

Combined Experiences of Thermal Hydrolysis and Anaerobic Digestion

Latest Thinking on Hydrolysis of Secondary Sludge Only

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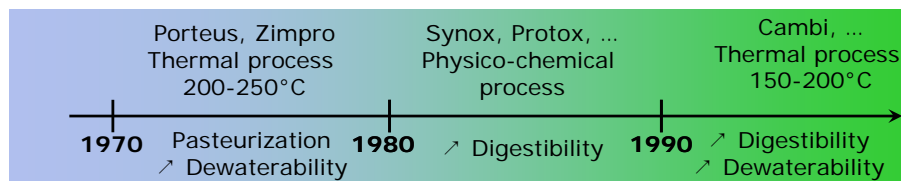
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INTRODUCTION

- As shown in the following historical review, the thermal treatment of sludge was improved in terms of process and goals.



- Regarding the limiting factor of anaerobic digestion process (hydrolysis), thermal hydrolysis process combined with anaerobic digestion is one of pertinent solutions available on the market. Cambi, a Norwegian Company has developed its own process based on the literature results and pilot plant studies. Since 1995, 20 plants have been built or are in construction (mainly in Europe).
- The optimum operating conditions found by Li and Noike (1992) and confirmed by Perez-Elvira (2006) are a temperature of 170° C during 30 and 60 minutes. In spite of the solubility increase, for temperatures higher than 170° C a reduction in biodegradability due to the formation of recalcitrant compounds is observed.



Typical Thermal Hydrolysis Plant

PERFORMANCES REVIEW AND RECENT STUDIES

An independent survey of a number of plants and lab scales was carried out by Degrémont, Suez Environnement, Valladolid University and Kläranlagen Beratung Kopp/PCS GmbH to check the main features of these plants as low digester volume and HRT, VS removal and high biogas yield, level of cake dewatering. For each site, Cambi process and digestion part were checked, sludge samples were taken and analysed by our laboratories.

1. VS removal and dewaterability

Plant results

- Significant improvement of VS removal for secondary digested sludge (42% compared to conventional 30%)
- Variable improvement of VS removal for mixed digested sludge (49-57% compared to conventional 45-50%).
- Significant improvement of dryness of secondary digested sludge (30% compared to reference dryness of 20%)

Visited Cambi sites: VS removal and dewatering technology, dryness results

Sludge quality	Site	Total VS removal	Technology	Dryness
Biological sludge	A	42%	Belt press	30%
	B	49%		
Mixed sludge	C	52%	Centrifuge	30%
	D	57.5%	Centrifuge	26%

Lab scale results

Sludge type influence

Disintegration factor and methane production increase are higher for secondary sludge than primary sludge and confirmed plant results.

Influence of the type of sludge on disintegration and methane production

Sludge	Disintegration factor	CH ₄ production increase
Primary	3.1	1.21
Biological	9.6	1.62

Biological sludge in admixture with unhydrolysed primary sludge compared to untreated mixed sludge

- Gas production increased by more than 25%
- Dewatering result increased from 22.7% DS to 30.8% DS

2. Return loads

The biodegradability of return loads (filtered fraction of digested sludge with 0.45µm), characterised by ultimate aerobic biodegradability tests are respectively:

- 68% for COD soluble
- 97% for TKN,
- 99% for N-NH₄⁺

The return loads are quite high, but in accordance with VS removal and solubilization ratio. Nevertheless, these loads are biodegradable and seem not to have big impact on the water treatment.

CONCLUSIONS

- Independent investigation of the vendors claims supports the data for the benefits claimed.
- The need for energy efficiency and the investment cost suggest that only secondary sludge thermal hydrolysis is a good way of getting maximum benefits.
- In this configuration, the expected benefits are at least 25% increase in digestion rate for short HRT digestion and an improvement of 8 points in dewatering.



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Abstract

The basic principles of batch thermal hydrolysis process (THP) are well known and have been put into full practice in 20 plants around the world. This paper reviews the historical development of the process and the latest thinking on the application of THP from a number of sources in Europe. An independent investigation of the vendors claims support the data for the benefits claimed to date. The need for energy efficiency suggests that only secondary sludge thermal hydrolysis is a good way of getting maximum benefits for minimum cost and energy demand. Furthermore the benefits can be obtained using a continuous THP that is more cost effective to operate. It is expected that there will be a number of plants in the future using continuous THP of secondary sludge mixed with unhydrolysed sludge. The research into this type of digestion and dewatering reviewed in the paper shows that benefits are expected to be at least 25% increase in digestion rate for short HRT digestion and an improvement of 8 points in dewatering. One full scale plant has been built in Germany where results are expected and others are being proposed.

