Département de Chimie

Université de Fribourg (Suisse)

Thermal runaway of the dried sewage sludge in the storage tanks :

from molecular origins to technical measures of smouldering fire prevention

THÈSE

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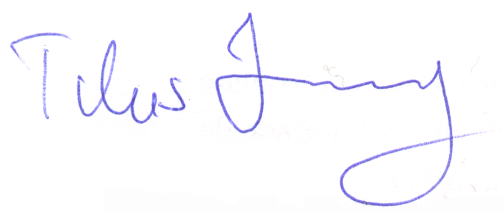Prof. Dr Peter Belser, Université de Fribourg, président du jury,

Prof. Dr Titus Jenny, Université de Fribourg, directeur de thèse, rapporteur,

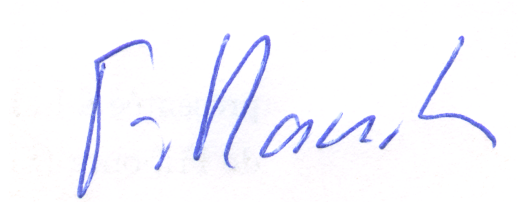Prof. Dr Carl-Wilhelm Schläpfer, Université de Fribourg, corapporteur,

Prof. Dr Serge Walter, École Nationale Supérieure de chimie de Mulhouse, corapporteur,

Dr Kurt Käser, École d'Ingénieurs et d'Architectes de Fribourg, corapporteur.

Fribourg, le 14 novembre 2007.

Le directeur de thèse et doyen
Prof. Dr Titus A. Jenny

Le vice-doyen
Prof. Dr Felix Mauch

'You do not solve problems by hitting them over the head,
but by gradually backing them into a corner from which there is no escape.'

<div align="right">HENRY FRANK</div>

À Jann

À ma famille et
mes filleuls Sven, Quentin et Lukas

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Résumé

Les boues d'épuration, sous forme de granulés séchés, sont en partie incinérées dans les cimenteries. Cet important déchet sert alors de combustible auxiliaire avant d'être réduit en cendre. Cependant durant le stockage des granulés, des augmentations de température ont lieu, causant parfois des emballements thermiques.

Ces augmentations de température dans les silos de stockage sont la conséquence d'une cascade de réactions chimiques initiée en premier lieu par l'oxydation du Fe(II). En effet le Fe(II) représente une grande part du fer total contenu dans les granulés de boues d'épuration (Fe_{tot} 7 - 12 % de la matière sèche), et se trouve principalement sous la forme de microcristaux de vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$). La chaleur libérée par l'oxydation du fer, ainsi que l'effet catalytique du Fe(III) formé permet d'initier l'auto-oxydation de la matière organique contenu dans ce déchet.

Parallèlement à l'oxydation du fer, le soufre sous forme de sulfure est également impliqué dans ce processus d'auto-échauffement. Les sulfures, présent principalement sous forme de sulfure de Fe(II), proviennent de la dégradation du matériel biologique et de la réduction des sulfates. Lors du stockage des granulés de boues d'épuration, les sulfures s'oxydent et forment des cristaux de soufre. Cette oxydation est liée au potentiel redox appliqué en grande partie par le système Fe(II) / Fe(III). Les cristaux formés correspondent à un allotrope du soufre métastable de haute température (soufre γ), confirmant le dégagement de chaleur lors de cette oxydation.

L'absorption d'eau par les granulés secs produit également de la chaleur par effet d'hydratation. L'apport d'eau sur le matériel a plusieurs origines, toutes contribuant à un dégagement supplémentaire de chaleur. De plus, l'eau favorise l'oxydation du sulfure et la formation de cristaux de soufre γ.

Les granulés de boues d'épuration sont d'excellents isolants thermiques, ce qui permet d'importantes augmentations de température lors du stockage dans de grands silos, et ce même lorsque la chaleur dégagée est faible.

Summary

A main portion of dried sewage sludge is incinerated in the cement industries. This important waste is reduced to ashes and its energetic content is used as a refuse derived fuel. During its storage, a significant temperature increase occurs which induces sometimes a thermal runaway.

Responsible for this sudden temperature increase is a cascade of chemical events which is initiated first by the oxidation of Fe(II), representing an important part of total iron (Fe_{tot} 7 - 12 % dried solids content). A large fraction of this ferrous iron consists of microcrystalline vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$). The heat release of this oxidation combined with the catalytic effect of the resulting Fe(III) enables to trigger the autoxidation of the organic matter.

Parallel to the iron oxidation, the sulfide is also involved in the self-heating process occurring during the dried granules storage. Sulfide comes from the degradation of the biological material and the reduction of the present sulfate. Principally captured as FeS, the sulfide is then oxidized to elemental sulfur due to the redox potential present in the sewage granules, which is mainly dictated by the iron redox system. High temperature metastable γ - sulfur crystals form spontaneously on the surface of stored granules, which confirms the important amount of heat released during this oxidation.

Water absorption by the sewage granules also produces further heat, because a exothermic hydration is taking place on the dried material. There are several sources of water in this solid biowaste, responsible for this additional heat release. Moreover the presence of water molecules favours the sulfide oxidation and therefore the formation of sulfur crystals at high temperatures.

Dried sludge granules are excellent thermal insulators with low thermal heat capacities. This explains the occurrence of a major temperature increase within big storage tanks even in the case of a small energy release.

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List of Abbreviations

AAS	:	Atomic absorption spectroscopy
BOD	:	biological oxygen demand
CEMSUISSE	:	Association of the Swiss Cement Industry
COD	:	chemical oxygen demand
DS	:	dry solids
DSC	:	differential scanning calorimetry
DTG	:	differential thermogravimetry
EIA-FR	:	École d'Ingénieurs et d'Architectes de Fribourg
		College of Engineering and Architecture of Fribourg
FOEN	:	Federal Office for the Environment, previously called Swiss
		Agency for the Environment, Forests and Landscape (SAEFL)
		Office fédéral de l'environnement (OVEF)
HT-XRD	:	high temperature X-Ray diffraction
ILC	:	ion liquid chromatography
LOC	:	limiting oxygen concentration
NMR	:	nuclear magnetic resonance
PAHs	:	polycyclic aromatic hydrocarbons
PCBs	:	polychlorinated biphenyls
PCDDs	:	polychlorinated dibenzodioxins
PTM	:	potentially toxic metals
SEM	:	scanning electron microscopy
STP	:	sewage treatment plant
	:	Abwasserreinigungsanlage (ARA)
THC	:	total hydrocarbons
TSS	:	total suspended solids
UNI-FR	:	Université de Fribourg
XRD	:	X-ray diffraction
XRF	:	X-ray fluorescence
%	:	mass ratio (x kg / 100 kg)

Part I

From sewage to sludge elimination

Chapter 1

Sewage sludge description

1.1 Formation

Sewage sludge is the final waste obtained in the wastewater treatment process. Urban wastewater consists of impure water released by residential, institutional, commercial and industrial facilities. The resulting sewage is also mixed with surface water and additional rainwater [1]. Such water carries all sorts of undesirable components and is therefore collected through the sewer and directed to a wastewater treatment plant for purification.

Wastewater contains organic and inorganic components, including toxic and polluting substances, as well as various micro-organisms among which several species present pathogenic or disease-causing properties. The main part of the organic components in wastewater are proteins, carbohydrates, fats and oils. In the inorganic part there are inert material such as calcite and quartz, minerals and heavy metal compounds. The treatment of wastewater is required to collect and remove the pollutants accumulated in the sewage before the purified water is released avoiding contamination of the nature.

Sewage is processed within a wastewater treatment plant for the following reasons. First, the biological decomposition of the organic materials in wastewater would consume oxygen and thus reduce the quantity available in the receiving waters for the aquatic life. In addition the decomposition would also produce large quantities of malodorous gases. Secondly, the numerous pathogenic or disease-causing microorganisms in untreated wastewater are health hazards to human beings. Third, its toxic compounds, especially heavy metals [2], can be dangerous to both plants and animals, and finally the presence of phosphate and nitrogen may lead to uncontrolled growth in aquatic plants.

Arriving at the wastewater treatment plant, the sewage therefore undergoes successive physical and biological processes in order to remove the present pollutants and to concentrate them within a sludge. The obtained sludge is brought to the desired dryness through several steps such as flocculation, centrifugation and drying process. As results of this treatment, on the one hand purified water is released into the effluents and on the other hand sewage sludge remains as final waste.

1.2   Processing

There are different ways of processing wastewater, which depend on the type of sewage entering in the wastewater treatment plant and treatment levels required by the authorities. Consequently the type of sludge produced at each sewage treatment plant (STP) varies considerably according to the facilities and these methods of operation.

Generally sewage sludge can be classified as primary, secondary (also called biological) and chemical sludge [3]. Depending on the facilities, sewage sludge can also be called tertiary, digested or activated sludge in function of the further performed treatments. The sludge is called raw sludge when it is not treated biologically or chemically for solids and pathogens reduction. The sludge can also undergo other treatments such as alkaline stabilization or composting.

1.2.1   Physical treatment

Most wastewater treatment plants use the physical process of primary settling to remove solids from raw sewage by sedimentation, which produces the primary sludge. The total solids concentration in raw primary sludge can vary between 2 - 7 % [1] dry solids (DS) content. Compared to biological and chemical sludges, primary sludge can be dewatered rapidly producing a drier sludge cake. However this sludge is highly putrescible and generates an unpleasant odor if it is stored without further treatment.

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[1]x % = x kg/100kg of material

1.2.2 Biological treatment

The primary sludge can be treated biologically resulting in secondary sludge, also known as biological sludge. There are several types of biological treatment processes producing different biosolids, which can be classified as aerobically or anaerobically digested or activated sludge. At that stage, the bacteria consume the soluble and insoluble organics forming the biological sludge with 1 - 4 % DS. This sludge is more difficult to dewater than the primary sludge because of the light biological flocs inherent in biological sludge.

1.2.3 Chemical treatment

Chemicals are used widely in wastewater treatment, especially in industrial STP, to precipitate and remove specific substances, and in some instances, to improve suspended solids removal. A typical example of chemical removal of a substance from wastewater is the chemical precipitation of phosphates by different chemicals such as lime, alum for instance aluminum potassium sulfate or some iron salts.

1.3 Thickening and dewatering

The purpose of reducing the volume of the sludge by thickening or dewatering processes (or both) is to increase the efficiency and decrease the costs of subsequent sludge-processing steps.

Thickening is a process to increase the solids concentration of sludge and decrease its volume by removing a portion of the water. The thickened sludge (generally up to 5 % DS) remains in the fluid state and is capable of being pumped without difficulty.

The dewatering is the removal of water from sludge to achieve volume reduction greater than that achieved by thickening. Dewatering the sludge results in a solid-semisolid material that is easier to handle. This treatment stage of the sludge is required before composting, thermal drying, incineration or disposal in landfills. However prior to dewatering, sludge requires conditioning by biological, chemical and physical treatment to enhance water removal.

1.4   Thermal processing

Thermal processing of wastewater sludge includes thermal conditioning, thermal drying, and incineration.

1.4.1   Thermal conditioning

Thermal conditioning consists in applying heat and pressure to the sludge to release bound water from solids, thereby enhancing its dewaterability without addition of conditioning chemicals. It also means thermal stabilization of sludge for instance with addition of dry lime, which leads to a pasteurization process caused by the exothermic reaction of quicklime and sludge.

1.4.2   Drying

Thermal drying is the process of evaporating water from sludge by heating means. With these techniques the moisture content is reduced below that achievable by conventional dewatering methods. Depending on the design and the operation of the dryer, the minimum moisture content of 5 % can be reached for ordinary municipal sewage sludge. The advantages of thermal drying include reduced transportation costs and further pathogen destruction.

Dryers are commonly classified on the basis of the predominant method of transferring heat to the wet solids being dried. For instance for direct drying performed by convection, heat transfer is accomplished by direct contact between the wet sludge and the hot gases. The heat of the inlet gas provides the latent heat required for evaporating the liquid from the sludge. The vaporized water is carried by the hot gases. Direct dryers such as flash dryers, direct rotary dryers, and fluidized-bed dryers are the most common types used in thermal drying of sludge.

With conduction (indirect drying) systems, heat transfer is accomplished by contact of the wet sludge solids with hot surfaces. A metal wall separates the sludge and the heating medium (usually steam or oil). The vaporized water is removed independent of the heating medium. Such indirect dryers include horizontal paddle, hollow-flight or disk dryers, and vertical dryers.

Finally in infrared or radiant heat dryers, heat transfer is performed by radiant energy supplied by electric resistance elements, gas-fired incandescent refractories, or infrared lamps.

1.4.3 Incineration

Incineration is the complete combustion, which is the rapid exothermic oxidation of combustible elements in sludge. It is known that dewatered sludge ignites at temperature of 420 - 500 °C in the presence of air. Temperatures of 760 to 820 °C are required for complete combustion of the organic solids. In the incineration of sludge, the organic solids are converted to the oxidized end products, primarily carbon dioxide, water vapor, and ash. Particles and other gases will also be present in the exhaust [4, 5]. Sludge containing 30 - 50 % DS is autogenous and therfore it can be burned without auxiliary fuel. By contrast sludge with only 20 to 30 % DS may require an auxiliary fuel for combustion such as coal or urban waste. The energy release by burning sludge reaches 10 - 30 MJ/kg (DS) depending on the use or not of an auxiliary fuel.

1.5 Sewage treatment plant of Bern

First it has to be said that the sewage treatment plant (STP) of Bern is a typical facility handling urban wastewater. There are not any particular manufacturing industries or specific industries in the area, where the sewage are collected.

1.5.1 Physical and chemical treatment

Mechanical removal of solid substances is the first step that raw sewage undergoes, while flowing through the sewer system to the wastewater treatment plant (Figure 1.1). Heavy pieces such as gravel and stones are separated out in the grit chamber, and the floating pollutants are removed from the sewage by coarse screens. The sand is then intercepted in aerated grit chambers.
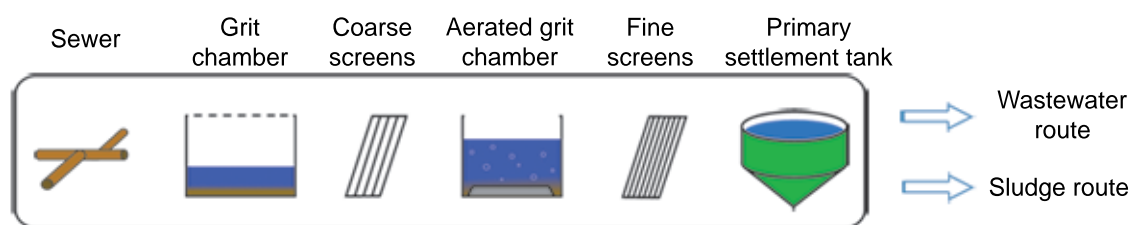
Figure 1.1: Physical treatments of raw sewage water

A chemical treatment is afterwards carried out in order to remove phosphates. Ferric chloride sulfate $(FeClSO_4)$[2] is added to the aerated grit chambers in order to precipitate $FePO_4$ and also to control the resulting odors from the microorganisms activity.   Any fine substances that have managed to pass through the coarse screen are finally stopped by a finer screen. Solids sink to the bottom of the primary settlement tank and are moved on from there to undergo the sludge treatment.

The STP of Bern uses a large amount of ferric chloride sulfate to remove all the phosphates. This procedure also prevents the release of smelly odours in the residential area where the STP of Bern is located.

1.5.2   Water processing

After the settlement process the sewage is split to two different treatment routes: on one hand the settled part of the wastewater follows the sludge route and on the other hand the remaining water is transfered to the wastewater route for further biological treatment. This water undergoes a biological treatment called BIOSTYR$^{©}$ process, which involves the action of microorganisms residing on support media. This process eliminates all biodegradable pollutants, including polluting organic compounds and organisms, measured by the chemical, respectively biochemical, oxygen demand (COD and BOD), and nitrogen (N-NH_4 and N-NO_3) and as well as total suspended solids (TSS) still present in water (Figure 1.2). The decomposition products are removed from the biofilter and are subsequently thickened (ACTIFLO$^{©}$ process). The thickened biosludge is pumped into the sludge treatment area for further processing. The last step of the water treatment is a sand filtration which removes the undissolved finest matter before the purified water is directed to the nearby river (River Aare).
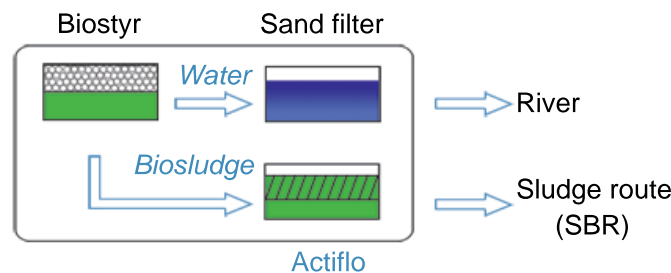
Figure 1.2: Wastewater treatment route

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[2] *Trifer 12.5* provided by Aregger Chemie, Riedholz (SO)

1.5.3 Sludge processing

The sludge treatment route starts after the primary settlement tank (Figure 1.3). After going through a prethickner tank, the sludge is heated to 37 ° C and is pumped into digesters for anaerobic microbial treatment [6]. There, specific bacteria decompose the organic substances producing digester gas which is used as fuel directly in the STP. The remaining sludge is then concentrated, aided by the addition of a polymer[3] to bind the sludge. After this biological treatment, the digested sludge is mechanically dewatered to 35 % DS using centrifuges. The dehydrated sludge can now be passed to a dryer for removal of the remaining water to produce the finished product, normally 92 % DS in form of dried sludge granules.
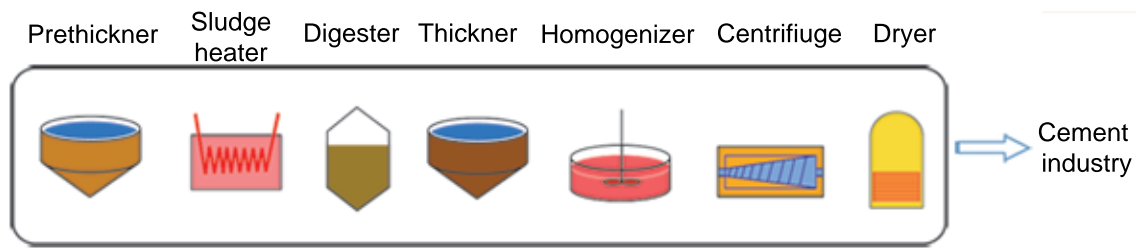
Figure 1.3: Sludge treatment route

The separated sludge liquor is channeled off to undergo a separate biological treatment stage in order to remove the nitrogen. Sludge liquor treatment consists of a process similar to biological wastewater treatment except that the microorganisms are freely suspended in flocks in the sludge liquor.

1.5.4 Air processing

Last but not least even the waste air is treated [7]. The odorous waste air from the tanks and the closed buildings is collected and pumped off to undergo a biological air treatment process. The purified air is then released into the atmosphere.

1.5.5 Dryer plant

The STP of Bern used first a dryer system consisting in a drum drying process called Swiss Combi ©. This dryer is a closed loop drying system, in which the heat is generated in a combustion chamber fired by oil or biogas. Then the heat

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[3]Superfloc A 90360 (polyacrylamid) provided by Kemira

is transferred to a heat exchanger where drying air is heated to 450 ° C. The sludge from the dewatering plant passed through drying drum where the drying air evaporates the water from the sludge.

In Fall 2001 a new dryer system was set up at the STP of Bern by the firm VA-Tech Wabag (DE). This new dryer plant consists in a fluid bed drying system, where the fluid bed is generated by blowing inert fluidization gas uniformly over the dryer cross-section. The dryer oven is heated by a thermo oil system creating a inert drying atmosphere at around 80 ° C.

The dewatered sludge ($\sim$ 35 % DS) is transfered from the centrifuges to the dryer plant by Archimedes' screws, where it is temporarily first stored in a dosing silo of 75 m^3 (Figure 1.4). Under this silo, three pumps feed the pipes transporting the dewatered sludge to the fluid bed dryer. The drying atmosphere consists in combustion gas with a low oxygen level ($<$ 1 % vol. in the dryer oven and $\sim$ 4 % vol. in the protective atmosphere)[4]. Before reaching the oven, one of these pipes goes by the dust recycler, where the wet sludge is mixed with the dust recycled from the dryer. At the entry of the oven, the sludge from the three pipes is chopped mecanically. The free-flowing granulates in the dryer begin to float and are at the same time mixed thoroughly due to the gas stream passing through the product layer. The dried sewage granules ($\sim$ 92 % DS) exiting from the dryer are then cooled down in a fluid bed cooler system before being transported mechanically to two large loading silos[5]. These silos are regularly emptied by loading their content by gravity directly into the transporting trucks. The material is then brought to the cement industries for incineration.
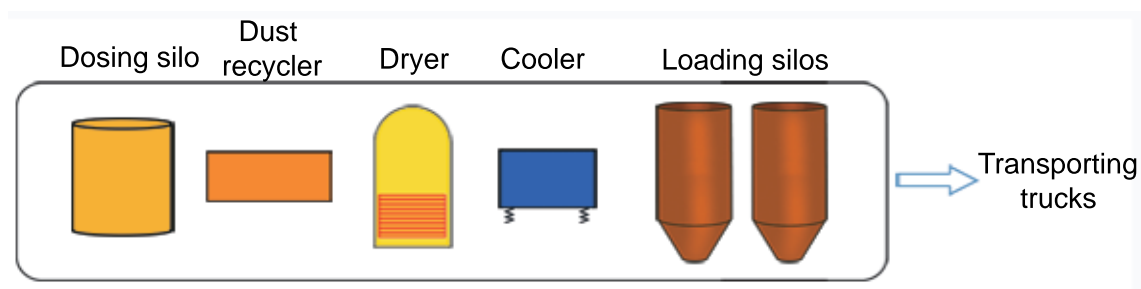
Figure 1.4: Dryer plant at the STP of Bern

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[4]operating limits $<$ 8 % vol. of oxygen
[5]capacity: 100 m^3 per silo, daily production: $\sim$ 24 t/d

1.5.6   Dried sewage granules composition

The dried sewage granules of the STP of Bern have a casual composition concerning the moisture content (8 - 10 % total mass), the ash content ($\sim$ 50 % DS) and the mineral composition (Table 1.1). However the iron content in the dried biosolids is very high as compared to the sewage waste produced in the other treatment plants, and reaches between 7 - 12 % DS of the dried granules (Table 1.2). This is due to the important amount of the added iron chlorosulfate in the raw wastewater to precipitate the phosphates.

Table 1.1: Composition of the dried sewage granules from the STP of Bern (State analysis of Mai 2006)

Analyses	Quantity	Units
Dry solids content	93.2	%
Ash	57.1	%
Total nitrogen	28	g/kg (DS)
Ammonium	2.4	g/kg (DS)
Calcium	68	g/kg (DS)
Phosphorus	29	g/kg (DS)
Magnesium	3.8	g/kg (DS)
Potassium	2.3	g/kg (DS)
Zinc	680	g/t (DS)
Copper	290	g/t (DS)
Lead	81	g/t (DS)
Chromium	42	g/t (DS)
Nickel	22	g/t (DS)
Cobalt	8.2	g/t (DS)

Table 1.2: Iron concentration in the dried sewage granules from the STP of Bern

State analyses	Fe concentration (% DS)
September 2003	10.4
August 2004	12.0
October 2004	8.2
February 2005	9.5
July 2005	11.0

Other elements and ions also takes part to the sewage sludge composition.

Heavy metals are present at low concentration (generally < 1 g / t DS). Total sulfur has also been analyzed several times and its concentration reaches generally 1 % DS. However during these routine analyses the anions concentration are not measured.

Chapter 2

Sewage sludge elimination

Sewage biosolids, the residues of wastewater treatment, represent an important waste in Switzerland ($\sim$ 200'000 tons DS per year) and an adequate disposal solution has to be chosen. The possible routes for the sludge disposal are recycling as fertilizers, landfill or dumping in the sea, and incineration. However, each elimination route presents some advantages and problems, which are described further. Some other techniques such as thermal gasification [8] or pyrolysis [9] are quite new and their optimization is still in progress.

2.1 Fertilizer in agriculture

Spreading or spraying of sewage biosolids onto the surface of the agricultural land or the injection of biosolids beneath the surface of the land conditions the soil or fertilizes crops grown in the soil [3]. Thanks to its high content of nitrogen and phosphorus, sewage sludge shows good fertilizer properties. Application of biosolids to agricultural land allows recycling of organic matter and nutriments in order to restore soils. By its contribution to the biocycle, the use of sludge replaces the application of synthetic fertilizers.

Dried sludge, usually in the form of granules or pellets, has the advantage of being convenient for the transport, because of its reduced volume and its important dry matter content (85 - 95 % DS) compared to dewatered sludge, which has only around 30 % DS. Farmers can also more easily handle dried sludge and there is also considerably less risk of infection when compared to the older methods for handling raw sewage.

However, sewage waste also contains heavy metals and other persistent pollutants such as organochlorine and brominated diphenyl ethers (BDEs) [10].

Such toxic substances may pose severe environmental hazards by polluting surface and ground water. By applying sewage biosolids in an injudicious way, further contamination may reach plants and animals by accumulation in the food chain.

Nevertheless this disposal of sewage sludge by application to agriculture is widely practiced and it is largely presumed to be environmentally beneficial. However the recycling of sewage sludge to grassland and forage crops must be tightly regulated to prevent detrimental effects on soil and animal health [11]. Sewage waste may adhere to herbage by repeated applications of these biosolids to grassland, which can lead to elevated concentrations of potentially toxic metals (PTM) such as Cd, Pb, Cu, Zn, Ni, Cr and Hg at the soil surface. Together with soil and herbage, grazing ruminants may ingest this contaminated feed. This may then lead to accumulation of some of these metals in the animal organs such as liver or kidney.

2.2 Landfill

Wastewater solids may also be disposed in definite areas. This surface disposal of sewage residues differs from the above application in that it uses the land for final disposal instead of using the biosolids to enhance the productivity of the land. The sewage biowaste may be disposed for instance in municipal solid waste landfills.

This technique presents some disadvantages principally concerning the leaching runoff, which can contaminate groundwater, surface water, and soil if the composition of the leachate waters is not controlled. Installation of leachate collection systems may be required to avoid pollution of the freshwater resources. Moreover methane gas monitoring systems must be installed at the sites where sewage sludge is covered, since methane gas is a byproduct of anaerobic decomposition of the organic matter and explosions may occur if a certain concentration range in air is reached.

2.3 Incineration

Incineration of wastewater sludge is the firing of sludge at high temperatures in an incinerator or furnace [12, 13]. There are several different incineration systems, however they all have to be equipped by air pollution control devices. These filters and precipitator systems are used to decompose further the remaining organic

compounds and to remove the fine particles and metals present in the exhaust gas coming from the incinerators.

The pollutant limits are defined for several metals present in the sewage sludge designated for incineration. The amount of total hydrocarbons (THC) in the biowaste is generally required before sending the sludge to the furnace. As a result of incomplete combustion, organic compounds may be found in the emissions, such as benzene, phenol and vinyl chloride. Therefore the THC concentration in the exhaust gas is also subject to regulation.

Chapter 3

Sewage sludge management in Switzerland

3.1 Earlier situation

The Swiss Agency for the Environment, Forests and Landscape (SAEFL), which is nowadays named Federal Office for the Environment (FOEN), presented in 2002 a report, which illustrated the trend in the quantity of all the waste produced, and served as a basis for future waste management [14]. From the 3.19 millions of tons of waste treated in 2000, 50'000 tons were sewage waste ($\sim$ 51 % DS) which were eliminated in regular household incineration plants and landfills like all the other combustible wastes at that time [15] (Table 3.1). However, the 404'300 tons of combustible waste incinerated in industrial furnaces or in cement industries were not taken into account for these data.

Table 3.1: Combustible wastes produced per habitant in Switzerland (2000) and the total quantity eliminated in household incineration plants and landfills [14]

Combustible waste	Production (kg/habitant)	Elimination (1000 tons) in incineration plant	in landfill
Urban waste	360	2'296	292
Workings waste	56	354	52
Other waste	20	110	38
Sewage sludge [a)]	7	42	8
Total	443	2'802	390

a) with average solid content of 51%

3.2   Use as energy source

Sewage sludge contains an important amount of organic material even after being treated. With this intrinsic chemical energy content, the biomass of sewage sludge can be used as refuse derived fuel in power stations for instance. Once dried other possible beneficial route can be explored such as fuel in power station or gasification. The ash remained after the combustion of the dried sewage sludge may be used in building materials like for the production of cement [16].

In 2000 some of the fossil fuel was already replaced by energetic waste by the means of urban and industrial wastes being eliminated through household incineration plants and discharges or in the industrial furnaces and cement industries [14]. This corresponded to 404'000 tons of energetic material eliminated that way (Figure 3.1).
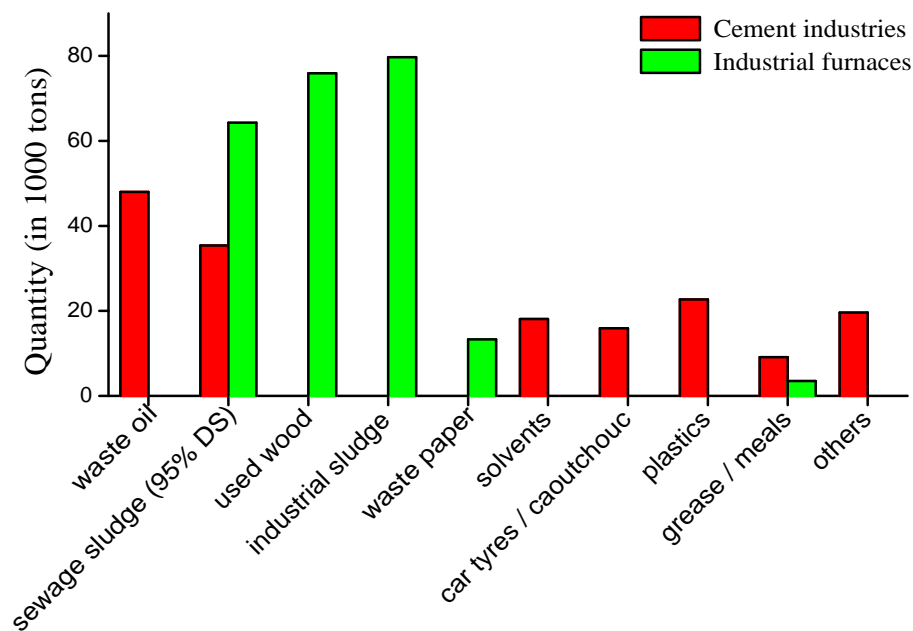
Figure 3.1: Waste incineration in Switzerland in 2000 [14]

3.3   Ban on the use as a fertilizer

Although sludge contains plant nutrients such as phosphates and nitrogen containing compounds, it also comprises a whole range of harmful substances and pathogenic organisms produced by industry and private households. For this reason, the Federal Council projects to ban the use of sludge as a fertilizer in order

to prevent any risk of irreversible damage to the soil. Such contamination due to the use of waste as fertilizers was studied [17] and presented the negative effects on the ecosystem, and then on animal [18] and human health. The quality of soil and plant, such as pasture and vegetables, could be spoiled by heavy metal ions and persistent organic pollutants such as dioxins (polychlorinated dibenzodioxins) (PCDDs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) [19] or pharmaceuticals [20, 21].

3.3.1 Perspectives and consequences

Energy production from waste elimination is expected to become a strategy of some importance, especially because waste from renewable raw materials provides energy with a CO_2 neutral value. The use of a CO_2 free fuel instead of fossil energy sources contributes towards the diminution of CO_2 releases and corresponds to the Swiss policy about the Kyoto protocol [22]. Therefore the use of sewage sludge represents a very attractive issue, as this biosolid is considered as a 'green' fuel in contrast to conventional fossil energy sources.

In August 1991, the SAEFL published a first report concerning sewage sludge incineration [23]. At that stage, 260'000 tons DS of sewage sludge were produced per year in Switzerland and 60'000 tons DS per year were already incinerated mainly in specific incineration furnaces (Table 3.2). This first study presented the incineration of sewage products as an attractive elimination route when this waste could no more be used as valuable fertilizer in agriculture. The incineration capacity of the household incineration plants was estimated to be sufficient to eliminate the remaining 200'000 tons DS of sewage sludge so far used in agriculture.

Table 3.2: Sewage sludge production and elimination in 1991 [23]

Elimination routes	Total quantity (tons/year)	Ratio (%)
Agriculture	200'000	77
Incineration		
- Specific furnaces	57'000	22
- Cement industries	3'000	1

In February 2003, another publication from SAEFL was reporting the results of the consultation process concerning the ban on the use of sludge as a fertilizer which will induce modifications of the Ordinance on Materials. Different offices, association and institutions were asked to communicate their points of view and impressions about the ban on the use of sludge as a fertilizer. Most of state governments and the environment and agriculture state offices expressed a favorable opinion. This point of view was supported by farmers and commercial associations, as well by consumers and environmental organizations. However several differences and oppositions were also declared principally by organizations with an economic interest on manure spreading: all together the use of sewage sludge was estimated corresponding to 7 millions CHF worth of fertilizer.

3.3.2   Decision and measures

On 26th March 2003 a press release from the Federal Office for the Environment announced that the use of sludge as a fertilizer has to be banned throughout Switzerland; in the future sludge will have to be incinerated using an environmentally friendly method[1]. The Swiss Federal Council has modified the Ordinance on Materials on 1st May 2003. The ban will be introduced in stages (Figure 3.2):

- from 1st May 2003, sludge may no longer be used in the production of fodder crops and vegetables;

- a period of transition lasting until 2006 at the latest has been accorded for other types of cultivation, which until now have been fertilized using sludge;

- in individual cases the cantonal authorities may extend this period until 2008. This decision is part of the Federal Council's implementation of precautionary provisions for the protection of soils and public health.

The ban was come first into force for the production of fodder crops and vegetables, because this sector represents the greatest risk to the health of humans and animals. From 2006 the ban had to be applied to all other types of cultivation, with extended periods of transition until Fall 2008 when accorded by the cantonal authorities. Exceptions to the ban included very small sewage treatment plants in remote areas. In such cases, sludge normally contains fewer problematic substances and the cost of transporting it to a larger treatment plant would be disproportional.

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[1]www.bafu.admin.ch
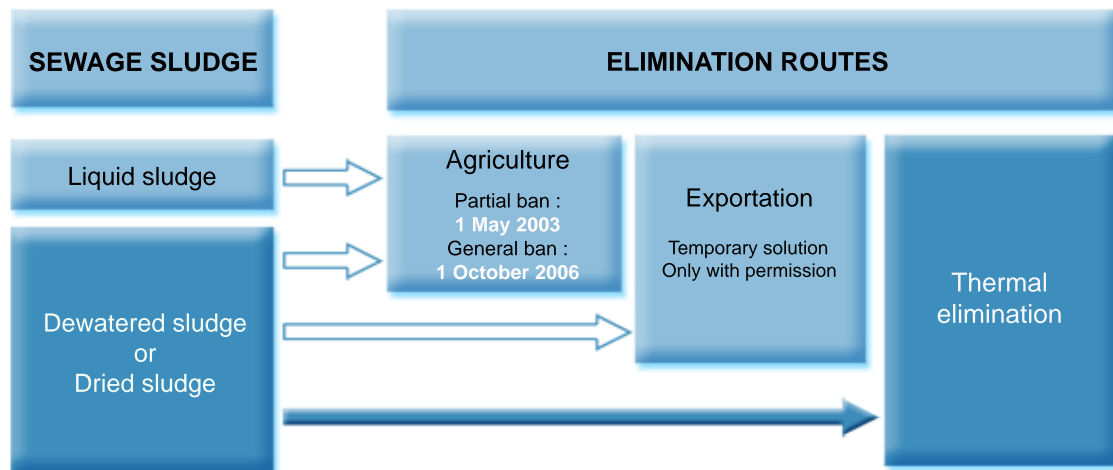
Figure 3.2: Sludge elimination in Switzerland [14]

At that stage, 60 % of all the sludge, corresponding to 120'000 tons DS per year, was already treated as waste and incinerated. For the remaining 40 % of sludge (80'000 tons DS), incineration routes had to be established until 2006. FOEN has set up a working group comprising representatives of the cantons, sewage and waste management and the cement industry in order to coordinate the sewage sludge incineration capacities.

3.4 Actual situation

The last report concerning the elimination of sewage waste was published in 2004 by the SAEFL [14] and presented the different routes to recycle sewage biosolids and the changes occurred between 2000 and 2002 (Figure 3.3). The updated federal laws wanted to upgrade this waste thanks to its energetic content. Moreover the collection, the transport and the storage of sewage sludge must be optimized in order to respect the environmental norms.
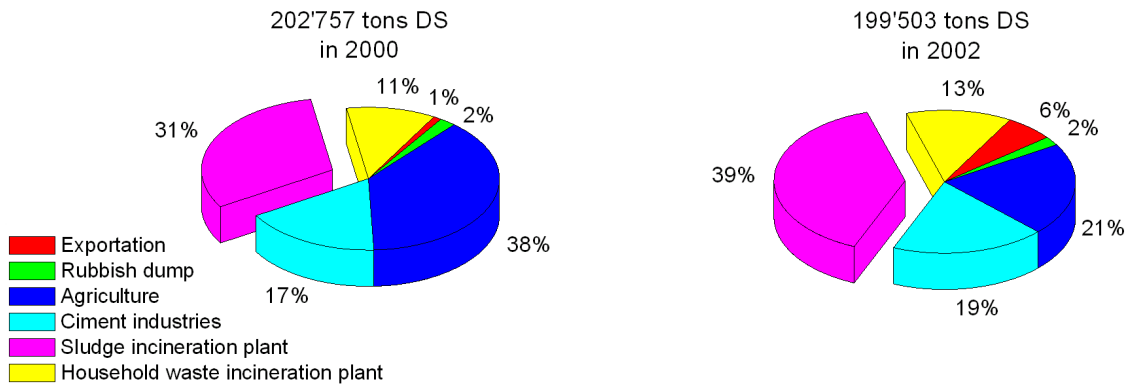
Figure 3.3: Waste incineration in Switzerland for 2000 and 2002 [14]

The banning of sewage sludge in agriculture was generalized on 1st October 2006 after the partial ban which started on 1st May 2003. From that stage, thermal treatment of sewage sludge represents the only elimination route in Switzerland (Figure 3.4). Such process must be performed in specific installations, such as cement industries, household waste and sewage sludge incineration plants or industrial furnaces. However to do so, sewage waste need to contain a minimum amount of dry matter corresponding to more than 30 % DS for all incineration plants and a minimum of 90 % DS for incineration in cement industries. Studies for other thermal elimination such as pyrolyse and gasification are at present in progress.
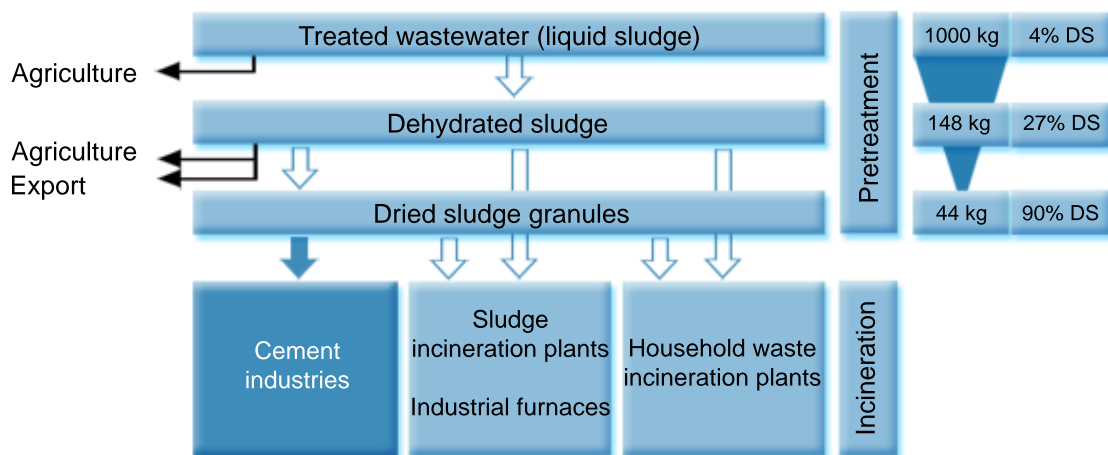
Figure 3.4: Treated stages of sewage sludge and incineration routes [14]

Part II

Spontaneous ignition and runaway processes

Chapter 4

Runaway and spontaneous combustion of diverse materials

The term 'spontaneous combustion' is defined as the temperature rise in a body made of combustible materials leading generally to a fire. This occurs as a result of the heat generated by some exothermic process taking place within the said body. Spontaneous combustion can happen when a substance with a relatively low ignition temperature begins to release heat. First, organic materials must heat to their ignition temperature via a spark, pilot flame, or other heating mechanisms. Then if the heat cannot escape and the temperature of the material rises above its ignition point and if sufficient oxygen is available, spontaneous combustion will occur. For example typical composting materials ignite at temperatures roughly in the 150 ° C to 200 ° C range.

In a 'runaway process', also called thermal runaway, the control of the temperature is lost [24, 25]. This happens when the rate of unwanted exothermic reactions is no more controlled by external conditions. Most of the time these reactions are oxidation or hydration processes of complex reaction mixtures.

Several dangerous situations may induce thermal runaways. However the homogeneous thermal runaway due to a too high temperature consists in the most frequent runaway behaviour. The Semenov theory describes an exothermic reaction according to the Arrhenius law [26]. The reaction is assumed to be an irreversible process. Under these conditions, the heat production increases exponentially with the temperature as shown in the following equation.

$$\frac{\mathrm{d}q}{\mathrm{d}t} \; = \; \dot{q}_G \; = \; V \cdot Q \cdot k^0 \cdot C^n \cdot exp\left(-\frac{E}{RT}\right) \qquad (4.1)$$

The power of heat loss is a linear function of the temperature as presented here.

$$\dot{q}_R \;=\; k \cdot S \cdot (T - T_a) \tag{4.2}$$

with

$\dot{q}_G$ = heat produced by the exothermic reaction (W)
$\dot{q}_R$ = heat removed by cooling (W)
V = volume (m^3)
Q = enthalpy of reaction (J·mol^{-1})
k^0 = Arrhenius factor ((mol·m^{-3})$^{1-n}$ · s^{-1})
S = heat exchange area (m^2)
T_a = ambient temperature (K)
C = concentration (mol·m^{-3})
n = order of the reaction
E = activation energy (J·mol^{-1})
k = overall heat transfer coefficient (W·m^{-2}·K^{-1})

There is some temperature limit above which the heat produced by the reaction is greater than the heat removed. Above this limiting temperature, the system temperature increases steadily causing the reaction rate to accelerate exponentially. Some typical examples of spontaneous combustion are discussed below.

4.1   Automobile shredder residues

In 1999 an article in the *Society of Automotive Engineers of Japan* presented a study about the thermal ignition characteristics and its mechanism for some solidified automobile shredder residues [27]. The combustion accidents of large quantities of piled shredder residue are well known, and it seems that the cause was spontaneous combustion.

To do so, the authors conducted two thermal ignition tests, one was an exothermic experiment using an adiabatic box (Figure 4.1), and the other was a heating experiment using an electrical heater. The self-ignition of automobile shredder residue was studied in relation with the thermal radiation and accumulation in the piles from different sizes. Three experiments were performed in the adiabatic box with an initial temperature of 60 - 70 °C obtained after cooling the treated residue with water. During the first two tests, temperature initially increased about 10 °C, but subsequently decreased, and finally reached ambient level. In the case
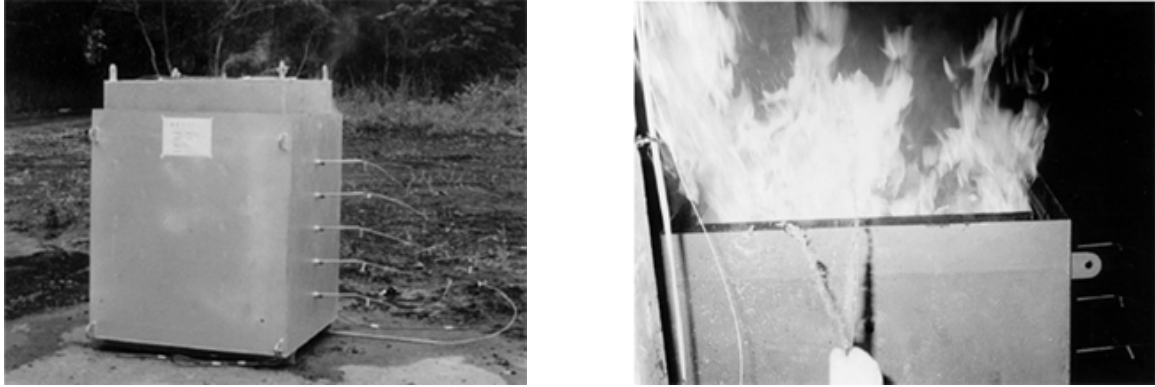
Figure 4.1: Adiabatic box used for the thermal ignition tests (left) and self-heating of automobile shredder residues causing spontaneous combustion when the adiabatic box was open (right) [27]

of the third test, made with uncooled shredder residues, temperature continuously increased and after 10 h, inside temperatures reached about 300 $^\circ$C and the pile caught fire.

Thanks to numerical calculations based on the Frank-Kamenetskii exothermic theoretical model it was possible to predict the spontaneous combustion characteristics for a large pile of automobile shredder residues. The obtained calculation results fitted successfully with the exothermic experimental results and demonstrated that the combustion temperature was inversely proportional to the pile height. The proposed mechanism was that the heat generated of the oxidation remained stored inside the piled shredder residues. Then more and more heat is stored in the pile and this causes ignition.

4.2 Shale spoils

Near Dallas (Texas), carbonaceous shale is excavated from the rocks for a sanitary landfill [28]. The shale, which contains 3 - 4 % of organic carbon, and no lignite seams, is piled loosely at one side of the landfill. In Fall 2000 steam with weak sulfur smell was first observed venting from the pile. In fact the shale deposits were spontaneously combusted (Figure 4.2). Maximum temperatures exceeded more than 500 $^\circ$C at several hot spots located approximately 4 m beneath the pile surface. It was explained that this spontaneous combustion was due to shale fines along with moisture trapped in the pile. These reactions generated heat faster than it could dissipate, leading to combustion.

Figure 4.2: Steams due to spontaneous combustion of shale spoils [28]

Even several months later, in July 2001, the pile continued to smolder. Excavations have enabled hot spots to vent more efficiently. Spreading the excavated material allowed it to cool down, and it stopped burning within a few hours. Colder winter temperatures cooled the pile, enabling more efficient venting, but did not quench the combustion. As solution it was proposed to spread the material in thin layers and compact it, which would inhibit air circulation and the segregation of fines that might otherwise lead to combustion.

4.3   Pyrophoric iron sulfide

Pyrite-containing shale mines sustain occasionally some hazards due to spontaneous combustion. It was also reported that in Estonia alum shale, which is a rock with high pyrite (FeS_2) content, has been altered at high temperature due to spontaneous combustion [29], where the temperature had reached up to 1200 °C. One suspected that pyrite in the shale tended to oxidize at high rates when exposed to the atmosphere (Eq. 4.3). It was demonstrated that under these specific conditions, depending mainly on the dump geometry, the exothermic reaction of pyrite oxidation causes a temperature rise in the order of tens of degrees. In such a case, this temperature rise triggered a high oxidation rate of the organic matter. In this mine alum shale samples contain 4 to 6 % of pyrite with typical particle size of 3 - 5 μm.

$$2\ FeS_2\ +\ (1.5+2x)\ O_2\ \longrightarrow\ Fe_2O_3\ +\ 4\ SO_x \tag{4.3}$$

Iron sulfide (FeS) is well-known to have pyrophoric properties and that it could be a source of ignition [30]. Iron oxide in the form of rust, which is formed by corrosion of the steel surfaces, may be exposed to atmospheres containing hydrogen sulfide. Rust and hydrogen sulfide react together to form iron sulfide (Eq. 4.4). Such formation of iron sulfide could occur in crude-oil cargo, distillation unites, storage tanks, gas lines... Further reaction of iron sulfide with elemental sulfur forms pyrite (FeS_2) (Eq. 4.5). When exposed to the air, iron sulfide species form pyrophoric material, which in contact with inflammable vapours may cause an explosion. For example in the seventies minor explosions occurred in the cargo tanks of an oil tanker which was discharging Qatar crude oil, having a high hydrogen sulfide content. A concentration of 5 % vol. gas has been measured in this oil [31]. Investigations showed that the formation of pyrophoric chemical species was the source of ignition.

$$2\,FeO(OH) \quad + \quad 3\,H_2S \quad \longrightarrow \quad 2\,FeS \quad + \quad S \quad + \quad 4\,H_2O \tag{4.4}$$

$$FeS \quad + \quad S \quad \longrightarrow \quad FeS_2 \tag{4.5}$$
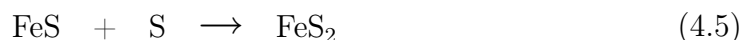
The sulfide mixture (FeS_2 and FeS) formed by the reaction of iron oxide with hydrogen sulfide presented an important oxidation reactivity when exposed to the air [32]. The study showed that at lower temperatures, an initial rise in temperature (first stage of oxidation) was followed by a temperature steady-state and then by a fast temperature increase (second stage of oxidation). At a temperature of 75 and 100 °C sparkling was even observed as soon as the sulfides were exposed to air.

As the formed iron sulfide mixture contains also elemental sulfur and water, the role of both co-products were analyzed. It turned out that sulfur-free iron sulfide presented the same pyrophoric reactivity as pyrite. The importance of water during this pyrophoric oxidation was also studied. Dried mixture of iron sulfide and elemental sulfur was exposed to air and the temperature variations were recorded. A first temperature increase up to 40 - 50 °C was followed by a steady temperature, which started to drop after a certain time. Water drops were then added to the sample without any changes during the following few minutes. Suddenly the temperature rose rapidly and the sample started to smoulder. Obviously the presence of moisture was very important for the pyrophoric activity.

Other oxidation experiments were performed on this dried iron sulfide mixture by exposure to air with various values of the relative humidity. This was done in order to investigate the effect of moisture concentration. On a sample of 3 g

at $20\,^\circ$C, experiments with relative humidity smaller than 50 % presented only a slight temperature increase followed by a slow return to ambient temperature. However the experiments performed at higher relative humidity showed a very fast temperature increase. This pyrophoric oxidation occurred as a one-stage thermal process in opposition of what was observed for raw sulfide mixture.

The temperature steady-state observed between the first and the second stages of oxidation of the raw sulfide mixture may therefore correspond to the evaporation of the bulk water which is an endothermic process [32]. Over this range of temperature, there would be a balance between the heat evolved during oxidation and the heat absorbed by evaporation.

