

# TU

## Technische Universität Wien

### DIPLOMARBEIT

## PRODUCING BIOGAS OUT OF WASTE WATER

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## Abstract

Diese Diplomarbeit behandelt das Thema „Produktion von Biogas aus Abwasser“. Der chemische Prozess der die Grundlage zu diesem Thema bildet ist die anaerobe Fermentation. Die Aufgabenstellung lautete eine Laboranlage aufzubauen, mit der man Biogas aus flüssigen Ausgangsprodukten produzieren kann. Die Einschränkung auf Ausgangsstoffe mit einem hohen Wassergehalt kommt daher, da mit der Art des verwendeten Rührers sonst keine ausreichende Durchmischung erreicht werden kann. Wenn die Anlage aufgebaut ist sollten einige Versuche durchgeführt um den Prozess der Fermentation besser zu verstehen und um zu sehen ob die Anlage korrekte Ergebnisse liefert. Die Ergebnisse sollten analysiert werden um Aussagen zu treffen, über die Qualität des Gases und über Zusammenhänge zwischen der Zusammensetzung des Wassers und der Produktion von Biogas. Diese Diplomarbeit soll einen guten Überblick über den Prozess der Fermentation und die Schwierigkeiten die bei diesem biochemischen Prozess auftreten können geben. Im Weiteren sollte eine Aussage abgegeben werden ob es sinnvoll ist dieses städtische Abwasser zur industriellen Produktion von Energie zu benutzen.

Um das produzierte Gas analysieren zu können, wurden das Volumen und die Zusammensetzung bestimmt. Die Apparate, die zum Einsatz kommen, werden in der Diplomarbeit in Kapitel 2 genauer erklärt. Die Anlage wurde aufgebaut und nachfolgend anhand von Versuchen optimiert. Für diese Tests wurde Wasser aus einer Kläranlage die in Nähe von Valencia liegt verwendet. Diese Kläranlage reinigt das Wasser unter anderem durch anaerobe Fermentation. Die in der Anlage produzierten Gase werden in der Anlage aber nicht weiterverwendet z.B. als Energieträger oder zur Deckung des Eigenenergieverbrauches. Im Prozess wurde das Wasser für die Tests direkt dem Fermenter entnommen. Das Wasser ist also zu einem Teil, der nicht bekannt ist, schon anaerob abgebaut. Festgelegt wurde, dass im Abwasser Carbonate, Nitrate, Sulfate und Ammonium bestimmt werden. Weiters wurde der BOD gemessen. Es wurde auch der Feststoffgehalt des Wassers bestimmt. Die jeweiligen Parameter wurden jeweils vor und nach dem Test bestimmt. Während der Versuche wurden das Redoxpotential und der PH gemessen. Diese Kennwerte geben Auskunft über den Verlauf des Prozesses.

Mit diesen gemessenen Werten werden dann offene Fragen beantwortet. Zum Beispiel welche Werte im Wasser ausschlaggebend sind, wie viel Biogas vollglick produziert wird und wie sich die Werte später auf die Zusammensetzung auswirken. Redoxkurven werden diskutiert, um den Prozess besser zu verstehen und Aussagen werden getroffen, ob der Prozess anaerob oder nicht abläuft.

Das Resultat der Arbeit war ein Apparat mit einfachem Versuchsaufbau. Die Apparatur besticht durch rasche Versuche von Abwasser mit ausreichend genauen Ergebnisse für die Analyse des Gases. Durch die Ergänzend gemessenen Parameter des Abwassers können interessante Schlüsse den Prozess betreffend gezogen werden. Für die Bestimmung des Gases sind keine Computer oder komplizierte Computerprogramme vonnöten. Die Kosten für die Tests sind gering die Ergebnisse jedoch brauchbar.

Diese kurze Vorschau soll einen kleinen Überblick über meine Arbeit geben.

## Abstract

This thesis deals with the topic fermentation and the production of biogas out of wastewater. The biochemical process, which builds the basis of this topic, is the anaerobe fermentation. The task was to build up an apparatus to produce biogas out of the given waste water. The fact, why the tests were only possible for products with a high amount of water, was the mixer. The mixer was not able to afford a good mixture with a high amount of solids in the fundamental material. After building up the plant some tests should be done to understand the process better and to see if the tests are correct or not. The results should be analysed and with the results it should be possible to understand the process better and give a statement if it is useful to use this waste water to produce energy in industrial way or not. This thesis should give a good overview about the process of fermentation and should show the difficulties which can occur when one are producing biogas.

To be able to analyse the gas, the composition and the volume of the gas was measured. The apparatus, which was used, is explained in part 2 of the thesis. The apparatus was assembled and afterwards optimised using the results of the continuous tests, which were made. For the tests water out of a water treatment plant in the ambience of Valencia Spain was used. This plant is already using anaerobic fermentation for water treatment. The gases produced in the factory are not having a further use, for example as energy source or to cover the energy own consumption of the water treatment plant. In the process the water was taken directly out of the digester. Due to this fact the water was already in an anaerobic status. So it is degraded until an unknown grade. The water was characterized by measuring carbonate, nitrate, sulphite and ammonium. Also the PH-value, the BOD and the solids in the water were measured. The mentioned parameters were taken every time before and after the tests. During the tests the redox potential and the pH value were measured. These parameter give information's about the course of the process.

With this measured parameters open questions were answered. For example which parameters can be inhibitors for the production of biogas and if they are inhibitors in the certain tests? The gas is analysed and the composition of the biogas is discussed in comprehended with the process conditions. Redox curves are discussed, to understand the process better. In the redox curves one can see how anaerobe the process is.

The result of the work was an apparatus with a simple test set-up. The apparatus captivate through fast testing with sufficient exact results to analyse the gas. With the additional measured parameter of the waste water, could be done interesting conclusion about the process. To measure the gas no computer or complicated computer programs are necessary. The costs for the tests are low but the results are practical.

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# 1 Objective

The objective was to build up an apparatus with existing components to produce biogas out of wastewater. Tests, which were made after building up the set up, should show if the apparatus is working correctly. With the tests the apparatus should be optimised. The apparatus should be able to produce biogas but it should also be possible to characterize the biogas for following analyses. With the results it should be possible to understand the process better and give a statement if it is meaningful to use wastewater for producing energy or not. All the results should be presented in a report with all the background information, which are necessary to understand the whole work.

## 2 Introduction / Theory Biogas

### 2.1 Introduction

This thesis deals with the topic “anaerobic fermentation of waste water”. The first part of the work gives information’s about the theory, which builds the basis of this work. Further some information’s about the state of the art in this field of the fermentation. The next part explains the set up with all the physical basics, used components and processes taking place. Following some explanations about the measurements and the process parameters. The main part of the work is about the testing. In the testing part there are all the results and the explanation leading through the tests. The results are analysed after the tests shown in the thesis. At the end there are all the calibration curves and measurement specifications, which were necessary to do the testing and to use the measurements.

### 2.2 State of the art <sup>[1]</sup>

The state of the art in the anaerobic fermentation of waste water is not basically to produce biogas. Normally it is used to stabilize wastewater. The sludge gets stabilized and the water removal capacity rise. A problem of the anaerobe fermentation is pathogens like salmonella, typhosa and others can survive the anaerobe digestion. Polio viruses similarly survive with little reduction in virulence. So an anaerobic digester cannot, therefore, considered as a method of sterilization. The fermentation function in the same way as it is mentioned in the theoretical part.

---

[1] Vgl. sludge treatment S 200 Environmental Engineering Veselind, Pierce, Weiner]

Complex organically components gets degrade into simple organic compounds. After a densification the sludge can be used as a fertilizer or burned to produce energy. If it is possible to use the sludge as a fertilizer depends on the amount of heavy metals in the sludge. The gas, which is produced in this process, gets burned in a gas engine or is collected to use it for cars or in power plants. Normally when one uses a gas engine to produce energy it is only for the own consumption of the water treatment plant. When one uses the gas for cars or in energy power plants one has to clean the gas before using it.

## 2.3 What is Biogas? [2]

Biogas is produced out of organic material in an anaerobe way of degradation, in which anaerobe bacteria are producing a gaseous energy source. It is a mixture of the main components methane and carbon dioxide. The useful component for producing energy is the methane. The composition of the Biogas varies upon the origin of the fermentation. Landfill gas typically has methane concentrations about 50%. Advanced waste treatment technologies can produce biogas with 55-75% CH<sub>4</sub>. [3]

| Matter                              | %         |
|-------------------------------------|-----------|
| Methane, CH <sub>4</sub>            | 55-75 %   |
| Carbon Dioxide                      | 25-45 %   |
| Nitrogen N <sub>2</sub>             | 0-0.3 %   |
| Hydrogen H <sub>2</sub>             | 1-5 %     |
| Hydrogen sulphide, H <sub>2</sub> S | 0-3 %     |
| Oxygen, O <sub>2</sub>              | 0.1-0.5 % |

**Table 1: Composition of Biogas** [4]

In this process there are three groups of bacteria involved. The three groups are hydrolytic bacteria, fermentative bacteria and methane producing bacteria. The feedstock gets degraded in sequenced steps into simple organic compounds, afterwards into low organic fatty acids and at the end into biogas.

[2] Vgl. Kapitel 15.1.1 Substrate S 641 Energie aus Biomasse ISBN 3-540-64853-4]

[3] Vgl. [www.oaktech-environmental.com/Juniper.html](http://www.oaktech-environmental.com/Juniper.html)]

[4] Vgl. <http://www.kolumbus.fi/suomen.biokaasukeskus/en/enperus.html>]

## **2.4 Biological Basics** <sup>[5]</sup>

In the methane fermentation bacteria's degrade organic biomass in a surrounding without oxygen. It is totally different to the aerobe degradation. In the nature it can be found in moors, on the ground of lakes, in wastewater treatment plants or in liquid manure plants. In biogas plants the fermentation processes are guided, to produce as much methane as possible. This methane is normally used to produce energy.

The anaerobe degradation functions with very different kinds of bacteria, which perform step by step and in symbioses. These bacteria groups have in reliant of the feedstock that is used, a certain speed of growing. The slowest growing bacteria limit the final speed.

Biomass is the raw material and it consists out of polymer organic compounds (for example carbon hydrate, fats, and proteins). As it is shown in **figure 2** the first step of the anaerobe degradation is the hydrolyse. Polymer and complex molecules gets degrade by hydrolytic bacteria into many low molecular compounds (amino acids, fatty acids, saccharide).

In a second step the fermentative bacteria are forming organic acids (propionic and lactic acid) and further connections like alcohol and acetic acid out of the reaction products of the first step.

The proportional composition of these intermediate products is affected by the hydrogen partial pressure. With low hydrogen concentrations a lot of acetic acid will be produced, though a higher partial pressure causes the formation of propanoic acid, butter acid and lactic acid as well as ethanol.

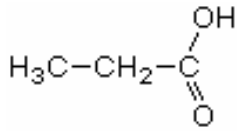
In a third step, the so-called acetic acid formation, the propanoic and the lactic acid are converted into forerunner substances from the fermentation gas, i.e. into acetic acid, carbon dioxide and hydrogen. As it is shown in **figure 1** in this step a lot of hydrogen is released. Though the hydrogen partial pressure rises not too high, the hydrogen is converted into methane. This process happens in the next step.

In the following fourth step, the biogas results out of the methane formation done by the methane bacteria. Approximately 70% of the fermentation gas is formed by splitting acetic acid into carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>). The remaining about 30% is developed by the connection of hydrogen and CO<sub>2</sub>, to CH<sub>4</sub> and water. The methane formation is very close attached to the dismantling of propane acid step three. Because the methane creator has to provide that the hydrogen partial pressure becomes not too high. Therefore the hydrogen constantly gets converted into methane. The formation of fermentation gas out of acetic acid on the contrary is energetically more unfavourable. It can be managed only by a part of the methane-forming bacteria but all methane bacteria's can build biogas out of hydrogen and carbon dioxide. Nevertheless the larger part of the fermentation gas is developed out of the acetic acid.

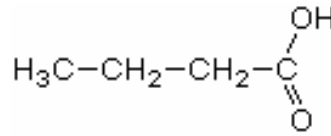
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[5] Vgl. 15.1.2 Biologische Grundlagen S 645-647 Energie aus Biomasse ISBN 3-540-64853-4]

**Propanoic acid ( CH<sub>3</sub>CH<sub>2</sub>COOH )**

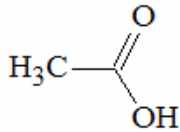


**Butter acid ( CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH )**



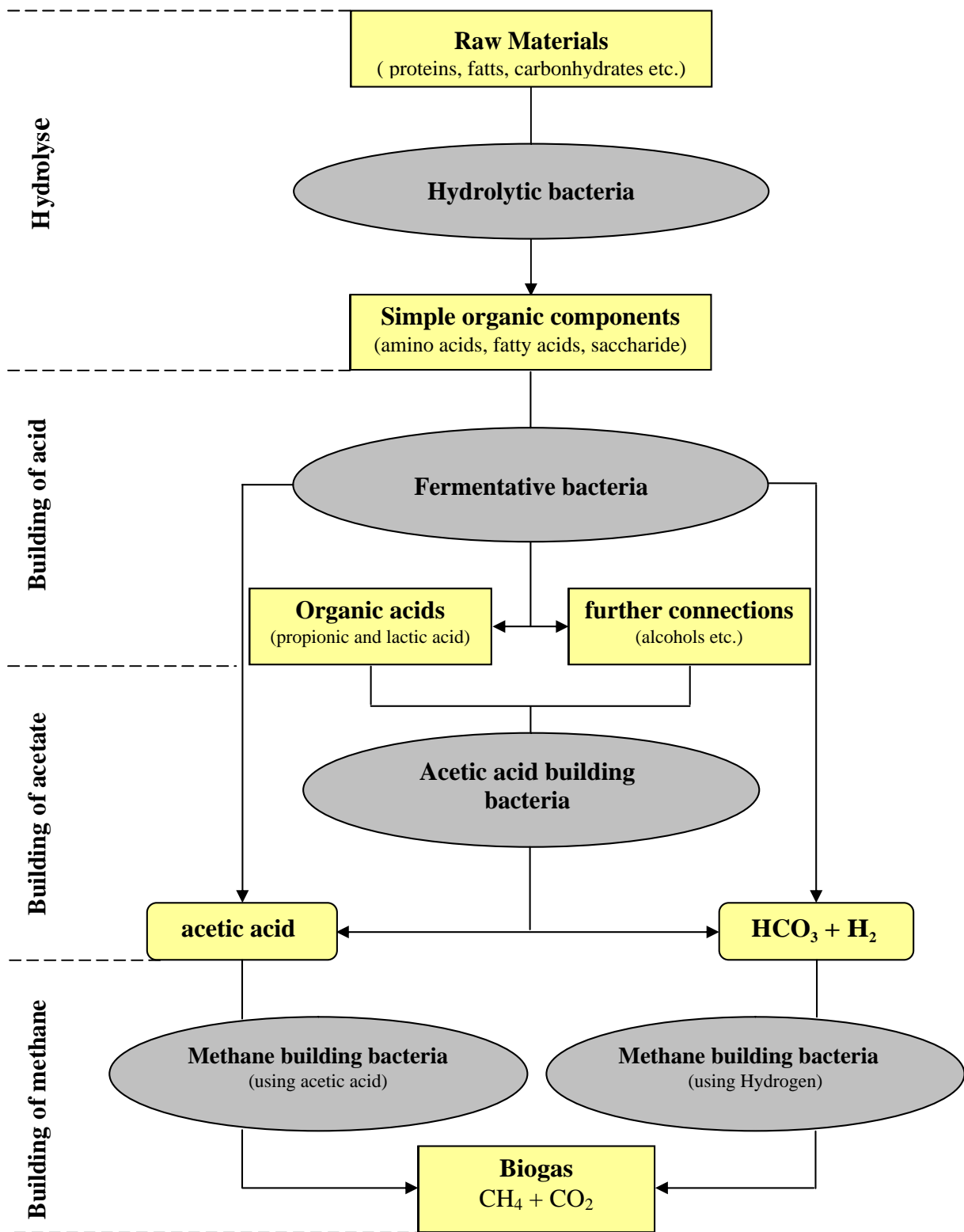
H<sub>2</sub> is released

**Acetic acid ( CH<sub>3</sub>COOH )**



**Figure 1: dismantling of the propanoic and butter acid**

All four mentioned processes run off in a biological gas facility at the same time, however often not with the same speed. The speed-determining step is normally the hydrolysis. Particularly cellulose and hemi cellulose are hydrolysed very slowly. Only if large quantities of easy degradable materials are present (e.g. in certain waste water of distillery or can dairies, in certain kitchen wastes), the methane formation becomes the speed-determining step.



**Figure 2:** anaerobic degradation of organic matter to biogas

## **2.5 Process factors**<sup>[6]</sup>

In the following part the main factors influencing the anaerobe fermentation process are discussed.

### **2.5.1 Temperature**

There are different types of bacteria, depending on the temperature. Psychrophile bacteria grow in a temperature range till approximately 25°C. Mesophile bacteria have a temperature optimum about 35°C and thermophile strains have an optimum at about 57°C. Although there are anaerobe degradations at lower temperature like on the ground of lakes at a temperature of 4°C, but the degradation is very slow.

In the technical processes particularly mesophile and thermophile bacteria strains are used. The anaerobe fermentation is not an exothermic process, therefore the substrate has to be heated up to the fermentation temperature by burning parts of the produced methane or with a heater. The selection of the temperature range depends up to the percentage of the water in the substrate. If the substrate is cold and the percentage of the water is high, a high fermentation temperature is not reasonable. The reason is too much of the produced gas has to be taken to heat the process. For wastes with a low amount of water, thermophile bacteria are advantageous, since at this temperature, the level of the pathogens and weed seed gets abolished better. For substrates with a higher amount of water a thermophile process can only be interesting when there is industrial wastewater at a very high temperature level (i.e. wastewater in the paper industry). Otherwise it's too expensive to heat the wastewater.

### **2.5.2 pH-value**

The optimum pH-value for the formation of methane is located between 7 and 7.5. Normally in a single-stage process the pH-value gets regulate automatically in the optimal range, because bacteria groups create a self-regulating system. The carbon dioxide (CO<sub>2</sub>), which is produced at the degradation, is in equilibrium with the hydro carbonate, buffering concentrations between 2,5 to 5g/l.

A decrease of the pH-value cause, that the process becomes instable. At low pH-value the methanogenic bacteria cannot work anymore. The acids accumulates, which leads to a further decreasing of the pH-value. The process gets acidic. In this case the feed of the substrate has to be reduced or stopped in order to give the methanogenic bacteria the chance, to degrade the already built acid. In an extreme case of a very hard acidification, lime or other alkaline acting substances can be introduced and if they do not succeed in increasing the pH, the reactor has to be cleaned.

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[6 Vgl. 15.1.3 Verfahrenstechnische Messgr. S 647-648 Energie aus Biomasse ISBN 3-540-64853-4]



### 2.5.3 Redox - potential

Life processes are every time linked with redox reaction. For the methane bacteria low redox potentials are necessary; i.e. for pure cultures potentials between  $-300$  to  $-330$  mV are the optimum. But in a digester the potentials can be much higher (in an extreme case till a maximum of  $0$ mV). To assure these low potentials, no oxidant and the main oxidants are oxygen, sulphide, nitrate and nitrite has to be introduced in the system.

### 2.5.4 Substances which hinder the process

In some cases substances can hinder the process. How hard the substance hinders the process depends normally on the concentration of the substance. The composition of the fundamental material and the adaptation of the anaerobe bacteria of the substance is the fact, which hinders the process.