Keywords: Anaerobic digestion, Biogas, Dewaterability, Heat treatment, Sludge, Thermal hydrolysis.

HISTORICAL DEVELOPMENT

In the first instance heat treatment was not seen as a method of pasteurisation or a way of improving anaerobic digestion but as a mean for improving dewaterability. A review of the literature shows that up to the late seventies this was the major emphasis. The major growth of heat treatment was during the sixties; temperatures were typically about 200°C – 250°C for the two main processes - Porteus and Zimpro. Many projects were shut down during the late sixties early seventies, mainly because of odour, high strength liquors and corrosion. Zimpro still operates in some projects at a lower temperature and under modified operating conditions to aid dewatering.

There was then a growing body of research starting in the late seventies to resurrect heat treatment at lower temperatures (150-200°C) to get the best compromise between dewaterability and digestibility. The researchers realised that the effect they were looking for was the optimum hydrolysis temperature. Most of this research has concluded that the ideal compromise temperature is about 170°C and that this is particularly effective for biological sludge such as activated sludge.

In the mid 80s, in response to the pending US 503 regulations and other national regulation in Europe, a growing number of technologies emerged based on hydrolysis using acid, alkaline, heat based and combinations. The idea was to have a one hit physico-chemical approach to produce a pasteurised product. None of these has been

successfully commercialised because they were expensive and did not make a good product – Synox and Protox are good examples of this. One process Cambi, has successfully combined the optimum thermal hydrolysis pre-treatment with anaerobic digestion.

Dewatering

It is well known that activated sludge is very difficult to dewater and has an adverse affect on dewatering when combined with primary sludge. A lot of work has been done on understanding the nature of water in sludge. It is generally assumed that there are different physical states of water. The aqueous phase is generally described as free water and bound water. The bound water needs a higher energy to be removed and some cannot be removed at all.

From a combination of size distribution analysis and electron microscopy, Jorand et al. (1995) have suggested a model of floc structure which is made up of three basic elements (Figure 1). The first level is composed of bacteria of average size $2.5 \mu\text{m}$. They are embedded in a gel like matrix of exopolymers, forming microcolonies of average size $13 \mu\text{m}$. The microcolonies aggregate together to form microflocs with an average size of $125 \mu\text{m}$. Snidaro et al showed that the microcolonies retained their integrity under 15 bar filtration and that microcolonies appear to be a waterproof structure. They concluded that these waterproof units within the sludge seem to be one of the main limiting factors in water removal efficiency. “Reaching higher dry solids content can only be done with thermal process or drying bedsor changing sludge structure.”

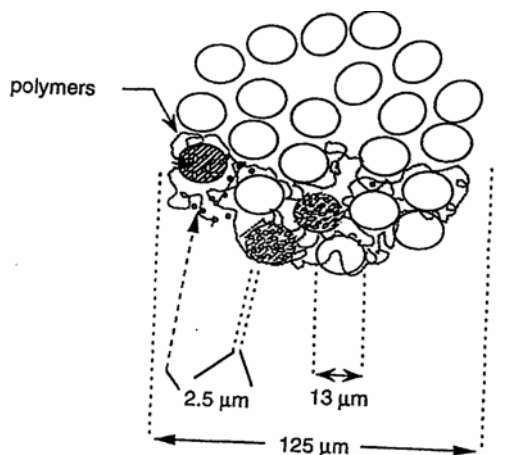


Figure 1: Microfloc model (Jorand et al., 1995)

First heat treatments

Porteous and Zimpro. The first Porteous process plants in the UK were at Halifax and Horsham in 1939. It was a method of heating sludge to batch cook the sludge at a minimum of 185°C , 30 minutes.

Raw sludge was forced by ram pump through a heat / heat exchanger and steam / heat exchanger into the reaction vessel and held for at least 30 minutes at about 200°C. From the reaction vessel the sludge was returned to the settlement tanks where the liquor was removed (**Error! Reference source not found.**). This process was developed into a continuous flow process and there were up to 30 installations in the late 60s. Most of these were operated to give optimum dewatering before incineration. Escalating energy costs coupled with operating problems led to the early closure of all of these plants throughout the seventies.