In other publications [33, 34], investigations of the ignition behaviour and the explosion characteristics of iron sulfide dusts have been undertaken. Determination of the critical particle size and the minimum ignition temperature for iron sulfide species such as pyrrhotite (FeS) and pyrite (FeS$_2$) has been determined in dust explosion tests [35]. It appears that the spontaneous heating of finely divided pyrite may be responsible for the ignition of stored pyrite and in pyrite mines [36]. In those cases mine fires were extinguished by flooding, however the fires were reignited again afterwards. In fact, some ferrous sulfide is produced by the partial oxidation of pyrite with water, present in large quantities due to fire extinguishing defense. Ferrous sulfide is a normal weathering product of pyrite, and as described previously, presents pyrophoric properties. Therefore when the water used for extinguishing is drained away, ferrous sulfide ignited spontaneously on contact with air.

Recently a new research was made on decomposition and oxidation of pyrite [37] and described precisely the mechanisms and kinetics of pyrite transformation in inert and oxygen-containing atmosphere.

4.4   Brown coal

The history of spontaneous coal combustion is as old as coal mining itself. Coal fires occurred during the mining, transportation and storage or stockpiling. Autogenous heating of coal can result in spontaneous combustion when other favourable conditions exist [38]. It has been observed that when coals are exposed to an oxidizing atmosphere even under ambient conditions, exothermic oxidative reactions may take place. Such heat release may lead to a temperature rise, if not appropriately removed. This may result then in smouldering processes and subsequent fires [39].

Coals of higher rank are less prone to oxidation such as lignite and bituminous coals, however rank dependency is not definitive. Rather, liability to spontaneous combustion differs with different coals and stockpiling or handling conditions. Moisture content within coals is suspected to play a role during the spontaneous heating like other conditions such as sulfur content, thermal conductivity, heat of wetting, porosity, air diffusion within the pile... [40].

Pyritic coal is specially known to exhibit a tendency towards spontaneous heating and ignition when stored in a place where there is access of air [36, 38]. It was proposed that the oxidation of pyrite in pyrite-rich coal to pyrophoric ferrous sulfide may be responsible for the generation of a lot of heat. The studied coals contain between 0.4 % of sulfur for high volatile bituminous coal up to 1.6 % of sulfur for lignite coal.

4.5 Linseed oil

Linseed oil (*Linum catharticum* L.) is a common ingredient in varnishes and oil-based house paints. It is used for its excellent drying quality, because linseed oil polymerizes and hardens when spread on a surface and exposed to air.

However linseed oil is known already for a long time to set cotton fibers such as rag on fire, even several hours after coming into contact with them [41]. A small amount of linseed oil is all that is needed to obtain this pyrophoric effect. Linseed oil, which consists of the mixed glycerides of oleic, linoleic and linolenic acid, autoxidizes rapidly in air. The autoxidation of these unsaturated fatty acids releases sufficient heat to ignite whatever was used to apply the linseed oil. Both autoxidation and polymerization give the linseed oil the capacity of self-heating up to self-ignition.

Other oils such as perilla oil (*Perilla frutescens* L. Britton) and tung oil (*Vernicia fordii* Hemsl.) may cause similar problems than linseed oil even under normal circumstances of use.

4.6 Fires at composting facilities

The composting process benefits from the ability of the mix of ingredients and microbes inducing self-heating. This property drives compost drying and physical degradation. This temperature increase allows also the pathogen killing. To maintain this useful heating cycle, the compost biology has to be continually furnished with appropriate environmental and nutritional feeding. In turn, this

vigorous biology loses about a third of the energy produced as heat, which makes the composting process successful by supporting an optimal biological activity [42].

Minor fires at composting facilities seem to be fairly common, however sometimes these fires turn out in a devastating events such as the ones in the US composting facilities of Hartford (Connecticut), Silver Creek (Texas), Hamilton (Ohio) and Cobb (Georgia) [43]. Composting is made of bulk organic materials and therefore it is prone to an oxidation. In opposition to a fire which is a rapid chemical oxidation, composting undergoes a biological oxidation. In fact, a simplified chemical equation for combustion by fire shows the same inputs and outputs as a simplified equation for composting (Eq. 4.6).

$$\text{Organic matter} \quad + \quad O_2 \quad \longrightarrow \quad \text{residue (ash)} \quad + \quad CO_2 \quad + \quad H_2O \qquad (4.6)$$

Generally composting fires result of spontaneous combustion. However, it is also known that fires at composting facilities also have developed from other causes, including lightning strikes, heat from equipment, sparks from welding activities, wildfires and arson.

The processes that initiate spontaneous combustion raise the material temperature above the lower temperature limit of runaway, where the self-heating reactions sustain themselves. For fires that occur in bulk organic materials, the first steps are usually due to biological self-heating. Respiration of living plant cells and microbial activity generate heat and start the temperature rise. Through biological activity, temperatures can reach 70 - 80 °C. At this point, the microorganisms die or become dormant and the biological heating stops. It has to be noted that there is a gap between the temperature limits of biological activity (80 °C) and temperatures at which organic materials ignite (150 °C). This gap is bridged by chemical processes which include chemical oxidation, slow pyrolysis, and adsorption or condensation of gases within dry charred particles. In particular, chemical oxidation of dry materials noticeably increases at around 80 °C.

In this chain of reactions that leads to spontaneous combustion of composting, following factors are needed: relatively dry materials or dry pockets, large well insulated piles or vessels, limited air flow, and time for temperature to build up. However the temperature rise can be moderated by heat loss from the evaporation of moisture, air movement and exposure to the cooler ambient environment. The

critical moisture range that supports spontaneous combustion is roughly 20 - 45 %. Above 45 %, there is enough moisture available for evaporation to hold down temperatures. Below 20 %, there is not enough moisture to sustain the biological activity that initiates the temperature rise. For composting, operating moisture contents range from 40 - 70 %, although the optimal range is typically 50 - 60 %. However, materials being composted often drop below 40 % moisture as process heat drives off water. Therefore in an active composting system, the possibility of spontaneous combustion grows as time increases because the compost dries. Moreover extremely dry piles of compost do not heat because biological activity is greatly reduced.

As conclusion it is worth mentioning that the ignition conditions and the risks caused by the fires at 'composting facilities' can be applied to nearly any facility that handles large volumes of bulk organic materials, including wood and bark grinding sites, paper mills that store wood chips, hay barns and mulch [42].

4.7 Haystack fires

Hay fires occur quite frequently and are due to self-heating processes which can lead to spontaneous combustion of whole stacks of hay.

The heating of hay is the result of a complex chain of biological events and chemical reactions and can be a result of the presence of excess surface moisture (rain, dew, flood water...) trapped inside hay at baling. It can also occur when the plants are too green (internal moisture) at baling or a combination of both. Therefore maximum moisture level within hay bales are suggested by agricultural offices to minimize the likelihood and danger of hay heating (Table 4.1). It was observed that if hay is baled with moisture contents well above the suggested level (> 3 %), the temperature will rise substantially.

Table 4.1: Suggested moisture contents for safe storage of various hay bales [44]

Hay bale type	Moisture content range (%)
Small rectangular bales	18 - 20
Round bales	14 - 18
Large rectangular bales	Under 14

The plant does not die when cut, and metabolic fuel is still available in the plant tissue [44]. This allows plant respiration to continue until the moisture concentration is low enough that metabolic activity is no longer possible. Therefore the initial heating occurs because of living processes, for instance the respiration of the plant material and bacteria activity, which continue for some time after plants are cut. The temperature can often raise about 45 °C through such biological processes (Table 4.2).

Table 4.2: Causative agents in the heating of hay and their active temperature range

Causative agents	Temperature range (°C)
Plants	up to 45
Fungi and bacteria	up to 65
Heat resistant fungi	45 to 85
Exothermic chemical reactions	from 70

The self-heating may then continue up to about 65 - 70 °C when organisms (fungi, bacteria), which are active at the higher temperatures, become active and generate heat through digestion. Then heat nests can appear at this stage, triggering heat resistant fungal spores before the fodder dries out. Hay stacks often cool down after this period when food for the organisms is used up and their activity diminishes. This will occur if the heat is able to be quickly conducted to the outside of the stack, like by loosely stacked bales. Chemical reactions are responsible if the temperature continues to rise above the changeover point of 70 °C. Once the stack reaches this temperature, a rapid rise to the spontaneous ignition point of 200 °C can be expected if enough oxygen is available, or up to 280 °C if oxygen is limited for instance in tightly stacked bales.

A small volume of wet hay surrounded by dry hay can cause spontaneous heating, which may dissipate within days, depending on the drying or storage conditions, or may continue to rise over a period of weeks. Most fires resulting from spontaneous ignition start between two and seven weeks after storage, but later fires have occurred in stored hay that has become wet by flooding.

Chapter 5

Sewage sludge fires

5.1   In Canada

The first thermal event on dried sewage pellets was recorded by the *Natural Life magazine* and happened during Summer 2001. On its website[1], the magazine announced that the sewage sludge pellets of the City of Toronto were on fire. In fact the sludge pellets were smoldering in a field where they had been dumped for storage. It was announced that sewage sludge pellets had undergone spontaneous combustion, and that one thought about a process where the microbial activity in the pile caused the pellets to heat to the point of burning.

An article published by the Ontario Fire Marshall's Office (Canada) confirmed that the City of Toronto had problems with the self-heating of sewage pellets in a storage silo [45]. In this article, fires and explosions taking place in other wastewater treatment works and storage places were enumerated:

- a smouldering fire in a sludge pellets stockpiled at a farm in Windsor (Canada);

- a series of explosions in a Windsor pelletization plant in October 2002;

- an explosion in the fertilizer plant at the STP of Milwaukee (USA) in 1996 caused serious injuries to a worker and $ 4.5 million worth of damage to the plant and property.

They pretended that when the moisture content of this material reaches between 5 - 10 % by weight of the product, aerobic biological decomposition occurs, causing self-heating. Water generated by this process is absorbed by the surrounding sludge, which intensifies the self-heating process. A smouldering fire may occur if the heat generated by this process is not dissipated to the surroundings.

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[1]www.life.ca

5.2   In the USA

In December 2005 a press release of the society *Cv Technology Inc.*, a cooperation specializes in the prevention and elimination of explosion hazards, presented the case of a dust explosion induced by a smoldering nest in large storage silo of dried sewage sludge [46]. The investigation concluded that the nest quickly changed from a smolder to a very vigorous combustion zone due to the increased air flow when the fans and vent were started. The dust was disturbed into a dust cloud that reached explosive concentrations very rapidly.

The society *Cv Technology Inc.* estimated that the smouldering nests in the case of sewage sludge was induced by:

- an aerobic reaction due to its organic composition, which releases heat;

- a critical material mass, in which such smouldering nests can form deeply inside.

5.3   In the United Kingdom

The recent changes in strategy of processing sewage waste cause a rapid increase in sewage sludge drying plants. This was specially induced by the new EC regulations, which effectively banned the disposal of sludge to sea and by the UK government which increased the taxes on the use of landfill [47].

It is known in UK, thanks to a report published in 2005, that several drying works sustained dust cloud explosions and fires [48]. These events were attributed to the production of explosive dust and that the finished product can self-heat leading to a smouldering fire.

For these reasons, some information documents are revised regularly, which contains for instance additional information on the application of limiting oxygen concentration (LOC) as a means for preventing explosions. Moreover the industry collected information on dried sewage sludge to establish if it should be classified as dangerous for transport by road.

In the majority of drying processes currently operating in the UK, the sewage dust produced within the dryer is classified in an St1 explosion class dust. This classification concerns the combustible dusts with an explosion constant between 0 - 200 bar·m·sec^{-1}. For comparison, wood flour is also in this explosion class with

an explosion constant of 90 - 190 bar·m·sec^{-1}. One suspected cause of the dust explosion is the ingress of metallic pieces or small stones into the drying process. Such pieces may provide an ignition source as they can produce sparks if they become jammed in the moving machinery giving rise to friction heating.

The main preventive measure proposed for safety within the dryer plants of the UK consist in avoiding a flammable atmosphere by inertisizing. The minimum oxygen level that will support an explosion is determined by the limiting oxygen concentration (LOC) of the dryer. Such a value ranges between 5 - 15 % vol. Usually the maximum permissible oxygen concentration is 2 % below the recommended LOC of the dryer.

5.4   In France

First it is worth mentioning that the thermal events occurring in France have been known only since May 2007, 3.5 years after the beginning of this PhD project. The performed analyses and the obtained results were discussed with the investigators of this French STP from that stage and until the end of this project.

Near Paris (France), the wastewater treatment plant of Valenton (SIAAP[2] - Seine Amont) experienced several unusual self-heating processes during the storage of dried sewage sludge. The used storage silos are 22 m high and 6 m of diameter. Even if the material has a temperature between 40 - 45 °C at the beginning of the storage, spontaneous temperature increases occurred regularly since June 2006. In fact these thermal event started, when it has been decided to reuse this waste in agriculture.

These sewage biosolids were in fact destined in the future to the agriculture for fertilizing purposes. To accomplish this goal, the whole dried sludge production has to undergo a traceability process, which consists in numbering and controlling every output batch. In addition of the production time, the quality controls extend the storage time of the dried biosolids. All together, the traceability process would need around 21 days. However, it is not currently possible to store the sewage granules for this period due to the self-heating and runaway events, which occur generally after only a few days of storage. In

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[2]Syndicat interdépartemental pour l'assainissement de l'agglomération parisienne (Greater Paris Interdepartemental Sanitation Authority)

consequence, actual storage of the dried sewage sludge was reduced to 5 - 7 days in order to insure a secure handling of the material. Unfortunately it is currently eliminated as a combustible waste, instead of being used as a fertilizer in agriculture.

In order to elucidate this phenomenon, the analyses made on the dried sewage sludge in 2001 were compared to a new set of analyses performed in 2006 and 2007. The study of the spontaneous heating process and the processing of the obtained results were assigned early 2007 to several consultants[3] well-skilled in environmental techniques and safety.

The characterization made in 2001 presented the expected results concerning the dry solids content ($> 92\%$) and the self-ignition temperature of 130 - 190 $°$C depending on the performed tests. The security tests carried out since 2006 consisted in a thermal analysis called ONU N4 used for the classication of self-heating solid material. These tests allow the monitoring of the inside temperature of a material contained in a cubic crucible made of metallic net. The crucibles are of different sizes and they are then placed in an oven ventilated with air at a definite temperature. The conclusion of this test was that the dried sewage sludge of Valenton may be classified as self-heating organic solid. Moreover the extrapolation of the ONU N4 test indicated that the storage conditions would lead to a self-heating behaviour. These results were confirmed by other tests performed in different safety laboratories.

Thermal analyses of the dried sewage sludge from the STP of Valenton were made in December 2006 by using differential scanning calorimetry (DSC) and thermogravimetry. As results an endothermic reaction was observed between room temperature and 200 $°$C, which was assigned to the water evaporation. Then a exothermic reaction starting at 233 $°$C led to a maximum spontaneous temperature increase of ~ 250 $°$C. In conclusion of this test, the dried sewage sludge was assigned to the class of the most reactive solids due to the low temperature limit of runaway.

In addition of the previous analyses, it has been noticed[4] in May 2007, that the tertiary sludge from Valenton, which contained an additional iron content due to the chemical precipitation process by ferric chloride, were a lot more reactive than the biological sludge (without any addition of iron).

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[3]Dr Thomas Haltmeier (independent consultant), Jean-Paul Chabrier (environmental consultant for SIAAP), Prof. Dr Serge Walter (The Mulhouse Graduate School of Chemistry)

[4]intern pre-report of Dr Thomas Haltmeier

The report presented in July 2007 by another consultant[5] consisted in the thermodynamic study of the self-heating and auto-combustion processes. The analyses made by differential scanning calorimetry presented a light exothermic event between 30 - 100 °C followed by two major exothermic events. Resulting from these analyses, it seems that the first large exothermic process already occurs at room temperature, but at a low reaction rate. Moreover the overall reaction enthalpy is largely sufficient to induce a temperature increase up to auto-combustion of the dried sewage sludge. Finally the role of iron in this spontaneous process was discussed. In fact, iron is suspected to be enrolled in some redox reactions due to its electrochemical properties. Such redox system would easily catalyze further reaction by electrons transfer.

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[5]intern report of Prof. Dr Serge Walter

Chapter 6

Sewage sludge fires in Switzerland

6.1   Situation in 2003

Early in 2004 the STP of Bern presented a summary about the sludge fires occurring at the cement industries to which they had delivered dried sewage granules for incineration. In 2003 several temperature increases, sometimes followed by spontaneous fires, took place in storage silos containing dried sewage granules (Table 6.1). The cement industries Vigier at Péry (BE) and Holcim at Untersiggenthal (AG) and at Eclépens (VD) all experienced temperature increases and fires in silos containing dried sewage granules. The transport to the furnace had to be interrupted several times due to the release of smoke and the formation of sintered granules obstructing the pipes and valves. Therefore the material incineration could not be made within the furnace of the cement industry for security reasons. The granules needed to be transported to an incineration plant for final elimination.

It was observed that the thermal events and the consecutive fires happened regularly after the delivery of sewage granules coming from the STP of Bern. Such incidents harmed seriously all the efforts performed to highlight the value of recycled dried sewage granules as a biofuel. In April 2003 the first reluctances for the incineration in cement furnace were expressed and difficulties to sell sewage granules to the Cemsuisse affiliated industries started (Table 6.2).

Table 6.1: Temperature increases and fires in silos containing the dried sewage granules from the STP of Bern

Date	Industries	Comments
Feb.2003	Vigier, Holcim	several fires in storage silo
20.02.2003	Vigier	strong temperature increase in storage silo
		stop introducing granules into the furnace
24.02.2003	Vigier	fire in storage silo
10.04.2003	Bern STP	temperature up to 100 $^\circ$C in the storage silo
24.04.2003	Holcim	strong temperature increase in loading silo
		stop introducing granules into the furnace
28.04.2003	Holcim	fire in storage silo
17.06.2003	Holcim	temperature between 85 - 100 $^\circ$C
02.07.2003	Holcim	fire in storage silo
		installation of an air dryer system and data logging
		devices for temperature and humidity monitoring
06.07.2003	Holcim	fire in storage silo containing sewage granules
		delivered 2 days before
08.08.2003	Holcim	fire in storage silo
28.09.2003	Holcim	fire in storage silo
09-12.10.2003	Holcim	high temperature in storage silo
21.12.2003	Vigier	fire in storage silo
24.12.2003	Holcim	temperature of 160 $^\circ$C in storage silo
03.02.2004	Holcim	high temperature in storage silo
		delivery stop of dried granules from Bern

Table 6.2: Observations and measures towards temperature increases and fires

Date	Measures, events & hypotheses
07.05.2003	Dried sewage samples from different STPs sent for analysis of the specific surface (Labor Spiez, CH)
15.05.2003	Dried sewage samples from STP of Bern examined at the Institute of Safety and Security for the determination of the explosion limit, smouldering temperature, etc.
16.05.2003	Information about a cement industry in Holland with a 450 m^3 silo specially made for sewage granules: no problem during storage
16.05.2003	Information about the use of sewage granules in tar industry: no problem observed
20.05.2003	Hypothesis of a biological reaction as trigger for the temperature increase
20.05.2003	Results from the Institute of Safety and Security: - no explosive behaviour of sewage granules from the STP of Bern - no reaction at 70 °C - smouldering fire only above 140 °C
21.05.2003	Second batch of dried sewage samples from STP of Bern submitted to the Institute of Safety and Security for analyses
21.05.2003	Information about a biological investigation in an external laboratory
22.05.2003	Hypothesis concerning the influence of the storage silo shape
04.06.2003	Delivery of granules from the STP of Bern to Vigier cement industry suspended due to the high risk of fire
02.07.2003	Hypothesis concerning the influence of humidity in storage silos Installation of an air dryer system and data loggers for temperature and humidity at Holcim (Untersiggenthal)
03.07.2003	Third batch of dried sewage samples from STP of Bern sent to the Institute of Safety and Security
08.07.2003	Proposition of storage experiments in an industrial silo (Hüntu) with air flow through the granules, investigation about the dryer influence, the transport and unloading processes
16.07.2003	temperature increase noted generally after ~12 hours
Summer 03	Two experiments in an industrial silo of 20 m^3

6.2   First attempts for the sludge fires elucidation

6.2.1   Physical analyses of granules from several STPs

During 2003 several analyses were carried out on sewage samples from the STP of Bern and compared to the other Swiss STPs (Table 6.3). This study was supervised by Ing. Hermann Kunz, chemical engineer at the STP of Bern. The report concerning the physical properties showed that the solid content in granules from Bern, which is around 92 % DS, is not exceptional since the solid content varies from 87 % DS for granules from the STP of Schwyz (SZ) to 95 % DS for samples from the STP of Altenrhein (SG).

Table 6.3: Characteristics of the dried sewage granules from several Swiss STP

STP	Dry solids (%)	Ash [a] (%)	Dust [b] (%)	Mean diameter (mm)	Density (kg/L)	Surface [c] (m^2/g)
Bern [d]	91.6	49.7	0.7	2.04	0.59	2.87
Altenrhein	94.7	51	12.4	1.27	0.71	
Biel	89.7	54	0.2	2.56	0.78	
Colombier	94.3	50	94.4		0.60	4.21
Oberraach	94.2	50	33.0	1.36	0.78	
Schwyz	87.1	52	17.5	1.52	0.52	

a) remaining solid after 2 h at 650 °C

b) fraction with mean diameter smaller than 0.56 mm

c) BET - specific surface determination by N_2 adsorption at 77 K

d) average value

The physical characteristics of granules from the STP of Bern corresponded to an average value for the ash content, density, diameter and surface. However it is worth to mention that the dust content is very low for the samples from the STP of Bern. Only the granules from the STP of Biel present a smaller dust content (0.2 %). Some other samples have important fractions of fine particles: for instance granules from the STP of Altenrhein (SG) and Schwyz (SZ) contain 12.4 % and 17.5 % respectively of fine particles. An extremly high dust ratio is measured for sewage material from the STP of Oberaach (TG) with 33.0 % dust content. Finally the STP of Colombier (NE) produces a very fine waste powder (94.4 % dust content).

6.2.2 Moisture content and particles size of the Bern granules

The humidity present in the dried granules from the STP of Bern is measured daily using a specific dryer device. The humidity contained within the sewage granules varies between 4 - 12 %, however the average humidity of 8 % is frequently noted.

The particles size is also analyzed regularly at the STP of Bern by sieving dried granules on a specific device composed of sieves from 0.56 mm to 3.15 mm meshsize. The mean diameter of the granules is approximatively 2 mm with some fluctuations from 1.6 to 2.3 mm for the granules mean diameter, depending of the analyzed batches. Generally the dust fraction (< 0.56 mm) and the large granules fraction (> 3.15 mm) vary a lot from one sample to another .

In Fall 2003 Ing. Hermann Kunz also studied the relationship between the humidity and sieving repartition in the dried granules of the STP Bern. The study represented a first step in the research concerning the self-heating process during the storage of dried sewage granules. A single sieving experiment was carried out in the civil engineering division of Bern University of Applied Sciences in Burgdorf. There the sieving analysis covered a larger sieving range from 0.125 mm to 32 mm meshsize in ten steps, with a meshsize doubling from one sieve to the next one (Figure 6.1).
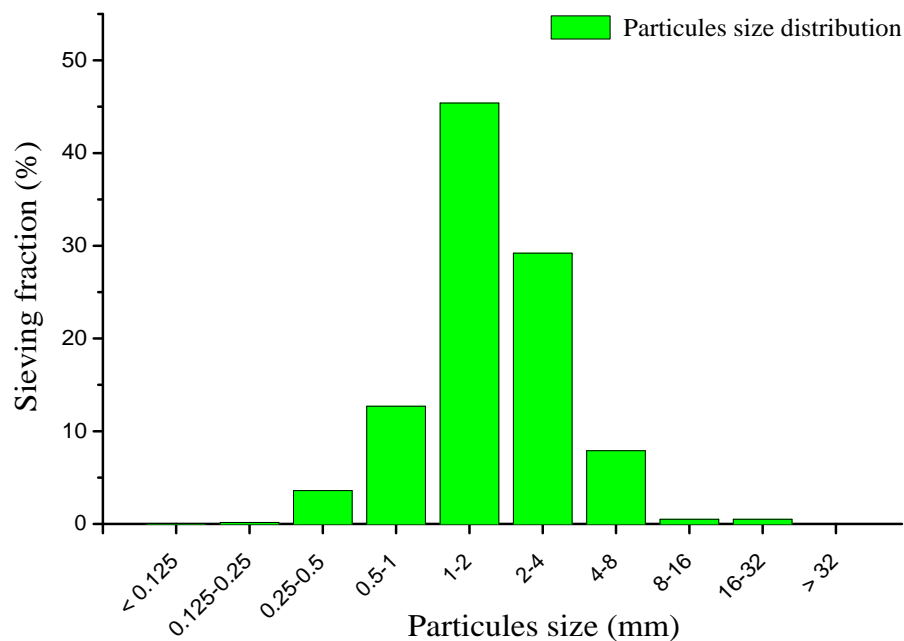
Figure 6.1: Particles size distribution of dried granules from the STP of Bern performed on a sieving device with sieves from 0.125 to 32 mm meshsize

This analysis also showed that the major fraction of the dried granules from the STP of Bern (45.4 %) has a particle size between 1 - 2 mm. Larger granules (> 4 mm) represented only 8.9 %. The humidity contained in these fractions was then measured and it turned out that the granules with a particle size smaller than 4 mm had quite the same humidity content about $\sim$ 7.5 % (Figure 6.2). However for larger granules, the humidity content increased and an important variation was observed from one analysed sample to another. Specially in granules with particle size larger than 8 mm the humidity content fluctuated between 9.2 to 40.5 %.
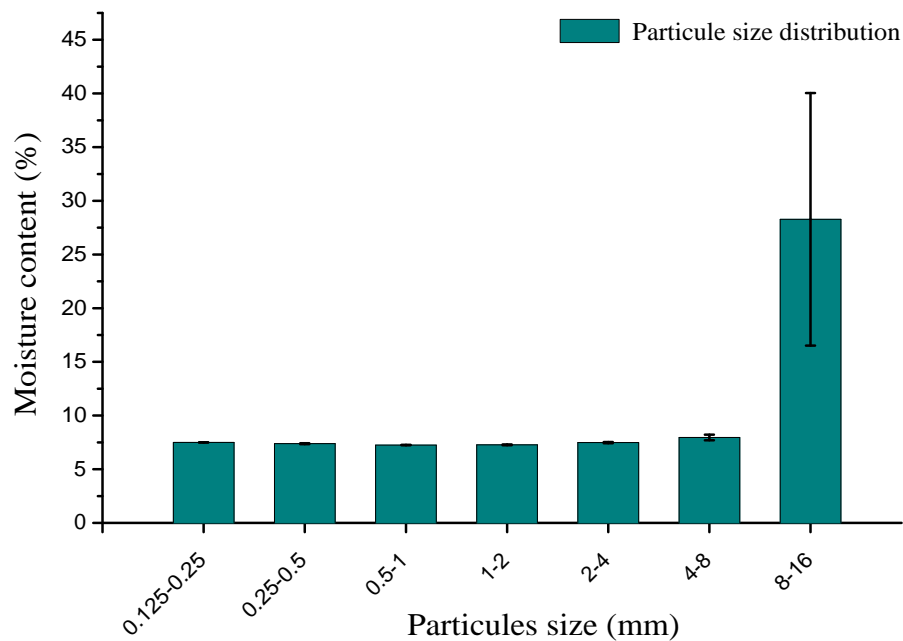
Figure 6.2: Moisture content in the sieved fractions of the dried granules from the STP of Bern

In the conclusion of this report, Ing. H. Kunz highlighted the presence of important and variable moisture content in large granules, corresponding to 1 % of the analysed granules. By the mean of photogaphies, the shape and the surface structure of the granules were also reported showing that the external apects of the large granules varied more than for the smaller ones.

6.2.3   Analyses from the Institute of Safety and Security

Several samples of dried granules from the STP of Bern were sent for analyses to the Institute of Safety and Security (Basel).

First set of analyses

Two samples were analyzed during this study. The first one was taken from the loading silo at the STP of Bern and was left during 14 days under normal atmosphere. The second sample, which came directly from the dryer plant, was kept under inert atmosphere and was immediately delivered to the Institute of Safety and Security. Several tests such as decomposition tests under air and nitrogen, tests of self-ignition in 400, 1000 and 1600 ml containers and dust explosion tests were carried out on both samples.

The first report of the Institute of safety and Security stated that both samples of these dried granules presented the same reactivity (Table 6.4). The first exothermic event occurred at temperatures above 130 °C under air, and no reaction happened up to 350 °C under nitrogen atmosphere. It was also demonstrated that the dried granules from the STP of Bern presented no tendency to self-heating even up to 70 °C. The tests concerning dust explosion tests showed negative results.

Table 6.4: Decomposition tests of sewage granules from the STP of Bern performed under air and nitrogen at the Institute of Safety and Security in Basel

	Samples [a]		1st exothermic event		2nd exothermic event	
Tests	Name	Prep.	Peak (°C)	ΔT (°C)	Peak (°C)	ΔT (°C)
Air	S1	received	130 - 270	166	270 - 350	117
Air	S1	dried	140 - 290	152		
N_2	S1	received	- [b]	-	-	-
N_2	S1	dried	-	-	-	-
Air	S2	received	140 - 320	144		
N_2	S2	received	-	-	-	-

a) S1 is the sample left during 14 days under air and S2 is the sample under inert atmosphere delivered directly to the Institute of Safety and Security. Both samples were analyzed twice: once received and once after being dried under N_2 at 130 °C during 4 hours

b) no exothermic event

As conclusion the report indicated that the observed temperature increase and the consecutive smouldering fire could not be explained by the performed analyses.

Second set of analyses

During this second set of thermal analyses, the tests of decomposition under air and the tests of dust explosion were repeated and presented the same results. In addition this time, the enthalpy change (ΔH) of the thermal events was analyzed using differential scanning calorimetry. The sample, without further treatment, was analyzed in a closed crucible under air with a heating rate of 4 K/min. The DSC analyses presented two exothermic peaks at 118 and 218 °C (Table 6.5).

Table 6.5: Peak maxima and enthalpy changes measured by DSC for samples of dried sewage granules from the STP of Bern

	Thermal events		Enthalpy change
	T_i - T_f (°C)	T_{max} (°C)	ΔH (kJ/g)
1st peak	68 - 156	118	- 32
2nd peak	191 - 257	218	- 19

This set of analyses was performed in order to determine the transport classification used for dangerous materials. The analyses showed that dried granules belonged to the transport class 4 for inflammable material without any further precision concerning the subclasses 4.1 for inflammable solid or 4.2 for self-inflammable materials.

Third set of analyses

A last set of analyses made by the Institute of Safety and Security confirmed the previous results. Theses tests allowed the determination of the transport subclassification and gave in fact positive results concerning the 4.2 subclassification used for self-inflammable materials.

6.2.4 Storage experiments in industrial silo

In order to find an explanation for the self-heating and runaway processes which were observed while the sewage sludge granules were stored, it has been decided by the STP of Bern to carry out several storage experiments in a large silo for further study of these thermal events. Therefore an industrial silo of 18 m^3 has been installed in a gravel pit called 'Hüntu' and in Summer 2003 two storage experiments with the sewage granules from the STP of Bern have been performed.

During these storage experiments, the silo was equipped with a ventilator placed at the top of the silo for aspiration, and a venting aeration system placed at the bottom of the tank (Figure 6.3). The temperature was monitored by two logging devices placed at position A and D at 20 cm depth, and also measured manually at position B, C and E at different depths twice a day. Carbon monoxide and humidity were also monitored by a logging device placed at the top of the silo.
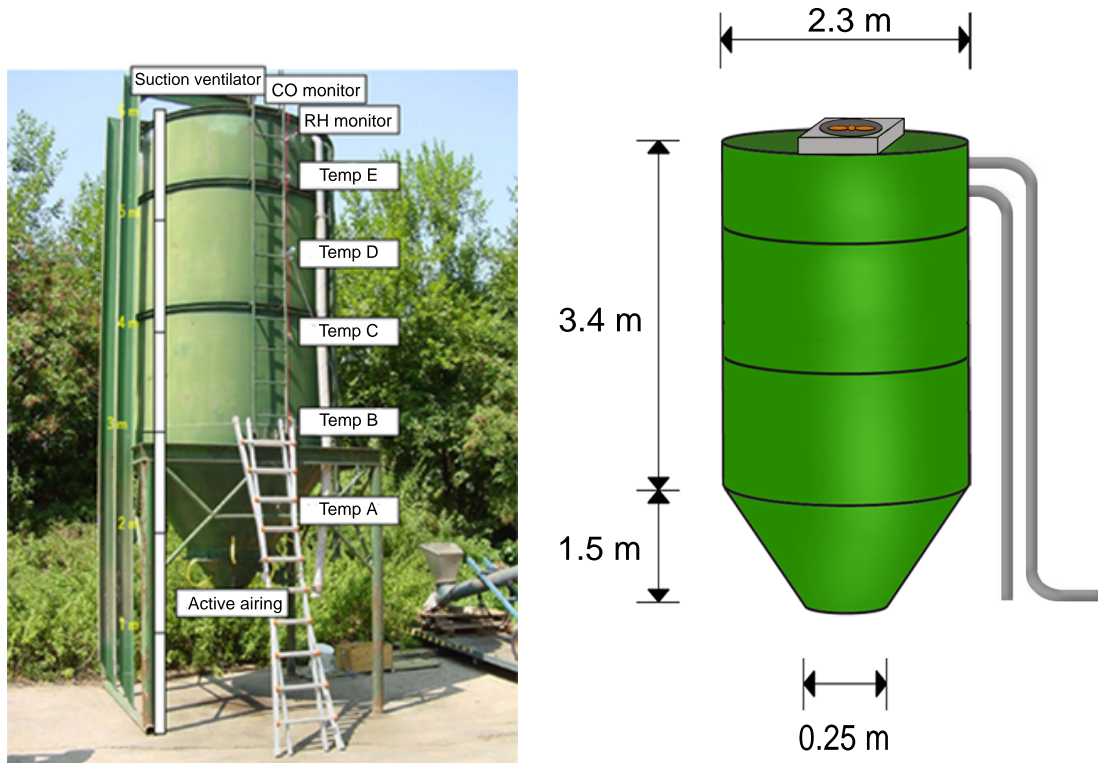
Figure 6.3: Industrial silo of 18 m^3 used for the storage experiments (report by Ing. H. Kunz) (left) and the scheme of the silo with the ventilator and the two pipes for the granules pneumatic transfer and the dust exit (right)

The storage experiments were divided in three main time periods consisting in first no airing of the stored granules and no aspiration neither, secondly an aspiration from the top of the silo, thirdly an active airing from the bottom of the tank.

First storage experiment

The first six hours of the storage experiment were performed without any air aspiration. During this period the inside temperature was around 50 ˚C. However, 24 hours later, a spontaneous temperature increase occurred and the temperature within the granules reached ∼ 80 ˚C. The silo was emptied after 1.5 days of storage because the inside temperature was still at 80 - 85 ˚C.

Second storage experiment

The second storage experiment was performed without any air aspiration at the top of the silo for the first eight days. During this first period of time, a temperature increase occurred at the bottom position of the silo (position B) reaching 80 °C. Then this temperature increase propagated upwards to the position C. When the aspiration at the top was started, the temperature increase up to 90 °C happened at a even higher position in the silo (position E). Two days later, the active airing was started without any changes in the temperature profiles within the stored granules. Even after six days under active airing and aspiration, only the upper part of the silo (position E) presented a temperature around 90 °C, elsewhere the temperatures were between 30 - 60 °C. The silo was finally emptied after 16 days of storage.

Part III

Aim of the work and Hypotheses

Chapter 7

PhD project

The final state of the treated sewage sludge at the STP of Bern consists in dried granules. This waste still needs to be incinerated, in the furnace of a cement production plant for instance. The dried granules are therefore loaded directly into a truck placed under the loading silos at the STP of Bern. After the road transport to the cement plant, the granules are transfered with compressed air into a large storage silo[1], where they are kept until being used as refuse derived fuel for the cement production.

Figure 7.1: Smouldering fire causes the formation of large piece of agglomerated granules (left) and smelt residue from sewage granules (right)

However there are problems of storing the dried sewage granules: self-heating occurred sometimes during the storage period, which may even trigger the auto-ignition of this combustible matter. Thermal runaway and consecutive smouldering fire might start after loading the sewage granules in the storage silo. At this stage, a steep temperature increase, the water condensation at the tank top, the raise of CO level, the smoke formation and a characteristic smell are observed. The

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[1] silo capacity: 175 m^3 (h = 10 m, d = 4.7 m), for the storage of the dried sewage granules at the Holcim cement plant at Untersiggenthal

burning material has to be removed immediately from the storage tank, because it might melt together and block the transporting pipes (Figure 7.1). All these observations give an idea about the reactivity of this waste and the risks induced by such spontaneous heating and combustion.

These smouldering fires in the storage silos disturb the working schedules and processes of the cement production plant and at the same time the timely elimination of the dried sludge from the sewage treatment plant. Therefore explanation of this phenomena and technical solutions to suppress it were needed. For these reasons the FOEN, the CEMSUISSE and the SPT of Bern (ARA Bern) decided to start a joint research project on the runaway of dried sewage sludge in storage tanks. The project was mandated to Prof. Dr Titus A. Jenny from the Chemistry Department of the University of Fribourg, who proposed to study the problem in a PhD thesis. This initial project was expanded by a collaboration with the College of Engineering and Architecture of Fribourg through a broader project financed by the Innovation Promotion Agency (CTI) of the Federal Office for Professional Education and Technology (OPET). The extension was supervised by Prof. Dr Kurt Käser from the Department of Industrial Technologies, College of Engineering and Architecture of Fribourg, a member of the University of Applied Sciences of Western Switzerland.

7.1   Goal

The aim of the project was to understand the thermal runaway occurring in dried sewage sludge storage tanks from its intrinsic origins to the resulting fire. It also consisted in providing some propositions of technical measures for the smouldering fire prevention.   This PhD project is therefore divided in two main parts: the experimental project and the research project.

7.1.1   Experimental project

Several smouldering fires and strong self-heating processes occurred in 2003. As the project started at the beginning of 2004, the first target was to find measures to avoid these spontaneous thermal events. Therefore it was proposed to start this project with large scale storage experiments in order to have a direct comparison with the real situations.

The first assumption was that the organic part of the sludge is spontaneously oxidized releasing enough energy to keep the process going or eventually to accumulate enough heat to start combustion of the organic material. This decomposition might be slowed down or completely suppressed by the addition of an anti-oxidant before that the dried granules are stored in silos, as it is used in the polymer industry to stop the oxidative degradation, which occurs during the processing of polymeric materials.

The experimental project therefore consisted in some storage experiments with sewage granules treated with antioxidants and to compare them to the storage experiments made with casual - untreated - granules under the same conditions. It was also the occasion to study the impact of the blowing process used for loading the granules from the transport truck to the silo. Actually at the cement plants, the granules are blown up from the truck tank to the storage silo with compressed air, which might be cooled beforehand.

7.1.2   Research project

In order to guarantee a long-term use of dried sewage sludge as alternative fuels for the cement industries, its transport and its storage must be safe and secure. This implies that the mechanisms leading to the thermal runaway and the resulting fires have to be known. Therefore a research project was proposed to investigate the phenomenon and its consequences.

As the runaway reaction occurring during the storage of dried sewage sludge is a complex system, this study needs a multi-field approach combining analyses and experiments in biology, physics and chemistry. The working hypotheses were formulated and checked one by one. The list of hypotheses were also completed as time went by.

7.2   Strategy

The strategy was to study first the physical and chemical properties of the dried sewage sludge (1) (Figure 7.2). With these data, some simulations could be carried out with the aim of understanding the storage behaviours (2). Finally several storage experiments could be performed in model and industrial storage tanks (3). It has to be noted that the analyses and experiments on sewage sludge granules were

performed at scales ranging from one single granule corresponding to microanalyses (a), then to a pile of dried sewage granules for the macroanalyses (b), up to large scale with storage in model tanks (c), and finally up to industrial scale with storage in a large silo (d) (Figure 7.3).
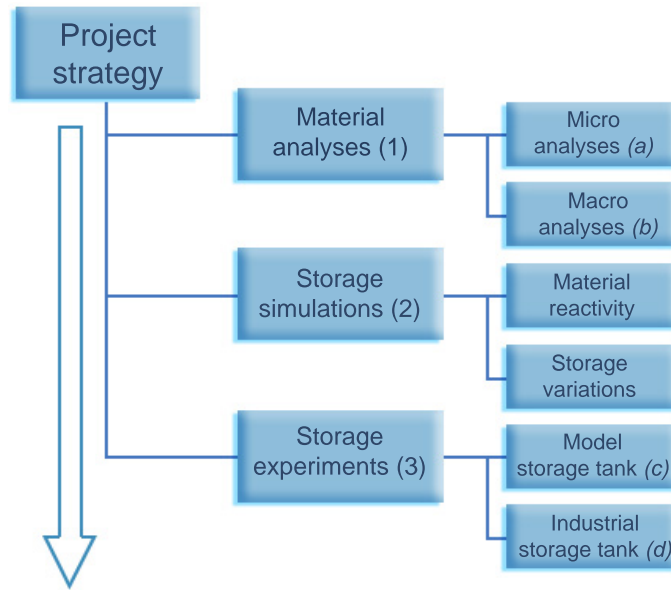
Figure 7.2: Project strategy: from material analyses to storage experiments
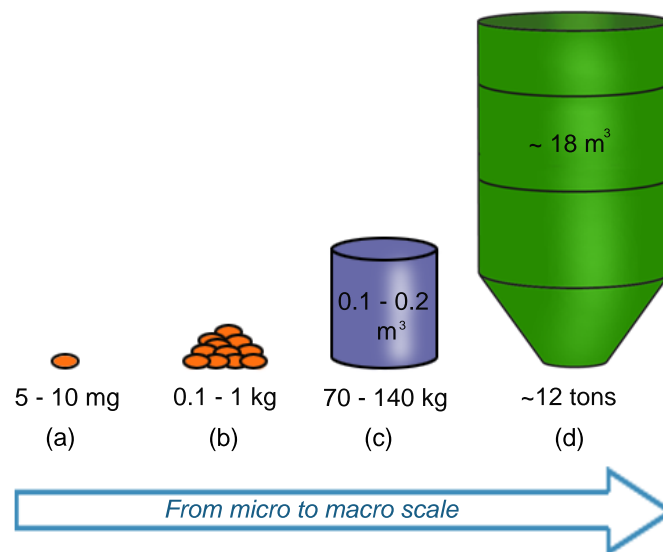
Figure 7.3: Project scale: a study from micro to macro scale

7.3 Working hypotheses

7.3.1 Experimental project

Fires in storage tanks at the cement industry seemed to happen more frequently when dried sludge from STP of Bern is stored. One of the main differences between dried sludge granules from STP of Bern and the other sewage treatment plants is its high iron content. The sludge granules from Bern STP contain between 7-12 % of iron with respect to dry solids content.

Starting assumptions

The combustible part of the sludge material (50 % DS) is assumed to be composed of non-biodegradable organic compounds such as long aliphatic chains originating from fatty acids for example, and aromatic compounds such as humic acids. The former hydrocarbon compounds can undergo autoxidation. Such degradation reactions occur when oxygen and heat or light is present. Autoxidation is a well known phenomenon, which is observed during the processing of polymeric materials. However this problem is suppressed by the addition of powerful antioxidants in the polymer industry. In analogy, similar antioxidants would be added to the dewatered sewage sludge before the drying process. Then storage experiments in a large silo of 18 m^3 would be carried out with treated and untreated granules. The ocurring runaway and smouldering fires would be studied in order to measure the impact of an antioxidative treatment.

Another reason for the start of the autoxidation might be the chemical heterogeneity of the dried granules. The autoxidation might be initiated locally by catalytic impurities, which might then lead to hot spots in the material. From that particular location, the heat would be released and propagated to the contiguous material triggering then a chain reaction.

Last but not least, the effect of using hot compressed air to blow the granules from the truck to the experimental silo would be examined. Indeed, the use of this hot compressed air provided by the transporting truck was suspected to initiate the autoxidation and to induce the thermal runaway within the dried granules stored at the cement industry.

Logistics and planing

The planned experiments in large storage silos implied before hand a study of the dryer characteristics of the STP of Bern. This study is necessary to achieve the adequate logistics for the future storage experiments. The dwell time of the sludge to pass through the dryer facility had to be known in order to collect the desired fraction of treated or untreated granules. The dwell time is determined by adding a marker to the dewatered sludge and its further detection in the dried sludge. The required concentration of the marker needed to be also determined for such a specific situation.

With the dryer characteristics in hand, the logistics would be worked out for the treatment procedure, the batching, the transport and finally for the storage experiments.

7.3.2   Research project

The research project relied on five initial hypotheses, completed by two additional hypotheses developed in the course of the study. The working hypotheses emerged from the actual knowledge on self-heating processes. The research was carried out for all hypotheses in parallel and proved to be an adequate strategy, as several investigations gave information about more than one hypothesis. All hypotheses had an exothermic process in common, which in combination with the high thermal insulating properties of the dried sewage granules would lead to a heat accumulation.

Hypothesis 1: low-temperature oxidation

Hypothesis 1 (H1) consists in a spontaneous oxidation of the organic material occurring at a low temperature range. Some specific conditions of humidity and air are needed to reach a system, which might self-oxidize. This exothermic process liberates heat, which accumulates within the storage tank due to the insulating properties of the material. The resulting temperature increase would then accelerate the oxidation and the self-heating processes.

Hypothesis 2: oxidation at the surface

Hypothesis 2 (H2) is based on the fact that sewage granules have a significant contact surface due to their small particle size (mean diameter: 2 mm) and their

important particle surface (around 2.9 m^2/g) (see section 6.2.2). Therefore an oxidation at the surface of these granules may be induced by the pneumatic transfer from the transport truck to the storage silo. As the blowing process is carried out with compressed air, the inert atmosphere surrounding the granules as a consequence of the specific drying conditions may be replaced by air creating an oxygen rich atmosphere. This would accelerate the autoxidation at the surface of the granules.

Hypothesis 3: external event

Hypothesis 3 (H3) follows from the idea that an external event could be the ignition source of a otherwise weakly reactive 'granules - air - humidity' system. This external factor might be more or less random and caused by many influences coming from the dryer plant itself, the transport procedures or the storage conditions. Therefore the potential source of self-heating, which may lead to spontaneous ignition, will be examined. Some of these ignition sources are for instance, the influence of the working days (dryer plant schedule), a potential electrostatic discharge during the unloading of the granules, and the heterogeneity of the material (hot spots).

Hypothesis 4: biological activity

Hypothesis 4 (H4) is related to the self-heating processes occurring within composting facilities and haystacks, where the first heating stage is due to the respiration of microorganisms. Residual bacteria spores present in sewage granules may grow in the 'granules - air - humidity' system and restart a biological activity under specific conditions. The heat release would accumulate within the material accelerating the biological processes up to a certain temperature. After a definite temperature, chemical reactions, e.g. autoxidation, would take place leading to the spontaneous combustion.

Hypothesis 5: catalytic autoxidation

Hypothesis 5 (H5) corresponds to a catalytic oxidative decomposition of the organic material with air. This autoxidation process is catalyzed by some transition metal species present as impurities. In the case of sewage sludge a large variety of elements may be potential catalysts. In the STP of Bern, an important amount of ferric chloride sulfate is added to raw sewage flows at the primary settlement tank

in order to remove phosphorus by precipitating soluble phosphate. Iron present in dried granules in a large excess (between 7 and 12 %) is therefore suspected to be mainly responsible for the catalytic oxidation of the organic part present in the sewage granules. Moreover the iron contained in the sewage sludge is reduced by the anaerobic conditions in the digester. Iron(II) might then oxidize spontaneously in iron(III) in contact of the air contributing to the heat accumulation in the dried sewage granules. The resulting iron(III) would also have a catalytic effect on the autoxidation of the organic matter.

Hypothesis A: pyrophoric iron sulfide

An additional hypothesis (HA), which was proposed during the project by Dr Thomas Haltmeier, consists in a self-heating of the material due to a pyrophoric reaction of iron sulfide. Actually Fe^{2+} present in sewage sludge due to the reducing condition of the biological treatment is known to decrease hydrogen sulfide concentration in the biogas by precipitation as iron sulfide. Therefore iron sulfide is suspected to be present in the final sewage sludge. Moreover as ferrous sulfide is black, it is said that the dark color of the dried sewage granules also proves the presence of iron sulfide. Pyrophoric oxidation of iron sulfide may release heat under specific conditions, which would also accumulate due to the insulating properties of sewage granules.

Hypothesis B: exothermic hydration

Another hypothesis (HB), which was also added to the five initial hypotheses, concerns exothermic hydration processes. For instance, dried calcium sulfate and calcium oxide are known to release heat while undergoing hydration. This chemical energy is stored within the compound, until the dehydrated salt gets in contact with water. Sewage granules from the STP of Bern contain $\sim$ 92 % of solid content: the remaining mass is moisture, either chemically bound as crystal water, or simply adsorbed on some hygroscopic surfaces. If mobilized, humidity may cause exothermic hydration of nearby drier particles.

Part IV

Results of the experimental project

Chapter 8

Antioxidant treatments

Dried sewage sludge granules is a resulting urban waste, which is made up of combustible matter ($\sim$ 50 % DS content) and of minerals for the remaining part. The organic part present in this material consists of non degradable organic compounds such as humic acids and long aliphatic chains, because it has already underwent the biological anaerobic treatment inside the digesters. In the mineral part of the biosludge, many metals are present such as iron mainly added in the process as $FeClSO_4$, calcium, magnesium, potassium, zinc, copper, and some heavy metals in smaller concentration. Iron represents a very important part of the dried sewage granules with a concentration around 7 - 12 % DS.

Material with this composition of organic non degradable substances and inorganic compounds may be easily subject to low temperature autoxidation processes analogous to polymeric materials which undergo autoxidation especially when metallic impurities are present.

8.1   Autoxidation

Any material containing hydrocarbon compounds (R-H) can undergo autoxidation when oxygen and heat or light are present [49, 50]. This is a free radical-initiated chain reaction, which proceeds auto-catalytically (Figure 8.1).

A radical ($R^\bullet$) formed by homolytic bound cleavage is the start of the radical reaction cycle. This radical reacts with molecular oxygen, catalyzed by transition metals, radical initiators or other active impurities, directly leading to the formation of peroxy radicals ($ROO^\bullet$) (Eq. 8.1). The peroxy radical is more reactive than a starting alkyl radical and will therefore readily abstract hydrogen from a new hydrocarbon compound forming a hydroperoxide and a new alkyl radical (Eq. 8.2).
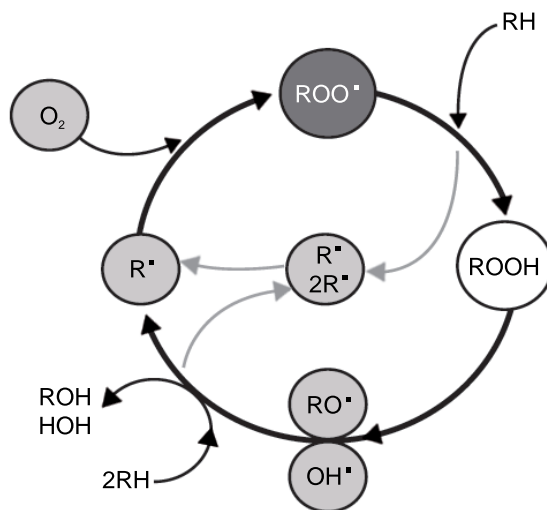
Figure 8.1: Cycle of autoxidation [49]

Then the hydroperoxide decomposes by heat, light or transition metal catalysis into two radicals: alkoxyl (RO$^\bullet$) and a hydroxyl (OH$^\bullet$) radical (Eq. 8.3, 8.4). Both radicals abstract hydrogen from a new hydrocarbon backbone and form two additional alkyl radicals (Eq. 8.5, 8.6).

