatering) and c) of secondary sludge (II scenario) from 12.3 (before dynamic thickening) to 0.25, 0.26 and 0.3 kg/m³ WW (after dewatering), respectively for thermal disintegration + digestion, ultrasound disintegration + digestion, and short aerobic thermophilic treatment. This means that for a plant capacity of 100,000 p.e. dry mass of secondary sludge to be transported to the fields for utilization can be evaluated in the range 6.3-7.5 t DS/d.

The two sub-scenarios of thermal treatment of mixed sludge or primary sludge are noticeably different regarding the emissions and the fuel consumption. While with on-site incineration the fluidised bed furnace does not need to be fuelled, on-site drying of mixed or primary sludge would require consumption of 72 and 34 L of CH₄/m³ WW, which are accounted to be 90 and 61.5%, respectively, of the total CH₄ production by digestion for the relevant scenarios. Moreover, total exhaust gas production in on-site incineration is 1.12 and 0.60 Nm³/m³ WW, respectively for mixed and primary sludge. Much more abundant production of exhaust gas is expected from on-site drying (7.54 and 3.63 Nm³/m³ WW, for mixed and primary sludge) and from off-site co-incineration (power plants, cement factories) or incineration (1.34 and 0.789 Nm³/m³ WW, for mixed and primary sludge). It therefore clearly appears that on-site incineration is much more sustainable from the environmental point of view.

Net CH₄ production from digestion (Nm³/m³ WW), considering the requirement for sludge and digester heating, was evaluated in 23.8 (mixed sludge), 20.8 (primary sludge), 10.9 (secondary sludge after ultrasound disintegration) and 13.5 (secondary sludge after Cambi thermal treatment). Separation of primary and secondary sludge processing seems to be a good chance to increase recovery of this valuable energy source (+33 and +44% according to the type of disintegration method for secondary sludge).

Proportion of COD to be recycled to the top of the plant by sludge side-streams (supernatant from gravity thickening and concentrate from dynamic thickening and dewatering) was accounted in 7.2 (mixed sludge) and 7.8-8% (primary + secondary sludge) of the influent COD.

In conclusions we can say that:

⇒ an enrichment of many contaminants occurs in primary sludge with respect to secondary one;

- ⇒ concentration of nitrogen and phosphorus of secondary sludge is at least 1.8-2 times higher compared to the primary sludge;
- ⇒ lab incineration tests evidenced that at 260% of stoichiometric oxygen and temperature > 850°C organic micropollutants emissions are practically negligible both from primary and from mixed sludge;
- ⇒ Cambi process or ultrasound disintegration can increase the performance of anaerobic digestion of secondary sludge. Cambi is a much more intensive treatment and the gain in digestion performance is higher. Their application strictly depends on the specific site (availability of space) and costs;
- ⇒ sludge on-site incineration can be carried out with an integrating process to perform the operation without any fuel requirement and minimizing the exhaust gas production;
- ⇒ on-site drying and off-site co-incineration (power plant or cement factories) or incineration (in combination with MSW) consume much more energy (fossil fuel) and produce much more flue gas to be vented to the atmosphere than on-site incineration;
- ⇒ separation of primary and secondary sludge processing seems very convenient to reduce disposal only to primary sludge and to increase production of methane from anaerobic digestion;
- ⇒ novel inertisation processes seem currently to be not as developed as incineration. Wet air oxidation and pyrolysis seem to play a future role in sludge disposal.

2. INTRODUCTION

Wastewater (WW) treatment and the management of sludge produced are global issues, with growing challenges, that must address the concerns of all of the stakeholders, including the facility administrators and operators, the regulators, the politicians, the scientific community, the wastewater generators, the taxpayers and the general public (Greater Moncton Sewerage Commission, 2008).

The volume of the sludge extracted from primary and secondary settling tanks is about 2% of the volume of treated WW. In spite of its negligible volume, sludge treatment and disposal entails very high capital and operating costs, which can be accounted as high as 50% of the total costs of the WW treatment plant, i.e. 25-35 €/(person × year).

Typical treatments for a large WW treatment plant include a first phase of concentration, generally carried out by gravity thickening, a biological aerobic or anaerobic stabilization, aimed to reduce biodegradable solids, odours and pathogens, and mechanical dewatering by centrifugation, belt-pressing or filter-pressing. In most cases sludge processing is designed according to the conventional systems, which might not be suitable for producing sludge with proper characteristics for its final disposal or utilization according to the legislative standards and avoiding any detrimental effects for the environment and any risk for the human health.

The current situation in most European countries is quite diverse. The Table 2.1 shows the current sludge disposal options in some European countries (Greater Moncton Sewerage Commission, 2008).

Table 2.1 Current disposal options in European countries (% of sludge produced)

	Landfill sites	Thermal treatments (incineration)	Composting	Agricultural utilisation	Non agricultural utilisation	Other
European Union	18	23	7	45		7
Austria		35	50	15		
Bulgaria	100			Only few cases		
Czech Republic	13	<1	50	17		20
Finland			73	3		
Flanders		88			12	
Germany	3-6	20 (mono-incineration)+17 (other thermal treatments including co-incineration)		32	25 (landscaping)	
Hungary	60	0.8		39		
Netherlands		58 (mono-incineration + 27 (thermal dried)	15			
Norway	7			65	12	16
Slovenia	30	47 (export to incineration)	15	7		1
U.K.	1.5	19.5		67	5.2	1.8

It may be seen that in many countries agricultural utilisation still plays an important role while in others it was completely banned. Composting seems to increase its importance while more stabilized and sanitized sludge could be obtained by using this process, due to the intense stabilization and the process temperatures as high as 70°C. The application of

thermal treatments is increasing as well as a result of progressively closure of the landfill disposal and agricultural use.

Table 2.2 (Greater Moncton Sewerage Commission, 2008) shows the sludge production per capita in different countries.

Table 2.2 Per capita sludge production (g/person × d) in different countries

Country	Sludge production (g/person × d)
Austria	55
Brazil	33
Canada	76
Italy	38
Finland	94
Hungary	48
Portugal	60
Slovenia	20
Turkey	60
Medium value	54

The sludge production range is quite large (20 – 94 g/person × d) thus indicating the different approach to WW treatment and sludge management in different countries. Sludge production more or less directly depends on the pollutants removal efficiency and chemicals added for phosphate precipitation and flocculation. Too high values, however, can indicate that the biological stabilization process is not completed. We generally can say that the appropriate values should be in the range of 45-65 g/(person × d), unless phosphorus removal process by chemical precipitation is performed.

In countries where technology is less developed, direct agricultural application or landfilling are the typical ways for secure sludge outlet from the WW treatment plants. In countries where the stakeholders and policy makers practically have forbidden land application and where the landfill directive implementation into the national legislation was stringent, only the high temperature destruction methods are available.

In this prospect, the Neptune project was addressed to discover new perspectives in sludge treatment which allow:

- a) to sustain agricultural utilization by producing a very clean and stabilized sludge;
- b) to set up new inertization processes that may allow to overcome the problems linked to dioxins and furans formation during the conventional incineration;
- c) to develop a new approach to conventional incineration aimed to minimize the exhaust gas production and fuel consumption as well as improving phosphate recycling.

The activities carried out on sludge management in the Neptune project are fully described in this report.

3. COLLECTION AND EVALUATION OF DATA OF PRIMARY AND SECONDARY SLUDGE QUALITY

Sewage treatment plants generate quite a large amount of sludge. Although rich in nutrients, organic substance and microelements, in some countries sewage sludge is not accepted as agricultural fertilizer due to the awareness regarding risks for contamination of typical products like milk, because of the possible presence of toxic compounds. A good stabilization is a preliminary condition both for sewage sludge agricultural use or landfill disposal. Anaerobic digestion was always considered the principal process to stabilize sewage sludge in the past years, at least for the big plants.

Separation of primary and secondary sludge could lead to more sustainable sludge management. Such an innovative concept is based on the following considerations: secondary sludge, poorer in pollutants than primary sludge, should be segregated and treated separately from primary sludge to increase chances of secondary sludge utilisation in agriculture. For example, linear alkylbenzene sulfonates (LAS) concentration was reported to be 4,000-7,000 mg/kg dry solids for primary sludge and of 300 mg/kg for activated sludge due to sorption on particulate material of the raw sewage and aerobic degradation in biological treatment (De Henau et. al., 1989; Siegrist et al., 1989).

Due to the low water solubility and lipophylic properties of polycyclic aromatic hydrocarbons (PAHs), these compounds are typically removed from sewage by adsorption on the particulate material in the primary settling tank (Angelidaki and Ahring, 1999). If such a primary sludge is blended with secondary it may render the mixed sludge no longer acceptable for agricultural use. Secondary sludge, on the other hand, is much richer in nitrogen and phosphorus than primary sludge (5-8% instead of 1.5-5% of dry solids for nitrogen, and 1.6-6.0% instead of 0.3-1.5% for phosphorus), with consequent better profit for crops, which need smaller amounts of sludge to balance nutrient requirements.

Separation of primary and secondary sludge treatment could also be advantageous from a technological point of view. Primary sludge, in fact, can be thickened, digested and mechanically dewatered much easier alone than in a mixture with secondary sludge (Kopp and Dichtl, 2001). Moreover, primary sludge treatment can be more easily optimised for energy recovery and for the final incineration.

3.1 Literature data

DPU, one of the partner of Neptune project, used some available data from two full scale plants (Böttrop and Duesseldorf South) to assess the quality of primary and secondary sludge. Each of the above plant serves a population over 1 million P.E. Between 5 and 12 samples (predominantly 24 h composite samples) were taken and analysed for each parameter per plant and measuring point. About 40 individual organic micropollutants were investigated during the period October/November 2004. Primary and excess sludge have been sampled from Böttrop WW treatment plant and analyzed. High variability in pollutant concentrations was noted.

Tables 3.1, 3.2, 3.3, 3.4, 3.5, 3.6 and 3.7 indicate that generally a significant difference between primary and secondary sludge cannot be observed, with the exceptions highlighted. The exceptions confirmed in both plants are relevant to DBP, BBzP, Bisphenol A, TCPP and TBEP. Concentrations of all the above contaminants are higher in primary than in secondary sludge. Tin organics seem to be equally distributed in primary and secondary sludge with a slight enrichment in secondary sludge. But it has to be considered that primary sludge is significantly more reduced in digestion than the secondary sludge that is already partly stabilized.

Table 3.1 Tin organics ($\mu\text{g}/\text{kg}$ dry solid) in primary and secondary sludge produced in the Böttrop (B) and Düsseldorf Sud (D) WW treatment plants

	Tributyltin-cation TBT	Monobutyltin-cation	Dibutyltin-cation	Monooctyl-cation	Diocetyl-tin-cation
Primary sludge (B)	13 \pm 9	35 \pm 23	89 \pm 63	17 \pm 14	22 \pm 23
Excess sludge (B)	41 \pm 21	162 \pm 100	250 \pm 144	53 \pm 32	45 \pm 27
Primary sludge (D)	130 \pm 11	883 \pm 126	621 \pm 105	29 \pm 3	19 \pm 3
Excess sludge (D)	153 \pm 19	892 \pm 271	683 \pm 137	42 \pm 8	22 \pm 7

Table 3.2 Phthalates ($\mu\text{g}/\text{kg}$ dry solid) in primary and secondary sludge produced in the Böttrop (B) and Düsseldorf Sud (D) WW treatment plants

	DBP	BBzP	DEHP	DOP
Primary sludge (B)	4,022 \pm 216	3,229 \pm 2,803	60,854 \pm 26,890	634 \pm 281
Excess sludge (B)	2,504 \pm 657	455 \pm 144	87,994 \pm 8,251	436 \pm 75
Primary sludge (D)	1,712 \pm 909	1,150 \pm 225	25,658 \pm 5,546	545 \pm 287
Excess sludge (D)	589 \pm 453	148 \pm 71	33,317 \pm 10,107	272 \pm 143

DBP: Di-n-butyl phthalate $\text{C}_6\text{H}_4[\text{COO}(\text{CH}_2)_3\text{CH}_3]_2$ BBzP: Benzylbutyl phthalate $\text{C}_{19}\text{H}_{20}\text{O}_4$ DEHP: Di-2-ethyl hexyl phthalate $\text{C}_6\text{H}_4[\text{CO}_2\text{C}_8\text{H}_{17}]_2$ DOP: Dioctyl phthalate $\text{C}_6\text{H}_4[\text{COOC}_8\text{H}_{17}]_2$ Table 3.3 Phenol ($\mu\text{g}/\text{kg}$ dry solid) in primary and secondary sludge produced in the Böttrop (B) and Düsseldorf Sud (D) WW treatment plants

	Nonylphenol	Octylphenol	Bisphenol A	Triclosan
Primary sludge (B)	24,605 \pm 19,093	939 \pm 495	2,383 \pm 877	32,561 \pm 30,277
Excess sludge (B)	11,042 \pm 2,423	460 \pm 130	557 \pm 30	22,668 \pm 814
Primary sludge (D)	39,149 \pm 12,002		2,187 \pm 1,931	7,209 \pm 4,005
Excess sludge (D)	35,154 \pm 14,137	3,608 \pm 2,856	553 \pm 379	7,514 \pm 3,859

Table 3.4 Organophosphate ($\mu\text{g}/\text{kg}$ dry solid) in primary and secondary sludge produced in the Böttrop (B) and Düsseldorf Sud (D) WW treatment plants

	T CPP	TiBP	TnBP	TCEP
Primary sludge (B)	6,058 \pm 2,641	129 \pm 56	391 \pm 202	196 \pm 213
Excess sludge (B)	2,855 \pm 393	168 \pm 55	409 \pm 100	91 \pm 12
Primary sludge (D)	6,626 \pm 4,100	227 \pm 103	236 \pm 112	475 \pm 556
Excess sludge (D)	1,085 \pm 353	39 \pm 22	51 \pm 15	173 \pm 74
	TDCP	TPP	TBEP	
Primary sludge (B)	81 \pm 33	698 \pm 554	956 \pm 522	
Excess sludge (B)	69 \pm 13	475 \pm 131	523 \pm 97	
Primary sludge (D)	186 \pm 69	1,079 \pm 935	1,358 \pm 684	
Excess sludge (D)	82 \pm 26	137 \pm 86	155 \pm 45	

T CPP: Tris (2-chloro-1-methylethyl) phosphate $\text{C}_9\text{H}_{18}\text{Cl}_3\text{O}_4\text{P}$ TiBP: Tris-isobutyl phosphate $\text{C}_{12}\text{H}_{27}\text{O}_4\text{P}$ TnBP: Tri-n-butyl phosphate $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_3\text{PO}$ TCEP: Tris(2-carboxyethyl)phosphine $\text{C}_9\text{H}_{15}\text{O}_6\text{P}$ TDCP: Tris[2-chloro-1-(chloromethyl)ethyl]phosphate $\text{C}_9\text{H}_{15}\text{Cl}_6\text{O}_4\text{P}$ TPP: Triphenyl Phosphate $(\text{C}_6\text{H}_5\text{O})_3\text{PO}$ TBEP: Tris(2-butoxyethyl)phosphate $\text{C}_{18}\text{H}_{39}\text{O}_7\text{P}$ Table 3.5 Musk scents ($\mu\text{g}/\text{kg}$ dry solid) in primary and secondary sludge produced in the Böttrop (B) and Düsseldorf Sud (D) WW treatment plants

	HHCB: Galaxolide PCM	AHTN: Tonalide PCM	Musk- ketone NM
Primary sludge (B)	2,482 \pm 496	516 \pm 126	74 \pm 3
Excess sludge (B)	7,503 \pm 937	1,626 \pm 192	124 \pm 14
Primary sludge (D)	8,147 \pm 1,756	2,005 \pm 471	
Excess sludge (D)	6,622 \pm 1,400	1,441 \pm 269	

Table 3.6 Estrogens ($\mu\text{g}/\text{kg}$ dry solid) in primary and secondary sludge produced in the Böttrop (B) and Düsseldorf Sud (D) WW treatment plants

Estrogene	17 β -Estradiol	Estrone	17-alpha-Ethinylestradiol
Primary sludge (B)	4 \pm 1	10 \pm 2	<1
Excess sludge (B)	<1	1.5 \pm 0.2	<1
Primary sludge (D)	7 \pm 1	5 \pm 2	
Excess sludge (D)	<1	1.1	

Table 3.7 Pharmaceutical compounds ($\mu\text{g}/\text{kg}$ dry solid) in primary and secondary sludge produced in the Düsseldorf Sud (D) WW treatment plants

	Atenolol	Bisoprolol	Bezafibrate	Ibuprofen	Sotalol
Primary sludge (D)	66 \pm 4	<50	92 \pm 10	101 \pm 8	52 \pm 2
Excess sludge (D)	51 \pm 14	15 \pm 5	<10	<10	117 \pm 30
	Trimethoprim	Phenazone	Metoprolol	Sulfamethoxl	Propanolol
Primary sludge (D)	66 \pm 7	<50	180 \pm 20	<50	<50
Excess sludge (D)	55 \pm 10	18 \pm 2	131 \pm 39	74 \pm 13	<10
	Erythromycin	Clofibrac acid	Carbama-zepine	Clarithromycin	Roxithromycin
Primary sludge (D)	<50	<50	263 \pm 55	<50	<50
Excess sludge (D)	<10	<10	303 \pm 32	<10	<10
	Naproxen	Diclofenac			
Primary sludge (D)	<50	75 \pm 23			
Excess sludge (D)	<10	127 \pm 12			

3.1.1 Tin Organics

Tributyltin-cation (TBT) is the main active ingredients in certain biocides used to control a broad spectrum of organisms. Uses include wood preservation, antifouling pesticide in marine paints, antifungal action in textiles and industrial water systems, such as cooling tower, refrigeration water systems, wood pulp, paper mill systems and breweries. TBT compounds are considered as toxic chemicals which have negative effects on humans and environment. Tributyltin compounds are moderately to highly persistent organic pollutants that bioconcentrate up the marine predators' food chain. One common example is leaching of TBT from marine paints into the aquatic environment, causing irreversible damage to the aquatic life.

3.1.2 Phthalates

Di-n-butyl phthalate (DBP) is commonly used as plasticizers and are used as an additive to adhesives or printing inks. They are soluble in various organic solvents (alcohol, ether and benzene). DBP is also used as an ectoparasiticide. It is a suspected endocrine disruptor.

Benzylbutyl phthalate (BBzP) is mostly used as a plasticizer for PVC. It is considered a toxicant. BBzP is commonly used as a plasticizer for vinyl foams, which are often used as floor tiles. Other uses are in traffic cones, food conveyor belts, and artificial leather.

Di-2-ethyl hexyl phthalate (DEHP) is the most important "phthalate", being the diester of phthalic acid and the branched-chain 2-ethylhexanol. This colourless viscous liquid is soluble in oil, but not in water. It possesses good plasticizing properties. Due to its suitable properties and the low cost, DEHP is widely used as a plasticizer in manufacturing of objects made of PVC. Plastics may contain 1% to 40% of DEHP. It is also used as a hydraulic fluid and as a dielectric fluid in capacitors. DEHP also finds use as a solvent in lightsticks. DEHP is used as an emollient in synthetic materials. In Germany, 90% of DEHP is used in PVC and about 10% in lacquers and paints. It is common to use DEHP as an antifoaming agent in paper production, as an emulsifier for cosmetics, in perfumes and pesticides. They aid in the production of different synthetic materials such as dielectric in condensers, and substitute for

substances such as PCBs and pump oil. DEHP specific emissions from various human activities have been identified from cellulose/paper production, DEHP production, plastisol-coating process, PVC production and processing, leaching from PVC products, leaching from landfills and waste incineration and uncontrolled combustion. DEHP is found regularly in municipal wastewater and because of its lipophilic properties it concentrates in sewage sludge.

3.1.3 Phenols

Nonylphenol is an organic chemical produced in large quantities in the United States. It is toxic to aquatic life, causing reproductive effects in aquatic organisms. Nonylphenol is moderately soluble and resistant to natural degradation in water. It is used as a chemical intermediate and is often found in wastewater treatment plant effluent as a breakdown product from surfactants and detergents. Nonylphenol is produced from cyclic intermediates in the refinement of petroleum and coal-tar crudes. It is manufactured by alkylating phenol with mixed isomeric nonenes in the presence of an acid catalyst. Nonylphenol is considered an endocrine disruptor chemical and induces production of vitellogenin in male rainbow trout. This is a process normally occurring in female fish in response to estrogenic hormones during the reproductive cycle. It also induces precocious development of ovaries and an intersex condition in some fish species.

Octylphenol (OP) is a commercial intermediate used primarily for the production of octylphenol polyethoxylate surfactants. No estrogen-like effects were observed.

Bisphenol A is used in the production of epoxy resins and polycarbonate plastics. These plastics are used in many food and drink packaging applications, whilst the resins are commonly used as lacquers to coat metal products such as food cans, bottle tops and water supply pipes. Some polymers used in dental treatment contain Bisphenol-A. Bisphenol A has a hormone disrupting effects and can also act as an antiandrogen.

Triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ester) has been used as an antimicrobial agent in soaps, shampoo and fabrics. While these compounds are regarded as low toxicity their 2-hydroxy isomers have been shown to undergo thermal and photochemical ring closure to form polychlorinated dibenzo-p-dioxins which are highly toxic.

3.1.4 Organophosphates

Tris (2-chloro-1-methylethyl) phosphate (TCPP) is a flame retardant. Physical-chemical properties of TCPP indicate a low viscosity and low acidity. Due to its properties and the excellent cost-efficiency, TCPP is widely used in PVC, rigid Polyurethane & Polyisocyanurate foams used in the construction industry, flexible Polyurethane foams, unsaturated Polyester resins, adhesives, coating and elastomers. TCPP has the potential to cause adverse effects on the human cell's genetic apparatus.

Tris-isobutyl phosphate (TiBP) is a phosphorus fire retardant used as antifoaming agent, penetrant, widely used in dyeing, printing, building, and oil field auxiliary. It is a colourless transparent liquid, with slight odour, it can be hydrolyzed in basic condition. It can be fired in heat, fire and oxidant condition, and produce toxic phosphorus oxide gas.

Tri-*n*-butyl phosphate (TnBP) is widely used worldwide as a solvent for cellulose esters, lacquers and natural gums as a primary plasticizer in the manufacture of plastics and vinyl resins in the formulation of fire-resistant aircraft hydraulic fluids and as an antifoaming agent, mainly in paper manufacturing plants. Although tri-*n*-butyl phosphate has been widely detected in air, water, sediment, and biological tissues, concentrations are usually very low. The production and use of tri-*n*-butyl phosphate pose a low risk for the environment and for the general population. The likelihood of long-term effects in occupationally exposed workers is small.

Tris(2-carboxyethyl)phosphine (TCEP) is a reducing agent frequently used in biochemistry and molecular biology applications.

Tris[2-chloro-1-(chloromethyl)ethyl]phosphate (TDCP) is produced only in two sites within the EU (total production about 10,000 tons/y). It is a flame retardant, potential substitute for the brominated compounds, such as the parent compound TCPP. TDCP is not readily biodegradable and the potential for abiotic degradation in soil and water (hydrolysis) is poor.

Triphenyl Phosphate (TPP) can be used as fireproof plasticizer in a cellulose resin, vinyl resin, natural and synthetic rubber. It possesses low volatility, high fireproof effect, excellent retention rate of mechanical property, transparency and softness. It is used as plasticizer and fireproof additive in cellulose nitrate, a wide variety of coatings, the thin ester and soft sheet of glycerol triacetate, hard polyurethane foamed plastic, engineering plastics, etc. It's a suspected immunotoxicant, neurotoxicant and skin or sense organ toxicant.

Tris(2-butoxyethyl)phosphate (TBEP) is used as the flame retardant agent for polyurethane, cellulose, polyethylene alcohol etc. TBEP is a colourless or light-yellow transparent liquid and it's characterized by low temperature. TBEP is also used in the floor polishers and as a plasticizer in rubber and plastics. Studies of concentrations in various environmental samples show that TBEP is readily biodegradable. Most potential exposure of the general population arises from the use of TBEP in packaging materials for food and from the possible contamination of drinking-water from synthetic rubbers used in plumbing washers.

3.1.5 Musk scents

Musk compounds are widely used as fragrance ingredients in washing and cleaning agents, air fresheners, and personal care products like shampoos, perfumes and cosmetics. Polycyclic musks (PCMs) are currently the largest production group of synthetic musks, with a worldwide production. The main representatives of the polycyclic musks, ranked by use, are: Galaxolide (HHCB), Tonalide (AHTN), Celestolide (ADBI), Phantolide (AHMI), Cashmeran (DPMI) and Traseolide (ATII).

Due to their extensive use, musk compounds have become ubiquitous in the environment, and they are prevalent in surface water. According to their lipophilic characteristics ($\log K_{ow} = 5.7$ and 5.9 for AHTN and HHCB, respectively) and slow bio-degradation rates (the half-life of HHCB in soils is approximately 128 days), considerable bioaccumulation of these compounds can be expected.

Musk ketone (NM) is a widely used artificial fragrance which has been identified in human fatty tissue and milk.

3.1.6 Estrogens

The human estrogen hormone (particularly 17beta-estradiol, estrone, and estriol) concentrations in the effluent of a conventional biological wastewater treatment plant (WWTP) typically range from a few ng/L to several $\mu\text{g/L}$. These micropollutants have properties of endocrine-disrupting chemicals and have been found to disrupt the endocrine system of many species including humans, even at ng/L. 17 β -estradiol is a sex hormone and represents one of the strongest estrogenic chemicals in the environment.

On the contrary, primary sludge is significant more polluted in nonylphenol, bisphenol-A, 17betaestradiol and estrone, whereas secondary sludge is more concentrated in DEHP (di-2-ethylhexylphthalate). Primary sludge resulted more polluted in the other phtalates species analyzed (DBP, BBzP, and DOP). Musk scents concentrate generally on excess sludge and chlorobenzol and PCB were always in concentrations under the detection limit, for both sludge types. Primary and excess sludge from Duesseldorf South WWTP have been also analyzed. From this evaluation no significant difference regarding tin organics and musk scents (PCBs and PAKs have not been determined), nonylphenol and triclosan has been noted. Primary sludge results more polluted in organophosphates, Bisphenol-A, 17- β estradiol, estrone, and phtalates except DEHP, which accumulates on the excess sludge (same result obtained also in the case of Böttrop). For Duesseldorf WWTP sludge, several pharmaceuticals have been also analyzed and the results for most of them show that they

are concentrated on primary sludge, with the exception of sotalol (a beta-blocker), sulfamethoxl (a sulfonamide bacteriostatic antibiotic) and diclofenac as a non steroidal anti inflammatory drug (see Voltaren).

3.2 Data from monitoring of Italian full scale plants

Three WW treatment plants in the Rome area were selected for a monitoring campaign, with the aim to assess the pollution load and the nutrient contents of primary and secondary sludge. This monitoring campaign was specifically designed to verify whether the idea of sludge separation may be a solution to sustain sludge utilisation in agriculture of the biological sludge that should be basically a clean soil improver where the presence of the non polar contaminants is expected to be negligible.

The 3 plants are Co.Bis. Cesano, 90,000 Population Equivalent (PE), Fregene 33,000 - 76,000 (PE) and Roma Nord 780,000 (PE). The quality of sewage sludge is subjected to some variation due to the mode of operation (sludge age) and maintenance of some units (especially the secondary settling tanks of Roma Nord WW plant).

3.2.1 Waste water treatment plant description

The municipal "Roma-Nord" WW treatment plant is one of the four wastewater treatment plants serving the city of Rome. The plant is conventional including screening, primary clarification and secondary treatment by activated sludge. This treatment plant serves about 780,000 p.e. and is operated with very high sludge age (20 d). The plant is designed to treat an average WW flow rate of 4.1 m³/s. Both primary and secondary sludges are mixed together and treated in two anaerobic digesters with a total capacity of 18,000 m³.

The Co.bis. Cesano WW treatment plant, which serves the cities of Cesano, Anguillara Sabazia, Bracciano, Manziana, Oriolo Romano e Trevignano, is designed to treat an average WW flow rate of 250 L/s. It is a conventional plant with primary clarification and secondary treatment by activated sludge; the sludge is aerobically treated and finally dewatered.

The Fregene WW treatment plant is located on the sea coast and therefore it is subjected to a quite large fluctuation of quantity and quality of the WW treated, due to the seasonal resident changes. This plant is designed to operate with a winter population of 33,000 p.e., treating 140 L/s of wastewater and with a summer population of 76,000 p.e., treating 336 L/s. The plant includes a primary settlement and a secondary treatment by activated sludge; the sludge treatment includes a pre-thickening step followed by a mechanical dewatering step (without any biological stabilization).

3.2.2 Sampling strategy

The sampling campaigns were performed on Roma Nord, Co.Bis. and Fregene WW treatment plants, taking both primary and secondary sludge 2 times a day for 5 consecutive days to achieve a representative sample. In the three WW treatment plants the sampling campaigns were carried out as reported in Table 3.8.

Table 3.8 Sampling campaigns in the three WW treatment plants

Roma Nord	Co.bis.	Fregene
June 2007	January 2008	
May 2008	August 2008	March 2009
December 2008	January 2009	May 2009

In each campaign 10 L of primary sludge and 25 L of the secondary sludge were collected. Moreover, 10 L of stabilized sludge were also collected in the WW treatment plants of Roma Nord and Co.bis., equipped with an anaerobic digester and an aerobic stabilization basin,

respectively. As in the Fregene plant the sludge is not stabilized, the mixed sludge (about 0.5 kg) was taken after dewatering by centrifugation.

In the WW treatment plants of Roma Nord and Co.bis. the primary sludge was sampled directly on the sludge extraction line from the primary settling tank. For Roma Nord plant this line takes the sludge to the pre-thickener while for the Co.bis. plant directly to the aerobic stabilization tank. The secondary sludges were sampled on the recycle line to the aeration basin.

In the Fregene plant primary sludge was taken directly from the primary settling tank and secondary sludge in the excess sludge line.

Table 3.9 shows the main characteristics of the treatment units of the three WW treatment plants.

Table 3.9 Main characteristics of the WW treatment plants

	Primary sedimentation	Biological section	Secondary sedimentation
Roma Nord	4 settling tanks $\Phi=60$ m H=2 m Residence time=2 h $S_{tot}=11,310$ m ²	2 aeration tanks 1 diffused air 1 rotors V_{tot} oxidation=56,000 m ³	8 settling tanks $\Phi=60$ m H=3,5 m Residence time=5 h $S_{tot}=22,619$ m ²
Co.bis.	4 settling tanks $\Phi=18$ m $V_{tot}=2,000$ m ³ $S_{tot}=1,018$ m ²	4 aeration tanks + 2 for denitrification V_{tot} oxidation=2,800 m ³ V_{tot} denitrific.=2,400 m ³ Residence time=2.8 h	4 settling tanks $\Phi=22$ m H=2.2 m $S_{tot}=1,520$ m ²
Fregene	2 settling tanks $\Phi=13$ m $V_{tot}=1,600$ m ³ $S_{tot}=265$ m ²	1 aeration tank V_{tot} oxidation=720 m ³ Residence time=1.3 h	2 settling tanks $V_{tot}=2,000$ m ³ $S_{tot}=402$ m ²

A third part of each sample was used to carry out the VS, TS, CST, MBAS, TKN and Total Phosphorus analyses; the other two third parts were freeze-dried to carry out the Heavy Metals, Organic Micropollutants and Thermal analyses, as shown in Figure 3.1.

3.2.3 Chemical characterization

Total and volatile solids (TS and VS) were determined according to the standard methods (APHA, AWWA and WPCF, 1995). The analysis of volatile solids, determined in triplicates, was carried out by a preliminary drying of samples at 105°C for 24 h and determining the concentration of dry solids. In a second step, the dry solids were brought to 550°C for 2 h. The residue typically represents the inorganic part of the dry solids. The difference between the total dry solids and the inorganic ones gives the volatile solids.

The CST was measured with a patented standard CST device. The Model 319 Multi-CST Triton Electronics was designed to comply with European and U.S. electromagnetic compatibility standards. Two 10- and 18-mm diameter funnels were applied for *fast* and *slow* filtering of light and heavy sludges respectively. Sludge was poured into a small open funnel (circular tube) placed on a piece of special chromatographic paper. Filtrate is extracted by capillary suction and a cake is formed at the bottom of the funnel. The CST is obtained from two electrodes placed at a standard interval from the funnel. The time taken for the waterfront to pass between these two electrodes constitutes the CST. CST typically represents a measure of filterability.

Nutrients (TKN and Total Phosphorus) were determined in triplicates by photometric determination using Nitrogen and Phosphate cell test by Spectroquant Merck.

MBAS were measured in duplicates by the standard method (APAT-IRSA 5170), after an ultrasonic extraction from dried sludge to a methanol phase.

C10-C40 – (EPA 5021 A 2003 + EPA 3540 C1996 + EPA 8015D 2003 Total hydrocarbons).

The heavy metals were determined using an Agilent 7500c ICP-MS equipped with a collision/reaction cell in the form of the Octopole Reaction System (ORS). The ORS-ICP-MS technique uses a collision/reaction cell to remove polyatomic interferences. The ions are extracted from the ICP-MS interface into an octapole cell which is positioned before the analyser quadrupole. Helium gas is bled into the cell operated in the Radio Frequency (RF) mode. The RF field focuses the ions, which then collide and react with molecules of the gas leading to the removal of polyatomic interfering ions. Analytic ions are then directed toward the quadrupole analyser. The instrumental operating parameters are reported in Table 3.10.