Zimpro was originally designed as a wet oxidation method in the US in 1954. The first Zimpro project in the UK was at Hockford STW, which took sludge from the nearby Central Veterinary labs. In this case destruction of organisms was seen as an advantage. The Zimpro method originally worked by high pressure wet oxidation of sludge solids at about 250°C and aimed to destroy up to 65% of COD. At this temperature the process became exothermic. However there were problems with odour, corrosion and liquor strength and all UK Zimpro plants were shut down. This process is still used industrially but Zimpro have modified the process for municipal sludge (LPO – low pressure oxidation). In this version temperatures are reduced to below 200°C, which produces very little oxidation and it is in reality a hydrolysis process. The added oxygen may give the product temporary stability but cannot stop the process of re-infection as there is no stabilising process.

Studies at lower temperatures. In 1971 Fisher and Swanwick reported on simulating these two processes (Porteous and Zimpro) over the range between 170°C and 230°C and for treating a wide variety of sludges. Their main conclusions were that there was very little difference between the two processes in the affect on dewaterability. As part of the study that looked at some selected liquors, they concluded that about a third of the liquor COD was not treatable – so called refractory or hard COD. The attached graph extracted from their work (Figure 2) shows that above 180°C dewatering becomes very easy but unfortunately this is the temperature at which the biochemistry of treatment goes wrong. After this time more research work was done to demonstrate the optimum temperature for both digestion and dewatering.

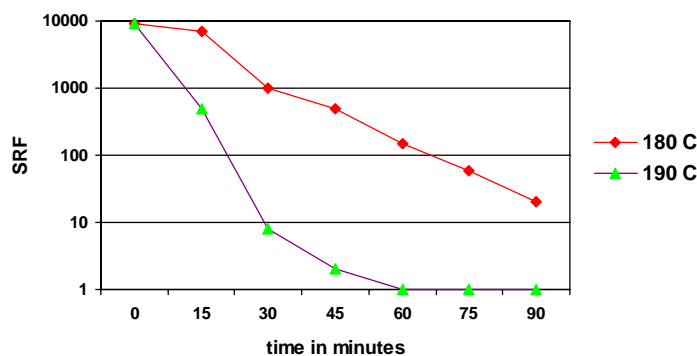


Figure 2 : Conditioning activated sludge by heat (Fisher and Swanwick, 1971)

In 1978, Haug et al worked on heat treatment at lower temperatures to see if they could combine some of the benefits of dewaterability with improved digestibility and at the same time avoid the problems that occurred with higher temperature heat treatments.

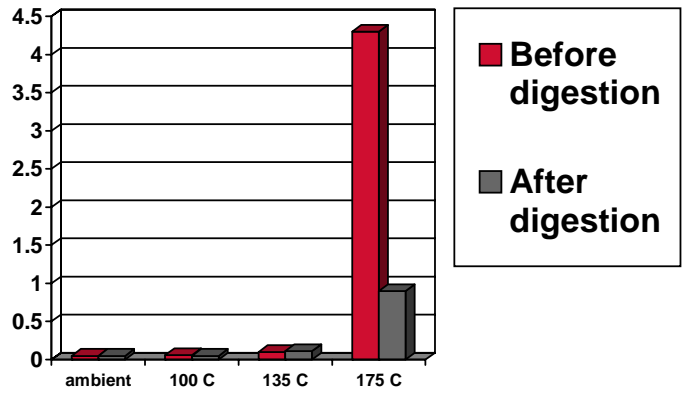


Figure 3: Effect of thermal pre-treatment on filterability of activated sludge (Haug et al., 1978)

Haug’s work showed that it was possible to get an improvement in dewaterability on undigested and digested sludges and that the temperature of 175°C was about the limit for digestibility before digestion was inhibited (presumably because of the formation of inhibitory and/or refractory compounds). He showed that the biggest effect on digestibility was for activated sludge but that all sludges tested dewatered better at 175°C (Figure 3).

Other conclusions/observations were:

- Thermal pre-treatment prior to anaerobic digestion may result in net energy production from the system because of increased biodegradability and reduced digester heating requirements.
- Recycling of liquid side streams from thermally pre-treated digested sludge should not significantly increase the oxygen demand on a biological treatment system.
- Odorous compounds normally associated with heat treatment are significantly reduced during digestion of thermally pre-treated sludge.

Elsewhere it has been observed that gas yield is improved if the temperature is dropped to 165°C which is slightly lower than the temperature in the Haug work. This optimum temperature is well illustrated in the work of Li and Noike (1998). This work is a wide ranging investigation into understanding and optimising activated sludge digestion.