The free radical-initiated chain reaction is slow at the start, generally associated with an induction period and accelerates with the concentration of the resulting hydroperoxides. For each complete cycle of this chain reaction, the number of radicals involved triples, leading to an exponential increase which speeds up the degradation rate.

$$R^\bullet \ + \ O_2 \ \longrightarrow \ ROO^\bullet \tag{8.1}$$

$$ROO^\bullet \ + \ RH \ \longrightarrow \ ROOH \ + \ R^\bullet \tag{8.2}$$

$$M^{n+} \ + \ ROOH \ \longrightarrow \ M^{(n+1)+} \ + \ RO^\bullet + \ HO^- \tag{8.3}$$

$$M^{(n+1)+} \ + \ ROOH \ \longrightarrow \ M^{n+} \ + \ ROO^\bullet + \ H^+ \tag{8.4}$$

$$RO^\bullet \;+\; RH \;\longrightarrow\; ROH \;+\; R^\bullet \tag{8.5}$$

$$HO^\bullet \;+\; RH \;\longrightarrow\; H_2O \;+\; R^\bullet \tag{8.6}$$
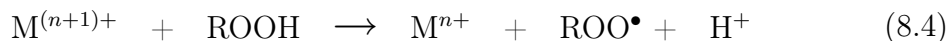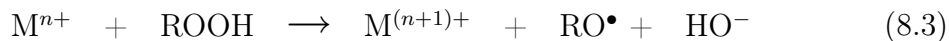
The main product of autoxidation is water. The remaining carbon backbone is oxidizes as well, but only to the stage of ketones or carboxylic acids. Autoxidation produces neither CO_2 nor CO. These typical combustion products require higher temperatures and C-C bound breaking reactions.

8.2   Inhibition of the autoxidation

Stabilizers are added to polymeric materials in small amounts to inhibit the oxidative degradation. These chemical substances are capable of trapping emerging free radicals, or reactive intermediate products such as hydroperoxides in the course of autoxidation, and to transform them into stable end products.

As the cycle of autoxidation is a chain reaction, different approaches may be used to inhibit one step or another of the degradation process using complexing agents, hydroperoxide decomposers, radical scavengers or $H^\bullet$ donors (Figure 8.2).

The metallic impurities, which are responsible for the formation of several radical species, may be deactivated by complexation. In principle, scavenging of the primary alkyl radicals would immediately stop the autoxidation. The metal deactivators are specially useful for application of polymers in direct contact with metals, such as cables with copper conductors and a polymer as insulator.

Another key step of the chain reaction is the abstraction of a hydrogen from the polymer backbone by the peroxy radical ($ROO^\bullet$) forming hydroperoxide. The latter reacts preferably with a hydrogen donor with higher reactivity than the hydrocarbon chain, and competes with the degradation. The $H^\bullet$ donor is characterized by the fact that they do not abstract a further hydrogen from the hydrocarbon backbone.

Radical scavengers present a high efficiency for inhibiting autoxidation. Moreover hydroperoxide decomposers suppress efficiently chain branching during autoxidation of the polymers and therefore are used as co-stabilizers. They decompose hydroperoxide into inert reaction products.
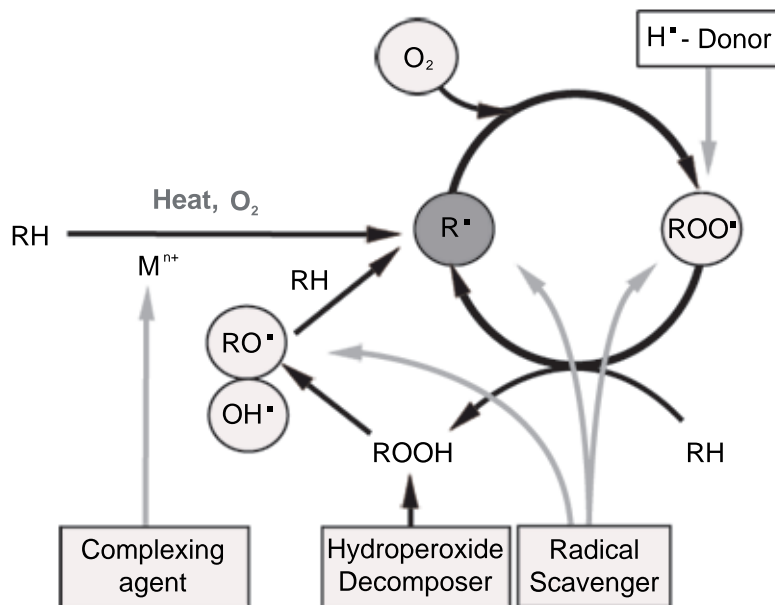
Figure 8.2: General scheme of the inhibition of a thermo-oxidative degradation [49]

8.3   Antioxidant mechanisms

To avoid autoxidation, inhibitors are usually used in the polymer industry. For instance stabilization of polymeric materials may be obtained by adding phenols and amines, which are both capable of highly efficiently inhibiting autoxidation [49].

Since the first assumption was that the auto-ignition of dried sludge granules is probably also due to an autoxidation process, the influence of some of these inhibitors would be tested. However because the industrial antioxidants are usually added during the production processes of polymers, they are principally organic compounds and consequently generally water insoluble. In the case of sewage sludge treatment, the antioxidants need to be added in the dewatered sludge ($\sim$35 % solid content) prior to the drying process in order to achieve a homogenous treatment and therefore they have to be water soluble.

The treatment of the dried granules with antioxidants is expected to inhibit the auto-ignition during storage. The storage experiments performed with treated dried sewage granules were done to observe the changes of the auto-ignition process when compared to the blank experiment.

8.4 Selected antioxidants

Three antioxidant compounds were tested by injecting them as an aqueous solution in dewatered sludge in order to prevent self-heating and runaway processes during storage of dried sewage granules. These compounds were selected according to three criteria: costs (sewage is not a compound of high added value like polymers), availability (including water solubility) and efficiency.

The first antioxidant is sodium hypophosphite (Na_2HPO_2), which is widely used for its stabilization properties in various fields (Treatment 1). It is known that sodium hypophosphite is an antioxidant working as free radical scavenger.

Two other products were kindly provided by Ciba Specialty Chemicals. These substances are routinely used as plastic antioxidants and stabilizers. Prostab$^©$ 5198, corresponding to 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy, was tested secondly (Treatment 2). This nitroxyl functional inhibitor blocks very efficiently the free radical chemical reactions[1]. The third antioxidant is 4-hydroxy-2,2,6,6-tetramethylpiperidine, known as HTMP (Treatment 3). This compound is a sterically hindered amine, which operates as efficient alkyl radical scavenger.
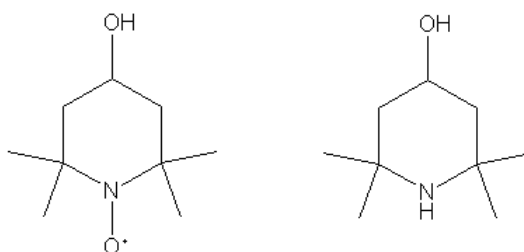
Figure 8.3: Prostab$^©$ 5198 (left) and HTMP (right) are two antioxidants provided by Ciba Specialty Chemicals and will be used for antioxidant treatments of sewage sludge (Treatment 2 and 3)

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[1]PROSTAB 5198, Ciba Specialty Chemicals, Additives, Date first Edition: March 1998

Chapter 9

Preparation of the storage experiments

9.1 Dwell time determination of the dryer plant

The dwell time of the sludge in the dryer system has to be known in order to select a specific fraction of the dryer output needed for the storage experiments. The dwell time was determined by using a marker, which was injected as an aqueous solution in the dewatered sludge before being dried in the dryer plant oven (Figure 9.1). Resulting marked granules may then be analyzed and the evolution of the marker concentration would give information about the time that sludge spends within the dryer and about the achievable steady state concentration of an added substrate.
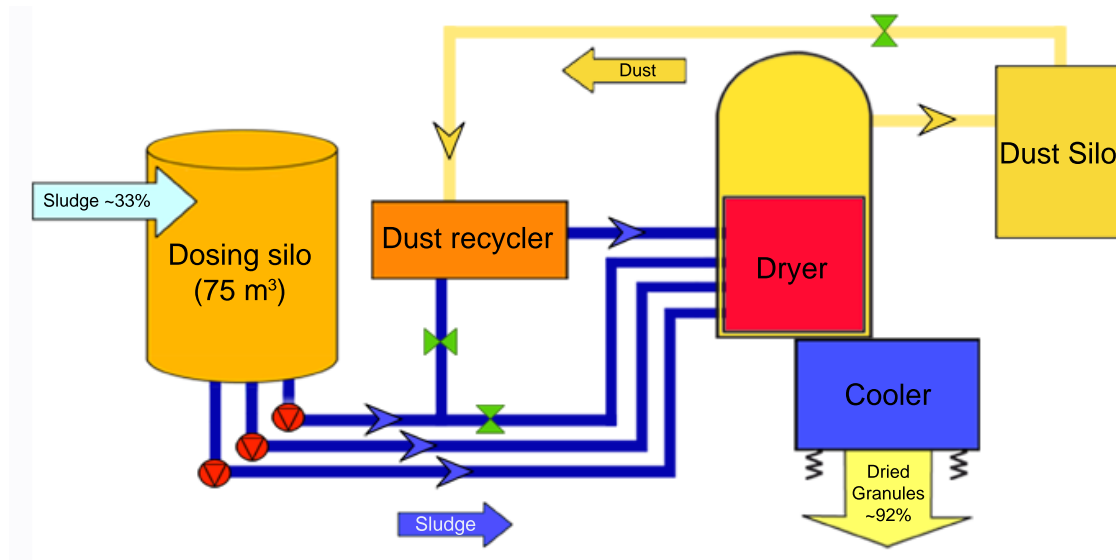
Figure 9.1: Scheme of the dryer plant composed of the dosing silo of dewatered sludge, three pumps injecting the sludge through the pipes connected to the dryer plant and to the dust recycler respectively, the oven, the dust silo and the cooler

9.1.1 Optical markers

The first idea was to use optical fluorescence marker detection to follow the evolution of the treatment, since this method would lend itself best for a continuous online monitoring. It was therefore planned to injected an aqueous solution of an optical marker in the dewatered sludge at the sludge pumps of the dosing silo and to process the optical detection after the fluid bed cooler system through an inspection window.

Fluoresceine

The first optical marker tested was fluoresceine. Several experiments were carried out to test the efficiency of fluoresceine as an adequate marker in the sewage biosolid. Aqueous solutions of fluoresceine free acid and fluoresceine sodium salt at various concentrations were prepared and mixed with dewatered sewage sludge. No fluorescence from the mixture could be observed directly under a UV lamp. A water extraction of the mixture gave a dark solution fluorescing while exposed to UV light. The fact that an extraction of each sample was needed in order to detect fluoresceine made online detection cumbersome. Nevertheless an injection of fluoresceine sodium salt solution (10^{-2} M) into the dewatered sludge was performed with a single head pump in one of the three sludge pipes (Table 9.1). The dried treated granules were sampled at the dryer plant exit after the cooler system and their extracts analyzed under UV light. From the 16 samples taken during the two hours following the start of the injection, no fluorescence could be detected in the dried granules upon UV light excitation. Even after extraction with water none of the solutions from the taken samples emitted under the UV lamp.

Table 9.1: Injection of fluoresceine solution in dewatered sewage sludge for the dryer dwell time determination by online optical detection

	Solution		Injection			Sampling [a)]		
	conc.	vol.	flow	time		dewat. sludge		dried granules
Exp.	(mol/L)	(L)	(L/h)	(h)	n	t_0 (+ Δt) (min)	n	t_0 (+ Δt) (min)
1	10^{-2}	11	6	1.8	5	10 (+ 2)	16	30 (+ 5)

a) n is the total number of taken samples, t_0 sampling time of the first sample after the injection start and Δt the additional time between the following samples

Anthracene

Anthracene was also tested as an optical marker for achieving online analyses of the dryer dwell time. This chemical compound emits in blue color when excited at 254 nm and even stronger at 365 nm even in its solid form. The poor water solubility of anthracene did not enable the injection of an aqueous solution, because the optical marker concentration would have been too low. Anthracene is soluble in acetone, but such solutions could not be used due to the incompatibility of the inside polymeric surface of the sludge pumps with organic solvents and the fire risks within the dryer oven.

During the mixing tests of anthracene with dewatered sludge, white suspensions of anthracene in water turned out to be an option as the obtained mixture was slightly emitting under UV exposure. Therefore two injections of anthracene suspension within the sludge were carried out with a single head pump in one of the three sludge pipes (Table 9.2). Dewatered sludge and dried granules were sampled and observed under a UV lamp. None of the dewatered sludge samples emitted neither directly upon excitation, nor after extraction with water. For dried granules samples some spots were observed under UV light. However it has to be noted that even untreated dried granules contained slightly emitting fragments, which caused difficulty to detect anthracene as an optical marker.

Table 9.2: Injections of anthracene suspension in dewatered sewage sludge for the dryer dwell time determination by online optical detection

	Suspension		Injection		Sampling [a]			
	conc.	vol.	flow	time	dewat. sludge		dried granules	
Exp.	(mol/L)	(L)	(L/h)	(h)	n	t_0 (+ Δt) (min)	n	t_0 (+ Δt) (min)
1	$5 \cdot 10^{-4}$	20	6.4	3.1	6	14 (+ 2)	9	45 (+ 15)
2	$2 \cdot 10^{-3}$	25	6.7	3.7	-	-	12	60 (+ 30)

a) n is the total number of taken samples, t_0 sampling time of the first sample after the injection start and Δt the additional time between the following samples

The two organic markers first chosen (fluoresceine and anthracene) turned out to be not suitable for the determination of the time that the dewatered sludge spent through the dryer plant. The emission provided by fluoresceine upon UV excitation is suspected to be quenched by the sludge and the emission provided by anthracene is not specific enough to be detected it in sludge.

9.1.2   Metallic ion markers

A metal salt solution was added in the wet sludge and the resulting dried sludge granules were analyzed by atomic absorption spectroscopy (AAS). As the concentration of the metals present in the sewage sludge are known from previous analyses, any variation of the concentration of the added metal ions versus time would therefore correspond to the evolution of the sludge treatment.

Copper sulfate with a single head pump

Copper has been chosen as metallic ion marker for several reasons: its toxicity is reasonable, its detection is easily feasible by analytical methods and its natural concentration in the sludge is low ($\sim$ 300 g/t solid content). All treated granules samples were dissolved in nitric acid and after dilution and filtration, the obtained solutions were analyzed by atomic absorption spectroscopy.

The first injection of a copper solution was made with a single head pump in one of the three sludge pipes and lasted 5.5 hours (Table 9.3). This first experiment showed an increase of the copper concentration starting after around 3 hours of injection. However the copper concentration was still increasing at the end of the experiment. This indicated that the steady state had not been reached yet. A new experiment was necessary with a longer time frame.

Table 9.3: Injections of copper sulfate solution in dewatered sewage sludge with a single head pump in one of the three sludge pipes for the dryer dwell time determination by atomic absorption spectroscopy

	Solution		Injection		Dried granules sampling [a]	
	conc.	vol.	flow	time	n	t_0 (+ Δt)
Exp.	(mol/L)	(L)	(L/h)	(h)		(h)
1	$2 \cdot 10^{-1}$	24	6.8	5.5	10	1 (+ 0.5)
2	$4 \cdot 10^{-1}$	24	6.6	7.5	19	2.5 (+ 0.5)

a) n is the total number of taken samples, t_0 sampling time of the first sample after the injection start and Δt the additional time between the following samples

The second injection was made with a twice more concentrated copper solution in the same injection conditions, but lasted 7.5 hours this time. AAS results showed again an increase of the copper concentration after $\sim$ 3 hours of dosing. However

the variation in the copper concentration in treated dried granules was not sufficient to allow the correct following of the treatment.

To obtain a better view of the treatment evolution, the difference of copper concentration in the normal sludge and in the treated sludge needs to be increased. As the experiment was done only on one pipe, only one third of the dry sludge was treated with copper sulfate. This treatment was clearly not sufficient: therefore an experiment with a triple head pump and a more concentrated copper solution was planned.

Copper and nickel sulfate with a triple head pump

To be sure that the increase of the concentration of the metallic ion marker was due to its addition to the dewatered sludge and not to the normal fluctuation of its concentration in sludge, a solution of two metallic ion markers (nickel and copper) was injected. By this way the evolution of the treatment can be proved by the simultaneous increase of both metals.

A nickel and copper sulfate solution was injected with a triple head pump in the three pipes transporting dewatered sludge to the dryer oven. This mixed solution, 0.7 M $CuSO_4$ and 0.4 M $NiSO_4$, was injected with a flow of 24.5 L/h during 4 hours. Under these conditions, the copper and nickel concentrations were expected to be respectively 3.7 and 12.8 times greater compared to their natural concentrations analyzed previously.

This time the variation of copper and nickel concentration was high enough for both metals to observe the evolution of the treatment, even if the expected concentration in dried granules had not been reached during this experiment. The obtained curve for the copper concentration was quite smooth, compared to the one for nickel (Figures 9.2 and 9.3). Actually the detection of nickel with atomic absorption may not be optimal since some interferences with other sludge constituents were suspected.

The decrease of copper and nickel concentration five hours after the start of the experiment is due to the stop of the injection one hour before (four hours of injection). This also indicates that the evolution of the treatment can be followed with this method. As the detection of the copper concentration in the dried granules seemed efficient enough, a longer injection time of copper as marker would be sufficient to determine the whole evolution of the treatment.
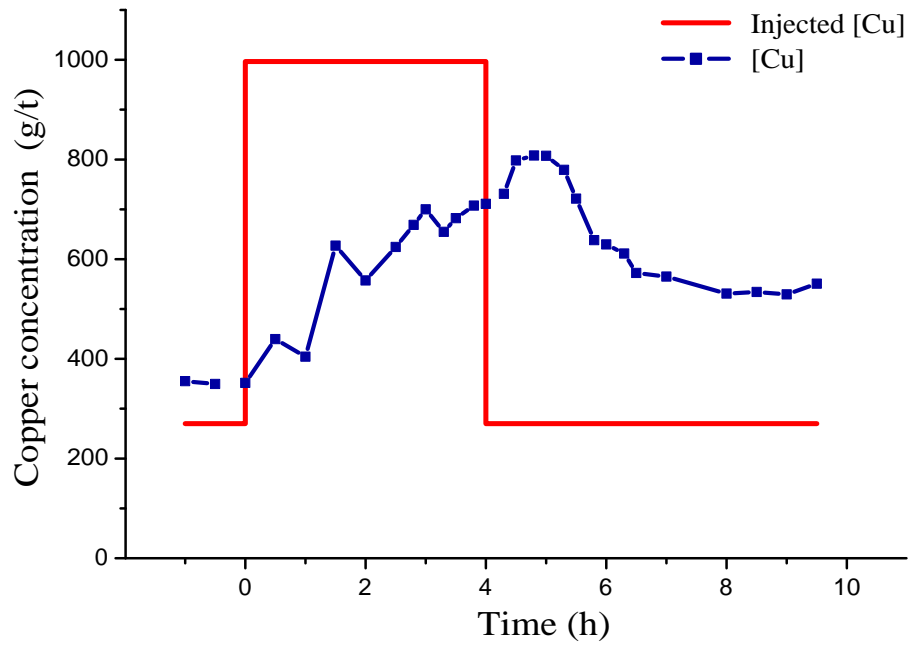
Figure 9.2: Copper concentration (dots) determined by AAS in samples of dried sewage granules during the injection of mixed metallic markers solution (line)
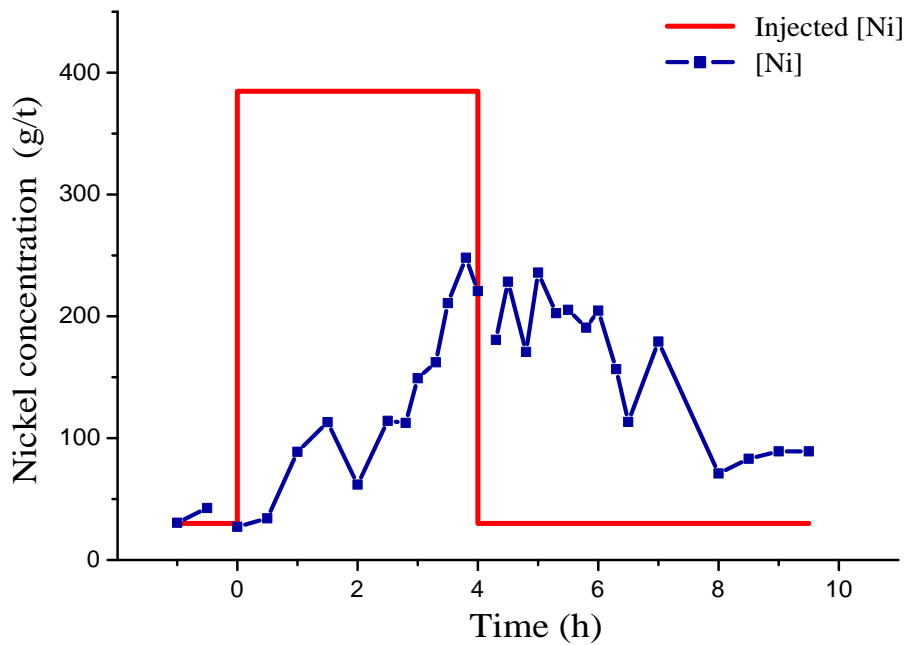
Figure 9.3: Nickel concentration (dots) determined by AAS in samples of dried sewage granules during the injection of mixed metallic markers solution (line)

Long range injection of copper sulfate

For this experiment, around 690 L of a 0.7 M copper sulfate pentahydrate (120 kg) solution has been prepared, and injected afterwards in the three pipes transporting the dewatered sludge to the dryer oven. With an injection flow of $\sim$ 24 L/h during 24 hours. Under dryer working conditions on the moment, the copper concentration was expected to be 3.7 times greater than its ordinary concentration in the dried sewage granules.

Samples of dried sludge granules were taken already the day before to determine a base line of the copper concentration. On the day of the experiment, the samples were taken every 30 minutes, starting 3 hours before the start of the injection and lasted 13 hours. Afterwards the sampling was performed every hour until the end of the injection. After the end of the injection, samples were still taken every 30 minutes again for 10 more hours.
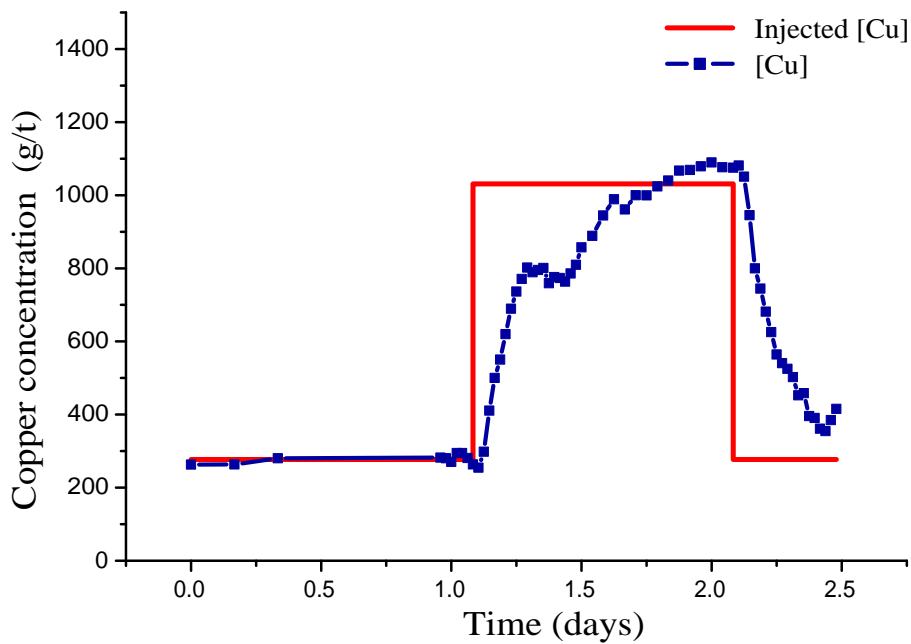
Figure 9.4: Copper concentration (dots) in samples of dried sewage granules during the 24 h injection of copper sulfate solution started at t_0 (line). Sampling began the day before the start of the copper injection in order to measure the natural copper concentration within the dried granules (baseline)

All 63 samples were prepared by microwave digestion in nitric acid 65 % and analyzed by atomic absorption spectroscopy. The measured copper concentration started increasing significantly after 1.5 hours of injection and reached a steady

state concentration after 19 hours (Figures 9.4). However the copper concentration did not increase as expected in a exponential decelerated curve. This phenomenon was not due to the AAS analyses as these analyses have been controlled by repeating the measurments twice: the first time with in increasing time order and the second time in a random order. Two similar curves were obtained with a maximal deviation from average copper concentration of ± 3.5 %.

The unevenness of the copper increase in dried sewage granules during the constant injection of a copper sulfate solution was related to the dust recycling process. Actually the dust recycler started working only when the dust silo is full (on / off system) which consisted to recover the dust from dryer and to mix it with the dewatered sludge. That was the reason why, after 5 hours of injection, the copper concentration curve showed a steady state even during a constant treatment of the dewatered sewage sludge (Figures 9.5). During the first dust recycling process, the dust did not contain already copper. This induced an important stall in the copper concentration increase. During the further dust recycling processes, dust recovered from the dryer contained additional copper, therefore the steady states were not so pronounced. Nine hours after the end of the injection, the copper concentration started to increase again. This phenomenon was due to a new dust recycling process which contained the copper added previously.
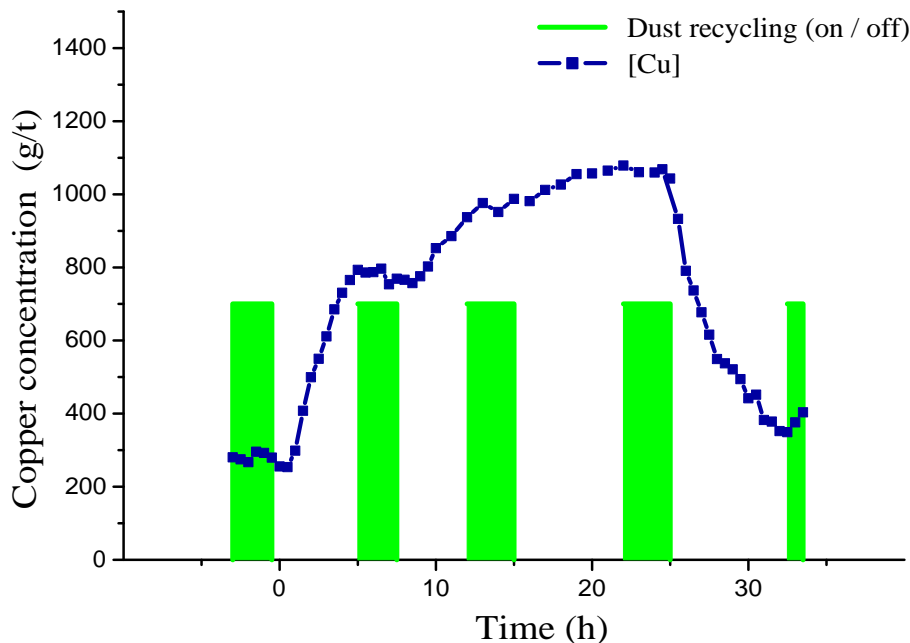
Figure 9.5: Relation between the copper concentration (dots) in dried sewage granules during the constant injection of a copper sulfate solution and the dust recycling 'on / off' processes (column)

Dwell time of dryer plant in the STP of Bern

In this experiment, 13 hours of injection were needed to obtain dried sludge granules which contained a concentration of at least 90 % of the maximum copper concentration added. That is the minimal time to wait, in this experiment, before collecting the desired fraction. However the increase of copper concentration is not regular versus time. It clearly depends on the dust recycling processes which starts automatically when the dust silo reaches a limiting level. As the dust recycling processes last between 2 and 3 hours, the average time to wait before collecting the right treated fraction must then take this data into account. In addition to this experiment, the mathematical modeling confirmed that at least 16 hours of injection were needed to ensure a homogenous treatment of the material.

9.2 Collecting the selected batch of granules

The storage experiments pose major logistic challenges, as a minor fault could totally invalidate the whole experiment especially during the production of treated dried sludge granules.

When dried, the granules leave the dryer facility and are stored into two large silos of 100 m³ each for temporary storage at the STP of Bern. The loading in one or the other silos runs automatically depending on the respective level of filling up.

Several procedure steps would be essential in order to collect the right fraction of sewage granules (Figure 9.6). The same procedures were also applied for blank experiments with untreated sewage granules:

- Start of the experiment (treatment of the dewatered sludge by injecting an antioxidant solution)

- Pretreatment phase of 16 hours (dwell time of the dryer plant). Pretreated dried granules are loaded in one of the silo (A) and will be eliminated as casual waste granules

- Emptying of the second silo (B) and get ready to collect the desired granules fraction

- Manual change of loading from silo(A) to silo (B)

- Production phase of 7 to 9 hours depending of the dryer working conditions. The production is collected in the empty tank (B) to obtain the required amount of (treated) sludge granules

- Manual change of loading from silo(A) to silo (B)

- Loading the granules fraction from the silo (B) in a transporting truck

- Start of the storage experiment
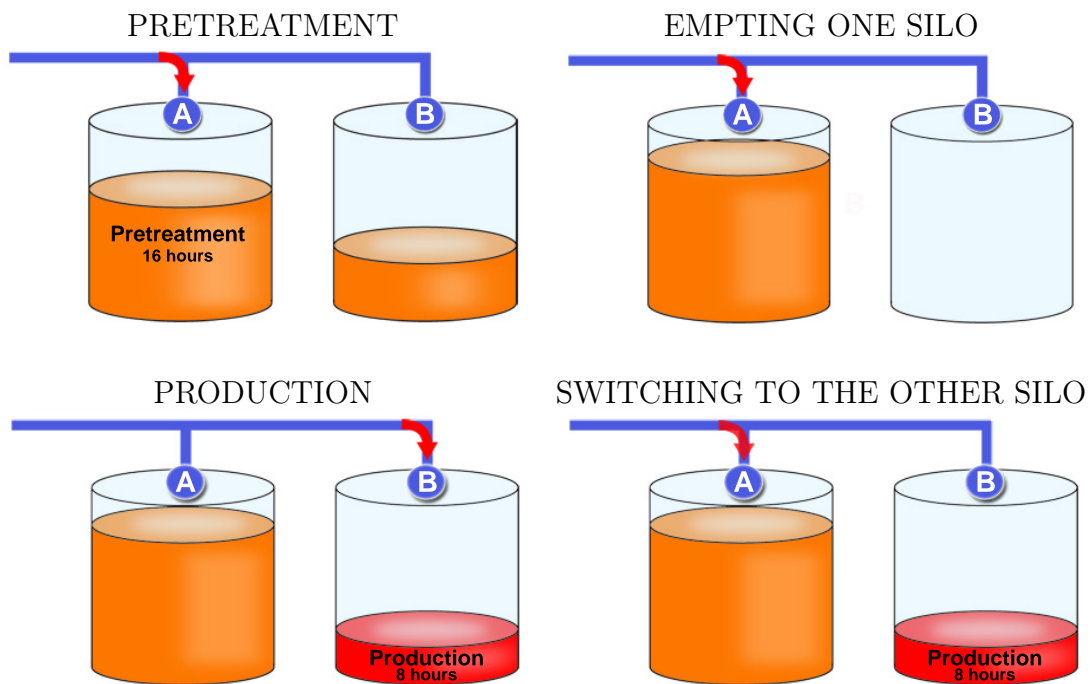
Figure 9.6: Four manual steps are required for collecting the desired fraction of dried granules: 1) the pretreatment phase (top left), 2) the emptying the silo destined for the production (top right), 3) the production phase (bottom left) and 4) the stop of collecting by switching to the other silo (bottom right)

9.3   Logistics

The storage experiments were performed in an industrial silo of 18 m^3 (see Figure 6.3) equipped with several measuring devices (Figure 9.7). Manual temperature measurements were performed at various heights, and at the front of the silo (T_1, T_3 and T_4) and on the side at right angle (T_2). For each position the temperature was measured at three different depths (0.6, 0.85 and 1.1 m). Two data logging devices were also used to measure continuously the temperature variations inside the granules: at 1.15 m depth for data logging device located at position L_1 and at 1.00 m depth for data logging device located at position L_2 at right angle. Humidity and CO concentration were also monitored by a data logging device on top of the silo (M). Two openings on the top of the silo and on the side of it (S_1 and S_2) allowed the sampling at various depths and at different periods of the storage for further analyses.
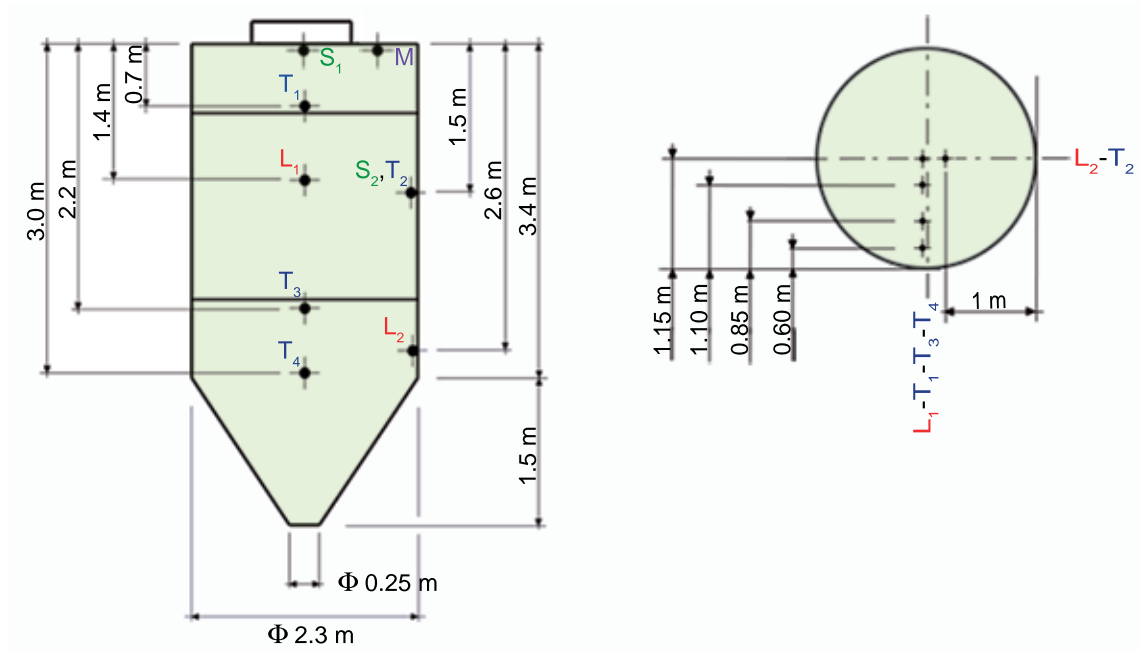
Figure 9.7: Side view (left) and top view (right) of the experimental silo of 18 m^3 with the different positions for the manual temperature measurements (T_1 to T_4), for the temperature logging devices (L_1 and L_2), for the sampling (S_1 and S_2), and for the carbon monoxide and humidity measurements (M)

Around 12 tons of selected fraction of dried sludge granules was transported by truck from the sewage treatment plant of Bern to the experimental storage place. There the granules were blown with compressed air into the silo through a flexible pipe connected to the top of the silo. The compressed air, provided by the

transporting truck, was very hot (up to 120 ˚C), excepted if a heat exchanger was used to cool down the compressed air. The dust was evacuated from the top of the silo by a second pipe (see Figure 6.3).

When the silo was filled up, a ventilator was fixed at the top for sucking the moist air at the surface of the stored granules. An air flow coming from the two open pipes connected to the top allowed ventilating continuously the surface of the loaded granules. This ventilation was needed for two reasons: on one hand in order to eliminate humidity (formed during the combustion) with the intention to avoid deterioration of the measurement elements (data logging devices) and on the other hand to mimic additional air intake, which normally occurred in real storage silos during further loadings.

The evolution of the whole process was followed by measuring the inside temperature until a critical situation (fire, smoke, high inside temperature…) was reached. At that stage the tank was emptied into an 25 m^3 open bucket by an endless screw.

Chapter 10

Storage experiments using hot compressed air

The following storage experiments were made in a rather 'small' silo of 18 m^3, as compared to the 175 m^3 silo used for temporary storage at the cement industry (e.g. Holcim, Untersiggenthal). They were performed in order to see if the auto-ignition could also happen at such a scale. This scale-down was important because it can give a first idea concerning the critical mass necessary for a runaway process and the consecutive fire.

Moreover large scale experiments with treated dried granules would also give direct information about the impact of processing the sewage sludge with antioxidant additives.

During these storage experiments, the assumption concerning the presence of *hot spots* caused by the autoxidation at a definite place would be studied. In fact, thanks to the temperature measurements performed at different places and depths, it would be possible to detect if the thermal events occurred locally at different positions within the stored mass or not.

Last but not least, the influence of using hot compressed air for blowing the granules from the tank of the truck to the experimental silo would be examined. By using cooled compressed air for filling up the storage silo, it would be possible to compare the thermal evolution of the stored mass in both situations.

10.1　Blank 1: with untreated granules

On Thursday 29th April 2004, a 8.5 hours production of untreated dried sludge granules was poured in the empty storage silo at the STP of Bern. The granules were let this way in the tank during the weekend. The first storage experiment started 4 days later on following Monday by loading the selected fraction of untreated granules in the transporting truck. At the experiment place, the granules were blown up with compressed air through the pipe into the silo. After filling, the average temperature in the storage tank ranged between 35 to 45 °C.

10.1.1　Manual temperature measurements

The next day the manual measurements indicated that the temperature had increased to 90 °C at the top position (T_1) for the three different depths. The position T_1 was the closest to the granules top surface and therefore the material at this particular place was suspected to be more in contact with fresh air than anywhere else inside the silo. The air present in the empty space just underneath the silo top was constantly renewed by the ventilation furnishing oxygen to allow a fast reaction with the granules in this region.

For the other positions placed below T_1, temperature increased also spontaneously and reached between 65 - 85 °C. During the three following days, the temperature at all positions and depths decreased slowly. Then suddenly at the fourth day, it raised to more than 150 °C at the top-center of the storage tank. From that time on, the temperature started to increase extremely at the top of the storage tank and this hot zone diffused from the top to the bottom of the silo. As the whole storage tank reached quite high temperature (between 150 - 200 °C), it was decided to stop the experiment and empty the tank.

10.1.2　Monitored temperature measurements

The study of the temperature measured by the data logging devices confirmed the average behavior of the experiment already observed with the manual temperature measurements. At the top position L_1 right in the center, the measurement showed a first temperature increase after a few hours of storage up to 95.8 °C followed by a small temperature decrease down to 90 °C (Figure 10.1). Then a constant temperature was maintained over 2 days. After three days of storage, a runaway occurred inducing high temperature and combustion processes.
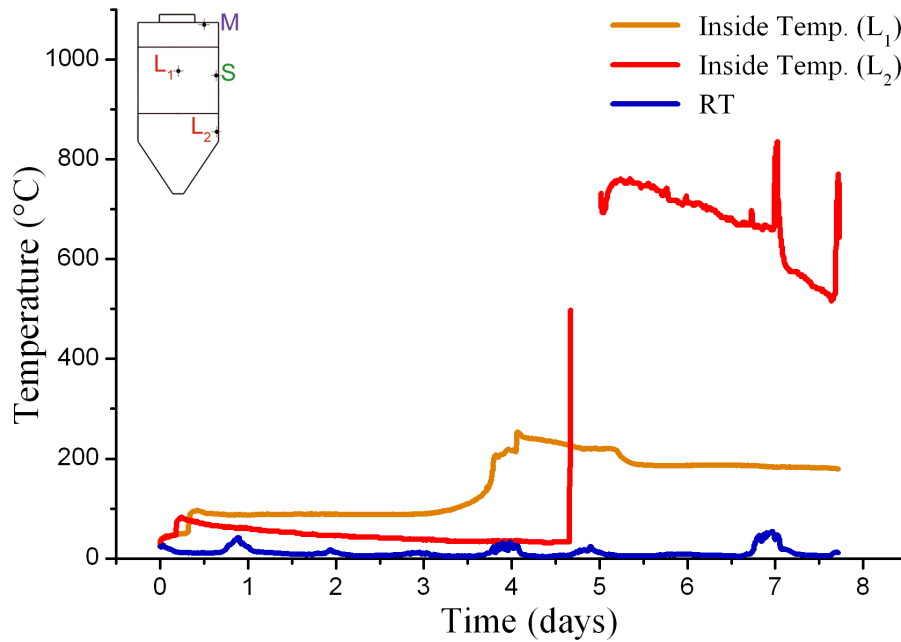
Figure 10.1: Inside temperature at position L_1 (depth = 1.15 m) and at position L_2 (depth = 1.00 m) and room temperature during storage of untreated granules (Blank 1)

The logging device L_2 measuring temperature at a lower position showed that temperature had the same profile than L_1. However it presented an important temperature decrease after the first thermal event instead of a steady-state temperature. The temperature decreased during nearly 5 days to finally reach 32.4 °C and then a runaway occurred rising the intern temperature up to more than 750 °C.

The peaks appearing on the temperature profile measured at the bottom position L_2 around the seventh and eighth day of storage corresponded to sampling times. The sampling at position S_2 was performed every day and by opening the sampling orifice some air was getting in the storage tank allowing the oxygen to stir up the fire. Through the opening for the sampling, glowing hot spots could even be seen!

10.1.3 Monitored measurements of CO concentration

The measured carbon monoxide had two separate origins. A minute amount of CO at the beginning came in fact from the gas surrounding the dried granules, which consisted in the inert gas used within the dryer plant for explosion prevention. This protective atmosphere is made up of combustion gas released by the heater

of the dryer plant. In fact it is a carbon dioxide rich atmosphere containing a small fraction of carbon monoxide. This protecting atmosphere allowed working conditions with only around 1 % vol. O_2 in the dryer oven and between 4 - 6 % vol. O_2 in the other parts of the dryer plant. The second source of carbon monoxide was due to the incomplete combustion induced by the thermal runaway and the combustion processes.
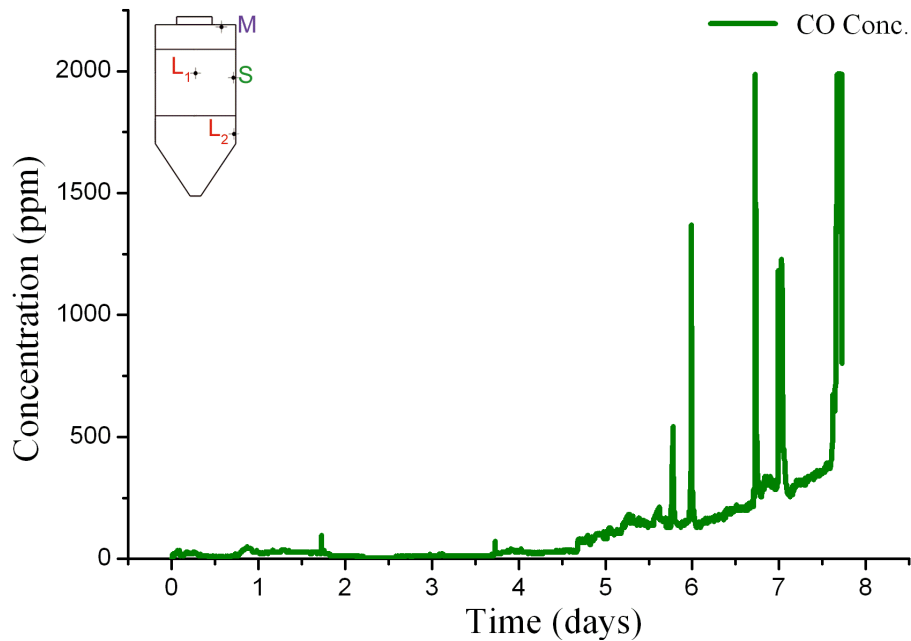
Figure 10.2: CO concentration at position M during storage of untreated granules (Blank 1)

The ventilation removed rapidly the CO present in the original inert atmosphere. This resulted in a very low carbon monoxide concentration at the beginning of the storage experiment (Figure 10.2). The CO logging device showed that the carbon monoxide concentration started increasing extremely from the fifth day, which fitted with the thermal runaway measured by the temperature logging devices. Some intense peak for CO concentration were observed which also corresponded to the sampling due to oxygen intake while opening. The increase of CO concentration proved that the dried granules self-heating process was sufficient to lead to an auto-ignition and a smouldering fire.

10.1.4 Description of the occurring thermal events

This first storage experiment showed well-marked thermal events: a first temperature increase, a quasi steady-state period and finally a thermal runaway (Table 10.1). The first self-heating process happened only a few hours after the loading of the material in the storage tank. This spontaneous temperature increase was measured manually at all positions and monitored by the two logging devices. Therefore it seemed that this thermal event was occurring at the same time anywhere within the granules. It is also worth mentioning that the measurements made at the upper positions (L_1 and T_1) indicates the greatest temperature increase, which can be intuitively related to the close distance to the top of the silo. It can be concluded that oxygen in the air contributes to this temperature increase.

Table 10.1: Onset and maximum temperature for the thermal events occurring during the first storage of untreated granules in the experimental silo (Blank 1)

Logger	1st thermal event [a)]		2nd thermal event	
	T_{onset} (t_{onset})	T_{max} (t_{max})	T_{onset} (t_{onset})	T_{max} (t_{max})
L_1	51.1 (0.3 d)	95.8 (0.4 d)	88.9 (3.0 d)	250.7 (4.1 d)
L_2	46.0 (0.2 d)	83.4 (0.2 d)	32.4 (4.7 d)	762.0 (7.2 d)

a) T_{onset} for the initial temperature at the beginning of the thermal event and T_{max} for the maximal peak temperature ($^{\circ}$C), occurring respectively at time t_{onset} and t_{max} (days)

A steady state temperature was observed within the granules at the upper positions of the silo, which indicates a running exothermic reaction without thermal runaway. Once again the closeness to the granules top surface, and consequently to the renewed air above it, was expected to be the clue of this sustained self-heating process. In fact the dried material was suspected to undergo an oxidation, which process was continuously fed by the constant fresh air intake.

The second observed thermal event corresponded to a thermal runaway, which occurred several days after the loading. The event started in the upper part and moved gradually down to lower levels within the silo. The monitored temperatures and CO concentration clearly indicated that a smouldering fire was occurring within the dried granules. Therefore it was possible to suggest that the runaway started in a certain region where sufficient oxygen was available (top part of the silo in this particular experiment). Then the heat was transfered to the adjoining material, which induced the stepwise propagation of the smouldering fire down to lower parts of the silo.

At the end of the storage experiment, the silo was emptied into an open bucket owing to an endless screw (Figure 10.3). The dried granules were stored in it before transporting them to the incineration plant. After 5 weeks the granules were still very hot (more than $100\,^\circ$C) at the top surface and turned red as a sign of a high concentration in ferric oxide. Therefore the material had to be cooled down with water before transport for safety reasons. In the further experiments, the smouldering granules would directly be transported to the incineration plant after draining the silo.

Figure 10.3: At the end of the first storage experiment (Blank 1), the smouldering granules were poured in a 25 m^3 open bucket, from which smokes were still emitted (left). The material kept on burning during several weeks and iron oxidized to red iron oxide (right)

10.2 Treatment 1: with sodium hypophosphite treated granules

Sodium hypophosphite is a commercial product known for its antioxidant properties. To avoid the temperature increase suspected to be due to a catalytic autoxidation process, 700 L of 0.67 M sodium hypophosphite (Na$_2$HPO$_2$ 50 kg) aqueous solution were prepared. Then this solution was injected in the three pipes transporting the dewatered sludge to the dryer oven. With an injection flow of ~ 27 L/h, the sodium hypophosphite concentration was expected to reach a ratio of 1.2 kg/t DS in dried granules under the dryer working conditions on the moment. After the preparation period of 16 hours, which corresponded to the time needed to ensure a treatment of 90 %, the treated granules produced during 8 hours were directly poured in the loading silo. The treated granules were kept this way in the storage tank from Thursday 13th May 2004 to the following Monday morning like for the previous experiment (Blank 1).

The production of treated dried granules was transported by truck to the working place. There the silo was filled up the same way as made previously. The data logging devices were placed at the same positions as well. The manual measurements started the next day at the same depths and position than for the previous experiment. The remaining granules (around 10 m^3) were taken back to the STP of Bern and poured out from the truck to a 25 m^3 bucket. These granules treated with sodium hypophosphite stayed for one week in this open bucket.

10.2.1 Manual temperature measurements

The temperature inside the storage tank was manually measured. The first day of storage, the temperature increased from the loading temperature of 50 °C to ∼ 90 °C at the top of the silo. The following day, only the temperature at the top position kept on increasing up to ∼ 100 °C for the three different depths. Meanwhile the temperature at the other places slightly decreased. On the third day the runaway started at the top of the silo and the temperature reached 140 °C even though the temperature at the bottom of the tank were only around 35 °C. From that stage on the whole tank started self-heating progressively from its top to the bottom. This heat evolution went on this way down to the cone of the silo. After 7 days the tank has been emptied the same way as for the blank experiment.

10.2.2 Monitored temperature measurements

Both monitoring presented the same temperature profile than those obtained during the storage experiment with untreated dried granules (Figure 10.4). Only the time when the thermal events started are slightly different between the two storage experiments (Table 10.2).