In **table 2** some substances are mentioned and the critical concentrations. The concentrations in the table are only an orientation. The concentration can differ depending on the bacteria population, on the process and on the digester, which is used.

|                  |   |
|------------------|---|
| <b>Potassium</b> | hinder at 3 g/l, interaction with sodium and Ammonium   |
| <b>Ammonium</b>  | In equilibrium with ammonia ( depends on the PH ); hinder between 2,7 and 10 g/l , ammonia hinder from 0,15g/l, interaction with organism with $Ca^{2+}$ or $Na^{2+}$ |
| <b>Sulphur</b>   | Compositions with sulphur hinder from 50mg/l $H_2S$ , 100mg/l $S^{2-}$ and 160 mg/l $Na_2S$   |
| <b>Nitrate</b>   | This substance are denitrificate in anaerobe environment  |

**Table 2:** main substances hinder the anaerobe fermentation

## 2.5.5 Composition of the gas

The composition of the gas can be influenced only in a limited way. The percentage of the methane, which is, in fact of the energy one can produce the most important component of the biogas. The amount of the methane depends on the following factors:

- Composition of the fundamental material. Here the grade of the oxidation counts. Material with a lot of fat and so on less oxygen gives - provided it doesn't appear in a to high amount - per mass more and better gas compared with carbon hydrates or proteins. Also easy degradable components have to be available as good as possible. To attain this substrate has to be prepared. For example with tearing.
- Amount of the water in the material for the fermentation. As thin the fermentation material is, as much carbon dioxide is solute and as much methane is in the biogas.
- Fermentation temperature: As high the temperature, as less CO<sub>2</sub> is solute in the water ( that means the amount of the CO<sub>2</sub> in the gas increase but also the amount of the gas increase because of the CO<sub>2</sub> )
- Pressure in the digester: As high the pressure, as much CO<sub>2</sub> is solute in the water and as much methane is in the biogas.
- Time of staying: As long the stay, as good is the degradation. In a later period of the process, when the hydrolyse which mainly produce CO<sub>2</sub> fade away, proportional more methane than normal is produced.

## 2.5.6 Dry mass and CSB – content

In earlier times the anaerobe fermentation was done mainly with very fluid substrate, but nowadays also solid waste is fermented. With solid waste materials are meant which contains over 15% dry mass. Sludge between 6 and 15% dry mass contains more or less much free water or a big amount of solids in suspension. Normally they have a high viscosity and because of that they are called half solid. Normal wastewater contains fewer than 6 % dry mass.

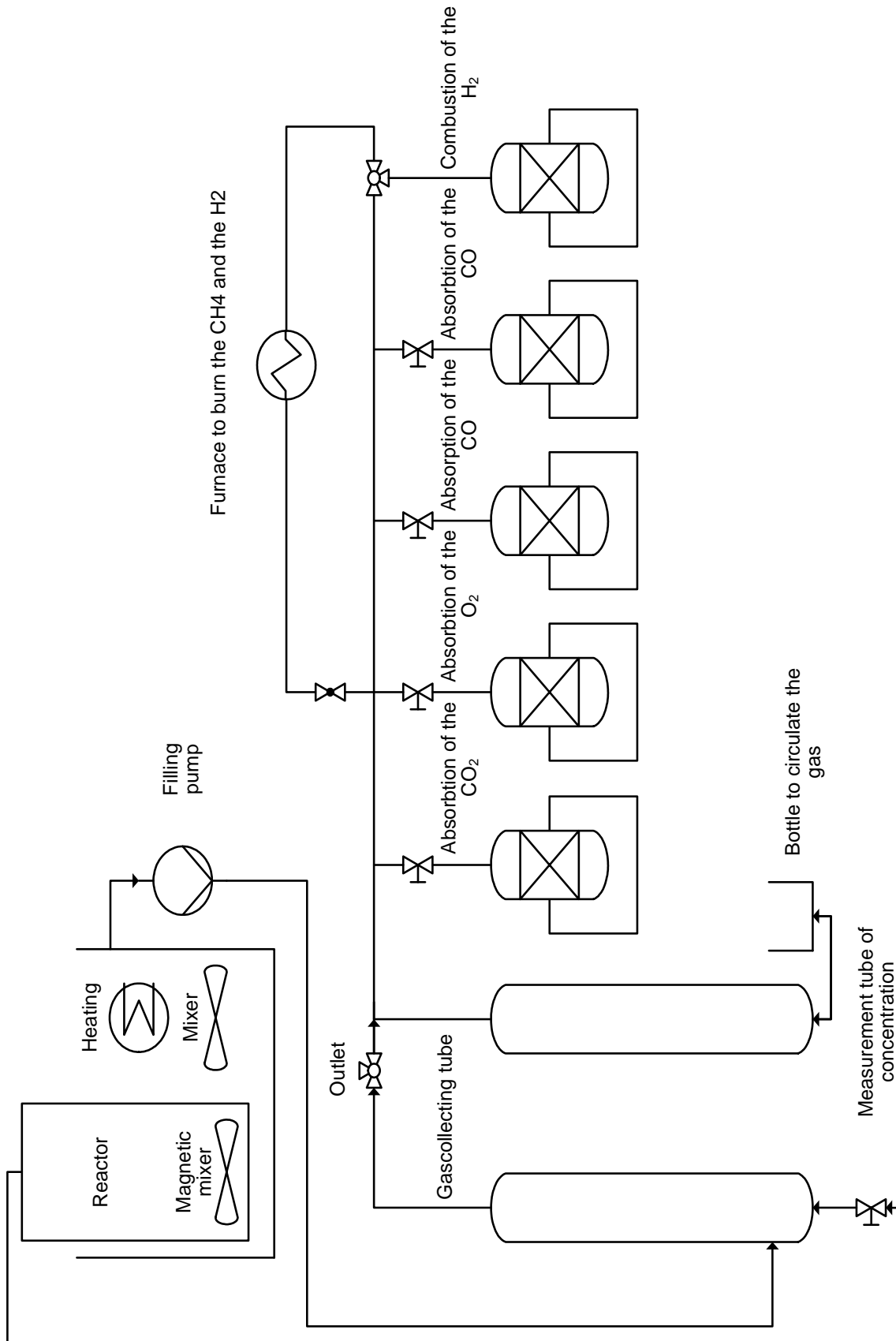
The amount of dry mass is measured by drying the substrate at a temperature of 105 ° till the weight is constant. The share of organic substance on the whole dry mass is measured by glowing the dry mass at a temperature of 550°C. Waste water, which organic mass is normally soluted in the fluid, is hard to measure, because some substance can build a connection with the water and vaporize.

In this case one works with the chemical oxygen demand. This value shows how much oxygen is needed to oxidize all the components, which can be oxidized.

## **3 The set up**

### **3.1 Flow sheet**

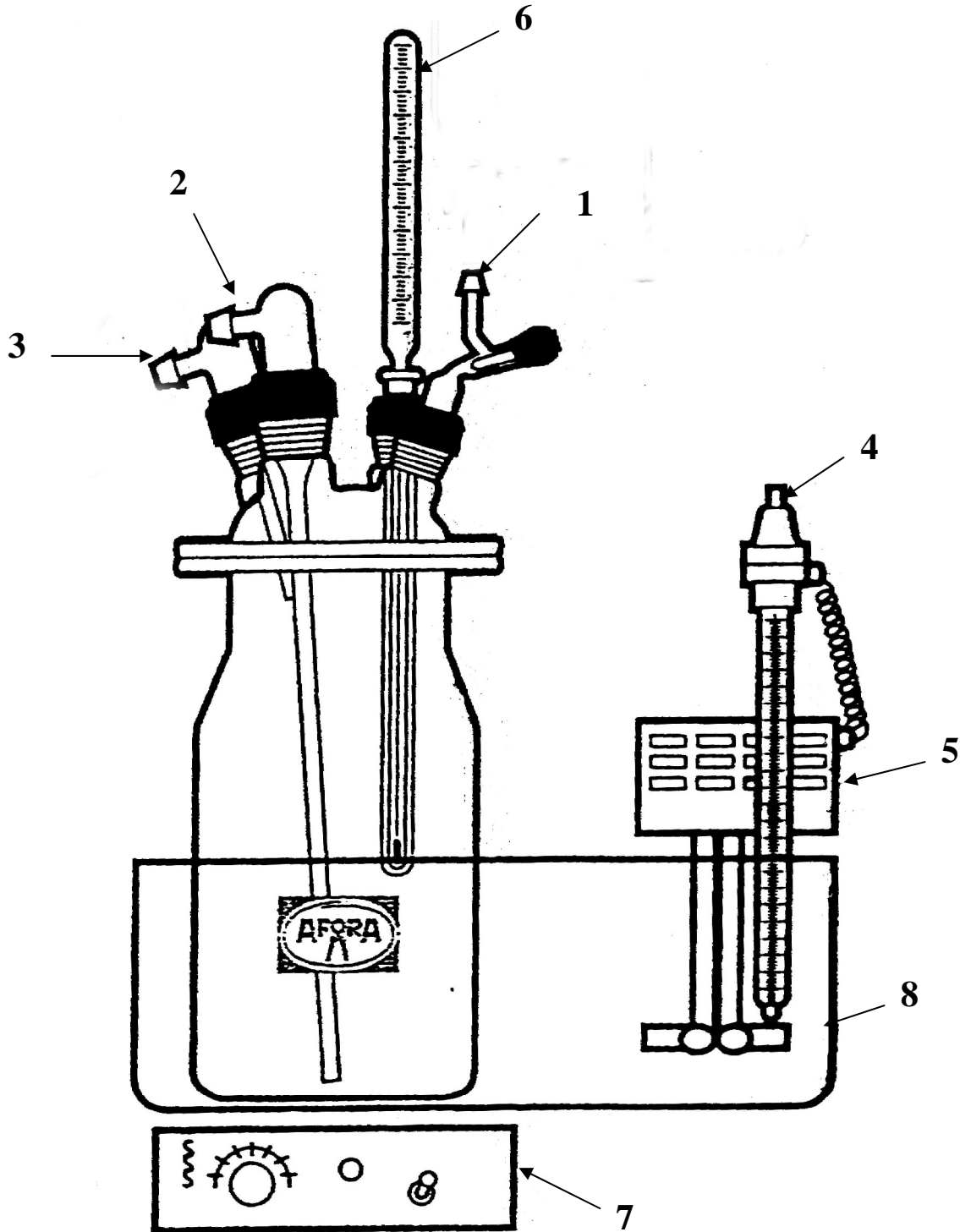
In the following flow sheet **figure 3** one can see the apparatus with all the important components. The main part, the reactor is situated in a water pool. The water pool together with a mixer and a heating keeps the reactor on a fixed temperature level. The reactor and the water pool are connected with the gas collecting tube. The gas collecting tube itself is connected with the apparatus for complete gas analyse. The border between the reactor with the gas collecting tube which is the part where the gas is produced and collected, and the apparatus for complete gas analyse builds the three way valve in the flow sheet, it is called outlet. The apparatus for complete gas analyse consists out of the measurement tube for concentration, 5 chambers for absorption and the furnace to oxidize the  $\text{CH}_4$  with copper oxide. The 5 chambers and also the furnace can be connected and disconnected with a 3-way valve.



**Figure 3:** flow sheet of the apparatus

### 3.2 The reactor

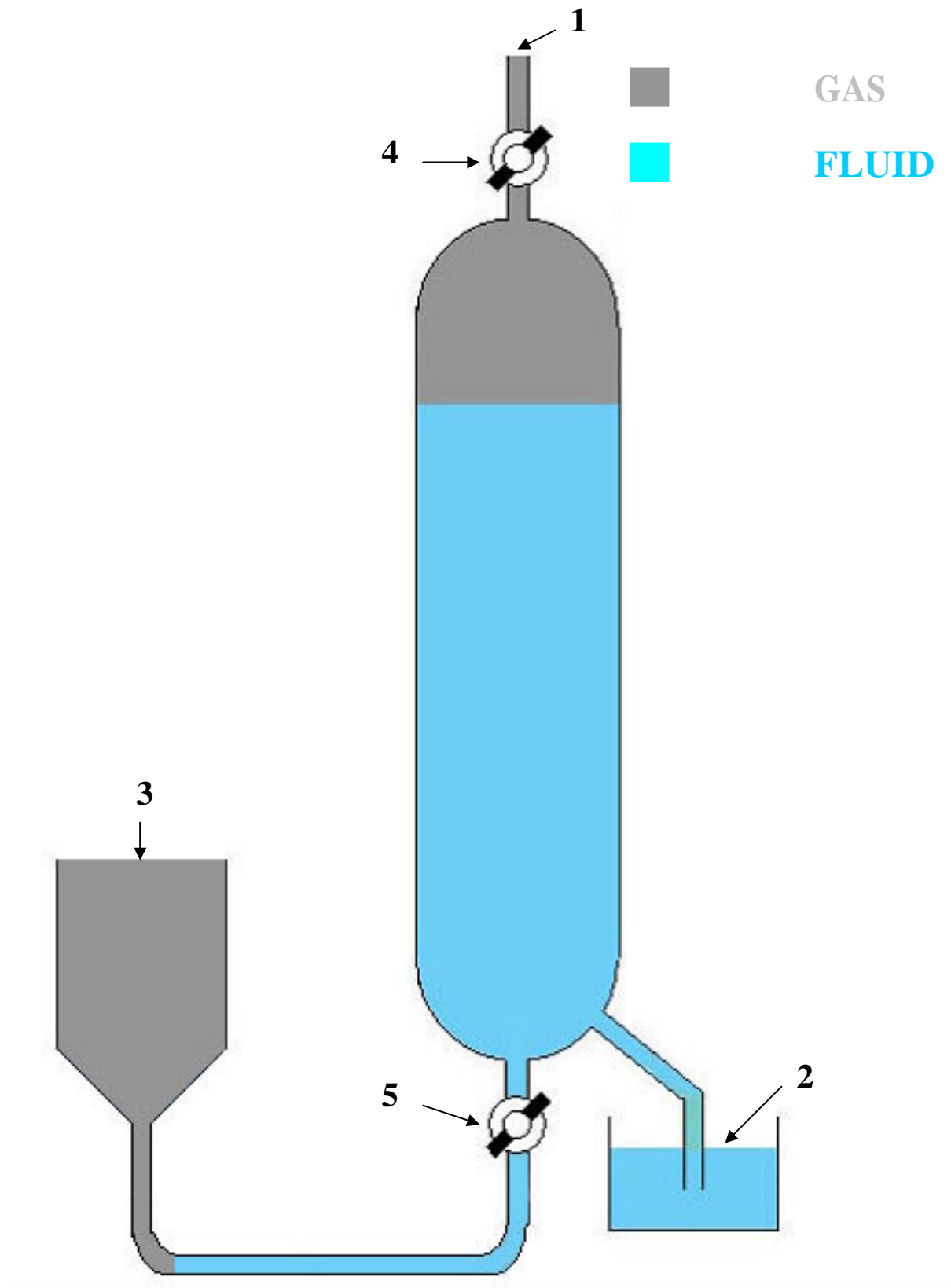
**Figure 4** shows the reactor and all the systems connected with the reactor like the heating and the mixer. Afterwards all the equipment is explained.



**Figure 4:** figure of the reactor and the heating

The reactor consists of a 2 litre glass chamber. In the chamber the biogas is produced. Further the glass chamber is connected with the gas collecting tube at **1**. **2** and **3** are normally connected to produce a circulation of the material with a pump. In this case the magnetic mixer is enough to produce the circulation because the material is fluid. **4** is a thermometer, which is connected with a controller **5**. It regulates the temperature in the tank **8**, which is filled with water and keeps the temperature at a certain value. With the thermometer it is possible to choose the temperature. To afford a circulation of the water, in order to keep a constant temperature in the water tank, a mixer is included in the controller. **6** is a thermometer to control the temperature in the reactor. The temperature of the water in the tank and the temperature of the water in the reactor are not at the same value. The difference is between 2 and 3 degrees. **7** is the magnetic mixer to afford the circulation in the reactor. The system is like in an industrial digester only a little bit simplified.

### 3.3 The gas collecting tube



**Figure 5:** figure of the gas collecting tube

**Figure 5** shows the gas collecting tube. This tube is used to measure the volume of the produced biogas. The technique is to fill the tube with water. In the process the water gets displaced with the biogas. The measurement tube is graduated to 1 litre in steps of 100ml.

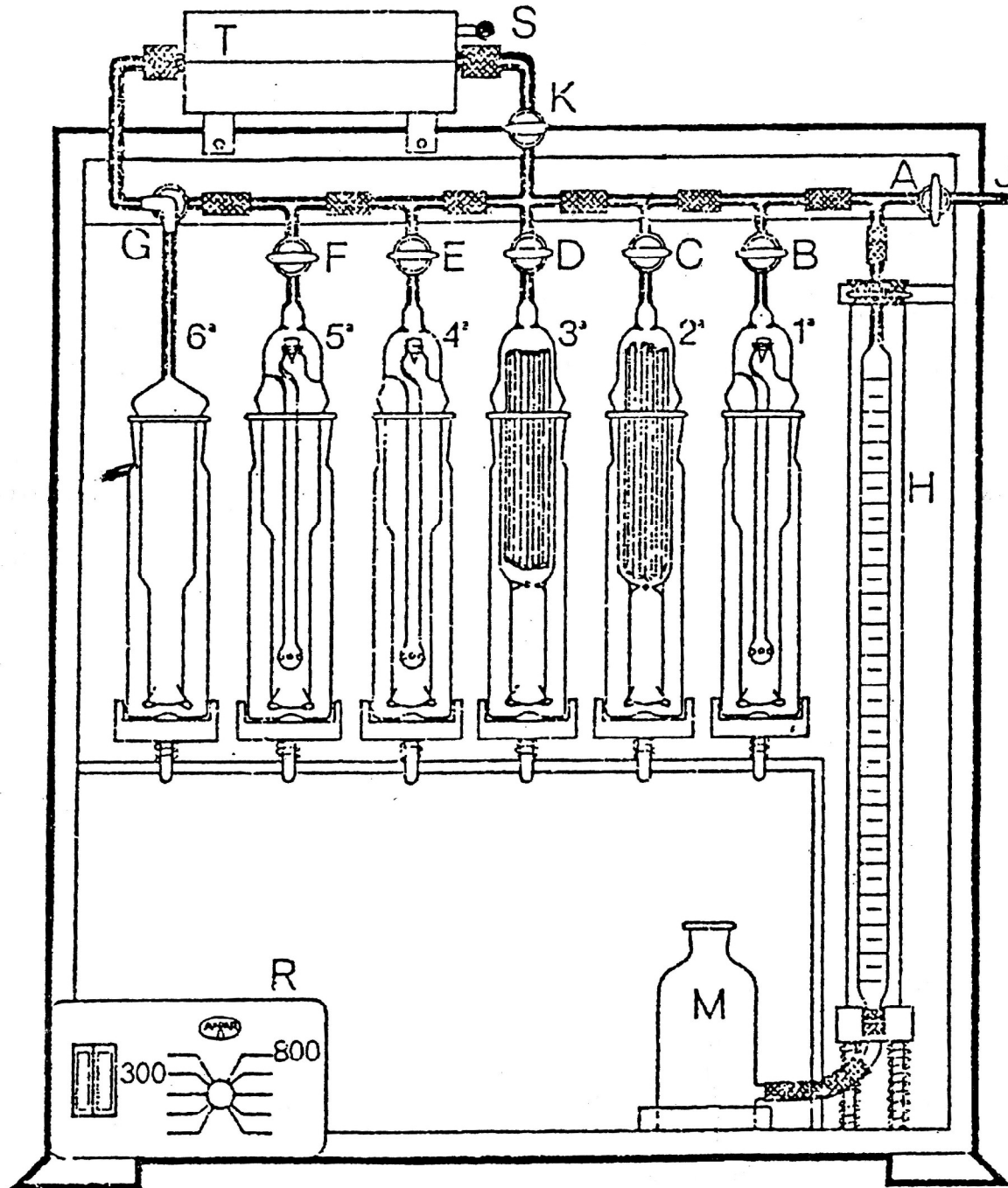
Now some words about the set up. **1** is a plastic tube, which is connected with the apparatus for complete gas analysis. **2** is the tank from where the measurement tube takes the water when it is filled and also the water is collected when it is displaced. **3** is the reactor where the gas is produced. **4** is a valve to disconnect and connect the tube with the apparatus for complete gas analyse. **5** is a valve to disconnect and connect the reactor with the measurement tube.