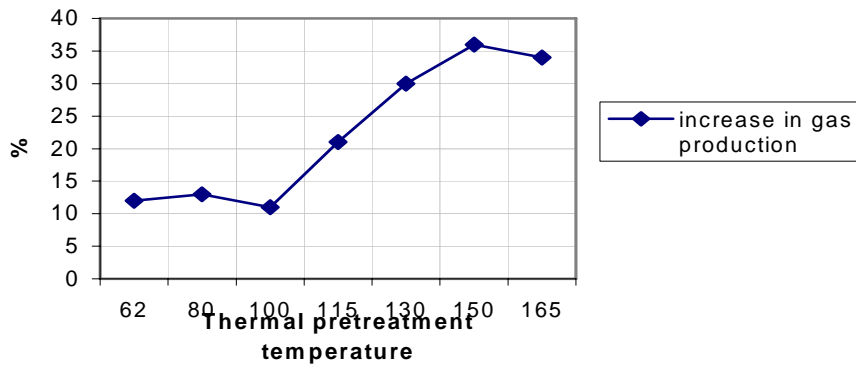


Figure 4: Effect of thermal pre-treatment temperature on gas production, (Li and Noike, 1998)

Initially they carried out test over a wide range of temperatures to identify the effective range (Figure 4). This shows that normal temperatures used for pre-pasteurisation of sludge have little effect on gas production.

They then carried out continuous testing on a narrower range of temperatures and measured COD removal as a measure of gas production (Figure 5).

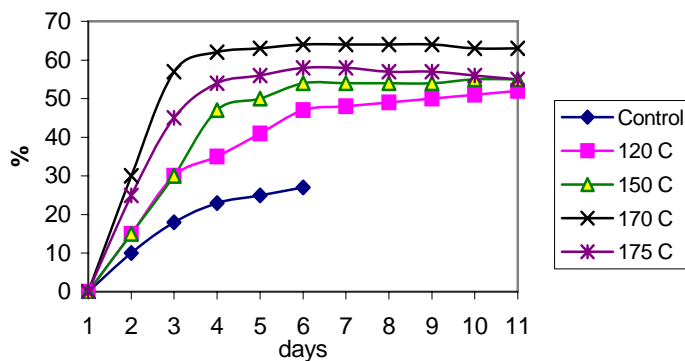


Figure 5: Effect of thermal pre-treatment temperature on COD removal (Li and Noike, 1998)

They concluded that 170°C for between 30 and 60 minutes was optimal and that the best hydraulic retention time was 5-10 days based on both gas production and studies on microbial populations of various species of methanogens. They observed that the hydrolysis effect was greater on carbohydrates and proteins than on lipids as would be expected from an understanding of their biochemistry. Li and Noike also observed that volatile fatty acids were present in high levels in the digester feed and converged to a common value which was slightly higher than the control. They concluded that this was evidence that there was little or no refractory COD effects at the temperatures used.

The Development of Cambi Thermal Hydrolysis Process

The process was developed during the period of 1990 to 1995 with pilot plant studies in Hamar (Norway). The idea for the Cambi process came from 2 separate directions: First as had been shown at laboratory scale that pressure cooking sludge in the range of 150-180°C had great benefits for digestion; second it was known that previous heat

treatment systems (Zimpro, Porteous with temperatures above 200°C) had a big effect on dewatering but had suffered from process problems of corrosion, scaling and difficult COD filtrate.

The Cambi process was invented to remove the process problems. Rather than use heat exchangers for adding heat to the liquid sludge, Cambi uses live steam to add heat to sludge cake. The process builds up the heat in the cake through 1 or 2 pre-heat tanks to get the sludge to nearly 100°C using recycled steam from the process (Figure 6). This avoids all the problems of pumping under pressure and corrosion in heat exchangers. Pre-heating the sludge avoids problems of adding steam to cold sludge which leads to major vibrations and unreliability.