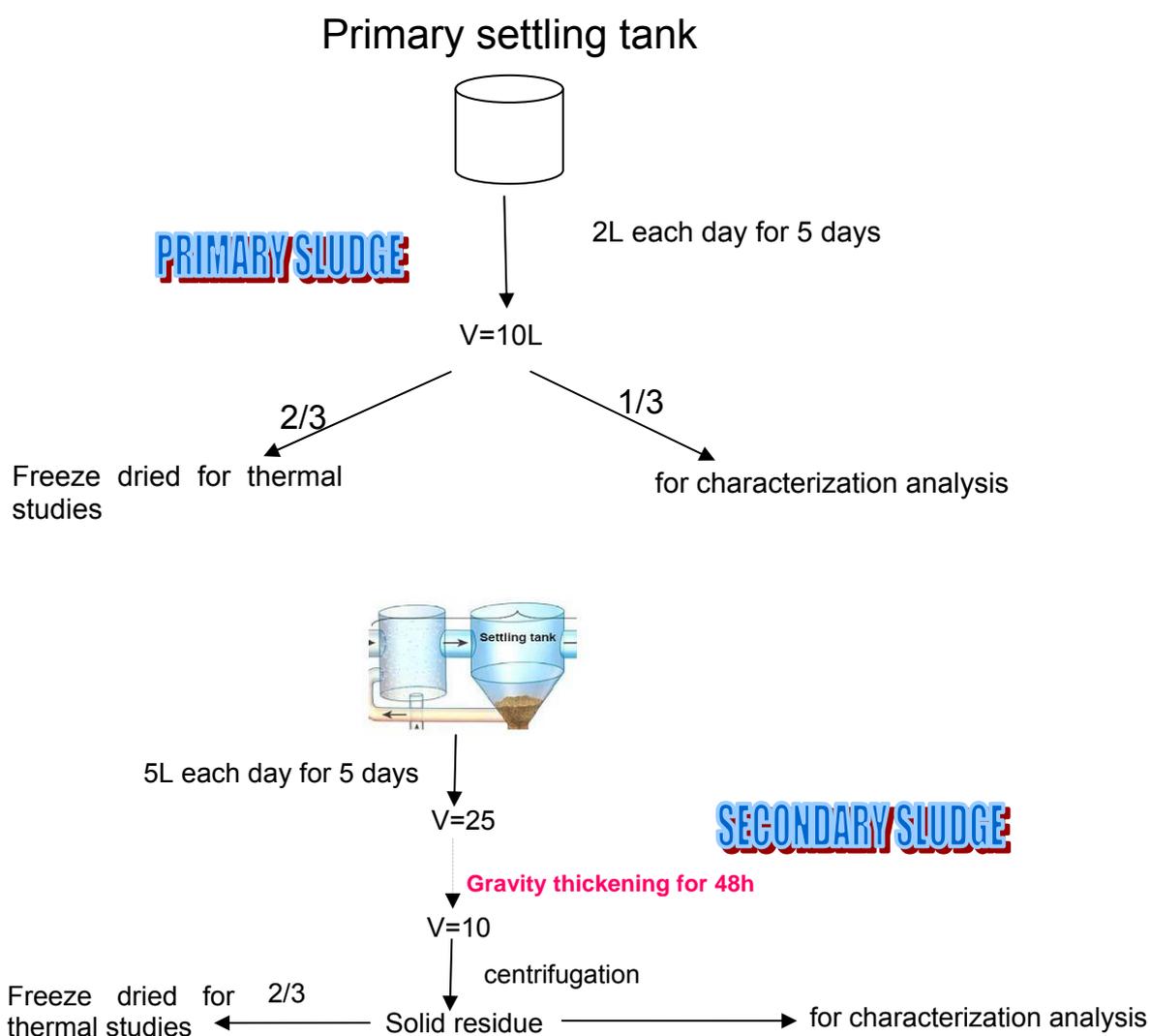


Figure 3.1 Sampling strategy

Throughout this study the octapole cell was pressurized with ultra high purity He gas. The Instrumental Detection Limit (IDL) values were calculated according to the section 3.5 of method 200.8 by USEPA (1994).

The Extractable Organic Halogens (EOX) were determined according to EPA 9023 method using the ECS 1000 analyzer by Euroglas Analytical Instruments (Delft, Netherlands). This

method does not allow detecting specific organic halogenated compounds, but only the total amount of Chlorine, Bromine and Iodine due to the organic halogens of the sample.

Table 3.10 Operating conditions adopted for ORS-ICP-MS analyses

RF power	1500 W
Sample depth	7 mm
Nebuliser	Babington
Nebuliser gas flow	1.10 L/min Argon
Spray chamber temperature	2° C
Sampler and skimmer cones	Nickel
QP bias	- 13.0 V
Octapole bias	- 7.0 V
Cell gas flow	2.5 mL/min He
Measurements	Integration time 0.3 s; 10 replicates
Instrumental tuning	Solution containing ${}^7\text{Li}$, ${}^{59}\text{Co}$, ${}^{89}\text{Y}$, ${}^{205}\text{Tl}$, ${}^{140}\text{Ce}$ at 5 $\mu\text{g/L}$ each; ${}^{156}\text{CeO}^+$, ${}^{140}\text{Ce}^+$, ${}^{70}\text{Ce}^{2+}$, ${}^{140}\text{Ce}^+$

3.2.3.1 Nutrients

Tables 3.11, 3.12 and 3.13 show the characterization, in terms of total and volatile solids and nutrient contents, of analyzed sludges sampled at Roma Nord, Co.bis. and Fregene WWTPs.

Table 3.11 Solid and nutrient content of Roma Nord sludges

	Roma Nord (1°campaign)		Roma Nord (2°campaign)		Roma Nord (3°campaign)	
	Primary	Secondary	Primary	Secondary	Primary	Secondary
Total Solids TS (g/L)	33.5	11.4	45.7	6.9	67.2	12.7
Volatile Solids VS (g/L)	15.6	6.2	19.9	3.2	22.7	4.5
VS/TS (%)	46.6	54.5	43.6	47.1	33.8	35.0
Total P (%TS)	1.0	1.4	0.8	1.4	0.7	1.2
Total N (%TS)	3.5	5.5	2.3	4.7	2.1	4.3

Table 3.12 Solid and nutrient content of Co.bis. sludges

	Co.bis. (1°campaign)		Co.bis. (2°campaign)		Co.bis. (3°campaign)	
	Primary	Secondary	Primary	Secondary	Primary	Secondary
Total Solids (g/L)	11.8	5.3	9.1	5.3	9.3	5.0
Volatile Solids (g/L)	8.7	3.8	6.8	3.9	6.2	3.4
VS/TS (%)	73.7	71.7	74.6	72.4	66.5	68.1
Total P (%TS)	1.4	3.5	0.5	0.8	0.2	0.5
Total N (%TS)	4.6	8.6	3.2	4.9	4.2	6.4

The average nutrient concentrations confirm that in the three WW treatment plants secondary sludge is richer in nitrogen (+60%, +130% and +170%) and phosphorus (+85%, +65% and +190%) than primary sludge. Volatile concentration of the Roma Nord sludges are quite low depending on the very prolonged sludge age and probably the inefficiency of the dewatering unit.

Table 3.13 Solid and nutrient content of Fregene sludges

	Fregene (1°campaign)		Fregene (2°campaign)	
	Primary	Secondary	Primary	Secondary
Total Solids (g/L)	9.4	5.7	27.8	5.8
Volatile Solids (g/L)	5.4	2.2	19.1	3.7
VS/TS (%)	57.2	39.4	68.8	62.9
Total P (%TS)	0.9	1.2	1.4	5.0
Total N (%TS)	3.3	3.9	0.4	6.8

Some values of nutrients reported in Tables 3.11, 3.12 and 3.13 are outside the typical range for secondary sludge (N 5-7 % of TS and P 1.5-3.0% of TS). Regarding the Rome Nord plant the values are a bit lower than the typical concentrations probably due to the quite diluted wastewater of Rome where we have a typical hydraulic loading of 500-700 L/(per × d). In the case of Cobis plant, it must be pointed out that a sewerage system collects all the discharges around the lake of Bracciano, which might be loaded with nutrients due to soil-leaching during the raining periods. Finally, as regards Fregene the low values of 1st campaign are certainly due to the high values of inert solids.

3.2.3.2 Heavy metals

Heavy metals are one of the main chemical classes of substances of water and soil pollution and can be found in various concentrations in wastewaters coming from both industries and municipal sewage (Chipasa, 2003). These elements, with a density above 5 g/cm³ (Nies, 1999), have a well-known toxicity to microorganisms and their effects on a wide range of physiological processes are continuously studied (Ehrlich, 1997; Jezierska and Witeska, 2001). Generally, metal ions dissolved in any aquatic environment are in a range between 3·10⁻¹¹ and 3·10⁻³ mol/L. Higher concentrations are often due to anthropogenic activities.

Adsorption of these ions on suspended particles and their deposit on sediments can cause damage to the equilibrium of aquatic systems. In many countries, water authorities are concerned with the problems related to heavy metal sludge disposal, because sludge with significant concentrations of toxic heavy metals is unsuitable for agricultural recovery and presents a potential environmental risk (Page et al., 1987).

Furthermore, it has been reported that significant increases of contamination potentially due to the presence of heavy metals in sludge-amended soils are produced by the formation of metal forms which are more easily extractable. The speciation of heavy metals significantly influences their environmental mobility and bioavailability determining a potentially high danger of environmental contamination. It is accepted that the primary environmental concern associated with the recycling of sewage sludge is the potential migration of heavy metals to the biosphere by the absorption in plants and consequently into the aquatic environment. The mobility of some of the most common toxic metals (Zn, Cd, Cu, Pb) usually contained in sewage sludge is very high and sludge application to soil increases the accumulation of metals in plants (Roy and Couillard, 1998).

Tables 3.14 and 3.15 show the metal content of primary and secondary sludges of Roma Nord and Co.bis.

Table 3.14 Heavy metals content (mg/kg) of “Roma nord” sludges

	1 st campaign		2 nd campaign		3 rd campaign		Limits of the Directive 86/278 for agricultural use
	Primary	Secondary	Primary	Secondary	Primary	Secondary	
Cd	0.04	0.05	0.7	0.8	0.3	0.2	20-40
Hg	0.89	0.64	0.7	0.6	0.2	0.1	16-25
As	16	15	20	17	9.5	12.7	
Ni	25	22	25	24	14	16.3	300-400
Cr	47	45	96	97	25.1	36.8	
Pb	140	124	142	134	115.8	119.3	750-1,200
Cu	184	162	174	179	80.2	110.4	1,000-1,750
Mn	293	283	271	274	187.5	226.1	
Zn	544	465	617	612	258.1	360.1	2,500-4,000

Table 3.15 Heavy metals content (mg/kg) of Co.bis. sludges

	1 st campaign		2 nd campaign		3 rd campaign	
	Primary	Secondary	Primary	Secondary	Primary	Secondary
Cd	0.05	0.06	0.6	0.4	0.3	0.4
Hg	0.33	0.8	0.9	0.9	0.4	0.3
As	20	12	29	13	9.5	7.9
Ni	13	18	29	21	9.9	10.7
Cr	33	42	102	40	36.1	23.9
Pb	71	67	97	78	73.8	78.2
Cu	282	369	357	354	91.8	184
Mn	142	681	172	686	124	395.9
Zn	595	460	9.741	586	300.8	381.9

In spite of the negligible difference between primary and secondary sludge in heavy metals content, it must be pointed out that primary sludge gets strongly reduced in digestion compared to secondary sludge. The heavy metal concentration of primary digested sludge should therefore be higher than the one of digested secondary sludge. All values are well below (1-3 order of magnitude) the present European limits.

The metal concentrations measured are found to be far from the maximum concentrations permitted according to Goi D. et al. (2006), demonstrating that these sludges are well suited for agricultural use.

3.2.3.3 Micropollutants

3.2.3.3.1 Organic halogen compounds

Contributors to the total amount of organic halogen compounds in municipal wastewaters and in sludge are washing detergents, disinfection byproducts, pesticides, varnishes, stain removers, flame retardants, cosmetics, pharmaceuticals, deodorants, etc. used typically in domestic activities, together with many other halogenated solvents and other synthetic materials consumed in handicraft activities and small industries connected to municipal sewers. The most common halorganics which can be found in municipal wastewaters are chlorinated hydrocarbons, chlorophenols (trichlorophenols, 2-chlorophenol, dichlorobenzene), trichloroethane, trichloroethylene, aldrin, dieldrin, polychlorinated biphenyls (PCBs).

The concentrations of these substances in municipal wastewaters usually are low so their toxicity phenomena on biomass are not a concern in traditional biological treatment plants. Biological processes are not very effective for their biodegradation, but rather these chemicals can be adsorbed and concentrated on biomass (WPCF, 1986; Bornhardt et al., 1997). Presence of organic halogen compounds in effluents of municipal WW treatment plants can preclude water reuse (Jekel et al., 1991).

It is important to underline that treatments which are traditionally carried out on sludge usually have no effect on the chemical properties of the halorganic compounds and therefore their removal from sludge can be carried out only through specific and generally expensive processes (Wild and Jones, 1989). If sludge is used to amend soils, these persistent halorganic polar compounds, which are less absorbed by soil, may reach the ground aquifer and pollute groundwaters (Klopffer, 1996).

In Figure 3.2 the extractable organic halogens contents of both primary and secondary sludge of Roma Nord and Co.bis. are reported.

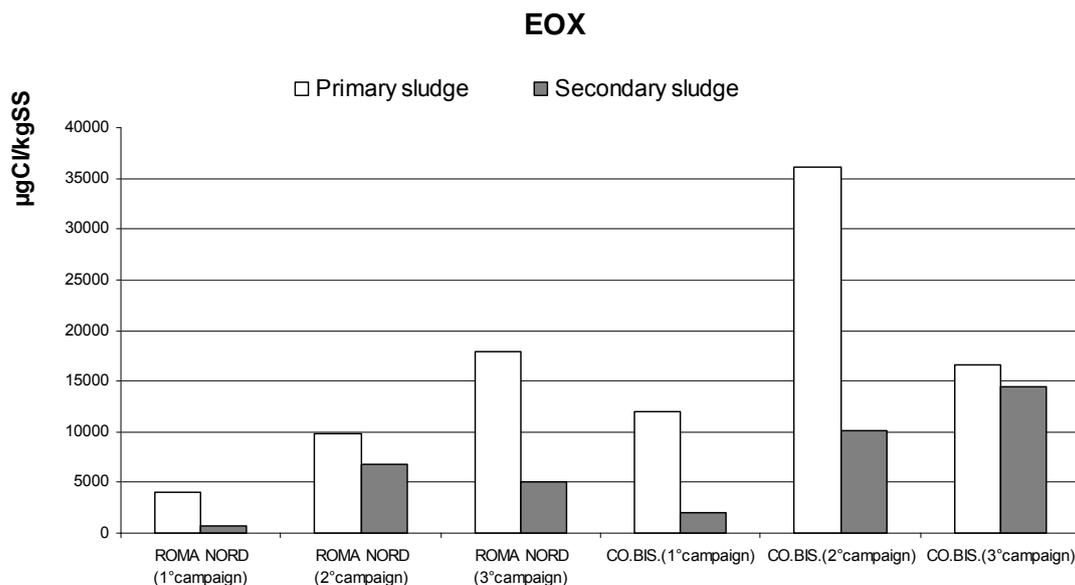


Figure 3.2 Extractable organic halogens (EOX)

Primary sludge is always richer in EOX content than the activated one.

3.2.3.3.2 Total Hydrocarbons

Total hydrocarbons are apolar compounds consisting of carbon and hydrogen, which are classified as aromatic or aliphatic, according to their content or absence of benzene rings. Hydrocarbons originally derive from various petroleum fractions and their toxicity increases according to the scale: paraffins, naphthalenes, olephines, and aromatic compounds. Generally, the smallest and most volatile molecules are the most toxic ones. Hydrocarbons are used as fuel, lubricants, solvents and raw materials for the chemical industry.

WWTPs located in urban areas were much likely to receive wastewaters contaminated by hydrocarbons and PAHs from road traffic and phthalates from industrial activities. These compounds could then be concentrated in sludge during primary settling. Some microorganisms are able to degrade organic compounds; for instance, in biological processes such as sludge composting or anaerobic digestion some PAHs and PCBs were reported to be eliminated by biodegradation (Lazzari et al., 2000; Bernal-Martinez et al., 2005). In settling tank, where the primary sludge is produced, oxygen concentration is low causing a slow fermentative biodegradation. On the contrary in aerated basin, where biological sludge is produced, oxygen concentration is higher and a high oxidative biodegradation is expected.

In Figure 3.3 the total hydrocarbons contents of both primary and secondary sludge of Roma Nord and Co.bis. are reported.

3.2.3.3.3 Methyl Blue Active Substances (MBAS)

Household detergents are the principal source of inorganic and organic chemical substances of domestic origin which are discharged into the environment, normally through wastewater drainage systems. The active matter of detergents is composed of natural and/or synthetic surfactants of different types. Linear alkylbenzene sulphonates (LAS) are the most frequently employed synthetic anionic surfactants. (Prats et al., 1997) and typically they represent 70-80% of MBAS.

Figure 3.4 shows the MBAS content in primary and secondary sludge of Roma Nord, Co.bis. and Fregene.

These results show that anionic surfactants, which are one of the focus pollutat affecting sludge utilization in agriculture, are mostly adsorbed in primary sludge.

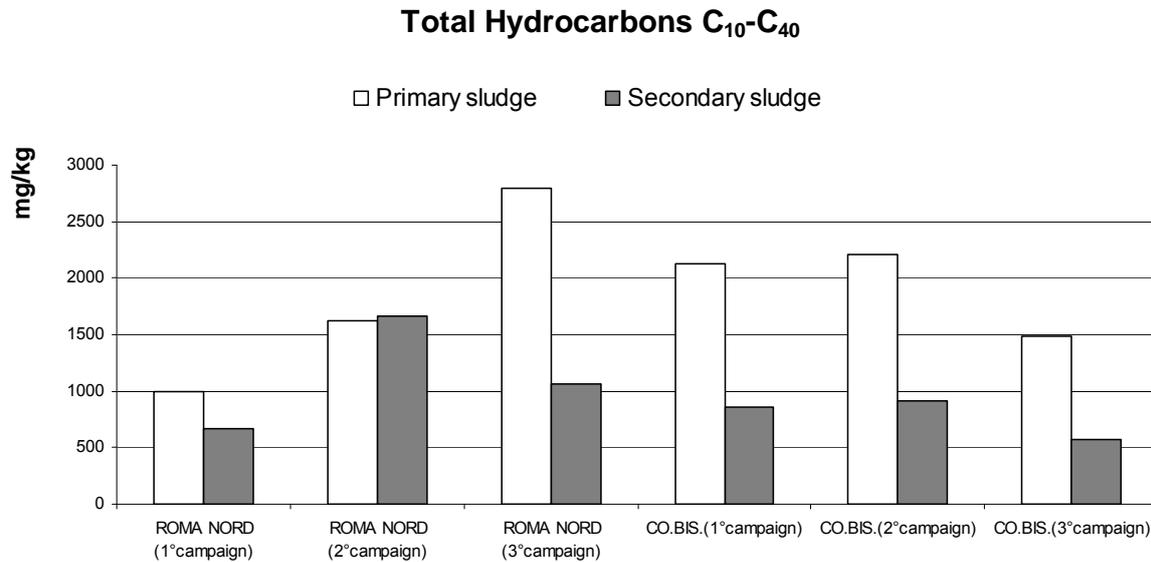


Figure 3.3 Hydrocarbons

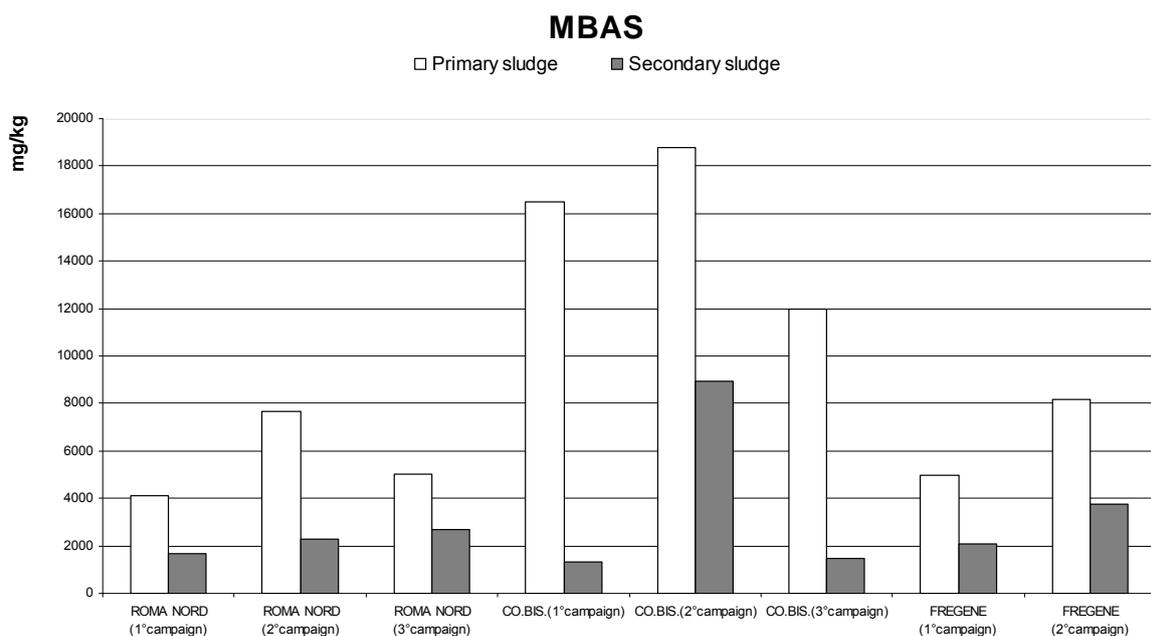


Figure 3.4 Anionic surfactants (one of the focus pollutant because inserted in the third draft of the proposed new directive on sludge utilization in agriculture) are mostly adsorbed in primary sludge (MBAS = methylene blue active substances)

3.2.4 Dewaterability of sludge

Capillary suction time is widely used to asses sludge dewaterability. The test is very rapid (some seconds) and as such is therefore a good alternative for determining filterability that normally should be assessed by specific resistance to filtration that is quite time consuming test. Only when sludge solid concentration is high and the predominant presence of

particulate as colloidal fraction renders filtration very difficult, CST may be as high as hundreds of seconds.

Tables 3.16 shows the CST values of the Roma Nord, Co.bis. and Fregene, respectively. It may be seen that practically there is no difference among different sludge types which show very good filterability.

Table 3.16 Sludge dewaterability

	Roma Nord					
	Primary			Secondary		
Sampling campaign	I	II	III	I	II	III
Capillary suction time (s L/g dry solid)	2.3±0.3	3.67±0.16	1.78±0.12	0.61±0.01	1.12±0.06	0.85±0.07
	Co.bis.					
	Primary			Secondary		
Sampling campaign	I	II	III	I	II	III
Capillary suction time (s L/g dry solid)	5.1±0.2	3.0±0.12	1.94±0.12	0.78±0.05	0.94±0.06	1.82±0.02
	Fregene					
	Primary			Secondary		
Sampling campaign	I	II	III	I	II	III
Capillary suction time (s L/g dry solid)	1.58 ± 0.08	1.65 ± 0.15		1.60 ± 0.03	1.94 ± 0.12	

3.3 Conclusions

Extensive data collected in two German plants show that there is not a constant enrichment of contaminants in primary or in secondary sludge. However, for TCP and TBEP (organophosphate contaminants), DBP and BBzP (Phtalates) and Bisphenol A it may be observed that primary sludge is always richer of such contaminants than secondary sludge, in both of the two monitored plants. For the other contaminants it is not possible to assess a predominant enrichment in one of the two sludge: only for tin organics a slight enrichment in secondary sludge is observed.

Extractable organic halogens (EOX), total hydrocarbons and methyl blue active substances (MBAS) were analyzed in three campaigns on two WW treatment plants in Italy. Table 3.17 shows the results. Enrichment of the above contaminants in primary sludge with respect to secondary one seems to increase in the order hydrocarbons, EOX, MBAS.

Heavy metals, present in the tested sludges at very low concentration, did not display any enrichment in primary or secondary sludge.

These results do not confirm completely that secondary sludge is less polluted than primary sludge but this is certainly true with respect to many contaminants. A deeper knowledge of speciation of contaminants according to their chemical-physical properties (principally KOW), and the other status conditions (pH, temperature, oxygen concentration, rH, interactions with other ions) would allow to understand when it is expected that such contaminants may enrich in primary or secondary sludge.

The presence of nitrogen and phosphorus in secondary sludge may be estimated to be 1.8 – 2.0 times than that in primary sludge. This means that agricultural use of secondary sludge according to nutrient requirement by crops would spread lower amounts of contaminants to land with respect to mixed sludge.

Table 3.17 Concentration of EOX, hydrocarbons and MBAS in Roma Nord and Co.bis. sludges

		Roma nord		
		EOX	Hydrocarbons C10-40	MBAS
I campaign	Primary	4,000	995	4,100
	Secondary	700	670	1,658
II campaign	Primary	9,890	1,620	7,665±461
	Secondary	6,820	1,670	2,261±334
III campaign	Primary	17,950	2,800	5,029 ± 1,276
	Secondary	5,100	1,070	2,681 ± 364
		Co.bis.		
		EOX	Hydrocarbons C10-40	MBAS
I campaign	Primary	11,950	2,125	16,479±1,240
	Secondary	2,000	865	1,323
II campaign	Primary	36,170	2,205	18,797±1,710
	Secondary	10,090	920	8,925±1,727
III campaign	Primary	16,630	1,480	11,958 ± 2,149
	Secondary	14,460	570	1,456 ± 98
		Fregene		
		EOX	Hydrocarbons C10-40	MBAS
I campaign	Primary			5,000
	Secondary			2,075
II campaign	Primary			8,171
	Secondary			3,775

4. INCINERATION TESTS

4.1 Introduction

Lab-scale thermal tests were performed with the sludge samples of Roma Nord and Co.Bis using a System for Thermal Diagnostic Studies (STDS) with the objective to verify whether the incineration of primary sludge separated from secondary one (land application) would lead to different emissions in comparison of the conventional incineration of mixed sludge.

Although incineration should theoretically result in the conversion of the hazardous organic compounds present in the sludge to innocuous end-products, often such conversion is not fully achieved due to the process variable inefficiencies observed in full scale incineration (Dellinger et al., 1988). Therefore, the control of toxic organics emitted from incinerators during combustion of wastes is an issue of principal concern (Fångmark et al., 1993; Ghorishi et al., 1995; Huang et al., 1995).

Theoretically, an inefficiency (or failure mode) of an incinerator can be defined as a situation where a fraction of the material is submitted to burning conditions less efficient than the average operating ones, thus resulting in an increase of potentially toxic organic emission (Tirey et al., 1989). In general, modes of failure can be thermal, temporal and fuel-oxidant mixing. The thermal failure mode is related to quenching of hot gases in the post flame zone (by cool secondary air and as boundary effects at cool combustor walls), to temperature gradients and heat transfer limitations. This failure mode is more likely to occur in the primary combustor than in the after-burning step. The temporal failure mode is related to the uncertainties in after-burning residence time distribution due to the plug flow assumptions. The fuel-oxidant mixing failure mode creates a poor micro-mixing resulting in the formation of zones in which oxygen starved conditions exist (pyrolysis pockets). This last mode of failure has been indicated as the primary source of products of incomplete combustion (PICs), although all failure modes likely contribute to their emissions (Dellinger et al, 1986 and 1991; Mascolo et al., 1999). Among the possible PICs formed during sludge incineration, particular attention should be given to aromatic hydrocarbons and polynuclear aromatic hydrocarbons (PAHs) because they could be the starting compounds for soot particle formation that, when adsorbed onto fly ash in incinerator regions where flue gas streams are cooled, are the initial reagents for *de novo* synthesis of chlorinated dioxins and furans (Milligan et al., 1993; Stieglitz et al., 1991; Fielder, 1996).

4.2 Experimental set-up

A lab-scale system for thermal diagnostic studies (STDS) was used (Figure 4.1).

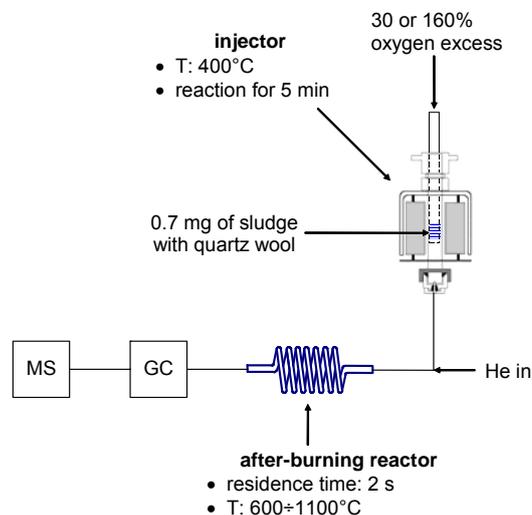


Figure 4.1 STDS instrumental set-up for lab-scale sludge incineration

Lab scale system includes four integrated sub-assemblies: a control console, a thermal reaction compartment, a cryogenic trapping gas-chromatograph (GC) and a mass spectrometer (MS). In the console sub-assembly the controls of gas flow rates, gas composition, pressures and residence time are located. The thermal reaction compartment is a modified GC equipped with a pyroprobe as injector (simulating the primary zone of the incineration) and a high temperature furnace that allocates an interchangeable quartz reactor (simulating the after-burning step). The pyroprobe, which allows a quartz probe carrying the sludge sample to be manually inserted in it through its silicon septa, is connected via a 3 mm i.d. silicosteel tube to the quartz tubular reactor and then, by another silicosteel tube, to the capillary gas chromatographic column located in a GC that is interfaced, through a transfer line heated to 350°C, to the capillary column of a Clarus 500 GC/MS system (Perkin-Elmer) equipped with an electron impact ion source. During the thermal experiments the GC analytical column was kept at -60°C in order to cryofocus the formed organic compounds into a small band. After completion of the thermal experiment, the compounds trapped at the top of the GC column, after purging and pressurising the column with helium, were separated by raising the oven temperature to 350°C at a rate of 15°C/min. Electron impact mass spectra, at an electron energy of 70 eV, were recorded by scanning the quadrupole from mass 35 to 600 Da. The background-subtracted mass spectra were matched against those of NIST mass spectra library and interpreted on the basis of the observed fragmentation.

Sludge used in the experimental tests was freeze-dried, then ground and sieved (100 µm). In a typical STDS experiment, 0.7 mg of sludge sample were placed into a quartz capillary tube (1.5 mm i.d., 15 mm length) and held in place by quartz wool at both ends. The quartz tube was inserted into the quartz probe which was, in turn, inserted into the pyroprobe, held at 400°C (simulating the thermal failure mode), for first thermal degradation step. The reaction in the pyroprobe was carried out under controlled oxygen rich atmosphere by feeding a variable helium/air mixture (total flow = 2.66 mL/min) through the quartz probe. Two different conditions were used being respectively 30 and 160% more than the stoichiometric oxygen theoretically required for the complete sludge combustion (i.e. 130 and 260% of the theoretical stoichiometric O₂). These two different oxygen concentrations were chosen in order to get oxygen-starved conditions (fuel-oxidant mixing failure mode) in comparison with high oxygen concentration, respectively. The excess oxygen was calculated taking into account the sludge volatile solids content of 57% and its elemental composition. The oxygen available for combustion can be calculated knowing the sludge reaction time (5 min) and the air flow rates which was 1.32 mL/min (260% of the theoretical stoichiometric O₂). The organics formed during the first incineration step were then swept into the other reactor and subjected to high temperature (600 - 1100°C) for a fixed residence time (2 s) obtained by properly setting the helium flow rate at the reactor inlet. The thermal reaction products were then transferred into the cryogenic trapping GC chamber where they were focused on a capillary GC column, separated by a temperature ramp, and identified by the MS.

4.3 Results obtained with Roma Nord sludge

As mentioned previously, three sampling campaigns were scheduled in order to cover several plants conditions in term of hydraulic loads as well organic pollutants concentration due to the different seasons. In figure 4.2 the amount of total alkanes and alkenes detected during incineration tests of collected sludge samples are reported. Total alkanes amount was recorded by means of an integration of the peaks of the chromatogram obtained extracting the characteristic ions of alkanes, namely those of m/z 43, 57, 71, 85, 99. Total alkenes amount was obtained in a similar manner using, i.e. using ions of m/z 41, 55, 69, 83, 97.

Experimental results (Figure 4.2) show that the three types of sludge (primary, secondary and mixed digested) gave rise to a similar formation of alkanes and alkenes, respectively. Also, alkanes amount is in the most cases higher than the one of alkenes. As far as the comparison of the two investigated oxygen excess is concerned, from the obtained thermal profiles it is possible to note that incineration with 130% of the theoretical stoichiometric O₂ always leads to a higher amount of both alkanes and alkenes than 260%. This result is

consistent with the fact that a higher oxygen concentration during incineration is able to convert a higher organic fraction of the sludge into CO_2 leaving a lower amount of alkanes and alkenes in the emissions.

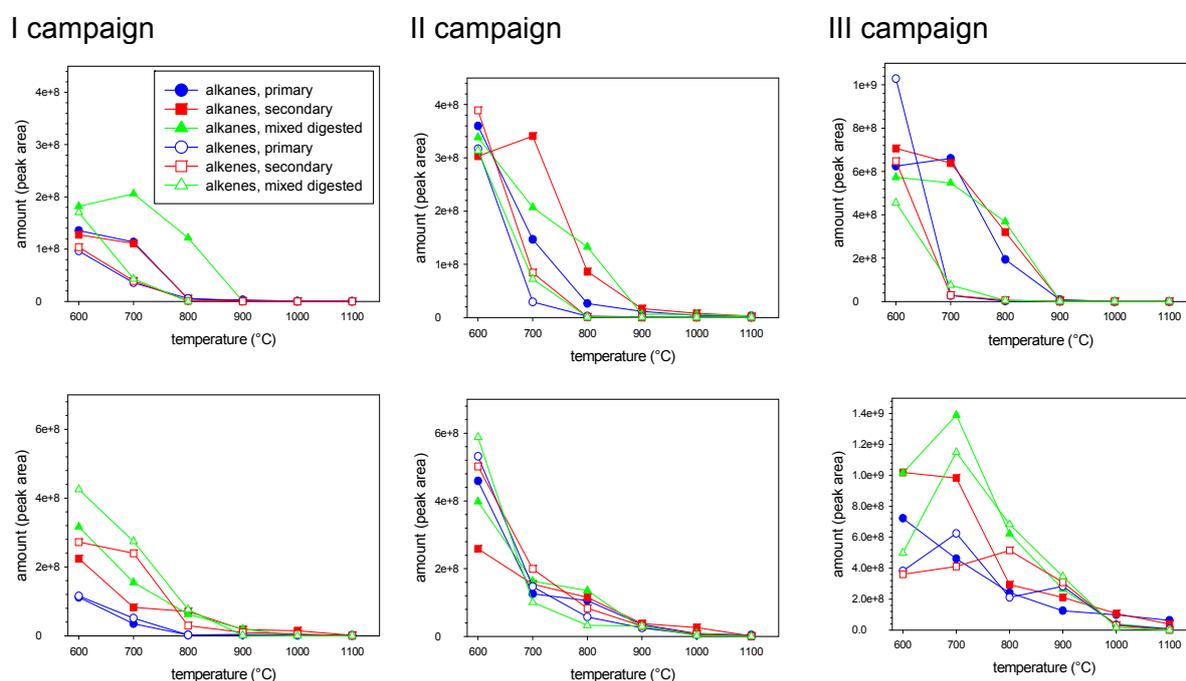


Figure 4.2 Thermal decomposition/formation profiles of total alkanes and alkenes during incineration of Roma Nord sludges (primary, secondary and mixed digested) performed with 260 and 130% of the theoretical stoichiometric O_2 (first and second row, respectively)

During STDS tests the formation of compounds with a single aromatic ring, with two aromatic rings and polinuclear aromatic hydrocarbons was also monitored. In Figure 4.3 the thermal profiles obtained for benzene and toluene are depicted, where it is possible to note that with 30% oxygen excess benzene is always more thermally stable than toluene being still present in the emissions even at temperature as high as $1,100^\circ\text{C}$. In addition, results confirmed already published findings (Mascolo et al., 1999), i.e. that the oxygen excess plays a major role in the minimization of the amount of these organics in the emissions. However, the comparison of the emissions formed by the primary and mixed digested sludge showed that they both gave rise to similar amount of benzene and toluene suggesting that the practice of sludge separation would not affect the emission of that sludge (the primary one) to be disposed of to incineration.