Table 10.2: Onset and maximum temperature for the thermal events occurring during the storage of sodium hypophosphite granules treated with sodium hypophosphite (Treatment 1)

Logger	1st thermal event [a]		2nd thermal event	
	T_{onset} (t_{onset})	T_{max} (t_{max})	T_{onset} (t_{onset})	T_{max} (t_{max})
L$_1$	48.8 (0.3 d)	96.2 (0.4 d)	84.4 (3.4 d)	312.4 (3.5 d)
L$_2$	49.0 (0.1 d)	86.5 (0.2 d)	42.0 (5.7 d)	495.5 (6.0 d)

a) T_{onset} for the initial temperature at the beginning of the thermal event and T_{max} for the maximal peak temperature (°C), occurring respectively at time t_{onset} and t_{max} (days)
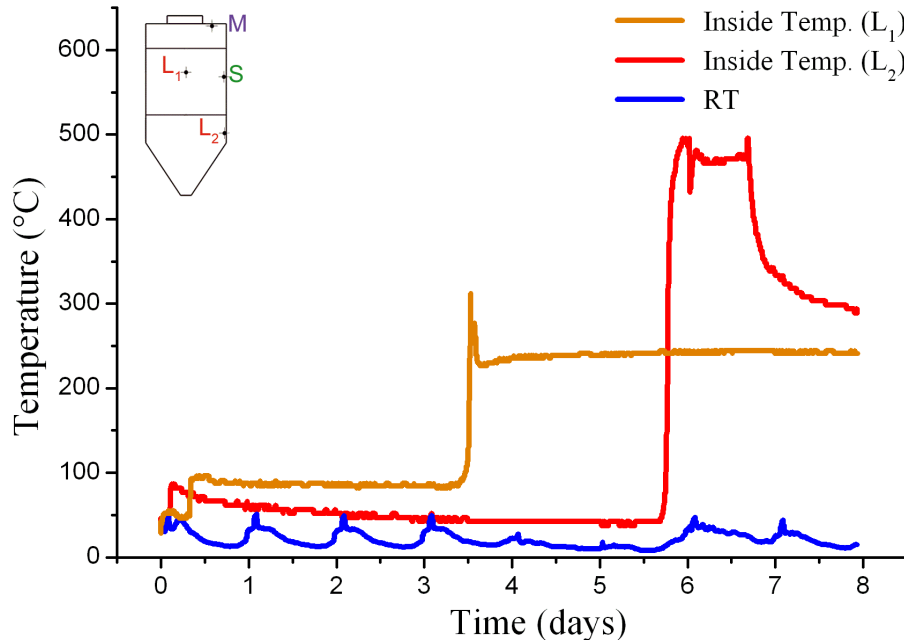
Figure 10.4: Inside temperature at position L_1 (depth = 1.15 m) and at position L_2 (depth = 1.00 m) and room temperature during storage of treated granules (Treatment 1)

10.2.3   Spontaneous combustion of waste treated dried granules in an open bucket

Too much treated granules were produced for this experiment. After filling up the experimental tank, quite a big amount of granules were still left in the truck. Therefore the surplus was taken back to the STP of Bern, where the remaining granules were poured in an open bin. After exactly one week, a smouldering fire took place in the large bucket of 25 m^3 kept inside the dryer hall (Figure 10.5).

An explanation for this fire was that these dry granules were in the truck tank while filling up the experimental silo. They were in fact blown inside the truck tank with hot compressed air, but instead of being transferred to the experimental silo, these granules were poured in an open bin. Contact with air allowed the material to self-heating up to a certain temperature where the spontaneous combustion triggered a smouldering fire.

Figure 10.5: Smouldering fire of a remaining batch of dried granules treated with a sodium hypophosphite solution as antioxidant processing. The fire occurred one week after having been placed in a 25 m^3 open bucket (left) and was extinguished by water addition (right)

10.3 Treatment 2: with Prostab $^{©}$ treated granules

Prostab $^{©}$ is the second antioxidant used for a stabilization attempt. Therefore 675 L of a 0.34 M aqueous solution of Prostab $^{©}$ (40 kg) has been prepared and injected in the three pipes transporting the dewatered sludge to the dryer oven. With an injection flow of $\sim$ 26.5 L/h under the dryer working conditions, the Prostab $^{©}$ concentration is expected to reach a ratio of 0.94 kg/t DS in dried granules. This concentration corresponds to a typical value of 1 ‰ of antioxidant additives as in polymers produced in industrial production. The preparation and the production periods lasted again 16 hours and 7 hours respectively. Instead of leaving the desired fraction of granules in the loading silo at the Bern STP, the production of freshly treated granules was directly transferred to the truck and transported to the gravel pit on Thursday morning 17th June 2004.

10.3.1 Temperature measurements

In this storage experiment, the monitored and the manual temperature measurements were carried out in the same way as for the preceding ones (Figure 10.6). The temperature profiles fit to the previous measurements with first a temperature increase up to 90 $^\circ$C after a few hours, then a steady-state temperature in the upper part of the silo and a temperature decrease down to 50 - 60 $^\circ$C in the lower part of the experimental tank (Table 10.3). After approximatively three

days of storage, a thermal runaway and the consecutive spontaneous smouldering combustion occurred. This thermal event started once again from the top of the silo and propagating downwards. Nevertheless the second temperature increase measured at position L_1 was less pronounced than during the two previous storage experiments.
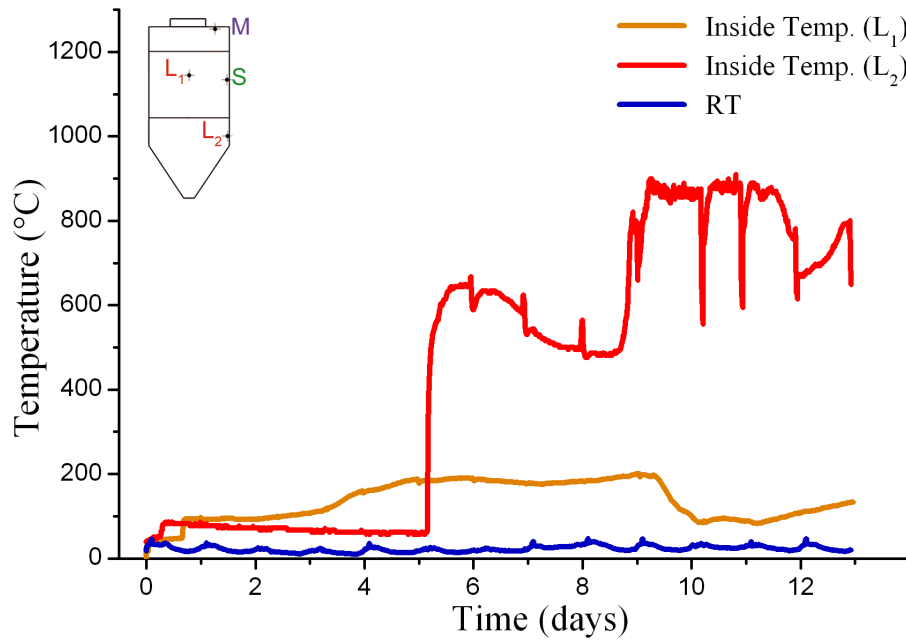
Figure 10.6: Inside temperature at position L_1 (depth = 1.15 m) and at position L_2 (depth = 1.00 m) and room temperature during storage of granules treated with Prostab [©] (Treatment 2)

Table 10.3: Onset and maximum temperature for the two consecutive thermal events occurring during the first storage of treated dried granules in experimental silo (Treatment 2)

	1st thermal event [a)]		2nd thermal event	
Logger	T_{onset} (t_{onset})	T_{max} (t_{max})	T_{onset} (t_{onset})	T_{max} (t_{max})
L_1	47.2 (0.7 d)	93.8 (0.7 d)	93.8 (2.2 d)	189.2 (5.0 d)
L_2	52.0 (0.3 d)	86.5 (0.3 d)	61.5 (5.2 d)	648.5 (5.8 d)

a) T_{onset} for the initial temperature at the beginning of the thermal event and T_{max} for the maximal peak temperature (°C), occurring respectively at time t_{onset} and t_{max} (days)

This storage experiment was planned on a longer time-range in order to observe the behaviour of the smouldering material after the runaway process. In the two previous experiments it has been noted that the inside temperature started to decrease after the thermal runaway. Therefore it was interesting to see if the whole batch of granules would cooled down itself or not. Unfortunately this was not the case, as the temperature rose again after the first thermal runaway. Moreover this additional temperature increase tallied the CO concentration, which started to increase extremely on the eighth day. Very high values (2000 ppm or more) have been reached due to the fire with insufficient oxygen (Figure 10.7). The exact CO concentration could not been measured as the maximal detectable value of the data logging device had been reached. The material inside the storage tank was clearly burning through incomplete combustion. The positive peaks in the CO concentration corresponded once again to the daily opening of the sampling orifice.
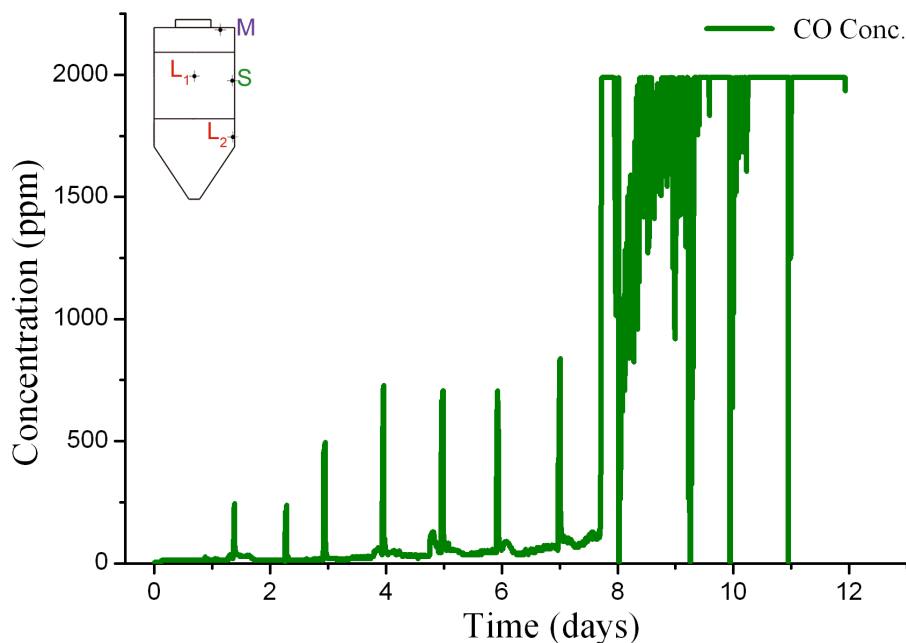
Figure 10.7: CO concentration at position M on top of the experimental silo during storage of treated granules (Treatment 2)

At the end of the storage experiment, the undeclared fire got to the bottom of the silo and also in its cone. The emptying of the smouldering material caused difficulties as the granules caught fire due to the fresh air contact (Figure 10.8). Moreover the cone of the silo was blocked by a very hard layer of sintered material. For security reasons, the whole silo had to be flooded with water to extinguish the fire. Only when the matter had completely cooled down, the obstructing block could be broken and removed.

Figure 10.8: The smouldering granules caught fire due to the fresh air contact during the emptying of the silo (left) and the draining of the very hot granules into the bucket (right)

Chapter 11

Storage experiments using cooled compressed air

The three first storage experiments ended up in catching fire. Obviously the favourable conditions for spontaneous combustion were all fulfilled. Since it was argued that a major factor resided in loading the granules pneumatically with very hot compressed air and a continuous air aspiration on top of the silo, the storage conditions had therefore been modified for a new set of experiments. The compressed air used to load the dried granules into the tank was cooled down with a heat exchanger (Figure 11.1). The compressed air, provided by the transporting truck, was now available at $\sim 15\,^\circ$C instead of $120\,^\circ$C like during the first set of storage experiments. The impact of such a technical measure would be evaluated, and in case of positive results, it can be directly applied at the everyday operation in the cement facilities.

Figure 11.1: Compressed air provided by the truck was connected to a heat exchanger in order to obtain cooled compressed air

The data logging devices for continuous measurement of the temperature and the CO concentration were placed at the same positions as in the first set of storage experiments. The temperature was also manually measured every day at three different depths for each position. The logistics and the dried granules production and transport were carried out in exactly the same manner as in the previous experiments.

11.1   Blank 2: with untreated granules

Around 12 tons of untreated granules were loaded in the truck and taken to the gravel pit where the experimental silo was located. There the material was blown up into the silo with cooled compressed air. After the loading process, the two flexible pipes connected to the top of the silo for loading and dust evacuation, were closed with suitable caps. Consequently no air flow passed at the top surface of the granules although the ventilator was running. The ventilator was only evacuating released gas and moisture present or formed inside of the storage silo.

11.1.1   Temperature measurements

The temperature curve was this time different from the observations made during the previous experiments: only a single temperature increase was measured (Figure 11.2). This thermal event corresponded to the first event also detected during the three past storage experiments with a spontaneous temperature increase from $\sim 40\,^\circ$C to $90\,^\circ$C for the logging device placed at the top position L_1 (Table 11.1). However the temperature did not stay at a steady-state value as observed previously, but decreased to $\sim 35\,^\circ$C within 13 days. Even after 13 days, no further thermal event occurred. The logging device placed at the bottom position L_2 showed first a smaller temperature increase, both with respect to the L_1 temperature and compared to the previous experiments, and then a faster temperature decrease as compared with measurement made at top position L_1.

Table 11.1: Onset and maximum temperature for the thermal events occurring during the second storage of untreated granules in the experimental silo (Blank 2)

| Logger | 1st thermal event [a] | | 2nd thermal event | |
	T_{onset} (t$_{onset}$)	T_{max} (t$_{max}$)	T_{onset} (t$_{onset}$)	T_{max} (t$_{max}$)
L$_1$	46.0 (0.2 d)	96.2 (0.5 d)	- [b]	-
L$_2$	44.1 (0.1 d)	61.8 (0.3 d)	-	-

a) T_{onset} for the initial temperature at the beginning of the thermal event and T_{max} for the maximal peak temperature ($^\circ$C), occurring respectively at time t$_{onset}$ and t$_{max}$ (days)

b) No other thermal event occurred after the first temperature increase
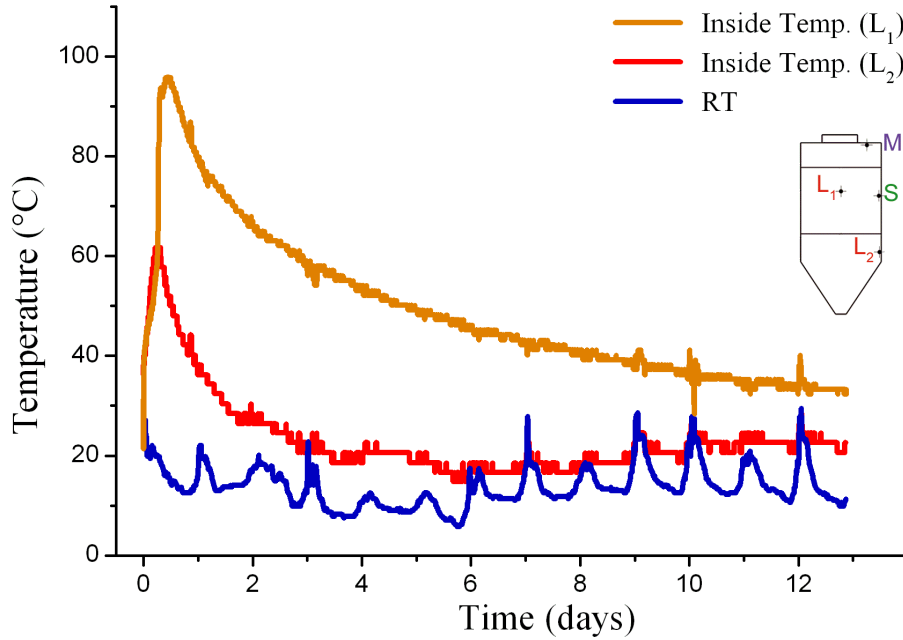
Figure 11.2: Inside temperature at position L$_1$ (depth = 1.15 m), inside temperature at position L$_2$ (depth = 1.00 m) and room temperature during storage of untreated granules (Blank 2)

11.1.2   Carbon monoxide concentration

The logging device, which monitored the CO concentration, showed a low amount of the monoxide concentration only at the beginning of the storage experiment (Figure 11.3). Then the CO concentration decreased rapidly. The peaks appearing on the CO curve corresponded to the sampling periods as already described.

Previously the CO concentration at the beginning of storage experiments was around 10 or 20 ppm. In this case the CO logging device measured higher concentration, up to 76 ppm, over a longer time-range.

This is probably due to the fact that there was no aspiration at the surface during this experiment and hence reduced venting. With the ventilator working and the open aspiration pipes, the gas among the granules was aspirated very quickly from inside the tank resulting in a very low CO concentration at the beginning of the storage experiment. However in this case, the starting CO concentration was not removed by the aspiration, because the aspiration pipes were closed. As the tank was not airtight, it can be easily supposed that a small intake of fresh air allowed the gas composition to reach the top of the silo. Hence, the carbon monoxide originally present within the dried matter may be measured by the device. When the whole CO amount has been removed, no more CO could be measured expect during sampling periods (peaks). No spontaneous combustion was detected as the CO concentration stayed very low.
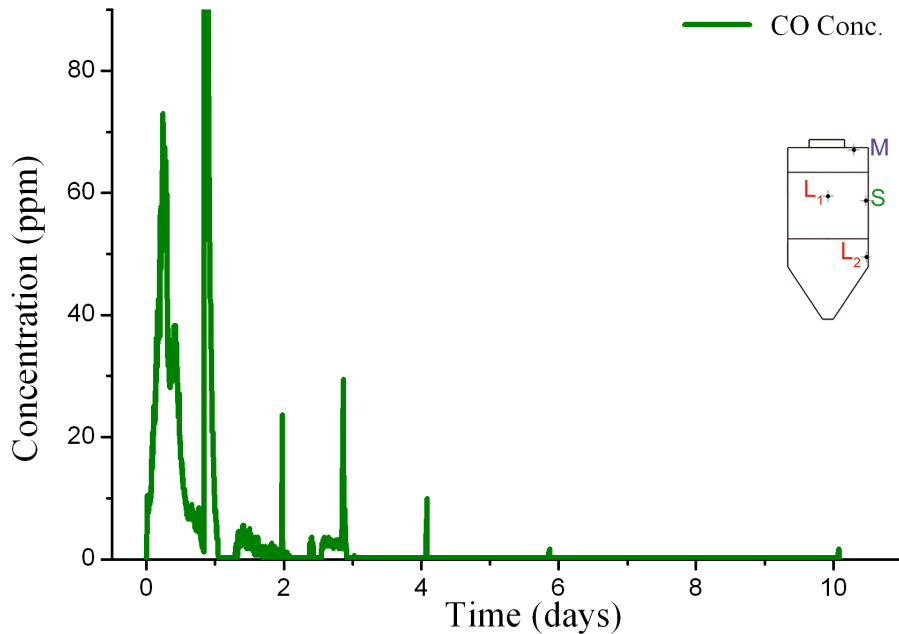
Figure 11.3: CO concentration at position M on top of the experimental silo during storage of untreated granules (Blank 2)

11.2 Blank 3: with untreated granules

As no thermal runaway has been observed during the blank experiment using cooled compressed air and closed pipes, a new storage attempt with untreated granules had to be made under some modified storage conditions. In fact the blank experiment should undergo a thermal runaway in order to see whether it could be avoided afterwards by treating the sewage sludge with antioxidant additives.

This time, after that the experimental silo had been filled up with the untreated granules by blowing them with cooled compressed air, the two loading pipes remained open. This opening caused an air flow at the surface of the granules due to the ventilator at the top of the tank.

The measured temperature at the top position (L_1) showed a single temperature increase of $50\,^\circ$C after 15 hours (Figure 11.4). Then it slowly increased from $\sim 90\,^\circ$C to a maximum of $110\,^\circ$C at the end of the 7 days of storage. No thermal runaway was measured at this position.

Figure 11.4: Inside temperature at position L_1 (depth $= 1.15$ m), inside temperature at position L_2 (depth $= 1.00$ m) and room temperature during storage of untreated granules blown with cooled compressed air (Blank 3)

The temperature measured at the bottom position (L_2) however presented the expected shape with two first temperature increases (Table 11.2). It finally turned in a spontaneous combustion at higher temperatures (around $1000\,^\circ$C).

Table 11.2: Onset and maximum temperature for the thermal events occurring during the third storage of untreated dried granules in experimental silo (Blank 3)

Logger	1st thermal event [a]		2nd thermal event	
	T_{onset} (t_{onset})	T_{max} (t_{max})	T_{onset} (t_{onset})	T_{max} (t_{max})
L_1	43.0 (0.7 d)	96.2 (0.9 d)	- [b]	-
L_2	56.5 (0.3 d)	86.5 (0.4 d)	76.5 (3.7 d)	678.0 (4.2 d)

a) T_{onset} for the initial temperature at the beginning of the thermal event and T_{max} for the maximal peak temperature ($^{\circ}$C), occurring respectively at time t_{onset} and t_{max} (days)

b) No other thermal event occurred after the first temperature increase. However the temperature kept on increasing smoothly up to 110 $^{\circ}$C

The concentration profile for the carbon monoxide fitted to the previous experiments. During the first days of storage a constant CO concentration (between 10 and 30 ppm) was measured, followed by an increase around the fourth day up to 150 ppm, which corresponded to the thermal runaway detected with the temperature logging device (L_2), and finally the smouldering fire caused very high concentration of carbon monoxide (2000 ppm and more).

11.3   Treatment 3: with HTMP $^{©}$ treated granules

After this satisfactory blank experiment had been obtained, the storage of treated dried granules was planed in the following conditions: cooled compressed air as blowing conditions and the two loading pipes remaining open like for the third blank experiment. Therefore dewatered sewage sludge sustained an antioxidant treatment in the sewage treatment plant of Bern. The obtained dried granules were used for the storage experiment as previously.

HTMP antioxidant is an additive provided by Ciba SC which is used for the stabilization of polymeric materials. A solution of this antioxidant was used for dried sewage sludge treatment in order to inhibit the self-heating and the runaway processes. Therefore 650 L of 0.49 M *HTMP* aqueous solution (50 kg) were prepared and injected in the three pipes transporting the dewatered sludge to the dryer oven. With an injection flow of $\sim$ 24.5 L/h under the dryer working conditions, the concentration of the *HTMP* antioxidant was expected to reach a ratio of 1.05 kg/t (solid content) in dried granules. This concentration fitted again the commonly used 1 ‰ of antioxidant additives in polymers produced in industry. The preparation and the production periods lasted 16 hours and 7 hours

respectively. The production of freshly treated granules was directly transferred to the truck and transported to the gravel pit on Thursday afternoon 28th October 2004.

11.3.1 Temperature measurements

Both temperature logging devices at the top position (L_1) and at bottom position (L_2) showed two consecutive temperature increases (Figure 11.5). The fact that the first temperature increase occurred later than observed in the past experiments was due to a dysfunction of the fan. Ventilation at the top of the tank was not working when the storage experiment was started. The fixing of the problem allowed to begin ventilating only after 17 hours of storage.
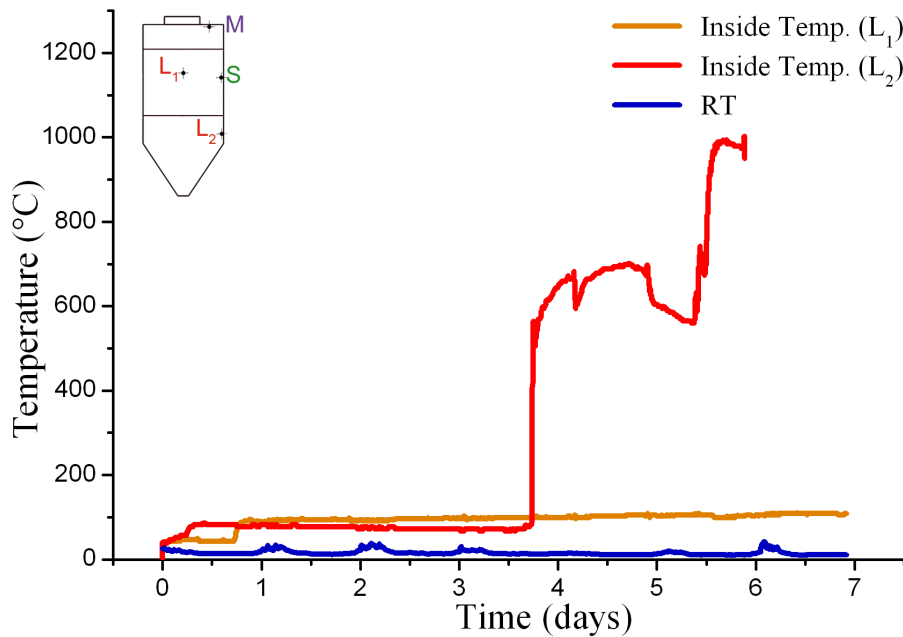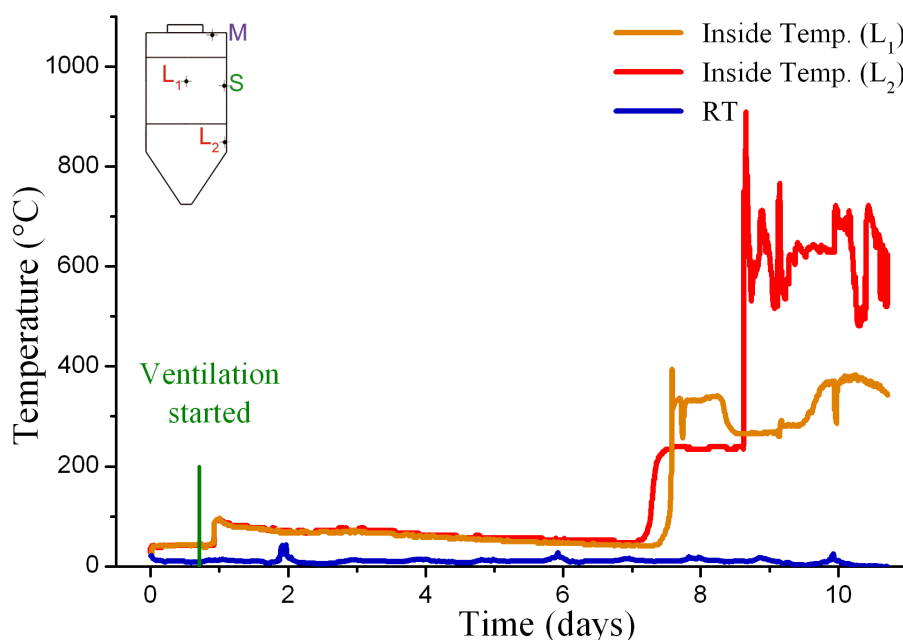

Figure 11.5: Inside temperature at position L_1 (depth = 1.15 m), inside temperature at position L_2 (depth = 1.00 m) and room temperature during storage of treated granules blown with cooled compressed air (Treatment 3)

It has to be noted that the onset and maximum time for the two consecutive thermal events corresponded to the other experiments if the 17 hours without ventilation were taken into account (Table 11.3).

The runaway occurring at the seventh day presented a smaller temperature increase at both measured positions (L_1 and L_2) than before. The temperature reached only 333 °C and 240 °C respectively on the top and the bottom posi-

tions. The lowest logging device however detected a third temperature increase, which occurred after a steady-state period of less than two days. A smouldering fire was clearly taking place before the ninth day despite the antioxidant present.

Table 11.3: Onset and maximum temperature for the thermal events occurring during the storage of treated dried granules in experimental silo (Treatment 3). Values given for the period under ventilation started 17 hours after loading

| | 1st thermal event [a)] | | 2nd thermal event | |
Logger	T_{onset} (t_{onset})	T_{max} (t_{max})	T_{onset} (t_{onset})	T_{max} (t_{max})
L_1	46.0 (0.2 d)	96.2 (0.3 d)	43.0 (6.7 d)	333.0 (6.9 d)
L_2	42.0 (0.2 d)	91.0 (0.2 d)	52.0 (6.4 d)	239.0 (6.9 d)

a) T_{onset} for the initial temperature at the beginning of the thermal event and T_{max} for the maximal peak temperature ($^{\circ}$C), occurring respectively at time t_{onset} and t_{max} (days)

11.3.2   Carbon monoxide concentration

During the first 17 hours of storage, there was no ventilation working on top of the experimental silo due to a technical problem. It is worth mentioning that the measured CO concentration was very low at that stage (4 ppm) and was therefore only coming from the inert dryer gas atmosphere present in the surrounding of the granules (Figure 11.6). When the ventilation was then started again, the curve for the carbon monoxide concentration showed an immediate increase to 20 ppm. After a steady-state period of 15 hours, the CO concentration reached 50 ppm and then decreased to 4 ppm.

A further increase of the CO concentration between the second and the third day of storage was due to a second stall of the ventilator. As the gas was no longer vented from the inside of the silo, the concentration of carbon monoxide accumulated to 470 ppm in the empty space above the surface of the granules. This proves that during the steady-state period occurring after the first temperature increase, a slow oxidation process is already running. This can easily be deduced from the important amount of CO, which can not come only from the original dryer gas surrounding the granules.

Moreover the concentration of carbon monoxide confirmed that a smouldering fire with a total carbon oxidation had already started on the sixth day of storage,

and before reaching extremely high values two days later (Figure 11.7). Again the sudden peaks in the CO concentration curve corresponded to the sampling sessions.
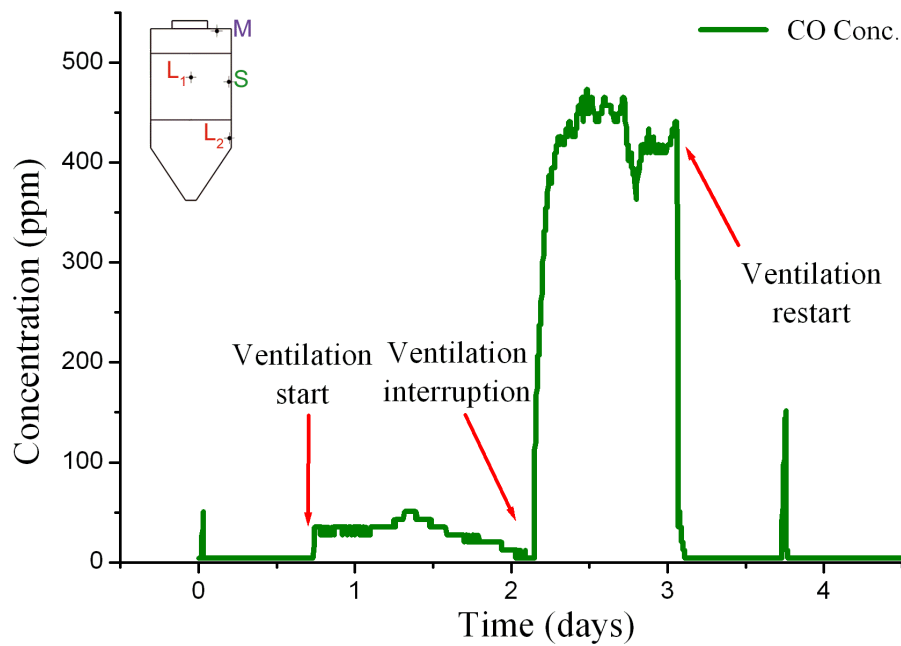
Figure 11.6: Zoom of the CO concentration at position M on top of the experimental silo during storage of treated granules (Treatment 3)
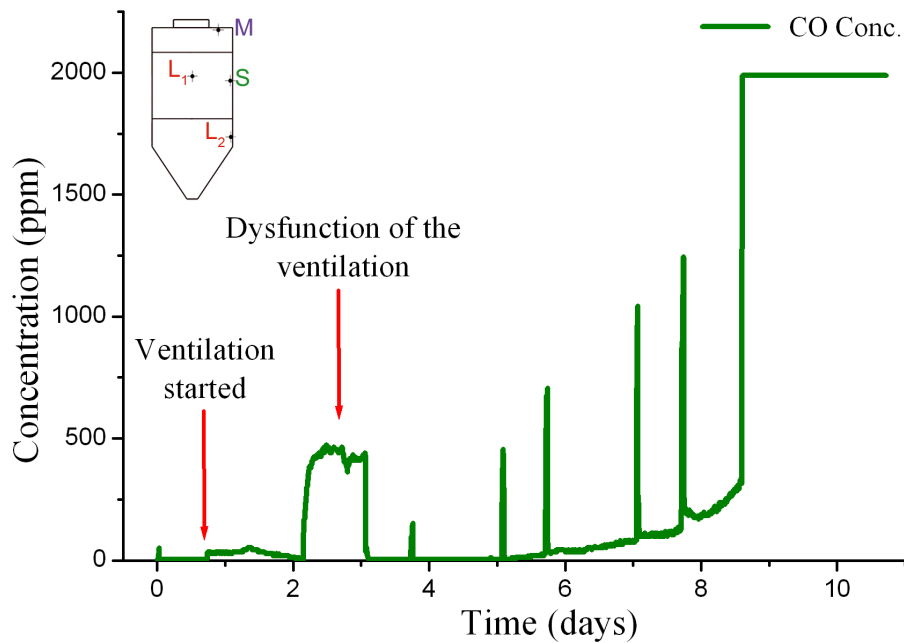
Figure 11.7: CO concentration at position M on top of the experimental silo during storage of treated granules (Treatment 3)

11.4   Conclusions

The six storage experiments made in an industrial silo can be separated in two groups according to the loading conditions of the dried sewage granules, respectively using hot compressed air or cooled compressed air. Five storage experiments showed similar well defined temperature developments independently if the granules were treated or not (Table 11.4). The temperature profiles consisted in a first temperature increase taking place in the first few hours (5 - 7 hours) after the loading, a steady-state period running on a few days (4 - 6 days), then followed by a thermal runaway and the consecutive smouldering fire (Figure 11.8).

Table 11.4: Spontaneous thermal events during the storage experiments of the dried sewage granules loaded with hot or cooled compressed air

	Untreated sludge			Treated sludge		
Loading	Blank 1	Blank 2	Blank 3	Treat. 1	Treat. 2	Treat. 3
Hot air	ΔT, fire [a]			ΔT, fire	ΔT, fire	
Cooled air		ΔT, no fire	ΔT, fire			ΔT, fire

a) ΔT used for the first temperature increase, and 'fire' for the thermal runaway

For the first thermal event, the temperature reached generally higher values at the logging device placed at the top position (L_1) as compared to the temperature measured beneath (L_2). This can be explained by the contact with the fresh air at the top part of the silo, which triggers the oxidation and releases heat. However in the major cases, this temperature increase was measured first with the logging device placed at the bottom position (L_2), which was attributed to the insulating properties of the material, because without any heat exchange with the air, as it occurs at the top of the silo, the heat released accumulates faster.

The second temperature profile is the steady-state period of several days occurring after the first temperature increase. At the top position, the temperature stayed more or less constant over this period of time, whereas the temperature measured in the bottom part of the storage silo decreased from 90 °C to the initial loading temperature ($\sim$ 40 °C). This steady-state period detected at the silo top position due to the continuously renewed atmosphere above the stored granules, made by the aspiration of fresh air via the open loading pipes. This process maintains the oxidation of the material at this location, whereas at the bottom position, no enough air intake enables the oxidation to continue, resulting in a slow temperature decrease.
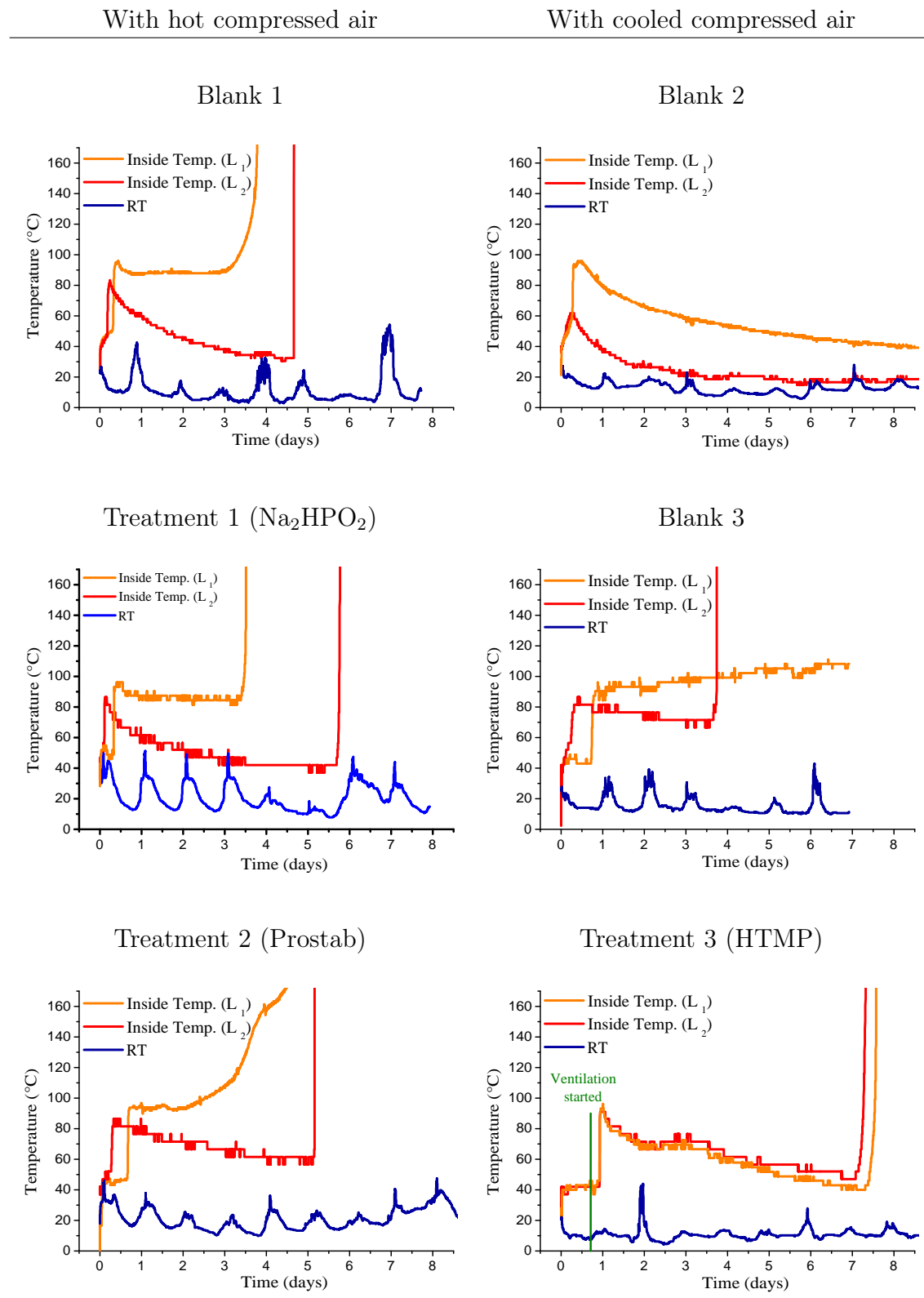
Figure 11.8: Temperature profiles measured during the storage experiments of dried sewage granules in an industrial silo

After this incubation period of several days, a thermal runaway occurred, which started from the top of the tank (position L_1) and propagated downwards (position L_2). This was confirmed by the thermal runaway delay measured between the two devices. Both the very high temperature and the large values for the carbon monoxide concentration confirmed a smouldering fire.

One storage experiment showed only the first temperature increase without further thermal events. Since in this case no air flowed over the top surface of the stored granules, due to the closed pipes, it clearly indicates that sufficient oxygen intake is required to maintain the oxidative processes leading to the steady-state temperature period and the thermal runaway. In contrast no additional air flow is needed for the first temperature increase to occur. This means that enough oxygen is present within the granules. This oxygen comes from the remaining oxygen present in the protecting atmosphere in the dryer plant ($\sim$ 4 - 6 %) and from the pneumatic loading using compressed air.

The antioxidant treatment only delays the beginning of the thermal events. However finally each stage of the temperature profile is observed in spite of the antioxidant treatment. Therefore under these storage conditions, fire risks can not be suppressed by an antioxidant treatment in concentrations of 1 $^0/_{00}$ solid content.

The use of cooled compressed air instead of hot compressed air for loading the material in the silo is not an issue as no significant changes was observed under these conditions. For the unique experiment with closed pipes (Blank 2), the absence of a thermal runaway is not due to the use of cooled compressed air, but by the absence of continuous renewal of the atmosphere above the top surface of the stored granules by fresh air.

Another fortuitous observation, due to the suboptimal working of the ventilator (occurred during the 'Treatment 3' storage experiment), shows that the thermal runaway also happens if air is not continuously flowing through the storage tank. This situation corresponds very much to the reality as loading new batches of dried sludge granules is not continuous, therefore air is not blown all the time, but an ignition may start anyway at any time after a sufficient contact with air!

The fact that the granules burn as well in an open bin is a very significant observation. Essential for an ignition is that the granules were blown up inside the truck with the compressed air and have contact with fresh air, when left in an open

bin. Therefore neither the shape of the container, nor the open or closed system is the clue of the auto-ignition of the dried granules. It is only the contact with air followed by thermal insulating conditions which supports the runaway.

The assumption concerning the presence of *hot spots* at a definite place, which triggered the autoxidation, was not confirmed. Actually the numerous temperature measurements showed that the thermal events did not happen at the definite location, but where sufficient air was available and where heat release was prevented. Therefore it can be concluded that there were no *hot spots* within the stored mass responsible for the self-heating at a specific position.

Chapter 12

Storage experiments in a quasi-adiabatic calorimeter (QuAC)

As part of the of the collaboration with College of Engineering and Architecture of Fribourg within the framework of a CTI project, several student projects were carried on under the supervision of the professors Dr Kurt Käser and Olivier Naef. These projects consisted first in the construction and the startup of a model silo for monitoring labscale storage experiments of the dried sewage granules. More precisely this model silo constituted a quasi-adiabatic calorimeter due to its large storage capacity between 100 and 200 L, and its insulating properties caused by the material itself and its controlled surrounding obtained by means of a thermostatted water bath.

12.1   QuAC 120

The first quasi-adiabatic calorimeter was made by the fitting of two steel barrels of 120 and 200 L separated by a glass wool insulation[1]. The top of the calorimeter was also insulated by a thick glass wool lid. Several temperature probes were placed at different positions and the temperature was measured continuously via several logging devices connected to a computer for saving and processing.

The QuAC 120 model silo was first tested by filling up the inside barrel with water and measuring the temperature variations within the system. Even with the glass wool insulation between the two steel barrels, it turned out that the daily fluctuations of the ambient air temperature had an impact on the measurements made inside the QuAC 120 model silo. Therefore it was decided to place the

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[1]made by Boris Droz (advanced work, EIA-FR 2005), Ludovic Clément and Nicolas Charbonnet (practical work, EIA-FR 2005)

calorimeter in a water bath in order to control the surrounding temperature while dried sewage granules were stored.

12.2   QuAC 100

A new macro calorimeter (QuAC 100) with a storage capacity of 100 L was built by the fitting of two stainless steel barrels of 100 and 200 L separated by a crushed glass insulation[2] (Figure 12.1). Other equipments such as air intake or cooling system by nitrogen or water addition were also installed. This was planned in order to study first the effect of air on the stored granules, and secondly to allow for an emergency measure in case of auto-ignition of the material.
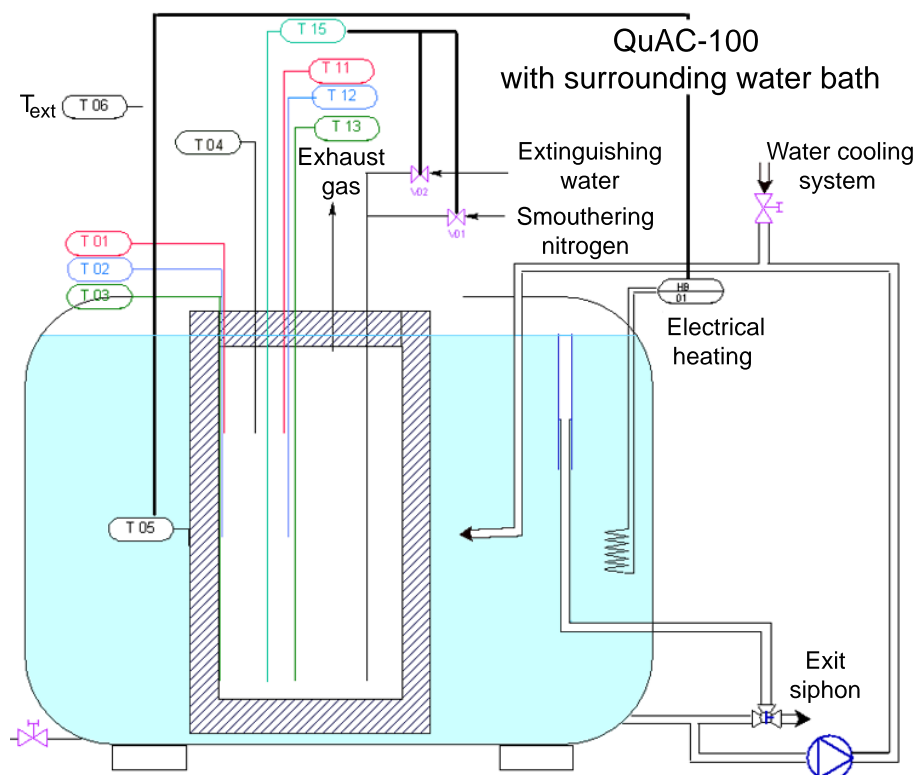
Figure 12.1: Scheme of the quasi-adiabatic calorimeter with a storage capacity of 100 L (QuAC100) placed in a water bath for controlling the surrounding temperature

All the temperature logging devices were installed and connected to a computer. A program was made with *Labview* for monitoring the data and for regulating the electrical heater. This program also allowed a continuous control of the inside

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[2]made by Alexis Delacrétaz (diploma work, EIA-FR 2005)

temperature by sending automatically regular e-mails for the actual temperature and emergency sms messages and e-mails if the limit temperature had been reached. Moreover some automatic emergency measures were programed in case that the stored granules would undergo a thermal runaway with a consecutive fire.

This new calorimeter was first tested to determine the thermal parameters of the system. This was again done by filling up the insulated barrel with water and by measuring the steady state temperature difference over the composite barrel wall in function of the power of an internal calibration heater. The alarm and the emergency measures were also tested during this first period.

12.2.1   Storage experiment at 40 °C

Afterwards the storage experiments of dried sewage granules could be started on the QuAC 100 model silo. To do so, an insulated barrel of 120 L was filled up with freshly prepared dried granules and the material was transported on a small truck from the STP of Bern to the College of Engineering and Architecture of Fribourg. There the QuAC 100 model silo was filled up manually within an hour with the dried sewage granules and closed for the storage experiment in a water bath at 40 °C (experiment A).

First it can be observed that an exothermic event occurred within the stored material (Figure 12.2). Indeed the temperature probes placed in the center of the model silo (T11, T12 and T13) and the one placed at the half-radius middle height (T04) presented all a temperature increase of 10 °C over the temperature of the water bath (40 °C). Moreover a trend can be observed, which consisted in a temperature increase starting from the top of the model silo (T11) down to the bottom of the silo (T13). This can be confirmed by the fact that the temperature rise was similar for the temperature probes placed in the center (T12) as compared for the one placed at the same hight, but at the half-radius of the silo (T04). The three temperature probes placed on the inside wall of the model silo (T01, T02 and T03) did not present an important thermal event due to the heat transfer towards the nearby water bath despite an insulating layer separating both media.

These experiences in this model silo confirmed the results of the large scale storage experiments for the first thermal event. However only the first temperature increase could be repeated in this model silo placed in a water bath at 40 °C.
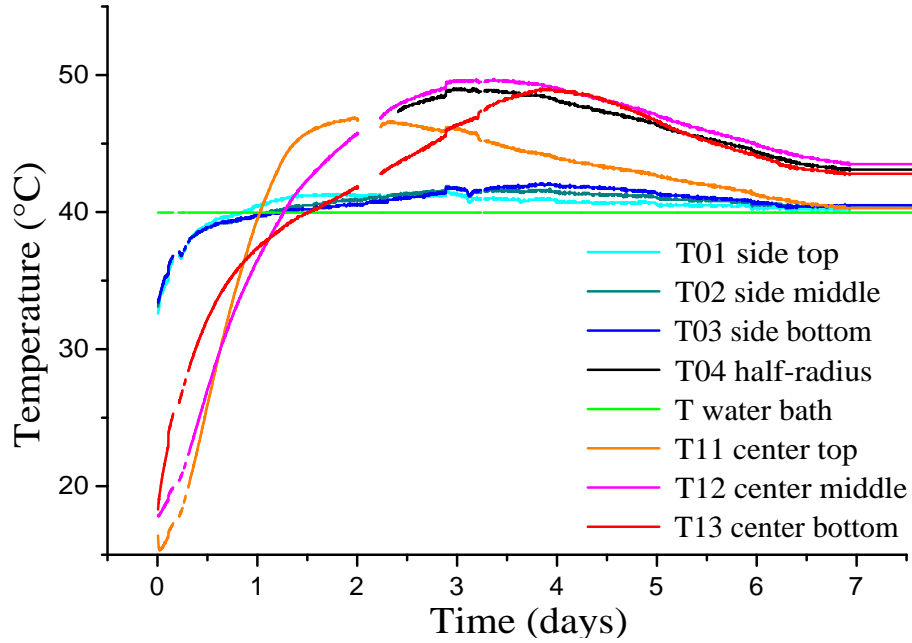
Figure 12.2: Temperature profiles measured inside the model silo QuAC 100 placed in a water bath at 40 °C (experiment A)

Under these quasi-adiabatic conditions, no thermal runaway events occurred during the storage of dried sewage granules. The trend of the temperature increase from the top to the bottom of the model silo was similar to the one in the large scale experiments. In the present set up, the model silo was not closed tightly and even though an insulating lid was placed on the top of it, fresh air intake was supposed to occur by thermal air flow.

During the last day of storage, airflow[3] of 1 L/min was forced on through the stored granules in order to see if an air intake would restart a self-heating process. However no thermal event occurred during the two hours of air intake through the system. This signifies that when this first temperature increase is over, it is not possible to reactivate it by adding oxygen. At a given temperature (40 °C) an oxygen intake can not start or restart an exothermic process once the first thermal event has ceased.