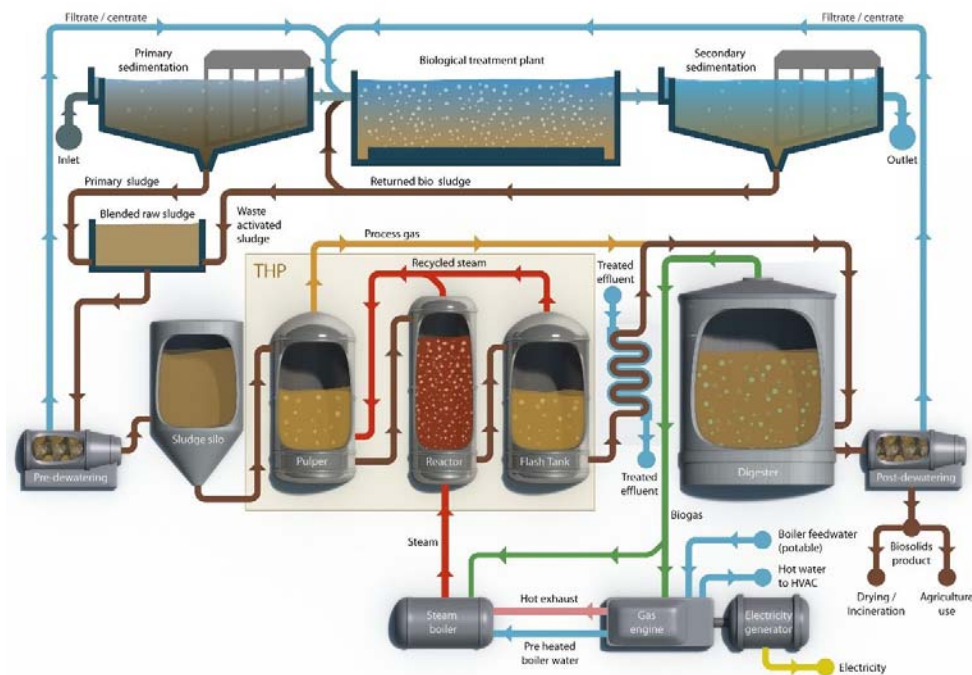


Figure 6: Process Flow Diagram of a 1 reactor THP shown in shaded area

The second major idea was to lower the temperature of previous heat treatment so that the sludge could be digested. In this case some of the extreme benefits of dewatering were sacrificed in order to have a hydrolysed digester feed that is very digestible and does not lead to the high levels of refractory COD encountered in other heat treatment process.

Since 1995 another 20 plants are built or in construction (mainly in Europe) and the sludge from approximately 8 million people is being treated this way.

The main features of these plants are : low digester volume and HRT, High biogas yield, well dewatered cake and pasteurised product.

Stated benefits are volatile bioconversion 52% (secondary only sludge) to 65% (2 stage digestion mixed sludge), increase of additional 8-12% points in cake dewatering, digester loading up to 6 kg VS/m³/day and guaranteed low odour pasteurised product with no bacterial regrowth.

A typical THP plant is shown below in Figure 7.



Figure 7: Typical Thermal Hydrolysis Plant for 20,000 dry tonnes sludge per year.

INDEPENDENT REVIEW OF PERFORMANCE

There is a large body of literature about the individual plants – see www.cambi.no. However to be sure of the claims of the manufacture, an independent survey of a number of plants was carried out by Degrémont and Suez Environnement. For each site, Cambi process and digestion part were checked, sludge samples were taken and analysed by our laboratories.

VM removal and dewaterability

The results concerning the VM removal and the DS content after the dewatering of the digested sludge are given in table 1 and in table 2.

Table 1 : Visited Cambi sites : VM removal.

Sludge quality	Site	Total VM removal
Biological sludge	A	42%
Mixed sludge	B	49%
	C	52%
	D	57.5%

Although these results of VM removal show the system's efficiency at one time and not represent necessarily what happens all along the year, they show the improvement of the Cambi process on the sludge digestibility.

Table 2 : Visited Cambi sites : dewatering technology and dryness results.

Sludge quality	Technology	Site	Dryness
Biological sludge	Belt press	A	30%
Mixed sludge	Belt press	E	25%
	Belt press	F	27%
	Centrifuge	D	26%
	Centrifuge	C	30%

The comments are the same as for the table 1. Besides, the benefits of the thermal pre-treatment are, here, more obvious, if we assume that, for example, the dryness of a classical digested biological sludge is about 20%.

Return loads

The determination of the impact of the return loads resulting from digested sludge dewatering was estimated from ultimate biodegradability tests on the parameters of soluble COD, TKN and $N-NH_4^+$. The soluble fraction was obtained from filtered supernatant of digested sludge ($0.45\mu m$). Under aerobic conditions, soluble COD, TKN and $N-NH_4^+$ of return loads were respectively biodegradable at 68, 97 and 99 %, as shown in Figure 8.