In Figure 4.4 the thermal profiles obtained for naphthalene and biphenyl are depicted. These figures show that when 130% of the theoretical stoichiometric O_2 was used a much higher temperature was required in order to get a negligible amount of the compounds in the resulting emissions. This demonstrates that incineration temperature plays a major role in minimizing the formation of organics in the emissions. However, It is necessary to point out that all results were obtained in flameless conditions, which are different from those of the industrial plants.

In addition, with such an oxygen concentration incineration of primary and mixed digested sludge did not show a remarkable difference in term of amount of naphthalene and biphenyl present in the emissions. Furthermore, oxygen excess plays a major role in the minimization of the amount of these organics in the emissions, which results in a very low residual amount of naphthalene and biphenyl in the emissions. It follows that when oxygen excess is not

enough (fuel-oxidant mixing failure mode) a much higher temperature should be used in order to avoid high emission of aromatic compounds.

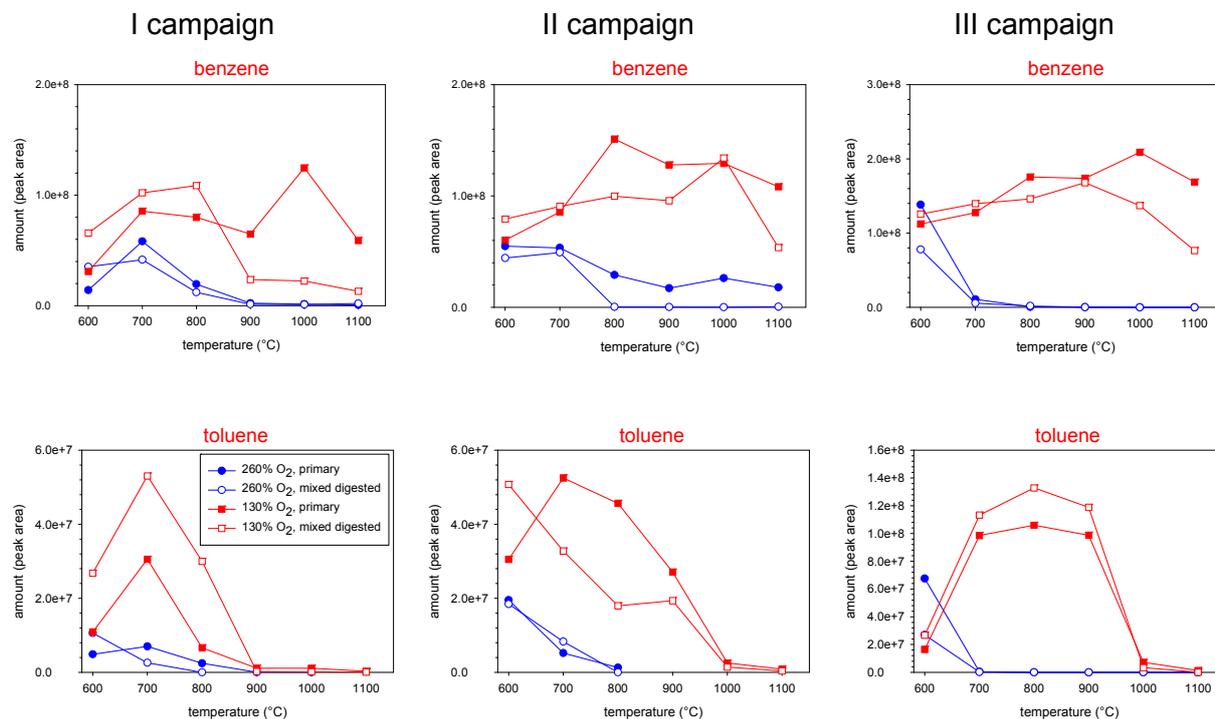


Figure 4.3 Thermal formation/decomposition profiles of benzene and toluene during the incineration of Roma Nord sludge (primary and mixed digested) performed with 260 and 130% of the theoretical stoichiometric O₂

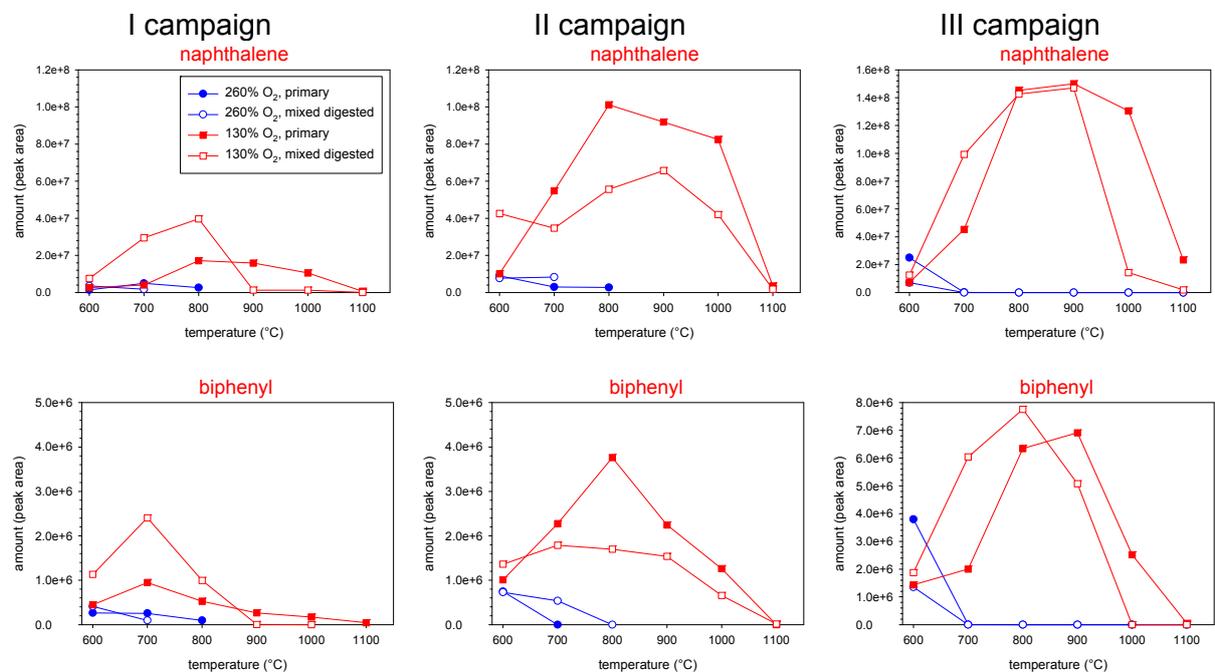


Figure 4.4 Thermal formation/decomposition profiles of naphthalene and biphenyl during the incineration of Roma Nord sludge (primary and mixed digested) performed with 260 and 130% of the theoretical stoichiometric O₂

The formation of both single and total PAHs was also monitored during STDS tests. In Figure 4.5 the thermal profiles of total PAHs and pyrene are depicted. Those of the other single PAHs monitored (acenaphthylene, naphthalene carbonitrile, cyanonaphthalene, fluorene, phenanthrene and anthracene) are similar to the thermal profiles obtained for pyrene. From such a figure it is possible to note that the obtained results were similar to those reported for naphthalene and biphenyl. In fact, it was found that a much higher temperature was necessary for reducing the compounds amount in the emissions when 130% of the theoretical stoichiometric O₂ was used.

With such an oxygen concentration the amount of total PAHs and pyrene present in the emissions was similar for primary and mixed digested sludge. Beside, once again experimental results showed that when incineration is carried out with a higher oxygen concentration (260% of the theoretical stoichiometric O₂) a minimization of the amount of PAHs and pyrene in the emissions is achieved. With such conditions there is practically no difference between incineration of primary and mixed digested sludge in terms of amount of the two compounds present in the emissions.

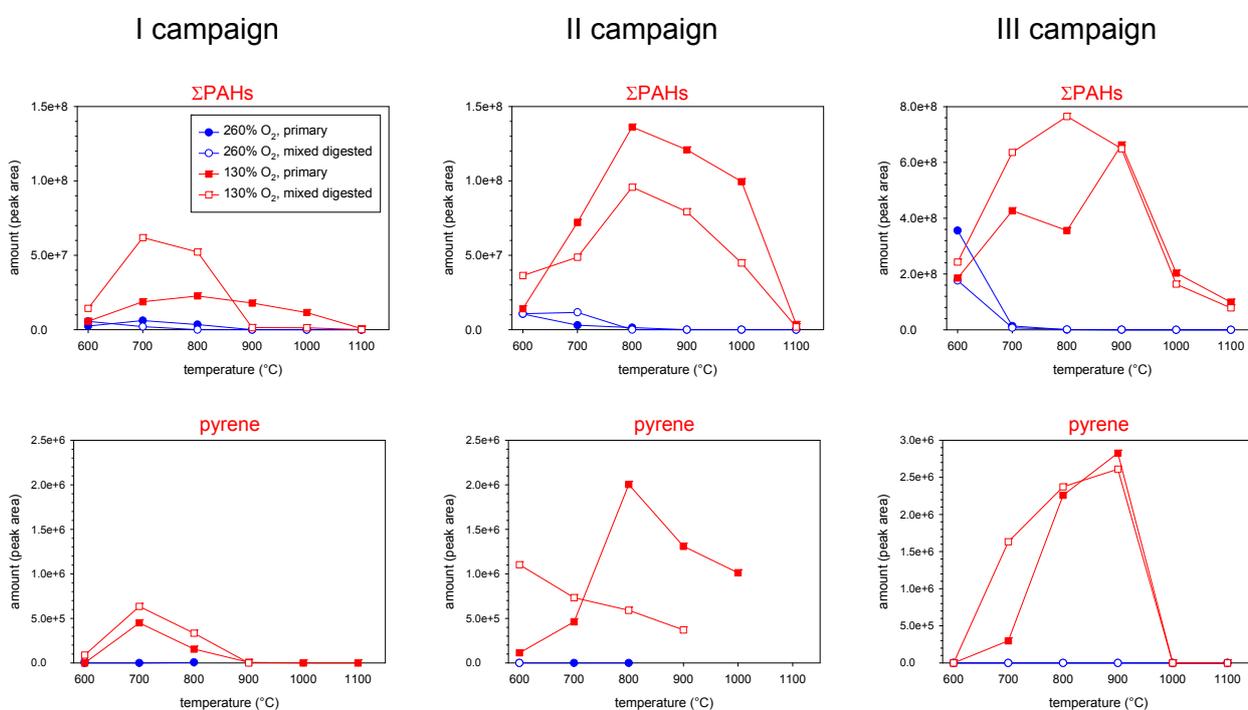


Figure 4.5 Thermal formation/decomposition profiles of total PAHs and pyrene during the incineration of Roma Nord sludge (primary and mixed digested) performed with 260 and 130% of the theoretical stoichiometric O₂

4.4 Results obtained with Co.bis sludge

The Co.bis plant was chosen as it is a medium size WWTP (90,000 p.e.) also having an industrial contribute in the influent wastewater. As for Roma Nord plant, three sampling campaigns were performed but in this report STDS tests carried out on the first two sampled sludge are discussed.

In Figure 4.6, the amount of total alkanes and alkenes, detected as already reported for tests carried out on Roma Nord sludges, are shown. Experimental results are similar to the one obtained for sludge samples of Roma Nord plant. In fact, the amount of both alkanes and alkenes in the emissions of each of the three sludges (primary, secondary and mixed digested) was similar (Figure 4.6). Accordingly, with test on Roma Nord sludges, alkanes amount was in the most cases higher than the one obtained for alkenes. Incineration at

130% of the theoretical stoichiometric O₂ leads always to a higher amount of both alkanes and alkenes than at 260%. This result is consistent with the fact that when a higher oxygen concentration is set a higher organic fraction of sludge is consequently converted into CO₂, leaving a lower amount of residual alkanes and alkenes in the emissions.

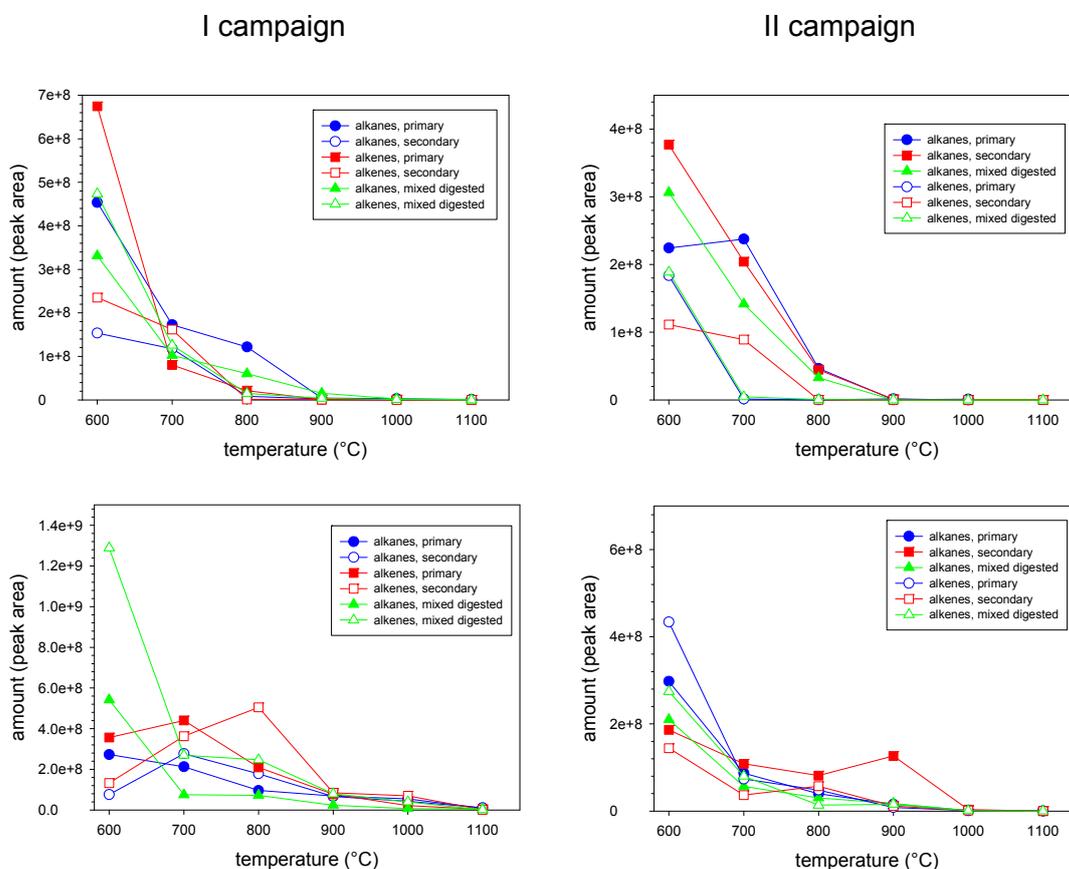


Figure 4.6 Thermal decomposition/formation profiles of total alkanes and alkenes during the incineration of Co.bis. sludge (primary, secondary and mixed digested) performed with 260 and 130% of the theoretical stoichiometric O₂ (first and second row, respectively)

Benzene and toluene appearance in the emissions vs. temperature is reported In Figure 4.7. At 130% of the theoretical stoichiometric O₂ benzene is always more thermally stable than toluene. In fact, it is still present in the emissions even at temperature as high as 1100°C. This confirms, once again, that the oxygen excess plays a major role in the minimization of these organics amount in the emissions. In addition, the comparison of the emissions formed during incineration of primary and mixed digested sludge showed that they both gave rise to similar amount of benzene and toluene. It follows that separate management of primary and secondary does not affect the emissions of the primary sludge incineration in comparison with incineration of mixed sludge.

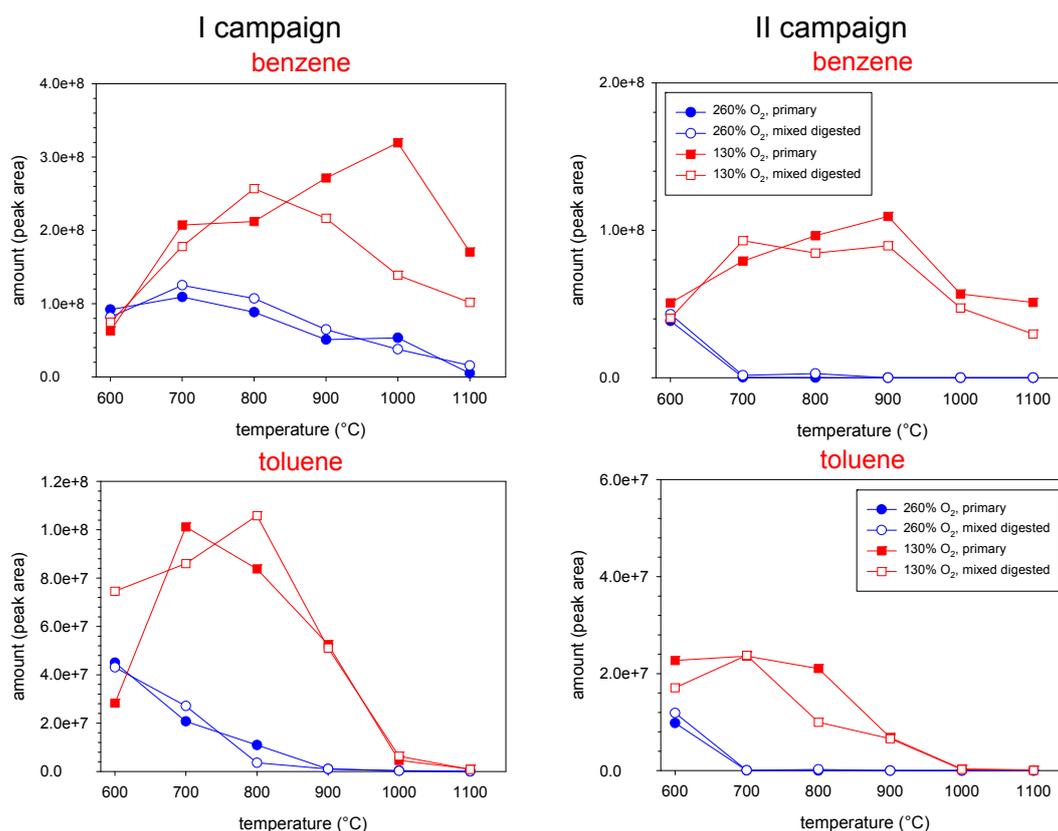


Figure 4.7 Thermal formation/decomposition profiles of benzene and toluene during the incineration of Co.bis. sludge (primary and mixed digested) performed with 260 and 130% of the theoretical stoichiometric O_2

In Figure 4.8 the thermal profiles obtained for naphthalene and biphenyl are depicted. It was confirmed that when of the theoretical stoichiometric O_2 was limited at 130% a much higher temperature was required to assure that such compounds are not present in the emissions. It follows that incineration temperature plays a major role in minimizing the formation of organics in the emissions when oxygen is not sufficient for a complete oxidation. With both oxygen concentrations tested incineration of primary and mixed digested sludge did not show a remarkable difference in term of amount of naphthalene and biphenyl present in the emissions. Furthermore, oxygen excess plays a major role in the minimization of the amount of these organics being the residual amount of naphthalene and biphenyl in the emissions very low.

The formation of both single and total PAHs was also monitored during incineration tests at lab-scale. The thermal profiles of total PAHs and phenanthrene are depicted in Figure 4.9. Phenanthrene was chosen as representative of the other single PAHs monitored (acenaphtylene, naphthalene carbonitrile, cyanonaphthalene, fluorene, pyrene and anthracene) which displayed quite similar thermal profiles. The results were similar to those reported for naphthalene and biphenyl. In fact, it was found that a much higher temperature was necessary in order to reduce the amount of the compounds in the emissions when 130% of the theoretical stoichiometric O_2 was used.

With this oxygen concentration, the amount of total PAHs and phenanthrene present in the emissions was similar for the primary and the mixed digested sludge. Beside, experimental results showed that when incineration is carried out with a higher oxygen concentration (260% of the theoretical stoichiometric O_2) a minimization of the amount of both total PAHs and phenanthrene in the emissions is achieved. With such conditions there is practically no difference between incineration of primary and mixed digested sludge in terms of amount of the two compounds present in the emissions.

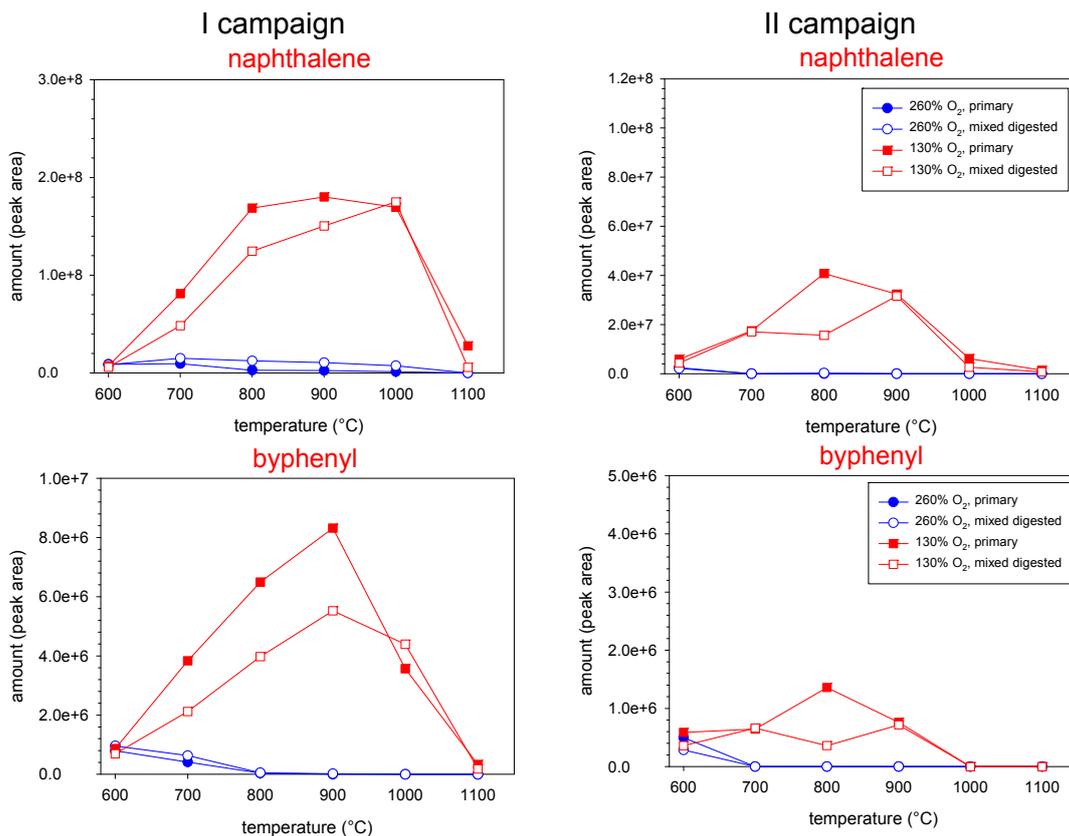


Figure 4.8 Thermal formation/decomposition profiles of naphthalene and biphenyl during the incineration of Co.bis. sludge (primary and mixed digested) performed with 260 and 130% of the theoretical stoichiometric O₂

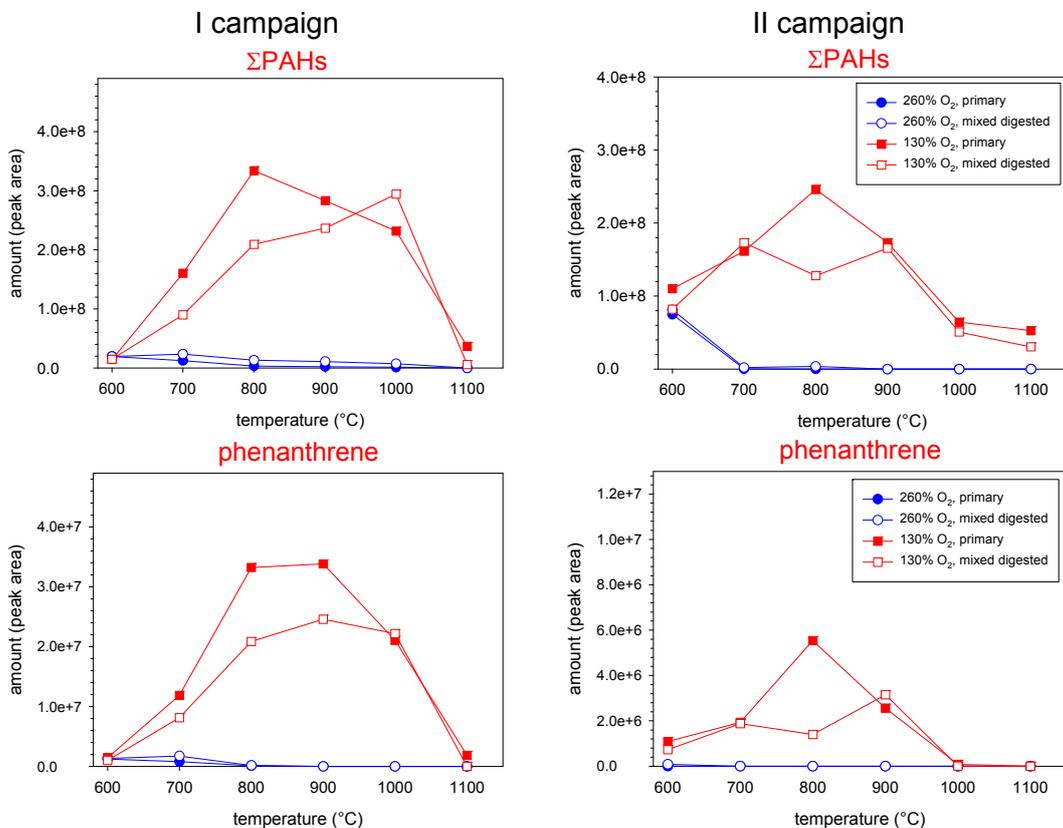


Figure 4.9 Thermal formation/decomposition profiles of total PAHs and phenanthrene during the incineration of Co.bis sludge (primary and mixed digested) performed with 260 and 130% of the theoretical stoichiometric O₂

5. DISINTEGRATION PROCESSES

5.1 Introduction

Municipal wastewater is generally treated by primary and secondary treatments, the latter one commonly carried out by activated sludge process generating considerable volume of sludge. Processing of secondary sludge is generally problematic due to its poor settling and thickening properties and to its scarce attitude to be digested.

The target goal of sludge processing is its volume reduction and removal of biodegradable substance, to be transformed into gases, to accomplish the European increasing stringent rules both for recovery and for disposal. One way to reach such results is to use enhanced biological mineralization, which is positively influenced by sludge disintegration.

Enhanced sludge mineralization by sludge disintegration has potential for sludge reduction as well in the activated sludge process as in sludge digestion. In sludge digestion it is also followed by an accelerated and higher biogas production. Subsequent sludge treatment steps (conditioning and dewatering) could be influenced positively.

5.2 Methods and application of sludge disintegration

5.2.1 Integration and operation of disintegration

Sludge disintegration can be added at different locations in the WWTP as shown in Figure 5.1. The disruption of resistant cell walls releases easily biodegradable organic matter for subsequent aerobic and anaerobic processes. Because of the high biomass content, best results are obtained if a fraction of the return sludge (A) or excess sludge (B) is treated. Disintegration of excess sludge increases the biogas production of the digester and reduces the digested sludge solids. Moreover, the treatment of the return sludge could improve denitrification and sludge settling conditions reducing excess sludge production.

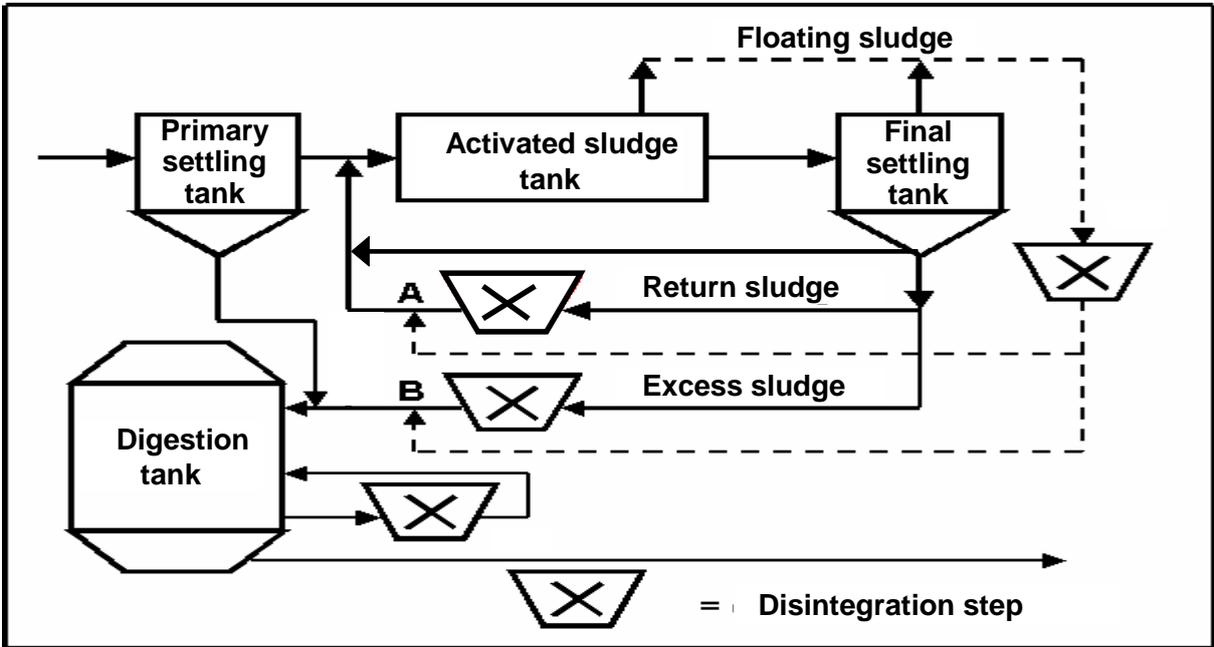


Figure 5.1 Various locations at a WWTP for biological sludge disintegration

In addition, the efficiency of sludge disintegration also depends on the sludge age because aerobically stabilized sludge (high sludge age) has a reduced organic content (Seiler and Pöpel, 1998, Neis and Tiehm, 1997). The highest degree of disintegration is achieved with

concentrated sludge (up to 6% TS; Winter et al. 2002, see also Figure 5.2), because the applied energy is then used most efficiently. Disintegration of digested sludge is also feasible because further biomass degradation results in increased biogas production (Parravicini et al., 2004, Vranitzky and Lahnsteiner, 2002, Scheminski et al., 1999). In contrast, disintegration of primary sludge is not recommended, as this sludge is easily hydrolysed by biological action. Disintegration of filamentous bacteria reduces foaming during digestion and leads to improved sludge settling ability (Boehler and Siegrist, 2004, Barjenbruch and Kopplow, 2003).

In full-scale applications, disintegration is mostly used as a pre-treatment step for anaerobic stabilization. Its main purpose is to increase biogas production as well as to accelerate sludge hydrolysis and reduce sludge production, especially in the case of overloaded digesters.

The effect of raw sludge disintegration decreases with increasing hydraulic retention time (HRT) in the digester (Parravicini et al., 2004). In low-energy applications, disintegration mainly accelerates the hydrolysis of particulate material that would in any case be degraded in digesters with a higher HRT. This has to be considered when comparing the efficiency of disintegration devices applied on different treatment plants. For high-energy applications, it is assumed that disintegration energy will also be used for the lysis of bacterial cells that are normally not destroyed in sludge stabilization. Disintegration should therefore be applied directly on the digested sludge.

5.2.2 *Methods of sludge disintegration*

In recent years, new processes for sludge disintegration have been presented and tested and are now increasingly available on a commercial basis. An overview of possible methods and areas of application is found in various reports of DWA, US EPA and Stowa (ATV, 2000, ATV, 2001, ATV, 2003, US EPA, 2007, Stowa, 2005) and in the WERF report by Stensel and Strand (2004).

Sludge disintegration implies floc destruction and cell disruption, which releases solubilized organic matter and can be achieved by various methods. The forces applied to solids can be mechanical, thermal, chemical, biological or a combination of these. So far, most full-scale applications have been based on the following methods:

- ⇒ Thermal hydrolysis: prior to digestion, sludge is dewatered to 15%–20% solids and fed through a hydrolysis vessel. The process involves the oxidation of sludge under elevated temperature (approximately 160°C) and pressure (approximately 7 bars). Under these conditions, cell structures and pathogens are destroyed, releasing energy-rich particulate and soluble compounds. After thermal treatment the sludge is fed to an anaerobic digester and after biological hydrolysis of the particulate material the fermentation results in a high volatile solids destruction (approximately 65%) and increased biogas production compared to conventional anaerobic digestion (see more details in section 5.3).
- ⇒ Ultrasound homogenizer: a generator supplies a high-frequency voltage in the range of 20-40 kHz. A ceramic crystal consisting of piezo-electrical material transforms the mechanical impulses, which are transmitted into the sludge by a sonotrode. Cavitation bubbles are created by alternating over and under-pressure. The subsequent implosion of the gas and vapour-filled bubbles produces high mechanical shear forces (hot spots), which tend to disintegrate bacterial cell material (see more details in section 5.4).
- ⇒ Chemical disintegration with ozone: the ozone disrupts the cell, the cell content is released into the bulk solution and the ozone partly oxidizes the solubilized organics. In addition, ozone reacts with less biodegradable organic aggregates, oxidizing them to smaller compounds which offer better bio-availability.
- ⇒ Biological treatment using enzymes: industrially produced enzymes are dosed selectively to the excess sludge for the lysis of cell-wall compounds and to support the natural

hydrolysis of particulate material. The results of enzymatic disintegration described in the literature vary considerably.

- ⇒ Stirred ball mill: this consists of a cylindrical grinding chamber of up to 1 m³ in volume that is almost completely filled with grinding beads. A rotor forces the beads into a rotational movement. The biomass is disintegrated due to the shear and pressure forces of the beads. For continuous operation, the beads are retained by a sieve so that the suspension can flow through the grinding chamber.