Now explanations about the steps which occur during the measuring. First one pumps the water from the water tank **2**. A hose pump was used to fill the tube. When one pumps the water in the tube valve **5** is closed and valve **4** is open. When the tube is filled close first valve **4** and then open valve **5**. Now the reactor is producing gas and the water is displaced with biogas. When the process is finished close valve **4** and open valve **5** afterwards. Pump the water back in the measurement tube that the gas is pushed through the tube **1** in the apparatus for complete gas analyse.



### 3.4 Apparatus for complete gas analysis

With this apparatus it is possible to analyse diverse gas mixtures. Normally it is used to determine oxygen, hydrogen, methane, oxides of carbon and nitrogen.



**Figure 6:** apparatus for complete gas analysis

### 3.4.1 Physical basics:

In this apparatus the operation of the absorption takes place. The individual gases are adsorbed by different type of fluids. In this case absorption means the penetration of a gas into a liquid. In the process of the absorption the mass transport takes place from the gas to the liquid ( absorbents ).

### 3.4.2 Description

The letters and numbers refer to **Figure 6**.

#### Inlet J

J is the tube where the gas enters and is connected with the gas collecting tube.

#### Valve A

Valve A is to close the passage with the pipes, which are connecting the chambers where the absorption takes place, and to empty the pipes and the apparatus.

#### Tube H

H is the measuring tube of 100 millilitre graduated in 1/5.

#### Chamber 1<sup>a</sup> of mumbing

In order to absorb **carbon dioxide** a caustic potash solution of 30% is used. The caustic potash, which is prepared in one litre of, distilled water and adding 320g pure caustic potash, in pastilles. Approximately  $1\text{cm}^3$  of this solution absorbs 40 a  $60\text{cm}^3$  of  $\text{CO}_2$ . So the chemical is sufficient at least for **100** measurements. The absorption of  $\text{CO}_2$  is a very fast reaction. In general, five passages in the laboratory guarantee an almost complete absorption. This reagent is not rigorously selective. If there is  $\text{SO}_2$ ,  $\text{C}_6\text{H}_6$  or  $\text{H}_2\text{S}$  in the gas, a proportion of these elements will be absorbed at the same time that  $\text{CO}_2$ .

#### Chamber 2<sup>a</sup> of contact

For the absorption of **heavy hydrocarbons** ( $\text{C}_n\text{H}_n$ ) bromine water is used. The bromine water is prepared with water distilled and pure bromine until saturation. It dissolves 7 to 8g of hydrocarbons per litre of water. Normally there are even less then 1% hydrocarbons in the biogas. So it leads for at least 1400 measurements

### **Chamber 3<sup>a</sup>, of contact:**

In order to absorb **oxygen** a solution of potassium pyrogallate is used. The solution is prepared by soluting 180 gr. of pyrogallole in 1 litre of caustic potash 30%. 1cm<sup>3</sup> of this solution absorbs approximately 12 cm<sup>3</sup> oxygen. The disadvantage is its sensitivity to the light and to the oxidation.

### **Chamber 4<sup>a</sup> and 5<sup>a</sup>:**

To absorb the **carbon monoxide** a solution of copper chloride and hydrochloric acid is used. The fourth chamber is for exhausted solution and the fifth for recent solution. This solution is prepared with 125 gr. of copper chloride and hydro chlorate acid 25% (density 1.135) up to 1 litre of solution. In order to conserve the solution it is necessary to place copper threads within the bottle, which contains the solution. In this case more than five passages are necessary to absorb the whole amount of CO.

### **Furnace of combustion**

The furnace is used to oxidize the methane and the hydrogen. The furnace consists of a quartz tube S, an electrical resistance T, and the regulator of power R together is the furnace. The quartz tube is filled with copper oxide.

### **Chamber 6<sup>a</sup>**

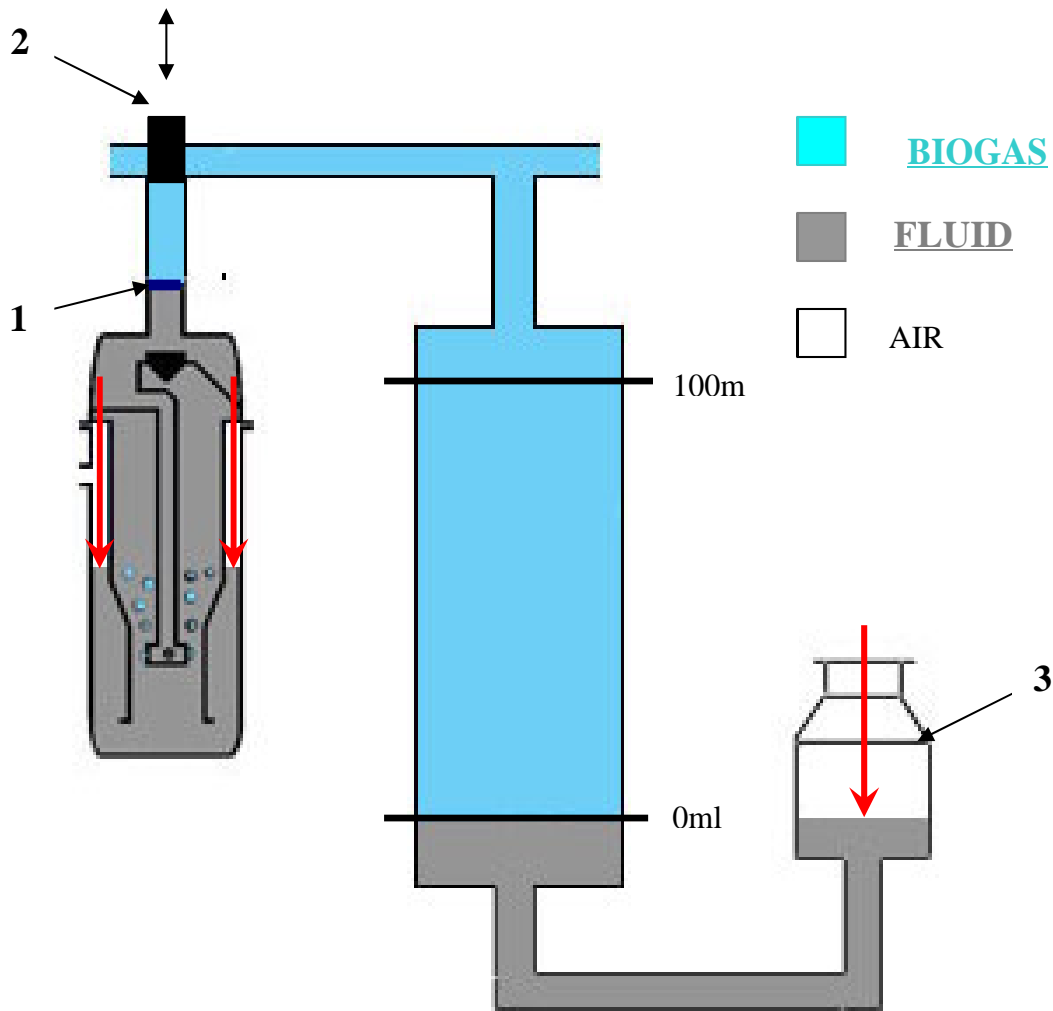
It is filled with water slightly acidic and is necessary to pump the gas through the quartz tube. Also it collects the water, which is produced when one heats the hydrogen up to 200 degrees and pumps it through the copper oxide. The copper oxide is used to oxidise the methane and the hydrogen.

### **Bottle M**

The measuring tube H is connected in its lower part, by a tube of rubber, to the bottle M in which about 200 millilitre of distilled water is. The bottle M is to pump the gas to the chambers of absorption

**Explanation of the process:**

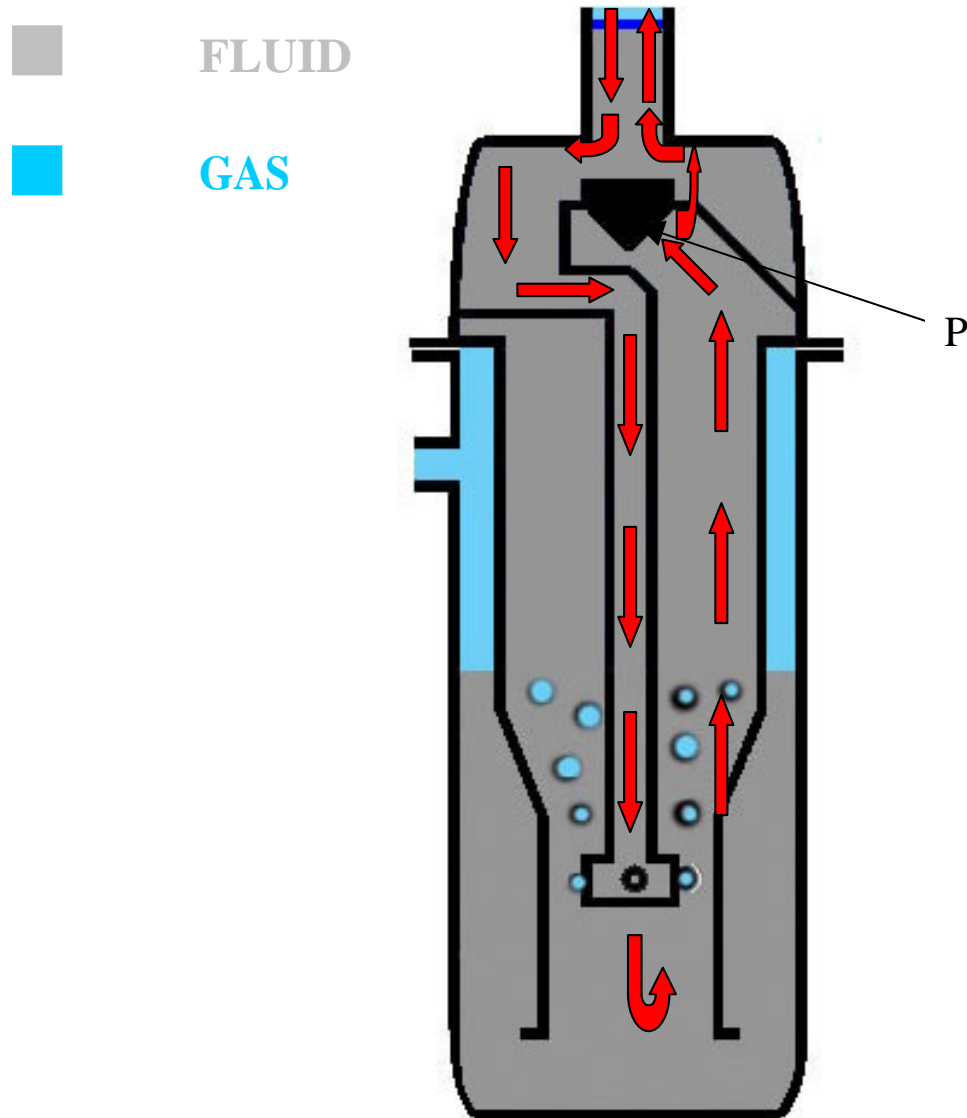
Now some words about the chemical and physical processes taking place in the apparatus for complete gas analyse. First some words about how to work with the apparatus and the physical background **figure 7**. The second **figure 8** shows the inside of a certain chamber for absorption.



**Figure 7: equilibrium of the forces**

In **figure 7** one can see the equilibrium between the columns in the apparatus for complete gas analyse. This figure gives an explanation why it is necessary to bring the chemicals in the chambers for absorption every time back to the blue marker **1**. In **figure 7** one can see that in the apparatus of complete gas analyse one have two water columns, which are separated because of the gas, which one measure. In the **figure 7** the situation is explained, how the apparatus should be prepared before every new measuring. The chemicals in the chambers for absorption are at the blue marker and the water column is at zero in the graduated measurement tube. **2** is a valve, which is closed at the beginning of the test. This explanation gives information about one chamber of absorption, which stands for all chambers. All the

chambers are functioning in the same way. When one opens the valve the columns get in equilibrium with the surrounding and the water in the measurement tube moves. Now one pumps the gas through the chemical. Now rise and sink bottle 3 and the water surface in the measurement tube follows the movement and pumps the gas through the chemical of absorption. Gas is absorbed and the amount of gas between the chemical of absorption and water falls. Now it is necessary to bring the level in the chamber of absorption back to the marker and close the valve **2** to know the real amount of the gas, which was absorbed.



**Figure 8:** chamber of absorption

In the **figure 8** one can see the way of the biogas through the chamber. How the gas enters and circulates. P is a one way valve. The gas enters through the pipe. At the end the gas gets pressed through small drilling. As a consequence the gas transform into bubbles. This changing improves the mass transport between the fluid and the gas. In form of bubbles the corresponding surface is very big. The absorption is very fast and complete. After the absorption less gas returns to the measurement tube. The difference between the amounts of gas before and afterwards can be measured.

## 4 Test leading

The testing starts every time with the filling of 2,5 litre wastewater into the reactor. Afterwards one put the reactor into the water chamber. The temperature at the controller is put at 37 degrees. With these settings it is sure that the temperature is 35 degrees in the reactor. The system loose like 2 degrees at the surface between the water and the reactor inside. Before the test is started one is filling up all the plastic tubes and all the tubes between the reactor and the other equipment with water, to guarantee that there is as less air in the system as possible. Then one has to wait for some time and afterwards one has to connect the reactor with the gas collecting tube. Normally at the first day the greatest amount of gas was produced. So one has to take more gas at the beginning and then everyday one or two tests depending on the amount of gas produced. One is never able to empty the whole gas collecting tube. It is only possible to empty the gas collecting tube until a certain limit. Then it is not possible anymore to make a whole test out of the remaining gas. The remaining gas, with which it is not possible to make a complete test, is left into the surrounding. To measure the volume one has to count also the remaining gas in the gas collecting tube. The goal was to measure all the gas and to calculate a mean with the measured concentrations. The result presents the whole gas volume produced during the testing. Some times there were problems with the apparatus for complete gas analyse. The system is complicate and quite sensible. For the explanation of the apparatus for complete gas analyse look chapter 8.10.

## 5 Measured Water Parameters

### 5.1 BOD

BOD - biochemical (biological) oxygen declares the amount of oxygen, which is required to biodegrade the available organic matter under specific circumstances and in a specific time. The BOD is mainly used to evaluate the quality of water.

Normally the BOD<sub>5</sub> (BOD after 5 days) is used. This parameter equals with the amount of oxygen in mg/l which bacteria or other in the water available microorganism at a temperature of 20°C in a period of 5 days use to degrade the biological degradable organic matter.

#### 5.1.1 BOD determination

##### Method of dilution and sowing:

In order to determine the BOD<sub>5</sub> the initially dissolved O<sub>2</sub> before the incubation is measured. After 5 days in incubation at 20°C, the dissolved O<sub>2</sub> was measured again with an oximeter and the difference is multiplied by the dilution factor is the BOD of the sample.

##### Procedure:

1. One has to prepare a dilution of 500 millilitre of the residual water sample using distilled water. Each group prepared a different dilution in agreement with the following table.

| DBOn Probable mg/l | Factor of dilution | Cleared result | Generally applicable |
|--------------------|--------------------|----------------|----------------------|
| of 3 a 6           | between 1 and 2    | 0,5            | R                    |
| of 4 a 12          | 2                  | 0,5            | R, E                 |
| of 10 a 30         | 5                  | 0,5            | R, E                 |
| of 20 a 60         | 10                 | 1              | E                    |
| of 40 a 120        | 20                 | 2              | S                    |
| of 100 a 300       | 50                 | 5              | S, C                 |
| of 200 a 600       | 100                | 10             | S, C                 |
| of 400 a 1200      | 200                | 20             | I, C                 |
| of 1000 a 3000     | 500                | 50             | I                    |
| of 2000 a 6000     | 1000               | 100            | I                    |

**R** = water of river

**E** = water of a sewage system biological

**S** = water of a sewage system or a industrial water little contaminated

**C** = water of a sewer

**I** = industrial water very contaminated



2. Introduce the wastewater in the appropriate bottle and measure the dissolved O<sub>2</sub>.
3. After finishing filling the bottle, put the bottle in incubation.
4. After 5 days take the bottle out of the incubation and measure the dissolved O<sub>2</sub>.
5. Now verify what dilution is the correct one. The correct dilution has to satisfy the following relation:

$$C1/3 \leq (C1 - C2) \leq (2 * C1)/3$$

C1 = concentration of O<sub>2</sub> dissolved, expressed in ppm.

C2 = concentration of O<sub>2</sub> dissolved, expressed in ppm, of a the same dissolution after n days.

6. One calculates the value of the DBO with the data collected of the correct dilution, in ppm of O<sub>2</sub>. The DBO given by the difference of concentrations of dissolved O<sub>2</sub> considering the conducted dilution.

$$DBO5 = F * (C1-C2)$$

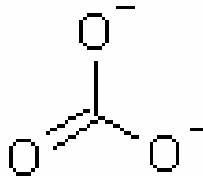
Where F is the dilution factor.

### **Crison OXI 45**

This measurement was used to measure the oxygen concentration to define the BOD. For more information's look up part 8.8 instrument specifications.

## 5.2 Carbonate <sup>[7]</sup>

Carbonates are the salts of the fully dissociate carbon acid. The appropriate double negative Anion is the carbonate  $\text{CO}_3^{2-}$ .



**Figure 9:** structure of carbonate

Also the ester of the carbon acid with the structure  $\text{R} - \text{O} - \text{C}(=\text{O}) - \text{O} - \text{R}'$ , whereas R and R' are the carbon consisting rests, are called carbonate. Carbonates are ionic salts and normally at ambient temperature crystalline solids. The carbonate anion brings no colour into the composition. Carbonate doesn't have any smell.

### Important Carbonates:

- Pottasiumcarbonate ( Potash )
- Sodium carbonate ( Soda )
- Magnesium carbonate
- Calcium carbonate
- Calcium-magnesium-carbonate

### Calibration

To calibrate the measurement different solutions with 125ppm, 250ppm, 500ppm and 1000ppm were prepared. Measuring the mV with the adequate electrode. The result was a diagram, which allows measuring mV, and one gets the correlative ppm out of the diagram.

### Weigh the amount of Carbonate

$\text{NaHCO}_3 = 84 \text{ g/mol}$

With the chemical  $\text{NaHCO}_3$  a solution of 1000ppm  $\text{CO}_3^{2-}$  was prepared. To produce the other necessary solutions dilute the 1000ppm solution. For the calibration curve and the measurements see **chapter 8**.

[7 Vgl. <http://de.wikipedia.org/wiki/Carbonate>]

## 5.3 Sulphide <sup>[8]</sup>

Formally, "sulphide" is the dianion,  $S^{2-}$ , which exists in strongly alkaline aqueous solutions formed from  $H_2S$  or alkali metal salts such as  $Li_2S$ ,  $Na_2S$ , and  $K_2S$ . Sulphide is exceptionally basic and, with a  $pK_a > 14$ , it does not exist in appreciable concentrations even in highly alkaline water, being undetectable at  $pH < 15$ . Instead, sulphide combines with protons to form  $HS^-$ , which is variously called hydrogen sulphide ion, hydrosulphide ion, sulfhydryl ion, or bisulphide ion. At still lower  $pH (<7)$ ,  $HS^-$  converts to  $H_2S$ , hydrogen sulphide. Thus, the exact sulphur species obtained upon dissolving sulphide salts depends on the  $pH$  of the final solution.