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[3]for an empty container this air flow corresponds to an air rising velocity of 6.3 mm/min and to a gas renewal of 1.7 h

12.2.2   Storage experiments at 60 °C

Two other storage experiments were performed with this model silo (experiment B and C). The loading of the QuAC 100 was similar than for the experiment carried out at 40 °C. Both storage experiments presented a similar temperature increase of ~ 10 °C above the temperature of the surrounding water bath (Figure 12.3). The temperature rise followed the already observed trend consisting in a temperature increase starting from the top of the model silo (T11) down to the bottom of it (T13). These data were used for modeling and computational simulations.
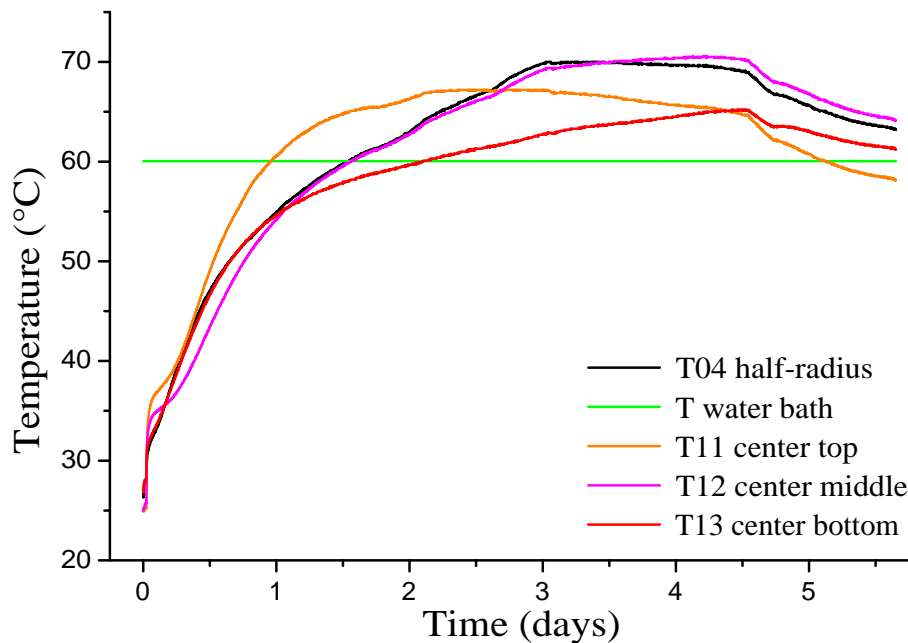
Figure 12.3: Temperature profiles measured inside the model silo QuAC 100 placed in a water bath at 60 °C (experiment B)

12.3   QuAC 200

In order to check the impact of forcing air through the stored granules, a third macrocalorimeter was built, consisting this time in a 200 L stainless steel barrel directly placed in the water bath without added insulation[4]. After the installation of this new system (including adequate preliminary tests), the QuAC 200 model silo was brought to the STP of Bern for filling it up directly with the dried sewage granules. Then the QuAC 200 model silo containing the dried biosolids was transported back to the College of Engineering and Architecture of Fribourg and

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[4]made in 2007 by Jean-Marc Juan (advanced work)

placed inside the water bath without any additional insulation. The temperature logging devices were installed at the same positions as in the previous storage experiments and the measurements directly processed with the developed program.

12.3.1   Storage experiment at 50 °C

The first storage of the dried sewage granules in the QuAC 200 was performed with a water bath at 50 °C. However some technical problems prevented the measurement of the inside temperatures for the first 19 hours of storage. After this time, the four temperature probes within the dried sewage granules (center top to center bottom: T01, T02, T03 and half-radius middle height: T04) showed temperatures around 5 °C higher than the surrounding water bath. The inside temperature decreased in a constant way until the eighth day, when air was added in a flow[5] of 4 L/min from the bottom of the silo. From this moment on, the temperature dropped below the temperature of the water bath due to this important injection of cold air. The fact that no temperature increase was observed at the beginning of the storage was only due to the 19 hours delay before the onset of temperature measurements. No further thermal event could be observed during the two weeks of storage, even with air injection.

12.3.2   Storage experiment at 70 °C

A second attempt was made with the QuAC 200 model silo. This time the water bath was planned to reach 70 °C. However, the intake of fresh water for compensating the water evaporation caused a steady state temperature at only $\sim$ 65 °C. Moreover a constant air flow[6] of 5 L/min was injected at the bottom of the silo via a metallic cannula, starting at the beginning of the storage experiment.

The temperature profiles for the probes placed within the material presented a steeper temperature increase for the first thermal event as compared to the previous experiments (Figure 12.4). A maximal temperature increase of nearly 22 °C above the water bath temperature was noted. The time to reach this temperature was only 10.3 hours. After the fourth day, the inside temperatures became constant again. The storage silo and the material inside were left that way for a whole week without any further temperature variations.

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[5]air rising velocity: 1.8 cm/min, gas renewal: 50 min
[6]air rising velocity: 2.2 cm/min, gas volume renewal: 40 min
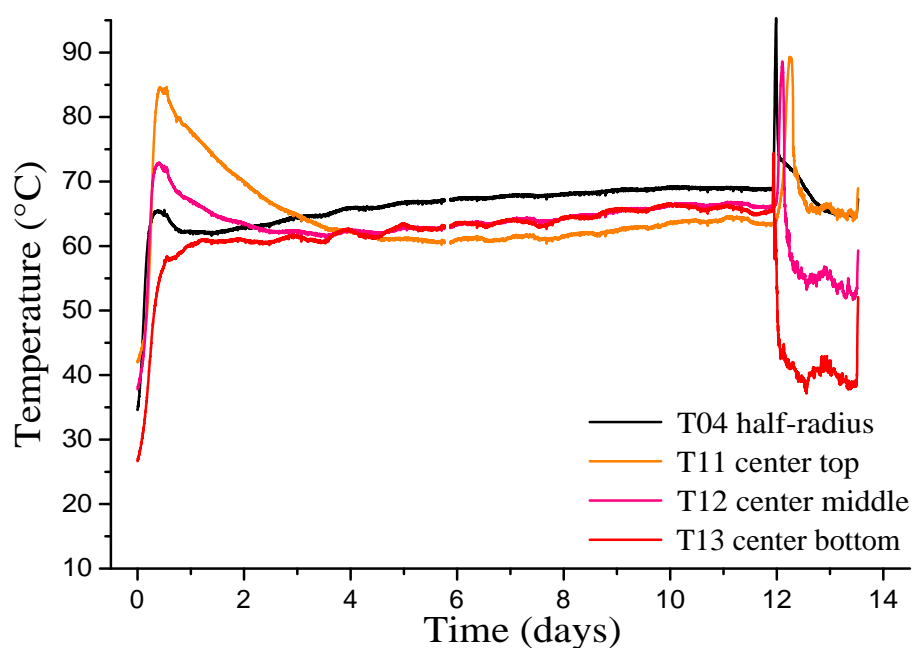
Figure 12.4: Temperature profiles measured inside the model silo QuAC 200 placed in a water bath at 70 ° C with a continuous air flow of 5 L/min

However, after 12 days of storage a new unexpected thermal event occurred and could be measured with the four temperature probes within the material. This exothermic process presented an even higher temperature increase as compared to the first thermal event. The maximal temperature increase reached more than 26 ° C above the previous steady-state temperature in only less than 2 hours for the temperature probe T04 at half-radius and middle height (Figure 12.5).

This second temperature increase could be explained later by some water overflowing from the bath into the stored dried granules. Some calcareous traces could be observed on the inside wall of the stainless steel barrel. This accidental water overflowing was caused by an obstruction of the siphon exit of the water bath by limestone residues (boiler scale), which allowed the water bath level to reach the top of the submerged container. The considerable low temperature after this exothermic event was assigned to the evaporation of the overflowing water within the hot granules mass. Actually the air flow was still injecting an important amount of cold air, which helped the evaporation process.
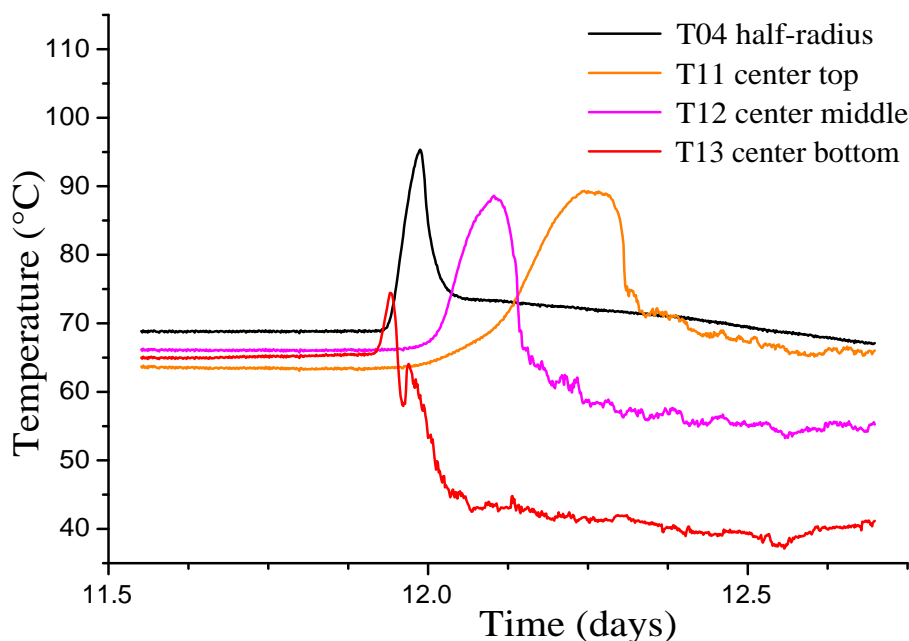
Figure 12.5: New exothermic process observed caused by a light overflowing of the water bath within the stored granules during a storage in the QuAC200 placed in in a water bath at 70 ° C

12.4   Conclusions

All five storage experiments in the quasi-adiabatic calorimeter presented a spontaneous temperature increase within the stored dried sewage granules (Table 12.1). The temperature increase and the time to reach the maximal temperature rise is enhanced when an air flow went through the stored dried sewage granules (entry 5). This greater temperature increase only occurred when the air flow through the material is started from the beginning of the storage experiment. However the addition of air after the end of the first thermal event did not present any further exothermic processes (entry 1 and 4). On the contrary, the temperature within the granules even dropped under the water bath temperature due to the injection of cold air.

The incident (flooding) in the last storage experiment with the QuAC 200 model silo gave an additional interesting hint on an exothermic process occurring when some water is added. The rate of addition could not be determined, but the calcareous traces on the inside wall of the stainless steel fit with a very faint water addition. Unfortunately the material could not be analyzed afterwards due to a

Table 12.1: Summary of the storage experiments in the model silos working as a quasi-adiabatic calorimeter QuAC 100 and QuAC 200

Model silo	Entry	$T_{waterbath}$ (˚C)	Air flow (L/h)	Start	ΔT_{max} [a] (˚C)	t_{max} [b] (days)
	1	40	1	end	10	3.4
QuAC 100	2	60		no	11	4.1
	3	60		no	10	4.3
QuAC 200	4	50	4	end	- [c]	-
	5	70	5	beginning	22	0.4

a) ΔT_{max} for the maximal temperature increase compared to the water bath

b) t_{max} for the storage time to reach the maximal temperature increase

c) No measured temperature increase due to a temperature logging problem

total overflowing of the QuAC 200 and the stored granules. In conclusion, a small water addition into the stored material induced an exothermic process, which was very suddenly releasing an important amount of heat.

Part V

Results of the research project

Chapter 13

Hypothesis 1: low-temperature oxidation

This hypothesis (H1) assumed a spontaneous oxidation of the organic part occurring at low temperature range induced for instance by some specific conditions of humidity and air. The heat released by this spontaneous degradation would accumulate within the storage tank due to the insulating properties of the material. The temperature increase would then accelerate the oxidation and the self-heating processes.

13.1 Dry solids content in sewage granules

The dry solids (DS) content in the sewage granules and the particles size repartition of this biowaste are measured and reported everyday at the STP of Bern. The data represent valuable information in order to control the evolution of the material in function of the dryer working conditions.

13.1.1 Relationship with the storage experiments

The DS content of the sewage granules used for the storage experiments using the industrial silo was also investigated in order to find the clue of the spontaneous combustion. From the data collected at the STP of Bern, it was obvious that the DS content of the granules fitted to the daily value (Table 13.1). Although the sampled sewage granules presented a significant variation in the amount of moisture, there was no correlation, which could explain the self-heating phenomena, since the only case with no runaway exhibited the usual state of dryness.

Table 13.1: Dry solids content of the sewage granules taken for the storage experiments using the industrial silo (collected data from the STP of Bern)

	Storage experiments	Dry solids content (%)	Runaway
Hot air	Blank 1	90.7	yes
	Treatment 1	92.0	yes
	Treatment 2	91.9	yes
Cooled air	Blank 2	92.3	no
	Blank 3	94.2	yes
	Treatment 3	89.2	yes

13.1.2 Sampling during the storage experiment (Blank 1)

During the first storage of dried sewage granules in an experimental tank, some samples were taken from the inside of the silo at the position S_2 (see section 9.3). These samples represented very well the whole batch of dried sewage granules, as important mixing occurred during the loading of the truck and during the filling of the storage tank with compressed air.

The sampling was performed at different depths from the silo side, at 75, 95 and 115 cm towards the center respectively. Various samples were taken over several days, even when the thermal events were occurring. Before the start of the experiment, a fresh sample of dried sewage sludge was taken at the STP of Bern and would be used as reference material.

Within the batch of granules taken during this storage experiment, there were some large moist granules, which have been sampled for further analyses. These granules contained only $\sim$ 85 % DS, which corresponds to an important amount of moisture. Such large granules were hardly ever observed, when the sampling was performed after the cooling part of the dryer plant. Therefore they had to be formed afterwards. It is possible that some water condensation occurred further in the loading silos. Actually the large loading silos at the STP of Bern are not insulated and temperature variations may allow the formation of moist granules, which agglomerated together to form larger units.

As the experiment progressed, the temperature increased in the storage tank as previously observed. Due to sustained heating by the first thermal event, the moisture was removed from the granules leading to a higher dry solids content

(Table 13.2). On the fourth day of storage, the sewage granules were completely free of moisture. This situation offered more favourable conditions to the spontaneous combustion as no more energy was actually needed to evaporate the remaining water. The released energy was accumulated as heat in this insulating system allowing the thermal runaway to occur.

Table 13.2: Dry solids (DS) and ash content of some samples of sewage granules taken during the first storage experiment (Blank 1)

Sampling time $t_0 + \Delta t$ (days)	Indicative Temp. (°C)	Depth (cm)	DS content (%)	Ash content from DS (%)
t_0	50	75	93.5	48.9
		95	93.6	48.4
		115	92.5	48.9
$t_0 + 1.0$	80	75	94.0	47.8
		95	96.0	49.0
		115	95.0	49.5
$t_0 + 3.8$	100	75	98.0	49.0
		95	98.0	49.2
		115	98.5	49.8
$t_0 + 4.0$	120	75	99.5	50.8
		95	100.0	50.8
		115	100.0	51.8
$t_0 + 5.0$	150	75	100.0	53.0
		95	100.0	52.5
		115	99.5	52.0

It is also worth mentioning that the ash content remaining after combustion[1] also increased as the storage experiment progressed. This highlighted that some organic part was already lost at that stage due to the autoxidation.

13.2   X-Ray fluorescence

The samples taken at different depths during the first storage of dried sewage granules (Blank 1) like previously described, were also analyzed by X-Ray Fluorescence. The aim of the XRF analyses consisted in determining the elementary

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[1]from DS, 3h at 650 °C

composition of the material in order to estimate the homogeneity of this biowaste within the stored mass. It would be worth knowing if the dried granules exhibited different chemical compositions at different locations in the storage silo, because such variation in the material composition could give clues pertaining to the origin of the autoxidation. As already mentioned the presence of *hot spots* responsible for the self-heating at a definite place was suspected.

The XRF analyses allowed the determination of chemical elements except the light elements such as H, N, C, O. As the dried sewage granules contain an important amount of organic material ($\sim$ 50 % DS), the XRF analyses gave only semi-quantitative results in this particular case. However this technique was suited perfectly for studying the elementary homogeneity within the biosolid samples.

13.2.1 Iron concentration

First of all the iron concentration in the dried sewage granules was analyzed. A comparison of the iron amount present in a reference sample, which was taken at the STP of Bern before the start of the storage, and in the collected stored samples was made. As the XRF measurements gave semi-quantitative results in this particular case, the measured iron concentration of the stored samples was normalized towards iron concentration of the reference sample. The iron concentration of this reference sample was determined by AAS and corresponded to 9.5 % DS.

The normalized iron concentration in the stored samples varied only slightly ($\pm$ 5 %) from the reference value (Figure 13.1). This indicated that the iron concentration was constant within all the samples taken during this storage experiment and fitted also to the reference sample checked with AAS.

The large moist granules were also analyzed by XRF and did not present any significant variation in the iron concentration either, when compared to the reference sample.

13.2.2 Other elements

The other elements present in this biowaste have also been analyzed by XRF. The two large moist granules and the samples taken during the storage experiments have been compared to the reference sample. These analyses gave the concentration
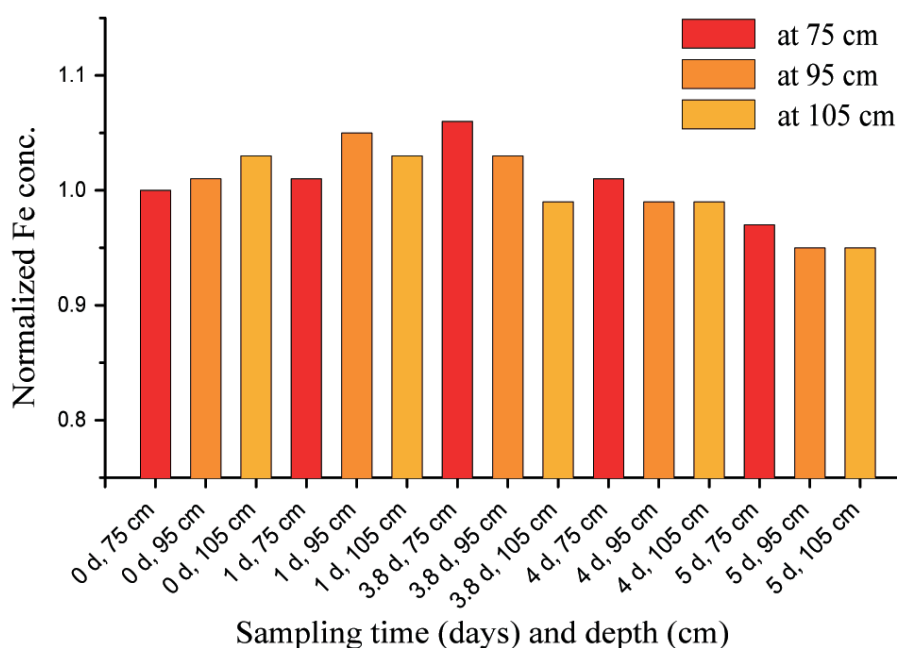
Figure 13.1: Iron concentration in dried sewage granules taken at different time and depths determined by XRF analyses. The concentration was normalized to the iron concentration of the reference sample

for 26 elements with a concentration of more than 100 ppm. It was quite surprising to notice that the concentration of all measured elements did not vary significantly from one sample to another. The results fit also to the analyses performed previously by the quality control laboratory. The elements present in a larger ratio than 1% DS in sewage granules were aluminum, silicon, phosphor, sulfur, calcium and iron. The other measured elements were present at a lower concentration or at trace concentration.

In conclusion it can be stated that the elementary composition of the dried sewage granules was quite constant over the 18 samples analyzed, which consisted in 1 reference sample, 2 samples of large moist granules and 15 samples of stored granules taken at three different depths over the five days of storage. With only a very slight variation of its elementary composition, the stored material consisted of a homogeneous material. Therefore the presence of hot spots due to an heterogeneous composition of the dried granules can be discarded at least for the main elements. The elementary composition of the light elements (H, C, N, O), which are not measured by XRF analyses, will still have to be studied.

13.3   Elemental analyses (CHN)

On the reference taken at the STP of Bern before the start of the first storage experiment (Blank 1), elementary analyses (CHN) have been performed (Table 13.3).

These values were confirmed by other CHN analyses made on different samples. Generally the amount of carbon within the sewage granules represented around 25 % of the biowaste and for hydrogen and nitrogen, 3.5 % and 3 % respectively. All the results of CHN analyses presented quite similar values, therefore no significant variation of the elementary composition could support the assumption of hot spots induced by the heterogeneity of the material.

Table 13.3: Dry solids (DS) content, ash content and the elementary composition (CHN) of the reference sample for the first storage experiment (Blank 1)

Analyses	DS content (%)	Ash content (% DS)	C (% DS)	H (% DS)	N (% DS)
1			26.5	3.94	3.18
	91.5	48.6			
2			26.4	3.91	3.14

According to the regularly performed state analyses, which gave information concerning the total amount of oxygen, sulfur and nitrogen present in the sewage granules, it was finally possible to estimate the elementary mass ratio of the organic phase of this dried biowaste, which corresponds to:

- $\sim$ 50 % Carbon

- $\sim$ 35 % Oxygen

- $\sim$ 7.5 % Hydrogen

- $\sim$ 5.5 % Nitrogen

13.4   Thermal analyses

On the same reference sample taken at the STP of Bern before the start of the first storage experiment (Blank 1), some thermogravimetry analyses (TG) and differential scanning calorimetry (DSC) measurements have been performed. The reference sample was analyzed in two different forms: as it was, in this case a single granule was directly used for the measurements, or as a powder from these granules.

This double measurement allowed the investigation of the difference between a single granule and a powder made by grinding a large number of granules. No significant differences between both sample preparations was found during all the following thermal analyses.

13.4.1   Thermogravimetry

First the different TG analyses performed on a single granule of dried sewage sludge showed always a total mass loss of around 48 - 50 % DS [4]. This result corresponded to the measurements previously made for the ash content determination.
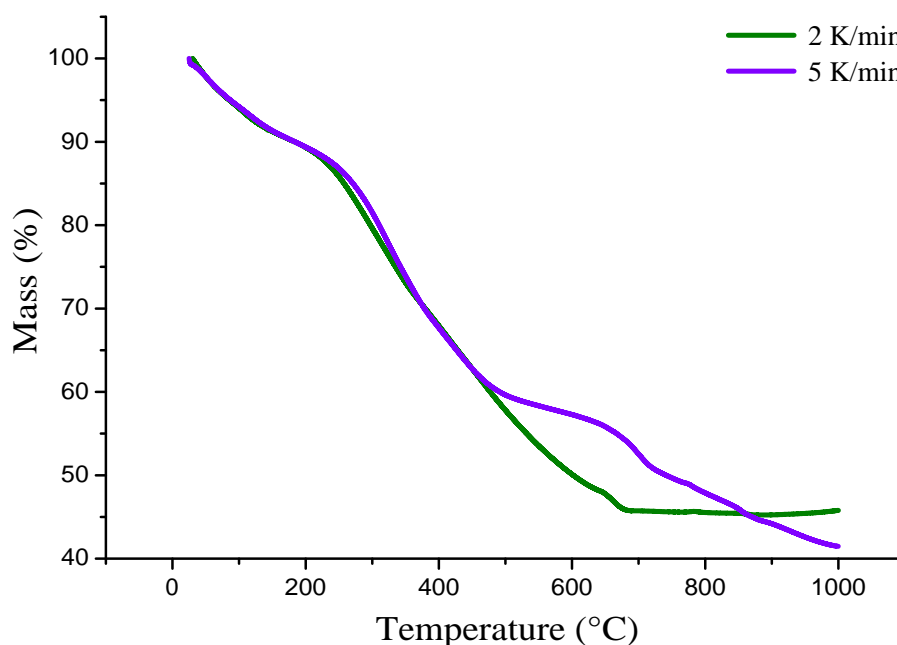
Figure 13.2: TG analyses of single granules from the reference sample (Blank 1) performed at 2 and 5 K/min, from 30 to 1000 ° C, under air flow of 50 ml/min

It has to be noted that the mass loss profile was similar for all the analyzed samples (Figure 13.2). Moreover in the first part of the analyses (up to 500 ° C), showed identical features, which indicated that the thermal decomposition of the combustible matter was the same for all the analyzed samples. At higher temperatures, some variations could be observed which certainly depended on the ash composition. At a temperature range from RT to 200 ° C, no stepwise decomposition, which would give a clue for the auto-combustion of the material, could be detected.

13.4.2   Differential scanning calorimetry

By using differential scanning calorimetry (DSC) on this reference sample, two main exothermic processes were detected (Figure 13.3). At 450 °C the thermal decomposition was not yet finished, which matches with the TG analyses showing mass loss up to even higher temperatures. These exothermic events corresponded to the combustion of the organic matter, because the DSC analyses were carried out under air flow. Therefore it can be assumed that two well-marked kinds of organic compounds constituted the dried sewage sludge.
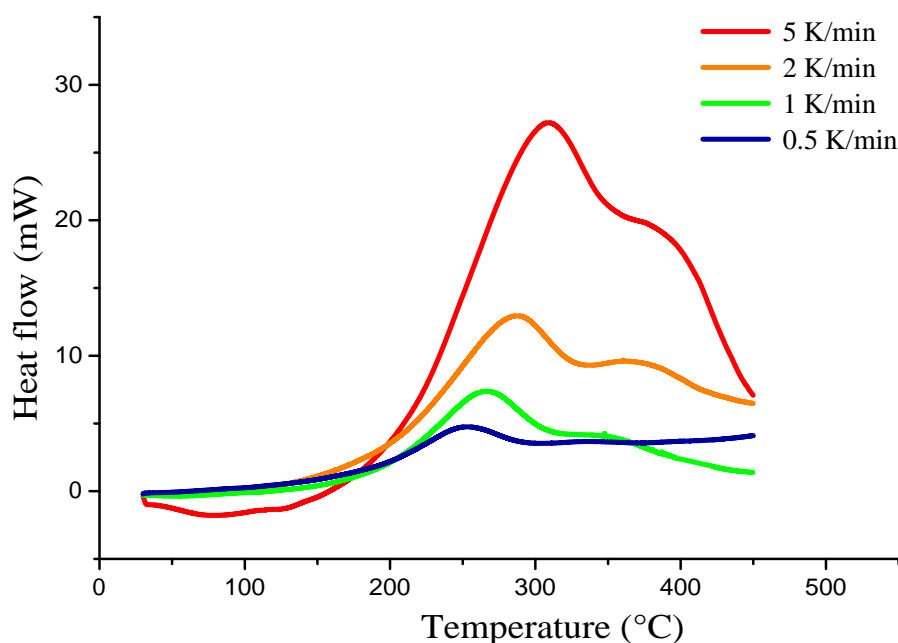
Figure 13.3: DSC analyses of single granules from reference sample (Blank 1) performed at 0.5, 1, 2 and 5 K/min, from 30 to 450 °C, under air flow of 100 ml/min

This combustion occurred at rather high temperature as compared to the storage temperature and therefore it can not be the direct origin for the auto-ignition of the dried sewage sludge. Moreover the combustion temperatures matched with the values for the combustion of other organic material. However the onset temperatures for the first large thermal event were quite low (Table 13.4), even though they could not be clearly determined. This was mainly due to a small thermal event that was observed between 70 and 120 °C. More surprising is that no endothermic peak for the evaporation of water was detected within this temperature range. It is suspected that a first exothermic event occurred at very low temperature, near the storage temperature, and that the released heat balanced the energy required for the water removal.

Table 13.4: Onset temperatures of the first large exothermic peak measured by DSC analyses on the reference sample (Blank 1)

Heating rate (K/min)	Onset temperature ($^\circ$C)
0.5	111
1	118
2	126
5	130

In order to determine the proportion of the exothermic peak balanced by the endothermic peak of the water evaporation, DSC analyses were performed on dried sludge granules using nitrogen and air atmosphere with a gas flow of 100 ml/min and a heating rate of 5 $^\circ$C/min.
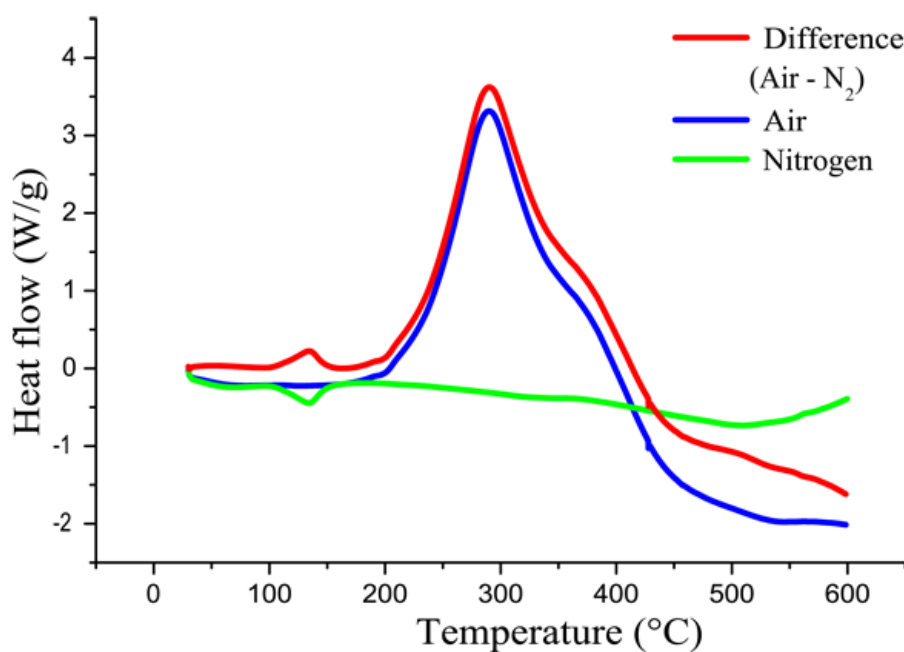
Figure 13.4: DSC analyses of single granules performed at 5 K/min, from 30 to 600 $^\circ$C, under air and nitrogen flow of 100 ml/min

The analysis made under air showed an important exothermic peak which started at 160 $^\circ$C with a maximum at 290 $^\circ$C (Figure 13.4). The first exothermic event could only be visible by zooming the DSC curve between 50 - 150 $^\circ$C. Under the nitrogen flow the large exothermic peak did not appear on the DSC curve. However an endothermic peak was present at lower temperatures starting at 100 $^\circ$C with a maximum of intensity at 134 $^\circ$C. This peak is assigned to the endothermic water evaporation.

The fact that this endothermic peak was only observed under nitrogen atmosphere and not at all during the analysis under air flow, indicated that an exothermic process compensated integrally the endothermic event. Subtracting the nitrogen curve from the air curve, the heat release can be evaluated. The peak integral for this exothermic process occurring under oxidizing atmosphere only was measured and reached - 67 J/g.

13.4.3   Derivative thermogravimetry

In order to investigate this first thermal event occurring between 70 and 120 °C, the mass loss at these temperatures need to be studied more in detail for this temperature window [51].

By means of the derivative thermogravimetry (DTG), two peaks were observed in the temperature range between room temperature and 200 °C (Figure 13.5). The first peak between 30 and 90 °C was assigned to the release of residual humidity. The second peak appeared between 90 and 170 °C and had a peak maximum at 126 °C. The second mass loss was assigned doubtlessly to water evaporation. In fact the mass loss between room temperature and 170 °C corresponded to 8.4 %, which matched very well with the usual moisture content in the dried sewage granules. In conclusion these two peaks indicated that not all the water was released at the same time. The remaining surrounding humidity was removed first and than at higher temperatures the chemically bound water, such as crystalline water molecules, was evaporated.

Moreover the two main peaks between 170 and 520 °C indicated two consecutive mass losses, which matched perfectly with the two large exothermic peaks observed in the DSC analyses. In conclusion a combustion occurring in a two-step process can be confirmed by the two distinct mass (DTG) and heat (DSC) releasing stages.

In conclusion it was also possible to calculate the exothermic energy of the first peak thanks to previous thermal analyses. With the DTG analyses, the limits of the peak can be established. Then the TG analyses gave the loss of water for the corresponding temperature section. The energy needed to evaporate the water can then be estimated. The energy due to the thermal process (exothermic) can then be obtained by taking into account the endothermic energy needed to evaporate the water. An exothermic value of - 111 J/g was obtained for the first thermal process.
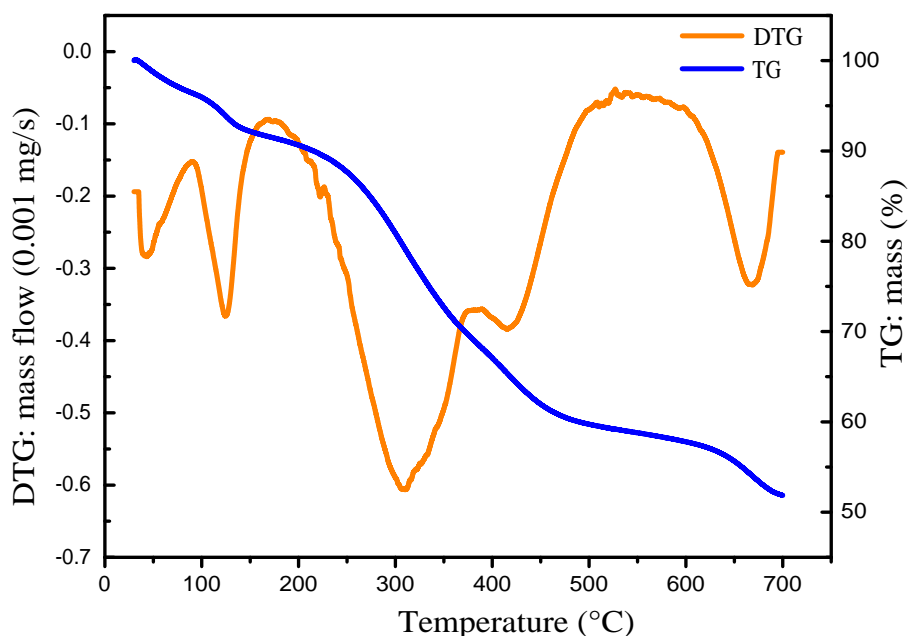
Figure 13.5: TG and DTG analysis of a fresh sample of dried sewage granules performed at 3 K/min, from 30 to 700 ° C under air flow of 100 ml/min

This value was in the same order of magnitude as the energy measured during the DSC analyses under air and nitrogen.

13.4.4   Thermogravimetry - mass spectrometry

In order to confirm the previous results concerning the release of water, which would balance the exothermic process, some thermogravimetry analyses coupled to mass spectrometry (TG-MS) were carried out on freshly sampled dried sewage granules. The use of TG-MS allowed the study of the exhaust gas in order to give some information concerning the first thermal event occurring at low temperature range [52].

The TG-MS measurements were first performed for defined masses such as for water and carbon dioxide, because the continuous scan over a large mass range did not yield good results due to insufficient sensitivity. It is worth mentioning that the TG-MS chamber containing the sample underwent a stabilization preheating period of 12 hours at 40 ° C for removing all present humidity and achieving therefore a stable baseline.

These TG-MS analyses showed that water started evaporating above 60 ° C with a maximum peak at around 125 ° C (Figure 13.6). In this temperature range,

water was the only substance released from the sewage granules. This was proved by the fact that the negative slope of the derivative thermogravimetry (-DTG) was perfectly fitting with the MS measurement for the water mass (MS-H_2O) between 60 and 125 °C. The former DTG analyses showed for temperatures beneath 60 - 70 °C a first mass loss assigned to residual humidity. Such humidity loss was not present anymore in the TG-MS analyses due to the stabilization preheating period. Above 60 °C, the water loss can be accounted for by the evaporation of crystal water. From 160 °C, a continuous release of water indicated the combustion of the organic products. Also, the CO_2-concentration started to increase from that temperature on.
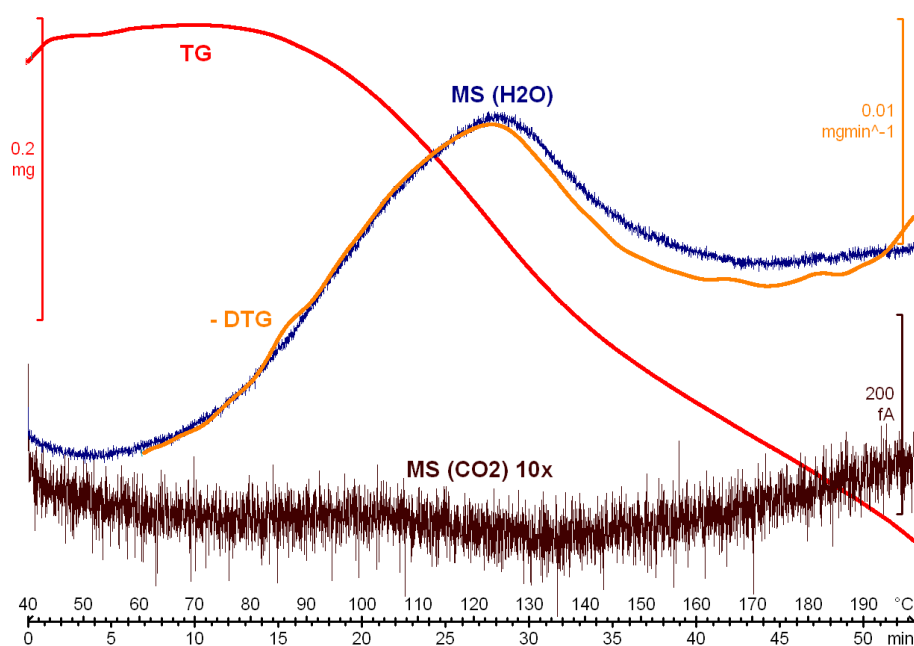
Figure 13.6: TG-MS analysis of dried sewage granules performed at 3 K/min, from 40 to 200 °C under air flow of 100 ml/min

Despite of the previous results, TG-MS analyses were also carried out for other defined masses with the aim of detecting some other gaseous molecules, which could be released during the heating. No recorded mass was corresponding to sulfur dioxide, nitrogen monoxide or dioxide, ammonia or methane. Therefore it could be concluded that these compounds were not formed during the first exothermic process. However it has been observed during all the performed TG-MS measurements that the carbon monoxide concentration decreased slightly from its initial concentration at the start of the measurement until $\sim$ 120 °C. This loss of CO with the increasing temperature was assigned to its desorption from the granules surface and its removal by the air flow utilized during the TG analyses.

13.5   Exhaust gas analyses

The exhaust gases were analyzed in order to find what type of degradation reaction occurred during the storage of the dried sewage granules. Therefore some samples of dried sewage granules were brought to the University of Applied Sciences of Offenburg (DE) to study the gas formation occurring during a heating process by means of an industrial gas detector.

The fresh samples were placed in a metallic cylinder closed by fine steel wool at both ends. The system consisting of the metallic cylinder and the stored granules inside, was then placed in an industrial oven for a heating program of $1\,^{\circ}$C/min. Moreover the system was connected to an entry tube providing a synthetic air flow of 1.7 L/min and to an exit tube connected to the industrial gas detector, working at a maximal gas flow of 1 L/min, and to an overpressure flask. The gas detector allowed the simultaneous measurement of oxygen, hydrogen, methane, carbon monoxide and carbon dioxide. The concentration of each gas was measured during the experiment allowing the detection of the released gases in function of the heating program.

Figure 13.7: The concentration of released gas from a stored sample of dried sewage granules sustaining a heating experiment under air flow

Already at around $30\,^{\circ}$C the O_2 concentration started to decrease indicating a consumption of oxygen even though the air flow through the system was constant (Figure 13.7). This pointed to an oxidation occurring already at a low temperature

range. The increase of the CO_2 concentration starting already at 60 °C clearly proved that an oxidative degradation of the organic material was occurring when the dried sewage granules heated in air under an important flow (1.7 L/min). It can not be the residual CO_2 form the dryer atmosphere surrounding the granules, because it would have already been removed by the air flow.

At 150 °C a sudden increase of the CO_2 concentration was detected accompanied with a smaller increase of the CO concentration. The release of the combustion gas was maximal at 160 °C and declined rapidly to a level of 1 - 1.5 % of CO_2. A second increase of both gases started at 180 °C. At 200 °C the heating process was stopped, because of the important formation of smoke and water, which could damage the industrial gas detector. From this first experiment, it is worth mentionning that no methane or hydrogen were formed during the heating process carried on the stored granules.
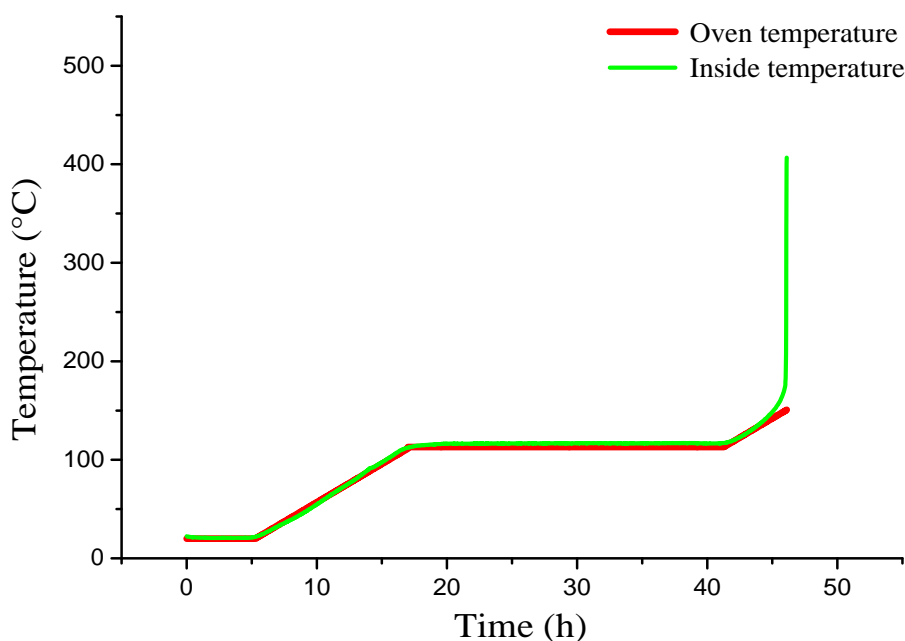
Figure 13.8: Inside temperature profile within a stored sample of dried sewage granules sustaining a heating experiment under air flow

During the second experiment the system containing the dried sewage granules was prepared exactly in the same way than for the previously one. However the heating conditions and the applied air flow were slightly different. After being introduced inside the industrial oven, the heating program consisted in a very

slow heating of 0.08 °C/min up to 115 °C with an air flow of 1.2 L/min. Then a constant temperature was applied for 22 hours, followed by a second heating also at 0.08 °C/min from 115 °C to 200 °C.

First it has to be mentioned that no exothermic event was measured in the first heating process and during the steady-state period at 115 °C (Figure 13.8). Then from the steady-state period of 22 hours at 115 °C, a constant temperature increase was started with 0.08 °C/min. However a thermal runaway clearly occurred meanwhile the second heating process and from ~150 °C the temperature began rising extremely. The combustion process was happening and was confirmed by the steep increase of the CO_2 concentration occurring at the same time (45 hours after the start of the experiment) and the simultaneous decrease of the O_2 concentration. The increase of the CO concentration was also small due to the constant air flow allowing a quasi-complete combustion. In this second experiment, methane and hydrogen were again not detected.
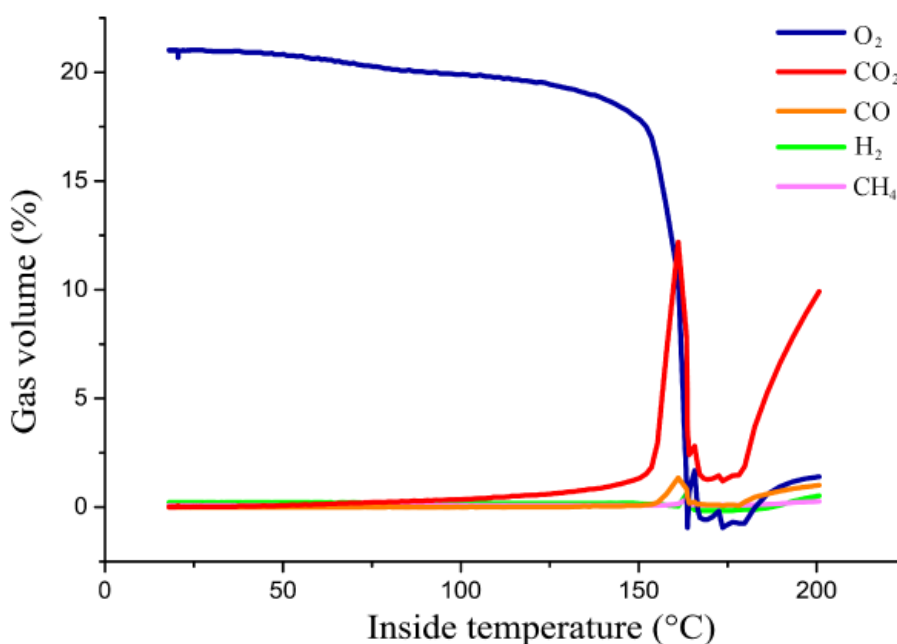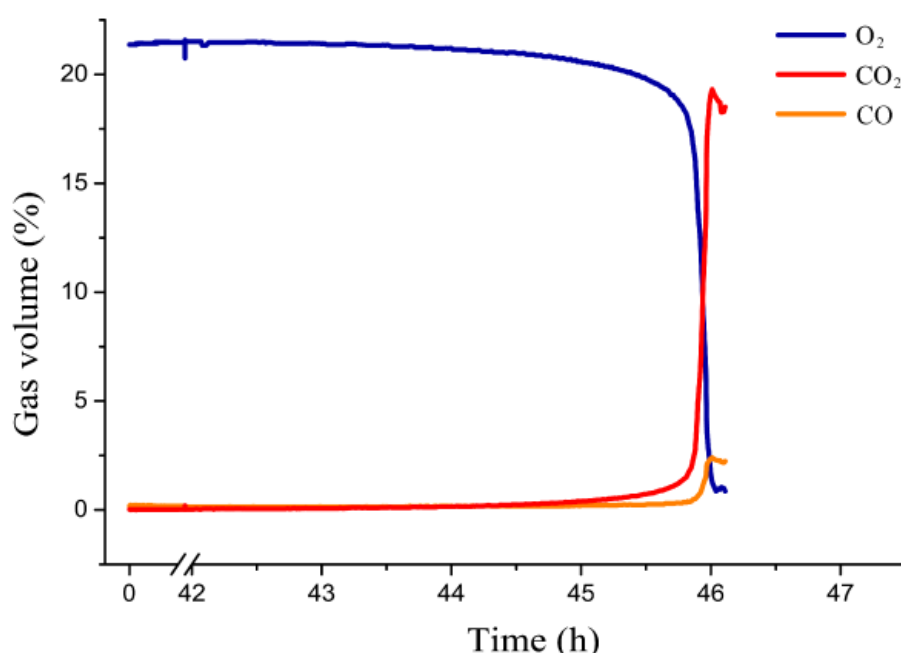

Figure 13.9: The concentration of released gas from a stored sample of dried sewage granules sustaining a heating experiment under air flow

13.6 Isotherm storage experiments

The first spontaneous temperature increase was also studied on small quantities of dried sewage granules. These labscale storage experiments included sample sizes between 100 g and 10 kg of dried biowaste, and in microscale storage experiments only a few granules of dried sewage. All the dried sewage biosolids were sampled at the STP of Bern from the orifice placed after the cooler part of the dryer plant (see section 1.5.5). The storage experiments were performed at a constant surrounding temperature chosen between room temperature and 70 ° C.

These storages in isotherm conditions allowed the determination of the critical mass for the first thermal event occurring on freshly produced dried sludge. It also enabled the study of the self-heating process of the material without the impact of external factors such as temporary storage in the loading silos at the STP of Bern or transport by truck to the cement industry.

13.6.1 Microscale storages

Some microscopic isotherm storage experiments were made by inserting a small amount of dried granules ($\sim$ 50 mg) in a DSC device and by running a isothermal program at a definite temperature between 40 - 70 ° C under a constant air flow. It turned out that even on a few granules only, an exothermic event at the beginning of the experiment could be observed (Figure 13.10). The thermal profile fitted to the one measured during the storage experiments made on the quasi-adiabatic model silo (see chapter 12). However this first exothermicity within the dried biowaste could not be observed in every microscale isotherm storage test.

13.6.2 Labscale storages

The labscale storage experiments were performed by storing the dried granules in insulating dewar containers of different sizes. The dewar filled with the dried sludge sample was placed in an oven at a defined temperature or left untouched at room temperature in the laboratory.
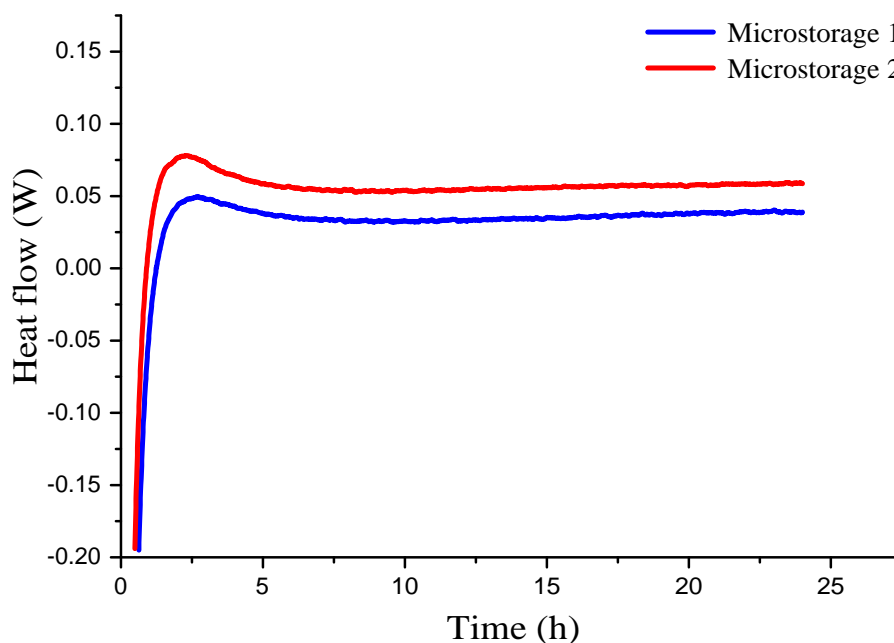
Figure 13.10: DSC analyses of dried sewage granules performed at 50 °C during 24 hours, under air flow of 100 mL/min

Aging processes

Some preliminary tests showed that only fresh samples of dried biowaste underwent a temperature increase during the storage under thermal insulating conditions. That meant that the dried sludge freshly produced sustained an aging process, because the old samples of dried sewage sludge did not systematically present the exothermic properties.

To control this aging process, a batch of freshly collected dried sewage granules was stored in the laboratory at room temperature. From this batch, some dried granules were taken to fill up a 1 L - dewar, which was stored in an oven at 50 °C for 48 hours. The measured inside temperature presented a spontaneous temperature increase fitting with the exothermic temperature profile already observed previously (see section 12). Two days later a new storage experiment was carried out with the dried granules from the initial batch. Under the same conditions, a thermal event was also observed, however the temperature difference was smaller (Table 13.5). The same experiment was repeated a third time without showing any exothermicity this time.

In conclusion it can be said that the first thermal event occurring on dried sewage granules is a degradation process already taking place at room temperature.

Table 13.5: Spontaneous temperature increase measured during the storage of fresh and old samples of dried sewage granules in a 1 L - dewar placed at 50 $^\circ$C

Entry	Δt before storage (days)	ΔT_{max} [a] ($^\circ$C)	t_{max} [b] (h)
1	0	9.2	10
2	2	5.8	10
3	4	- [c]	-

a) the maximal temperature increase

b) the time to reach the maximal temperature increase

c) thermal event not clearly defined

This could be determined by the fact that the fresher the dried sewage granules were, the more important the temperature increase was. Therefore with the aim of studying this first thermal event, the samples needed to be rather fresh, because otherwise the material would have undergone already some aging processes.