5.2.3 Energy consumption, assessment and comparison of disintegration methods

The success of a disintegration method depends strongly on the amount of organic matter that is solubilized: it is quantified by the degree of disintegration. This parameter is determined by the COD released or solubilized compared to the total initial COD or TSS (Müller, 1996). The performance of various disintegration methods can be compared on the basis of the specific energy applied per mass of solids treated (ATV, 2000). Figure 5.2 shows the release of COD solubilized for excess sludge as a function of the solids contents and exposure time to ultrasound treatment in batch experiments.

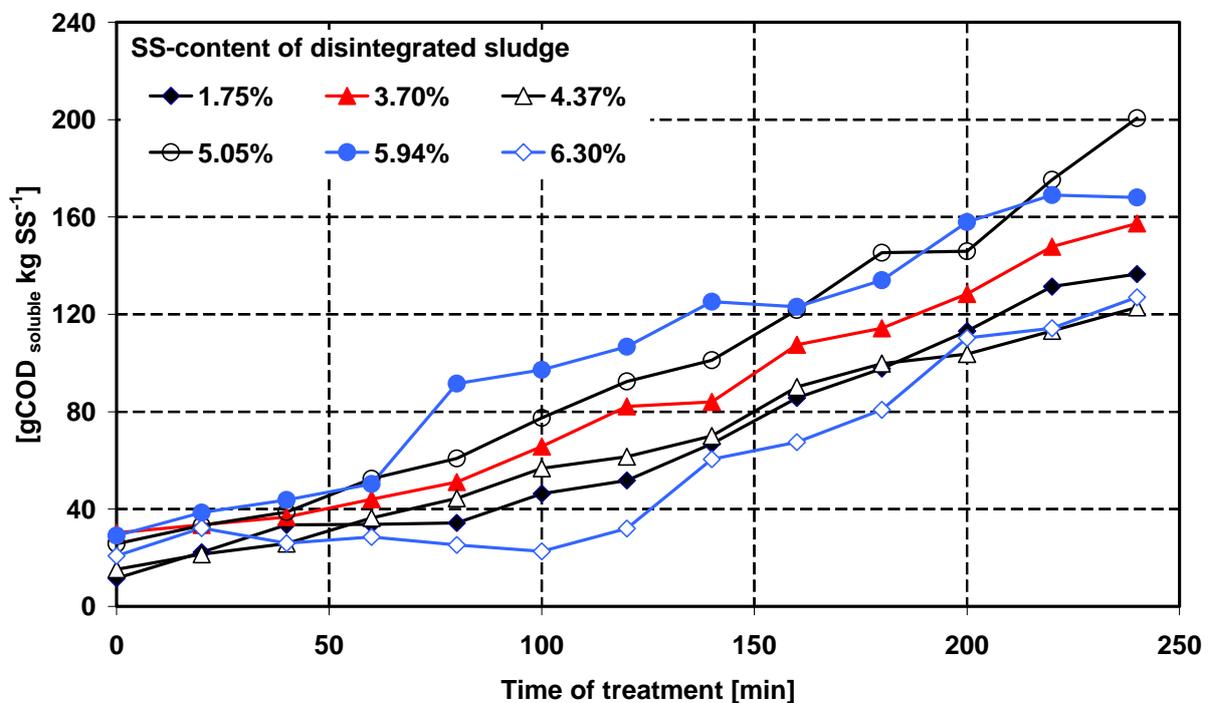


Figure 5.2 COD solubilized with ultrasound at different activated sludge concentrations

The relation of the specific energy to the degree of disintegration is presented in Figure 5.3 for different disintegration methods (Boehler and Siegrist, 2006). All investigations by chemical disintegration with ozone resulted in high COD release, whereas considerably less COD was released with mechanical disintegration. The degradability of the solubilized COD depends on the disintegration method. The attainable released COD of a certain disintegration method is in literature mostly related to the COD released with the NaOH decomposition method. Müller (1996) and Neis and Tiehm (1997) gave a ratio of about 0.5 g COD released with the NaOH decomposition method per g COD_{tot} measured with the K₂Cr₂O₇ method. In Figure 5.3 this ratio is adopted for an activated sludge with a COD content of 1 g COD g SS⁻¹.

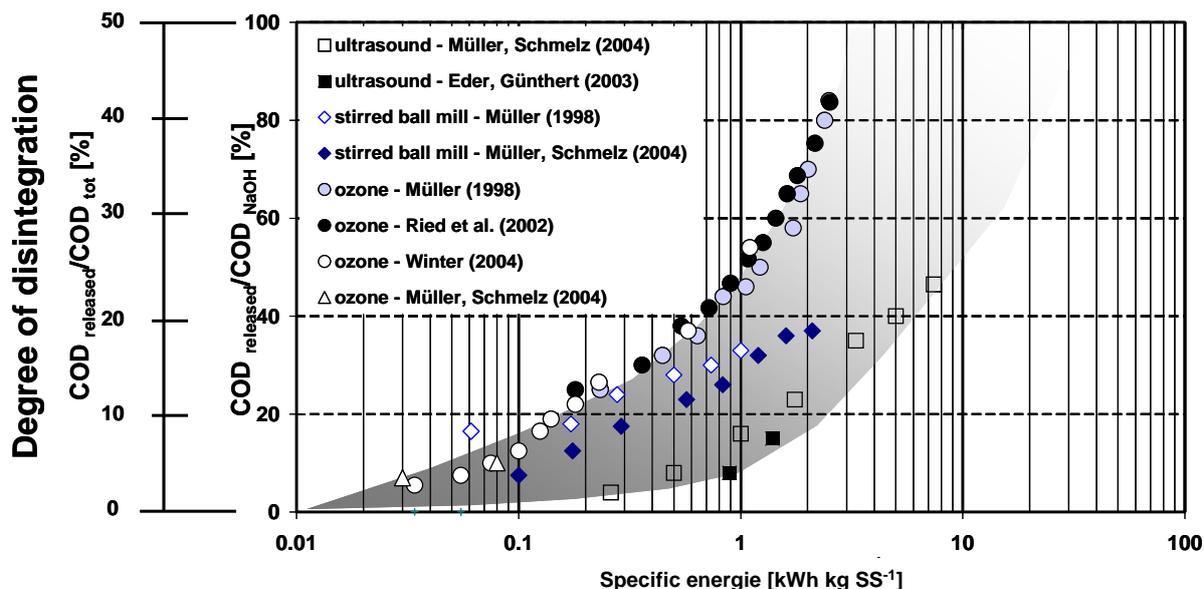


Figure 5.3 Degree of disintegration as a function of the specific energy for various disintegration methods ($\text{COD}_{\text{NaOH}} \approx 0.5 \cdot \text{COD}_{\text{tot}}$: COD detected from decomposition with NaOH and $\text{K}_2\text{Cr}_2\text{O}_7$ respectively). (Boehler and Siegrist, 2006)

Sludge solubilization and reduction strongly depend on the energy input. If activated sludge is treated with a specific energy of about 1 kWh kg SS^{-1} , a solubilization of about 20% can be expected (Figure 5.3). Assuming a $\text{COD}_{\text{tot}}/\text{SS}$ ratio of 1 and 90% degradability of the solubilized organics, $0.18 \text{ kg COD solubilized kg SS}^{-1}$ will be available for biological processes.

In case of anaerobic stabilization, about 90% of the solubilized COD will be transformed into biogas and the remaining fraction into biomass. Incineration of the additional biogas results in $2.3 \text{ MJ kg SS}^{-1}$ treated ($14 \text{ MJ kg COD}^{-1} \cdot 0.18 \cdot 0.9$), and $0.19 \text{ kWh kg SS}^{-1}$ of electricity ($2.3 \text{ MJ} \cdot 0.3/3.6$) could be additionally produced if about 30% efficiency is assumed for electricity generation. Due to the disintegration of activated sludge, about $0.01 \text{ kg NH}_4 \text{ kg SS}^{-1}$ of additional ammonia is released and has to be nitrified with $0.04 \text{ kg O}_2 \text{ kg SS}^{-1}$, which corresponds to an energy consumption of about $0.04 \text{ kWh kg SS}^{-1}$. The net electricity production is therefore only $0.15 \text{ kWh kg SS}^{-1}$ and thus significantly lower than the energy input for the sludge disintegration (about 1 kWh kg SS^{-1}).

5.3 Thermal Hydrolysis

5.3.1 Introduction

Thermal hydrolysis is a process used to increase sludge digestibility. High temperature and the pressure allow transforming recalcitrant organic solids into soluble material having more chance to biogas conversion in a subsequent anaerobic process, thus reducing the final quantity of sludge to be disposed and increasing its biological stability. During thermal treatment, sludge is heated at the high temperature and pressure for several minutes. Microbial cell walls in the sludge are destroyed, releasing more easily digestible organic compounds contained within the cells.

The advantages of combining thermal hydrolysis and anaerobic digestion are high volatile solids (VS) destruction, increased biogas production and better dewatering of the remaining sludge. Currently, the most known commercial thermal hydrolysis technologies are Cambi® and BioThelys®.

In the 1990's thermal hydrolysis was evaluated in Norway, and was developed into a viable technology that has received considerable attention in Europe, primarily through the efforts of Cambi, a company that grew out of the research in Norway. The Cambi system is based on a batch operation mode and consists of a series of three high pressure, high temperature hydrolysis tanks. Continuous thermal hydrolysis systems are still in the early stages of development. This technology may be retrofitted ahead of existing digesters, or may be incorporated into the new facilities. Key advantages of thermal hydrolysis are the ability to operate digesters at high feed solids concentrations (around 10 percent) due to the improvements in viscosity through the process, the improvement of biosolids dewaterability and the ability to achieve better pathogen reductions. Hydrolysis of the feed solids increases biogas production and volatile solids removal. Capital costs are quite high due to the temperature and pressure conditions that occur in thermal hydrolysis, requiring the use of high-pressure stainless steel tanks. Operating costs are high too, for the heating purposes and for the need of the high skill operators. At present this process seems to be cost-effective only where costs of sludge reuse/disposal are very high.

The Biothelys system, commercialized by Veolia, is similar to Cambi. It combines thermal hydrolysis (a THELYS® process) with downstream biological treatment. According to the company many types of sludge (industrial, municipal, primary, secondary, produced from extended aeration) can be treated by this process. During thermal hydrolysis, a part of the suspended solids is dissolved, producing a more readily biodegradable liquid sludge; that can be subsequently anaerobically digested. According to the vendor, Biothelys system can reduce the quantity of sludge up to 80% compared to the conventional methods.

Thermal hydrolysis in combination with digestion ensures that the thermal hydrolysis process is self-sufficient in energy while still producing "green energy".

5.3.2 Technology Description, performance and application

As the continuous steam hydrolysis is in the early stages of development, this review will focus only on the Cambi (Figure 5.4) and the BioTHELYS batch systems (Figure 5.5).

In the Cambi process, a three tank system is typical. Pre-dewatered sludge, up to 15% solids concentration, is added to the feed tank where it is held until the reactor is ready for a batch conversion. Sludge is then pumped to this reactor where it is held for a minimum of 20 minutes at 170°C and 8.5 bar. Live steam is added to achieve this temperature and pressure. Steam is vented to the feed tank. At the end of the batch, solids are allowed to flow to the flash tank where the rapid expansion causes the cells rupture. The resulting sludge has a lower viscosity. The temperature is also reduced by flashing, so the temperature in the digester is about 38°C. Due to the water condensation and the cell disintegration the resulting sludge concentration to digestion is 10 - 12%, which does not pose any problem of pumping and stirring. Normally, no further heating is needed for digestion. Although the Cambi process requires considerable heat for steam, some heat is recovered in the process and is used for digestion. In spite that in Europe the full sludge stream is treated, including primary and secondary sludge, the hydrolysis affects mainly secondary sludge. Therefore the process can be more cost effective by applying thermal hydrolysis only to the secondary sludge, thus reducing the tankage and the steam required. The secondary sludge could then be mixed with unheated primary sludge to reach the temperature of 37-38°C required for mesophilic digestion. The Cambi thermal hydrolysis system is modular, with the limitation being the reactor vessel, which has a maximum size of 12 m³. One reactor can treat 4,000 to 5,000 dry t/year, with a 90 minute cycle time for each batch feed. This is equivalent to a treatment plant with a flow capacity of around 40.000 to 50.000 m³/d. The size of one train is limited to six reactors in parallel, with one pre-heat tank and one flash tank per train. Larger systems will require multiple trains.

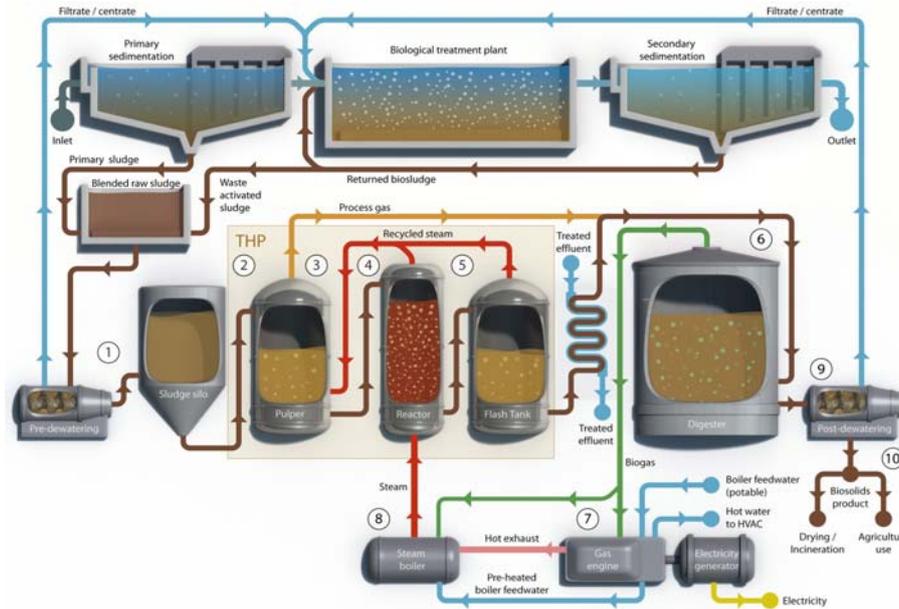


Figure 5.4 Flow sheet of the Cambi process

- Primary and secondary sludge is mixed and dewatered in centrifuges to approx. 16% dry solids.
- The dewatered sludge is led to a storage silo and then fed into the pulper (2).
- In the pulper the sludge is pre-heated by injecting recycled steam from the reactors and the flash tank. The sludge is mixed by circulation pumps. All process gases are compressed and injected into the sludge pipe to the digester(s), thereby avoiding odour.
- Pre-heated sludge is pumped into the reactor(s) (4) where thermal hydrolysis at high pressure and temperature takes place at approximately 165°C for 30 minutes. Then a pressure release valve at the top of the reactor is opened gradually and the pressure is reduced.
- After thermal hydrolysis, sludge is passed in to the flash tank (5), where the pressure and temperature of the hydrolysed sludge are decreased to approximately 105°C by flashing steam back to the pulper. The sludge is cooled to the required digestion temperature.
- The THP process is followed by anaerobic digestion (6), converting the organic matter (*volatile solids*) to biogas, mainly consisting of approximately 65% methane (CH₄) and 35% carbon dioxide (CO₂).
- The biogas is utilised in a gas engine (7) with generator producing electricity.
- Steam is produced in a waste-heat boiler (8) using exhaust gas from the gas engine. A small part of the produced biogas is fired directly in the steam boiler. Engine jacket cooling water preheats boiler feed water.
- The digested sludge is dewatered with to a biosolids product in a centrifuge or belt-press to 30 – 34% .
- The resulting cake/biosolids is applied directly on agricultural land or dried and used as fuel or fertilizer.

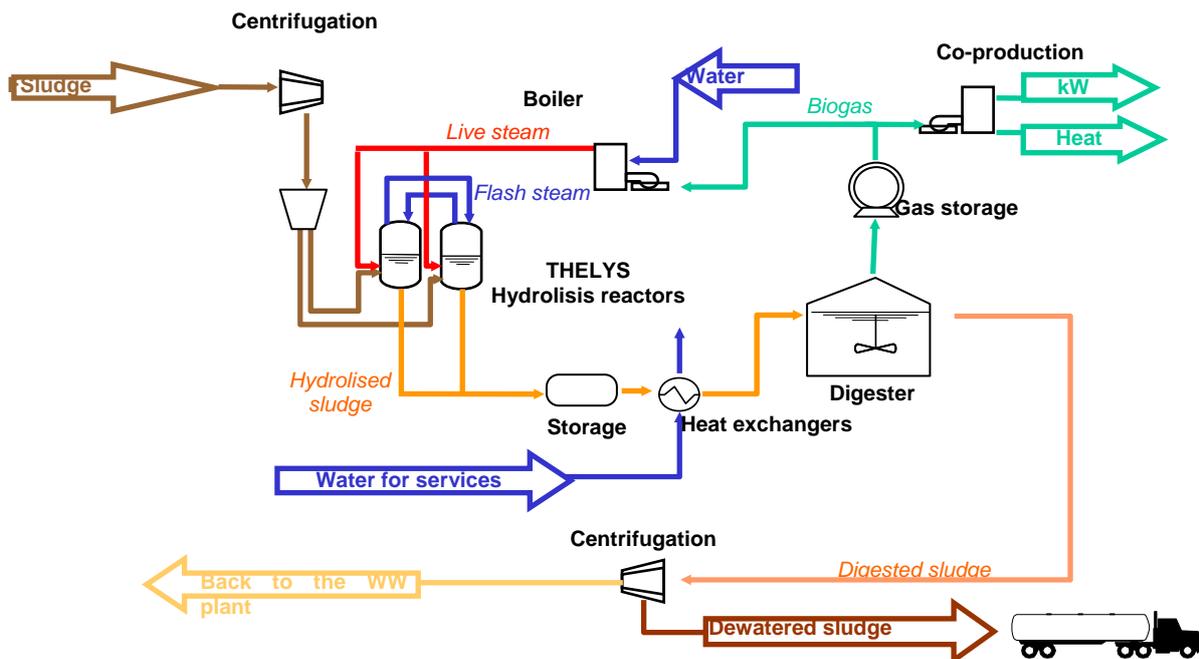


Figure 5.5 Flow sheet of the BioThelys process

Laboratory experiments on Cambi process (Bougrier et al. 2007) were carried out using WAS collected from the municipal WW treatment plant of Toulouse (500,000 p.e.). Sludge was diluted in order to obtain total solids concentration of 14.5 g/L. The total volatile solids (VS) content was equal to 81% of TS. The 1 L stainless reactor was equipped with a magnetically coupled mixer. The process was carried out at a temperature of 135°C and 190°C for about 30 min and 15 min, respectively. Three anaerobic reactors inoculated with the same anaerobic sludge were run in parallel at 35°C with organic load of 1 g COD/(d × L). The first one was fed with raw sludge (control reactor), the second one with sludge treated at 135°C and third one with sludge treated at 190°C. COD solubilisation was 34% and 46% for sludge treated at 135 and 190 °C, respectively. After digestion the total COD removal increased from 52% (control reactor) to 58% (reactor operated at 135 °C) and to 63% (reactor operated at 190 °C). Hydraulic retention time was fixed at 20 days and organic loading rate was around 1 kg COD/(m³ × d) of reactor. Biogas production increased from 173 mL/g of added COD (control reactor) to 194 mL/(g of added COD) for the reactor fed with sludge treated at 135°C and to 217 mL/(g of added COD) for the reactor fed with sludge treated at 190°C.

The primary driver for development of thermal hydrolysis in Europe has been regulations on pathogen content of biosolids for land application, and a drive to reduce sludge volumes as costs for reuse/disposal have been increasing. Thermal hydrolysis assists in these aims, as hydrolysis improves digester performance and volatile solids destruction, and thermal conditioning improves the viscosity of the solids and improves the dewaterability. Thermal hydrolysis may be particularly beneficial at plants which have overloaded digesters, as the viscosity improvements through thermal pre-treatment allow digesters to be fed at the solids concentrations up to 10 percent. Resulting sludge can be dewatered at much higher cake concentration due to its better quality in terms of dewaterability and input solid concentration, thus resulting in a lower volume of solids for disposal (Commonwealth Energy Biogas/PV Mini-Grid Renewable Resources Program Process Selection Report for Wastewater Treatment Plants; Task 2.2.1 Final Report, California Energy Commission - Public Interest Energy Research Renewable Program; 2003).

Based on the applications of this process in Europe, the typical operating results claimed by Cambi may be so summarized:

- ⇒ Increased VS destruction and biogas production in the range of 20 to 30% so that VS destruction is typically higher than 60%;
- ⇒ significant improvement in sludge dewaterability, so that cake concentration can be in the range of 30-50%;
- ⇒ increased digester potentiality, considering that feed sludge concentrations may reach 10% solids: it is estimated that 50% of digester volume is saved, compared with conventional digestion;
- ⇒ the high dry solids concentration hydrolysis results in increased ammonia concentrations requiring a dilution of digester content to limit the NH₄-N concentration to the maximum value of 2.400 to 2.600 mg/L. Dilution can be performed either with water or with the effluent from WW treatment plant;
- ⇒ thermal hydrolysis shortens the retention times in the digestion to 10 - 12 days;
- ⇒ the process has been certified by Norwegian authorities to fulfil the requirements for sludge pasteurisation and its subsequent use in agriculture.

The first full-scale installation of a batch thermal hydrolysis process with direct steam injection was started in 1995 in Norway. The present European installations with the Cambi process and BioTHELYS system are reported in Table 5.1.

Table 5.1 Full scale installation in Europe with Cambi and BioThelys processes

Plant denomination	Throughput		Year of installation	Type of process
	dry t/year	p.e.		
Hamar (NOR)	3,500	90,000	1996	Cambi
Chertsey (U.K.)	8,000	300,000	1999	Cambi
Næstved (DEN)	1,600		2000	Cambi
Fredericia (DEN)	8,000			Cambi
Aberdeen (U.K.)	16,500			Cambi
Dublin-Ringsend (Ireland)	36,000	1,300,000		Cambi
Saumur, (France)	1,400	62,000	2004	BioThelys
Château-Gontier (France)	1,000	38,000	2004	BioThelys

The eight wastewater installations in Europe present site-specific conditions that prompted application of Cambi or BioThelys systems. For example, two of the plants, in Norway and Denmark, had high industrial loads (over 50 percent). The Fredericia plant in Denmark does not have primary treatment and the solids from the extended aeration process were difficult to digest without some form of a pre-treatment. The Dublin plant is located on an island, and therefore the cost of sludge transporting off the island made the Cambi process economical. It does not appear that other pre-treatment options, such as ultrasound, were considered as alternatives.

Thermal hydrolysis may prove cost-effective for installation at treatment plants where some or all of the following conditions apply:

- ⇒ low digester retention times that results in lower stability and performance;
- ⇒ low digester volatile solids destruction and gas production;
- ⇒ high ratio of secondary to primary sludge (over 45% secondary);
- ⇒ high sludge reuse/disposal costs (over 50 €/wet ton);
- ⇒ plants with foaming in the digesters;
- ⇒ plants with low dewatering performance.

5.3.3 Full scale plant experiences

5.3.3.1 WWTP Hamar (NOR) (90,000 p.e.)

The thermal hydrolysis part of the overall treatment process consists of two pulping tanks, one reactor tank and one flash tank. The sludge is fed into the pulping tanks where it is homogenised, pre-heated and cut to a particle size of less than 3 mm in a macerator pump. It is then passed to the reactor tank for thermal hydrolysis by treatment at high pressure (around 10 bar) and temperature (160°C) for 30 minutes. The pressure and temperature are reduced in the flash tank. The average operating parameters are shown in Table 5.2.

At this moment the energy content of the biogas is solely used for the heat generation.

The thermal hydrolysis module has been operated continuously since the start at the turn of the year 1995/96.

Earlier thermal hydrolysis processes gave problems with wear on the valves; this problem has been minimised by reducing the temperature and the pressure stepwise. The flash tank was designed to shut down the hydrolysis plant during the weekends however, since the hydrolysis plant can be operated 24 hours a day, the tank is oversized. To minimise the total energy consumption, a heat exchanger transfers heat from the flash tank back to the pulping tank to assist the pre-heating. The daily operation of the entire sludge treatment, including external sludges, is today in the hands of one operator. The plant's maintenance staff

contributes with 1/3 of a man-year. The steam boiler operation calls for people with a boiler certificate. The steam boiler needs to be inspected every 84 hours. An inspection includes water analysis, leakage control, and general maintenance control.

Table 5.2 Average values of Hamar operating parameters

Water consumption for steam production	2,500 m ³ /year
Live steam for the hydrolysis process	8,800 kWh/d
Recovered energy (at flash tank heat exchanger)	6,100 kWh/d
Net energy consumption for hydrolysis	2,700 kWh/d
Net energy production in digester	15,000 kWh/d
Surplus energy	12,300 kWh/d
Volume treated	2,700 dry t/year
Mass reduction	50%
COD removal	59%
Gas production	2,500 Nm ³ /d (70% methane)
Dewaterability of digested sludge	35% can be achieved, currently 28%

The thermal hydrolysis of sludge releases strong odours. An installed biofilter proved to be insufficient. Currently the air is injected into the aeration basins of the activated sludge process (Fjærgård T. and Sander O., 2002).

5.3.3.2 WWTP Ringsend (Dublin, Ireland) (1,6 milion p.e.)

Sludge is pasteurised and hydrolysed thermally by holding a batch at 165°C for 24 minutes at 6 bar pressure. The combination of the high temperature during the cycle and the pressure drop at the end of the cycle breaks open cells making the sludge more readily biodegradable. The Dublin WW treatment plant (Figure 5.6) treats up to 11.3 m³/s of flow. The equivalent population is 1.6 million of which ½ million is industrial load.



Figure 5.6 View of the Dublin WW treatment plant

All the sludge at Dublin is screened through 10 mm sludge screens, pre-dewatered and then fed to the CAMBI process. In the Cambi process the pressure is raised to 6 bar whilst the temperature rises to 165°C in batches of about 7,5 m³. This condition is maintained for 24 minutes, a time established as optimum for the nature of the sludge in Dublin.

The Cambi thermal hydrolysis plant at Dublin heats the sludge under pressure, the hydrolysis converts approximately 50% of the biological and 10% of the raw particulate COD to a more digestible form. The flow sheet of the process performed in Dublin is shown in Figure 5.7.

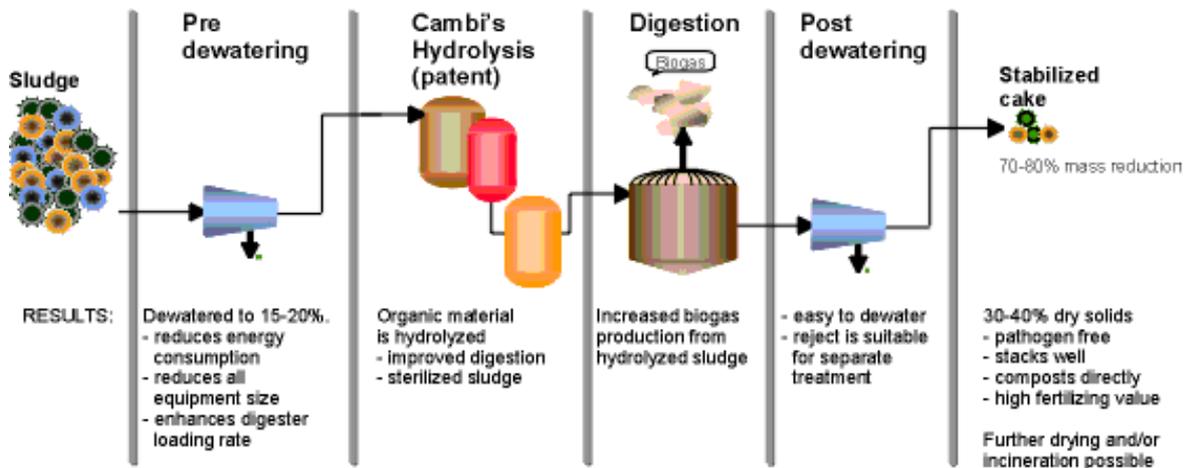


Figure 5.7 Flow sheet of the Cambi process in Dublin WW treatment plant

A blended primary and activated sludge mix is pre-dewatered at concentration higher than 18% using a piggy back combination thickening and dewatering belt presses. The cake is then diluted with hot water (Brian Pickworth et al.). The sludge passes through two stages of pulper tanks where it is homogenised and heated up to 100°C with recovered steam from the process. The sludge is fed to one of the eight batch reactor tanks, where it is heated to 165°C and put under at least 6 bar pressure. The cycle time from starting to fill a reactor to when a reactor is empty is typically 90 to 110 minutes.

The hydrolysed sludge is passed to a flash tank, to a heat exchangers and then to the digesters. Steam produced in de-pressurisation from 6 bar to atmospheric pressure is directed back to the two pulpers to pre-heat the sludge.

The plant runs 24 hours a day processing 90 - 100 dry t/d. As a result of the hydrolysis process the subsequent digestion stage achieves a reduction in volatile solids of 62% and a reduction of dry solids of 50%. Thus the 100 tonnes fed to the process results in only 50 tonnes for drying and shipping off to agriculture.

The biogas production has been stable at approx 0.7 Nm³/kg VS destroyed and this has correlated well back to the COD fractionation of the wastewater and site sludge production.

The digesters are fed with a hydrolysed and pasteurised sludge at 11-12% solid and operate at 15 days hydraulic retention time. The 4,250 m³ Dublin digesters (bottom fed and mechanically mixed) are currently loaded at 6 kg VS/(m³ × d). The digesters are stable with ammonia concentrations over 2,000 mg/L as the pH is between 7.6 and 8.0 units. Thermal pre-treatment inhibits foaming. The microbial community in the digester is stable because the digester is fed by a sterile sludge. Both systems are energy neutral because the heat required to treat the sludge is recovered from the engines which burn the biogas to produce electricity or the steam boilers running on biogas.

5.3.3.3 WWTP Saumur (France) (62.000 p.e.)

The first functional full-scale BioThelys® installation has operated at Saumur in France since 1998. This plant treats 1,400 dry t/year. Coupling BioThelys with anaerobic digestion resulted in reducing the quantity of wet sludge to be disposed by 44% (Chauzy et al., 2007).

The plant at Saumur in the Loire Valley treats sludge from an extended aeration plant serving a population equivalent of 60,000. Since the thermal hydrolysis process operates at a temperature of 160°C, an important sustainable criterion is to minimise the energy needed for heating. This is achieved by dewatering the raw sludge to about 30% solids concentration using a centrifuge to reduce the volume and, hence, the heat input. The dewatered sludge is pumped to the two hydrolysis reactors working in parallel. Each reactor in turn goes through a two-hour multi-step cycle. The reactor is filled with raw sludge and preheated with recycled flash steam from the other reactor. Heating to hydrolysis temperature is completed by injecting live steam into the reactor from a steam generator fired with biogas. There are no mechanical rotating parts in the thermal hydrolysis reactors, sufficient mixing of raw sludge being achieved by steam injection. Once hydrolysis temperature has been reached, it is maintained for a period of 30 minutes before the pressure is reduced generating flash steam, which is recovered for pre-heating the other reactor. Finally the reactor is emptied using the residual pressure in the reactor to aid discharge to the buffer tank where the hydrolysed sludge is stored prior to being cooled to about 40°C and pumped continuously to the anaerobic digester. The digester is mechanically mixed by a top-entry agitator, and there is no recirculation or heating system. The digester temperature is regulated by controlling the temperature of the hydrolysed sludge feed by means of a heat exchanger at the buffer tank outlet. The digested sludge is dewatered and stored in covered cells for nine months and then it is spread on agricultural land.

The thermal hydrolysis process is self-sufficient in energy, using some of the biogas produced by the anaerobic digestion. Excess biogas is fed to two 20 kW CHP (Combined Heat and Power) plants that generate power for the Saumur works and also preheat the softened water feed to the steam generator.

The BIOTHELYS® process followed by mesophilic anaerobic digestion at Saumur is currently achieving about 45-50% removal of volatile suspended solids compared to 30-35% removal typically achieved by a single stage mesophilic digestion treating similar extended aeration sludge. That means a reduction in sludge for disposal of about 15%.

The biogas production is increased in the same proportion, and the Saumur biogas is 75% methane and only about 24% carbon dioxide. Without the thermal hydrolysis step, the digester volume would have been almost 1,500 m³, about three times the size of the installed plant. This means that retrofitting thermal hydrolysis as a pre-treatment for existing digesters could increase their capacity by up to three times.

5.3.4 Pilot trial results of thermal hydrolysis to enhance sludge digestion: a new approach combining hydrolysis with temperature phased anaerobic digestion

Aquafin performed pilot scale tests to evaluate thermal hydrolysis (THP) with the Cambi technology followed by temperature phased (thermophilic–mesophilic) anaerobic digestion (TPAD). These tests followed earlier pilot trials conducted in San Francisco which indicated high VS conversion and biogas production in temperature phased anaerobic digestion following thermal hydrolysis. However, full scale implementation of this process on the WWTP of Hamar indicated that the thermophilic digestion step was unstable and difficult to control (Fjaergard et al. 2006).

Within Neptune it was investigated whether shorter residence times in the thermophilic digestion step – focusing on acidification rather than gas production - could lead to a more stable operation with high VS-conversion and biogas production in mesophilic digestion.

The set-up is shown in Figure 5.8.

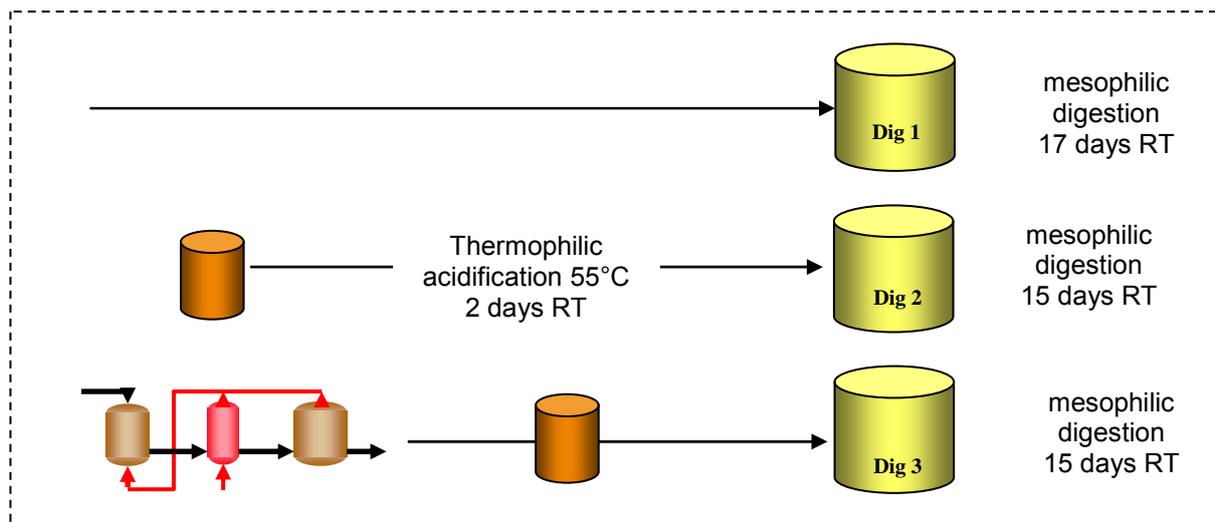


Figure 5.8 Experimental set-up Cambi thermal hydrolysis + TPAD

A reference digester (Dig 1) with a total volume of 1,000 L was compared to two temperature phased digesters, one of them fed with raw sludge (TP+MD, Dig 2), the other one with thermal hydrolysed sludge (THP+TP+MD, Dig 3). The two temperature-phased digesters had a total volume of 25 L.