### Calibration

To calibrate the measurement different solutions with 125ppm, 250ppm, 500ppm and 1000ppm were prepared. Measuring the mV with the adequate electrode. The result was a diagram, which allows measuring mV, and one gets the correlative ppm out of the diagram.

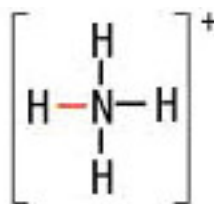
### Weigh the sulphide

$Na_2S = 78,05 \text{ g/mol}$

With the chemical  $Na_2S$  a solution of 1000 ppm  $S^{2-}$  was prepared. To produce the other necessary solutions dilute the 1000ppm solution. For the calibration curve and the measurements see **chapter 8**.

## 5.4 Ammonium <sup>[9]</sup>

The ammonium ion  $NH_4^+$  is the conjugated acid to the base  $NH_3$  ammonia.



**Figure 10:** structure of ammonium

The ammonium ion is a cation, it reacts in the same way like an alkali metal ions. Also it forms salts with the same structure. In the nature normally ammonium is formed at the degradation of proteins

[8] Vgl. <http://en.wikipedia.org/wiki/Sulphide>

[9] Vgl. <http://de.wikipedia.org/wiki/Ammonium>

## Calibration

To calibrate the measurement different solutions with 125ppm, 250ppm, 500ppm and 1000ppm were prepared. Measuring the mV with the adequate electrode. The result was a diagram, which allows measuring mV, and one gets the correlative ppm out of the diagram.

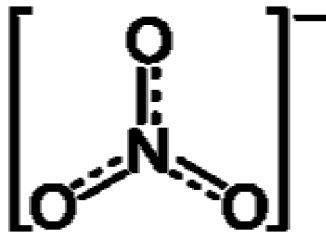
## Weigh the amount of ammonium



With the chemical  $\text{NH}_4\text{NO}_3$  a solution of 1000 ppm  $\text{NH}_4^+$  was prepared. To produce the other necessary solutions dilute the 1000 ppm solution. For the calibration curve and the measurements see **chapter 8**.

## 5.5 Nitrate <sup>[10]</sup>

In inorganic chemistry, a nitrate is a salt of nitric acid with an ion composed of one nitrogen and three oxygen atoms. In organic chemistry the esters of nitric acid and various alcohols are called nitrates.



**Figure 11:** structure of a nitrate

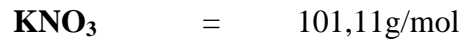
The nitrate is an ion with the empirical formula  $\text{NO}_3^-$  and a molecular mass of 62.0049. It is the conjugate base of nitric acid, consisting of one central nitrogen atom surrounded by three identical oxygen atoms in a trigonal planar arrangement. The nitrate ion carries a formal charge of negative one and is commonly used as an example of resonance. Almost all nitrates are soluble in water at standard temperature and pressure. In organic chemistry a nitrate is a functional group with general chemical formula  $\text{RONO}_2$  where R stands for any organic residue. Examples are methyl nitrate formed by reaction of methanol and nitric acid, the nitrate of tartaric acid and the inappropriately named nitroglycerin.

## Calibration

To calibrate the measurement different solutions with 125ppm, 250ppm, 500ppm and 1000ppm were prepared. Measuring the mV with the adequate electrode. The result was a diagram, which allows measuring mV, and one gets the correlative ppm out of the diagram.

[10 Vgl. <http://en.wikipedia.org/wiki/Nitrate>]

### Weigh the amount of nitrate



With the chemical  $\text{KNO}_3$  a solution of 1000ppm  $\text{NO}_3^-$  was prepared. To produce the other necessary solutions dilute the 1000 ppm solution. For the calibration curve and the measurements see **chapter 8**.

## 5.6 PH

This measurement was used to measure the process factors pH and redox potential. For further information's look up part 8.9 instrument specifications.

## 6 Tests

This part is the practical part of the work. The interesting tests when the apparatus was working correctly are shown in this part. In the work 3 tests are presented. The first test only shows four results of the measured gas. The fact is some problems appeared at the beginning of the test but have been corrected. The second test was perfect with the water directly out of the digester and no problems during the 7 days of measuring. The third test is with water, which was already during the second test stored. It was stored at room temperature. Also the water was characterized at every test. All the water values were measured before and after the test to see the changes, which occur in the water because of the fermentation. The PH and redox potential are measured during the tests to see changes in the process during the fermentation. The Tests were all made at a temperature of 35 degrees.

### 6.1 Test 1

#### 6.1.1 Produced gas

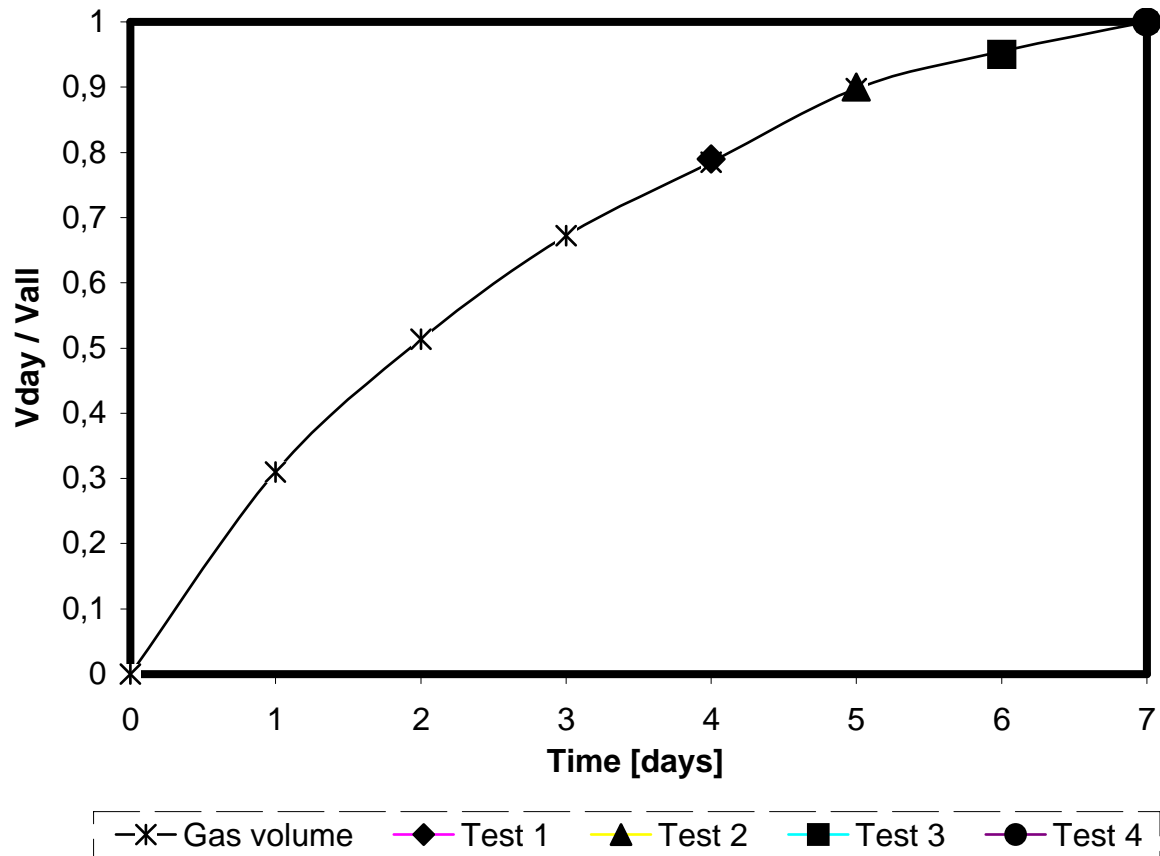
In this part of the work something about the results of the tests. In **table 3** the amount of the produced gas in ml during the testing is shown for the days of experiment. In the third line the volume of every day is divided with the whole amount of the volume, which is **2210 ml**. For the testing **2,5 l** of wastewater was taken. The test was made at **35** degrees.

|   |   |      |      |      |      |     |      |     |
|---|---|------|------|------|------|-----|------|-----|
| <b>Time [days]</b>                                | 0 | 1    | 2    | 3    | 4    | 5   | 6    | 7   |
| <b>Volume [ml]</b>                                | 0 | 685  | 450  | 350  | 250  | 250 | 125  | 100 |
| <b><math>V_{\text{day}}/V_{\text{all}}</math></b> | 0 | 0,31 | 0,51 | 0,67 | 0,79 | 0,9 | 0,95 | 1   |

**Table 3: composition of the measured biogas corrected**

In the following tables the word test is used for single measurements which are performed at certain days.

In diagram 1 one can see the volume of the produced biogas. The biogas, which is produced every day, is divided with the whole amount of biogas and the individual results per day are mount up to 1.

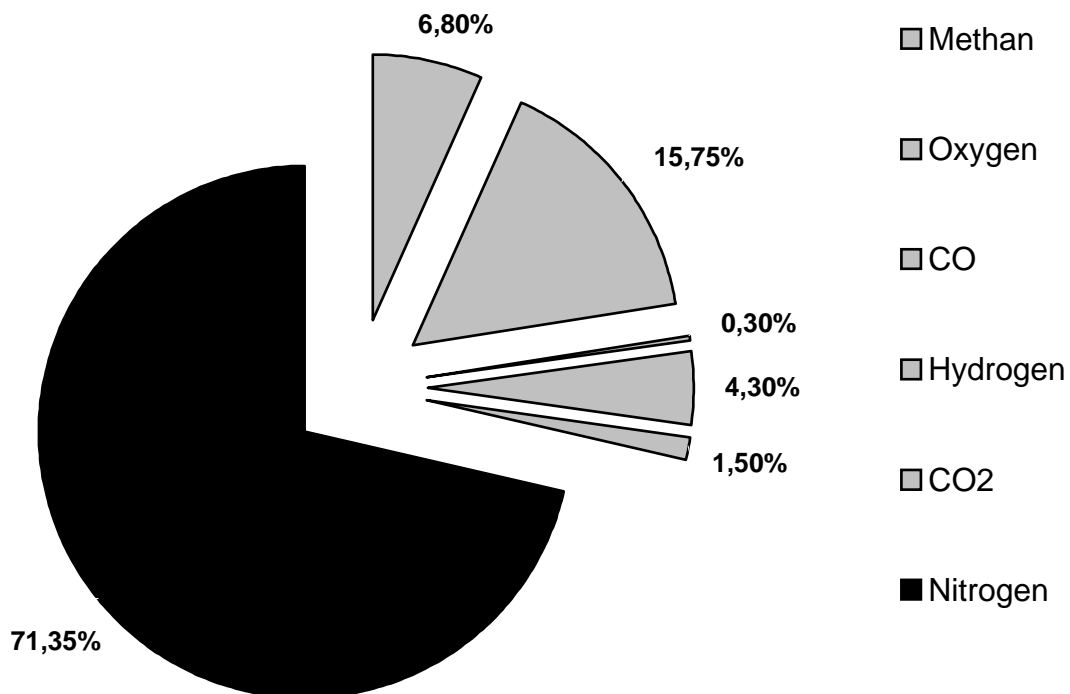


**Diagram 1:** Mount of the produced Biogas with the individual tests

**Table 4** shows four tests of the gas with the main components. In this table there is a mistake because of the air, which was coming in the reactor during the tests. The time is the time when the tests were made. The volume means the amount of gas needed for every measuring of the gas.

| Components  | 1Test | 2 Test | 3 Test | 4 Test | Mean          |
|-------------|-------|--------|--------|--------|---------------|
| Methane     | 4,8%  | 11,2%  | 5,4%   | 5,8%   | <b>6,80%</b>  |
| Oxygen      | 18,2% | 16,0%  | 16,0%  | 12,8%  | <b>15,80%</b> |
| CO          | 0,4%  | 0,0%   | 0,2%   | 0,6%   | <b>0,3%</b>   |
| hydrogen    | 4,0%  | 1,0%   | 6,0%   | 6,6%   | <b>4,3%</b>   |
| CO2         | 0,4%  | 0,8%   | 0,6%   | 4,2%   | <b>1,50%</b>  |
| Nitrogen    | 72,2% | 71,4%  | 71,8%  | 70%    | <b>71,35%</b> |
| Time [days] | 4     | 5      | 6      | 7      |               |
| Volume [ml] | 125   | 125    | 125    | 100    |               |

**Table 4:** composition of the measured biogas



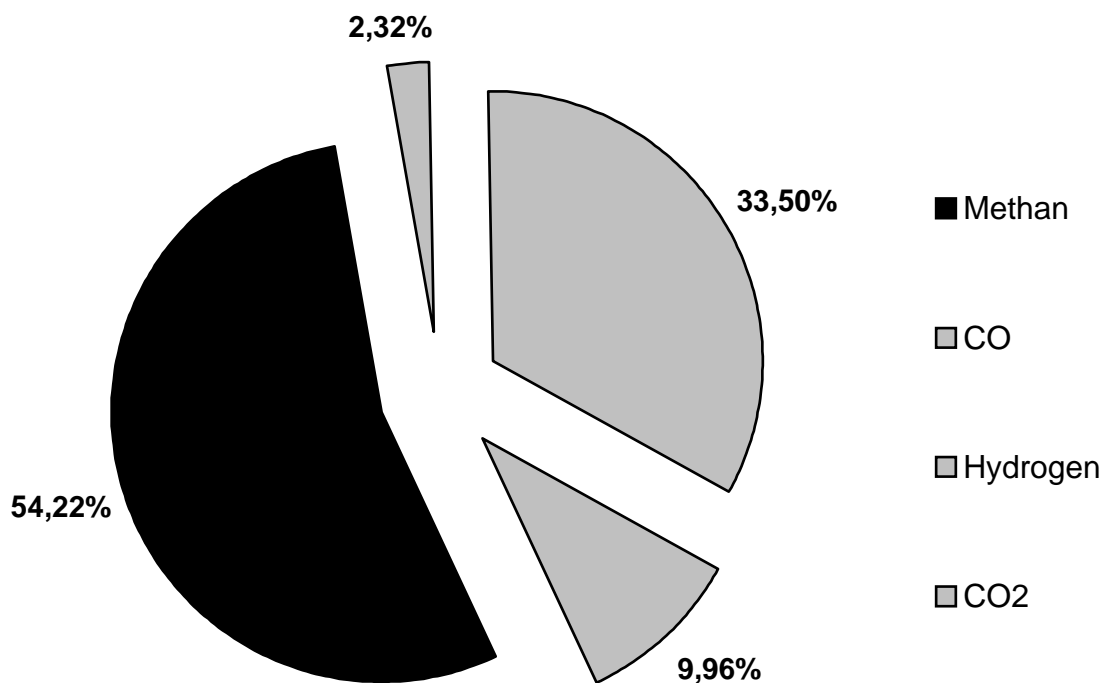
**Diagram 2:** composition of the measured biogas



In **table 5** the volumes have been corrected with the average composition of air (78% nitrogen 21% oxygen). I corrected only the amount of nitrogen and oxygen. The result was that now oxygen and nitrogen disappear in the biogas

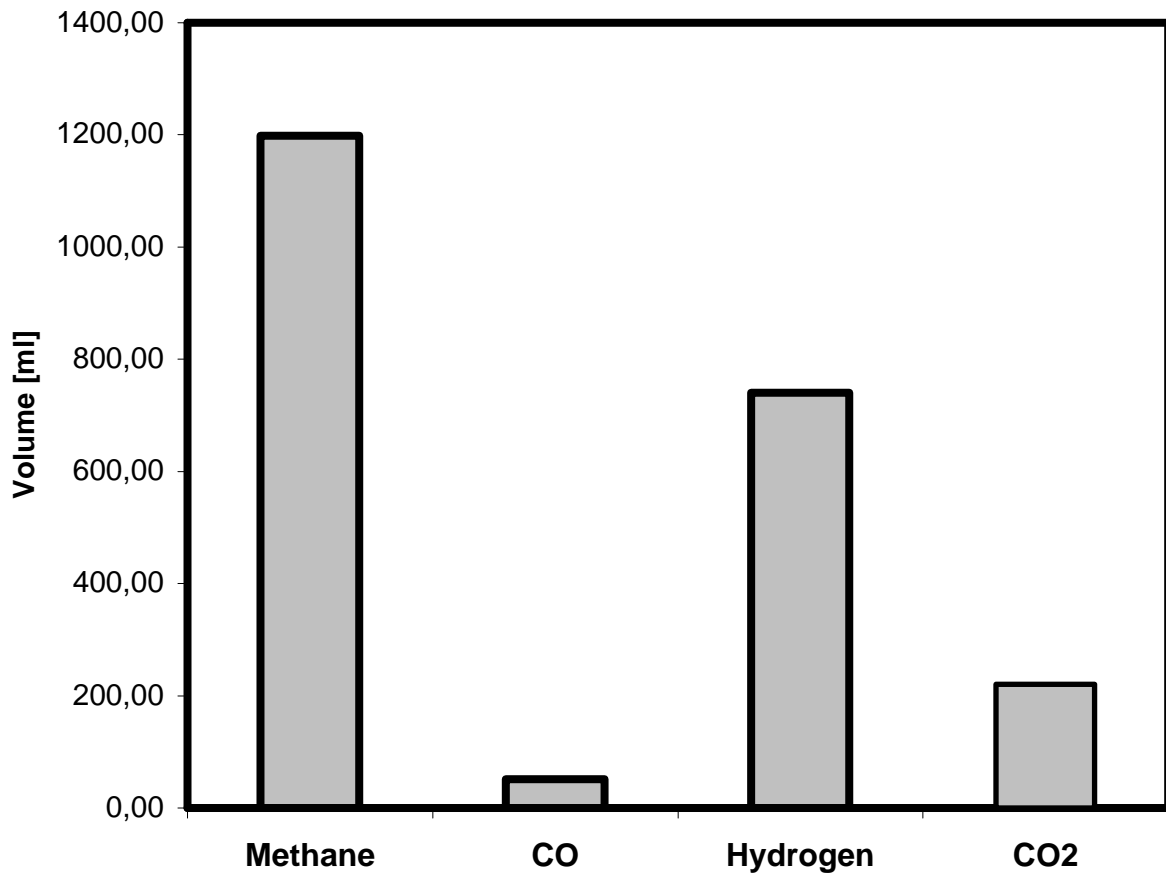
| Components  | 1Test | 2 Test | 3 Test | 4 Test | Mean          |
|-------------|-------|--------|--------|--------|---------------|
| Methane     | 50%   | 88,9%  | 44,3%  | 33,7%  | <b>54,22%</b> |
| CO          | 4,2%  | 0,0%   | 1,6%   | 3,5%   | <b>2,32%</b>  |
| Hydrogen    | 41,7% | 4,8%   | 49,2%  | 38,4%  | <b>33,5%</b>  |
| CO2         | 4,2%  | 6,4%   | 4,9%   | 24,4%  | <b>9,96%</b>  |
| Time [days] | 4     | 5      | 6      | 7      |               |
| Volume [ml] | 125   | 125    | 125    | 100    |               |

**Table 5:** composition of the measured biogas corrected



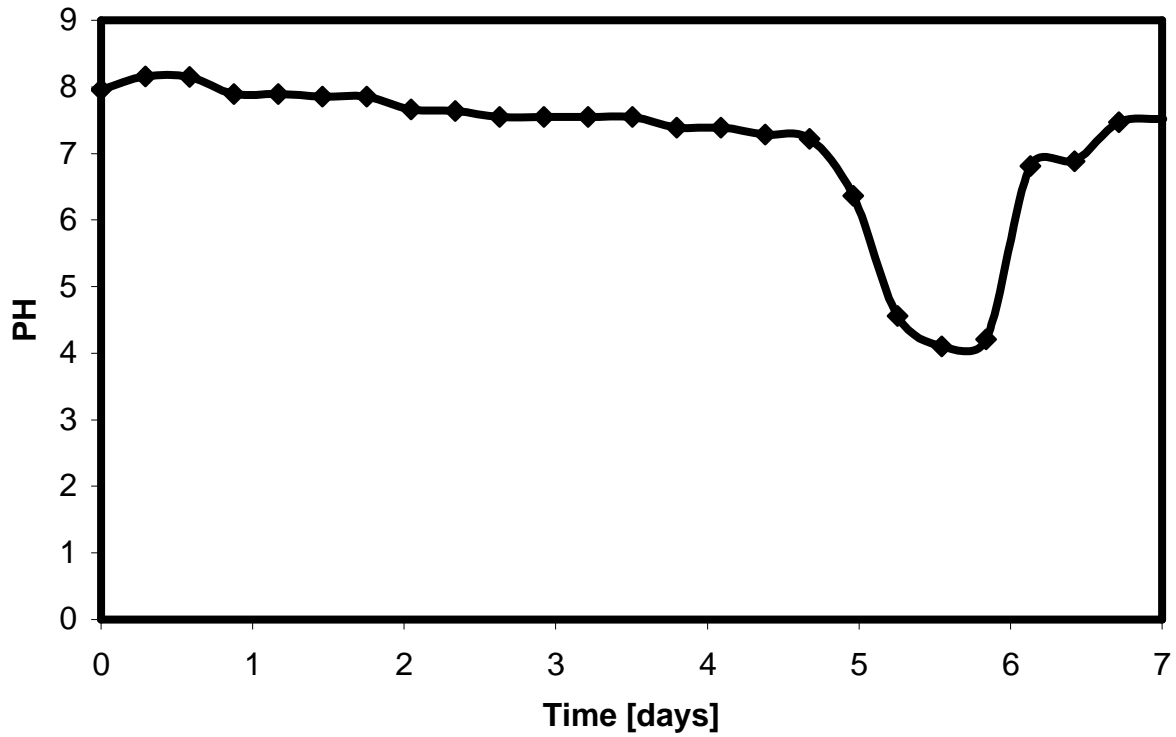
**Diagram 3:** composition of the measured biogas corrected

In **diagram 4** one can see the composition of the biogas in ml calculated out of the whole volume produced and the composition of the measured biogas corrected.