However, on one hand when the thermal event was completely over, no new spontaneous temperature increase during such storages could be observed. On the other hand it had been observed that even some old samples of dried sewage granules presented occasionally a self-heating process, when stored after a while in a 1 L - dewar, which was placed in a oven. In those cases, it can be proposed that the first thermal event was not yet over and that this exothermic reaction, which was already running at room temperature, has been accelerated by the oven temperature.

Critical size

The large number of labscale storage experiments in various dewars of different sizes showed that the first temperature increase was only observed for volume equal or larger than 1 L. No thermal event occurred during the storages made in dewars of a volume between 90 mL and 750 mL. In the larger insulating containers, the inside temperature increased spontaneously of by about 10 $^\circ$C and the maximum temperature rise occurred after a few days (Figure 13.11).

All the performed storage experiments presented similar temperature profiles. As expected the relationship between the amount of stored granules and the temperature increase was proportional (Table 13.6). Moreover from these storage experiments, no relationship between the spontaneous temperature increase and the working schedule of the dryer plant could be established.
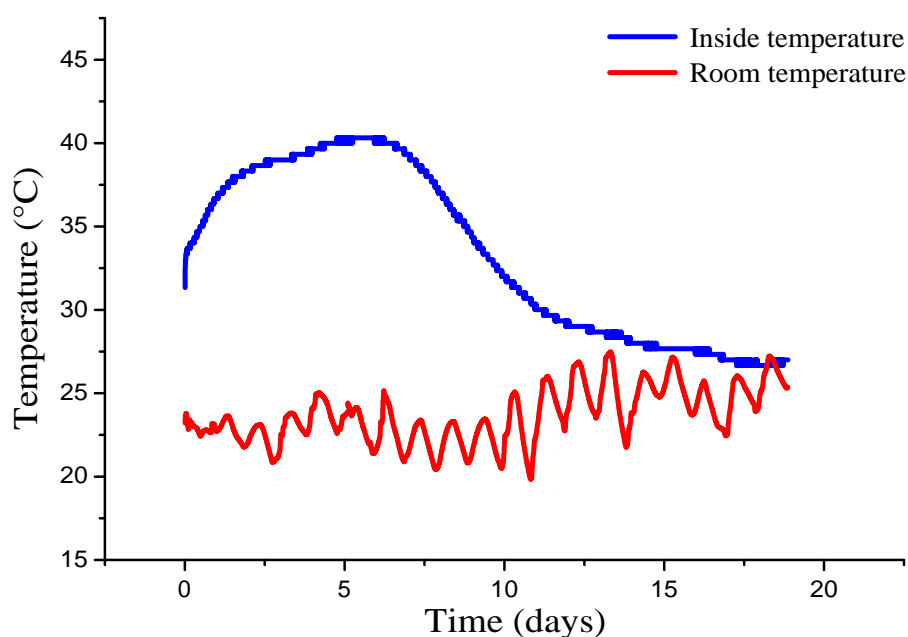
Figure 13.11: Spontaneous temperature increase measured during the storage of freshly sampled dried sewage granules in a 6.7 L - dewar placed at RT

Table 13.6: Spontaneous temperature increase measured during the storage of freshly sampled dried sewage granules in dewars of different size placed at RT

Dewars (Vol.)	A (1 L)		B (6.7 L)		C (8.5 L)	
Stored mass (kg)	0.6		4.4		5.6	
	ΔT_{max}	t_{max}	ΔT_{max}	t_{max}	ΔT_{max}	t_{max}
Storage [a]	(°C)	(days)	(°C)	(days)	(°C)	(days)
Wed 3rd May 06	6.0	0.6	8.0	1.6	8.3	2.2
Tue 23rd May 06	2.3	0.2	- [b]		9.7	5.3
Fri 2nd June 06	3.7	1.7	6.0	0.5	7.3	5.5
Wed 7th June 06	6.0	0.4	5.3	0.9	- [c]	

a) ΔT_{max} for the maximal temperature increase and t_{max} for the time to reach the maximal temperature increase

b) thermal event not clearly defined

c) no storage experiment performed

13.7   Solid state NMR spectroscopy

In order to have an idea about the main organic composition of the dried sewage granules and about its evolution during the storage period, several analyses with solid state NMR spectroscopy were carried out. For these experiments the dried biosolids were ground and sieved and the resulting fine powder was analyzed directly or after storage of the material under defined conditions.

13.7.1   Fresh samples of dried sewage granules

The two first ^{13}C NMR measurements were performed on freshly sampled granules allowing a first investigation of the original organic composition. Both solid state NMR spectra presented some distinguishable regions of peaks even though an important background noise did not enable the precise integration of the spectra. The five main regions of peaks could be assigned to a type of functional groups (Table 13.7).

Table 13.7: Peak regions, and the corresponding functional groups, observed from the solid state ^{13}C NMR analyses performed on dried biosolids freshly sampled

	Shift	Peak region integral	
Functional groups	(ppm)	Analysis 1	Analysis 2
C in carbonyl (ester, acid, amide, . . .)	165 - 190	1.0	1.0
C sp^2 (double bond, aromatic, heterocycle)	120 - 145	0.9	0.8
C sp^2 (aromatic) + connected to O	90 - 120	0.2	0.3
C sp^3 + connected to O	50 - 90	4.3	3.1
C sp^3 (methylene, methyl)	10 - 50	2.7	1.9

13.7.2   Stored samples of dried sewage granules

With this ^{13}C NMR fingerprint of the dried sewage biosolids, the evolution of the organic matter during the storage of the granules can be performed. To do so, the solid state NMR measurements were done on fresh and stored samples and the resulting spectra were compared in order to find variations.

At room temperature

During the storage of dried sewages granules, the first exothermic event occurred spontaneously at the loading temperature (30 - 40 ˚C). To evaluate the impact

of the storage on the organic phase, the following solid state NMR analyses were performed first on a fresh sample and secondly on a sample stored at room temperature in a 1 L - dewar during 3 days. It has to be noted that this stored sample sustained a spontaneous temperature increase, which was maximum 17 hours after the beginning of the storage and reached a temperature difference of 7.6 ° C.

Both solid state ^{13}C NMR analyses presented the same regions of peaks than in the previous analyses. A slight variation between the measurements made on fresh and on stored granules could be seen for the peak region at 160 - 190 ppm. Actually it was the only peak region, which did not completely overlay when the two NMR spectra were superimposed. However a better integration of the peak regions was prevented by an important background.

It can therefore be proposed that the first temperature increase occurring at the storage temperature was not related to the organic phase. In fact no significant variation of the organic composition could confirm that an autoxidation of the aliphatic region was taking place at a low temperature range.

At high temperature

The impact of the temperature on the organic phase was studied by repeating the ^{13} C NMR measurement on a fresh sample of dried granules. Afterwards the analyzed powder was stored within the NMR stator for two consecutive storages at 80 and 120 ° C. Therefore solid state ^{13}C NMR analyses at RT, 80 and 120 ° C could be compared, which allowed studying the organic degradation which processed at higher temperature.

These three successive measurements presented interesting variations of the organic composition at the different storage stages (Table 13.8). The fresh sample of dried sludge granules showed the following differences compared to measurements made after storage at 80 and at 120 ° C:

- important peak in the region 20 - 40 ppm disappears on heating to 80 ° C;

- peak in the region 40 - 60 ppm decreases after storage (peak region 2);

- small peak in the region 100 - 110 ppm increases after storage (peak region 5);

- no peak in region the 140 - 155 ppm appears after storage (peak region 7).

Table 13.8: Peak regions of the solid state ^{13}C NMR analyses performed on dried granules freshly sampled and on samples stored consecutively at 80 and 120 °C

| | Peak shifts | Peak region integral | | |
Regions	(ppm)	Fresh sample	Storage at 80 °C	Storage at 120 °C
1	20 - 40	0.8	0.1	0.2
2	40 - 60	0.9	0.6	0.5
3	55 - 90	1.9	1.7	1.8
4	85 - 100	0.4	0.3	0.3
5	100 - 115	0.2	0.5	0.6
6	110 - 155	0.9	0.7	1.62
7	140 - 155	- a)	0.8	
8	155 - 180	1.0	1.0	1.0

a) no peak
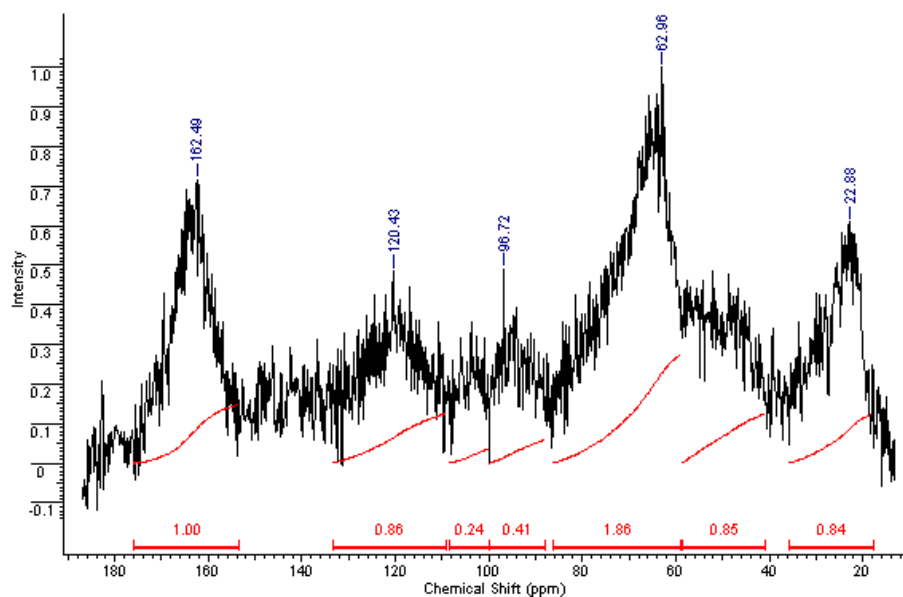
Figure 13.12: Solid state ^{13}C NMR spectrum of powdered fresh dried sludge granules before storage

The organic part of the dried biowaste definitively underwent some degradation processes at high temperature (Figure 13.12 - 13.14). An important amount of aliphatic carbons (20 - 40 ppm and 40 - 60 ppm) decreased after the first storage in an oven. Moreover the peaks variation between measurement on fresh sample (RT) and on stored sample at 80 °C is more important than between both measurements after storage at different temperature in an oven. Therefore the main part of the degradation process occurred during the first storage at 80 °C.
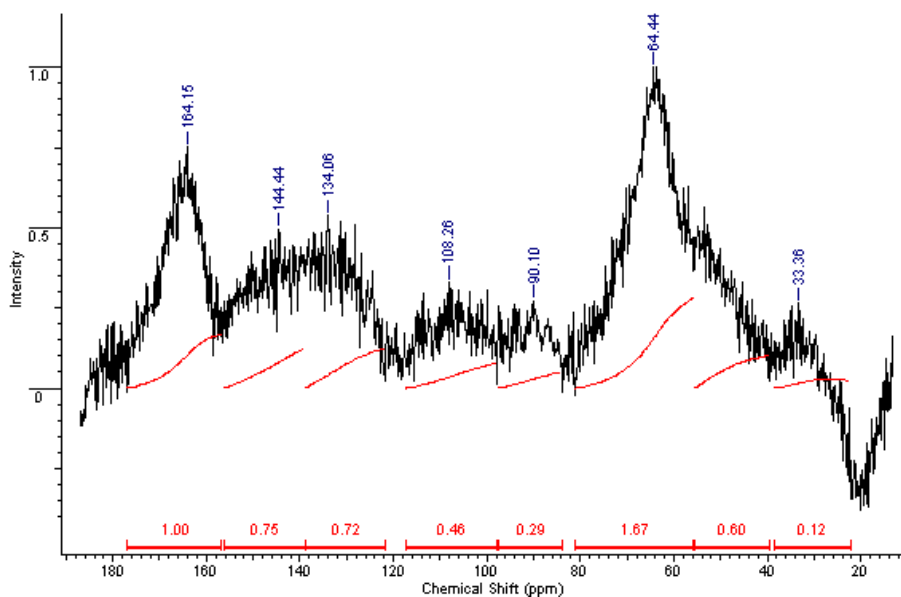
Figure 13.13: Solid state ^{13}C NMR spectrum of powdered dried sludge granules after first storage at 80 °C
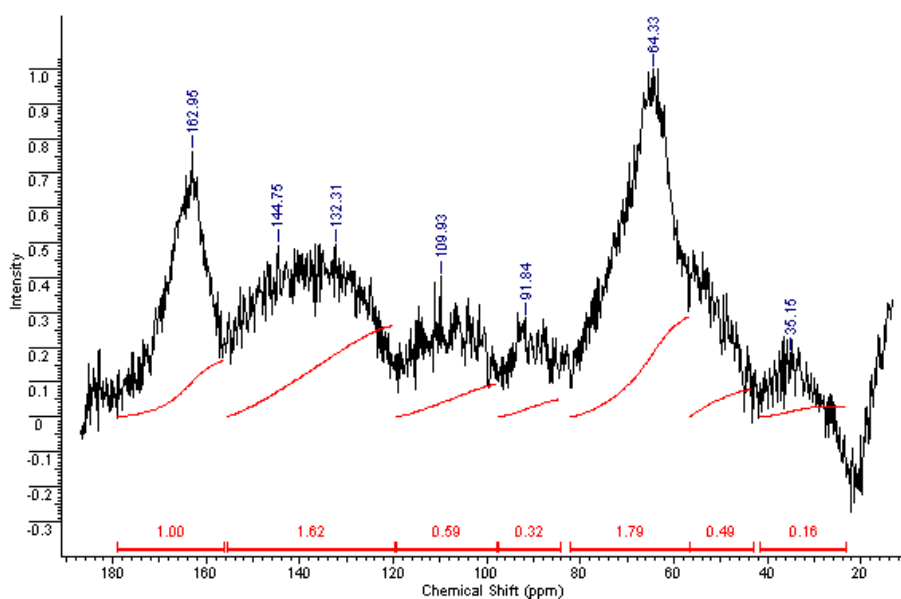
Figure 13.14: Solid state ^{13}C NMR spectrum of powdered dried sludge granules after consecutive storage at 120 °C

However due to the important background noise and some problems in the phase correction of the spectra, these ^{13}C NMR measurements gave only qualitative information about the evolution of the organic phase contained within the sewage granules. It just can be concluded that at 80 °C already hydrogen bearing aliphatic carbons underwent degradation and that unsaturated carbons were formed by then.

13.8 Insulating properties

Thermal conductivity and thermal diffusivity are physical properties, which are needed as input parameters for the modeling and simulations. [53]. They were measured at the University of Applied Sciences of Offenburg (DE), and in fact completed the already determined physical properties (Table 13.9).

Table 13.9: Physical properties of dried sewage granules

Physical property	Values	Units	Method
Density	0.66	kg/L	Measured in laboratory
Overall reaction heat	5 - 6	kJ/g	DSC
Heat capacity	1.2	kJ/(kg K)	DSC [a]

a) determined by Alexis Delacrétaz during his diploma work (2005, EIA-FR)

13.8.1 Thermal conductivity and diffusivity

The thermal conductivity (λ) was determined using the following equation

$$\dot{Q} \;=\; \lambda \cdot \frac{2\pi \cdot L \cdot (T_{int} - T_{ext})}{ln\left(\dfrac{d_{ext}}{d_{int}}\right)} \tag{13.1}$$

by measuring the radial heat flux ($\dot{Q}$) through a cylindrical layer of dried sewage granules of known thickness (L). This heat transfer induced a radial temperature drop (ΔT) within the material, which can be determined when steady state conditions were reached.
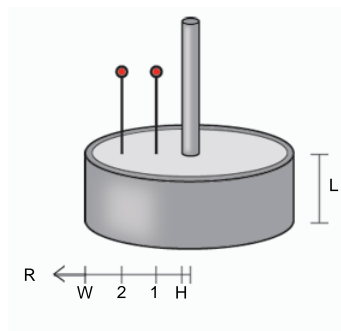
Figure 13.15: Scheme of the special container used for the thermal conductivity determination

At room pressure

The experiment was performed by heating a sample of dried sewage sludge (91.0 % DS) stored in a cylindrical container closed by a fitting insulating cover (Figure 13.15). An electrical heater placed in the center of the container allowed a constant heating from that postion. When steady state conditions were reached, the temperature was measured at different radial distances (r_H, r_1, r_2 and r_W) between the heater surface (H) to the wall (W) of the container. Knowing the temperature difference ($T_{int} - T_{ext}$) for two radial distances (d_{ext} and d_{int}), the thickness of the dried sewage sludge layer inside the container (L) and the thermal power applied by the heater ($\dot{Q}$), the thermal conductivity (λ) can be calculated (Eq. 13.1) and gave a mean value of 0.33 Wm^{-1}K^{-1}. For comparison, this value corresponds to the thermal conductivity of wood granules.

Then the thermal diffusivity (α) can be calculated using the following equation

$$\alpha \quad = \quad \frac{\lambda}{\rho \cdot C_p} \tag{13.2}$$

from the thermal conductivity (λ), the apparent density (ρ) and the heat capacity (C_p). The value obtained for the thermal diffusivity of dried sewage granules is 0.44 mm^{2}s^{-1}. In conclusion, the rate at which heat is conducted through the dried sewage granules is similar to that of glass.

Under applied weights pressure

The previous analysis was performed at room pressure. However in the case of a large storage silo of dried sewage waste, the mass of the stored granules and the resulting pressure may play a role in the thermal properties of the material.

Therefore a fresh new sample of dried sewage sludge (92.1 % DS) was analysed for determing the thermal conductivity and the thermal diffusivity under various applied pressures. The granules were placed in the experimental device in the exact way as before, however different weights were placed on the free insulating cover for simulating the mass of stored material at a definite place. The applied pressures corresponded to the mass of granules in the experimental and the model storage silo at different heights (Table 13.10). For instance, at the half-height and at the bottom of the experimental tank, the calculated pressure reached 0.125 bar and 0.249 bar respectively, and at the bottom of the model silo 0.041 bar (QuAC 100).

Table 13.10: Thermal conductivity and applied pressure on samples of dried biosolids

Entry	Applied pressure (bar)	Thermal conductivity (Wm^{-1}K^{-1})	Thermal diffusivity (mm^{2}s^{-1})
1	0	0.33	0.44
2	0.041	0.53	0.67
3	0.071	0.49	0.62
4	0.113	0.51	0.64
5	0.149	0.52	0.66
6	0.264	0.49	0.62

Clearly the two experiments are not directly comparable, but the thermal conductivity of the dried granules seems not being dependent of the pressure. Therefore the isolating properties of this material are not expected to fluctuate in function of the position inside the storage silo and overlaying old granules with new batches does not trigger a runaway due to higher pressure among the former.

13.9 Simulations of the exothermic events

Several simulation programs were used in order to develop the understanding of the reactivity of the stored material. Moreover some computational modeling attempts have been performed.

13.9.1 AKTS

Modeling of the thermal runaway occurring during the storage of the dried sewage granules was attempted by using a simulation program called AKTS[2]. From the DSC analyses performed on the dried sewage solids, the activation energy could be estimated and this value could be used further to simulate the reaction under various thermal conditions such as isothermal, non-isothermal, temperature rate... It was expected to evaluate the kinetics of the self-heating reaction by this program.

However the simulation of the reaction could only be done for the two main peaks present in the DSC curves. Therefore the first event that occurred at a low temperature range could not be taken into account for such a simulation.

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[2]www.akts.com

It turned out however that these simulation attempts were not optimal for the present case. Even if the simulations fitted partially with the observed thermal events, too many parameters still needed to be adjusted in order to obtain a perfect matching. This was probably due to the fact that the kinetics were mainly based on the two combustion processes clearly visible in the DSC curves. Even though the overall reaction enthalpy of 5.9 kJ/g was estimated by this program[3].

13.9.2 STAR-CD

A second set of computational simulations of the thermal runaway were performed by using a simulation program called STAR-CD. This was done in collaboration with the Department of Mechanics of the College of Engineering and Architecture of Fribourg.

Previously the heat released from the first thermal process was estimated by taking into account the energy needed for the water evaporation. The energy from the first exothermic event was evaluated to be 70 and 110 J/g.

With these values, the simulation of the first exothermic process could be done. To do so, all the physical data about the stored material, such as density, heat capacity, thermal conductivity... have to be entered to the program. The case of the storage in the large experimental silo of 18 m^3 was studied and the temperature increase (ΔT) could be calculated with the following equation

$$\dot{Q} = m \cdot C_p \cdot \Delta T \tag{13.3}$$

with the released heat flux ($\dot{Q}$), the heat capacity (C_p) and the stored mass (m) of the dried sewage granules.

For a storage of 12 tons of dried sewage granules, the simulated temperature increase was calculated to be 92.5 °C. This first value matched approximatively the first thermal event, which consisted in a temperature rise from the loading temperature (30 - 40 °C) to around 95 °C. However no further simulations could be done due to the complexity of the occurring reactions.

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[3]DSC curves and AKTS simulations made by Alexis Delacrétaz (diploma work, EIA-FR 2005)

13.9.3　Modeling of the chemical reactions

Some mathematical modeling of the exothermic reactions have also been tried. The first attempt[4] consisted in the modeling of a dynamic system in function of the temperature and the reactants consumption. By the means of a computational program based on *Labview*, the modeling of the temperature increase was started with the values obtained during the first storage of the dried sewage granules in the QuAC 100 with a water bath at $60\,^{\circ}$C (see section 12.2).

By varying each parameter of the modeling equation, it was possible to obtain a temperature increase matching with the measured temperature profile during the storage of the sewage biosolids. This modeling was confirmed by another mathematical model elaborated by Prof. Dr Kurt Käser.

However this modeling of the exothermic process did not match with the temperature profiles from the other storage experiments. In fact the modeling of the temperature profiles from the other storage experiments gave different parameters for the modeling equation. This means that the model equation and its parameters represented only the analyzed temperature increase, and not the general thermal event.

13.10　Conclusions

The first working hypothesis concerning a low-temperature oxidation of the organic material of the dried sewage granules has been discarded because the organic fraction of the dried granules did not undergo a significant oxidative degradation when stored at room temperature. This was confirmed by several thermal analyses, which showed two mass losses between 30 - $90\,^{\circ}$C and 90 - $170\,^{\circ}$C assigned to the humidity and to the remaining water respectively. No other substances were released from the dried sewage granules while stored in air at a low temperature range. However the endothermic peak of the water evaporation is completely balanced by an exothermic process taking place in the same temperature range. This exothermic process is oxygen demanding, because the oxygen concentration decreases already at low temperature ($30\,^{\circ}$C).

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[4]made by Alexis Delacrétaz (diploma work, EIA-FR 2005)

The assumption of 'hot spots' responsible for a local spontaneous temperature increase was also discarded because the composition of the sewage granules can be considered to be homogeneous over a limited production time with respect to the dry solids content and the elemental composition.

The first thermal event is induced by the material itself because a spontaneous temperature increase can even be measured during the isotherm storage of rather small quantities (a few milligrams). During the storage experiments in larger recipients, a temperature rise of about ten degrees takes place, reaching the maximal temperature increase after a few days. However the temperature increase is proportional to the aging state. When the first thermal event is completely over, the self-heating process is completely prevented. This last result gives already a first clue concerning a safety storage of the dried sewage granules: if the first thermal event could be forced in controlled conditions and the released heat removed, the material could then be handled without further difficulties.

Chapter 14

Hypothesis 2: oxidation at the surface

The hypothesis H2 is based on the fact that the sewage granules have a significant contact surface, therefore an oxidation at the surface of these granules may be the cause of the self-heating leading to autoxidation and runaway processes.

14.1   Gas volume within the granules

Within a heap of stored sewage biosolids, there is a lot of space in between the solid granules. At the STP of Bern, the atmosphere surrounding the dried material is controlled and the protecting gas contains around 1 % vol. of oxygen within the dryer itself and between 4 - 6 % in the recycled protecting gas consisting mostly of CO_2. During the loading process at the cement industries, the dried granules are tranfered from the transport truck into the storage silo by pneumatic transfer. Therefore the previously inert atmosphere among the granules is replaced by air during the blowing process with compressed air. This situation would allow for oxidation at the surface of the granules.

Therefore the effective volume of solid parts of the sewage granules has been studied. In fact the gas volume among the granules seemed at first quite important. In order to determine the ratio between the solid and the gaseous part in a heap of stored sewage granules, a system was installed consisting in a round flask equipped with a pressure gauge and a valve connected to a gas inlet and to the vacuum. This system allowed the addition of a desired gas after having removed the surrounding protecting gas and the residual humidity from the granules heap. By weighting the system containing the defined mass of granules at different stages of the experiment, respectively under atmospheric pressure, after vacuum and after the gas addition,

it was possible to determine the gaseous volume (ΔV_{gas}) among the dried sewage granules by the following equation

$$\Delta V_{gas} \quad = \quad \frac{\dfrac{\Delta m_{gas}}{M_{gas}} \cdot R \cdot T}{\Delta p} \tag{14.1}$$

by measuring the added mass of gas (m_{gas} - m_{vac}), the difference of pressure (p_{gas} - p_{vac}), the temperature (T) and by using the molar mass of the gas (M_{gas}) and the gas constant (R).

With the volume of added gas (V_{gas}) and the exact volume of the round flask (V_{tot}), the volume of the solid part of the granules heap (V_{tot}-V_{gas}) can be determined. Moreover the effective density of the solid part of the dried granules (ρ_{solid}) can be calculated with the mass of the stored granules (m_g) using the following equation

$$\rho_{solid} \quad = \quad \frac{m_g}{V_{tot} - V_{gas}} \tag{14.2}$$

This experiment was performed by using argon and nitrogen for replacing the surrounding inert atmosphere among the dried granules, which were placed in two different round flasks of 500 and 1000 ml. Each experiment was repeated three times and gave a mean value of 2.2 kg/L for the effective density of the solid part of the dried granules.

Table 14.1: Determination of the effective density of the solid part within the dried granules and the resulting gas - solid ratio

| | Density | Solid ratio | Gas ratio |
Heap of granules	(kg/L)	(% vol.)	(% vol.)
Total heap	0.66		
Solid part	2.2	∼ 30	
Gaseous part			∼ 70

With the effective density of the solid part of the dried granules and the density of the heap of granules, it was possible to calculate the ratio between the solid and the gaseous part in a heap of stored sewage biosolids (Table 14.1). It was rather surprising finding an important ratio for the gaseous part reaching ∼70 %

of the heap volume. If this volume of protecting gas among the granules would be completely replaced by air during the blowing process, this would represent an important intake of oxygen, corresponding to about 15 % vol. of O_2 in the total volume of stored granules without taking into account specific adsorption phenomena.

14.2   Impact of pneumatic transfer

This potential oxidation at the surface was therefore suspected to be induced by the pneumatic transfer of the dried granules from the transport truck into the storage silo. As the blowing process is carried out with hot compressed air, the inert atmosphere surrounding the granules is replaced by air creating an oxygen rich atmosphere. In this case, the granules after loading would start an oxidation at the surface and should therefore be different from the sewage samples taken before loading.
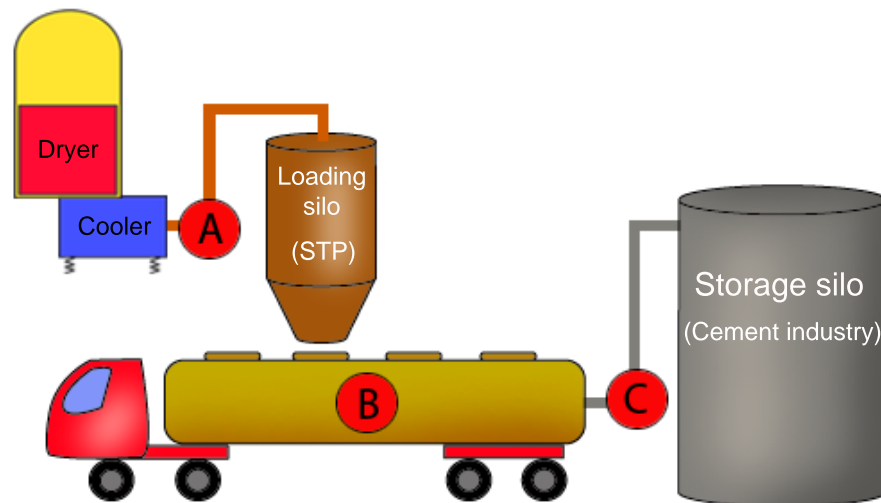
Figure 14.1: Scheme of the sampling performed for the study of the pneumatic transfer impact

In order to study the impact of the pneumatic transfer with compressed air, three samples were taking during the loading of the dried granules into a storage silo at a cement industry. The first sample was taken the day of the production directly at the cooler (location A), the second sample (B) was taken in the transporting truck (the granules already loaded in the truck for 24 hours) and the last sample (C) was taken after loading with cooled compressed air (15 °C, $\sim$ 1 bar) at the cement

industry (Figure 14.1). Such sampling has been carried out twice, which enabled repeating the analyses on fresh samples and estimated the confidence limit of the measured values. Elemental composition and thermal behaviour were analyzed.

14.2.1   Chemical analyses

If a surface oxidation would occur, it would be expected that the elemental composition of the samples of dried granules taken after pneumatic transfer (C) would be different from the two other samples (A and B).

Dry solids and ash content

First the dry solids and ash content were measured (Table 14.2), but the results presented standard values for the three samples without any significant deviation for the sample after loading (C). Moreover the moisture content in the three sample was not influenced by the transport and the blowing process.

Table 14.2: Dry solids (DS) and ash content of dried sewage granules during the pneumatic transfer

| | | 1st Analysis | | 2nd Analysis | |
Origin	Samples	DS (%)	Ash (% DS)	DS (%)	Ash (% DS)
Dryer plant	A	93.3	50.0	93.1	49.7
Transporting truck	B	93.5	50.8	92.0	51.1
After transfer	C	93.8	51.7	92.3	50.4

Elemental analyses (CHN)

Elemental analyses (CHN) were made on the three samples (A, B and C) from the first series, once on pristine granules, and once on powdered samples.

All CHN results matched perfectly to the previously obtained values. Furthermore no CHN variation appeared for the powdered samples. However for the pristine granules, a significant decrease in the C, H and N content from the sample taken at the dryer plant (A) to the one taken after the pneumatic transfer (C) emerged from these results (Table 14.3). The ratio of the measured CHN concentration compared to the initial values clearly decreased at the same rate for carbon, hydrogen and nitrogen.

This may be interpreted in two different ways:

- a release of a volatile compound or a mixture of compounds with such a chemical composition that the CHN ratio decreases at the same rate for the three elements;

- an addition of a new substance, which induces the decrease of the CHN concentrations without modifying their elemental ratios.

Table 14.3: Elemental analyses (CHN) of dried sewage granules from the first pneumatic transfer experiment and the ratio of the measured CHN concentration compared to the starting values of sample taken at the dryer plant (A)

Origin	Samples	C (%)	Ratio	H (%)	Ratio	N (%)	Ratio
Dryer plant	A	23.7	1.00	3.7	1.00	2.7	1.00
Transporting truck	B	21.9	0.92	3.3	0.90	2.5	0.93
After transfer	C	20.9	0.88	3.1	0.84	2.3	0.87

In this case, the adsorption of oxygen at the surface of the granules would be the only possibility, which would match with the obtained results. These results would support the present assumption. The fact that no variation in the CHN concentration can be observed in the powdered samples could be explained by the sample preparation. Indeed the crushing process may destroy the adsorption surface and release the adsorbed oxygen giving identical CHN values for the three samples aside the pneumatic transfer.

DrLange analyses

Additional analyses were performed with a DrLange device to measure the concentration of non metallic ions such as nitrate, nitrite, phosphate, total phosphorous and ammonium. The chemical oxygen demand (COD) was also measured. The aim of these analyses was to observe if there was a difference in the composition of the samples before and after the pneumatic transfer.

Some fluctuations for some ion concentrations were measured, however, the repetition of these analyses did not confirm the originally observed variations. Therefore no systematic variation of the ionic composition could be found between samples before and after the pneumatic transfer.

14.2.2 Thermal analyses

The first sample series regarding the pneumatic transfer, was analyzed by DSC in order to check for significant differences induced by the blowing process.

A comparison between sample A and sample C revealed that both DSC curves presented the same profile consisting in two principal exothermic peaks with peak maxima around 300 °C and 380 °C respectively, under these measuring conditions (Figure 14.2). There were no additional peaks or peaks missing, which would hint to a significant difference between both samples. However it was rather surprising to find a more important energy content for the sample taken at the dryer plant (A) as compared to the sample taken after pneumatic transfer (C). The peak integral for the two exothermic events together showed a value of 5.7 kJ/g for sample A and 4.7 kJ/g for sample C. This may signify that the sample C has already released some of its energy content.
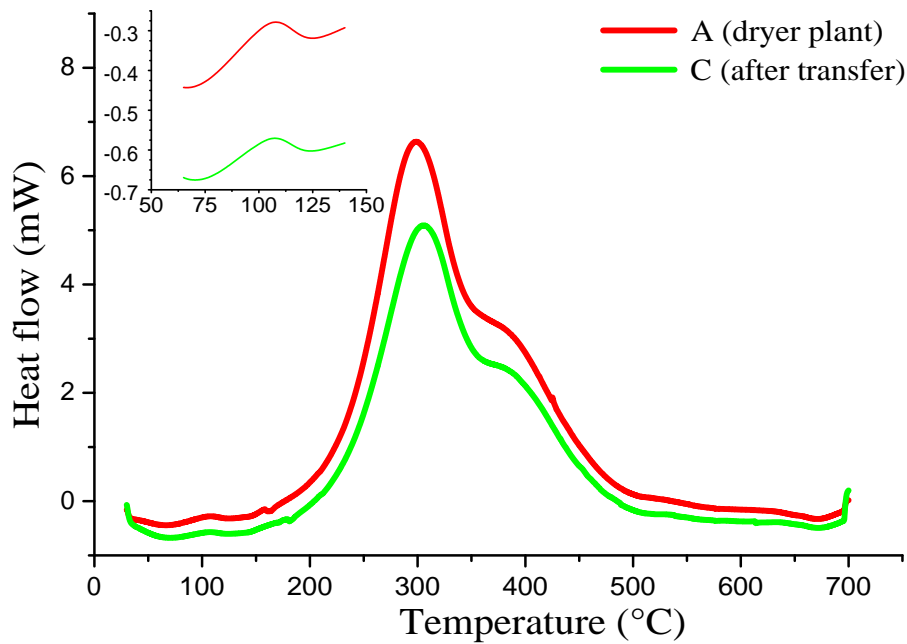
Figure 14.2: First set of DSC analyses of dried sewage granules taken at the dryer plant (A) and in the pipe after the pneumatic transfer (C) performed at 10 K/min, from 30 to 700 °C, under airflow of 50 ml/min. In the top corner, a zoom of the DSC curve between 60 and 140 °C

Moreover a small exothermic peak was clearly detected at lower temperatures with a peak maximum at 108 °C. This confirmed the earlier observed exothermic event (see section 13.4.2). As these DSC analyses were performed at a high heating

rate (10 K/min), this fine but sizeable event was easily detected, because the heat released from this exothermic process was not consumed within the system for the water evaporation.

To confirm these last results, the thermal study about the impact of the pneumatic transfer experiment was repeated. After sampling, DSC analyses were carried out on a new set of samples A, B and C at heating rates of 0.5, 1, 2, 3 and 5 K/min in air.

Once again all the DSC curves presented similar profiles consisting in a first weak exothermic event followed by two major exothermic processes (Figure 14.3). Within all the measurements performed at different heating rates, it appeared clearly that the sample A presented a higher energy content as compared to samples B and C. However, the difference in the released energy amount decreased more importantly between sample A and B than from B to C, when the loading process took place.
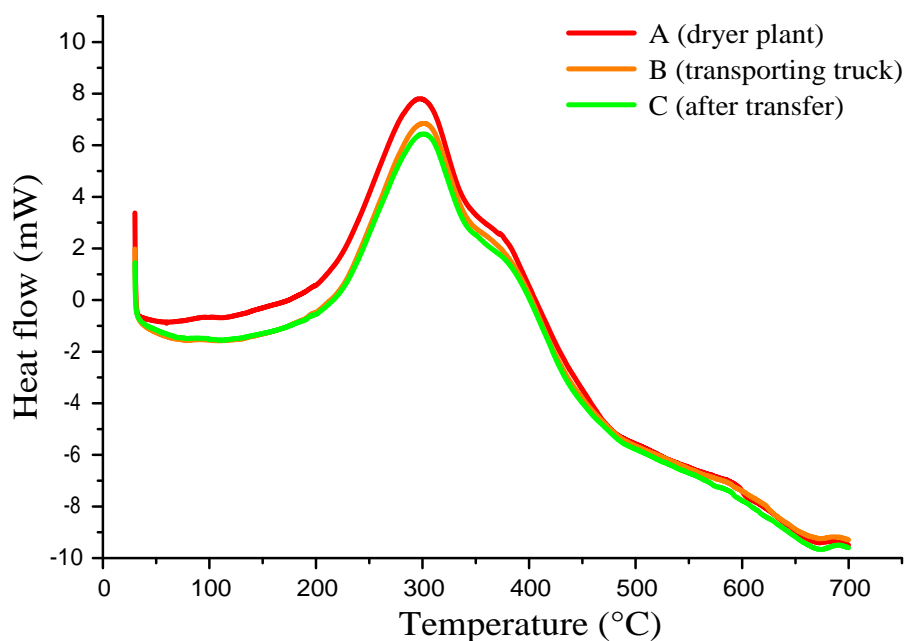
Figure 14.3: Second set of DSC analyses of dried sewage granules taken at the dryer plant (A), in the transporting truck (B) and in the pipe after the pneumatic transfer(C) performed under air flow at 3 K/min, from 30 to 700 °C

With these results it can be concluded that the more energetic sample consisted in the one taken directly at the dryer plant after the cooler system (A). The fact that this sample had a higher energy content as compared to the other samples was

interpreted to be due to the protective atmosphere present at the cooler exit. In this quasi inert atmosphere, no degradation reactions have been started yet.

The variation of energy content in the samples (B and C) taken before and after the pneumatic transfer was only minor. Therefore it can be concluded that the impact of the pneumatic transfer with compressed air has no significant effect on the oxidative degradation of the material itself. Thus this procedure is not directly responsible for the autoxidation and the consecutive runaway occurring during the storage of dried sewage granules.

14.3   Labscale storages under inert conditions

To confirm that the first temperature increase was not due to a reaction with the oxygen added somewhere after the dryer by air intake, some new labscale storage experiments were done by using inert gas as a surrounding atmosphere among the granules. First the overpressurized protective gas of the dryer plant, which contained less than 6 % of oxygen, was used. Then argon was also used as inert atmosphere. In both cases, the storages as made previously was also performed in order to compare the impact of using an inert atmosphere.

To do so, a plastic glove box was attached to the dewar and to the sampling orifice placed after the cooler part of the dryer plant. This installation allowed the sampling of the dried granules under more or less the same inert conditions as present in the dryer plant and to fill up the dewar under the light overpressure of the dryer gas or by an additional flow of argon.

The storages performed without any protective atmosphere, as blank experiments, presented a temperature increase corresponding to the temperature profiles already observed during isoperibolic storages (see section 13.6). The temperature rise reached a maximum of 7.3 - 11.2 $^\circ$C after 1.6 -2.5 days of storage in the 6.7 L - dewar (dewar B).

For the storages under inert atmosphere it was rather surprising to measure spontaneous temperature increases within the dried sewage granules similar to what was observed for all the previous storage experiments (Table 14.4). Even with inert surrounding gas such as the dryer gas or argon, the material underwent a self-heating process. This observation clearly confirms that the first temperature increase can start without any additional air intake.

Table 14.4: Spontaneous temperature increase measured during the storage of freshly sampled dried sewage granules in dewars at RT under inert atmosphere

Dewars (Vol.)	A (1 L)		C (8.5 L)		C (8.5 L)	
Atmosphere	Dryer gas		Dryer gas		Argon	
Storage [a]	ΔT_{max} (°C)	t_{max} (days)	ΔT_{max} (°C)	t_{max} (days)	ΔT_{max} (°C)	t_{max} (days)
Thu 22nd June 06	1.0	0.6	11.9	2.5		
Tue 4th July 06	7.9	0.5	9.0	3.2		
Fri 14th July 06	6.6	0.8			9.6	8.1
Thu 26th July 06	- [b]				6.6	3.5

a) ΔT_{max} for the maximal temperature increase and t_{max} for the time to reach the maximal temperature increase

b) thermal event not clearly defined

Most strikingly the time required for reaching maximum heating varied more than an order of magnitude between the different experiments, with shortest times for the smaller dewar. Air leakage despite the protective atmosphere is the most reasonable explanation.

14.4 Labscale storages under an air flow

Previously it has been shown that no air intake was necessary for the first spontaneous temperature increase to take place. However the study of an additional air intake through the stored material needed to be investigated. Therefore storage experiments were carried out by placing freshly sampled dried sewage granules in large insulating dewar containers of 6.7 L and 8.5 L. After having closed the dewars, a glass tube was inserted through the cover. The exit of the glass tube was placed at the half-height of the dewar. A light air flow ($\sim$ 0.5 L/min) was blown through the material while the temperature was measured continuously during the whole storage period.

A spontaneous temperature increase also occurred during these storage experiments (Figure 14.4). However the self-heating event was largely greater than what was measured without any air intake (Table 14.5). The temperature rise was more than the double and the time for reaching the maximum temperature increase was significantly shortened.
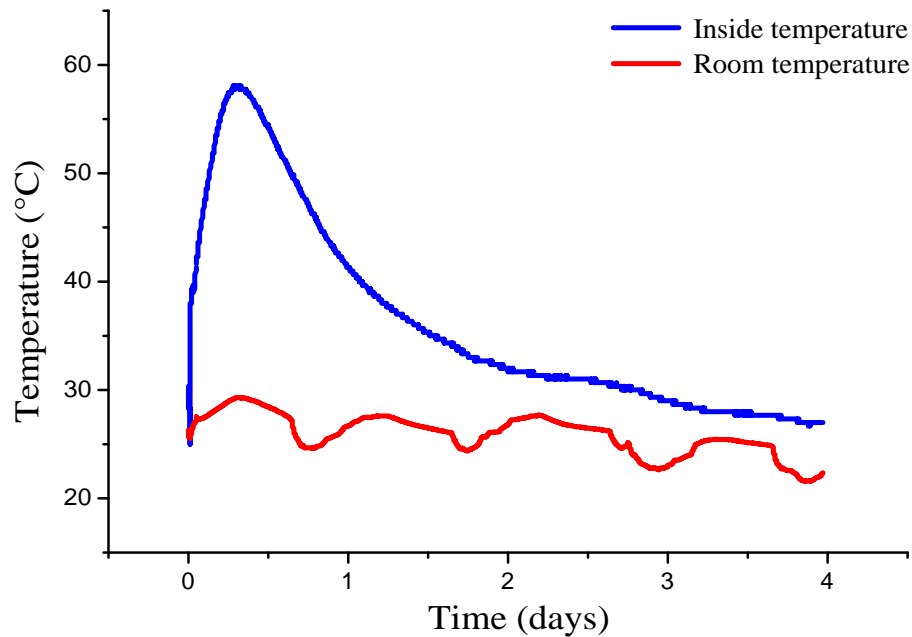
Figure 14.4: Spontaneous temperature increase measured during the storage of dried sewage granules in a 6.7 L - dewar placed at RT with a constant air flow

This clearly proves that the spontaneous first heating event is oxygen dependent working with traces of oxygen already. Since excluding traces of oxygen on a technical scale and during the whole 'lifetime' of the sewage granules is virtually impossible, an inert atmosphere will only postpone the spontaneous self-heating of the material.

Table 14.5: Temperature rise and time to reach the maximal temperature increase occurring during the storage of dried sewage granules under a constant air flow

Dewars (Vol.)	B (6.7 L)		C (8.5 L)	
	ΔT_{max}	t_{max}	ΔT_{max}	t_{max}
Storage [a]	($^\circ$C)	(h)	($^\circ$C)	(h)
Mon 18th June 07	21.1	7.1	25.1	4.2
Tue 3rd July 07	25.3	7.6	29.9	6.7

a) ΔT_{max} for the maximal temperature increase and t_{max} for the time to reach the maximal temperature increase

14.5 Conclusions

The gaseous part within a heap of dried sewage granules reaches $\sim 70\,\%$ of the total volume. After the loading process with compressed air, the air replaces gradually the protective dryer atmosphere. Even though, there is sufficient available oxygen within the granules to already start the oxidation. Nevertheless the hypothesis about an oxidation at the surface induced by the pneumatic transfer of the dried biosolids from the truck to the storage silo is discarded, because no significant variations can be observed in the samples taken before and after the pneumatic transfer. For instance the CHN ratio for the raw former samples showed a trend to lower CHN values. This regular decrease is assigned to the adsorption of oxygen at the surface of the granules. However the transfer of the granules with compressed air has no major impact on the energetic content of the dried sewage sludge, therefore this procedure can not be made directly responsible for the subsequent thermal events.

Moreover the first thermal event can not totally be suppressed under inert conditions, because the remaining traces of oxygen or the air leaking-in suffice to sustain the self-heating process. These results put aside the installation of a pneumatic system for the granules loading using an inert gas such as nitrogen or the combustion gases as compressed gas. This measure would not prevent the first temperature increase, which would lead to a very reactive system suitable for thermal runaway.

However, an additional air flow within the material clearly accelerates the self-heating, which results in a much steeper temperature rise. This corresponds to the reality, because the addition of a new batch of granules supplies fresh air to the stored material, which maintains the oxidation and the resulting heat. This observation gives a solution to trigger the first thermal event in order to obtain a safer material. As the first thermal event could not be prevented, it could be forced in controlled conditions, meanwhile the released heat should be evacuated.

Chapter 15

Hypothesis 3: external event

The third hypothesis advanced several blames of the self-heating to an external event, which triggers the ignition of an otherwise only weakly reactive 'granules - air - humidity' system. This external factor may be more or less random and could be caused by all sorts of factors coming from the the dryer plant itself, the transport procedures or the storage conditions. Therefore a correlation between the thermal event and the dryer plant schedule was attempted. Some electrostatic discharge during the unloading of the granules and the heterogeneity of the material which may cause locally specific reactions, were also suspected to lead the material to a spontaneous ignition.

15.1 DS content in function of the dryer plant

The dry solids content in the sewage granules is measured and reported everyday at the STP of Bern. These data represent valuable information in order to control the dependence of the dry solids content as a function of the drying system and the dryer working conditions.

The thermal runaway events started after the installation of the new dryer plant at the STP of Bern. This dryer consists in a fluid bed drying system working under a inert drying atmosphere at around 80 ° C and less of 1% vol. of oxygen within the oven. The dried sewage granules are then cooled and stored under a 4 - 6% vol. oxygen atmosphere. The previous dryer was working on very different conditions, which consisted in a closed loop drying system using drying air heated up to 450 ° C.

It was important to study the differences between the two drying processes. The first point was to compare the dried matter content in the granules produced by both dryers (Figure 15.1).
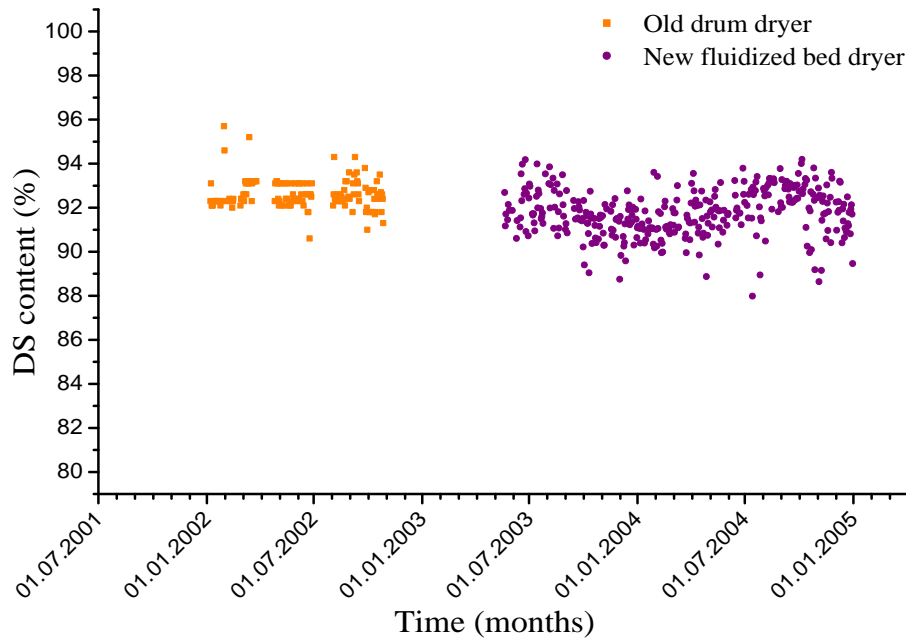
Figure 15.1: Comparison of the dry solids content in sewage granules produced by the previous dryer (Swiss Combi $^{©}$ drum drying process) and by the new dryer (VA-Tech Wabag fluid bed drying system) from January 2001 to December 2004

In 2002 (January to September) the average dry solids content in the dried sludge granules was 92.6 %. After the construction of the new dryer, from May 2003 to December 2004, this mean value was 91.8 % DS. It seemed that the fluctuations in the DS content were more important after the installation of the fluid bed drying system. However no significant trend could be observed which would explain the beginning of the thermal runaway in relationship with the transition to the new drying system. In addition, no correlation between recorded thermal runaways and extreme values could be found.

Moreover the data about the dry solids content in the dried sludge granules was also analyzed in function of the working days on the dryer plant. The new dryer plant works generally during the week and is switched off for the weekend. It was observed thanks to these data that there were no variation in the DS content in relationship with the weekly schedule.

15.2   Discharges of static electricity

Another assumption for a triggering event of this temperature runaway was the formation of static electricity during loading of the dried sewage granules from

the transporting truck to the storage silo. Electrostatic charging could occur by induced friction during granules transfer and the resulting discharges could act as an ignition source.

Before the third storage experiment with untreated granules (Blank 3), a metallic cylinder was suspended in the middle of the tank by the means of electrically insulated strings. Before loading the dried biogranules, the cylinder was connected to an electrostatic voltmeter and consequently worked as an electrode (Figure 15.2). It appeared that static electricity was accumulating in the empty space of the tank (electrostatic tension until 2 kV) during the loading, however no electrostatic discharges were recorded.
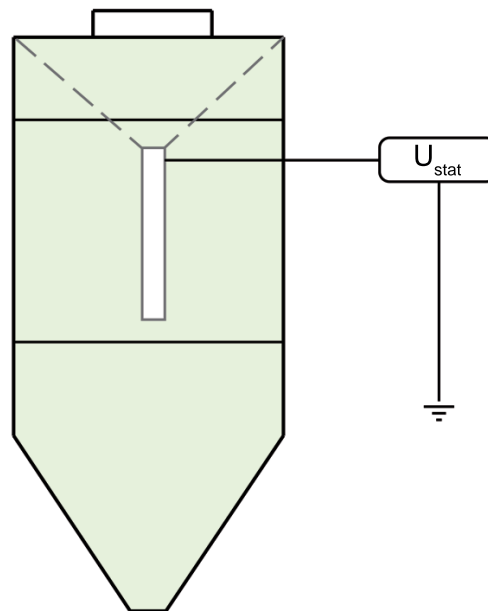
Figure 15.2: Scheme of the electrode (metallic cylinder) suspended by strings in the middle of the industrial silo and connected to an electrostatic voltmeter for the measurement of electrostatic discharges

After a time corresponding to around half loading, no static electricity could be measured anymore, since at this stage the metallic detector got in touch with the granules, which showed a sufficient conductivity. Electrostatic fields have also been measured at the surface of the pipes connecting the truck to the silo. However no electrostatic discharges manifested by abrupt changes of the voltage were detected during this experiment, neither inside the tank, nor in the connecting pipes.