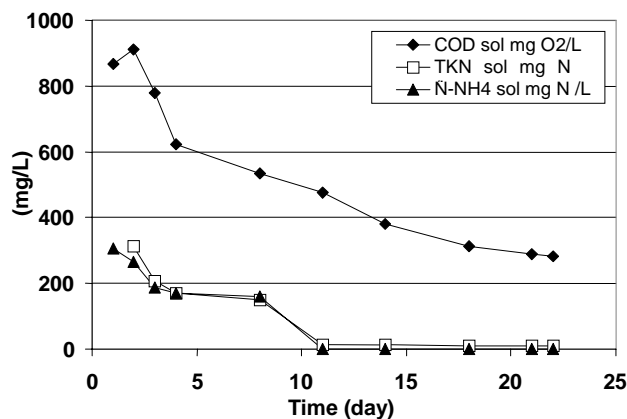


Figure 8: Evolution of soluble COD and TKN, NH_4^+ during ultimate biodegradability tests carried out on supernatant of digested sludge.

The return loads are quite high, but in accordance with VM removal and solubilization ratio. Nevertheless, these loads are biodegradable and seem not to have big impact on the water treatment.

RECENT STUDIES ON THE EFFECT OF THERMAL HYDROLYSIS ON SECONDARY SLUDGE IN ADMIXTURE WITH UNHYDROLYSED PRIMARY SLUDGE

Cambi digested sludge dewateres extremely well. It has been shown by reverse staining to have a very low content of extra cellular polymer. This has been shown as a feature of heat treatment compared to other forms of pre-digestion hydrolysis (Figure 9). Barjenbruch & Kopplow (2003) showed the relative effect of treatments

using enzymatic hydrolysis, High Pressure Homogenization (600 bar) and heat treatment up to 121 °C on the content of ECP using the reverse staining technique.

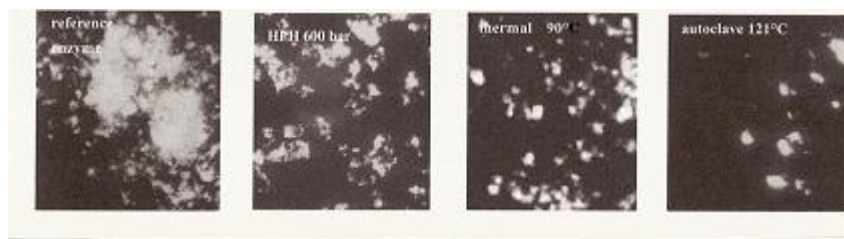


Figure 9 : Barjenbruch &Kopplow (2003), The effect of treatment processes on secondary sludge.

To date all the Cambi plants have been treating the whole sludge from the WWTP. It has been known from the original work that the main benefit comes from the effect on the secondary sludge that contains the very high level of ECP.

Lab scale investigation in Germany

A lab scale investigation was conducted in 2005/6 by P.C.S. Pollution Control Service GmbH in Germany in preparation for a full-scale application of the Cambi process at a German wastewater treatment plant. During thermal hydrolysis, the excess sludge was pressure cooked at 165°C and 6 bar pressure, for approximately 30 minutes and was subsequently digested mesophilically for 20 days together with primary sludge as a mixture. As a reference sample, the untreated excess sludge was digested under the same conditions together with primary sludge and was designed to reflect the full scale plant. The digesters were fed quasi-continuously over several weeks using online monitoring of gas production. The degree of degradation was quantified using COD reduction. After a period of adaptation, gas production increased steadily by more than 25% in the sludge where the secondary sludge had been treated. Mechanical dewatering parameters were determined for the digested sludge samples (Table 3).

As a result of enhanced degradation during digestion, the dewatering result increased from 22.7% DS to 30.8% DS, i.e. by approximately 8 percent points DS. Although the sludge particles are of smaller size, they are markedly more compact (Figure 10). Due to the compact floc structure, less water is bound as interstitial water by the capillary forces and the dewatering result is correspondingly higher.

Table 3 : CAMBI-Process results

Parameters	Digested Sludge	Digested Sludge pre-treated with CAMBI
DS [%]	2.1	2.0
VSS [%]	62.1	58.5
pH [%]	7.4	7.4
DS dewatering [%]	22.7	30.8
Polymer demand [kg WS/MgTR]	10.5	12.8
Particle size [µm]	71	48
COD in the centrate [mg/l]	482	939
NH4-N in the centrate [mg/l]	734	847
total P in the centrate [mg/l]	27	29

The sludge flocs of the two tested samples formed after conditioning with 10.5 kg/t DS and 12.8 kg/t DS respectively. The mixture of sludge and the previously ascertained optimal polymer rate has been mixed in a beaker with a stirrer for about 30 seconds at 1000 rpm. The liquor of the CAMBI sludge displays a clearly darker yellow shade than that of the untreated sludge.