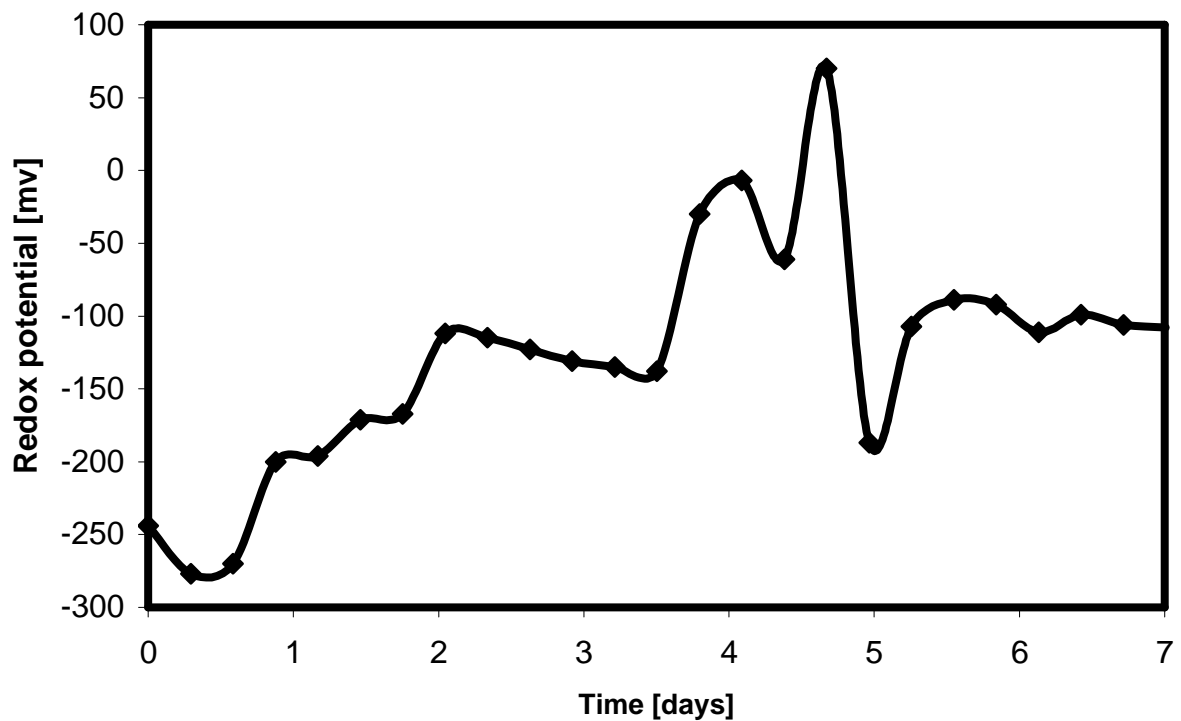
**Diagram 4:** composition of the biogas in ml

In **diagram 5** one can see the PH value during the testing.



**Diagram 5: PH value during the testing**

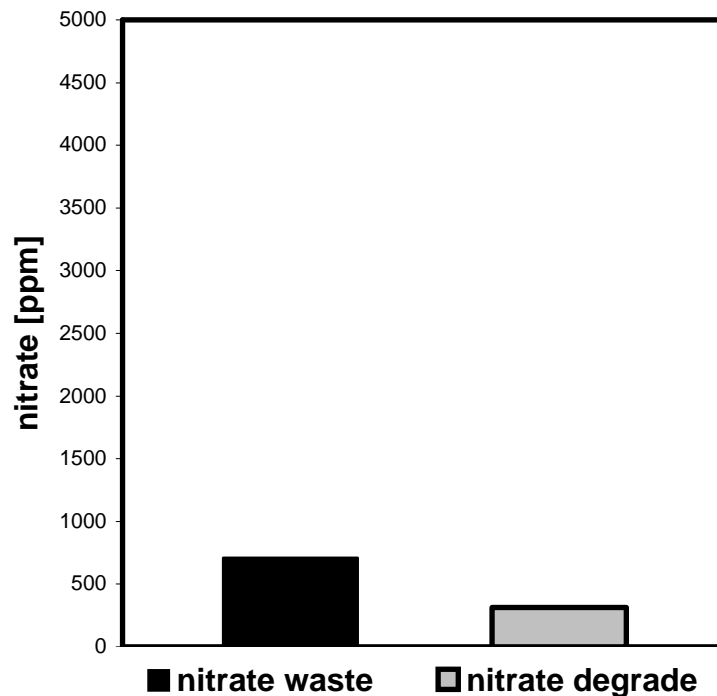
In **diagram 6** one can see the value of the redox potential during the testing.



**Diagram 6: redoxpotential during the testing**

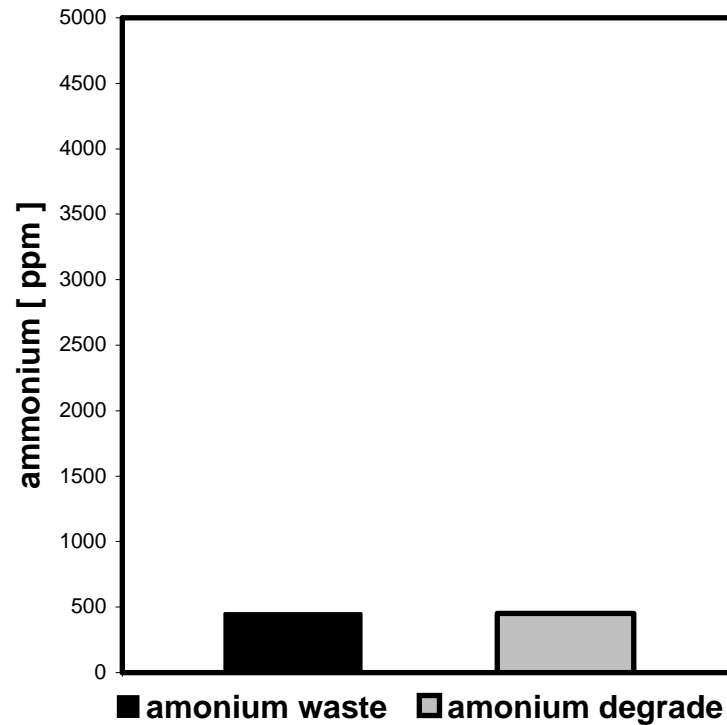
## 6.1.2 Measured water

In this part one can see the values of the waste water before and after the test. Following one can see the amount of the nitrate, ammonium, carbonate and sulphide. This ions are building the nutrient for the bacteria. In **diagram 7** one can see the nitrate. Before the testing the value of the nitrate is **710 ppm** and after the testing the value is **315 ppm**.



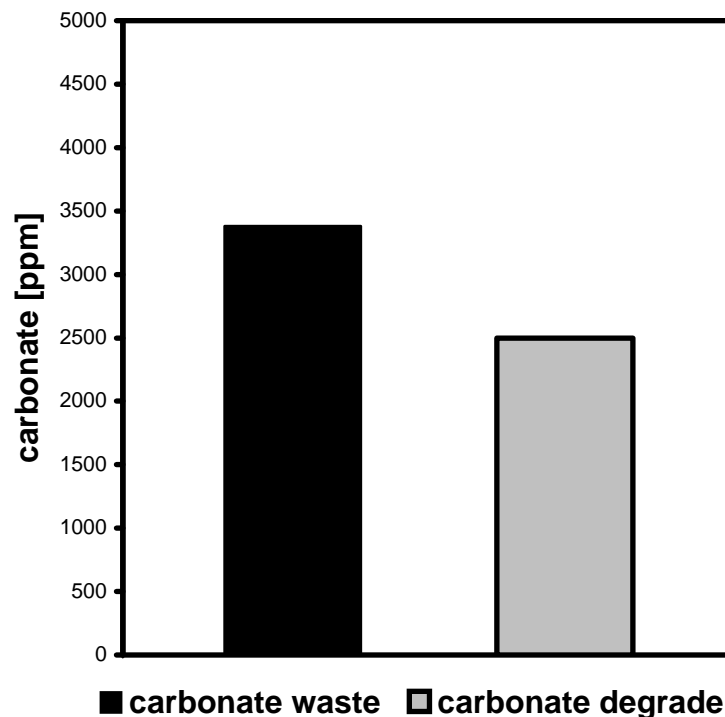
**Diagram 7:** comparing the nitrate in solution before and after the testing

In **Diagram 8** one can see the amount of ammonium in ppm before and after the testing. The amount before the test is **450 ppm** and after the test the amount is **450 ppm**.



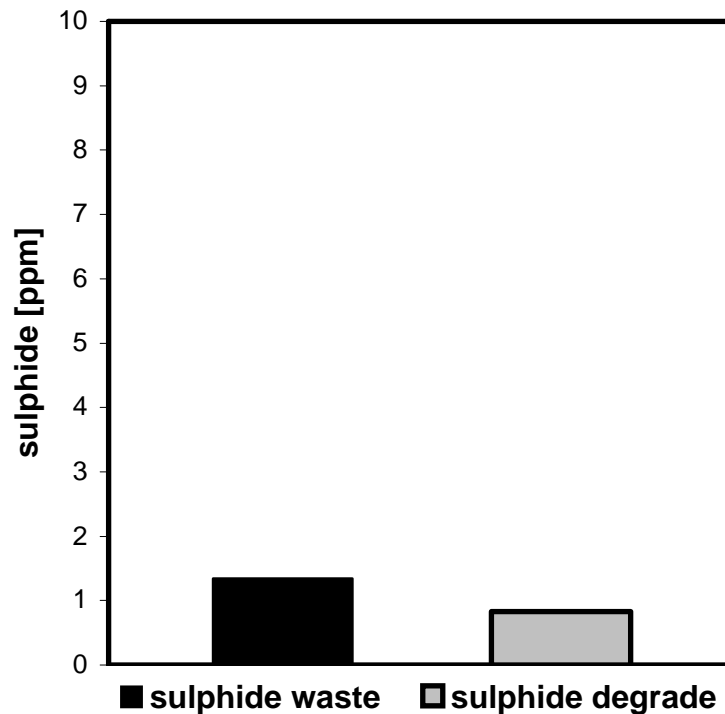
**Diagram 8:** comparing the ammonium in solution before and after the testing

In **diagram 9** one can see the amount of carbonate in ppm before and after the testing. The amount before the test is **3380 ppm** and after the test the amount is **2500 ppm**.



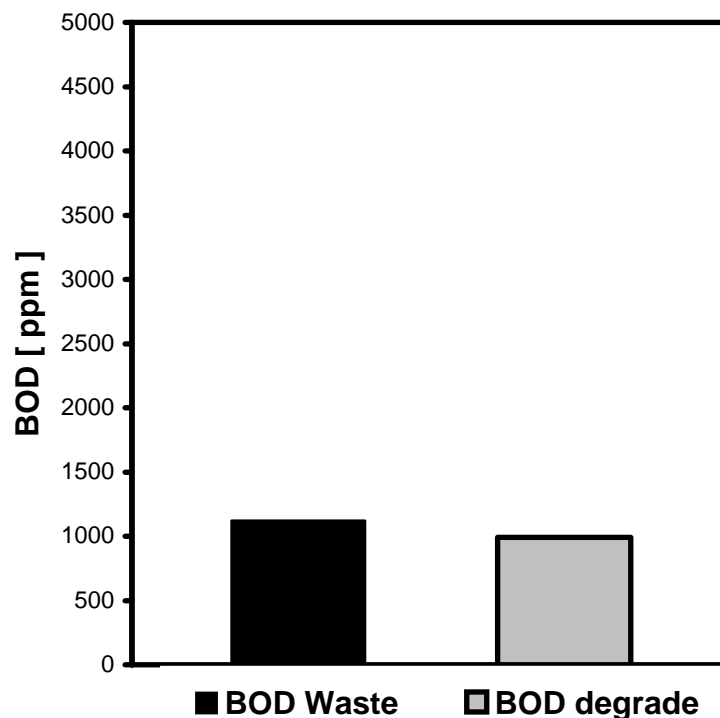
**Diagram 9:** comparing the carbonate in solution before and after the testing

In **diagram 10** one can see the amount of sulphide before and after the testing. In this case the scale has been changed because the value of the sulphide is too small for the normal used scale. The amount before the test is **1,34 ppm** and after the test the amount is **0,83 ppm**.



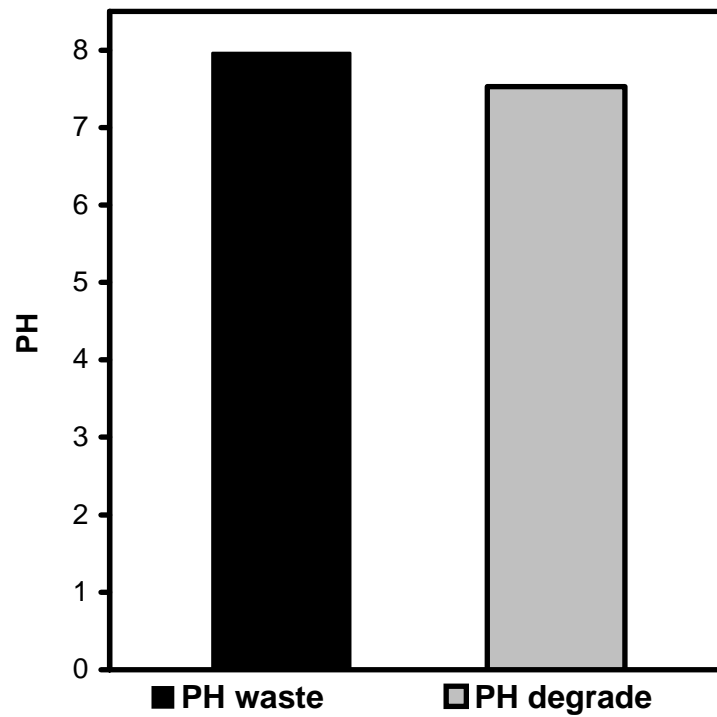
**Diagram 10:** comparing the sulphide in solution before and after the testing

In **diagram 11** the amount the biological oxygen demand ( BOD ) which gives information about the amount of the biodegradable substances in the waste water before and after the test. The amount before the test is **1120 ppm** and after the test the amount is **992 ppm**.



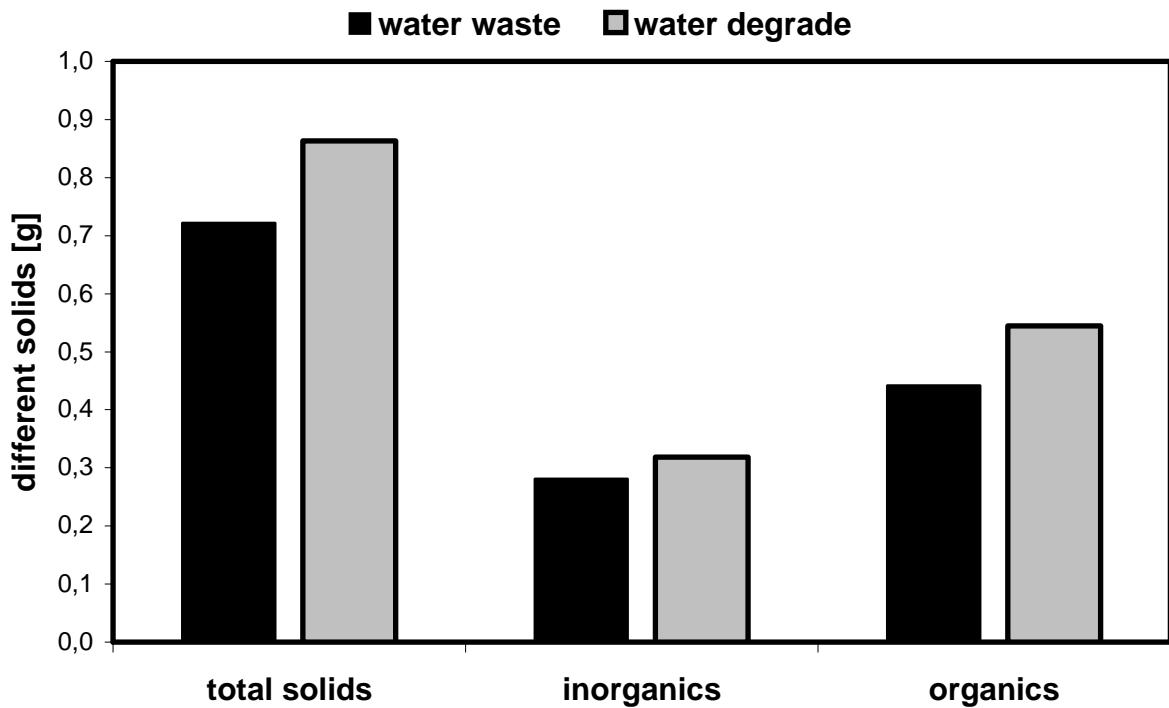
**Diagram 11:** comparing the BOD before and after the testing

In **diagram 12** one can see the value of the PH before and after the testing. The PH before the test is **7,96** and after the test the amount is **7,52**.



**Diagram 12:** comparing the PH before and after the testing

In **diagram 13** one can see the amount of the solids in g. For the test 25ml wastewater was taken. The amount of the total solids before the test is **0,722 g** and the amount after the test is **0,863 g**. The amount of the inorganics before the test is **0,281 g** and after the test it is **0,318 g**. The amount of the organics before the test is **0,441 g** and after the test it is **0,545 g**. The percentage of the total solids before the test is **2,9%** and after the test it is **3,4%**.