15.3   Tendency towards explosion

In order to study the explosion tendency of the dried sewage granules, some cook-off experiments[1] were carried out, which consisted in long-time range thermal analyses for macro samples (0.1 - 1 kg). These analyses were achieved with a specific temperature program which corresponds to the American military norm MIL-STD2105B and the standard agreement STANAG 4382.

Three cook-off experiments were performed on around 200 g of dried sewage granules. The experiments consisted in filling up a stainless steel cylinder with the fresh samples (Figure 15.3 left). For the study of auto-ignition of this biowaste, the cylinder was not hermetically closed as usually made for the cook-off experiments, but a fine wire netting was placed at both sides to allow some air circulation through the material. One thermocouple was placed inside the cylinder among the material and two thermocouples were placed on the external surface of the cylinder at both sides. Then the system, composed of the cylinder, the thermocouples and the stored granules, was inserted in a thermally isolated oven, which was placed in a bunker for standard security norms. The temperatures at different positions were measured while the cylinder sustained a slow heating rate program ($3.3\,^\circ$C/h). During the third cook-off experiment, an air flow was continuously injected through the material in order to study the effect of such a constant air intake within the dried sewage granules (Figure 15.3 right). The air flow came from a compressor and was directly injected in the crucible without preheating or drying processes.

In parallel to these cook-off experiments, for each samples the dry solids and ash contents were determined and thermal analyses (TG and DSC) were performed. The results did not indicate any characteristic differences from the other analyzed samples.

Firstly no explosive tendency was observed during the three cook-off experiments. The temperature inside the cylinder and at the surface of it increased in a constant way and matched well with the temperature program of the oven (Figure 15.4). No runaway or sudden thermal events were detected. Only a slight exothermic process appeared on the cook-off curves starting at $140\,^\circ$C and reaching a maximal temperature difference of $5.5\,^\circ$C at $180\,^\circ$C. This corresponds to the self-ignition of organic matter and the resulting combustion induced the additional temperature increase. The observed exothermicity is smaller than in the other thermal analyses (DSC) due to the extremely slow heating rate ($0.055\,^\circ$C/min).

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[1]performed in the laboratories of ARMASUISSE thanks to the coordination of Dr P. Folly
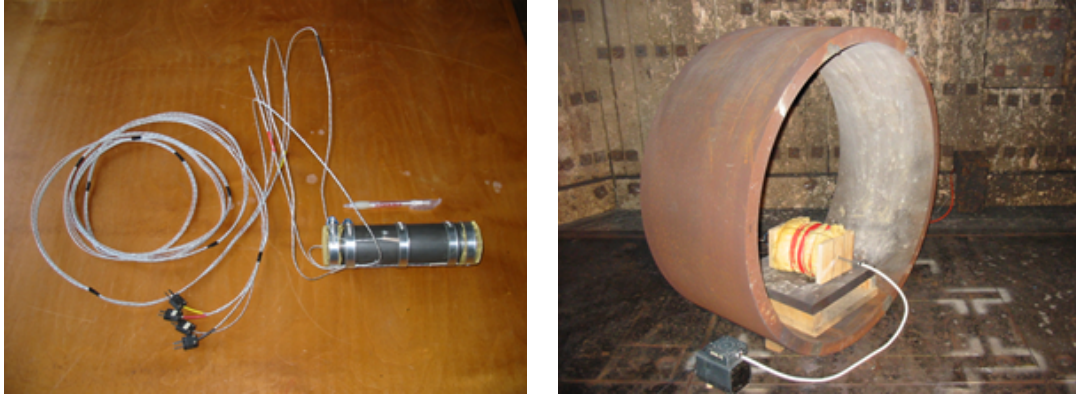
Figure 15.3: Macro scaled crucible used for cook-off experiments, which consisted in a stainless cylinder closed by fine wire nettings at both sides and connected thermocouples (left). The crucible was placed in a thermally insulated oven. During the third experiment compressed air was injected continuously (right)
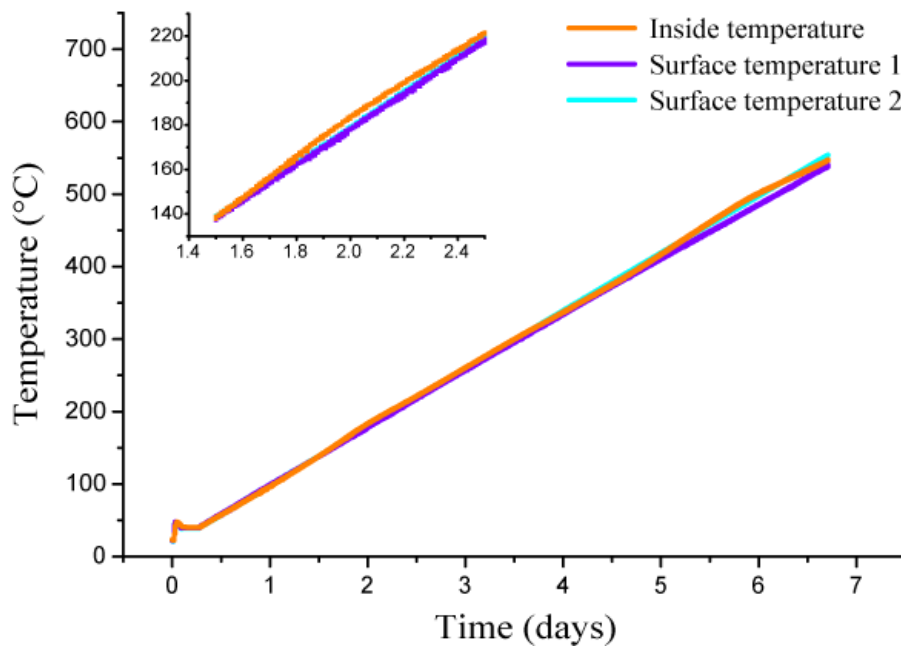
Figure 15.4: Temperature profile of the dried sewage granules stored inside the cylinder and the temperature at the surface of it and zoom of the exothermic event due to the combustion of the material

During the third cook-off experiment the inside temperature was even lower than the oven temperature due to the cooling effect of the airflow, which overbalanced the expected more pronounced exothermicity resulting from the combustion.

15.4   Conclusions

An external event induced for instance by the working conditions of the dryer plant, an electrostatic ignition source or a self-explosion tendency can be excluded. Moreover no clear trend was noted concerning the dry solids content related to neither the transition between the two drying systems, nor to the weekly schedule of the new dryer plant.

Chapter 16

Hypothesis 4: biological activity

The fourth hypothesis is related to a self-heating process occurring within the organic material such as noted in the composting facilities or haystacks. In these cases the first heating stage is due to the decaying plants respiration and the biological activity of the present microorganisms. After the drying process, the remaining microorganisms become latent because of the lack of humidity necessary for their growth activity. Therefore these bacteria spores, present in sewage granules, may become active again if specific conditions are attained. The restart of their biological activity would release heat [54], which could accumulate within the material further accelerating the biological processes until a critical temperature would be reached.

16.1 Standard biological analyses

Different samples of dried sewage granules from the STP of Bern were brought to the state agricultural and veterinary laboratory in order to carry out biological analyses.

The first sample underwent a qualitative analyses in order to detect what sort of bacteria spores were present within this dried biowaste. These biological tests were carried out on specific media allowing the rapid growth of the microorganisms. However the results of this analysis would indicate only the total presence of dormant microorganisms and not in any case their biological activity (Table 16.1).

With the aim of understanding the role of the microorganisms in the self-heating process of the dried sewage granules during storage, the biological analyses are investigated more deeply with the germs counting (Table 16.2).

Table 16.1: Qualitative biological analyses of dried sewage granules

Bacteria	Qualitative presence [a]	Biological activity
Enterobacteria		
Bacillus cereus	++	aerobic
Bacillus sp.	+	aerobic
E. coli	+	aerobic
Proteus sp.	+	aerobic
Clostridium perfingens	+	strict anaerobic

a) + and + + indicated respectively a small and a medium amount of grown bacteria

The two analyses gave extremely different results from each other, which indicated that an important variation within the quantity of bacteria spores in the material. Another disadvantage of this standard method consisted in the fact that the bacteria in their resting form were not distinguishable from the ready-to-duplicate cells. Therefore the plate counts method can not give valuable information about the corresponding heat release, because the growth evolution and the metabolic activity have not yet been taken into account.

Table 16.2: Germs counting made for the biological analyses of dried sludge granules

	Bacteria spores (CFU/g) [a]	
Bacteria	Analysis 1	Analysis 2
Bacillus cereus (Enterobacteria)	21'000	560
E. coli (Enterobacteria)	< 10	9'000
Clostridium perfingens	100'000	0

a) CFU is the number of colony forming units from the bacteria spores on a selective medium

16.2   Specific biological analyses

Other biological analyses were started at the Department of Plant Biology of the University of Fribourg under the supervision of the assistant professor Dr Liliane Sticher. This was done for searching the presence of fungi and bacteria spores within the dried sewage granules. In presence of moisture, such spores may develop and even release heat during their growing process.

The previous biological analyses, made by the state agricultural and veterinary laboratory, were performed by using nutritive culture media. Moreover the media were specific to the selected groups of microorganisms. However if there would be a biological activity responsible for the thermal runaway during the storage of dried granules, it had to occur only with the surrounding medium, which consisted in the sewage granules themselves.

Therefore the following tests were performed to study the biological activity of fungi and bacteria within the dried sewage granules as single growing medium. It was planned to test the biological activity of the dried sewage sludge on nutritive medium[1] and on non nutritive medium such as on agar only. Both experiments, on nutritive and non nutritive media, would be made at different temperatures from room temperature to 50 ° C.

On nutritive medium

Some dried sewage granules were placed on biological plates containing specific nutritive culture medium and were left at different temperature for growing process. Several bacteria and fungi developed on the various plates, however it turned out they were too many colonies to allow a correct determination. Therefore only the experiments on non nutritive medium was carried on.

On non nutritive medium

Some dried sewage granules were placed on biological plates containing only agar (non nutritive medium). Various temperatures (RT, 37 ° C, 50 ° C) and preparation (direct application of granules or powder, suspension of the powdered granules in water with or without centrifugation) were used for these biological experiments (Table 16.3).

The white colonies grew as rings around the dried sewage granules and on the suspensions made with the powdered granules. Some yellow colonies appeared as dots only in the plate containing the centrifuged solution of sewage solids. However the amount of these yellow colonies was minimal and was probably due to a contamination.

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[1]nutritive media V8, PCA, PDA and LB

Table 16.3: Colonies formed on non nutritive medium from bacteria spores present in the dried sewage sludge granules

	Direct application		Suspension in water	
Growing conditions	Granules	Powder	Non centrifuged	Centrifuged
Room temperature	w [a)]	w	w	w
37 °C, in oven	w	- [b)]	w	w + y
50 °C, in oven	w	-	w	w

a) w for the detected white colonies of microorganisms, and y for the yellow colonies

b) - when no colonies of microorganisms were observed

To make further analyses, the white and yellow colonies were picked up and restreaked on a two different culture media:

- on non nutritive medium (agar only)

- on nutritive medium (LB: *Luria Bertani Broth*)

The new biological cultures were placed at 37 °C in an oven and at RT, giving large enough colonies after several days (Table 16.4). It was then possible to proceed a determination of the colonies by Gram staining [55, 56]. The observation of the resulting stains by microscope indicated that the ring-shape white colonies were in fact Gram-negative (red stain) and rods bacteria, which corresponded to *Escherichia Coli*. The presence of these optionally aerobic enterobacteria was expected with respect to the origin of the material. Their growth in a small amount on a non nutritive medium, such as on dried sewage sludge itself, and in a large amount on specific nutritive culture medium fitted with this type of microorganisms.

Table 16.4: Picking and restreaking of developed colonies of dried sewage sludge granules for determination by Gram stain

		Culture medium	
Source	Colonies	Nutritive	Non nutritive
Centrifuged suspension (RT)	y [a)]	+ [b)]	+
Non centrifuged suspension (37 °C)	w	+ + +	+
Granules (37 °C)	w	+ + +	+

a) w for the detected white colonies of microorganisms, and y for the yellow colonies

a) quantity of grown colonies: + small, + + + large

The dot-shape yellow colonies were also Gram-negative (red stain) and rods bacteria. By microscope observation these bacteria turned out to be much smaller than *Escherichia Coli.* No further determination could be done on them. As these yellow dots colonies were present in only one of the twelve biological cultures, they were suspected to be due to a external contamination.

16.3 Conclusions

Even though the analyses performed on specific media show the presence of bacteria spores within the dried sewage granules, the self-heating could not be assigned to the biological activity of the residual microorganisms. Indeed the biological processes need enough time (days or weeks) and moisture (20 - 45 %) to self-heat, whereas the spontaneous temperature increase within the stored biosolids takes place on the one hand in a few hours only, and on the other hand with very a low moisture content ($\sim$ 8 %).

Moreover on non nutritive medium (only on dried sewage sludge), colonies of *Escherichia Coli* are the principal microorganisms to grow. *Escherichia Coli* is a typical mesophile and its maximum growth temperature is 48 °C [56], preventing any further biological activity at higher temperature. In conclusion the first spontaneous temperature increase is not caused by biological processes.

Chapter 17

Hypothesis 5: catalytic autoxidation

This hypothesis assumes that the organic part of the sludge undergoes an oxidative degradation, which would release enough energy to keep the self-heating process going or eventually to accumulate enough heat to start combustion of the organic material. Autoxidation processes are known to be catalyzed by transition metals, such as iron, present in abundance in the sewage granules: an important amount of ferric chloride sulfate is added to raw sewage flows arriving at the STP of Bern for precipitating phosphate and by adding weight to the biowaste for faster sedimentation. Iron is therefore present in dried granules in large quantities (between 7 and 12 %) and is suspected to be mainly responsible for the catalytic autoxidation of the sewage granules.

17.1 Presence of vivianite (ferrous phosphate)

During the storage experiments performed in the industrial silo, some samples of granules freshly stored and of sintered granules left after the fire were taken for X-ray diffraction (XRD).

The unsintered sewage granules contain an important part of amorphous materials, which gives a diffuse bump in the baseline of the XRD spectrum (Figure 17.1). Nevertheless some crystalline phases were detected indicating the presence of quartz (SiO_2), calcite ($CaCO_3$) and vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$). The presence of iron phosphate was expected, because of the addition of ferric chloride sulfate in raw wastewater for the purpose of phosphate precipitation. However the presence of crystalline ferrous phosphate, called vivianite, indicated that iron had been reduced during the sludge treatment. In the digesters, the sewage sludge underwent an anaerobic biological degradation. Under these reducing conditions Fe(III) is converted presumably totally in Fe(II) leading to the formation of vivianite [57].
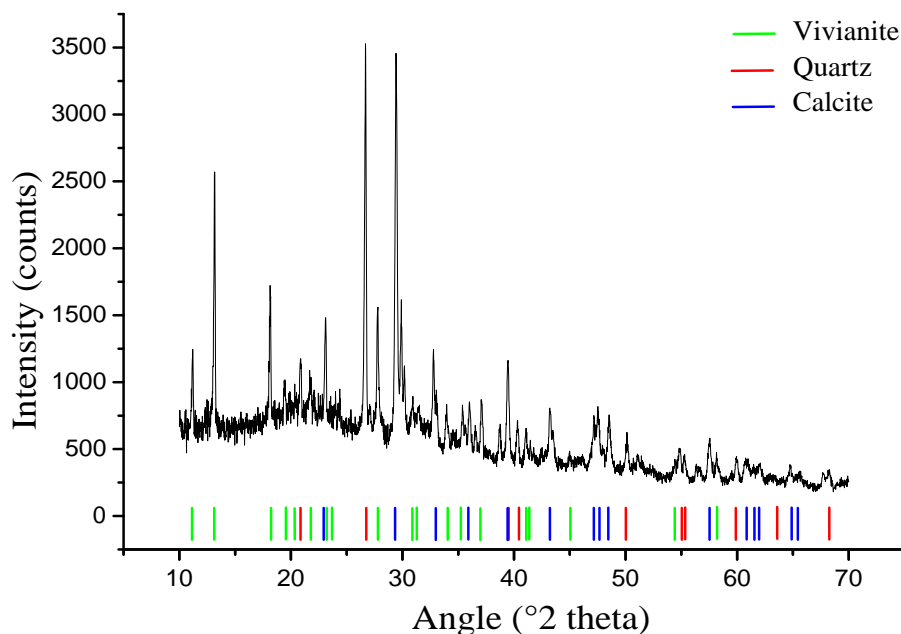
Figure 17.1: XRD measurement of the dried sewage granules from the STP of Bern. Presence of three main crystalline phases: vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$), quartz and calcite within an important amount of amorphous matter

Vivianite was the only iron compound detected by XRD, neither iron carbonate called siderite ($FeCO_3$), nor iron oxides such as hematite (Fe_2O_3) or magnetite (Fe_3O_4) was present in sewage granules, or at least not in a crystalline phase.

In the analysis of the sintered samples, no diffuse bump in the baseline of the XRD spectrum appeared anymore. As the amorphous phase was absent after the smouldering fire, it can be concluded that the amorphous part is mainly composed of organic material. Quartz and calcite were still present in the sintered samples, but the crystalline phase of vivianite could no longer be observed in the XRD spectra. Obviously vivianite decomposed during the smouldering fire.

17.2   Vivianite quantification in the dried granules

The vivianite detected by XRD consisted only in the crystalline phase of the ferrous phosphate octahydrate. Amorphous vivianite or microcrystalline phases were not detected by this method. Quantitative determination of the amount of the crystalline vivianite would therefore give only limited information about how much iron was left in the amorphous phase.

Crystalline vivianite was quantified by spiking the material with a reference crystalline phase of known concentration. Then the obtained XRD diffractograms were processed using the Rietveld method. The Rietveld method is a method for extracting detailed crystal structural information from X-ray powder diffraction. With a software for quantitative powder XRD phase analysis based on this method, it was possible to quantify the various crystalline phases and the amount of the amorphous or microcrystalline part present in a sample.

Table 17.1: Amorphous and crystalline phases in dried sewage granules

| Spiking with ZnO | Phases content (%) [a] | | | |
	Amorphous	Quartz	Calcite	Vivianite
2.5 %	91.3	2.3	1.8	4.5
10.0 %	90.9	1.6	1.8	5.6

a) from the dry solids content

The dried sewage granules were spiked with 2.5 and 10 % of zinc oxid. The results of this phase characterization indicated that around 91 % of the dry solids content was amorphous (Table 17.1). The quantification of the crystalline vivianite gave around 5.1 % DS, which corresponds to 1.7 % of iron in this phase. This amount represents around 20 % of the total iron present in the dried sewage granules.

17.3   Evolution of vivianite as a function of storage

The behaviour of vivianite under storage was studied because the presence of ferrous phosphate ($Fe_3(PO_4)_2 \cdot 8\ H_2O$) in its crystalline form was suspected to play a role in the first exothermic event observed during the large scale storage experiments and the thermal analyses. In fact the spontaneous oxidation of iron(II) in the presence of oxygen was expected to contribute to the heat release leading finally to the autoxidation of the organic material.

In order to verify this assumption, XRD analyses were made on different samples of dried sludge granules stored at different temperatures for detecting any changes in the concentration of the crystalline ferrous phosphate. A first test with dried sludge granules stored at 110 °C during 24 hours showed that the crystalline phase of vivianite had completely disappeared under these conditions.

Therefore the next sample was separated in two fractions stored at room temperature and at 90 °C. This temperature was chosen because it corresponds to the temperature reached after the first temperature increase observed in the large storage experiments.
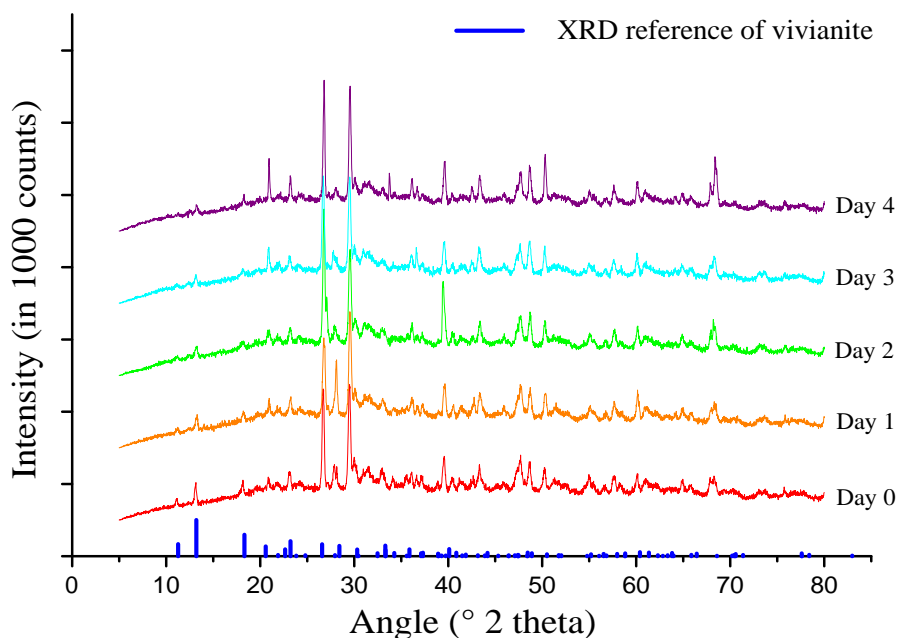
Figure 17.2: XRD measurements of the dried sewage granules stored at 90 °C during four days

The XRD analyses were made once a day during the four days of storage at RT and 90 °C. At RT the vivianite peaks did not show any significant changes. However it can be observed in the powder XRD patterns from the storage at 90 °C that the amount of crystalline vivianite decreased in this time frame (Figure 17.2). Actually the three major peaks of the vivianite phase, which appeared at 11.2, 13.2 and 18.2 ° 2θ, decreased when stored at 90 °C. This decrease can already be observed after the first day of storage.

17.4   Evolution of vivianite towards of temperature

The decomposition of vivianite [58, 59] as a function of temperature was studied using high temperature X-Ray diffraction (HT-XRD). The stability of this crystalline Fe(II) compound at different temperatures would give information about its impact within the dried sewage granules, since on decomposition the crystal water amounting to 28.7 % of the vivianite is set free.

Samples of dried sewage sludge were ground and sieved in order to obtain a fine powder. The freshly powdered granules were directly placed within the HT-XRD device without any further treatment. The sample sustained a temperature program while a certain number of XRD measurements were made, each at a defined time interval.

The more intense peak of the powder XRD pattern of vivianite was known from the reference data to be at $13.2\,°\,2\theta$. The peak position was confirmed by the XRD pattern of the dried sewage granules performed at room temperature. Therefore the XRD scans were carried out by measuring between $12.5\,°\,2\theta$ and $13.5\,°\,2\theta$ at $0.02\,°\,2\theta$ steps. The temperature program allowed a first XRD measurement at room temperature and then several successive XRD scans at the chosen temperature. The decrease of this major peak from the vivianite XRD pattern was recorded with respect to temperature and time.
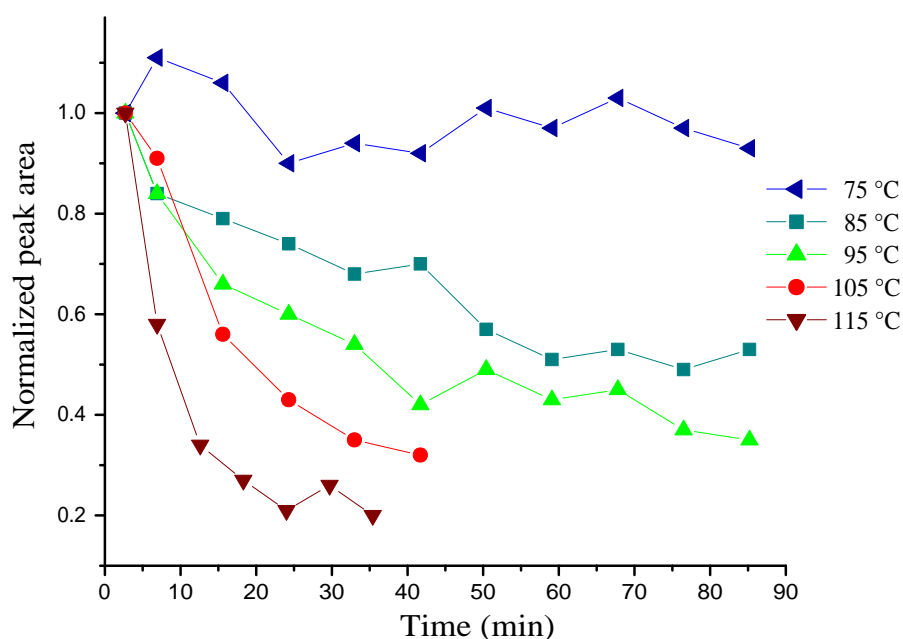
Figure 17.3: Evolution of the major peak area from the vivianite XRD pattern as a function of the time of storage during the isotherm temperature HTXRD program

The HT-XRD study showed a decrease of the peak area for isotherm storages at 85 °C and over (Figure 17.3). The decomposition of the vivianite crystalline phase occurred quite rapidly in this temperature range. At 85 °C, for instance, half of the crystalline vivianite has already decomposed after one hour. When stored at 75 °C however, the crystalline phase of vivianite was quite stable, even though the peak area showed some fluctuations. At 55 and 65 °C the vivianite crystalline

phase from the dried sewage granules did not show any significant decomposition even after two hours of storage as revealed by HT-XRD measurements.

The data about the crystalline phase decomposition can be studied further to obtain kinetic information [60]. Indeed the thermal decomposition follows a logarithmic equation called the *Avrami* equation (Eq. 17.1)

$$y = 1 - \exp(-kt)^n \tag{17.1}$$

with the transformed fraction y, rate constant k, an empirical parameter n and the experiment time t. To extract values of the rate constant k from the Avrami equation, linearization of the vivianite decomposition towards temperature is used by plotting $\ln(-\ln(1\text{-}y))$ against $\ln t$ (Eq. 17.2).

$$\ln(-\ln(1 - y)) = n \ln k + n \ln t \tag{17.2}$$
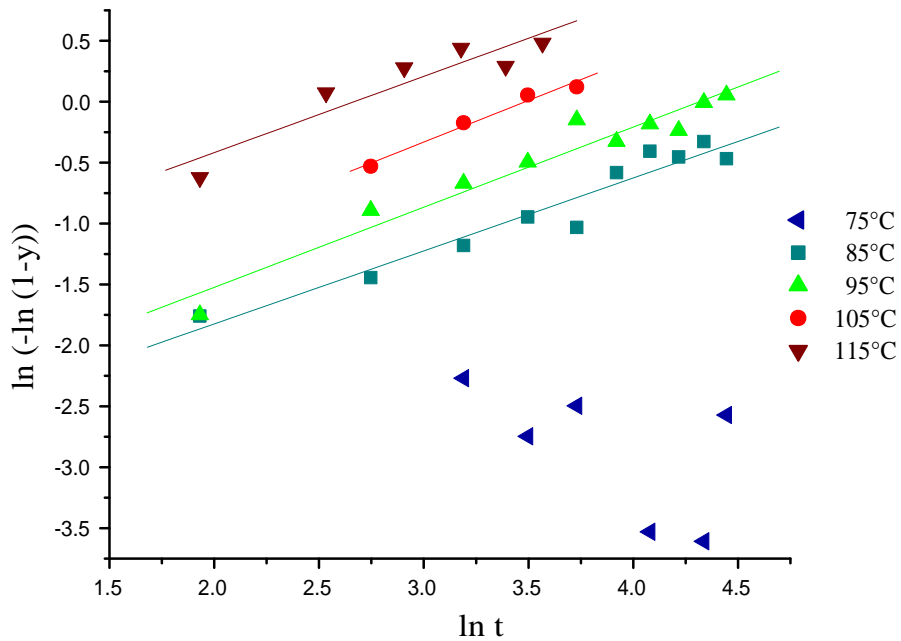
Figure 17.4: Avrami plot of the vivianite decomposition towards temperature

On the Avrami plot (Figure 17.4) the decomposition of vivianite as a function of the temperature was represented by the linear regressions except for the measurement made at 75 °C. Even though a faint decomposition trend can be noted at 75 °C, some normalized peaks showed greater area as compared to the initial XRD pattern, which prevented the linear regression. The identical slope for the decomposition at different temperatures indicated that the mechanism of

decomposition did not change within the temperature range (isokinetic process). However it also meant that the decomposition of vivianite started above 75 °C.

Moreover the rate constant k and the empirical parameter n are determined by the Avrami linearization giving $\bar{n} = 0.64 \pm 0.04$ (Table 17.1). Then the empirical activation energy E_a is obtained by the means of the Arrhenius equation (Eq. 17.3), when $\ln k$ is plotted against $1/T$ (Figure 17.5). From the slope $-E_a/R$, the resulting empirical activation energy is (92.0 ± 3.3) kJ/mol.

Table 17.2: The rate constant $\ln k$ and the constant n for the decomposition of vivianite in function of the temperature

Temperature (°C)	constant n	rate constant $\ln k$ (min^{-1})
85	0.60 ± 0.06	-5.05 ± 0.34
95	0.66 ± 0.06	-4.32 ± 0.32
105	0.68 ± 0.07	-3.48 ± 0.35
115	0.63 ± 0.12	-2.67 ± 0.59

$$k = A \exp\left(\frac{-E_a}{RT}\right) \qquad (17.3)$$

In conclusion it can be said that crystalline vivianite was stable up to 75 °C. At higher temperature, the crystalline phase started to decompose. However it was not possible to elucidate if this decomposition was due to the oxidation of iron or to the collapse of the vivianite lattice by the loss of water molecules.

On the one hand it is well known that the unaltered form of vivianite is colorless when pure, but even though most pristine crystals of vivianite have a greenish to bluish hue. This color change is attributed to the partial oxidation of the total iron within vivianite [61]. In fact vivianite is particularly susceptible to oxidation processes. Due to oxidation of iron, the formula of vivianite ($Fe_3(PO_4)_2 \cdot 8\ H_2O$) varies from its strict mineral composition of an hydrous phosphate of ferrous iron to an oxidized form corresponding to

$$Fe^{2+}_{3-x}Fe^{3+}_x(PO_4)_2(OH)_x \cdot (8\text{-}x)\ H_2O \text{ where x} < 1.2$$
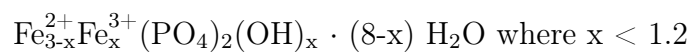
Usually, when more than 40 % of the iron has been oxidized, the monoclinic vivianite lattice collapses to the triclinic symmetry of metavivianite [62].
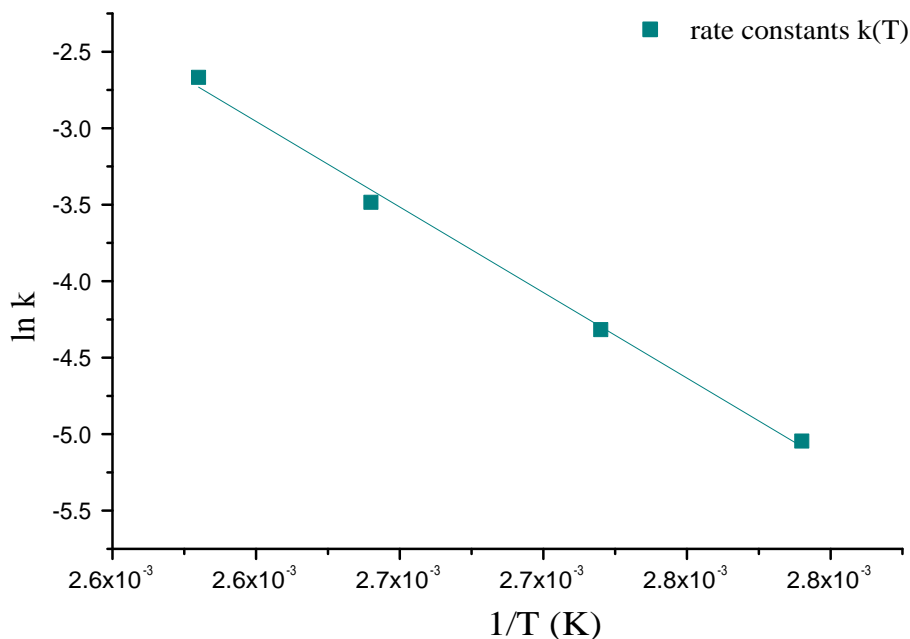
Figure 17.5: Arrhenius plot using the rate constant k(T) obtained by the Avrami linearization of the vivianite decomposition towards temperature

One the other hand the dehydration of vivianite has also been studied by thermal analyses [58]. Natural vivianite was found to show a major differential thermal response over the 65 - 316 $^\circ$C attributed to an endothermic loss of structural water combined with the oxidation of Fe(II). However the performed TG analyses showed the first weigh loss only at 105 $^\circ$C assigned to water by TG-MS.

17.5   Determination of the iron/phosphate ratio

The vivianite detected by XRD consisted only in the crystalline phase, however it has been shown that crystalline vivianite corresponded only to 20 % of the total iron. The remaining iron was present in the amorphous phase. In order to study the iron in an amorphous phase, some analyses were performed using the DrLange device.

Three samples of dried sewage sludge were prepared and the obtained solutions were analyzed for total iron and phosphate determination. In vivianite the Fe/PO_4^{3-} mass ratio is 0.88. The results showed a higher Fe/PO_4^{3-} ratio around 1.2 indicating an excess of iron as compared to the available phosphate (Table 17.3).

Table 17.3: Iron / phosphate ratio in the dried sewage granules

| Samples | Concentration (%) [a] | | | Mass ratio |
	Fe_{tot}	P_{tot}	Calculated PO_4^{3-}	Fe_{tot} / PO_4^{3-}
1	9.79	2.65	8.12	1.21
2	9.98	2.73	8.36	1.19
3	9.95	2.70	8.28	1.20

a) from dry solids content

To double check these results, the analyses carried out regularly by the State laboratory on the dried biosludge were studied. Even though these composition analyses are made several times a year, iron concentration was not always measured. Therefore all the data from the starting up of the dryer plant were collected and the total iron and phosphate concentration was worked out.

Table 17.4: Calculated iron / phosphate ratio in dried sewage granules from State analyses

| Analyses | Concentration (%) [a] | | | Mass ratio |
	Fe_{tot}	P_{tot}	Calculated PO_4^{3-}	Fe_{tot} / PO_4^{3-}
September 2003	10.4	1.8	5.4	1.9
August 2004	12.0	3.6	11.0	1.1
October 2004	8.2	3.9	12.0	0.7
February 2005	9.5	4.6	14.1	0.7
July 2005	11.0	3.5	10.7	1.0

a) from dry solids content

The results given by the State laboratory using atomic emission spectroscopy with inductive coupled plasma (ICP-AES) gave Fe_{tot} / PO_4^{3-} ratios varying considerably (Table 17.4). Nevertheless during most of the sampling periods iron was clearly in excess of phosphate with a ratio above 0.88.

17.6 Iron redox speciation in the sewage sludge

The former analyses showed that dried sludge granules from the STP of Bern generally contained a high level of iron, which is due to the addition of ferric chlorosulfate to incoming wastewater at the beginning of the treatment process.

This chemical handling is needed to remove soluble phosphate by precipitation. The precipitated iron phosphate follows then the whole sewage sludge treatment route. One of the biological treatments occurs in digesters, where the organic matter is decomposed to their reduced forms. In these digesters Fe(III) is also reduced into Fe(II) due to anaerobic bacterial conditions.

Indeed the present Fe(II) is suspected to have a catalytic activity responsible for the autoxidation of organic material contained in dried sludge granules. Therefore the redox species of iron were determined in the sewage sludge samples [63] and the variation of the Fe(II) and Fe(III) ratio during storage was studied [64].

17.6.1 Fe(II) and Fe(III) ratio in sewage sludge samples

Sewage sludge samples were taken at different stages of the drying process for the determination of the respective Fe(II) and Fe(III) concentration. Therefore liquid sludge (~ 4 % DS) taken after the digesters, dewatered sludge (~ 35 % DS) taken after the centrifuges and dried sludge granules (~ 92 % DS) taken after the dryer plant were freshly sampled and stored under argon atmosphere. All the samples were carefully prepared for ion liquid chromatography (ILC). In parallel the samples were also prepared under argon for the determination of total iron concentration by means of AAS.

The ILC analysis was repeated three times using the same sampling and working conditions. The average Fe(II) and Fe(III) concentration showed that the iron contained in the liquid and dewatered sludge was mainly Fe(II) corresponding to ~ 80 % of total iron (Figure 17.6). During the drying process the iron underwent a partial oxidation decreasing the Fe(II) / Fe(III) ratio to ~ 50 %.

The total iron concentration for the analyzed samples measured by AAS corresponded to the expected values between 7 - 11 % DS. Moreover the summed concentrations of Fe(II) and Fe(III) of each sample measured by ILC matched pretty well with the total iron concentration.

17.6.2 Evolution of the Fe(II) and Fe(III) ratio towards aging

The evolution of the Fe(II) and Fe(III) ratio was studied during the aging process. Therefore some fresh dried sewage granules were sampled and placed in dewars of 1 L (dewar A) and 8.5 L (dewar C) for several days. They were stored at room temperature or at higher temperature when placed in an oven. The inside temperature was recorded during the whole storage experiment.
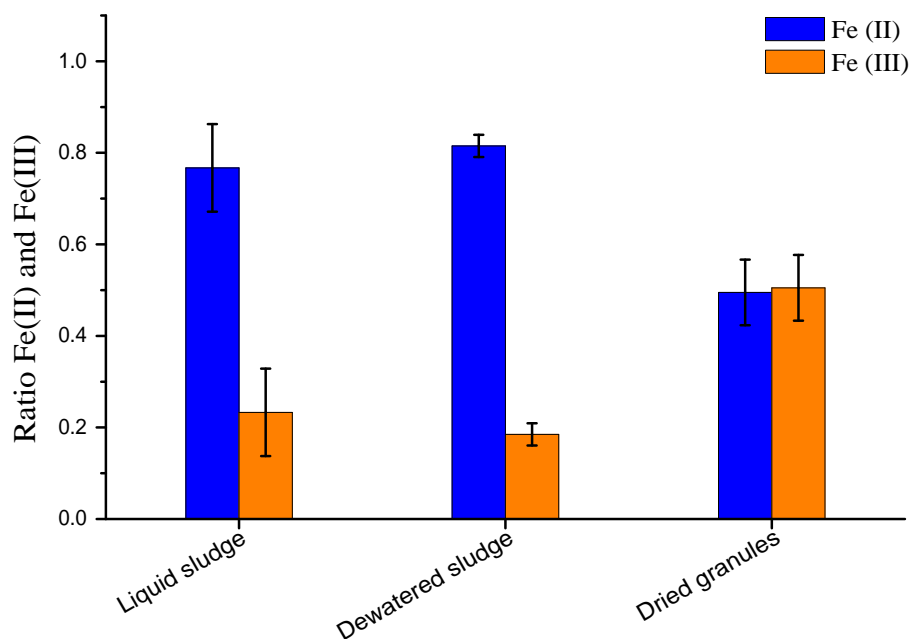
Figure 17.6: Ratio of Fe(II) and Fe(III) contained in fresh samples of liquid sludge, dewatered sludge and dried sewage granules

At the end of the storage experiment, the samples were prepared for ILC analyses. The tendency resulting from the various performed experiments consisted in the spontaneous oxidation of Fe(II) during the storage period (Figure 17.7). For nearly all the storage experiments, the concentration of Fe(III) had increased after that the granules were stored, however there were some important variations of the Fe(II) and Fe(III) ratios from one storage to another.

Spontaneous oxidation of the Fe(II) contained in the dried sewage granules occurred during the storage period. However due to the important fluctuations of Fe(II) and Fe(III) ratio from one storage to another, no trend concerning the impact of the storage conditions could be noted.

17.7 Conclusions

During the sewage sludge treatment, Fe(III) added as iron chloride sulfate in raw wastewater is reduced to Fe(II) under the anaerobic conditions of the digesters. This was confirmed by the iron speciation of liquid sludge samples, in which nearly 80 % of the total iron content is Fe(II). After centrifugation, this Fe(II) / Fe(III) ratio stays constant for the dewatered sludge samples, whereas after the drying
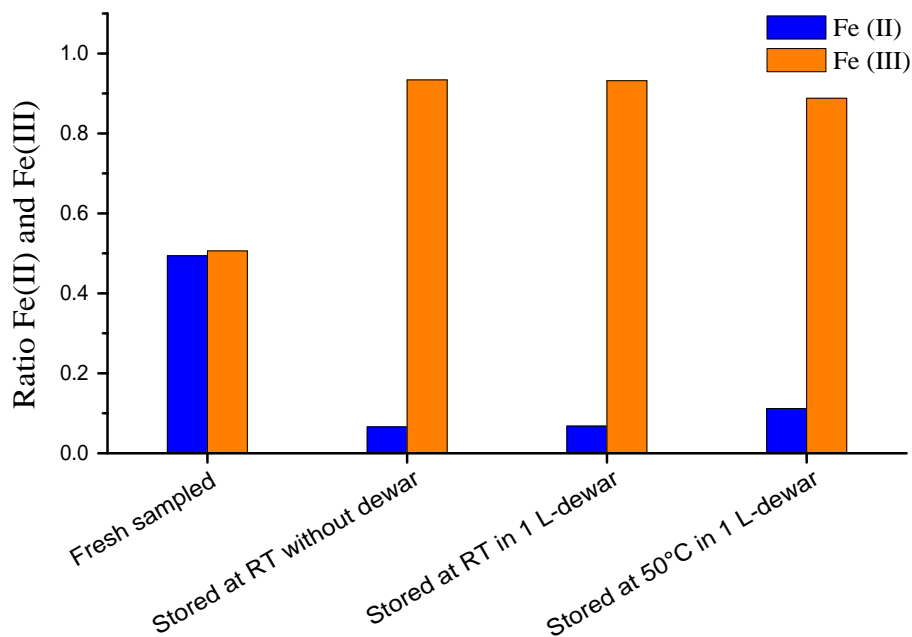
Figure 17.7: Ratio of Fe(II) and Fe(III) contained in the dried sewage granules freshly sampled and the usual variation of the Fe(II) and Fe(III) ratio occurring during the storage in several conditions

process the Fe(II) / Fe(III) ratio drops to 50 %. This oxidation occurs under the dryer working conditions at $\sim 80\,^{\circ}$C and under a low oxygen atmosphere. During the storage of the dried sewage granules, iron oxidation continues due to the presence of residual oxygen (4 -6 % vol.) and air leakage through the lid.

In the dried sewage granules, 50 % of the total iron content is ferrous species, present principally as crystalline ferrous phosphate (vivianite). This crystalline phase corresponds to at least 20 % of the total iron present in the dried biosolids. The remaining iron is on the one hand microcrystalline iron phosphate, which was not detected by this XRD analysis, and on the other hand amorphous iron compounds. Even though the crystalline vivianite within the dried granules is stable up to $75\,^{\circ}$C, the microcrystals and the amorphous ferrous compounds are suspected to oxidize spontaneously at lower temperature.

In conclusion the spontaneous oxidation of iron within the sewage granules was observed first during the drying process and secondly during storage of the material. Depending on the oxygen and moisture content surrounding the stored material, this oxidation leads to a specific Fe(II) / Fe(III) ratio, which may explain the important variations of the Fe(II) and Fe(III) concentrations from one storage to another.

Chapter 18

Hypothesis A: pyrophoric iron sulfide

The hypothesis A added at a later stage of the work explains the self-heating of the material by to a pyrophoric reaction of iron sulfide (FeS), which is suspected to be present in the treated sewage sludge. The State analyses on dried sludge granules from the wastewater treatment plant of Bern determined always a total sulfur concentration of ~ 1 % without further speciation. It is said that hydrogen sulfide formed within the digesters is then precipitated by the surplus of present iron resulting in the formation of black iron sulfide. Iron sulfide is easily detected, since upon HCl addition H_2S forms.

18.1 Gas analyses under acid conditions

In order to analyze the liberated gases from the dried sewage granules, and specially hydrogen sulfide, some experiments were performed on fresh samples with an acid treatment. The gas measurements were made with a security device[1] sensitive to hydrogen sulfide, methane, carbon monoxide and oxygen.

A fresh sample of dewatered sludge was placed in a flask connected to the gas analyzer device. A nitrogen flow went through the system to allow the device pump to suck the liberated gas. Then some water was added to obtain a thick slurry to which a HCl 2M solution was added dropwise. During this experiment, some very small amounts of hydrogen sulfide, with a maximum concentration of ~ 30 ppm, were measured.

Then a sample of dried sewage granules was also tested under the same conditions. The presence of hydrogen sulfide was also detected with a maximum concentration of ~ 20 ppm.

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[1]Miniwarn, Dräger

18.2   Gas release during storage

Three storage experiments of dried sewage sludge were performed under different conditions, while the released gas from the biosolids was analyzed continuously. The dried sewage granules were placed in a 1 L - dewar at room temperature, the first time without any air addition, the second time with a small nitrogen flow, and the last time with a small air flow. It has to be noted that during these three experiments no temperature increase was observed.

During these storage experiments, only a very small amounts of hydrogen sulfide were detected (2 - 3 ppm), even under a flow of air or nitrogen for removing the gas present within the granules. Meanwhile the CO concentration was also measured and presented a maximum concentration when the gas analyzer device started to pump (23 ppm) followed by a stable concentration afterwards (12 ppm). No methane was detected during these tests.

18.3   Presence of iron sulfide

As a potential source of ignition, presence of iron sulfide in dried sludge granules was studied. In order to prove that iron sulfide was indeed contained within the dried sludge, some untreated samples of dried granules and some other samples spiked with FeS were acidified with HCl (1M). The released hydrogen sulfide would precipitate as PbS, a black suspension, while bubbling in a $Pb(OAc)_2$ solution ($2 \cdot 10^{-2}$ M) :

$$FeS \quad \text{in dried sludge} \quad + \quad HCl \quad \longrightarrow \quad H_2S \quad \xrightarrow{Pb(OAc)_2} \quad PbS \downarrow$$

The total sulfur concentration reaches ~ 1 % DS in the sewage sludge produced at the STP of Bern. The spiking of the biowaste aimed of doubling the initial sulphur content. First the system was tested by acidifing FeS only. The formed gas bubbled in a $Pb(OAc)_2$ solution by the mean of a light nitrogen flow. The solution turned black after the addition of 1 mL of HCl 1M proving the release of H_2S (Table 18.1, entry 1).

The experiment was then repeated on dried sewage granules, to which between 15 and 30 mL hydrochloric solution was added dropwise, giving an acidic slurry at the end. However no black precipitate was observed after the addition of HCl on dried sludge (entry 2). More surprisingly no H_2S was released after HCl addition

to FeS-spiked sludge powder (entry 3 - 4). The formation of hydrogen sulfide from FeS under acidic conditions was tried again and in fact needed only a few drops of hydrochloric acid (entry 5). Therefore the presence of iron sulfide within sludge granules could not be evidenced.

Table 18.1: Presence of iron sulfide by acidification of the raw and spiked samples of dried granules

Entry	Granules (g)	Mass FeS (g)	Added S as FeS (% DS)	Vol. HCl 1M (mL)	Precipitation in Pb(OAc)$_2$ sol.
1	-	0.17		1	yes
2	5.00	-		31	no [a]
3	5.02	0.15	1.2	31 [b]	no
4	5.07	0.17	1.3	15.5 [c]	no
5	-	0.17		2 drops	yes

a) light brownish precipitate probably corresponding to PbCO$_3$

b) stirring the two powders together before the addition of HCl

c) grinding the two powders together before the addition of HCl

To understand why no hydrogen sulfide was formed from a mixture of dried sewage sludge and iron sulfide powder, additional control experiments were carried out, which consisted in testing on one hand the matrix (sewage granules) and on the other hand the sulfide source.

The first test consisted in mixing iron sulfide and calcinated sand, used as an inert matrix. After the addition of 2 mL of HCl to the mixture, a black suspension appeared in the Pb(OAc)$_2$ solution (Table 18.2). This confirmed the release of H$_2$S from the blend.

Table 18.2: Occurrence of iron sulfide within an inert matrix

Entry	Calcinated sand (g)	Mass FeS (g)	Vol. HCl 1M (mL)	Precipitation in Pb(OAc)$_2$ sol.
1	5.00	0.15	2	yes

In the second test Na$_2$S instead of FeS was added as spiking compound. This experiment showed that after the addition of 2 drops of HCl 1 M, a black suspension appeared in the Pb(OAc)$_2$ solution (Table 18.3). This experiment

confirmed that H_2S was directly released, when the mixture of sewage sludge and Na_2S was acidified. This proved that iron sulfide within the granules undergoes a transformation, which prevents the formation of hydrogen sulfide.

Table 18.3: Occurrence of sodium sulfide within dried sewage granules

Entry	Granules (g)	Mass Na_2S (g)	Added S as Na_2S (% DS)	Vol. HCl 1M (mL)	Precipitation in $Pb(OAc)_2$ sol.
1	5.00	0.15	1.3	2 drops	yes

Several explanations for that can be proposed for this interesting observation:

1. Iron sulfide is strongly bound within the dried granules and can not be released as H_2S by addition of HCl;

2. In situ formed H_2S reacts with another compound within the mixture (unlikely since added Na_2S liberates H_2S);

3. There is no sulfide as such in the dried sludge;

4. The sulfide in iron sulfide is converted to S_2^{2-} due to the redox potential present in the sewage granules.

18.4   Crystals formation during storage experiments

This last explanation received some unexpected support by the observation of some sparkling effects seen on the stored granules while draining the containers at the end of the storage experiment in the large dewars. The sparkling could be observed on all the stored granules at any position within the dewar, which meant that these crystals were not formed by a located reaction, but in the whole stored mass.

A closer observation of these sparkling granules to the naked eye and by optical microscope showed that there were single little transparent crystals at the surface of the dried biowaste. The formation of these crystals occurred during the storage of dried sewage granules in large insulating containers only. Moreover they were not visible at the beginning of the storage and neither during the first few days of storage, but only at the end of the storage when the inside temperature has more or less reached again the surrounding temperature.

18.4.1 Crystals occurrence

Since the formation of these sparkling structures was observed, many storage experiments in dewars were performed under the same conditions. However it seemed that the formation of these crystals not always happened (Table 18.4). It has to be mentioned that when they were formed, the stored granules always sustained a spontaneous temperature increase similar to what was observed previously (see section 13.6), but not inevitable the inverse way.