Following optimal conditioning, sludge RS-0 required a polymer dose of 10.5 kg active/t DS. Treated sludge RS-C required 12.8 kg active/t DS. Hence, the polymer requirement slightly increased after treatment with the CAMBI process which is attributable above all to the increased amount of colloids in floc structure. It is expected that the polymer demand can be further reduced by a combination of flocculation agents.

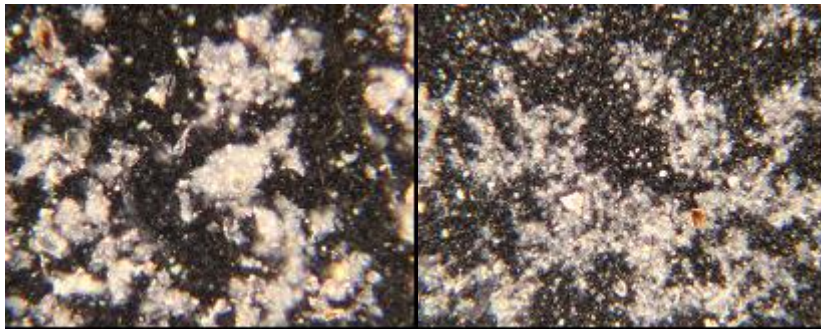


Figure 10: Floc structure of the digested reference sludge sample (left) and that of the digested sludge sample pre-treated with the Cambi-Process (dark field 100 times).

Based on the success of the tests a full scale reactor has been installed in Germany and full scale results will be available at the time of presentation.

Lab scale investigation in Spain

During 2006 experiments were carried out at the University of Valladolid to develop continuous thermal hydrolysis and energy integration in sludge anaerobic digestion.

A scheme of the thermal hydrolysis pilot plant designed and constructed for the treatment of sludge with direct steam injection is shown in Figure 11.

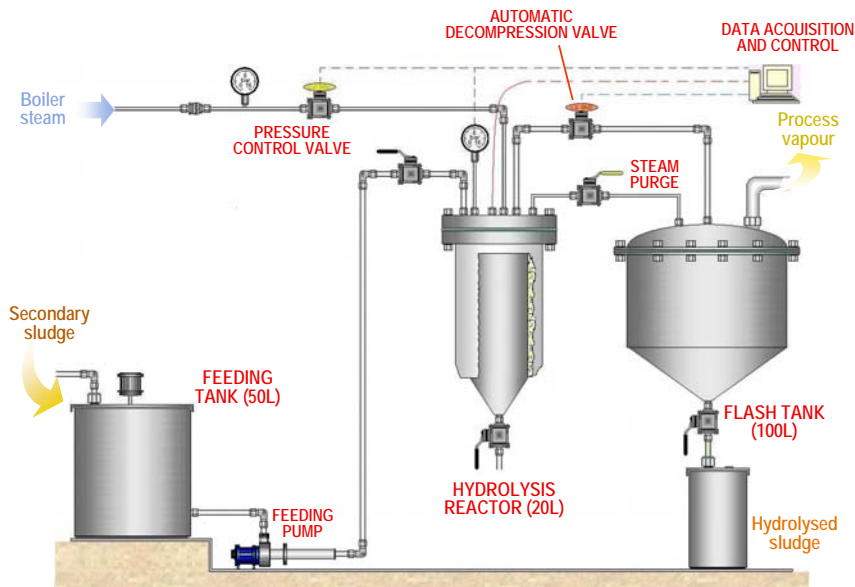


Figure 11: Thermal hydrolysis pilot plant with direct steam injection heating.

Anaerobic biodegradability was calculated following the methane production, using an automatic patented equipment. All the tests were made by duplicate.

Pressure and temperature influence. The objective is to experimentally verify the bibliographic values for different operating conditions (temperature-pressure), feeding the reactor with secondary sludge. Figure 11 shows the disintegration factor values calculated for different hydrolysis temperatures. The results demonstrate that in the range tested the degree of sludge solubilisation is directly related to the hydrolysis temperature. Analyzing the biodegradability factor (methane increase) at different temperatures, Figure 11 shows a clear maximum at 170 °C. In spite of the solubility increase, for temperatures higher than 170 °C a reduction in biodegradability due to the formation of recalcitrant compounds is observed. This confirms the findings of Li and Noike (1992) and the full scale operating parameters of existing Cambi plants as being fully optimal.