**Diagram 13:** comparing total solids, inorganics, and organics before and after the testing



### 6.1.3 Discussion

The discussed data are shown in chapter 6.1. In **diagram 1** one can see the amount of gas produced every day divided with the amount of gas produced during the whole test. It can be noticed that at the first day the amount of the gas produced is higher than at the following days. Also the tests which have been done and at what day the tests have been done. In **table 4** one can see the 4 Tests which have been done together with the corresponding composition. Also one can see again at what day the tests were made and the volume of each of the tests in ml. Between the tests there are quite big differences in the composition. One can see the first test is on the 4<sup>th</sup> day because with the tests on the first 3 days there have been problems with the apparatus for complete gas analyse. The quality of the results was not satisfying and it was not possible to use them in this work. In **diagram 2** one can see the mean of the data in **table 4**. To make the analyse of the biogas it is better to use the following **table 5** and **diagram 3**. In **diagram 2** and **table 4** there is still an error because of the air, which came into the apparatus during the tests. The tests have been corrected with the composition of the air (78% nitrogen and 21% oxygen). In **table 5** one can see the composition of the biogas without the corrected failure of the air and the amount of hydrogen is quite the same at all the tests only in the 2<sup>nd</sup> test the amount is lower. In the 2<sup>nd</sup> test the percentage of the methane is quite high. In test 4 the amount of the CO<sub>2</sub> is high compared with the other tests. This differences results of, how the test has been done, which is explained at the beginning of chapter 6 and out of the different density of the gases. Hydrogen is the lightest gas so it is more located on the top of the tube. CO<sub>2</sub> is the heaviest gas and more located on the bottom of the tube. In the tests one can see this fact. Also there are every time fluctuation in the tests because of the different time left between the tests and the different amount and composition of the biogas produced during the test. In **diagram 3** one can see the percentage of biogas without the air. The amount of hydrogen is quite high. If the time of staying is longer, the degradation is better <sup>[11]</sup>. At a later point of the degradation, when the CO<sub>2</sub> emitting hydrolyses is nearly over, a lot of methane is produced and so on a Biogas with a higher energy amount is produced. In my case the waste water is already degraded and there have been only tests from the last four days. Also when the initial material is quite fluid more CO<sub>2</sub> is soluted in the water and the amount of CO<sub>2</sub> is lower <sup>[12]</sup>. Because of this fact in the tests the amount of CO<sub>2</sub> is quite low and as a consequence the amount of hydrogen is higher. In **diagram 4** one can see the composition of the biogas in ml. During the tests an amount of 2210 ml of biogas is produced. To use the waste water for industrial energy production the amount is not enough but for the own consumption of the waste water treatment plant it is every time useful.

[11 Vgl. 15.1.3 Verfahrenstechnische Messgr. S 651 Energie aus Biomasse ISBN 3-540-64853-4]

[12 Vgl. 15.1.3 Verfahrenstechnische Messgr. S 651 Energie aus Biomasse ISBN 3-540-64853-4]

In **diagram 7,8,9 and 10** one can see the amount of nitrate, sulphide, carbonate and ammonium before and after the testing. These parameters characterise the fluid part not the solid part of the wastewater. During the fermentation a part of the mentioned ions change into solids and another part change into the gaseous form. The bacteria eat the parts of the water they need for living and remove some parts into solids and the other part they remove into biogas. This changing one can see in the **diagram 7,8,9 and 10**. Now some words about the problematic of these components when they are soluted in water when one are producing biogas. Ammonium is normally in equilibrium with ammonia and is an inhibitor between 2,7 and 10 g/l that's like 10000 ppm<sup>[13]</sup>. The wastewater in the test has an amount of 450 ppm. Ammonium in equilibrium acts also as a puffer of the PH at lower concentration. Nitrate normally gets denitrified in an anaerobe ambience. Sulphide is an inhibitor at concentration higher than 100mg/l S<sup>2-</sup><sup>[14]</sup>. In my case the amount is 1 ppm that's more or less 1mg/l.

The BOD **diagram 11** is also higher before the test then afterwards. The BOD is a number, which gives advice, how much biodegradable material is in the product. It has been measured, that the BOD before the test is higher than afterwards. That's normal because the components in the wastewater gets degrade anaerobe. As a result there are fewer biodegradable components in the water after the testing.

In **diagram 13** one can see that the solids are more after the fermentation than before. The reason why it is more, results out of the living process of the bacteria. The bacteria eat components out of the water and produce solids and biogas. Also after some time a part of the bacteria die and they change into the solid part. Also the number of bacteria increases during the tests by splitting. Another fact why the amount is more afterwards, results since that there is nearly no degradation of the solid part in the waste water. The reason is, that to degrade solids it needs a lot of time. In my case the tests last 7 days, which is to less to degrade the solids. The fact to clean the water with the anaerobe degradation is not exact, it is more a stabilisation of the bacteria. It is not the fact to reduce the solids but the solids are more stabilized after the anaerobe degradation. Also the amount of water, which is hold back in the sludge, is less after the fermentation.

The PH **diagram 5** is at the beginning a little bit high when one compares it with the optimum mentioned in the theory. In the theory they say the optimum is between 7 up to 7,5<sup>[15]</sup>. In this case the PH starts at 7,9612 and ends at the 7,4712. At the end one can see a certain acidification. Normally in a single-stage process the pH-value gets regulate automatically in the optimal range, because bacteria groups create a self-regulating system. The carbon dioxide (CO<sub>2</sub>), which is produced at the degradation, is in equilibrium with the hydro carbonate, buffering concentrations between 2,5 to 5g/l<sup>[16]</sup>. In the process of anaerobe fermentation in the second step fermentative bacteria are forming organic acids out of amino acids, fatty acids and saccharide. When this process is the fastest or the number of the fermentative bacteria increases it is possible that the puffer system is not working anymore and there is an acidification. Another explanation one can see in the graphs in the same time or a little bit earlier the redoxpotential rises. So it seems the fermentative bacteria are working better than the methane building bacteria when there is an amount of oxygen in the system. When there is a decreasing of the PH it makes the process instable.

[13] Vgl. 15.1.3 Verfahrenstechnische Messgr. S 650 Energie aus Biomasse ISBN 3-540-64853-4  
[14] Vgl. 15.1.3 Verfahrenstechnische Messgr. S 650 Energie aus Biomasse ISBN 3-540-64853-4  
[15] Vgl. 15.1.3 Verfahrenstechnische Messgr. S 648 Energie aus Biomasse ISBN 3-540-64853-4  
[16] Vgl. 15.1.3 Verfahrenstechnische Messgr. S 648 Energie aus Biomasse ISBN 3-540-64853-4

The optimum of the redoxpotential normally in the theory is between  $-300$  and  $-330$ <sup>[17]</sup> but the process works also at higher levels. In **diagram 6** the redoxpotential starts at  $-244$  mV and ends at  $-106$  mV. The increasing of the redoxpotential effects, because at the beginning oxygen was present in the reactor. Oxygen is an oxidant like sulphide and nitrate. When there is oxygen in the system the redoxpotential increase. It is not possible to eliminate all the oxygen in a discontinuous process. It have been tried to fill up the reactor totally with wastewater to minimize the amount of oxygen but still there is oxygen. This oxygen one can see in **diagram 6**. Also one can see that the decreasing of the PH and the increasing of the redoxpotential occur nearly at the same time. The explanation why the redoxpotential rises is that it have been put on the mixer stronger because it have been thought it accelerate the production of the gas. The result was the contrary, it have been nearly stopped the whole process. The fact was in the moment it have been mixed the fluid harder, more oxygen was dissolved in the fluid. After stopping the mixer the system stabilized again and the redox potential arise again.

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[17 Vgl. 15.1.3 Verfahrenstechnische Messgr. S 648 Energie aus Biomasse ISBN 3-540-64853-4]

## 6.2 Test 2

### 6.2.1 Produced gas

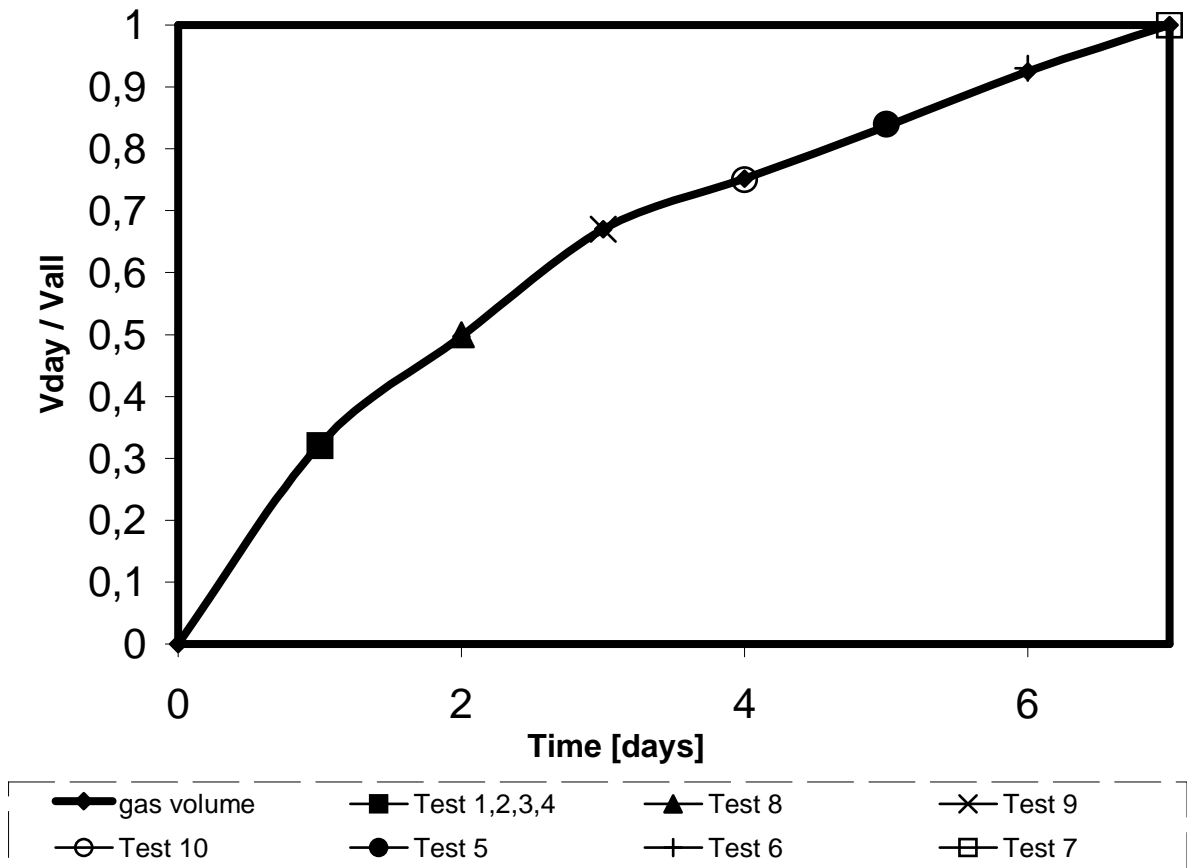
In this part of my work something about the results of my tests. In **table 6** one can see the amount of produced gas in ml at every day during the testing. In the third line the volume of every day is divided with the whole amount of the volume, which is **1470 ml**. For the testing **2,5 l** of wastewater was taken. The test was made at **35** degrees.

|   |   |      |      |      |      |      |      |     |
|---|---|------|------|------|------|------|------|-----|
| <b>Time [days]</b>                                | 0 | 1    | 2    | 3    | 4    | 5    | 6    | 7   |
| <b>Volume [ml]</b>                                | 0 | 475  | 255  | 255  | 120  | 125  | 130  | 110 |
| <b><math>V_{\text{day}}/V_{\text{all}}</math></b> | 0 | 0,32 | 0,50 | 0,67 | 0,75 | 0,84 | 0,93 | 1   |

**Table 6:** composition of the measured biogas corrected

In the following tables the word test is used for single measurements which are performed at certain days.

In **diagram 14** one can see the volume of the produced biogas. The biogas, which is produced every day, is divided with the whole amount of biogas and the individual results per day are mount up to 1.

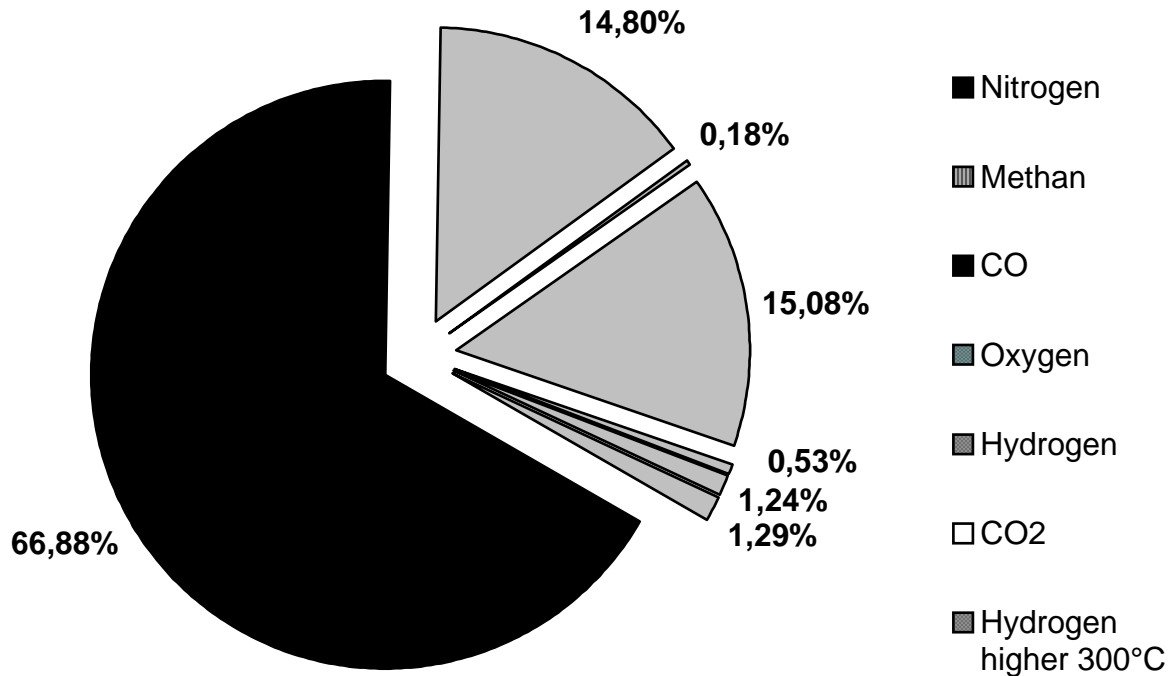


**Diagram 14:** Mount of the produced Biogas with the individual tests

**Table 7** shows 10 tests of the gas with the main components. In this table there is a failure because of the air, which was coming in the reactor during the tests. The time is the time when the tests were made. The volume is the amount of gas which has been took for every measuring of the gas.

| Components            | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | Test 6 | Test 7 | Test 8 | Test 9 | Test 10 | mean          |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|---------------|
| <b>Methane</b>        | 12,4%  | 17,4%  | 33,6%  | 22,6%  | 17,7%  | 18,2%  | 8,7%   | 10,0%  | 7,4%   | 2,8%    | <b>15,08%</b> |
| <b>Oxygen</b>         | 12,2%  | 15,6%  | 13,0%  | 15,6%  | 16,8%  | 14,8%  | 17,0%  | 14,6%  | 14,0%  | 14,0%   | <b>14,75%</b> |
| <b>CO</b>             | 0,4%   | 0,2%   | 0,2%   | 0,0%   | 0,2%   | 0,2%   | 0,2%   | 0%     | 0,2%   | 0,2%    | <b>0,18%</b>  |
| <b>Hydrogen</b>       | 4,8%   | 2,6%   | 1,4%   | 1,2%   | 2,8%   | 2,2%   | 1,2%   | 0%     | 2,0%   | 0,0%    | <b>1,82%</b>  |
| <b>CO<sub>2</sub></b> | 1,2%   | 1,0%   | 2,2%   | 1,0%   | 1,0%   | 1,2%   | 1,4%   | 1,4%   | 1,0%   | 1,0%    | <b>1,24%</b>  |
| <b>Nitrogen</b>       | 69,0%  | 63,2%  | 49,6%  | 59,6%  | 61,5%  | 63,4%  | 71,5%  | 74%    | 75,0%  | 82,0%   | <b>75,08%</b> |
| <b>Time [days]</b>    | 1      | 1      | 1      | 1      | 2      | 3      | 4      | 5      | 6      | 7       |               |
| <b>Volume [ml]</b>    | 125    | 110    | 125    | 115    | 125    | 135    | 120    | 125    | 130    | 110     |               |

**Table 7:** composition of the measured biogas

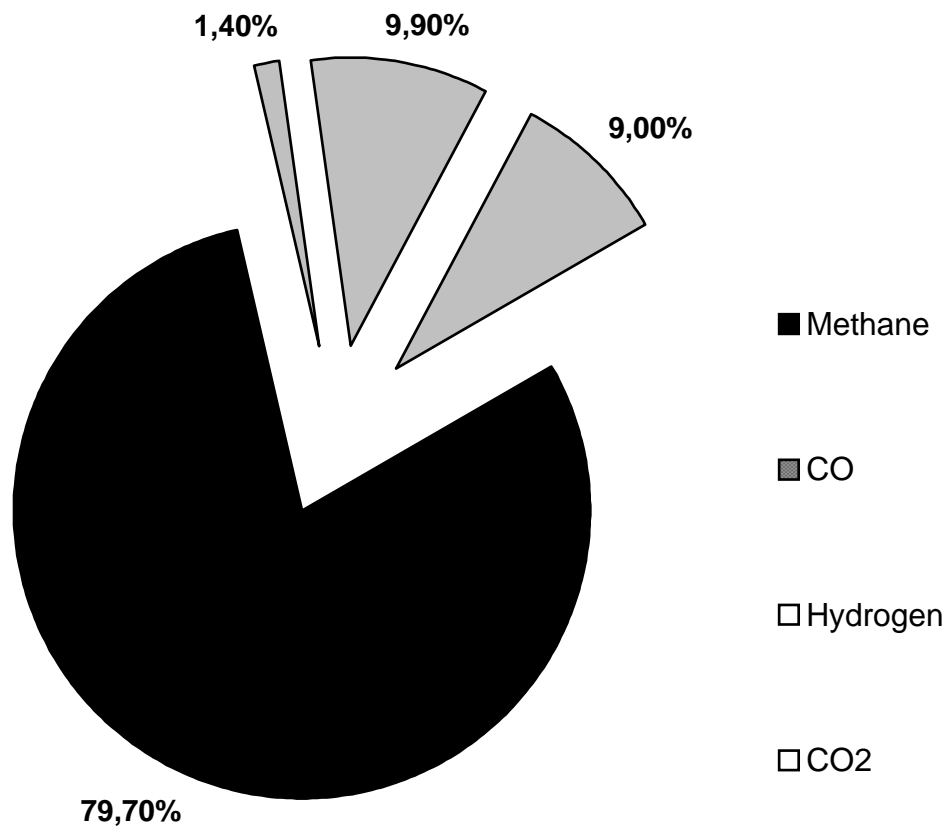


**Diagram 15:** composition of the measured biogas

In **table 8** the volumes have been corrected with the average composition of air. It have been corrected only the amount of nitrogen and oxygen. The result was that now oxygen and nitrogen disappear in the biogas