Raw secondary sludge was taken from the WWTP of Antwerp South, a 190,000 PE WWTP with extended aeration. The sludge was thickened on a thickening table to $\pm 6\%$ DS. All three digesters were inoculated with digested sludge from the same WWTP.

Thermophilic pre-treatment was performed by introducing steam to a batch (± 4 L) of sludge until a temperature of 150°C and pressure of 6 bar. Residence time under these conditions was 20 minutes. After 20 minutes, the pressure is decreased to 2.5 bar and the sludge is led to the flash tank where it cools down till 100°C . Because of the steam addition, the sludge volume is increased to 6 L leading to 150% dilution of the organic matter. The hydrolysed sludge was stored in a refrigerator at 4°C and used as a feed for Dig 3.

The COD balance over the thermal hydrolysis is shown in Figure 5.9. Dilution could partially explain the lower total COD values of the sludge after thermal hydrolysis. However there was also a considerable loss of 10-20% of total COD, which was explained by the conditions in the pilot THP plant allowing some volatilisation of VFA.

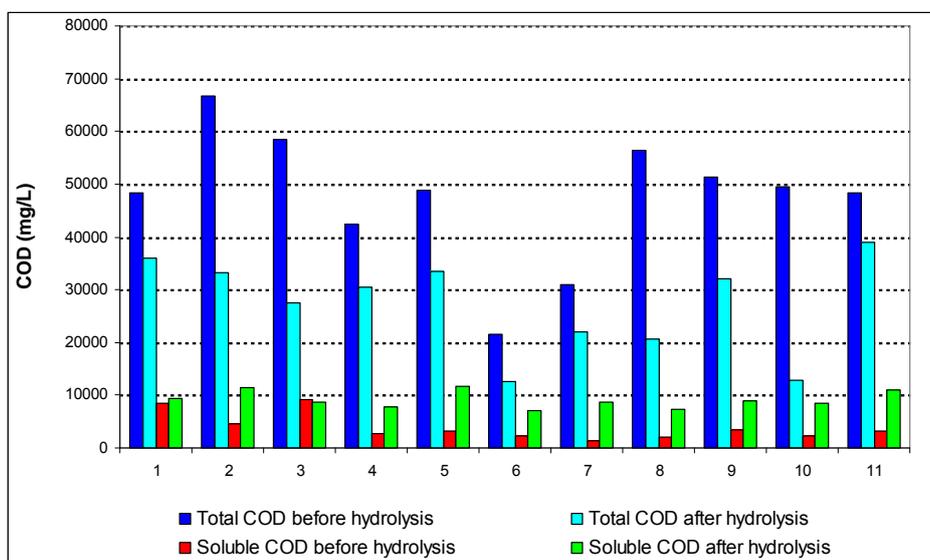


Figure 5.9 Total and soluble COD of the raw sludge before and after thermal hydrolysis (11 batch experiments)

In total, approximately 30% of the total COD was converted to soluble organic matter.

The results of pilot experiments are shown in Figure 5.10.

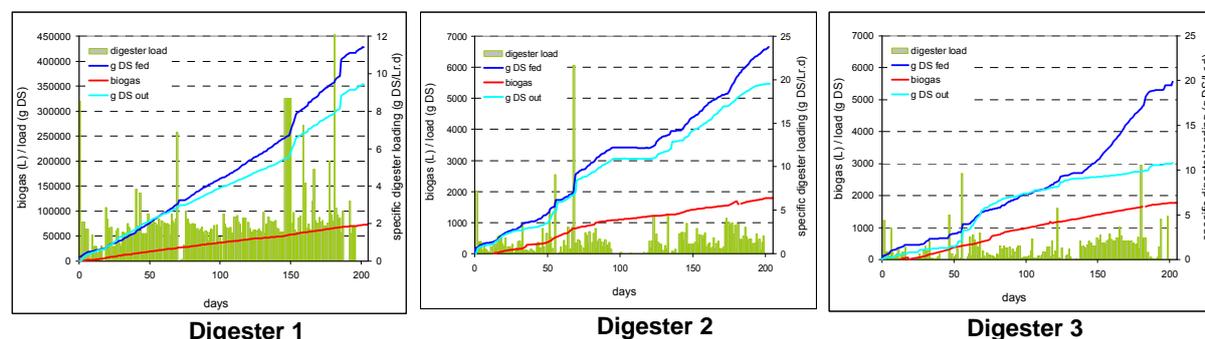


Figure 5.10 Dry solids and biogas production in THP + temperature phased digester (Dig 3)

During six months experiments, the two temperature phased digesters no. 2 and no. 3 had to cope with frequent blockages, unfortunately leading to a lower organic loading rate of the digesters. No other problem of reactor instability was observed.

The mass balance was calculated using three different approaches (COD balance, Van Kleeck formula, ash compensated balance) to account for the uncertainties in the DS-results caused by settling and blockages in the experimental set-up. The mean VS-removal was 24% for the reference digester, 31% for the temperature phased digestion and 35% for the temperature phased digestion preceded by the thermal pre-treatment.

Both temperature phased digesters showed an improved biogas production compared to the reference (mesophilic) digester. Thermal hydrolysis pre-treatment of the sludge could increase the biogas production as well as VS-removal.

Results from full scale Cambi references often reflect much better results for VS removal and biogas increase. This can be explained by a loss of VFA which evaporate when the sludge has to be taken out of the THP-pilot. Earlier experiments with the pilot plant indicated a VS loss of 12% (Wilson et al., 2008). The differences in loading rate, settling in the digesters and the VFA loss in the pilot THP plant were suggested to be responsible for the poorer result.

The dewaterability was evaluated using a lab scale dewatering device. The most appropriate polymer was selected by means of coagulation-flocculation tests. The dewaterability was evaluated using different polymer doses. The results of the obtained DS-content after dewatering are illustrated in Figure 5.11.

The thermally hydrolysed sludge showed a higher DS-content after dewatering, but coupled with a significantly higher polymer dosage.

5.4 Ultrasounds

5.4.1 Introduction

Ultrasound technology for improved anaerobic digestion was tested at laboratory scale as early in the 1960's. However, at that time, ultrasound generating technology was not sufficiently developed to provide a process that could cost-effectively be implemented at full-scale. In the last five years, advances in ultrasound equipment have generated renewed interest in this technology for hydrolysis of municipal solids. The technology provides an easy retrofit option for existing wastewater treatment plants, and has a relatively low cost compared to options such as thermal hydrolysis. The simple installation and operation of this technology makes it particularly attractive as a potentially cost-effective method for optimizing gas production at municipal plants.

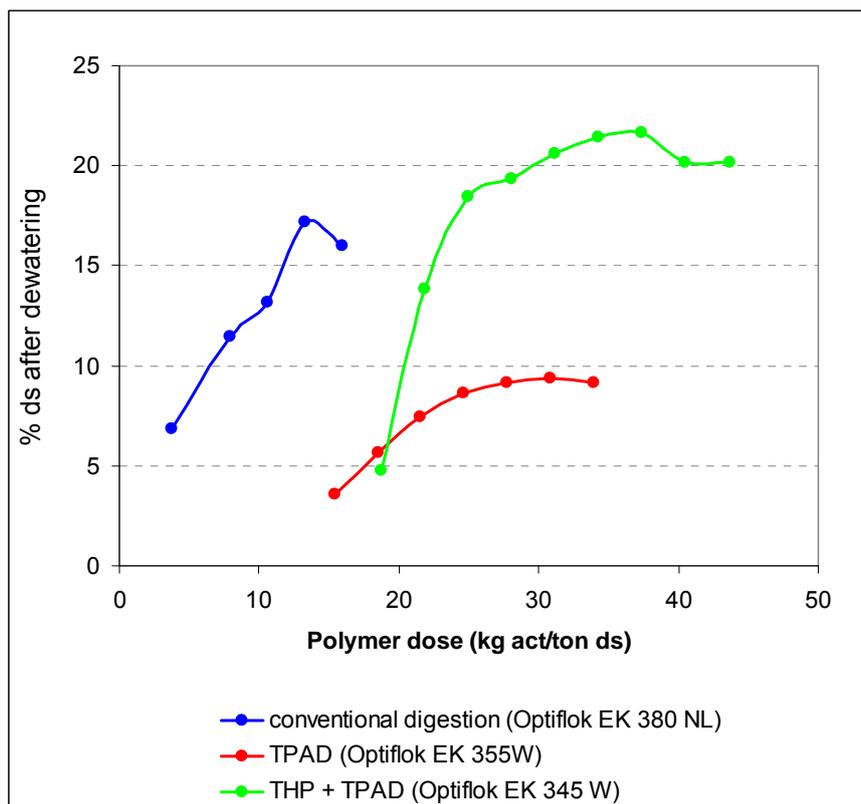


Figure 5.11 Dewatering results of the (hydrolysed) digested sludges

There are three primary suppliers with systems developed for municipal applications, and these suppliers are continuing to develop and optimize their equipment to improve cost-effectiveness. The early ultrasound units used on secondary sludge were in the range of 1 to 2 kW each, and the cost-effectiveness of installing large numbers of these units at medium to large treatment plants is questionable. Therefore, to make the units more cost-effective and enable one ultrasound probe to treat a greater amount of sludge, developments have focused on designing probes which operate at higher powers, between 6 to 16 kW each, and on probe designs that maximize the intensity of the power exerted by the probe. These developments aim to reduce the sonication retention time required, and thereby increase the capacity of a single ultrasound probe. These new high power ultrasound probes are in the early stage of development on full-scale digestion applications, and operational issues, equipment life and reliability, efficiency of transducer, cooling systems, and actual cost-effectiveness of these new systems is yet to be demonstrated. The different manufacturers have also been making other specific design modifications to their ultrasound equipment to improve the cost-effectiveness. These numerous recent developments in equipment mean that this technology is still in the developmental phase, and work still needs to be done to evaluate the application of this technology in optimizing gas production at municipal treatment plants. Most of the work to date has been conducted in Europe.

Research on the application of ultrasound for improved anaerobic digestion has shown that greatest impact occurs when secondary sludges are sonicated. Secondary sludge consists primarily of cellular material which is harder to breakdown and it's rate limited by the hydrolysis step. The increase in the gas production is much lower when primary sludge is sonicated, as these solids are readily putrescible and less limited by hydrolysis. Therefore, application of ultrasound for digestion has focused on the treatment of secondary sludge.

Sludge flocs, or agglomerations of cells, are first broken up. The cell walls are then damaged by the effects of cavitation. The impact of sonication on the sludge can be approximated by the increase in soluble organics, typically measured as the increase in soluble chemical oxygen demand (COD), through the ultrasound reactor. Besides, there are a number of

process improvements benefits which have been observed when sludge disintegration by ultrasound is coupled with anaerobic digestion:

- ⇒ increased volatile solids destruction;
- ⇒ increased biogas production;
- ⇒ increased digester capacity (due to shorter retention times).

The increase in solids destruction results in an increase in gas production, and the ability to operate digesters in a stable manner, even at low retention times of 12 to 15 days, enables plants which are restricted by digester capacity to operate more effectively.

The footprint is small, and operation of the system is simple. The energy demand of an ultrasound system is small, and the net energy balance of the digestion process can be positive. This technology is certainly less expensive than the processes based on thermal disintegration. Although ultrasound disintegration has been tested at the feed concentrations up to the 10% solids, it is not clear whether the power input would need to be increased at the feed solids concentrations over 6.5% due to the high sludge viscosities.

5.4.2 Technology Description

Ultrasound equipment typically consists of an ultrasound generator, which changes the frequency of the applied electric current from 50 Hz to the typical frequency of 20 kHz used for sludge disintegration. This high frequency electric current is passed into a transducer, which contains piezoelectric crystals which convert electrical energy into resonant mechanical energy. A metal or ceramic ultrasound probe or horn is attached to the transducer, and the resonations are transferred to the horn, which vibrates in the fluid being treated producing a phenomenon known as “cavitation”. Cavitation is the formation, growth, and rapid collapse through implosion of micro-bubbles in a liquid. Implosion of these cavitation bubbles creates localized hot spots with conditions similar to those on the sun, with temperatures up to 5,000°K and pressures of 510 bar. Disintegration of sludge requires the maximum intensity of cavitation, and this is achieved at the lowest end of the frequency range. As the frequency increases, the cavitation intensity decreases.

Most high-power ultrasonic transducers operate in the range of 20–35 kHz, which is an optimum range for delivering peak power to the fluid. In WW applications, the ultrasound probes are typically made of titanium, as this provides the best material strength at the optimum vibration.

Ultrasound systems have a number of key design parameters. These are listed below:

- ⇒ intensity power supplied per unit area of the probe (W/cm^2);
- ⇒ density power supplied per unit volume of fluid in the reactor (W/L);
- ⇒ dose energy supplied per unit volume treated (Wh/L);
- ⇒ specific energy input per unit mass of solids in the reactor (Wh/kg, or kJ/kg);
- ⇒ amplitude (distance of the vibration) or displacement, of the ultrasonic probe (μm).

5.4.3 Lab scale tests

Ultrasound assisted biological sludge degradation has been extensively studied in laboratory, pilot and full-scale (Bougrier et al., 2005; Müller et al. 2003; Tiehm et al., 2001; Lafitte-Trouque and Forster, 2002; Onyeche et al., 2002; Brown et al., 2003; Braguglia et al., 2006; Khanal et al., 2007). The performance of anaerobic digestion processes is commonly assessed by means of volatile solids (VS) reduction (de la Rubia et al, 2006) The amount of VS degraded and transformed into the biogas depends on the sludge characteristics, temperature and the organic loading rate (OLR). It is well known that the OLR of a digester, as the hydraulic residence time (HRT), is one of the most important factors for anaerobic digestion system control. For example, a digester fed with the sonicated sludge and operated at 12 d HRT showed a better performance in comparison with a parallel one fed with the untreated sludge and operated at 22 d HRT (Tiehm et al., 1997). Such results were confirmed by Mao et al. (2006).

Table 5.3 shows results of a study by Braguglia et al. (2007) to assess the effectiveness of disintegration by ultrasound to improve performance of the secondary sludge anaerobic digestion. Secondary sludge was taken from the “Roma-Nord” WW treatment plant operated at a quite high sludge age (20 d). The disintegration by ultrasound was performed with an ultrasonic processor UP400S (dr. Hielscher, Germany) operating at 255 W and 24 kHz. The sonotrode has a diameter of 22 mm making the device suitable for sample volumes of 500 mL. The degree of sludge disintegration was calculated according to Braguglia et al. (2006). Sonication energy input was varied between 0.35 and 1.4 kWh/kg dry solid on 500 mL of waste activated sludge (1.5-5.0 % TS) placed in 1 L beaker with the probe allocated at 3 cm above the beaker bottom. Digestion of sludge was carried out using two anaerobic digesters operated in a semi-continuous mode under the same conditions. One reactor, as control unit, was fed with a raw secondary sludge, and the second one with the same sludge after disintegration by ultrasound. Both jacketed reactors (7 L) were completely mixed and maintained at the constant temperature of 37 °C.

Table 5.3 Operating conditions and results of the anaerobic semi-continuous tests

Test #	1		2		3	
Test duration (d)	67		101		76	
HRT (d)	20		10		10	
OLR (g VS L ⁻¹ d ⁻¹)	0,7		1,4		3	
Sonication Energy (kWh kg ⁻¹ TS)	1.4		1.4/0.7		0.33	
	R ¹	S ¹	R ¹	S ¹	R ¹	S ¹
TS feed (%)	2.13	2.10	2.51	2.49	5.12	5.06
VS/TS	63.8%	64.3%	55.0%	55.4%	56.1%	56.1%
Cumulative biogas production (NL)	85	116	201	255	362	394
VS removal (%)	34	37	32	39	35	36

¹R = raw sludge, S = sonicated sludge

In test #1 the reactors were operated at an HRT of 20 d with a corresponding OLR of 0.7 g VS/(L·× d), considering that VS of feed sludge was approximately 13,600 mg L⁻¹. In test #2 the organic load was increased to 1.4 g VS/(L·× d) by shortening the HRT to 10 d, whereas in test #3 the sludge was preventively thickened to a TS concentration of about 5%, still maintaining HRT of 10 d. Data were collected in steady state conditions, i.e. after reaching constant specific biogas production.

In the test #1, 2 and 3 cumulative biogas production increased in the reactors fed with sonicated sludge in comparison with the reference reactor of 36, 26 and 9%, respectively.

The WAS sampled from the WWTP and used for the tests was characterized by a quite low VS content (55-64%) due to its high sludge age. With ultrasound pre-treatment, VS removal increases from 34 to 37 % for test #1 and from 32 to 39 % for test #2, in spite of the lower specific energy for sonication. In test #3, performed with thickened sludge at 5% TS and with an OLR of 3 g VS/(L × d), the improvement due to the sonication was negligible. These low VS removals are typical of WAS digestion while higher values (up to 50%) are observed for digestion of mixed sludge (Metcalf and Eddy, 1991; Bolzonella et al., 2005).

5.4.4 Vendors

In the last decade, much of the fundamental research for ultrasound in environmental engineering applications was done at the University of Hamburg-Harburg and the Fraunhofer Institute in Dresden.

Both of these institutes have set up spin-off companies to commercialize their know-how, known as Waves and IWE Tec, respectively. A third company, Sonico, was established following applied research funded by a consortium of U.K. and U.S. water agencies, led by Atkins, an engineering firm based in the U.K. These suppliers have a number of demonstration installations in Europe. VTA, an Austrian company, has gained valuable

experience in recent year by applying its technology to 21 WW treatment plants in Austria, Germany, Italy, Poland and Switzerland.

5.4.4.1 IWE Tec Ultrasound System

The IWE Tec approach to ultrasound application for municipal sludges is based on partial treatment of the secondary sludge stream which is the most cost-effective approach. The increase in gas production is attributed to the release of soluble COD from cell lysis, as well as stimulation of enzyme activity. IWE Tec also claims that dewaterability of the digested sludge is improved by a partial treatment and decreases if a larger portion of the flow is treated. Bioflocculation is considered to be the reason for improved dewaterability – cell lysis exposes the inner cell walls to the oppositely charged outer cell walls, allowing agglomeration of particles. Excessive particle disintegration by ultrasound can result in the production of too many very fine particles which cannot be captured by dewatering devices and makes dewatering more difficult.

The IWE Tec system operates at sonication times of 30 to 60 seconds. IWE Tec considers the amplitude to be a key parameter in achieving the required sludge disintegration and therefore set the probes to run at 90 to 95% of maximum amplitude. The operating power draw is a function of an amplitude and load or resistance on the probe, and the systems are usually designed to run between 50 to 75% of the maximum power, to provide a buffer and prevent the units cutting out due to power overloads. Some of the recent advances made by IWE to improve the cost-effectiveness of the system are:

- ⇒ increase in the maximum amplitude from 25 μm to 50 μm ;
- ⇒ Increase in probe power, from 4 to potentially 16 kW. Probes over 4 kW have a new water cooling system;
- ⇒ the probe design has been changed from single cast piece to a two-piece probe to allow the lower portion, which has the most wear, to be replaced more frequently, while the upper portion can be replaced less frequently.

These are potentially significant changes regarding the cost-effectiveness of ultrasound application. The performance and operational impacts of these changes require validation through a demonstration testing. Data from IWE in Germany show that the older design, using 2 kW probes at the lower amplitude range typically provided improvements in anaerobic digestion as follows:

- ⇒ Increase in volatile solids destruction of 20 - 25%;
- ⇒ Increase in gas production of 25 - 30%;
- ⇒ Improved dewaterability of 0 - 5% points.

Actual results vary depending on digestion performance without ultrasound, digester retention times and the proportion of secondary solids in the digester feed.

5.4.4.2 Sonico Ultrasound System

The Sonico ultrasound system consists of individual radial horns that are shaped like a ring donut. The horns are mounted in series in a reactor that typically contains three or five horns, as shown in Figure 5.12.

The reactor is designed with flanges at either end which connects to a six inch diameter pipe. The radial horn design and reactor design are covered by patents. The research for this system was conducted using 2 kW and 3 kW horns. The design of the ultrasound system was improved producing higher powered horns at 6 kW.

The Sonico approach to ultrasound application for municipal sludges is based on treatment of the entire secondary sludge stream. Research conducted in developing this system has shown that maximum gas production is achieved by maximizing the fraction of sludge that

receives ultrasound treatment. Sonico has not yet done much work on evaluating improvements in dewaterability.



Figure 5.12 Inline ultrasound unit, 3 kW horns

However, during the demonstration tests conducted at Orange County Sanitation District small-scale dewaterability tests were run using laboratory-scale belt press equipment. The data showed an improvement of 1.2 to 2.5% in dry solids content.

The Sonico system operates at sonication times of around 2 s. Sonico consider the ultrasound density and dose to be the key parameters in achieving the required sludge disintegration. The system is designed to typically run at 70 to 75% of the maximum amplitude, which provides buffering for changing loads. Some of the recent advances made by Sonico to improve the cost-effectiveness of the system are:

- ⇒ increase in the maximum amplitude from 12 to 16 μm ;
- ⇒ increase in power, from 3 to 6 kWh;
- ⇒ improvements in the transducer cooling system.

Data from Sonico ultrasound systems show that the older design, using 3 kW probes at the lower amplitude range, typically provided improvements in anaerobic digestion as follows:

- ⇒ Increase in volatile solids destruction of 30 - 50%;
- ⇒ Increase in gas production of 30 - 50%;
- ⇒ Improved dewaterability of 0 - 2.5% points.

5.4.4.3 UltraWaves Ultrasound System

The Technical University of Hamburg-Harburg (TUHH), Germany, has been conducting research in environmental engineering applications of ultrasound for many years. A spin-off company, known as Waves, has been set up to commercialize their know-how. The company currently uses an ultrasound system provided by a German manufacturer, Sonotrode.

The Ultrawaves ultrasound system consists of short cylindrical probes arranged in series, within a reactor which provides a serpentine flow path, as shown in Figure 5.13. The reactor typically contains five probes. Each probe is a 2 kW unit, and the systems typically operate at 50% power draw. Waves does not develop higher powered probes as its manufacturer states that this would reduce the life and reliability of its transducers; cooling of larger transducers with more piezoelectric rings is a key design issue. Ultrawaves has also focused on the

application of ultrasound systems at smaller treatment plants, and considers its current system cost-effective for these types of facilities. A test unit is now operating at the Hamburg wastewater treatment plant, Germany.



Figure 5.13 Flow path through the Waves ultrasound unit

Ultrawaves, like IWE Tec, also treats only part of the secondary sludge flow, although its approach is different. Waves has shown that the greater the amount of sonication, the greater the increase in gas production. However, it has found its system to be most cost-effective when treating 30 to 50% of the secondary sludge flow. It does not attribute the improvement in digester performance to enzyme activity, only to cell lysis. Research by the TUHH has found that dewaterability impacts are complex and not well understood and Ultrawaves does not make claims in this regard without site testing. It has found that higher cationic polymers are often required due to the presence of smaller particles (Eder B., Guenther F.W.; 2002).

The Ultrawaves system operates at sonication times of around 2 s. Ultrawaves considers the ultrasound density and dose to be the key parameters in achieving the required sludge disintegration, and they found that the intensity was highest with the shorter probes. The maximum amplitude on the Ultrawaves system is 40 μm , although the operating set point is fixed at 25 μm . Ultrawaves has found that for their system, operating at higher amplitudes reduces the life of the equipment.

Data from Ultrawaves ultrasound systems using its current 2 kW probes typically provided improvements in anaerobic digestion as follows:

- ⇒ Increase in gas production of 10 - 50%;
- ⇒ Increase in volatile solids destruction corresponding to gas production.

The average specific energy dose of the ultrasound units is generally 0.04-0.05 kWh/kg DS (or 159 kJ/kg DS).

Actual results vary depending on digestion performance without ultrasound, digester retention times and the proportion of secondary solids in the digester feed.

5.4.4.4 VTA

The Reverse Flow Disintegration Unit, developed and patented by VTA Technology Ltd., achieves the disintegration effect by means of ultrasound at 25 kHz frequency. A part of the surplus sewage sludge continuously flows top down through the disintegration reactor. The ultrasonic transducers are located in this reactor. By means of an agitator the sludge

suspension is treated by continuously being passed through the ultrasonic oscillators. Depending on the residence time of the sludge in the reactor, the flow rate, the rotation speed of the agitator and the energy input of the integrated ultrasonic elements, the disintegration rate can be selected. The treated sludge is subsequently transferred to the digestion process.

5.4.5 Cost/Benefit of technology

Vendors claim that ultrasound systems will have a pay back period from two to five years, depending on factors such as:

- ⇒ ratio of secondary to primary solids and digester retention time;
- ⇒ value of energy, whether measured in terms of natural gas off-set or purchased electricity costs;
- ⇒ actual impact on dewaterability and potential for savings on polymer and for production of drier cake;
- ⇒ cost of recovering or disposing sludge;
- ⇒ concentration of feed secondary sludge because the more diluted it is, the larger the size of ultrasound system is required and the lower the increase in gas production per installed ultrasound unit is expected;
- ⇒ site-specific installation costs, such as surge tanks, pressure regulating systems, installation on the secondary sludge line or on the digester recirculation line.

Preliminary installed ultrasound cost estimates for a 130,000 m³/d plant are 1.3 - 1.6 million €, and would depend on what ancillary equipment, such as holding tanks, may be required at the site. The larger the power input, the fewer the number of probes required. This improves the cost-effectiveness of ultrasound systems for medium to large plants. IWE Tec does not recommend the installation of more than six units in series, at least with the 2 and 4 kW probes. This is mainly due to head loss across the probes. Sonico similarly recommends a maximum of five reactors, each containing five horns, to be installed in series. Additional parallel trains may be installed.

5.4.6 Performance at specific full-scale installations

5.4.6.1 Meldorf (Germany) WWTP (65,000 pe)

A full-scale installation was implemented at Meldorf WWTP (65,000 PE) in February 2005 after a three-month test period. The plant was experiencing problems with foaming in the anaerobic digester as a result of an excessive growth of filamentous bacteria (*Microthrix parvicella*) in the waste activated sludge. The purpose of the ultrasound installation was to eliminate the source of the foaming problems and thereby ensuring an undisturbed anaerobic digestion. Sonication was applied to 100% of the thickened waste activated sludge flow before it was fed to the two anaerobic digester tanks present at the plant.

A short time after the installation of the ultrasound equipment at the Meldorf WWTP, the problems with foaming sludge were no longer an issue. This, in turn, provided the conditions necessary for a smooth and effective digestion of the sludge when it reached the fermenter. The VS, expressed as percent of dry solids, were reduced from 60 to 45% in the stabilized sludge. With regard to biogas production, a 30% increase after the ultrasound installation was noted as compared to before the installation. These improvements correspond to improved self-sufficiency with regard to energy supply and a reduced sludge mass for disposal. In addition, the feeding of co-substrates was made possible as a result of the improved stability of the anaerobic digestion process. The plant was able to accept process liquids from a local food producer, which serves the interests of both parties. (Neis U. et al.; 2008)

5.4.6.2 Bamberg (Germany) WWTP (330000 pe)

A full-scale installation with two ultrasound reactors was completed in August 2004 at the WWTP in Bamberg, Germany (actual load 330,000 PE). The ultrasound application had previously successfully been tested at the plant during a trial period that lasted for four months. The purpose of the ultrasound application was to enhance the VS-degradation to a minimum of 45% in order to avoid the costly task of constructing another anaerobic digester. The HRT in the digesters was 18 days.

In order to improve the VS degradation, 25% of the thickened waste activated sludge flow (TWAS) was sonicated before it was led to the anaerobic digester.

Ideally, organic material that is available to the organisms in the sludge is converted to methane in the anaerobic food chain. The gas production, compared to conventional digestion, increases as a greater amount of organic material is made bio-available through the sonication. By feeding the digester with ultrasonically treated sludge, the gas production has been shown to increase by almost 30% at the WWTP in Bamberg (Figure 5.14). The methane content also increased slightly making the biogas a more attractive and energy rich product. The residual VS content in the digested sludge was reduced from 60 to 54%. The desired goal to reach a minimum of 45 % VS-degradation was met and surpassed.

An increase in VS-destruction and biogas production was apparent at the Bamberg WWTP after ultrasound had been installed. As compared to a conventional digestion, VS-destruction increased by 28 % and biogas production increased by nearly 30 % in the digester fed with US-treated sludge. The energy consumed by ultrasound treatment was 2.6 kWh/m³.

The increase in VS-destruction implies that more of the organic matter in the sludge was metabolized in the digestion process. This coincides with the increase in gas production; less organic matter in the sludge means that the carbon source must have been metabolized in the digestion process to yield biogas. Through the increase in gas production, the self-sufficiency of the plant with regard to energy supply was improved. To a larger extent, the plant was able to supply its operative processes with energy obtained from its anaerobic digestion process. This is of course advantageous seen from an economic perspective.

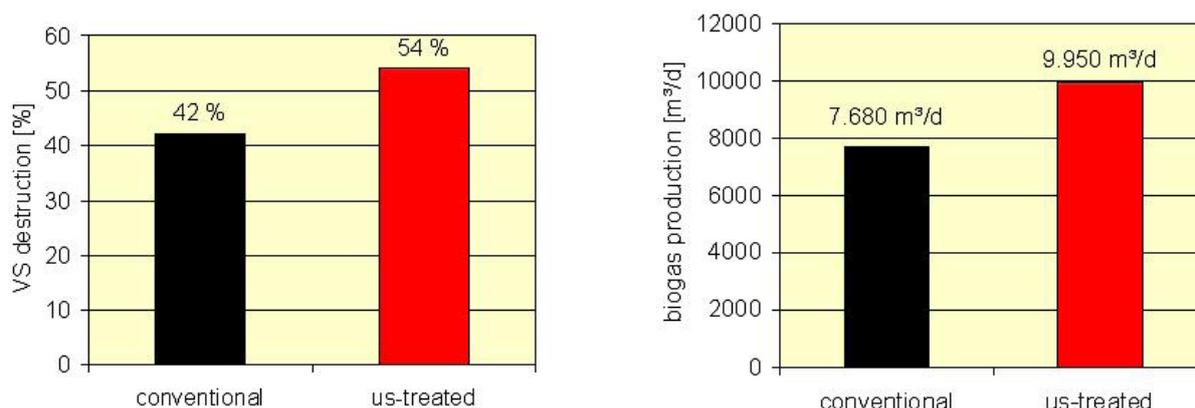


Figure 5.14 VS destruction and biogas production

5.4.6.3 Mannheim (Germany) WWTP (725.000 p.e.)

Surplus activated sludge (WAS) is continuously thickened (TWAS) by centrifuges up to 12% dry matter as well as primary sludge (TPS, also thickened to approximately 10% dry matter content). Complete stream of thickened sludge (TWAS plus TPS) is charged to digesters in order to generate biogas and to reduce total sludge mass. Biogas is mainly used in combined heat power units for energy production and also to run an aeration compressor. Handling such high concentrated, high viscous sludge requires special equipment for pumping as well as very effective stirring systems in the digesters (3 digesters, 7.500 m³

each) and reliable control technology. After digestion stabilized sludge is dewatered with centrifuges under use of flocculants up to a dry matter content of about 25% and subsequently dried.

Remaining water content in the outcome of drying process is about 5%. Biogas from digestion as well as the natural gas is used for dryer's thermal energy supply.

In order to keep charges for water as low as possible, in 2002 a research project common with Fraunhofer IKTS Dresden was started to figure out effects of a full scale ultrasound part stream disintegration system with regard to increase of biogas production, reduction of total sludge mass, reduction of flocculants demand and savings on energy. The initially installed high-power-ultrasound system ran successfully for more than three and a half years. Effects on sludge treatment process were convincing, so in the 2006 an update of the TWAS disintegration process started after a 8 month pilot phase with the new Disintegration Module System, developed again by Fraunhofer IKTS. That new treatment system needs 45% less energy compared to the formerly installed ultrasound technique and has significantly lower maintenance costs, with an operation time of nearly 24 h/d every day. First ultrasound probes installed in spring 2006 are still in operation today.

Due to the application of the part-stream disintegration process for treatment of TWAS at WWTP Mannheim, a stable increase in biogas production of 20% is achieved, which equals to an additional electrical power generation of about 5.600 kWh/d and extra thermal energy of 8.970 kWh/d. Additionally the decrease in amount of sludge before drying stage is 20 m³/day. All this enables a daily saving of 12.700 kWh primary energy, which otherwise would have to be produced by burning natural gas.

Energy balance of used disintegration system at WW treatment plant of Mannheim is very positive due to the significant effects on subsequent processes for a daily total gain of energy of about 27.300 kWh primary energy, out of them only 288 kWh of electricity are required for the disintegration system (Hein A., 2008).

5.5 Conclusions

The disposal of sewage sludge by landfill is decreasing due to more stringent regulations in Europe (Directive 99/31). Agricultural use of stabilized sludge is decreasing too in many European countries, like Austria, Netherlands and Switzerland due to specific local situations many times reflecting the interests of stakeholders and the market.

An increasing fraction of sewage sludge must therefore be dewatered, dried, incinerated and the ashes disposed of in landfills. These processes are cost-intensive and also lead to the loss of the valuable phosphate resources incorporated in the sludge ash. The implementation of processes that could reduce sludge by higher degradation with higher biogas production, better dewatering and potential for phosphate recycling is therefore recommended.

Sludge disintegration by mechanical, chemical or thermal methods to reduce its production will therefore become of greater interest in future.

The efficiency of disintegration of raw sludge decreases with increasing hydraulic retention time of the digester (Figure 5.15). This has to be considered in comparing different disintegration devices. Since a fraction of the energy is used to accelerate hydrolysis of particulate material that would be degraded in digesters with longer HRTs, disintegration of (pre)-digested sludge may be more economic.

The energy balance for sludge disintegration introduced to improve biogas production is often negative with today's disintegration devices. The evaluation of the effectiveness of full scale applications of disintegration in praxis is difficult, because WWTPs often have no second digestion lane as a reference for a direct comparison. A representative sludge sampling and analysis of sludge characteristics like VSS, TS and TSS is often difficult and defective. These parameters have big impact on the mass and energy balances.