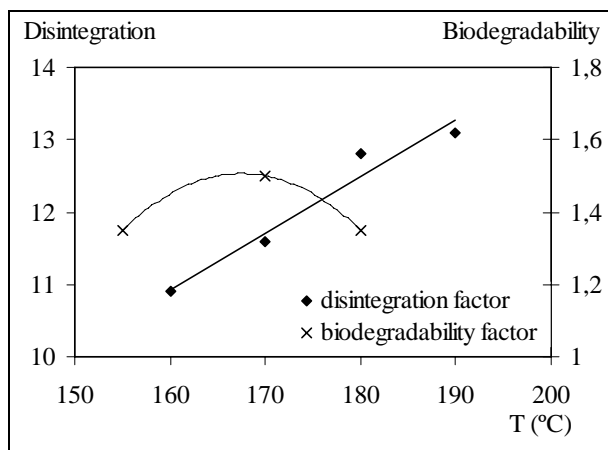


Figure 12: Disintegration and biodegradability factors for different hydrolysis temperatures

Sludge type influence. To verify the effectiveness of the process on the different types of sludge, experiments with thickened primary sludge and secondary sludge (biological sludge) were performed. The more relevant results appear in Table 4. Both disintegration factor and methane production increase are higher for biological sludge. Therefore, thermal hydrolysis seems suitable as pre-treatment for biological sludge, being hardly justifiable in the case of primary sludge.

Table 4: Influence of the type of sludge (primary and secondary)

Sludge	Disintegration factor	Methane production increase
Primary	3.1	1.21
Secondary	9.6	1.62

Continuous operation. Taking into account the results obtained for methane production increase and centrifugation in the batch experiments, the operation parameters chosen to work trying to obtain a steady state with continuous feed and exit were: temperature 170°C, pressure 7 bar, residence time 30 minutes. Maintaining these values, the control system was modified to work in continuous. The decompression valve opening/closing is temporized so that the volume that arrives at the flash tank is the sum of feeding and heating steam condensed in the reactor.

In order to test the effectiveness of the thermal pre-treatment process, the pilot plant was operated at the Municipal Wastewater Treatment Plant of Vic (Spain), using fresh mixed sludge (primary + secondary). Hydrolyzed sludge feeds two anaerobic reactors ($V = 200L$) placed in parallel; one operates in the mesophilic range (35 °C) and the other in the thermophilic range (55 °C). Both of them are continuously fed.

Mesophilic reactor : The mesophilic reactor was inoculated with anaerobic digested sludge and directly fed with thermally hydrolyzed mixed sludge using a hydraulic residence time of 20 days, without any acclimation period. The hydraulic residence time was decreased step by step until it reached a stable value of 12 days.

Thermophilic reactor : The thermophilic digester was also inoculated with anaerobic digested sludge and temperature suddenly risen to 55 ° C. Starting with 120 days hydraulic residence time an following a pseudo-steady state strategy, measuring VFA concentration and biogas production, the volume of hydrolyzed sludge fed was gradually increased.

The main average operation data for both anaerobic digesters working in continuous after a period of 16 weeks appears in Table 5. Methane production increase was calculated taking as reference values obtained in the full scale mesophilic digester fed with the same mixed sludge. These results indicate that operating at short residence time it is possible to increase by 50% the methane production decreasing the final amount of sludge to be disposed.

Table 5 : Mesophilic and thermophilic anaerobic digesters behaviour.

Reactor	HRT (d)	VS _{remov} (%)	Biogas (L/kg VS _f)	CH ₄ incr. (%)
Mesophilic	12	45 - 60	445	36
Thermophilic	16	40 - 55	405	30

CONCLUSIONS

The basic principles of batch THP are well known and have been put into full practice in 20 plants around the world. Independent investigation of the vendors claims support the data for the benefits claimed. The need for energy efficiency suggests that only secondary sludge thermal hydrolysis is a good way of getting maximum benefits for minimum cost and energy demand. Furthermore the benefits can be obtained using a continuous THP that is more cost effective to operate. It is expected that there will be a number of plants in the future using continuous THP of secondary sludge that will be mixed with unhydrolysed sludge. The benefits are expected to be at least 25% increase in digestion rate for short HRT digestion and an improvement of 8 points in dewatering. One such plant has been built in Germany and others are being proposed.

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