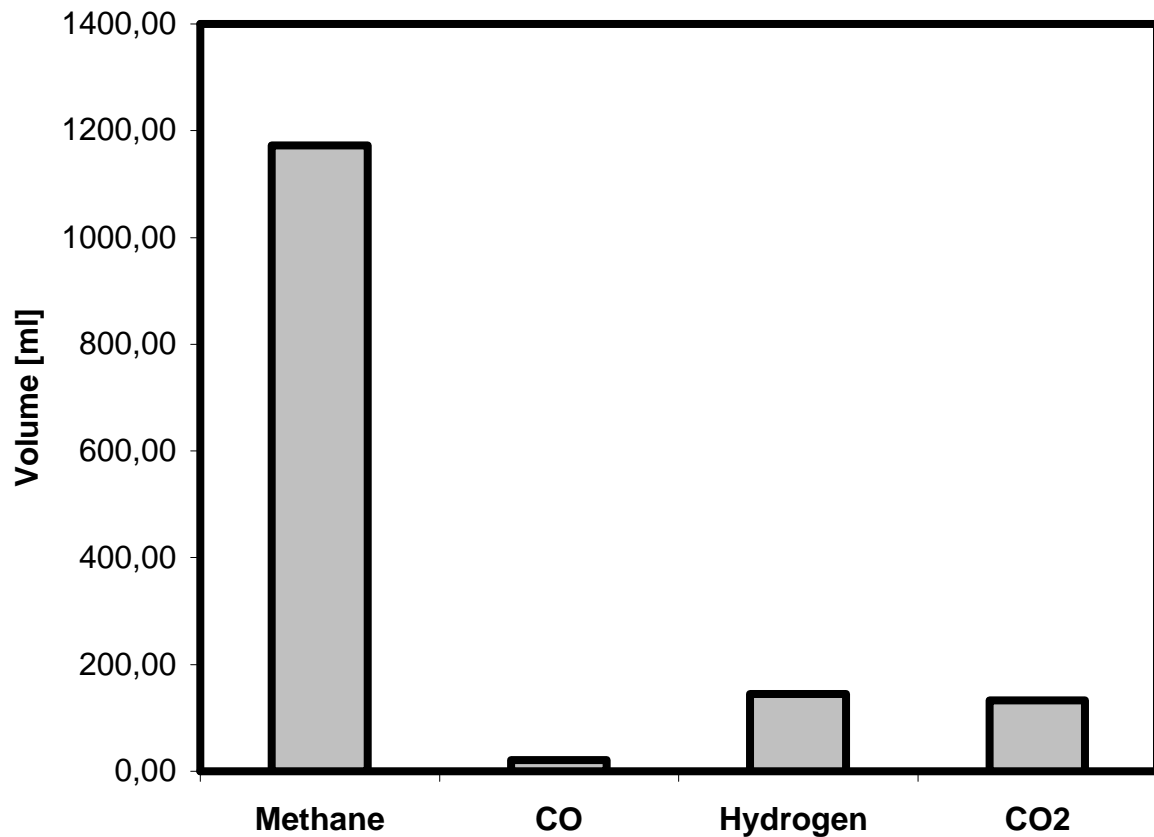
| Components            | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | Test 6 | Test 7 | Test 8 | Test 9 | Test 10 | mean         |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|--------------|
| <b>Methane</b>        | 66%    | 82,1%  | 89,8%  | 91,1%  | 77,3%  | 83,5%  | 75,7%  | 87,7%  | 69,8%  | 70%     | <b>79,7%</b> |
| <b>CO</b>             | 2,1%   | 0,9%   | 0,5%   | 0,0%   | 0,9%   | 0,9%   | 1,7%   | 0%     | 1,9%   | 5%      | <b>1,4%</b>  |
| <b>Hydrogen</b>       | 25,5%  | 12,3%  | 3,8%   | 4,8%   | 12,2%  | 10,1%  | 10,4%  | 0%     | 18,9%  | 0,0%    | <b>9,9%</b>  |
| <b>CO<sub>2</sub></b> | 6,4%   | 4,7%   | 5,9%   | 4%     | 4,4%   | 5,5%   | 12,2%  | 12,3%  | 9,4%   | 25,0%   | <b>9,0%</b>  |
| <b>Time [days]</b>    | 1      | 1      | 1      | 1      | 2      | 3      | 4      | 5      | 6      | 7       |              |
| <b>Volume [ml]</b>    | 125    | 110    | 125    | 115    | 125    | 135    | 120    | 125    | 130    | 110     |              |

**Table 8:** composition of the measured biogas



**Diagram 16:** composition of the biogas minus the oxygen and the nitrogen

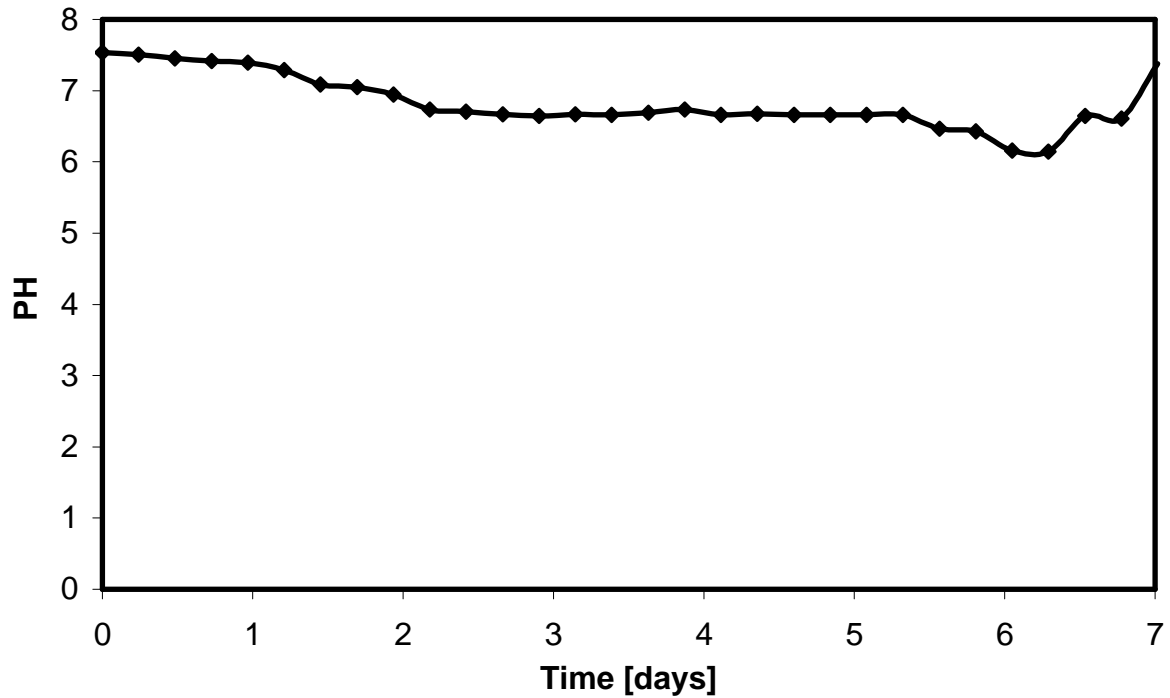
In **diagram 17** one can see the composition of the biogas in ml calculated out of the whole volume produced and the composition of the measured biogas corrected.



**Diagram 17: composition of the biogas in ml**

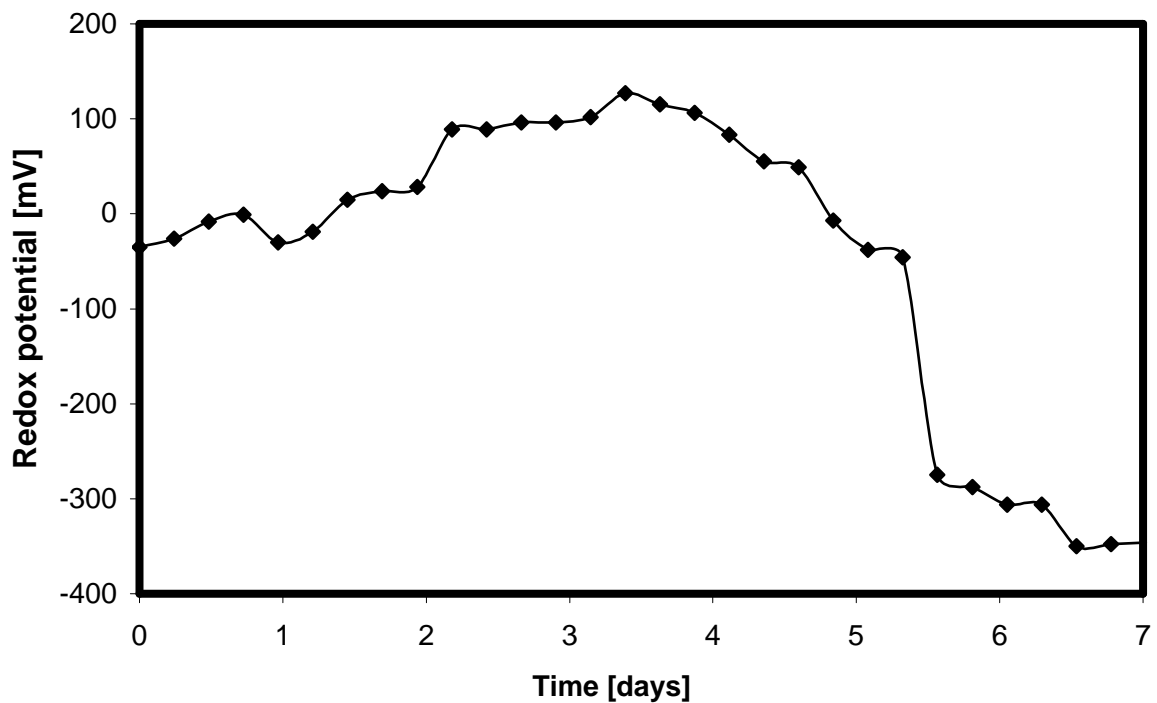


In **diagram 18** one can see the PH value during the testing.



**Diagram am 18: PH value during the testing**

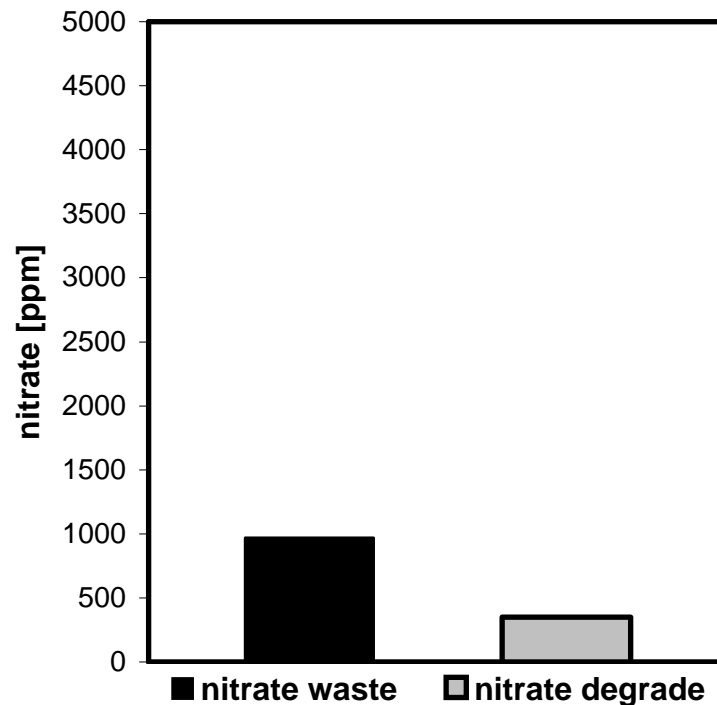
In **diagram 19** one can see the value of the redox potential during the testing.



**Diagram 19: redox potential during the testing**

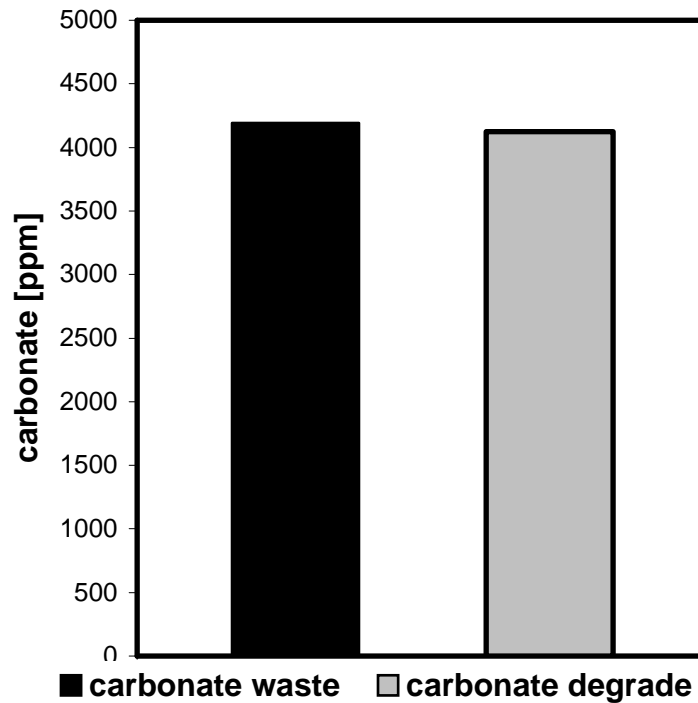
## 6.2.2 Waste water

In this part the values of the waste water before and after the test. Following nitrate, ammonium, carbonate and sulphide. This ions are building the nutrient for the bacteria. In **diagram 20** one can see the nitrate. Before the testing the value of the nitrate is **970 ppm** and after the testing the value is **350 ppm**.



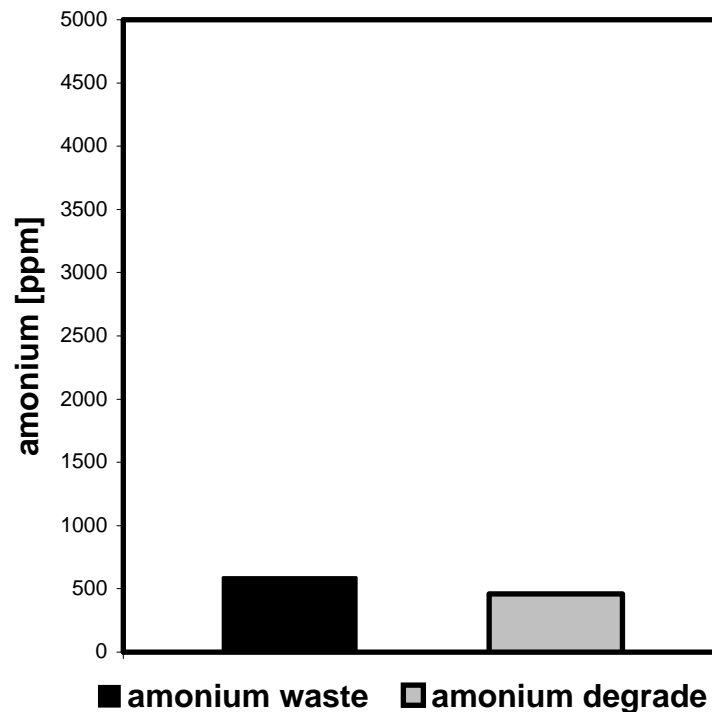
**Diagram 20:** comparing the nitrate in solution before and after the testing

In **diagram 21** one can see the amount of carbonate in ppm before and after the testing. The amount before the test is **4190 ppm** and after the test the amount is **4125 ppm**.



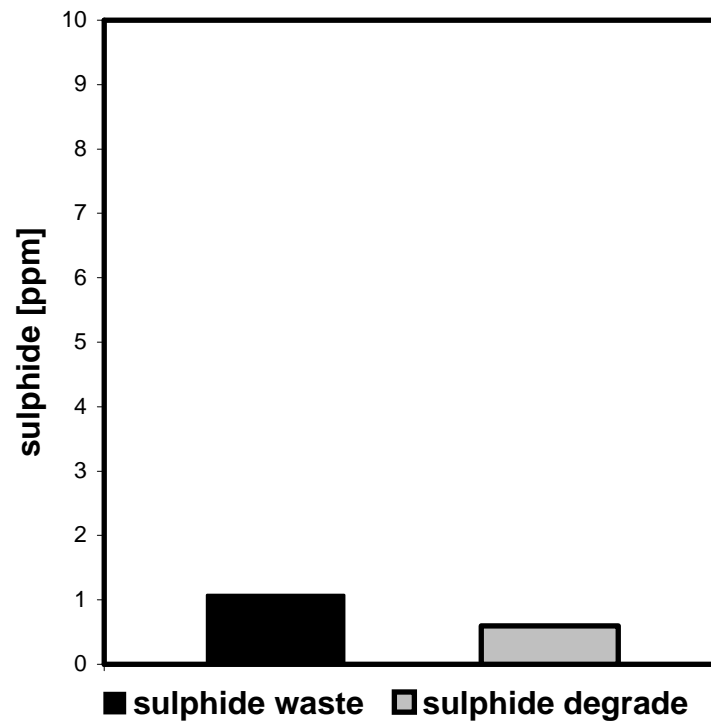
**Diagram 21:** comparing the carbonate in solution before and after the testing

In **diagram 22** one can see the amount of ammonium in ppm before and after the testing. The amount before the test is **590 ppm** and after the test the amount is **458 ppm**.



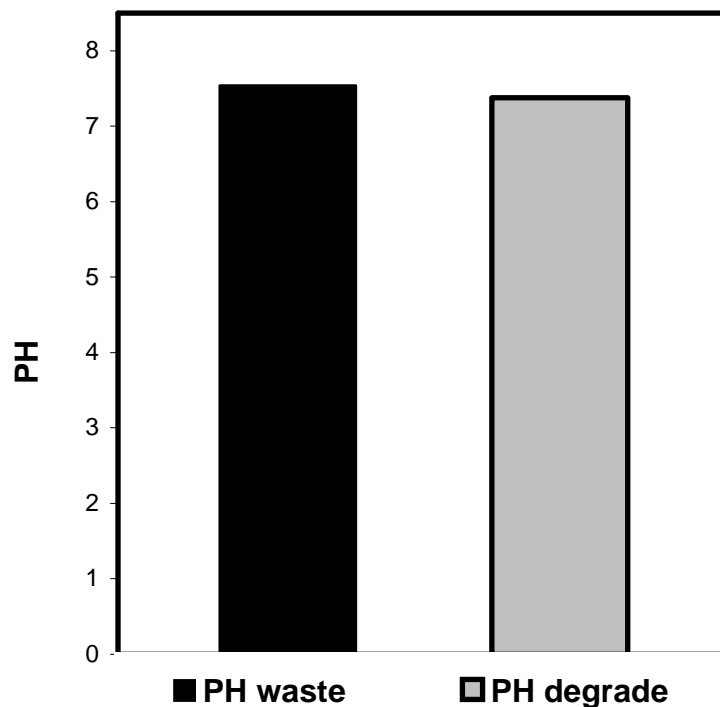
**Diagram 22:** comparing the ammonium in solution before and after the testing

In **diagram 23** one can see the amount of sulphide before and after the testing. In this case the scale has been changed because the value of the sulphide is too small for the normal used scale. The amount before the test is **1,08 ppm** and after the test the amount is **0,59 ppm**.



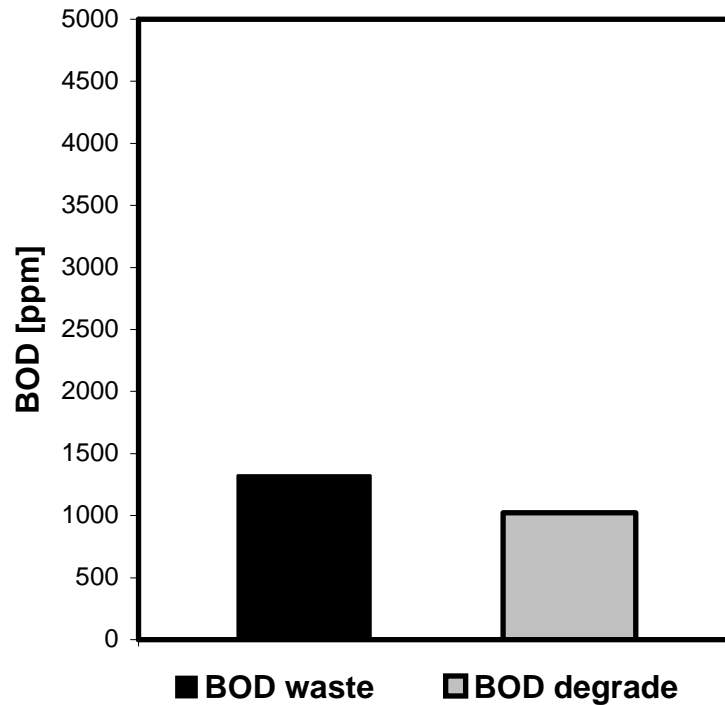
**Diagram 23:** comparing the sulphide in solution before and after the testing

In **diagram 24** one can see the value of the PH before and after the testing. The PH before the test is **7,54** and after the test the amount is **7,38**.