Table 18.4: Occurrence of sparkling crystals during the storage experiments in the large dewars

| | Sparkling crystals | |
Dewars (Vol.)	B (6.7 L)	C (8.5 L)
Fri 14th July 06	yes	yes
Wed 26th July 06	yes	yes
Thu 31st Aug 06	no	no
Mon 25th Sept 06	no	no
Tue 07th Oct 06	no	no
Thu 16th Nov 06	yes	yes
Thu 14th Dec 06	yes	no
Wed 17th Jan 07	yes	yes
Thu 06th Feb 07	no	no

In addition these crystals were not stable for a long time. After having been kept a few days at room temperature no crystals could be observed on the surface of the sewage granules anymore. Therefore the thermal stability was first tested by storing the granules with crystals on them at RT, 50 °C and 80 °C for a few hours. At 80 °C, no more crystals were present. At 50 °C, only a few crystals stayed. At RT the crystals disappeared after a few days.

18.4.2 Crystals characterization

The determination of these crystals formed during the labscale storage of dried sewage sludge in large dewars was carried out with the aim of finding the clue of the self-heating process.

Ion liquid chromatography

Some samples of dried sewage granules containing crystals were prepared for ILC analyses directly at the end of the experiment. The results of the Fe(II) and Fe(III) ratio measured by ILC and the total iron concentration determined by AAS did not presented any significant trend, but corresponded to the reference stored samples without sparkling crystals.

Powder X-ray diffraction

Other samples of dried sewage granules with crystals on top of their surface were also prepared for powder XRD analyses. The crystalline phases of vivianite, calcite and quartz were present and the ratio of each crystalline phases corresponded to the previous measurements. No additional crystalline phases were observed, which would be due to the presence of news crystals. In conclusion even if the sparkling crystals were visible to the naked eye on the stored granules, the XRD measurements of these powdered granules samples did not show any significant variations of one of the present crystalline phases or the apparition of any new crystalline phases, meaning that the amount of these crystals was below any detection limit.

It was observed that when the granules with crystals on top of their surface were stored in a glass vessel the crystals settled at the inside wall of the recipient. By fractionating a sample of these granules in many glass vessels, it was possible to collect enough crystals for further analyses.

After having collected the crystals from the inside wall of the glass vessels, a powder XRD analysis was performed. This powder XRD pattern of these crystals was compared to crystalline phases measured within dried sewage granules (Figure 18.1) without any matching. The comparison of the XRD pattern of this unknown crystalline phase with other iron compounds like metavivianite and siderite, and also to iron sulfide compounds such as pyrite, mackinawite and pyrrhotite was made without success neither.

Scanning electronic microscopy and EDS microanalysis

On the collected crystals, an analysis by scanning electronic microscopy (SEM) was performed, which showed clearly well-defined crystals (Figure 18.2). On the same sample a X-ray microanalysis has also been done by using energy dispersive X-ray spectroscopy (EDS). It turned out that the crystals were composed of sulfur only.
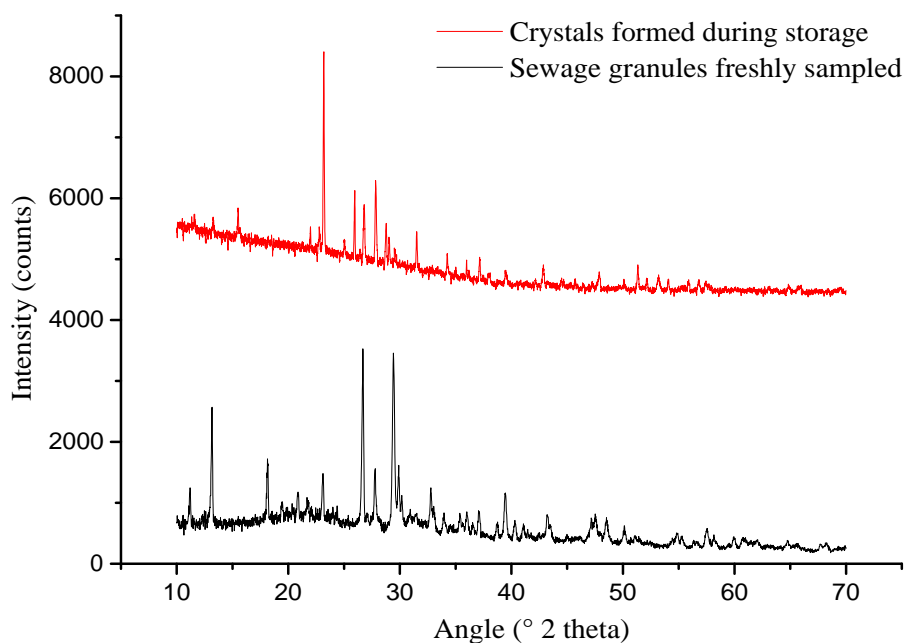
Figure 18.1: Powder XRD patterns of the crystals formed during the storage of dried sewage granules and of the crystalline phases contained in the dried sludge
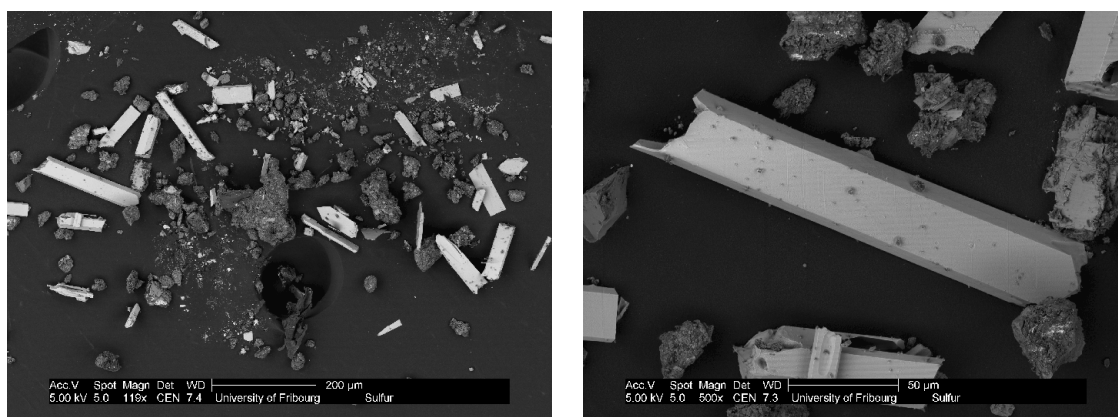
Figure 18.2: SEM analyses of the crystals formed during the storage of dried sewage granules

With this information it was then possible to compare the powder XRD pattern of the unknown crystals with the various polymorphous crystalline phases of sulfur (Figure 18.3). In fact it matched perfectly with the powder XRD reference pattern for orthorhombic α - sulfur [65].

Figure 18.3: Powder XRD pattern of the crystals formed during the storage of dried sewage granules and the reference powder XRD pattern of orthorhombic α - sulfur

Single crystal X-ray diffraction

A single crystal XRD analysis was also performed on the crystals found on the surface of the dried sewage granules with the aim of determining the crystal unit cell parameters. Therefore the largest crystal was picked up using polarized light microscopy for a better selection. This crystal was fixed on a capillary for single crystal XRD analysis.

Table 18.5: Determined unit cell of the crystal formed during the storage of dried sewage granules and reference unit cell of orthorhombic α - sulfur [65]

	Unit cell parameters [a]	
	Crystals from the storage	Orthorhombic sulfur
a	8.18	10.45
b	8.39	12.48
c	13.08	24.46
α	90.18	90
β	89.88	90
γ	112.68	90

a) the distances a, b and c are in Å and the angles α, β and γ in degrees

A crystalline unit cell was obtained for the analyzed crystals, however it was rather surprising that the obtained unit cell parameters did not correspond to orthorhombic sulfur (Table 18.5). In fact this unit cell corresponded to another polymorphous phase of sulfur called Rosickyite and also known as γ - sulfur [66], which has a monoclinic unit cell. Moreover the powder XRD of the γ - sulfur Rosickyite did not match at all with the crystals formed during the storage of the dried sewage solids (Figure 18.4). The single crystal XRD analysis was repeated and gave the same monoclinic unit cell again.

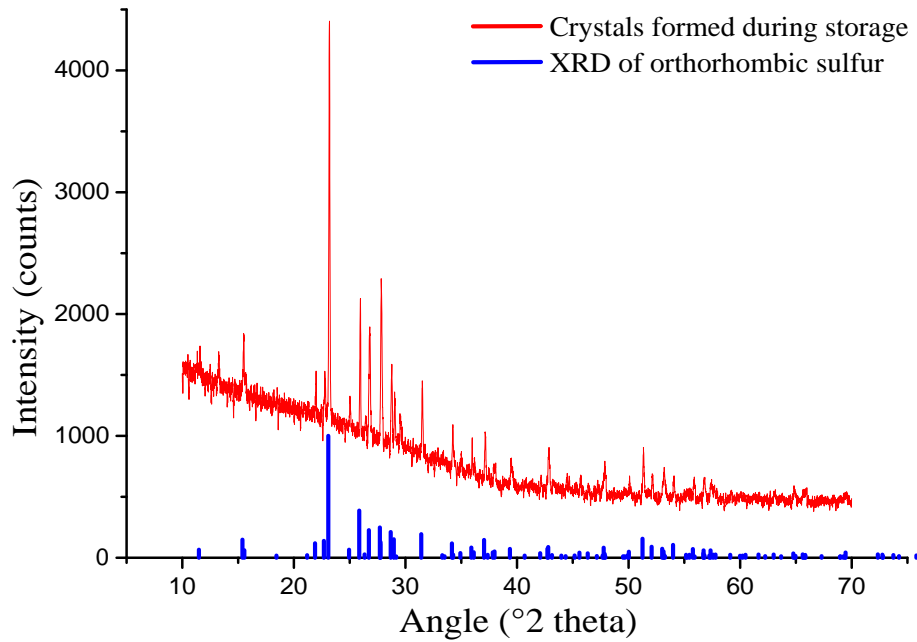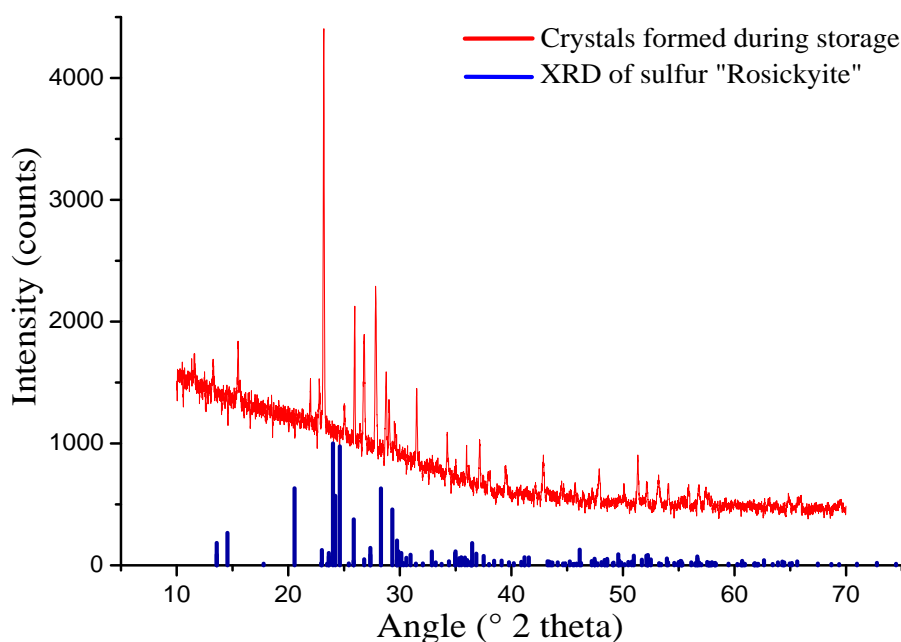Figure 18.4: Powder XRD pattern of the crystals formed during the storage of dried sewage granules and the reference powder XRD pattern of monoclinic γ - sulfur Rosickyite

Orthorhombic sulfur is the stable form at room temperature, but when heated above $100\,^\circ$C, it is converted to monoclinic sulfur. This allotropic phase of monoclinic sulfur consisting of elongated, transparent, needle like structures as present in this case. According to the phase diagram of sulfur, monoclinic sulfur is stable only between 100 - 115 $^\circ$C at low pressure (Figure 18.5).

In conclusion, it can be proposed that sulfide was oxidized first in presence of the redox system Fe(II) / Fe(III) to S_2^{2-} and afterwards to elemental sulfur. This happened during the spontaneous temperature increase that underwent the stored
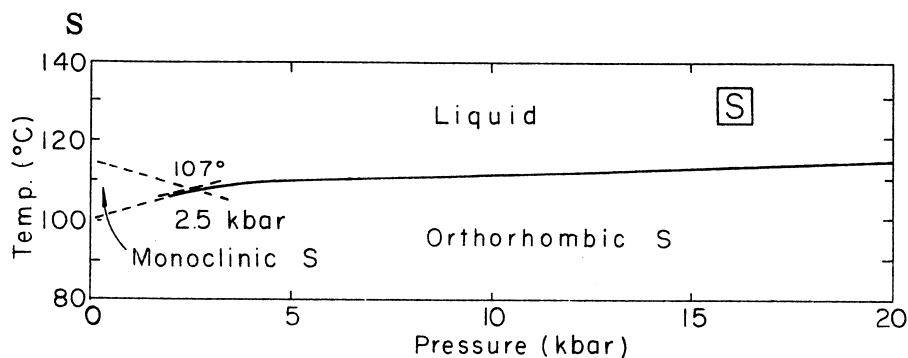
FIG. 3940.—System S; P-T diagram.

Figure 18.5: Phase diagram of sulfur [67]

dried granules. This oxidation required moisture as evidenced by its acceleration in presence of traces of water. This moisture may have various origins such as residual humidity, moisture diffusion from large granules to smaller ones, or released crystal water during vivianite degradation.

The resulting sulfur crystals were first present in a monoclinic crystalline phase due to high local temperature. This metastable phase remained for a certain time after the emptying of the material from the dewars. However after a certain time the monoclinic crystals sustained a phase transformation towards orthorhombic sulfur.

The single crystal XRD was performed under nitrogen atmosphere and at 200 K which allowed the determination of the monoclinic unit cell. In opposition the powder XRD was carried out at room temperature, which enabled the phase transformation and the measurement of the powder XRD pattern of orthorhombic sulfur.

18.5   Conclusions

The presence of iron sulfide within the sewage sludge could not be proved. In fact upon an acid addition on the dried granules, no H_2S forms. Moreover even with FeS-spiked granules treated with HCl, no hydrogen sulfide was released neither. The redox potential applied mainly by the Fe(II) / Fe(III) system is suspected to convert sulfide in S_2^{2-} species, which prevents the formation of H_2S. Further oxidation is leading to elemental sulfur. This was proved by the presence of high temperature monoclinic γ - sulfur crystals on the surface of stored granules. This high temperature metastable sulfur allotrope undergoes then a phase transformation to the stable orthorhombic α - sulfur. Therefore a pyrophoric reaction of iron

sulfide as the cause of the self-heating process of the dried sewage sludge can be excluded, because no iron sulfide is present as it is within the material. However the formation of the γ - sulfur crystals indicates clearly an oxidation with locally high temperature increase.

Chapter 19

Hypothesis B: exothermic hydration

The second additional hypothesis involves an exothermic hydration processes. It was suspected that the dried sewage sludge (~ 92 % DS) of the STP of Bern would heat up when undergoing hydration by any source of humidity. This heat would then accumulate due to the insulating properties of the material.

19.1 Moisture transfer between the stored granules

In order to study the moisture transfer between the granules stored in insulating containers, several storage have been performed in two large dewars of 6.7 L (dewar B) and 8.5 L (dewar C). Some characteristics such as the dry solids content, the average diameter of the dried granules and particles size repartition were analyzed before and after the storage experiment.

19.1.1 Dried sewage granules freshly sampled

First the relationship between the DS content and the granules size was established. Therefore five fresh samples of dried sewage sludge was analyzed (Table 19.1). The four first samples were taken daily during the same week (Exp 1 - 4) and the last one was sampled four weeks later (Exp 5). All the samples presented expected values for the DS content and the granules mean diameter.

The five samples of dried sewage granules were sieved, which gave the particles size distribution for each sample. Then the DS content of every obtained fraction was measured (Figure 19.1). The principal fraction consisted in granules of 1.6 - 2.5 mm size. It has to be noted that some variation appeared in the particles size distribution for the analyzed samples. However the DS content presented only

Table 19.1: Mean diameter and DS content of fresh sampled dried sewage granules

Exp	Sampling	Mean diameter (mm)	DS (%)
1	Mon 13rd Nov 06	2.09	93.1
2	Tue 14th Nov 06	1.70	93.2
3	Wed 15th Nov 06	1.86	92.4
4	Thu 16th Nov 06	1.97	92.5
5	Thu 14th Dec 06	2.03	92.6

small fluctuations for the different sieved fractions except for the granules with a large diameter (> 3.2 mm). For these large granules the moisture content may even reach 18 %.
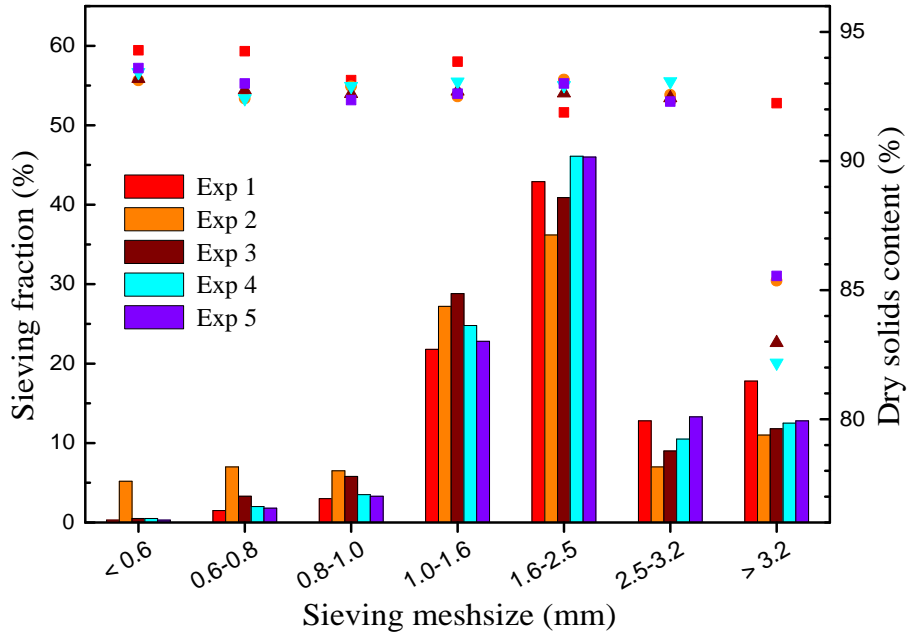
Figure 19.1: Sieved fractions of several samples of fresh dried sewage granules and the respective DS content

19.1.2   Stored sewage granules

With the aim of studying the moisture transfer which may occur between the stored sewage granules, the particles size repartition and the DS content of each sieved fraction was measured at the beginning and at the end of a storage experiment performed in two large dewars. Therefore the variation of the moisture content towards granules size would be analyzed.
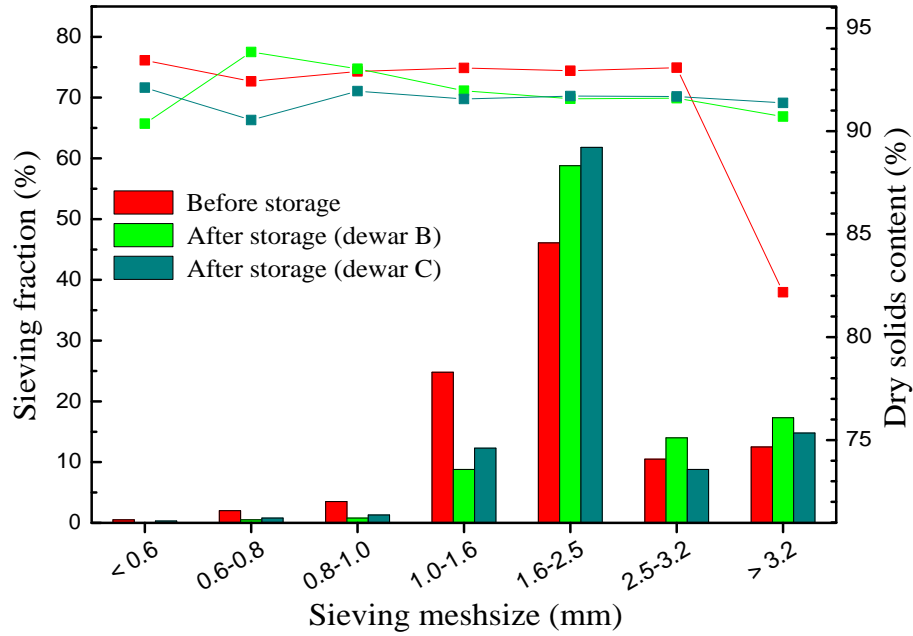
Figure 19.2: Moisture transfer from the large sewage granules to the small ones during the storage in large insulated containers

It is worth mentioning that the exceptionally moist larger granules with a particle size greater than 3.2 mm lose their moisture during the storage (Figure 19.2). Both samples taken after the storage experiment from dewars B and C presented a DS content greater than 90 %. It can also be noted that the particules size distribution changed for the stored granules. In fact it seemed that the fractions of granules larger than 1.6 mm increased during the storage. This was compensated by a depletion of granules smaller than 1.6 mm in diameter.

This experiment was repeated two more times. The obtained results confirmed the tendency for the large granules (> 3.2 mm) getting drier during the storage and the decrease of the fractions containing small granules (< 1.6 mm) in favour of the large granules (> 1.6 mm).

The fact that there were less small granules after the storage and more large granules after the storage confirmed that a moisture transfer took place from the big granules to the small ones, which become bigger and reduce the number of small granules.

19.2   Labscale storages sustaining water addition

During the last storage experiment performed with the quasi-adiabatic model
silo (see section 12.3.2) it has been noted that a small intake of water induced a
spontaneous temperature increase. Therefore the impact of such water addition
needed to be investigated. In order to do so, some new storage experiments were
carried out by placing freshly sampled dried sewage granules in a large insulating
container of 14.2 L (dewar D). After having closed up the dewar, a thermocouple
was inserted though the cover and placed 30 cm deep into the stored material. The
system was left this way during one month meanwhile the inside temperature was
measured continuously. Bidistilled water (60 mL) was injected at 30 cm depth on
the inside wall of the dewar at different stages of the storage.

As expected a first temperature increased happened with a maximum tempera-
ture rise of 4.6 ˚C after 5.7 days (Figure 19.3). However a new temperature increase
occurred fifteen days after the beginning of the storage, which corresponded to
the second water addition. Even if the inside temperature has nearly reached the
surrounding temperature, a new self-heating event could occur due to this small
second intake of water (60 g of water over 9.4 kg of stored granules). One week
later a third addition of water (60 mL) under the same conditions did not induce
another exothermic event anymore.

The same experiment was repeated, but this time the water was added in the
center of the stored granules also at 30 cm depth. Again a consecutive temperature
increase occurred spontaneously (Table 19.2). A second water addition, which was
performed several days later, did not cause a new temperature increase.

Table 19.2: Temperature rise and time to reach the maximal temperature increase
occurring during the storage of dried sewage granules with water addition

Storage	ΔT_{max} (˚C)	t_{max}(days)
Mon 18th June 07	4.8	2.0
Tue 3rd July 07	4.2	3.1

During both experiments the exothermic process corresponding to the water
addition could clearly be observed over several days. Even if the temperature
rise was not so important as compared to the first thermal event induced by the
oxidation, the released heat from this process could also accumulate within the
material and enable further reactions within the dried sewage sludge.
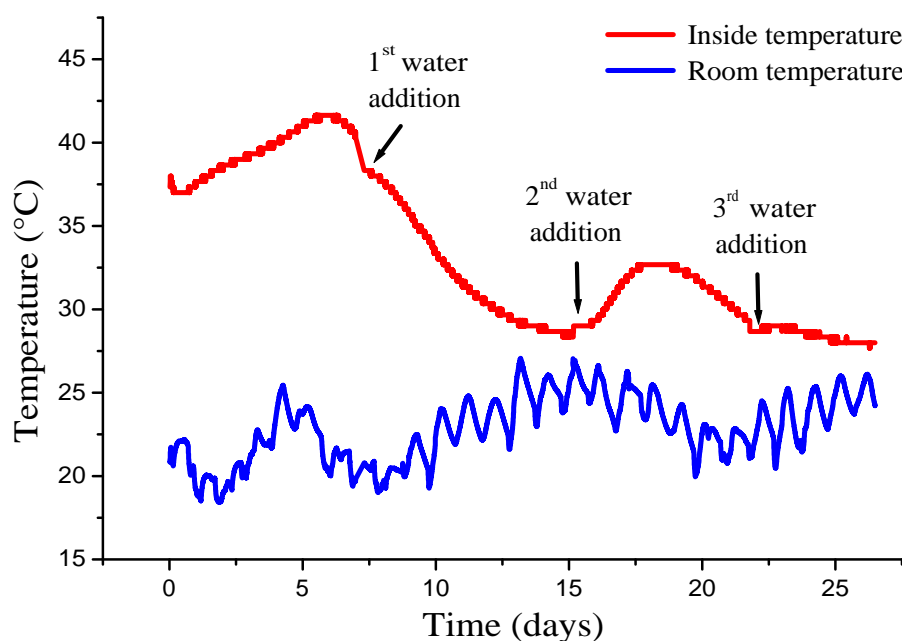
Figure 19.3: Spontaneous temperature increase measured during the storage of dried sewage granules in a large dewar (14.2 L) with water addition

Moreover it has been observed that the formation of the sulfur crystals at the surface of the stored sewage granules occurred more regularly during the experiments performed with the water additions. In addition more crystals were visible when the dewars were emptied at the end of the storage experiments. It seemed that moisture contributed to the oxidation of sulfide and the consecutive formation of the sulfur crystals.

19.3 Conclusions

This hypothesis was confirmed by the sizeable measured temperature increase, which occurs when small quantities of water are added to the stored sewage granules. Moreover the occurrence of sulfur crystals is directly related to this additional moisture content, proving its impact on the sulfide oxidation within the granules. Therefore moisture transfer from the larger granules to the smaller ones contributes to the overall heating processes.

Chapter 20

Discussion and perspectives

20.1   Causes of the thermal runaway

The performed analyses and experiments showed that the spontaneous temperature increase in the stored dried sewage granules is not caused by a single event, but that several chemical reactions are involved in the overall process. Indeed the whole runaway is the consequence of a cascade of events.

The iron contained in the dried sewage granules (7 - 12 % DS), which comes principally from the addition of the ferric chlorosulfate for the phosphate precipitation, undergoes two successive reactions of oxidoreduction. First the iron(III) in the wastewater is reduced, when it goes through the digester for biological degradation under anaerobic conditions, resulting in up to 80 % of the total iron present as Fe(II) in the dewatered sludge. Then this Fe(II) reoxidizes during the drying of the dewatered sludge, reaching a Fe(II) / Fe(III) ratio of around 50 % in the final dried biowaste. In addition iron continues oxidizing during the storage of the granules. This oxidation is due to the presence of remaining oxygen (4 - 6 % vol.) in the surrounding atmosphere.

Parallel to the iron oxidation, the sulfide is also involved in the self-heating process occurring during the storage of dried sewage granules. On the one hand sulfide comes from the degradation of the biological material, and on the other hand some additional sulfide is produced in the biological digester by reduction of the abundant sulfate, mainly coming from the added $FeClSO_4$. The sulfide principally captured as FeS is then oxidized to elemental sulfur due to the redox potential present in the sewage granules, which is mainly dictated by the iron redox system. This oxidation liberates locally a significant quantity of heat, which accumulates within the material due to its insulating properties. If the consecutive temperature

rise reaches temperatures above 75 °C, the decomposition first of the microcrystals of vivianite ($Fe_3(PO_4)_2 \cdot 8\,H_2O$), and then of larger vivianite crystals is enabled. The collapse of the vivianite unit cell is on the one hand due to the oxidation of Fe(II), and on the other hand to the loss of crystal water molecules. Absorption of this liberated water by the other compounds produces further heat, because a exothermic hydration is taking place on the dried granules. There are several other sources of water responsible for this additional heat release, such as the humidity of air entering the silo when a new batch of granules is added, or by the release of water from moist larger granules during the storage. Moreover the presence of water molecules favours the sulfide oxidation and therefore the formation of sulfur crystals at high temperatures (100 - 115 °C).

As the sewage granules become hotter, other chemical reactions are starting to take place. First the autoxidation of the organic material starts already at 80 °C catalyzed by the presence of transition metals, especially iron. This can lead to even higher temperatures resulting finally in the self-ignition of the dried granules, when the material reaches temperatures above 140 °C in the presence of air.

Thus, these different processes are starting at different onset temperatures ranging from room temperature to higher temperatures. Even the combustion process observed by DSC under an air flow starts already in a medium temperature range ($\sim$ 80 °C). This cascade of chemical reactions with specific onset temperatures starting from room temperature to medium temperature range is a very reactive system, which consequently leads to the thermal runaway.

The thermal runaway could be prevented if the first events of this succession of chemical reactions would be suppressed or controlled. However these first chemical reactions are not easily avoided, because it is not economically feasible to totally suppress the presence of oxygen or moisture. Oxygen and moisture is present in small quantities through out the dryer plant and during the road transfer, however their concentration increases since they are transfered pneumatically from the truck to the storage silo.

In addition, the presence of most of the sulfide in the sewage sludge could be avoided by replacing the ferric chlorosulfate, used for the phosphate precipitation, by alternative products. However the use of this product follows first some economical constraints because of the low cost of the ferric chlorosulfate solution, and secondly technical constraints because of the hydrogen sulfide removal from the

biogas by sulfide precipitation with the excess of iron. The presence of hydrogen sulfide in the biogas need to be prevented because of its further reactions with the steel of the containers, its toxicity and the resulting stench.

20.2   Recommended technical measures

Some technical measures could be taken in order to prevent these thermal runaways to occur during the sewage granules storage, because the complete suppression of this cascade of events is not conceivable. The first step of the self-heating process would occur in the material itself anyway, however the consecutive autoxidation and smouldering fire can be prevented by the following measures:

1. running the drying process at the highest oxygen level possible (this preventive measure advances the iron and sulfur redox reactions and spreads them out in time);

2. the separate storage of the most reactive material (high iron and sulfur content) in a dedicated silo;

3. the use of dry compressed air for the pneumatic transfer into the storage silo;

4. the installation of a O_2 detection device in the storage silo, with an alarm system set for the case that the O_2 concentration starts to drop below a defined level (indication of an acceleration of the autoxidation);

5. the installation of some temperature logging devices in the storage silo, with an alarm system set at reaching a defined temperature level (for instance at 80 °C);

6. the possibility to adjust the granules consumption in the furnace of the cement industry in order to perform a quick elimination in case of a starting self-heating process.

The use of a separate storage for the most reactive material allows a faster consumption of the dried biowaste, due to the adapted capacity of the silo. Moreover the adjustment of the flow of granules towards the furnace in the case of the oxygen concentration and/or the temperature limits have been reached, enables the elimination of the self-heated material on time. The control of the oxygen concentration is well-adapted because already a small oxygen consumption indicates an accelerating reaction, like is the present case. As the thermal

runaway is exponential process, there is a critical decrease of the oxygen concentration, which still leaves enough time for the application of fire prevention measures.

Some of these technical measures are already applied at the cement industry Vigier at Péry (BE) and obviously present a good solution, as no smouldering fire occurred since their application.

Part VI

Experiment part

Chapter 21

Analytical techniques

All used chemicals were purchased from Fluka, Acros, Aldrich and Merck and were used without further purification. The gases used for the storage experiments under controlled atmosphere of the dried sewage granules and the sensitive sample preparations were argon 48 or nitrogen 45, provided by Carbagas.

Dry solids (DS) and ash content

The DS content of the sewage samples was determined at the STP of Bern with a Precisa XM60 and a Sartorius MA30 devices. The ash content was obtained after having placed the sewage samples in a oven at 650 °C during 3 hours.

Sieving analyses

The sieving analyses were made at the STP of Bern with a Retsch AS200 basic device using an amplitude of 60 % during 10 minutes.

X-ray fluorescence

The XRF spectrometer is a Philips PW 2400 with a rhodium anode tube and the data are collected with UNIQUANT 5 program. The samples preparation consisted in grinding finely around 20 g of dried sewage granules. The obtained powder is then dried at 110 °C at 700 mbar during 24 hours. The dried sludge power (6.4 g) is mixed up with a wax (1.44 g) (Licowax C Micropowder PM, BM-0002-1, FLUXANA). The mixture is pressed to obtain a pill which is kept in dry conditions.

Powder X-ray diffraction

Room temperature powder X-Ray diffraction

The powder X-ray diffraction analyses of the dried sewage sludge granules were performed at the Geoscience Department of University of Fribourg on a Philips PW 1800 X-Ray diffractometer of Bragg-Brentano geometry equipped with a Philips PW 1808 multiple samples changer, variable primary slit, primary and secondary Soller slits, receiving slit, graphite monochromator, and a detector with proportional counter. The X-ray source consisted of a CuKα beam. The working tension and current were respectively 40 kV and 40 mA. Diffraction patterns were recorded from 10 to 70 ° 2θ with a step scan of 0.02 ° 2θ per step and between 1 and 3 seconds per step. XRD data were recorded by the PC-ADP program and were collected with X'Pert softwares (X'Pert Organiser and X'Pert Graphics & Identity) and compared with reference patterns. After conversion with the ConvX program, the data were further treated with Excel or Origin.

The samples of dried sewage granules were ground in an agate mortar. The freshly obtained powder was poured in the specific round support and compressed softly. All prepared samples were placed in a multiple samples changer and charged for the batch analysis. The RT XRD analyses were carried out under normal atmosphere.

For the determination of the crystalline phases, a very fine powder of dried sewage granules was mixed with 2.5 and 10 % of zinc oxid. The mixture was ground. The obtained powder was placed in the multiple samples changer and charged for the batch analysis like standard room temperature XRD analyses. The resulting XRD diffractogramms were treated with the Siroquant software for quantitative powder XRD phase analysis.

The dried sewage granules with the crystals formed at the surface were stored in several glass vessels. The crystals settled on the inside glass wall were directly collected and placed in a glass capillary (Hilgenberg). The powder XRD analysis was performed at the Chemistry Department of the University of Fribourg on a STOE FR590 diffractometer and the data were analyzed using the STOE WinXPOW package (version 2.12).

High temperature powder X-ray diffraction

The powder HT-XRD patterns were also performed at the Geoscience Department of University of Fribourg using a Philips PW 1830 diffractometer connected to a temperature control unit (TCU 2000 from Paar Physica). The X-ray source consisted of a CuKα beam. The working tension and current were respectively 40 kV and 40 mA. The diffracted X-ray intensity was measured by a scintillation detector mounted on a goniometer with Bragg-Brenteno geometry and equipped with divergence and soller slits on both the tube and the detector side. XRD analyses were performed under various temperature programs, which consisted in a first scan at RT, in defined number of scans and waiting periods at high temperatures (between 75 - 115 $^\circ$C) and in a last scan at RT again. The XRD measurements were done between 11 - 13 $^\circ$ 2θ at 0.02 $^\circ$ 2θ per step, 1.5 - 3 seconds per step depending on the temperature program. XRD data were recorded by the PC-ADP program and were directly treated with Excel or Origin.

For the powder HT-XRD analyses, the crude powder of dried sewage granules was placed directly within the device on the sample holder consisting in a 1 cm wide platinum strip serving as heat source. By resistance heating temperatures up to 1500 $^\circ$C can be reached. The temperature is controlled by a thermoelement attached on the lower side of the platinum strip. The HT-XRD analyses were carried out under normal atmosphere.

Single crystal X-ray diffraction

Single crystals were mounted on a glass fiber and all geometric and intensity data were taken from this crystal. The data collection with Mo$_{K\alpha}$ radiation (λ=0.71073 Å) was performed at 200 K, at the Chemistry Department of the University of Fribourg on a STOE IPDS-II diffractometer equipped with an Oxford Cryosystem open flow cryostat. The crystal unit cell was determined with the program STOE X-Area version 1.38.

Elemental analyses (CHN)

The CHN analyses were carried out at the College of Engineering and Architecture of Fribourg on a CE instruments (EA-CHNS). The samples were analyzed as raw granules or as a fine powder, obtained by grinding finely around 20 g of dried sewage granules.

DrLange analyses

The analyses were performed at the sewage treatment plant of Bern on the DrLange devices DR2800 and Cadas 50. The sewage granules ($\sim$ 20 g) are ground, sieved (filter meshsize: 0.7 - 0.8 mm) and ground finely a second time. For each sample, exactly 500 mg of powder are dissolved in 250 ml of bidistilled water or hydrochloric solution depending of the analyzed species. The obtained solutions are stirred with a magnet stirrer or placed in an ultrasonic bath at 40 °C for 30 to 90 min. After dilution and filtration on a paper filter, the solutions are analyzed with a DrLange device using the selected DrLange cuvette-tests for iron (LCK 321), nitrate (LCK 339), ammonium (LCK 303 and LCK 304), nitrite (LCK 341), total nitrogen (LCK 238), phosphate (LCK 350 and LCK 349), chemical oxygen demand (LCK 114 and LCK 514) and biological oxygen demand (LCK 554).

Differential scanning calorimetry

The DSC analyses were carried out at the College of Engineering and Architecture of Fribourg on a calorimeter Mettler Toledo DSC821e, with an Tambiance oven, and a heating program from room temperature to 700 °C, without any cooling system. The program for the data collection is the STARe software 8.1. The DSC measurements were performed at a scanning rate between 0.5 - 10 °C under a nitrogen or air flow of 100 ml/min.

Thermogravimetry analysis

The TG analyses were also performed at the College of Engineering and Architecture of Fribourg using a oven Mettler Toledo TGA/SDTA 851e and the program for the data collection is again the STARe software 8.1. The TG analyses were carried out with a scanning rate between 0.5 - 10 °C under a nitrogen or air flow of 100 ml/min.

The TG-MS analyses were achieved with a quadrupole mass spectrometer Prisma QMS200 from Balzers Instruments and a vacuum system Thermostar GSD300 from Pfeiffer, and using the QuadSTAR program.

Scanning electron microscopy

The SEM analyses were performed at the Geoscience Department of University of Fribourg with a FEI XL 30 Sirion FEG microscope using a Schottky field emitter electron gun. The EDS analysis was carried out using a X-ray detector from EDAX.

Ion liquid chromatography

Standards and samples preparation

250 mg of Fe(II) from iron(II) chloride tetrahydrate were diluted in 500 mL degazed bidistilled water. After dilution, these solutions were used as Fe(II) standards. 125 mg of Fe(III) from anhydrous iron(III) chloride were dissolved in 10 mL 65 % HNO_3 and placed in a microwave oven for two times one minute at maximum power. After dilution these solutions were used for Fe(III) standards.

The sewage sludge samples were collected and stored in a closed recipient previously flushed with argon. Around 10 g of liquid sewage sludge ($\sim$4 % DS), 3 g of dewatered sewage sludge ($\sim$35 % DS) and 1 g of dried sewage sludge granules ($\sim$92 % DS) were dissolved in concentrated hydrochloric acid (20 mL). The obtained slurries were stirred for 30 minutes under argon. Then bidistilled water (20 mL), previously degassed with argon for 15 - 30 minutes, was added and the resulting suspension was placed in ultrasonic bath for further 30 minutes under argon. After filtration on filter paper, the solutions were diluted to the chosen concentration for ILC measurements. The stored samples of sewage sludge were prepared using the same procedure. All prepared samples were also analyzed by AAS for the total iron determination.

Eluents preparation

A solution of 100 mM sodium sulfite was prepared for the deoxygenating treatment of the ionic column. The freshly made eluent consisted in 7.0 mM of pyridine-2,6-dicarboxylic acid (PDCA), 66.0 mM potassium hydroxide, 74.0 mM formic acid and 5.6 mM potassium sulfate. The measured pH for this eluent, called PDCA eluent, was 4.2 $\pm$ 0.1 and corresponds to documentation.

The post-column reagent contained 0.5 mM 4-(2-pyridylazo)-resorcinol monosodium salt monohydrate (PAR), 1.0 M 2-dimethylaminoethanol, 0.5 M

ammonium hydroxide and 0.3 M sodium bicarbonate. Prepared PDCA and sodium sulfite solutions were degassing during 30 minutes in ultrasonic bath and stored in reservoirs pressurized with nitrogen.

ILC device

The ILC analyses were performed at the College of Engineering and Architecture of Fribourg using a Dionex DX-120 Ion Chromatograph was used with a guard column (Dionex, IonPac CG5A 4 mm Guard) and an ionic analytical column (Dionex, IonPac CS5A 4mm Analytical). Nitrogen was used for flushing and pressurizing processes. The operating pressure of $\sim$ 2200 psi was applied on the column and the post-column reagent PAR was introduced at 50 psi by a pneumatic controller (Dionex PC10) connected to nitrogen gas. After the column the mixing with the post-column reagent occurred in a 375 μL knitted reaction coil. The complexes formed between the metals and the postcolumn reagent PAR were measured by UV-vis detector (HP Series 1050) at 530 nm.

Column conditioning was achieved by pumping first 0.1 M sodium sulfite eluent through the column at 1.0 mL/min for about one hour. Working with PDCA eluent at the same flow, standards and sewage samples were injected for analyses in ILC using 2 mL syringe equipped with a filter. Ultra-pure water was used for rinsing between injections.

Atomic Absorption Spectroscopy

The AAS analyses were performed at the Chemistry Department of the University of Fribourg on an AAS 3300 Perkin Elmer system using an acetylene flame.

Iron standard solution for atomic spectroscopy, $c(Fe) = 1,000$ g/L from $FeNO_3$ in $\sim$ 0.05 M HNO_3, was used for the preparation of atomic absorption standards.

Solid state ^{13}C NMR spectroscopy

The solid state NMR was performed at the Chemistry Department of the University of Fribourg on a Bruker Advanced DPX 400 (^{1}H 400 MHz; ^{13}C 100 MHz), together with a SB-MAS probe head. Magic angle adjustments were performed using oxalic acid-d_2. All needed parameters were optimized prior each measurement. The solid state NMR measurements were made by Dr Olivier Aebischer.

Around 20 g of dried sludge granules, which were freshly sampled or stored in specific conditions, were ground in a mortar. The obtained powder was sieved and ground a second time. The solid state NMR stator was filled up with this fine powder, which was manually compressed and then closed up. The system stator containing the powdered granules was inserted within the NMR device for measurement, which were carried out during several days.

Chapter 22

Storage experiments

Thermal measurements

Type K (Chromel / Alumel) and Type J (Iron / Constantan) thermocouples were used as temperature sensors. The data were recorded by the Hobo® Data Loggers, and then exported using BoxCar® Pro (version 4.3) and Onset Hoboware® (version 2.1.1) programs. Finally the temperature curves were treated with Excel or Origin.

Storage experiments

Storage experiments under normal conditions

At the cooler part of the dryer plant, the desired amount of dried sewage granules freshly produced was taken from the sampling orifice and placed in an insulating container (dewar). When filled up, the dewar was closed by a homemade insulating plug, which was fixed by large adhesive tape. Through a small hole in the top plug, the thermocouple was inserted within the stored granules at middle-height of the container. The closed system was left at room temperature or placed in an oven at a defined temperature for several days. Meanwhile the inside temperature was measured by the thermocouple connected to a temperature logging device.

Storage experiments under air flow

Using the procedure previously described, the sewage granules were placed in an insulating dewar container. Through the insulated plug, a glass tube was inserted in the center of the container allowing an air ventilation thought the stored material. Meanwhile the inside temperature was measured by the thermocouple connected to a temperature logging device.

Storage experiments with water addition

Using the procedure previously described, the sewage granules were placed in an insulating dewar container. Through the insulated plug or on the inside wall of the insulating container, water was injected slowly via a syringe. Meanwhile the inside temperature was measured by the thermocouple connected to a temperature logging device.

Storage experiments under inert atmosphere

A plastic gloves box was attached to the dewar and to the sampling orifice placed after the cooler part of the dryer plant. When the sampling orifice was open, the overpressure inside the dryer plant blew the plastic box up. The inert gas were removed three times by compression of the plastic box. Then the dried sewage granules were taken and placed in two storage tanks of different size under the dryer gas atmosphere. Two other storage tanks were filled up as usual: with a surface air contact only. These four tanks were left closed for several days at RT meanwhile the inside temperature was measured by a thermocouple connected to a temperature logging device. The experiment was repeated by replacing the dryer gas atmosphere with argon.

Cook-off experiments

The samples of dried sewage granules were placed in a stainless steel cylinder (intern volume: 338 cm^3: intern diameter: 47 mm, length: 195 mm, wall thickness: 4 mm) and then the cylinder was closed with fine wire netting at both sides. For the last experiment, a stainless perforated tube was placed within the cylinder in order to inject air in a continuous way. The thermocouples were connected at the surface of the cylinder (2 measurements) and inside the cylinder (1 measurement) and the data were collecting during the whole cook-off experiment.

For the first experiment, a fresh sample of dried sewage granules (223.82 g) was put inside the cylinder. The temperature program for this cook-off experiment presents a preheating phase from 20 to 40 °C during 20 min, a stabilization phase of 6 hours at 40 °C and a heating program from 40 to 550 °C during 6.5 days corresponding to a heating rate of 3.3 °C/h.

The second experiment was performed on 225.32 g of the dried granules. The same temperature program was used except that the heating program went from 40 to 340 °C during 2.5 days, which corresponded to a heating rate of 5 °C/h.

The last cook-off experiment used 222.34 g of granules. After the same preheating and the stabilization phases, the temperature program consisted in a heating program went from 40 to 340 °C during 3.8 days, which corresponded to a heating rate of 3.3 °C/h. An airflow from a small compressor was injected within the granules without preheating or drying processes.

Chapter 23

Other experiments

Gas volume within the granules

In order to determine the effective volume of solid part within a dried sewage granules heap, a system with vacuum and gas addition was first installed. Then the total volume of the two round flasks of 500 and 1000 mL used for the experiments was exactly determined.

The round flasks were filled up with dried granules and closed with a valve. The system (round flask, granules and valve) was weighted under atmospheric pressure. Then air and humidity are evacuated with vacuum and argon was then added to the system. The pressure and the mass of the systems are measured before and after the addition of argon, allowing the calculation of the added gas volume and the determination of the volume of the solid part of a granules heap.

Combustion gas analyses

Two gas analyses have been done on fresh samples of dried sewage sludge granules undergoing different heating programs. The dried granules were placed each time in a metallic cylinder that contained fine steel wool at both ends. The cylinder was connected to an entry tube providing the air flow and to an exit tube connected to the industrial gas detector (ACF-NT provided by ABB) working at a maximal gas glow of 1 L/min, and to an overpressure flask. The cylinder contained the material was then placed in an industrial oven for the heating program.

The first combustion gas analysis was performed on 221 g of fresh dried granules sustaining a constant heating rate of $1\,^\circ$C/min under a synthetic air flow of 1.7 L/min from room temperature to $200\,^\circ$C.

The second combustion gas analysis was made on 330 g of material, by applying a heating rate of 0.08 °C/min from room temperature to 115 °C under an air flow of 1.2 l/min. A constant temperature was then applied for 22h followed by a second heating also at 0.08 °C/min from 115 °C to 200 °C.

Hydrogen sulfide analyses

A fresh sample of dewatered sludge (2 g, $\sim$ 35 % DS) have been placed in a flask connected to a security gas analyser device (Miniwarn, Dräger) sensitive to hydrogen sulfide, methane, carbon monoxide and oxygen. A nitrogen flow went through the system to allow the device pump to suck the liberated gas. Then 1 mL H_2O was added to obtain a thick solution to what 2 mL HCl 2M was added dropwise.

A ground sample of dried sewage granules (1 g, $\sim$ 92 % DS) have been placed in the same system. Then 20 mL H_2O was needed to obtain a solution to what 15 mL HCl 2M was added dropwise. The liberated gas were measured with the security gas analyser device.

Part VII

Appendices

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EDUCATION

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'*Thermal runaway in dried sewage sludge storage silos: from molecular origins to technical measures of smouldering fire prevention*'
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Chemistry diploma   1997-2001
'*Synthesis of a Binuclear Ruthenium (II) / Osmium (II) Complex with a Bisdipyridophenazine Bridging Ligand*'
Prof. Dr P. Belser, University of Fribourg (CH)

'*Structure Elucidation of a New C-Glycosidic Flavonoid Isolated from Dark Bleached Barley (Hordeum vulgare L.) Leaves*'
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EXTRA EDUCATION

Business workshop, 'venture challenge' (venturelab)   2006-2007

Business workshop, 'young entrepreneurs' (IVE Institute)   2006
First prize award for best business plan, offered by Credit Suisse SA

Academic didactic   2004-2006
Post-graduate education, University of Fribourg (CH)

Biochemistry education   2002-2003

Courses and training, University of Fribourg (CH)

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PROFESSIONAL EXPERIENCE

Scientific researcher   2002-2003

'*Development of a new medicine for AIDS treatment, optimization and scale-up of a successive multi-steps synthesis*'

College of Engineering and Architecture, Fribourg (CH)

Trainee in analytical chemistry   2002-2003

'*Elaboration of an HPLC method to analyze impurities in a new generic anti-arthritis medicine*'

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Trainee in organic chemistry   2002-2003

'*Improvement of the oxidative color developers for capillary dyes, organic syntheses in the field of aromatic amines*'

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TEACHING EXPERIENCE

Teacher   2005

Courses in organic and inorganic chemistry, physics and maths for 1st and 2nd laboratory technicians apprentices

Professional school, Fribourg (CH)

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Training representative   2002-2007

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Personal improvement centers (ASFL, Perform, CPI)

Teacher   1999-2001

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SCIENTIFIC CONTRIBUTION

Publications

'*Dissociative electron attachment and electron energy-loss spectra of phenyl azide*'
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Oral presentations

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Fall Meeting, Swiss Chemical Society   2007

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CERC3 Young Chemists'Workshop, Göttingen, Germany   2007
3rd and 5th Swiss Snow Symposium of Young Chemists   2005-2007

Posters

'*PhD project: Thermal runaway during the storage of dried sewage sludge*'
Fall Meetings, Swiss Chemical Society   2005-2006
Annual open days, College of Engineering and Architecture, Fribourg   2005-2006

'*Synthesis and scale-up of NU 1320: new drug for AIDS treatment*'
Annual open days, College of Engineering and Architecture, Fribourg   2002-2003

WORKSHOPS ATTENDED

CERC3 Young Chemists' Workshop   2007
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3rd-5th Swiss Snow Symposium for Young Chemists   2005-2007

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'*Fundamental Kinetics and Thermodynamics in (Metallo) Supramolecular Assemblies*', '*Progress in Analytical Chemistry*'
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IUPAC Symposium   2005
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Annual Spring and Fall Meetings, Swiss Chemical Society   since 2002