Due to disintegration, nutrients incorporated in the sludge will be released again and have to be treated in the wastewater plant which is energy intensive. Sludge disintegration could therefore significantly increase the overall energy consumption of the plant.

Actual investigations show that sludge disintegration is only economic in the case of high sludge-disposal costs and of interest if operational problems such as foaming and bulking sludge can be reduced. The application of sludge disintegration must consequently be carefully evaluated for every application.

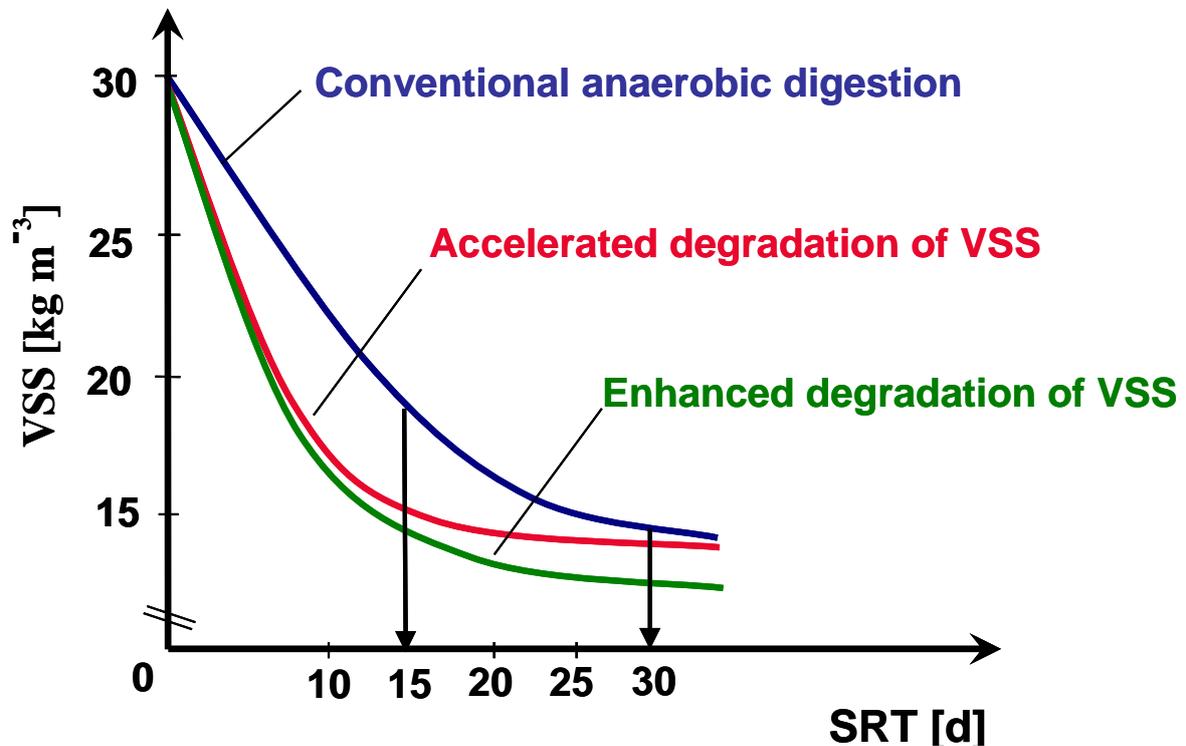


Figure 5.15 Accelerated and enhanced degradation of VSS (Parravicini et al., 2004)

6. INERTIZATION PROCESSES

6.1 Sludge inertisation methods

The major characteristics of sludge inertisation processes are that they are being performed at elevated temperatures ranging from 250°C to 1,300°C. Some of the processes require high pressure as well (wet oxidation and super critical water oxidation) while for incineration, pyrolysis and gasification pressure is normal. Elevated temperature ensures complete destruction of pathogenic bacteria, degradation of organics and micropollutants from sludge as well as reduction of the waste volume for the final disposal. The energy is gained back either in the form of heat or could be stored if gas or oil are being produced. However, a commercial oil or gas production is still not a common practise, in the most cases due to the high amount of impurities comprised in the obtained products, which requires high purification costs.

6.1.1 Ultra high temperature sludge Pyrolysis

Sludge ultra-high temperature pyrolysis includes sludge exposure to the temperatures >1,000°C in the absence of oxygen. Ultra-high temperature allows for avoiding the oily liquid phase in the product while C-C bonds will be destroyed, whereas the absence of oxygen allows for the production of CO, H₂ and CH₄ (instead of CO₂ and H₂O) so that the sludge energy content could be stored and used in other form than heat energy.

At the same time, organic micropollutants and microorganisms present in the sludge are completely destroyed. Schematic layout of the process, together with the major energy input and output, is given in the Figure 6.1.

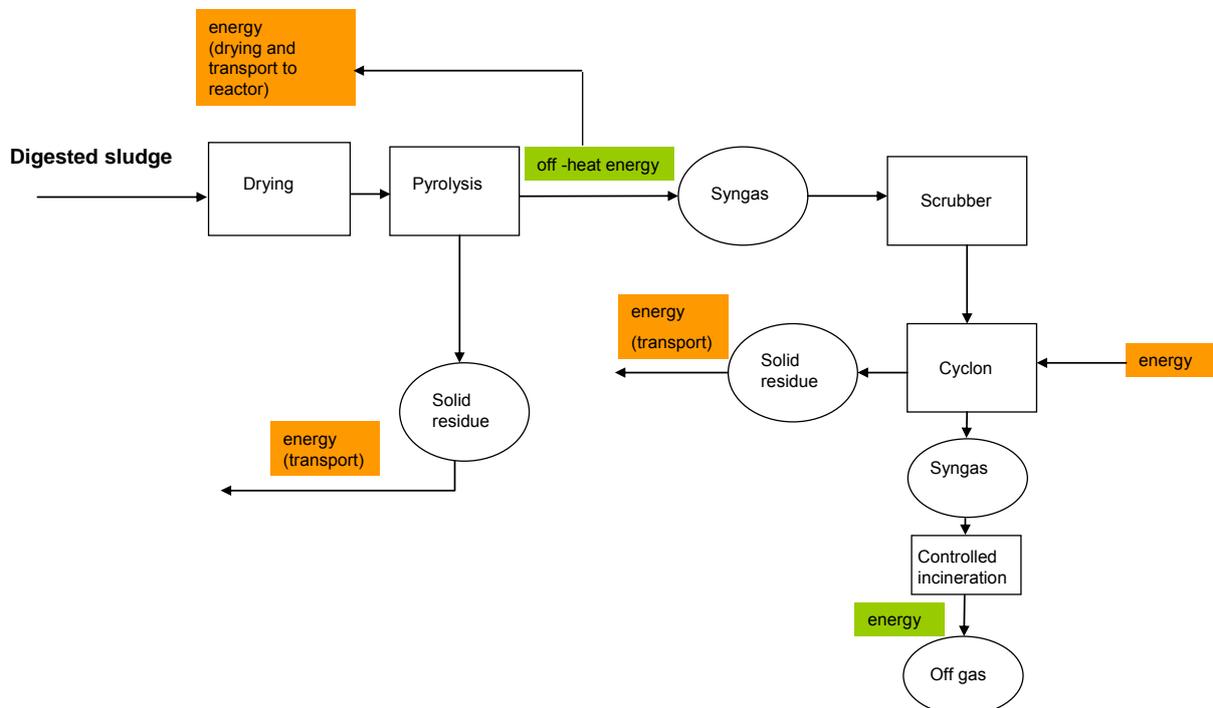


Figure 6.1 Schematic layout of the ultra-high temperature gasification process

Digested and dried sludge (TS>70%) is fed to the reactor. The sludge is heated with an electrical, low-energy consumption induction system in the specially developed tube that can withstand temperatures in the range of 1,000°C-1,500°C over a long period of time without corrosion. As a result, hydrocarbons are converted to a gas with low content of CH₄ and high content of CO, corresponding to the composition of the syngas, which is 85% CO and H₂ with

smaller portion of CO₂ and CH₄. Syngas can be used as an intermediate for the production of synthetic natural gas, organic chemicals, fertilizers, hydrogen, steam, transportation fuel or electric power production. The obtained solid inert inorganic product, to be classified as non hazardous waste, can be safely disposed since it is free of any hazardous organic micropollutants. Due to its high phosphorus and low heavy metal content it could be used as raw product for the fertilizer industry.

The process data obtained from the industrial size plant with a capacity of 25 t/d treating sludge, which has been operated for two years in Emmerich, Germany and one year in Neustadt, Germany are given in the Table 6.1.

Table 6.1 Basic data for the pyrolysis process

Pyrolysis process	
Capacity:	7000tTS/year
TS :	70-90%
Electricity consumption:	100kWh/tonTS
Oxygen consumption:	none
Solid mineral out:	250kg/tonTS
Gas out (to the atmosphere)	none
Operato and maintenance:	4men/year
Energy gain:	960kWh/tonTS
Investment costs:	9million € (for 25ton/d unit)
Personal costs	200'000€/year

6.1.2 Wet Oxidation (WO)

Wet oxidation (WO) is a reaction in the liquid phase between organics and oxygen at elevated temperature and pressure. It could be used for different kind of industrial and urban effluents, which contain high amount of organic compounds. The basic process layout is given in Figure 6.2.

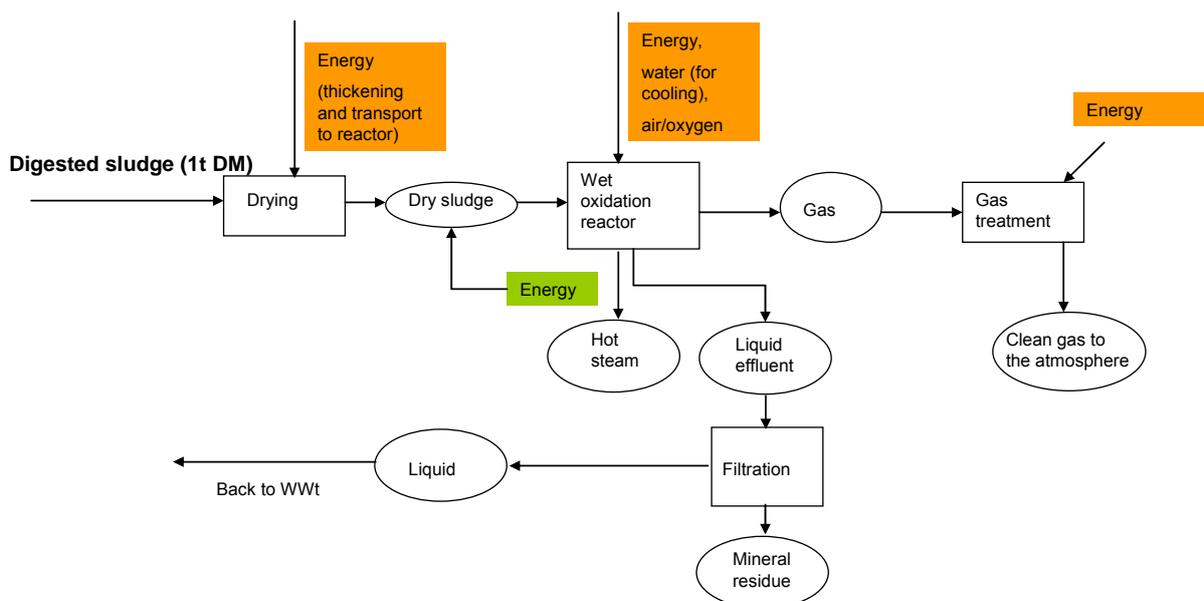


Figure 6.2 Schematic layout of the WO process

The sludge which enters the process could either be digested or raw sludge with a water content of more than 85%. The feasibility of the treatment is determined by the concentration of organic compounds, which should be in the range of 70-120 kg/m³ COD. The residence time should be in the range of 30-60 minutes. Optimal temperature and pressure are in the range 250-300°C and 60-100 bar. Compressed air or pure oxygen is mixed with sludge and the mixture is preheated in the heat exchanger, by using the heat of the liquid after reaction. The WO reaction occurs in a vertical tubular reactor, which operates as a pressurized bubble column. The temperature of the medium will increase in the reactor since the WO is an exothermal process.

If the organic content of the sludge is high, the excess heat can be used for industrial steam, hot thermal or hot water production. After the recovery of excess heat, the fluid is used to preheat the incoming liquid. After cooling, the liquid/gas mixture is separated in a phase separator and decompressed using regulation valves. The gas phase is composed mainly of CO₂ and excess of O₂, but it may contain traces of CO and VOC.

The major process achievement is stable mineral solid product with less than 3% content of organic matter. The mineralization of organic matter is not complete (25%); however, the organics dissolved during the process and returned to the digester are easily biodegradable and enhance the methane production.

Basic process data are given in the Table 6.2.

Table 6.2 Process data for the WO unit (average data for year 2006)

Capacity	120 kg TS/d
TS :	9,80%
COD:	99 g/L
Electricity consumption	350 kWh/t TS
Oxygen consumption	875 kg O ₂ /t TS
Oxidized liquid out (to the digester)	9,25 m ³ /t TS
Solid mineral out	735 kg/t TS
Gas out (to the atmosphere)	900 kg/t TS
Operator	0,5 man/year
Maintenance	25 d/year
Operational costs ^a	550 €/t TS
Excess heat recovered	
Hot water	2,5 GJ/t TS
Heat	0.9 GJ/t TS

^athe value decrease significantly with the increase capacity

6.1.3 Gasification

Middle temperature sludge gasification of sludge occurs in fluidized bed, which provides conditions for the fast, uniform and complete reaction. The process is initiated by the preheated air with the remark that only one third of air volume is required compared to the amount which would be needed for complete combustion. During the exothermal process, by controlling the oxygen amount the temperature will be increased up to the value of 850°C, at which the typical gasification reactions take place. Large organic compounds will be converted into the more simple gaseous compounds and inorganic part of the sludge will leave the reactor as the inert solid product. The major process characteristics are very similar to the one for the WO process (Figure 6.3).

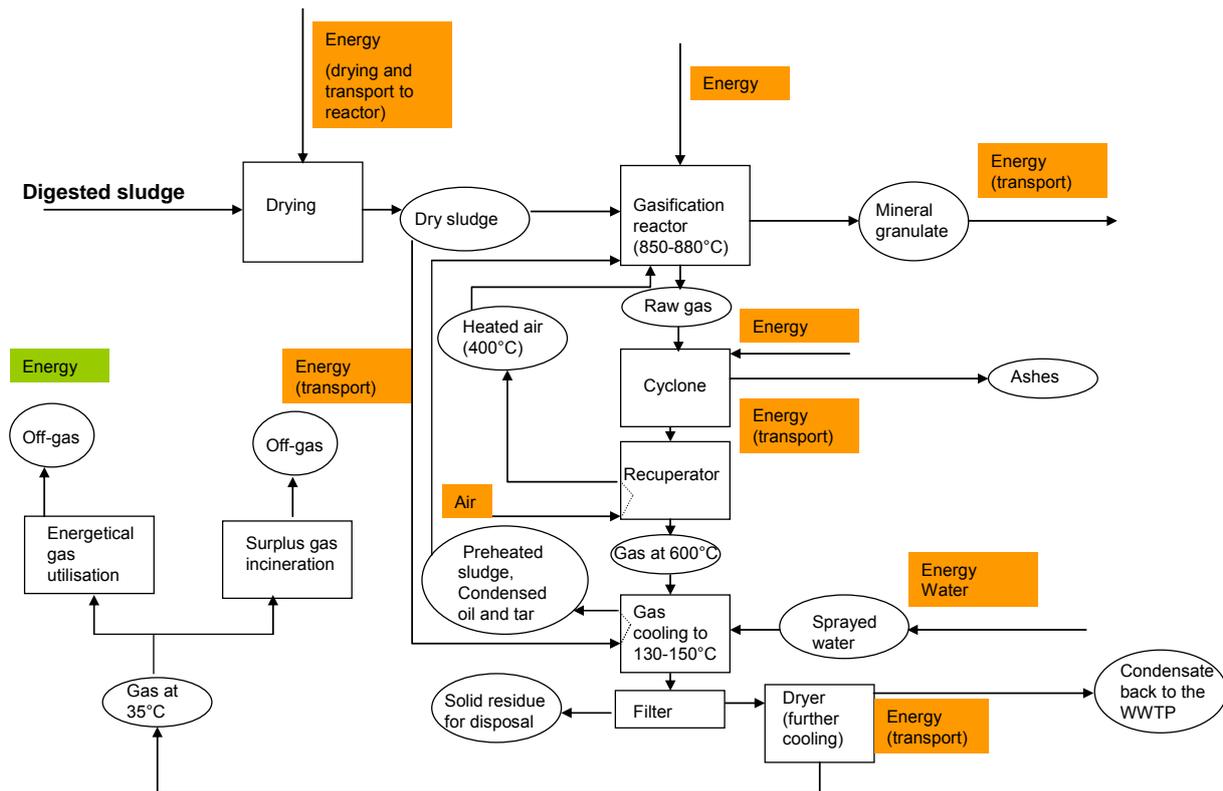


Figure 6.3 Schematic layout of the gasification process

However, due to the higher temperature the total solids (TS) reduction is much higher: 50% for the gasification process compared to 25% reduction during the WO process. Table 6.3 gives the basic process data.

Table 6.3 Process data for the gasification process (Kleinhapfl et al., 2007, Burgbacher, 2006)) (calculated for 1 t TS)

Gasification unit	
Capacity:	170kgTS/h
TS :	70-85%
Electricity consumption:	350kWh/tonTS
Air consumption:	900m ³ /tonTS
Condensate after gas drying, returned to the WWTP :	0.35m ³ /tonTS
Solid mineral out:	500kg/tonTS
Gas out (to the atmosphere):	1765m ³ /tonTS
Operational costs: *)	350-375€/tonTS
Energy gain	
Electrical energy:	500kWh/tonTS
Heat:	3.6 GJ/tonTS

*) Reinhold, 2002

6.1.4 Super Critical Water Oxidation (SCWO)

SCWO is an effective process for the treatment of organic rich sewage sludge. Under the conditions of T=374°C and P=22 MPa water reaches the supercritical phase in which vapour and liquid phases are no longer distinguishable. Therefore, super critical water (SCW) has

properties which are between those of a gas and a liquid. While the density of SCW is similar to the density of liquid water, the viscosity and diffusivity are more like that of a gas. Most organic compounds as well as oxygen are completely soluble in SCW while inorganic compounds become more or less insoluble (Stendahl and Jäfverström, 2003). High viscosity and temperature exclude mass transfer limitations and complete destruction of organic compounds, with products listed in the next table, occurs in less than 60 seconds.

The main process stages as well as the process data could be represented by the scheme given in Tables 6.4 and 6.5 and in Figure 6.4.

Table 6.4 Transformation of the sludge components during the SCWO process

Components	Products
Carbon	CO ₂
Organic and inorganic nitrogen	N ₂
Sulphonated organic and inorganic	Sulphuric acid
Metals	Oxydised to a highest valency
Phosphorus	P ₂ O ₅

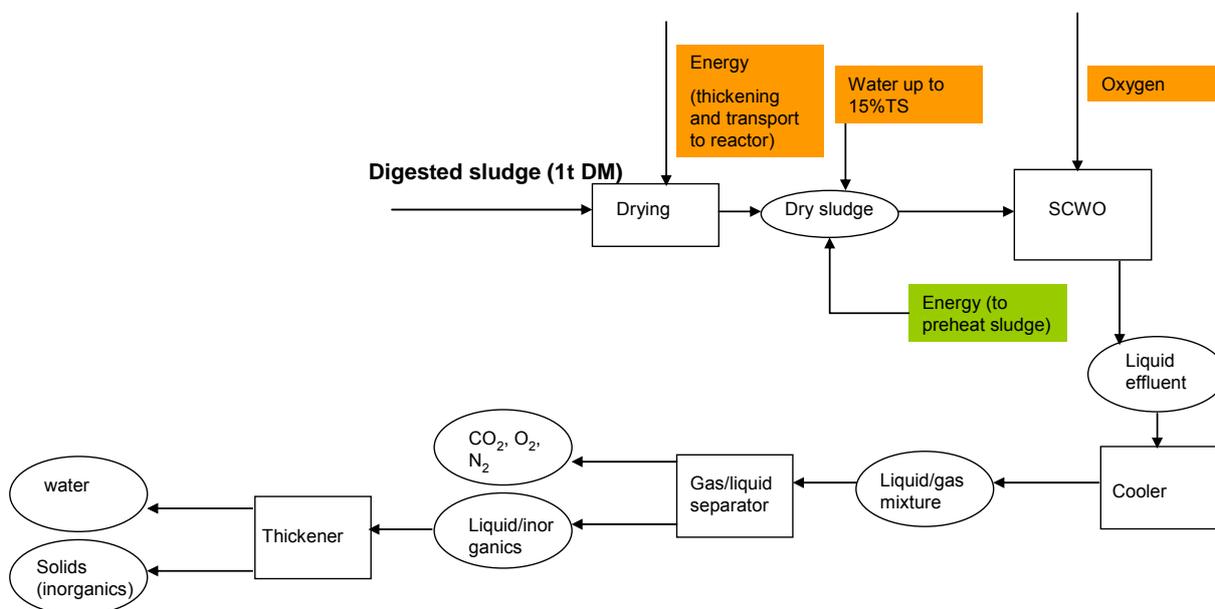


Figure 6.4 Schematic layout of the SCWO process

Table 6.5 Process data for the SCWO process; calculated for 1ton TS (Svanstrom et al, 2003)

SCWO process	
Capacity:	1tTS/h
TS :	15.00%
Electricity consumption:	300kWh/tonTS
Oxygen consumption:	875kg/tonTS
Solid mineral out:	400kg/tonTS
Gas out (to the atmosphere)	800kgO ₂ +34kgN ₂ /tonTS
Operato and maintenance:	4.4menhour/tonTS
Energy gain:	3.2MWh/tonTS
Investment costs:	1.9million € (for 10t/d unit)
Maintenance:	612'000€/year

6.2 Thermal drying and incineration by fluidised bed furnace

6.2.1 Introduction

This activity is addressed to demonstrate that sludge incineration can be efficiently carried out using an integrated process including an indirect dryer, a fluidised bed furnace and a boiler minimizing the unit size as well as the auxiliary fuel consumption, if needed. Moreover, for large plants (capacity $\geq 500,000$ p.e.) a more sustainable sewage sludge management could be attained through a separate processing of primary sludge to be incinerated from the secondary one to be possibly recovered in agriculture. This innovative sludge management strategy is evaluated in terms of size of the operating units needed for sludge incineration and in terms of energy balance for a plant serving 500.000 p.e. Results, under different scenarios of cake concentration, are compared with those of a conventional plant (without sludge separation) and also with corresponding options not including drying.

6.2.2 Composition and production of primary and mixed sludge

According to the fixed values of raw influent characteristics (Table 6.6) and the TSS removal efficiency in the primary settler of 60% (Metcalf & Eddy, 1991), a production of primary sludge of 48 g/(pers \times d) was evaluated and a concentration of 4% of total solids (TS) was assumed with a fraction of VS of 75%. The VS in primary sludge may be approximated to the formula $C_{18}H_{19}NO_9$ with a corresponding COD of 1.425 g/g VS.

Table 6.6 Raw influent characteristics

Parameter	Units	Value
Specific flow rate	L/(pers \times d)	250
COD	g/(pers \times d)	140
N tot	g/(pers \times d)	13
Total Suspended Solids (TSS)	g/(pers \times d)	80
VS/TSS ratio		0.75

Modelling of a typical WWTP was carried out utilizing ad hoc ASCAM (Activated Sludge Computer Aided Modelling) software (Tomei et al., 1993). The procedure is based on the solution of the algebraic system obtained by considering the kinetic, stoichiometric and mass balance equations for all the components and units involved in the COD and nitrogen removal processes. Secondary sludge production of 27.1 g/(pers \times d) at a total solids concentration of 1.1% with a fraction of loss on ignition (VS) of 75.1% was estimated by model application.

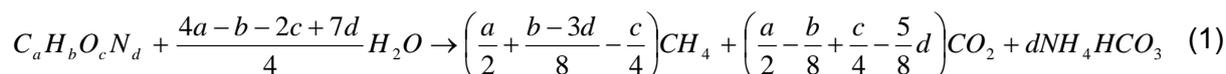
For secondary sludge, the typical formula of $C_5H_7NO_2$ (corresponding COD of 1.48 g/g VS) was considered.

6.2.2.1 Gravity thickening

Concentrations of primary and secondary thickened sludge were assumed to increase from 4 and 1.1% to 8 and 2.5% as TS, respectively, considering lower values of the range reported by Metcalf & Eddy (1991). Accordingly, the concentration of mixed thickened sludge was calculated as 4.6 %.

6.2.2.2 Anaerobic digestion

According to U.S. EPA (1979) VS destruction was estimated as 50 and 30 %, for primary and secondary sludge, respectively. Corresponding VS destruction for mixed sludge was therefore computed as 42.8 %, on the basis of the VS proportion between the two sludges. Biogas production was calculated by the following equation (Buswell and Müller, 1952):



On the basis of assumed composition of VS of primary and secondary sludge, biogas production was calculated as 0.97, and 0.92 Nm³/kg VS destroyed for primary and mixed sludge, respectively. Total biogas production for a plant serving 500,000 persons was estimated as 8,721 and 11,541 Nm³/d for primary and mixed sludge.

Vapour content of biogas was evaluated assuming saturation at 35°C with corresponding vapour partial pressure of 41.827 mm Hg (molar fraction 0.055). According to biogas composition, water loss due to evaporation was estimated as 4.53, 3.71 and 4.33% of volatile solids destruction for primary, secondary and mixed sludge.

6.2.2.3 Mechanical dewatering by centrifuge

Final cake production was finally evaluated in 30 and 51 g/(pers·× d), for primary and mixed sludge, respectively, with VS presence of 60 and 63% of TS. Four different scenarios were considered regarding final cake concentration after mechanical dewatering both for primary and mixed sludge according to Table 6.7.

Table 6.7 *Scenarios of solid concentration of primary and mixed sludge after mechanical dewatering*

	Cake concentration (weight %)	
	Primary sludge	Mixed sludge
Pessimistic value	25	15
Typical value	30	20
Optimistic value	35	25
Very optimistic value	40	30

6.2.2.4 Drying and incineration

In this study an integrated process was considered where sludge was dried before incineration utilizing saturated steam at medium pressure (1.22 MPa and 188°C) produced in a boiler where heat is recovered from the exhaust gas from the furnace. Steam condensation in the dryer allowed recovering 1,984 kJ/kg of steam. The process flow sheet is shown in Fig. 6.1.

Basic assumptions for mass and enthalpic balances of the drying/incineration process are shown in Table 6.8. Gross heat value of VS was calculated according to the Du Long equation (Task Force on Thermal Destruction, 1992):

$$GHV (kcal / kg) = 7,840 \cdot C + 33,989 \cdot \left(H - \frac{O}{8} \right) - [523 \cdot N \cdot (1 - Conv_{NO}) + 1,551 \cdot N \cdot Conv_{NO}] \quad (2)$$

where C, H, O and N represent the weight fraction of the elements in VS and Conv_{NO} is the fraction of nitrogen in VS converted to NO during combustion.

Enthalpies of different gas compounds were evaluated at temperature T using the following equation:

$$H_{compound} = \int_0^T c_p dT \quad (3)$$

Specific heat values c_p of CO₂, H₂O, NO, N₂ and O₂ as a function of temperature are given in Perry and Green (1984). The enthalpy of water was evaluated by adding to the enthalpy of the gas the evaporation heat at 0 °C (2,504.5 kJ/kg).

Table 6.8 Assumptions for enthalpic and mass balances in sludge drying and incineration (Task Force on Thermal Destruction, 1992)

Parameter	Values
Elementary analysis of volatile fraction of dry solids (VS)	Primary sludge: C 54.96%, H 4.83%, O 36.64%, N 3.56% Mixed sludge: C 54.29%, H 5.33%, O 33.64%, N 6.75%
Extraction of incondensable gas from the dryer	1.5 kg/kg evaporated moisture
Gross heat value (GHV) of VS	Primary sludge 18,309 kJ/kg; Mixed sludge 19,245 kJ/kg
Gross heat value of methane	38,083 kJ/Nm ³
Heat losses (% of inlet and/or developed)	5% in the furnace and condenser; 7% in the dryer and the boiler
Excess air for methane combustion with respect to the stoichiometric value	20%
Excess air for VS combustion	What is needed to attain 6 % of oxygen in the exit gases
Conversion of nitrogen presence in VS to NO	5%
Exit conditions from condenser	Saturation of gas
Specific heat of solids	1.255 kJ/(kg °C)
Conversion of heat to electric energy	10,050 kJ/kWh
Minimum temperature of exhaust gas from boiler	250°C

6.2.3 Description of the algorithm

Sewage sludge is basically a poor combustible material and therefore attention has to be put in designing the process (Figure 6.5) which has to be optimised to perform two main goals: minimization of size of furnace, boiler, dryer and other units of the exhaust gas treatment and minimization of auxiliary fuel consumption. The dryer has to be dimensioned to produce a cake at the minimum solid content, possibly allowing autogenous combustion. When the enthalpy of the exhaust gas from the fluidised bed furnace is not high enough to provide the heat for thermal drying, it is necessary to fuel the furnace with a consequent reduction of cake concentration in the feed to the furnace. Such a process has to be strictly considered as disposal operation (D 10) according to the European Directive 91/156. Recovery of energy would be practically possible only through an intensive use of fuel in the furnace fed directly by dewatered sludge not previously dried. Such an approach could not be considered as recovery operation.

An algorithm was developed to calculate the characteristics (flow and temperature) of different currents shown in Figure 6.5. Composition of the exhaust gas from the furnace (current 16) was also calculated at each iterative step imposing oxygen concentration of 6% by volume and adjusting excess of air accordingly.

The flow diagram of the algorithm is shown in Figure 6.6.

The fluidised bed furnace is dimensioned considering a height of 2 m of the bed under fluidisation and 5 m of free board (Mininni, 2001) with an up-flow velocity of 1.1 and 0.8 m/s in the bed and in the freeboard, respectively. Dryer surface area was calculated considering a specific surface requirement of 0.08 m²/(kg/h of evaporated moisture) (Mininni et al. 1997).

The same approach can be used for a plant not including the dryer and condenser. In this case the model is simplified as the enthalpic and mass balances are referred only to the furnace. The same assumptions for temperatures and oxygen concentration are still valid.

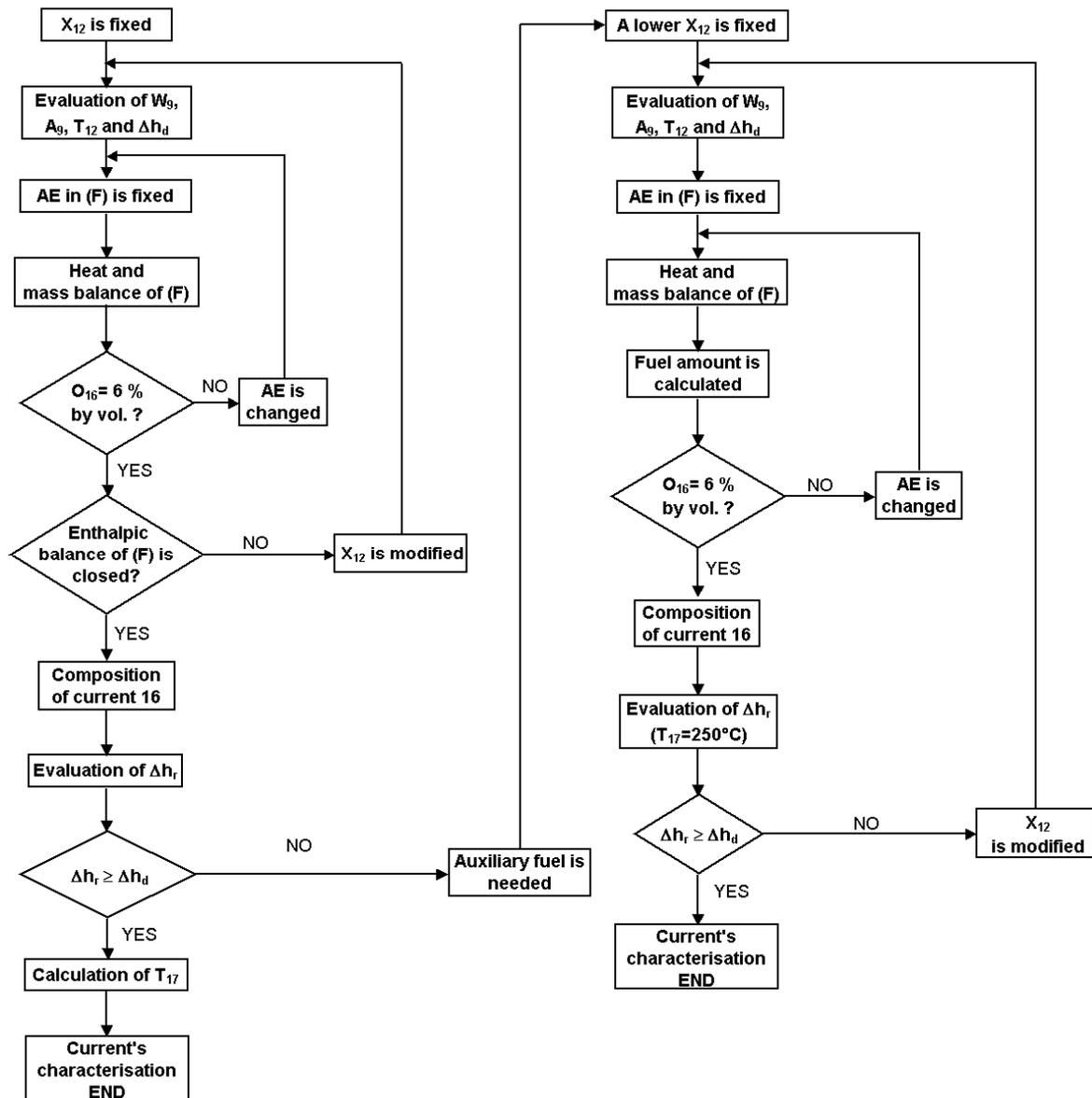


Figure 6.6 Flow diagram of the algorithm to evaluate enthalpic and mass balance of the process shown in Fig. 6.5. The number as subscript is referring to the current index.

A air flow rate, AE excess of air, F fluidised bed furnace, O oxygen concentration, T temperature, W water content, X dry solids concentration, Δh_d heat required for sludge drying, Δh_r sensible heat available in the exhaust gas with $\Delta T=600\text{ }^\circ\text{C}$

Figure 6.9 shows cake concentration of the feed sludge to the furnace as function of corresponding input concentration before drying. The graph displays an increase up to values of input cake concentration allowing autogenous operation (30% both for primary and secondary sludge). In fact, optimal cake concentration before incineration strictly depends on the input cake concentration only under non autogenous conditions. On the contrary when autogenous conditions are performed the average cake concentration before incineration slightly decreases due to the lower heat recovery as a consequence of lower amount of exhaust gas from the dryer (current no. 9) to be fed to the furnace.

Table 6.9 Characterisation of different currents in the flow sheet of Fig. 1 in different scenarios (Incineration of primary sludge)

Current no.	Description	Flow rate (t/d)									
		Primary sludge				Mixed sludge					
1	Sludge from dewatering	(t/d)	60	50	42.9	37.50	170	127.50	102	85	
		X ₁	0.25	0.30	0.35	0.40	0.15	0.20	0.25	0.30	
2	Feed sludge to dryer	(t/d)	99	74	52	35	310	220	167	118	
		T ₂ (°C)	63	60	56	52	68	66	63	60	
3	Recycle of dryer		53	37	24	14	186	126	90	59	
4	By-pass of dryer		14	13	15	17	46	33	25	26	
5	Sludge from dryer		66	49	35	23	206	147	111	79	
6	Condensed steam from dryer		49	38	26	18	154	110	84	60	
7	Exhaust gas from dryer (dry air)		49	38	26	18	154	110	84	60	
7	Exhaust gas from dryer (saturated vapour)		33	25	17	12	103	73	56	39	
8	Water to condenser		423	317	221	149	1321	942	714	503	
9	Incond. to furnace (dry air)		49	38	26	18	154	110	84	60	
9	Incond. to furnace (saturated vapour)		4.2	3.2	2.2	1.5	13.2	9.4	7.1	5.0	
10	Water from condenser to wastewater treatment plant		452	339	236	159	1411	1006	763	537	
11	Air to dryer		49	38	26	18	154	110	84	60	
12	Feed sludge to furnace	(t/d)	27	25	26	26	67	54	46	46	
		T ₁₂ (°C)	43	45	42	38	32	37	42	41	
		Average conc. %	56	60	58,1	57.4	30,7	47,2	55	55,8	
13	Fresh combustion air to furnace		47	55	66	74	60	79	90	112	
14	Fresh combustion air to burner		11	0	0	0	123	51	7	0	
15	Methane to burner		0.5	0	0	0	6.0	2.4	0.3	0	
16	Exhaust gas from furnace		139	121	120	119	424	306	235	222	
17	Exhaust gas from boiler to treatment	(t/d)	139	121	120	119	424	306	235	222	
		T ₁₇ (°C)	250	328	485	602	250	250	250	404	
18	Steam to dryer		49	38	26	18	154	110	84	60	

Table 6.10 and 6.11 show throughputs and dimensions of different units for the different options with primary and mixed sludge, respectively. Size of all the equipment sharply decreases with the increase of cake concentration after dewatering. The decrease of furnace volume for primary sludge vs. input cake concentration is much less pronounced.

Boiler thermal capacity of the plant without drying increases in the range 180-310% (primary sludge) and 180-210% (mixed sludge) comparing to corresponding values of integrated process. Similar results are observed for the furnace volume with increases of 80-190% (primary sludge) and 140-185% (mixed sludge).

Electric energy production for the options A2 is quite poor and probably it is not convenient considering the higher capital cost of boiler with respect to the options A1.

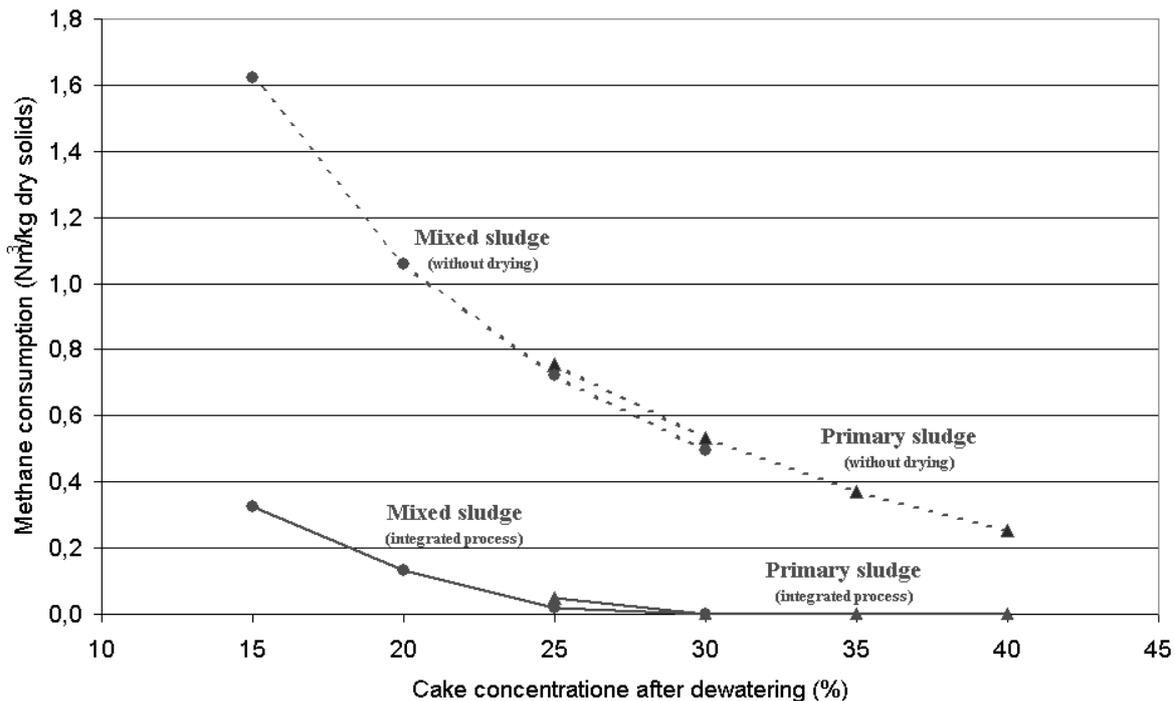


Figure 6.7 Specific methane consumption (Nm³/kg dry solids) for integrated and non integrated processes

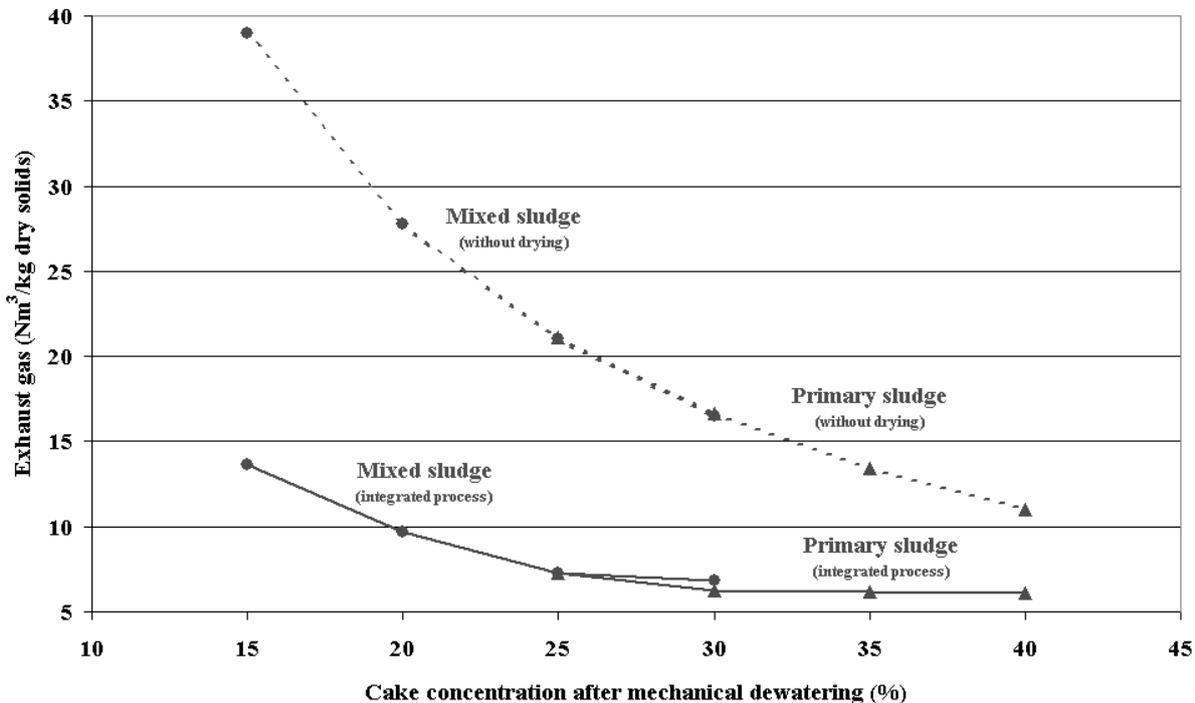


Figure 6.8 Specific exhaust gas flow rate for integrated and non integrated processes

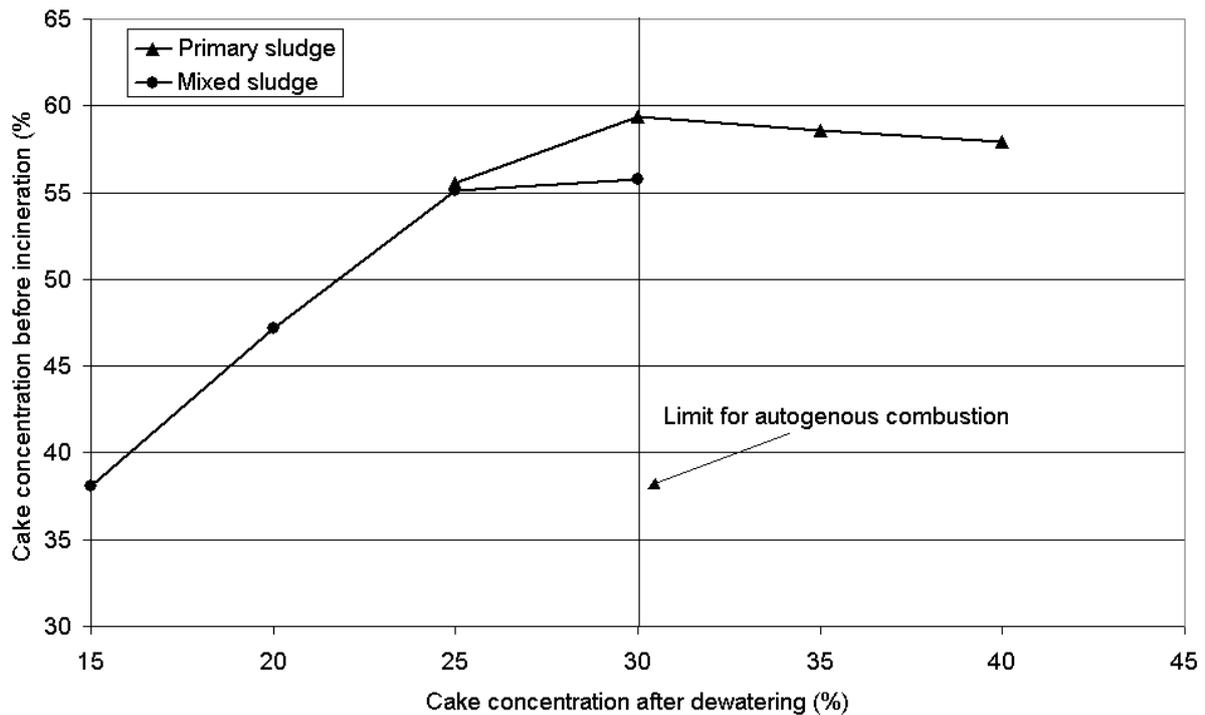


Figure 6.9 Cake concentration of feed sludge to the furnace vs. input cake concentration

Table 6.10 Equipment design for the options with primary sludge

Equipment	Parameter												
	Cake concentration after dewatering (%)	25	25	30	30	30	35	35	35	40	40	40	
	Alternative options for energy recovery	A1	B	A1	A2	B	A1	A2	B	A1	A2	B	
Dryer	Exchange surface (m ²)	115		86	86		60	60		40	40		
	Evaporation capacity (kg/h)	1374		103	103		719	719		48	484		
Boiler	Steam production at 1.22 MPa and 188 °C for A1 and A2 and at 4.05 MPa and 400 °C for B (t/h)	2.1	4.5	1.6	1.8	3.5	1.1	1.8	2.9	0.7	1.8	2.4	
	(MWhth)	1.2	3.4	0.9	1.1	2.7	0.7	1.0	2.2	0.4	1.0	1.8	
Fluidised bed furnace	Diameter of fluidised bed (m)	1.2	2.1	1.1	1.1	1.8	1.1	1.1	1.6	1.1	1.1	1.5	
	Diameter of free board (m)	1.4	2.4	1.3	1.3	2.1	1.3	1.3	1.9	1.3	1.3	1.7	
	Volume of the furnace (m ³)	10.2	30	8.7	8.7	23.3	8.6	8.6	18.8	8.6	8.6	15.4	
Turbine	Electric energy production (MW)	0	1.2	0	0.05	1.0	0	0.1	0.8	0	0.2	0.7	

A1 = Integrated process without electric energy production;
 A2 = Integrated process with electric energy production when heat is still available after drying purpose;
 B = Process without drying

Table 6.11 Equipment design for the options with mixed sludge

Equipment	Parameter									
	Cake concentration after dewatering (%)	15	15	20	20	25	25	30	30	30
	Alternative options for energy recovery	A1	B	A1	B	A1	B	A1	A2	B
Dryer	Exchange surface (m ²)	344		245		186		131	131	
	Evaporation capacity (kg/h)	4294		3061		2321		1636	1636	
Boiler	Steam production at 1.22 MPa and 188 °C for A1 and A2 and at 4.05 MPa and 400 °C for B (t/h)	6.4	14	4.6	9.9	3.5	7.6	2.5	3.3	6.0
	(MWhth)	3.8	11	2.7	7.6	2.1	5.8	1.5	1.9	4.6
Fluidised bed furnace	Diameter of fluidised bed (m)	1.7	2.8	1.4	2.4	1.2	2.1	1.2	1.2	1.8
	Diameter of free board (m)	1.9	3.3	1.6	2.8	1.4	2.4	1.4	1.4	2.1
	Volume of the furnace (m ³)	19	55	14	39	10.	29	9.5	9.5	23
Turbine	Electric energy production (MW)	0	3.8	0	2.7	0	2.1	0	0.2	1.6

A1 = Integrated process without electric energy production;

A2 = Integrated process with electric energy production when heat is still available after drying purpose;

B = Process without drying

6.2.5 Conclusions

Sludge is basically a poor material with a calorific value of 2,500 or 3,300 kJ/kg wet weight, for mixed or primary sludge at their typical cake concentration after dewatering (20 and 30 %, respectively). Incineration, which is practically the unique option for sludge disposal for large plants, has therefore to be carried out with the primary objective to reduce or better eliminate auxiliary fuel. At the same time, optimisation of plant design must be addressed to minimize the unit size. The proposed integrated process, including a drying stage before incineration to concentrate sludge up to a level allowing autogenous combustion, can attain both the goals. This study evidenced that, when primary sludge is separated from secondary one, autogenous incineration of primary sludge is possible in most of the cases (for input cake concentration $\geq 30\%$). In these operating conditions, in fact, the heat recoverable from the exhaust gas is sufficient to dry the sludge from the input concentration to the minimum one (55-60%) assuring autogenous combustion. Incineration of mixed sludge (no sludge separation) is instead more difficult because typical input concentrations are lower and therefore auxiliary fuel is needed in the furnace.

It is worth to note that, when input cake concentration is very high, the calorific value of the sludge is exuberant with respect to drying requirement and therefore extra steam can be recovered in the boiler for electric energy production. Unfortunately, such a possibility does not appear practically convenient because in the most optimistic case (primary sludge at 40 % input concentration) only 214 kW can be produced for a plant of 500.000 inhabitants (3.75 kWh/person/year).

Finally, it is to remark that an incineration process without drying is never autogenous and methane consumption may be often prohibitive (up to 1.62 Nm³/kg dry solids for mixed sludge at 15% input concentration). Boiler, furnace and exhaust gas treatment units are 2-3 times larger than those required for an integrated process. In this case the huge amount of exhaust gas produced, due to the intensive use of fuel in the furnace, certainly makes convenient electric energy recovery, which was estimated at a maximum value of 66.7 kWh/person/year for mixed sludge at input cake concentration of 15%. This energy recovery derives from the intensive use of fuel and cannot be certainly linked with recovery from the organic matter content of sludge.

6.3 Fate of phosphorus and heavy metals during sludge inertisation methods

Phosphorus content in the stabilized sludge is in the range of 18-40 g/kg TS (Siegrist et al., 1989), which represents 40-95% of the total phosphorus entering the WWTP. Phosphorus recovery from wastewater and sludge, instead of simply removal, incineration and final disposal was recognized as a necessity for the future wastewater and sludge treatment technologies, since easy accessible phosphorus resources will be depleted within the next 80 years (Herter et al., 2001). Phosphorus content in the domestic sewage sludge is 5 times higher compared to the content in the household rubbish. Therefore, sludge mono-incineration is recommended as an additional measure, in order to separately store the ash with the high phosphorus content and low heavy metal concentration, which will reduce the costs of the recovery.

All processes for recovery of phosphorus, either from sewage sludge or from the sewage sludge ash, consist of a chemical treatment (alone or combined with the thermal treatment), so that phosphorus is transferred into the liquid phase together with other pollutants (mainly heavy metals), followed by the selective phosphorus precipitation. The processes for phosphorus recovery from the sludge ash include the following:

The BioCon Process includes ion exchangers for the phosphorus recovery (Østergaard, 2000) from the sulphuric acid solution.

The SEPHOS-Process includes sludge treatment with sulphuric acid. The separation of phosphorus from heavy metals is achieved by stepwise pH increase with caustic soda (Schaum et al., 2004).

The Aqua Reci Process consists of the super critical water oxidation (SCWO) process followed by the separation of the phosphorus from the inorganic sludge which leaves the reactor, by the addition of base (Svanström et al., 2004). Stark et al., (2006) have shown that phosphorus could be recovered either by usage of acid or base. Acid leaching will release more phosphorus but will be more contaminated by heavy metals compared to the phosphorus obtained by the base leaching. However, acid leaching opens possibilities for the metal recovery as well, as shown by Stendahl et al., (2004) who recovered Fe and Al together with phosphorus. They also reported that 0.33 t H₂SO₄ and 0.1 t MgO is needed for treatment of the inorganic residue obtained after treatment of 1t TS of sludge. For 1 t DS the process will deliver 0.1 t of iron phosphate, 0.1 t of Alunite (KAl₃(SO₄)₂(OH)₆) and 0.3 kg heavy metals, which together with recovered energy and savings due to the sludge volume reduction should compensate the total costs of 248 €/t TS needed for the sludge treatment by the Aqua Reci process.

The Rotary Furnace Process is based on the thermal treatment of the sludge ash in the rotary furnace with an addition of KCl or MgCl₂, in order to improve the heavy metals evaporation and to produce the clean residue which could be used as a fertilizer (Kley et al., 2004). A phenomenon of increased heavy metal evaporation, on the example of domestic waste incineration by building metal chlorides, has already been noticed by some authors. Greenberg et al. reported that chloride concentration in the urban waste combustion fly ash is 14-20%, which might be the concentration high enough to enable building of heavy metal chlorides in the gas stream during the combustion. The idea was further developed within the EU Project Susan (www.susan.bam.de/eng_home-project-objectives.htm).

The idea of using the solid residue obtained after sludge inertisation directly as a fertilizer was further developed within the EU project Neptune. One of the reasons for performing the *Rotary Furnace Process* as a separate process is the corrosion of the equipment if chlorides are added to the sludge before the incineration process. However, the materials used for the construction of the Pyrolysis reaction tube (section 4.2.1) can withstand the temperatures up to 1300°C and it could be possible to enhance the heavy metals evaporation during the process itself, by adding some source of chlorides, which will save energy needed for an additional ash treatment process. Another important issue is that parallel to the metal-

chlorides formation, heavy metals react with oxygen to form oxides, which will keep them in the solid residue and not separate from the phosphorus. Since Pyrolysis is performed without any oxygen addition, the metal chlorides formation is enhanced and oxides formation can be avoided.

Sludge inertisation processes, described in the chapter 6.1, were investigated for the heavy metals and phosphorus distribution as well as for the leaching properties (SCWO was not included in the research since a lot of literature data regarding phosphorus recovery are available). According to Liu et al., 2003, thermal treatment process either incorporates heavy metals in solid residue due to the built up of aluminum-sodium-silicate matrix, or transforms them to a gas phase by evaporation. However, it is very hard to predict the distribution of heavy metals among solid and gas phase during the high temperature treatment, since there is a number of factors which have influence on the thermal process; process temperature, treatment time, physical and chemical properties of the metal species and the residue.

The content of the heavy metals and phosphorus in the solid residues, obtained after different sludge inertisation methods, as well as the maximum values allowed for the fertilizers in some European countries (Adam et al., 2007), is presented in Figure 6.10.

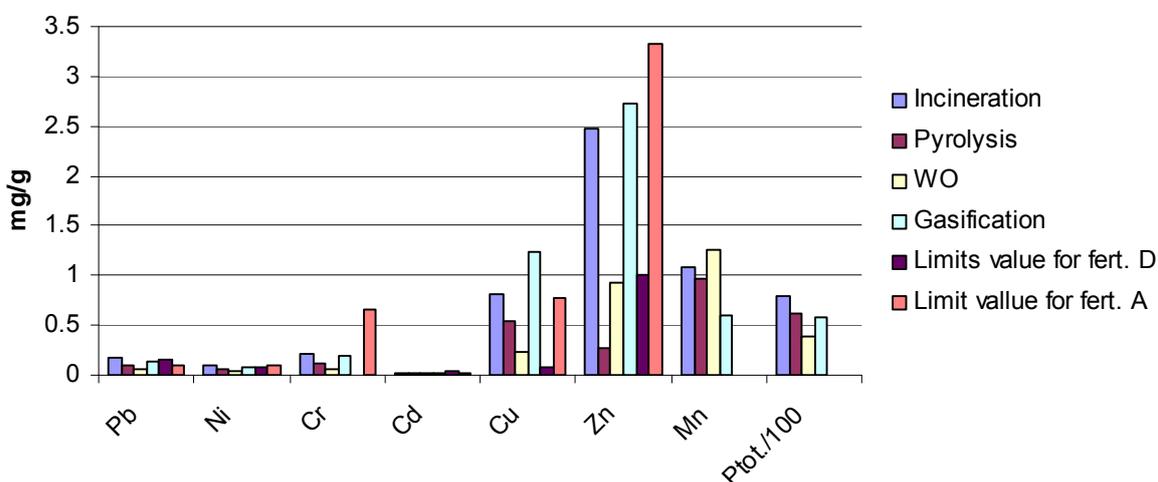


Figure 6.10 Heavy metals content in the solid residues of different sludge inertisation methods (total solids mass reduction for Incineration, Pyrolysis, WO and gasification are 95%, 80%, 25% and 50% respectively; treated digested sludge was from different WW treatment plants for all inertisation methods)

Content of the majority of the metals is below the fertilizer limits for almost all of the sludge inertization methods included in this research, without any enhancement of heavy metals evaporation. The stability of the metals was tested by leaching test performed by placing 1g of sample in 20 mL of water and constant shaking during the 5 days period. Results of the experiment are given in the Figure 6.11.

When the amount of solids, which leave the reactor is taken into account, the results shown in Figure 6.12 are obtained (mg of heavy metals and phosphorus leached per 1 g of TS treated with the specific process).

The higher values obtained for the WO as well as the big improvement for incineration are due to the TS reduction of 50% and 95% respectively.

Phosphorus bioavailability of the recycled phosphorus was tested by dissolving the residue in 2% citric acid (1 g of material in 20 mL 2% citric acid during the 2 h period). The aim of this experiments was to show if phosphorus present in the samples could be used by plant as a fertilizer.

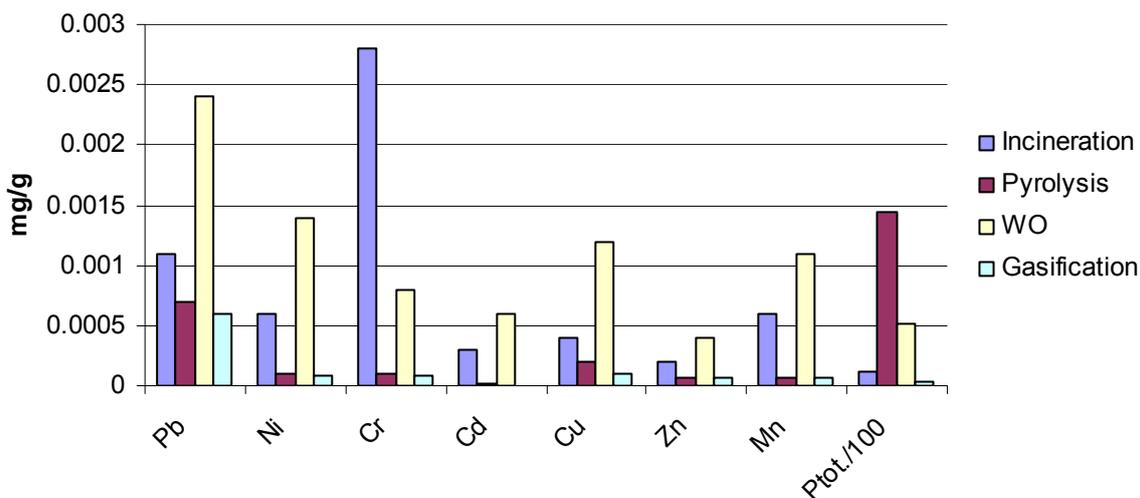


Figure 6.11 Heavy metals leached from the solid residues of different sludge inertisation methods, calculated for 1g of solid residue (1 g of material in 20 mL of water, 5 d shaking)

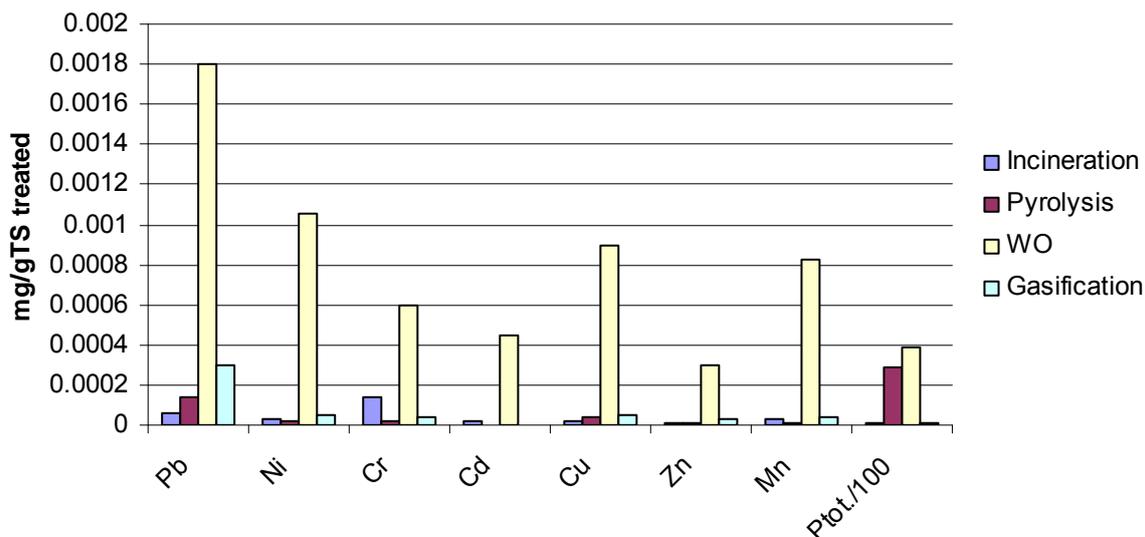


Figure 6.12 Heavy metals leached from the solid residues after different sludge inertisation methods (1 g of material in 20 mL of water, 5 d shaking); calculated per 1g of TS which enter the process

Table 6.12 indicates the great advantage of all novel sludge inertisation technologies when compared to the incineration in terms of phosphorus reuse. Life Cycle Assessment (LCA) studies, also carried out within the EU project Neptune, will show the overall impact of all novel technologies presented here compared to the nowadays widely applied incineration.

Table 6.12 Phosphorus bioavailability from the solid residue obtained after different sludge inertisation methods (1 g of material in 20 mL of 3% citric acid during 2 h time)

	<i>Ptot. init.</i> (mg/g)	<i>Percentage leached</i>
Incineration ash	58-90	0.07%-0.12%
Wet Oxidation solid residue	81.1	8.90%
Pyrolysis (TS80%, 1200°C, 10min)	60.58	9.92%
Gasification in Balingen	58.56	16.48%

6.4 Conclusions

The different inertisation processes described in the Chapter 6 are commercially developed at different level. The incineration process by fluidised bed furnace is applied in several full-scale plants in Europe, in the States and in the Far East, including Japan. Fluidised bed incineration, both by bubbling and circulating furnaces, is at present the most used sludge disposal technology in the world. In spite of the bad reputation of municipal waste incineration, sludge incineration appears to have much lower emissions especially if it is coupled with indirect drying thus performing an integrating process with internal thermal recovery. In fact the steam which can be produced in a recovery boiler downstream the fluidised bed furnace using the sensible heat of the exhaust gas leaving the furnace at approximately 850°C is generally overabundant with respect to the steam required for sludge drying to increase the solid concentration to the minimum target value required for self-sustaining combustion. This mode of operation allows to minimize the exhaust gas production, which for a quite big plant serving 500.000 p.e. is lower than 7.000 Nm³/h (< 8 Nm³/kg dry solids treated by the furnace). Therefore, such a plant might be therefore assimilated to a pilot plant rather than to a full-scale plant.

Moreover, it is worth mentioning that chlorine concentration of sewage sludge is so low, unless sludge is dewatered using FeCl₃ as conditioner, that formation of PCDD/F and other chlorinated toxic compounds is quite unlikely. Generally, the heat recovery in the boiler can be stopped when exhaust gas reaches a temperature of 350-400°C that is sufficient to guarantee the steam production required for sludge drying. This option is an intrinsic security to avoid any formation of PCDD/F for the de-novo synthesis.

Among the other inertisation processes presented in this report, currently wet air oxidation seems the technology with the major full-scale applications. The process is carried out in liquid phase by injecting pure oxygen into a reactor where the temperature increases up to 250-300 °C and the pressure correspondingly to 6-10 MPa. Typical residence time is 0.5-1.0 h. The advantage of this process is that the sludge has not to be previously dried considering that it is conducted in liquid phase. The problems are generally connected with the sludge-sludge heat exchanger which is used to recover the heat from treated sludge. It generally experienced clogging problem and performance reduction due to deposits and incrustations. These problems can be overcome by using live steam for sludge heating avoiding the use of sludge-sludge heat exchanger. Obviously, this type of process entails higher energy consumption. The degree of mineralization is not completed (25% of organic substance not completely oxidized still remains at the end of the process) but in spite of this the organic content of treated sludge might be very low (< 3%). This can be explained by the great proportion of the organic matter that is solubilized and has to be recycled with liquid side-stream (9.25 m³/t dry solid) to the top of the plant. Literature data show that consumption of electric energy and pure oxygen can be accounted in about 350 kWh/t dry solid and 875 kg pure O₂/t dry solid, respectively. Production of effluent gas to be vented to the atmosphere is under 1 Nm³/kg dry solid which is really negligible, only 10% of that from incineration.

Supercritical wet air oxidation is similar to the above process but in this case it is conducted above the critical point of water (374 °C and 22 MPa). Consumption of oxygen and electric

energy are similar to those of wet oxidation, but in the supercritical conditions a complete mineralization of organic matter occurs in less than 1 minute. A big advantage of such process is that heavy metals are transformed into insoluble oxides. Therefore the residue appears practically inert.

Sludge pyrolysis at high temperature ($> 1,000^{\circ}\text{C}$) seems to be a promising technology which can reduce considerably the production of effluent gas, in comparison with both conventional incineration and wet air oxidation. The process carried out in total absence of oxygen takes to the production of a syngas, constituted by 85% of CO and H_2 , to be used for energy production. Currently, very few plants are in operation very few plants most of them on pilot scale: therefore this technology still has to be improved. One of this, with a capacity of 25 t/d of sludge at concentration of 70-90% solids (7,000 t/year), was in operation for about 3 years in two locations of Germany. Electric energy consumption was about 100 kWh/t dry solid and therefore less than 1/3 of that of wet air oxidation. Sludge was completely transformed into inert material (250 kg/t dry solid). Investment cost for such a plant were estimated to about 1,800 €/t/year of dry solid to be treated) i.e. 16-20 million € for a plant serving 500,000 p.e. The sludge has to be previously dried and this cost is not included in the above data. However, the required heat can be balanced by using off-heat from the process.

Sludge gasification is generally carried out at the same temperature as incineration (850°C) or even higher. Gasification is an incomplete combustion of the organics in order to breakdown the molecules into a syngas by carefully controlling of the amount of oxygen present. The core of gasification process is that the oxygen (about $\frac{1}{3}$ of the stoichiometric value) reacts with carbon to produce CO_2 which further reacts with un-combusted C to give production of CO. Hydrogen in the organic matter is converted to H_2 gas instead to H_2O as in incineration. It is well known that gasification of coal and char coal was used during the second world war to produce the so-called town gas, i.e. the mixture of CO + H_2 . On a pilot plant treating 170 kg/h of sludge the following data were obtained: electric energy consumption 350 kWh/t dry solid, air consumption 0.9 Nm^3/kg dry solid, exhaust gas production 1.8 Nm^3/kg dry solid.

One of the advantages of gasification and pyrolysis is that they offer more scope for recovering products from waste than incineration. When waste is burnt in an incinerator only energy can be produced by means of a steam turbine. Pyrolysis and gasification can be used in conjunction with the gas engines, gas turbines or coupled gas/steam turbines (integrated gasification combined cycle, IGCC) in order to obtain higher conversion efficiency. Moreover the syngas could not only be used as a fuel but as a feedstock (secondary raw materials) for the petrochemical industry as well as for other applications provided that it is purified.

Other advantages of wet oxidation, pyrolysis and gasification are linked with the possibility to recover phosphorus from the ashes, due to its better solubility in comparison with the incineration ash.

7. STRATEGIES FOR A SUSTAINABLE AND SAFE SLUDGE MANAGEMENT

7.1 Introduction

In the near future it is expected that, at least for large WW treatment plants, the only possible sludge disposal system will be inertisation. The present European Directive 99/31 and the Decision of the European Commission of 19 December 2002, establishing criteria and procedures for the acceptance of waste at landfills, are certainly restricting this disposal route, especially in those countries where the implementation of the above criteria in national legislations were stringent. In fact, landfilling is in many countries a feasible disposal option only for inert and non recoverable wastes, considering that the limits of organic carbon of 4-5 % in wastes to be disposed of have been set for the acceptance of both non hazardous and hazardous wastes. Guidelines for agricultural utilisation will become progressively more stringent due to increasing health concerns about the widespread diffusion of pathogen and micropollutants in the environment (European Commission, 2000). In any case, agricultural utilisation involving large amounts of sludge to be spread on land does not seem feasible for the following reasons:

- ⇒ large volume of cake would require large extensions of fields and therefore long distances would have to be covered from WW treatment plants to the site of spreading;
- ⇒ a large storage volume would be required when sludge cannot be used (winter periods and when the fields are flooded);
- ⇒ influent WW of large cities are often polluted by non controlled industrial discharges that might hinder agricultural utilisation of resulting sludge.

A more sustainable sewage sludge management could be attained through a separation of primary and secondary sludge before their treatment and disposal. It would thus be possible to maintain agricultural utilisation for the biological sludge (secondary) and to convert to inert material by different inertization processes only the primary sludge (Mininni et al. 2004). In fact, characteristics of primary and secondary sludge are quite different in terms of quality (pollutants and nutrients) and in terms of suitability for thickening, digestion and dewatering. Secondary sludge is expected to be less polluted than primary sludge, and should be segregated and treated separately from primary sludge to increase chances of secondary sludge utilisation in agriculture. Primary sludge can be much better thickened, digested and mechanically dewatered than mixed primary and secondary sludge (Kopp and Dichtl, 2001). Therefore, primary sludge can be treated more efficiently, thus allowing energy recovery and the production of a final cake more suitable for inertization processes.

A sampling campaign carried out in the Neptune project specifically designed to assess the different quality of primary and secondary sludge has highlighted that enrichment factors of extractable organic halogens (EOX), total hydrocarbons and methyl blue active substances (MBAS) in primary sludge with respect to secondary one increase in the order hydrocarbons, EOX, MBAS. Extensive data collected in two German plants showed, however, that there is not a constant enrichment of contaminants in primary sludge. This effect was confirmed for TCPP and TBEP (organophosphate contaminants), DBP and BBzP (Phthalates) and Bisphenol A. For the other contaminants it is not possible to assess a predominant enrichment in one of the two sludge types but only for tin organics a slight enrichment in secondary sludge is observed. The presence of nitrogen and phosphorus in secondary sludge was detected to be 1.8 – 2.0 times higher than that in primary sludge.

These findings demonstrate that agricultural use of secondary sludge according to the phosphorus requirement by crops, which is the limiting factor among the nutrients, would take lower amount of contaminants to land with respect to mixed sludge.

On the other hand, separate treatment of secondary sludge can be impaired by its poor characteristics in terms of biodegradability and thickenability. It requires pre-treatments aiming at increasing digestability (biogas production) and stabilisation. Literature data suggest that pre-treatments may also enhance removal of recalcitrant organic contaminants (Tiehm and Neis, 2005, Tiehm et al., 2000).

The sludge separation strategy may also give flexibility to sludge management, decreasing dependency on conventional disposal options (as required in the Directive 2008/98) as more sludge of high quality can be used in agriculture while the remaining primary sludge can be treated by inertization processes. The challenge in the coming years will be, in fact, assuring the greatest flexibility in sludge management, maximizing recovery of valuable products and energy sources and reducing disposal only to inert materials which cannot be recovered any more.

7.2 The innovative sludge management

The innovative sludge management policy in the WW treatment plants is based on the following concepts:

- ⇒ increased pollutant removal (metals, organics, pathogens) in primary sedimentation eventually enhanced by coagulation, to improve secondary sludge quality;
- ⇒ digestion of primary sludge to be finally treated by inertization processes;
- ⇒ sonication or thermal pre-treatment like Cambi as pre-treatment of secondary sludge before anaerobic digestion;
- ⇒ short aerobic thermophilic treatment to get sanitized secondary sludge in small plants.

The effort to improve the performance of the anaerobic digestion involves mainly secondary sludge, containing up to 70% of bacteria and the hydrolysis of these bacteria is the limiting step of the whole anaerobic process. Sludge disintegration treatments attacks bacterial cells wall and the bacterial eso-enzymes are released into solution and therefore are able to biocatalyse hydrolytic reactions. Sludge disintegration can therefore accelerate the breakdown of organic material into smaller, readily biodegradable fractions. The subsequent increase in the amount of biodegradable material improves bacterial kinetics resulting in lower sludge quantities and, in the case of anaerobic digestion, increased biogas production. The technologies already in use for sludge disintegration like ultrasounds, by means of shear forces, have proved that energy input can be accounted for 1-2 kWh/kg dry solids (Müller, 2001). But additional electrical energy gained is mostly significantly lower than energy input.

In this context, IRSA has carried out anaerobic digestion tests, in batch and semi-continuous mode, with sonicated secondary sludge to investigate the effect of pre-treatment on digestion performances and on particle surface charge, affecting dewaterability. It is worth mentioning that ultrasound pre-treatment (specific energy 5,000 kJ/kg TS i.e. about 1.4 kWh/kg TS) accelerates considerably the reaction rate (k values are doubled) and the biogas production was always higher for sonicated sludge (up to 30% more biogas).

Thermal pre-treatment by Cambi process may give even better results as a consequence of the more drastic conditions of this disintegration process (temperature of 160-170°C, pressure of 6-9 bar, residence time of more than 20 minutes). The Cambi process combined with anaerobic digestion allows of increased VS removal and biogas production of 40-50% in comparison to sludge conventional anaerobic digestion without disintegration.

7.3.1.1 Sludge production

Wastewater flow rate: 250 L/(per × d);
 COD concentration: 480 mg/L (120 g/(per × d));
 BOD₅ concentration: 240 mg/L (60 g/(per × d));
 N concentration: 48 mg/L (12 g/(per × d));
 P concentration: 8 mg/L (2 g/(per × d));
 COD removal in primary sedimentation: 35%;
 SS removal in primary sedimentation: ~ 50%;
 SS concentration of primary sludge: 4%;
 VS concentration of primary sludge: 75% of SS;
 Production of secondary sludge according to Monod eq. with the following kinetic constants:
 Y 0.45, K_d 0.08 d⁻¹, θ_c 6 d;
 COD removal in secondary treatment: 90%;
 SS concentration in secondary sludge 1%;
 SS in the effluent 10 mg/L;
 Elemental composition of primary sludge (% of VS): C 54.41%, H 4.79%, O 36.27%, N 3.53%, S 1%; (% of SS) K 0.33%, P 0.7%.
 Elemental composition of secondary sludge (% of VS): C 54.55%, H 6.36%, O 29.09%, N 10%; (% of SS) K 0.5%, P 3.06%.
 Density of dry solids=1,500 kg/m³;
 Density of water=1,000 kg/m³.

7.3.1.2 Sludge thickening

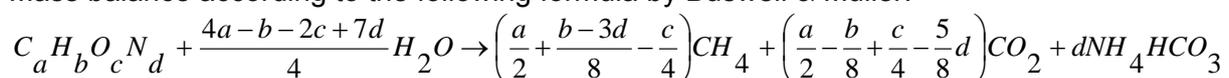
$SS_{output} \text{ (weight fraction)} = (3.1 - 30 SS_{input}) SS_{input}$, but not higher than 7%; SS_{input} (weight fraction);
 SS concentration of supernatant: 3,000 mg/L (from primary sludge thickening), 1,500 mg/L from secondary sludge thickening, 2,000 mg/L (from mixed sludge thickening);
 $SS_{output} \text{ (weight fraction)} = 0.045 + 2.045 SS_{input} \text{ (weight fraction)}$ (dynamic thickening of secondary sludge).

7.3.1.3 Sludge digestion

$$\text{Volatile solid removal (weight fraction)} = \frac{k_d \theta}{1 + k_d \theta}$$

where k_d = 0.06 d⁻¹ for primary sludge, 0.04 for secondary sludge, 0.05 for mixed sludge, 0.048 for secondary sludge after ultrasound disintegration, 0.064 for secondary sludge after thermal disintegration by CAMBI process;

Mass balance according to the following formula by Buswell & Müller:



Molar fraction of water in biogas=5.504%;

H₂S concentration in biogas produced from primary and mixed sludge digestion=600 ppm (in volume);

P solubilisation 70%;

Decrease of temperature of digester for heat losses= 1 °F/24 h;

Digestion time= 15 d;

Sludge temperature=20°C;

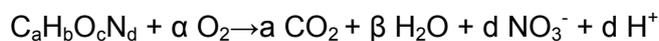
Digester temperature=37°C.

7.3.1.4 Short aerobic thermophilic stabilization

$$\frac{VS_{out}}{VS_{in}} = \frac{1}{(1 + K_{20^{\circ}C} \gamma^{(T-20)} \theta)^n}$$

Where $K_{20^{\circ}C}=0.025 \text{ d}^{-1}$, $\gamma=1.03$, $\theta=5 \text{ d}$, $n=\text{number of reactors in series}=1$, $T=45^{\circ}\text{C}$.

Mass balance according to the following formula:



$$\text{where } \alpha = \frac{4a + b - 2c + 5d}{4}, \quad \beta = \frac{b - d}{2}$$

7.3.1.5 Dewatering by centrifuge

$SS_{out} = 0.087 + 0.00205 SS_{in}$ where SS_{out} and SS_{in} (weight fraction);

SS concentration of centrate=3,000 mg/L;

Polyelectrolyte dosage=5 g/kg SS;

Polyelectrolyte to sludge particles=90% of input poly;

Polyelectrolyte solution concentration=3 g/L;

7.3.1.6 On-site indirect drying + incineration (integrated process)

The process is performed according to the flow sheet shown in Figure 6.5 (pag. 67).

Heat loss of fluidised bed furnace (FBF): 5% of total input enthalpy;

Heat loss of boiler: 7% of input heat;

Heat loss of dryer: 7% of input heat;

Heat loss of condenser: 5% of input heat;

Excess of air for methane combustion: 20%;

Operating temperature of FBF: 850°C;

Minimum oxygen concentration in exhaust gas from FBF: 6% by volume;

SS concentration of dried sludge: 90%;

Minimum solid concentration to the dryer to avoid clogging: 60%;

Output temperature of exhaust gas from dryer: 100°C;

Output temperature of exhaust gas from condenser: 50°C;

Water temperature to condenser: 10°C;

Input fresh air to indirect dryer: 1.5 kg/kg water to be evaporated;

Conversion of organic N to NO: 5% of input N in VS;

Enthalpy from steam condensation in the indirect dryer: 474 kcal/kg.

7.3.1.7 On-site direct drying

Concentration of water in the exhaust gas from drying (kg/kg)=0.1 of dry gas (about 14% by volume).

7.3.2 Results

Tables 7.1 and 7.2 show the major and minor components, respectively, during sludge processing for the flow sheet shown in Figure 7.1 without sludge separation. Total mass of sludge is reduced from 16.24 (fresh mixed sludge) to 0.724 kg/m³ WW (dewatered sludge) and to 0.1795 kg/m³ WW (dried sludge), respectively -96% and -99%. Correspondingly, COD and VS are reduced of 52% and SS of 43%. Figure 7.3 shows the progressive reduction of major components.

Table 7.1 Mass of major components (kg/m³ WW, 0.25 m³/per × d) in the currents of the flow sheet without sludge separation (see Figure 7.1)

	COD	SS	VSS	Water	Total mass	SS (%)	VS (% SS)
A Mixed sludge before thickening	0,2962	0,2815	0,2045	15,9572	16,2387	1,73%	72,64%
B Thickened sludge	0,2743	0,2607	0,1893	5,5679	5,8285	4,47%	72,64%
D Mixed digested sludge	0,156	0,1763	0,1081	5,5215	5,7296	3,08%	61,33%
E Dewatered mixed sludge	0,1433	0,1614	0,099	0,5578	0,7242	22,31%	61,33%
L Dried sludge from on-site drying	0,1433	0,1616	0,099	0,018	0,1795	90,00%	61,27%
C Supernatant from thickening	0,0219	0,0208	0,0151	10,3963	10,4101	0,20%	72,64%
F Centrate from dewatering	0,0127	0,0149	0,0091	4,9695	5,0121	0,30%	61,33%

Table 7.2 Mass of minor components (g/m³ WW) in the currents of the flow sheet without sludge separation (see Figure 7.1)

	N with particulate	N-NH ₄	Tot. P	Ortho P	S	K
A Mixed sludge before thickening	12,737	0	4,859	0	1,191	1,138
B Thickened sludge	11,795	0	4,5	0	1,103	1,054
D Mixed digested sludge	6,71	5,085	4,5	3,15	1,036	1,054
E Dewatered mixed sludge	2,168	0,679	1,692	0,421	0,976	0,992
L Dried sludge from on-site drying	2,168	0,679	1,692	0,421	0,976	0,992
C Supernatant from thickening	0,942	0	0,359	0	0,088	0,084
F Centrate from dewatering	0,751	4,405	2,807	2,729	0,06	0,061

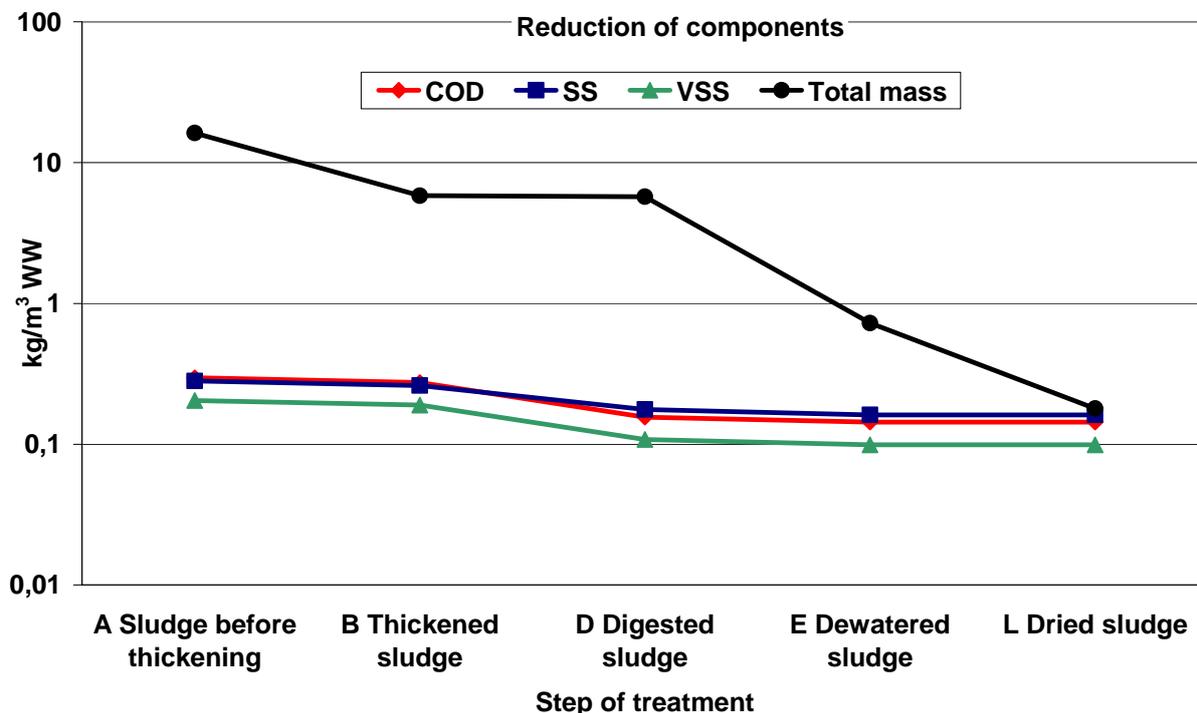


Figure 7.3 Reduction of major components during treatment of mixed sludge

Proportion of COD lost in gravity thickening and dewatering, to be recycled to the top of the plant by the side streams, is accounted in 11.7% of the corresponding COD of fresh mixed sludge and in 7.2% of the influent COD (Table 7.5).

Tables 7.3 and 7.4 show the major and minor components, respectively, during sludge processing for the flow sheets shown in Figure 7.2 with sludge separation. Total mass of primary sludge decreases from 3.97 (fresh primary sludge) to 0.363 kg/m³ WW (dewatered sludge) and to 0.1028 kg/m³ WW (dried sludge), i.e. -91% and -97%, respectively. Correspondingly, COD and VS are reduced of 52% and SS of 42%.

Total mass of secondary sludge decreases from 12.27 to 1.54 kg/m³ WW (dynamic thickened sludge) and to 0.25-0.26 kg/m³ WW after thermal or mechanical disintegration, anaerobic digestion and dewatering and to 0.30 kg/m³ WW after short aerobic thermophilic treatment and dewatering, i.e. up to 98%. It is interesting to note that total mass of secondary sludge is more than 3 times higher than that of primary sludge while the total dry solid of secondary sludge is only 75-80% of that of primary sludge.

Proportion of COD lost in primary and secondary sludge processing (gravity or dynamic thickening and dewatering), to be recycled to the top of the plant by the side streams is accounted in about 12.7-12.9% of the corresponding COD of fresh primary + secondary sludge and in 7.8-8.0% of the influent COD.

Figure 7.4 shows the progressive reduction of major components during primary and secondary sludge processing.

Table 7.3 Mass of major components (kg/m³ WW) in the currents of the flow sheet with sludge separation (see Figure 7.2)

	COD	SS	VS	Water	Total mass	SS (%)	VS (% SS)
A Primary sludge before thickening	0,1680	0,1588	0,1191	3,8109	3,9697	4,00%	75,00%
B Thickened primary sludge	0,1624	0,1535	0,1151	2,0388	2,1922	7,00%	75,00%
D Primary digested sludge	0,0847	0,0981	0,0605	2,0101	2,1199	4,63%	61,67%
F Dewatered primary sludge	0,0800	0,0924	0,0570	0,2686	0,3630	25,49%	61,67%
M Dried primary sludge	0,0800	0,0925	0,0570	0,0103	0,1028	90,00%	61,60%
P Secondary sludge before thickening	0,1282	0,1227	0,0854	12,1463	12,2690	1,00%	69,59%
R Dynamic thickened secondary sludge	0,1057	0,1008	0,0702	1,4385	1,5398	6,55%	69,59%
S Secondary sludge after short aerobic thermophilic treatment	0,0839	0,0863	0,0556	1,4464	1,5392	5,61%	64,46%
T Secondary sludge after US disintegration and AD	0,0615	0,0694	0,0408	1,4203	1,5085	4,60%	58,89%
V Secondary sludge after thermal disintegration and anaerobic digestion	0,0540	0,0644	0,0359	1,5584	1,6443	3,91%	55,70%
Y Dewatered secondary sludge after US disintegration and AD	0,0583	0,0655	0,0386	0,1896	0,2580	25,43%	58,89%
X Dewatered secondary sludge after thermophilic aerobic treatment	0,0803	0,0824	0,0531	0,2165	0,3001	27,49%	64,46%
Z Dewatered secondary sludge after thermal disintegration and anaerobic digestion	0,0507	0,0602	0,0336	0,1876	0,2510	24,02%	55,70%
C Supernatant from primary sludge thickening	0,0056	0,0053	0,0040	1,7721	1,7775	0,30%	75,00%
Q Centrate from dynamic thickening of secondary sludge	0,0229	0,0219	0,0152	10,9117	10,9336	0,20%	69,59%
H Centrate from primary sludge dewatering	0,0057	0,0057	0,0035	1,9045	1,9205	0,30%	61,67%
AA Centrate from dewatering of secondary sludge after thermophilic aerobic treatment	0,0041	0,0042	0,0027	1,3877	1,3085	0,30%	64,46%
AB Centrate from dewatering of secondary sludge after ultrasound disintegration and anaerobic digestion	0,0034	0,0038	0,0023	1,2822	1,3024	0,30%	58,89%
AC Centrate from dewatering of secondary sludge after thermal disintegration and anaerobic digestion	0,0035	0,0041	0,0023	1,3766	1,3995	0,30%	55,70%

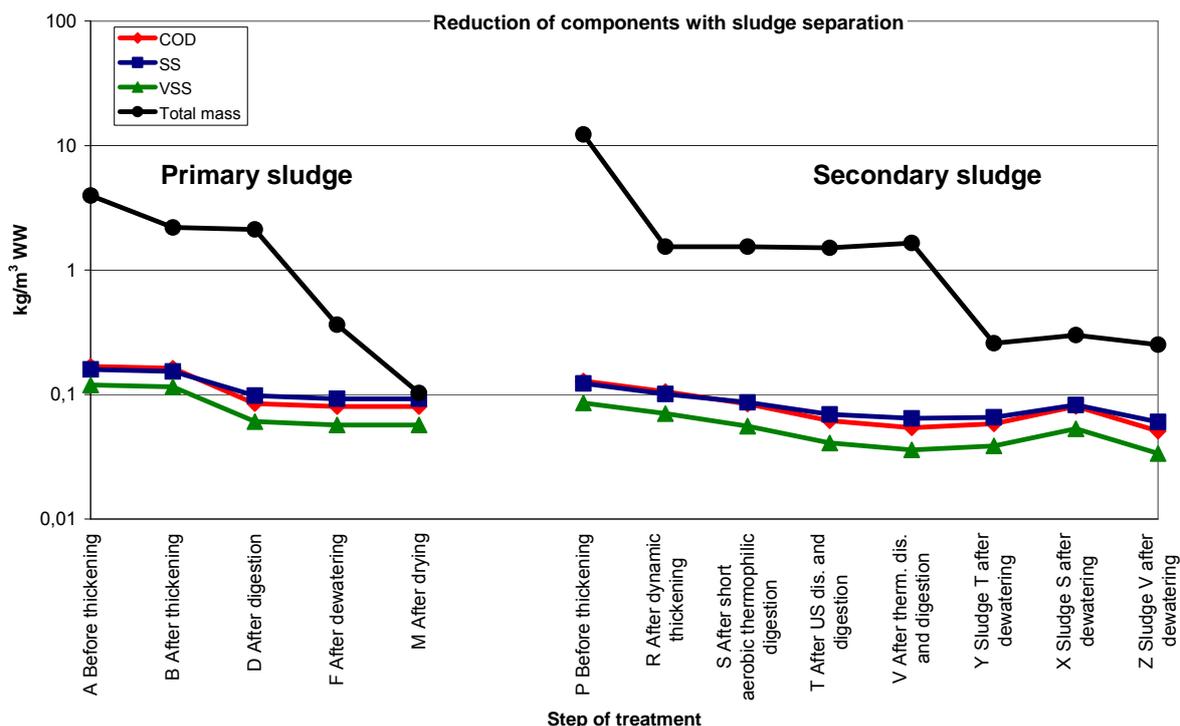


Figure 7.4 Reduction of components during treatment of primary and secondary sludge

Table 7.4 Mass of minor components (g/m³ WW) in the currents of the flow sheet with sludge separation (see Figure 7.2)

	N with particulate	N-NH ₄	Total P	Ortho P	S	K
A Primary sludge before thickening	4,200	0,000	1,109	0,000	1,191	1,109
B Thickened primary sludge	4,059	0,000	1,072	0,000	1,151	1,072
D Primary digested sludge	2,117	1,942	1,072	0,750	1,103	0,509
F Dewatered primary sludge	0,424	0,260	0,403	0,100	1,039	0,480
M Dried primary sludge	0,424	0,260	0,403	0,100	1,039	0,480
P Secondary sludge before thickening	8,537	0,000	3,750	0,000	0,000	0,611
R Dynamic thickened secondary sludge	7,016	0,000	3,081	0,000	0,000	0,502
S Secondary sludge after short aerobic thermophilic treatment	5,589	1,456 ¹	3,083	0,000	0,000	0,502
T Secondary sludge after US disintegration and AD	4,100	2,945	3,083	2,158	0,000	0,502
V Secondary sludge after thermal disintegration and anaerobic digestion	3,599	3,446	3,083	2,158	0,000	0,502
Y Dewatered secondary sludge after US disintegration and AD	1,484	0,394	1,159	0,288	0,000	0,473
X Dewatered secondary sludge after thermophilic aerobic treatment	4,399	0,195 ¹	2,903	0,000	0,000	0,473
Z Dewatered secondary sludge after thermal disintegration and anaerobic digestion	0,604	0,460	1,159	0,288	0,000	0,473
C Supernatant from primary sludge thickening	0,141	0,000	0,037	0,000	0,040	0,037
Q Centrate from dynamic thickening of secondary sludge	1,522	0,000	0,668	0,000	0,000	0,109
H Centrate from primary sludge dewatering	1,693	1,683	0,669	0,650	0,064	0,030

AA Centrate from dewatering of secondary sludge after thermophilic aerobic treatment	1,272	1,347 ¹	0,192	0,000	0,000	0,031
AB Centrate from dewatering of secondary sludge after ultrasound disintegration and anaerobic digestion	2,616	2,552	2,097	1,869	0,000	0,029
AC Centrate from dewatering of secondary sludge after thermal disintegration and anaerobic digestion	2,995	2,986	1,923	1,869	0,000	0,029

¹N-NO₃⁻

Total and net methane production, i.e. the methane production in excess with the respect to the requirement for sludge and digester heating, from anaerobic digestion is shown in Figure 7.5. It clearly appears that total net CH₄ production from primary and secondary sludge digestion (flow sheets with sludge separation) is higher than from mixed sludge digestion without separation. This is due to:

- the increased biogas production from secondary sludge due to the mechanical or thermal disintegration;
- the reduced biogas to be used for sludge heating and for balancing the heat loss of the digester due to the higher sludge concentration from secondary sludge dynamic thickening.

The net methane production after CAMBI thermal treatment of secondary sludge resulted about 24% higher than the corresponding production from secondary sludge disintegrated by ultrasound.

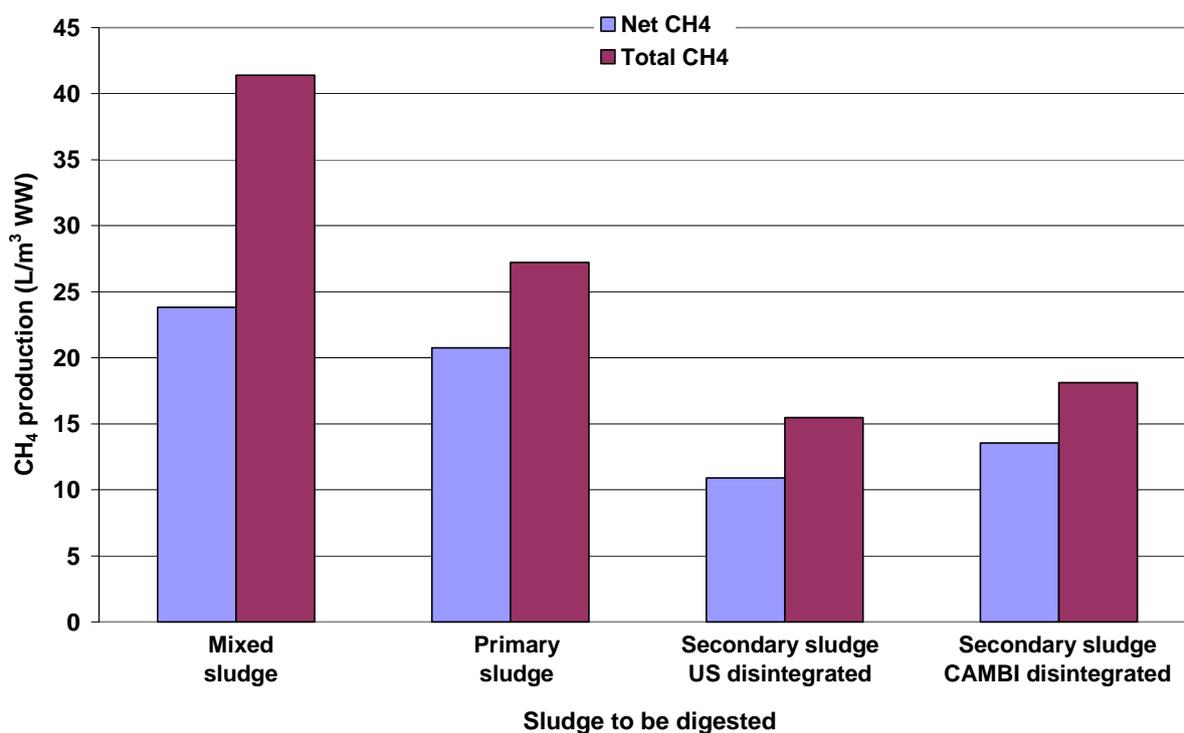


Figure 7.5 Net biogas production from anaerobic digestion

Table 7.5 shows the proportion of COD, SS, VS, N and P to be recycled to the top of the plant with sludge side-streams compared to the input load of sludge and to input load with WW.

Table 7.5 Load to be recycled to the top of the WW treatment plant with sludge sidestreams

With sludge separation	COD	SS	VSS	Tot. N	Tot. P
Load to be recycled with sludge sidestreams (% of input with raw sludge)	12,7-12,9%	13,1-13,2%	12,2-12,4%	36,3-49,9%	32,2-71,4%
Load to be recycled with sludge sidestreams (% of input with WW)	7,8-8,0%	11,5-11,6%	10,4-10,6%	10,5-14,4%	19,6-43,4%
Without sludge separation	COD	SS	VSS	Tot. N	Tot. P
Load to be recycled with sludge sidestreams (% of input with raw sludge)	11,7%	12,3%	16,9%	43,1%	65,2%
Load to be recycled with sludge sidestreams (% of input with WW)	7,2%	10,8%	14,4%	12,5%	39,6%

No significant differences of the flow sheets with or without sludge separation may be observed, the former option entailing a slight higher recycling with the exception of the option including short term thermophilic aerobic stabilization which allows of reduced recycling of nitrogen and phosphorus.

Figure 7.6 shows the production of off gas in thermal treatments of dewatered mixed and primary sludge (current E of Figure 7.1 and current F of Figure 7.2). From on-site incineration by the integrated process shown in Figure 6.5 (pag. 54) total production of off-gas is estimated to be 1.12 Nm³/m³ WW (mixed sludge) and 0.598 Nm³/m³ WW (primary sludge), i.e. respectively 5,800 and 3.100 Nm³/h for a plant serving 500.000 inhabitants. An incineration plant of municipal solid waste (MSW) serving the same population would produce instead at least 120.000 Nm³/h of exhaust gas. This means that incineration of sewage sludge is much less environmental problematic considering the much lower exhaust gas production, only 5% for mixed sludge and only 2.6% for primary sludge with respect to that from a MSW incineration plant serving the same community. Moreover, it should be observed that production of mutagenic compounds like PCDD/F during sludge incineration is not expected considering that the chlorine presence in sewage sludge is generally negligible.

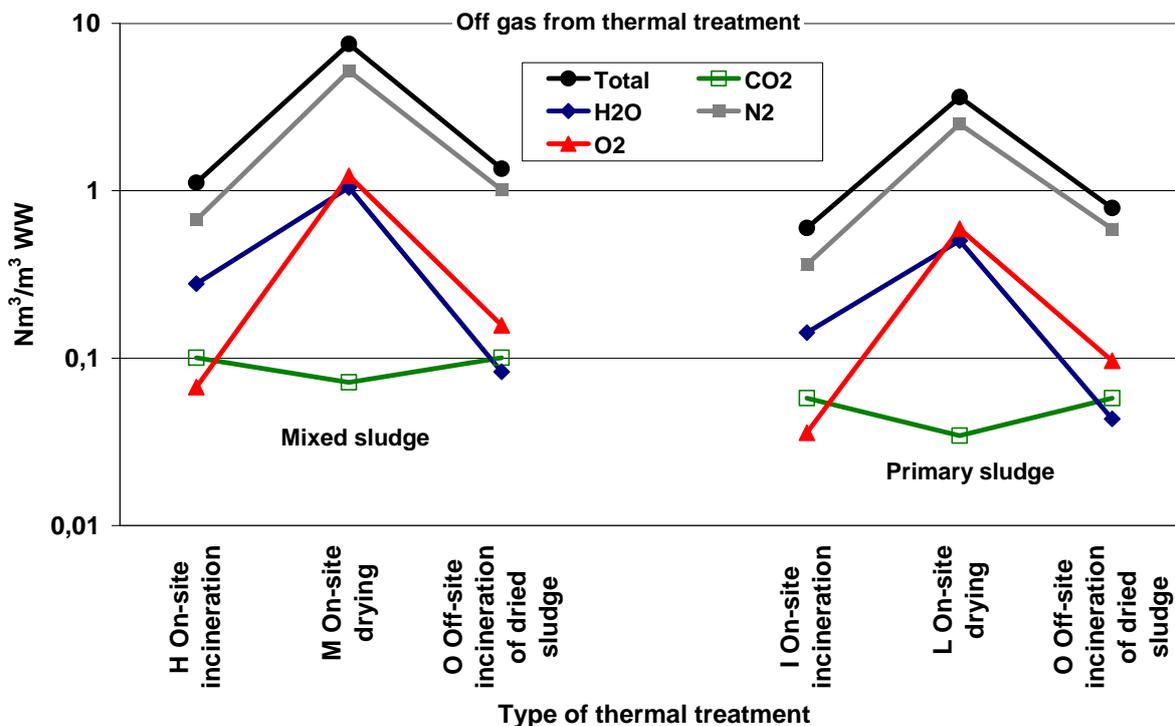


Figure 7.6 Production of off gas from thermal treatments

It is quite surprising that thermal drying by a direct contact dryer produces much more gaseous effluent (7.543 and 3.634 Nm³/m³ WW for mixed and primary sludge, respectively). This is due to the great dilution required by fresh air in order to keep the temperature of inlet gas to the dryer lower than 300 °C to avoid problems of combustion in the dryer and possible explosions due to the presence of fine particulates. Moreover the humidity of exit gas from dryer should be kept lower than 0.1 kg/kg of dry gas to guarantee that a sufficient gradient of water vapour is present in each section of dryer for performing the operation with not so large equipment. The subsequent incineration of dried sludge in an off-site plant would produce an additional exhaust gas of 1.353 (mixed sludge) and 0.789 Nm³/m³ WW (primary sludge). Total volume of exhaust gas from on-site drying and off-site incineration of dried sludge is therefore 8.9 (mixed sludge) and 4.42 Nm³/m³ WW (primary sludge), which means 46.300 and 23.000 Nm³/h for 500.000 persons, respectively (7-8 times the volume of exhaust gas from on-site drying and incineration).

It clearly appears that on-site drying and off-site incineration of dried sludge is not a convenient option also considering that a methane consumption of 71.7 (mixed sludge) and 34.4 L/m³ WW (primary sludge) is required for thermal drying (90 and 61.5%, respectively, with respect to methane production in sludge digestion). Therefore, in some cases the balance could hardly be reached, especially for the flow sheets without sludge separation.

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