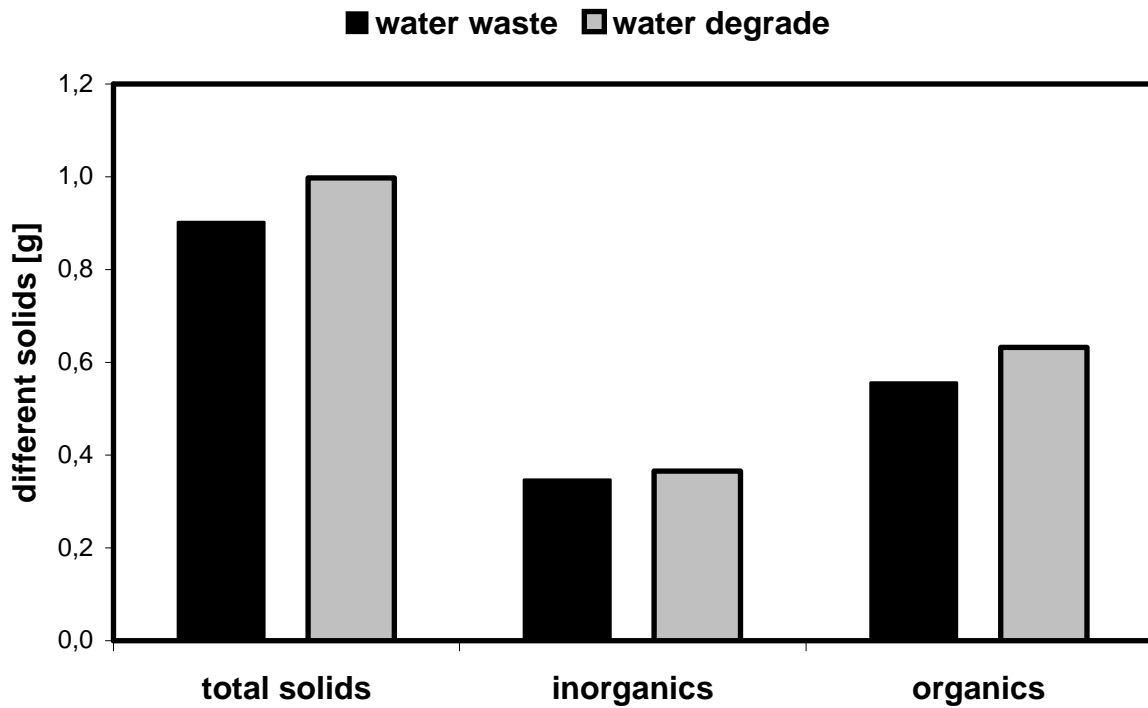
**Diagram 24:** comparing the PH before and after the testing

In **diagram 25** one can see the amount the biological oxygen demand ( BOD ) that gives information about the amount of the biodegradable substances in the wastewater before and after the test. The amount before the test is **1323 ppm** and after the test the amount is **1022 ppm**.



**Diagram 25:** comparing the BOD before and after the testing

In **diagram 26** one can see the amount of the solids in g. For the test 25ml wastewater have been taken. The amount of the total solids before the test is **0,833 g** and after the test it is **1,063 g**. The amount of the inorganics before the test is **0,327 g** and after the test it is **0,365 g**. The amount of the organics before the test is **0,506 g** and after the test it is **0,698 g**. The percentage of the total solids before the test is **3,4%** and after the test it is **4,3%**.



**Diagram 26:** comparing total solids, inorganics and organics before and after the testing

### 6.2.3 Discussion

In this part some analyse about the data shown in chapter 6.2. In **diagram 14** one can see the amount of gas produced every day divided with the amount of gas produced during the whole test. One can see that on the first day the amount of gas produced is higher, than at the following days. Also one can see the tests which have been done and on what day the tests have been done. In **table 7** one can see the 10 Tests have been done with the corresponding composition. Also one can see at what day the tests have been done and the volume of each of the tests in ml. Between the tests there are small differences in the composition. In **diagram 15** one can see the mean of the data from **table 7**. To make the analyse of the biogas it is better to use the following **table 8** and **diagram 16**. In **diagram 15** and **table 7** there is still an error because of the air, which came into the apparatus during the tests. The tests have been corrected with the composition of the air ( 78% nitrogen and 21% oxygen). In **table 8** one can see the composition of the biogas corrected. In the tests one can see that the amount of the hydrogen is quite high at the beginning and the CO<sub>2</sub> is quite high at the end. The methane is the most in the middle of the process. This differences result of, how the test has been done, which is explained at the beginning of chapter 6 and out of the different density of the gases. Hydrogen is the lightest gas so it is more located on the top of the tube. CO<sub>2</sub> is the heaviest gas and more located on the bottom of the tube. In the tests one can see this fact. Also there are every time fluctuation in the tests because of the different time left between the tests, the different amount and composition of the biogas produced during the test. In test 2 the percentage of the methane is quite high. In test 4 the amount of the CO<sub>2</sub> is high compared with the other tests. In **diagram 16** one can see the percentage of biogas without the air. One can see the amount of hydrogen is quite high. If the time of staying is longer, the degradation is better <sup>[18]</sup>. At a later point of the degradation when the CO<sub>2</sub> emitting hydrolyses is nearly over, a lot of methane is produced and so on a Biogas with a higher energy amount. In this case the waste water is already degraded in the water treatment plant. Also when the initial material is quite fluid more CO<sub>2</sub> is soluted in the water and the amount of CO<sub>2</sub> is lower <sup>[19]</sup>. The amount of CO<sub>2</sub> is quite low and as a consequence the amount of hydrogen is higher. In **diagram 17** one can see the composition of the biogas in ml. In all tests an amount of 1470 ml of biogas is produced. To use the waste water for industrial energy production the amount is not enough but for the own consumption of the waste water treatment plant it is every time useful.

In **diagram 20,21,22 and 23** one can see the amount of nitrate, sulphide, carbonate and ammonium before and after the testing. The amounts are quite the same at in the test shown in chapter 6.1. With 1.08 ppm sulphide and 590 ppm ammonium the components are not inhibitant for the process. For further informations look up chapter 5.

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The BOD **diagram 25** is also higher before the test then afterwards like expected because of previous test. For further information look up chapter 6.1.

In **diagram 26** one can see the amount of the solids before and after the test. Like in the previous test the amount is more after the testing then before. For the explanation look up chapter 6.1.

The PH **diagram 18** is more or less in the optimum range only at the beginning it is a little bit too high and in the middle of the test it's a little bit to low with PH 6.6 to 6.1 . In the theory they say the optimum is between 7 up to 7,5<sup>[20]</sup>. In my case the PH starts at 7,54 and ends at the 7,38. The explanation of the fluctuation is the Ph depends on how much oxygen is transported into the system. Normally when the redox potential falls and as a consequence the amount of oxygen decrease the PH arises. For further information's look up chapter 6.1

The optimum of the redox potential **diagram 19** normally in the theory is between  $-300$  and  $-330$ <sup>[21]</sup> but the process works also at higher levels. In my case the redoxpotential starts at  $-36$  mV and ends at  $-346$  mV. In the middle it's till 106. The explanation is that at the beginning there is oxygen in the reactor . Till this oxygen is not processed the redox potential arises. Later the redox potential falls till  $-346$  mV. This fact one can see in the diagram.

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## 6.3 Test 3

### 6.3.1 Produced gas

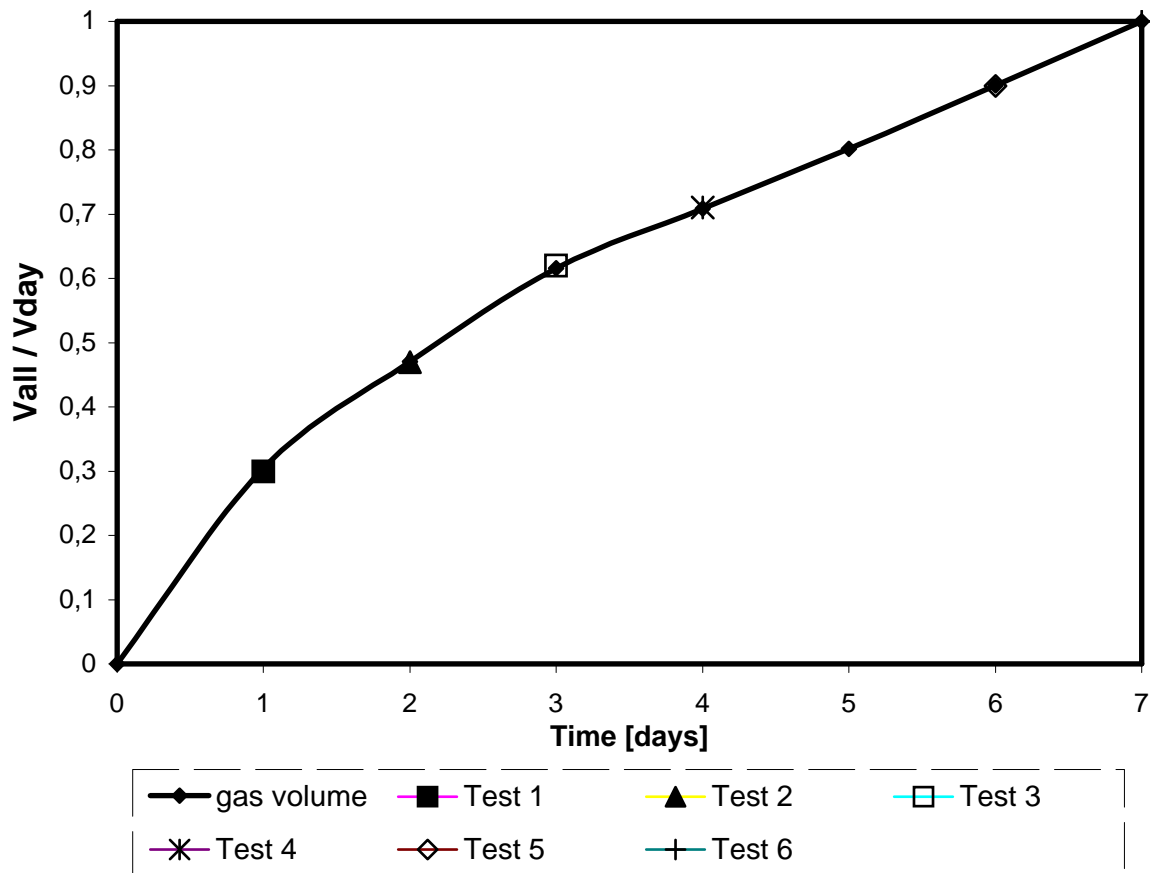
In this part of my work something about the results of my tests. In **table 9** one can see the amount of produced gas in ml at every day during the testing. In the third line the volume of every day is divided with the whole amount of the volume, which is **755 ml**. For the testing **2,5 l** of wastewater was taken. The test was made at a temperature of 35 degrees

|   |   |      |      |      |      |      |      |    |
|---|---|------|------|------|------|------|------|----|
| <b>Time [days]</b>                                | 0 | 1    | 2    | 3    | 4    | 5    | 6    | 7  |
| <b>Volume [ml]</b>                                | 0 | 230  | 125  | 110  | 70   | 70   | 75   | 75 |
| <b><math>V_{\text{day}}/V_{\text{all}}</math></b> | 0 | 0,30 | 0,47 | 0,62 | 0,71 | 0,80 | 0,90 | 1  |

**Table 9:** composition of the measured biogas corrected

In the following tables test is used for single measurements which are performed at certain days.

In **diagram 27** one can see the volume of the produced biogas. The biogas, which is produced every day, is divided with the whole amount of biogas and the individual results per day are mount up to 1.

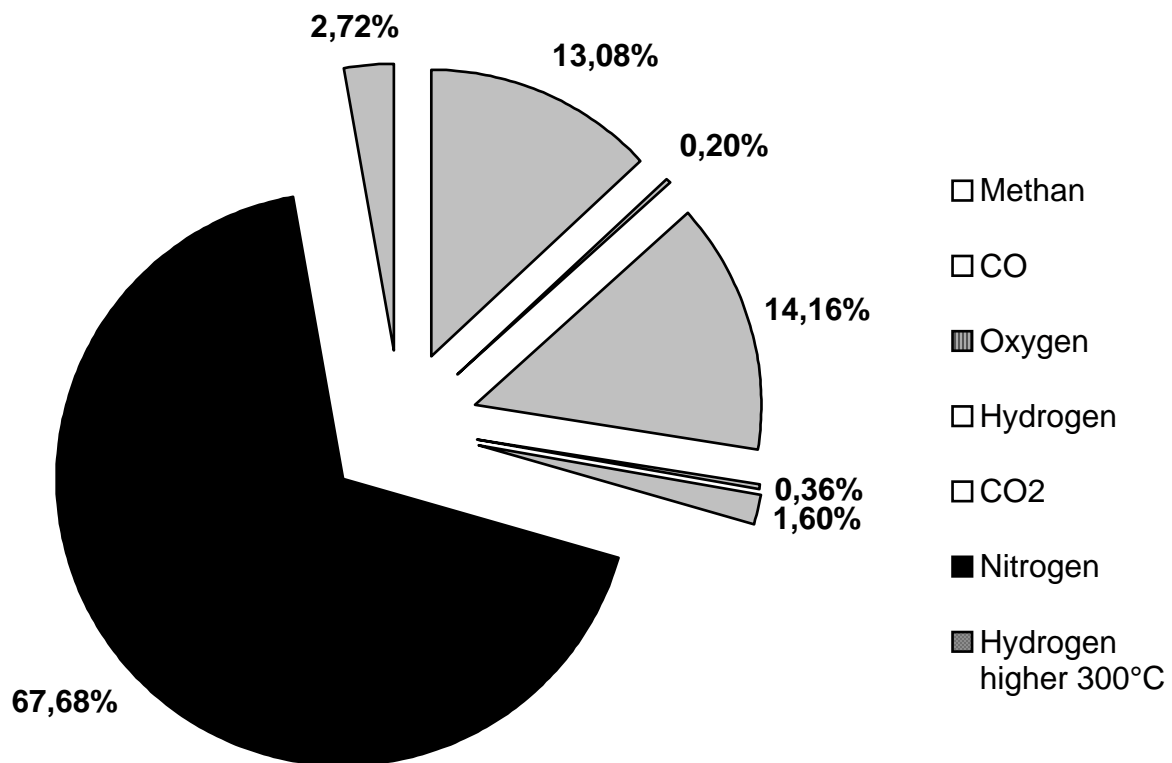


**Diagram 27:** Mount of the produced Biogas with the individual tests

**Table 10** shows 6 tests of the gas with the main components. In this table there is a mistake because of the air, which was coming in the reactor during the tests. The time is the time when the tests were made. The volume is the amount of gas which has been taken for every measuring of the gas.

| Components      | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | Test 6 | mean         |
|-----------------|--------|--------|--------|--------|--------|--------|--------------|
| Methane         | 7,40%  | 9,00%  | 9,00%  | 15,80% | 9,00%  | 15,20% | <b>10,9%</b> |
| Oxygen          | 16,40% | 10,40% | 13,80% | 8,60%  | 13,80% | 7,80%  | <b>11,8%</b> |
| CO              | 0,20%  | 0,40%  | 0,00%  | 0,00%  | 0,00%  | 0,40%  | <b>1,0%</b>  |
| Hydrogen        | 0,40%  | 5,80%  | 2,20%  | 1,60%  | 1,60%  | 3,80%  | <b>2,6%</b>  |
| CO <sub>2</sub> | 0,60%  | 2,20%  | 1,00%  | 1,80%  | 0,60%  | 1,80%  | <b>1,3%</b>  |
| Nitrogen        | 75,00% | 72,2%  | 74,00% | 82,2%  | 75,00% | 71,00% | <b>74,9%</b> |
| Time [days]     | 1      | 2      | 3      | 4      | 6      | 7      |              |
| Volume          | 105    | 125    | 110    | 70     | 75     | 75     |              |

**Table 10:** composition of the measured biogas

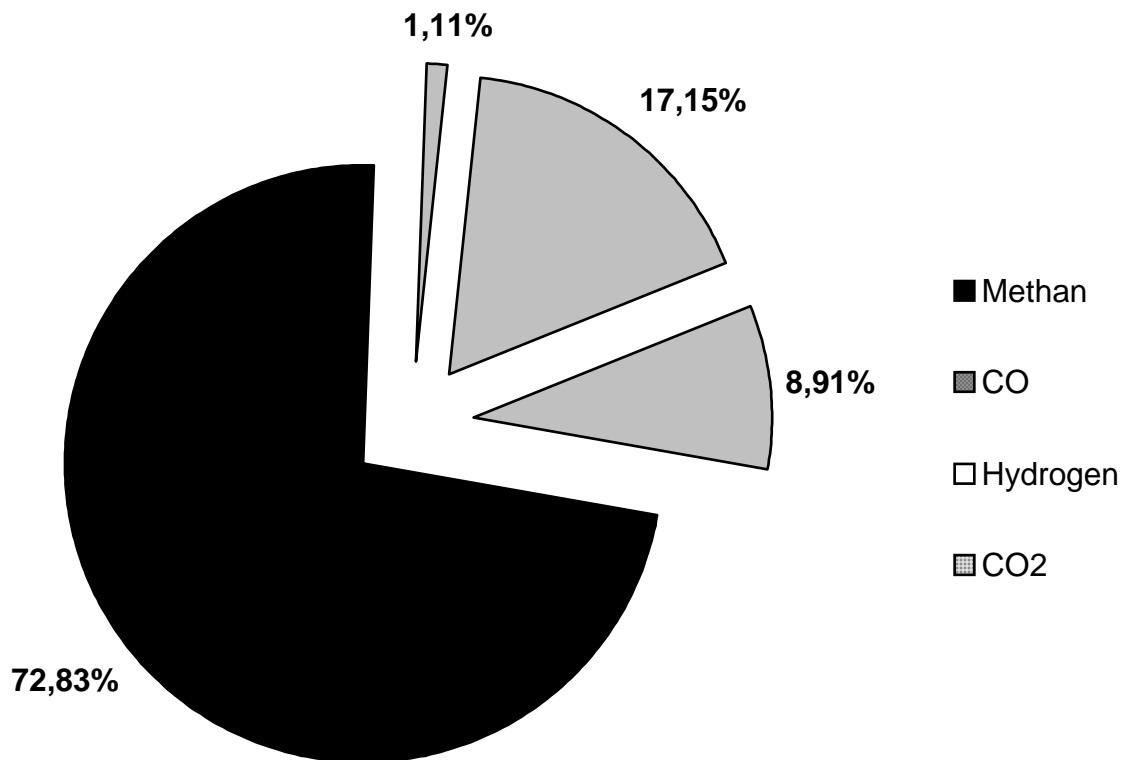


**Diagram 28:** composition of the biogas

In **table 11** the volumes have been corrected with the average composition of air (78% nitrogen, 21% oxygen). Only the amount of nitrogen and oxygen has been corrected. The result was that now oxygen and nitrogen disappear in the biogas

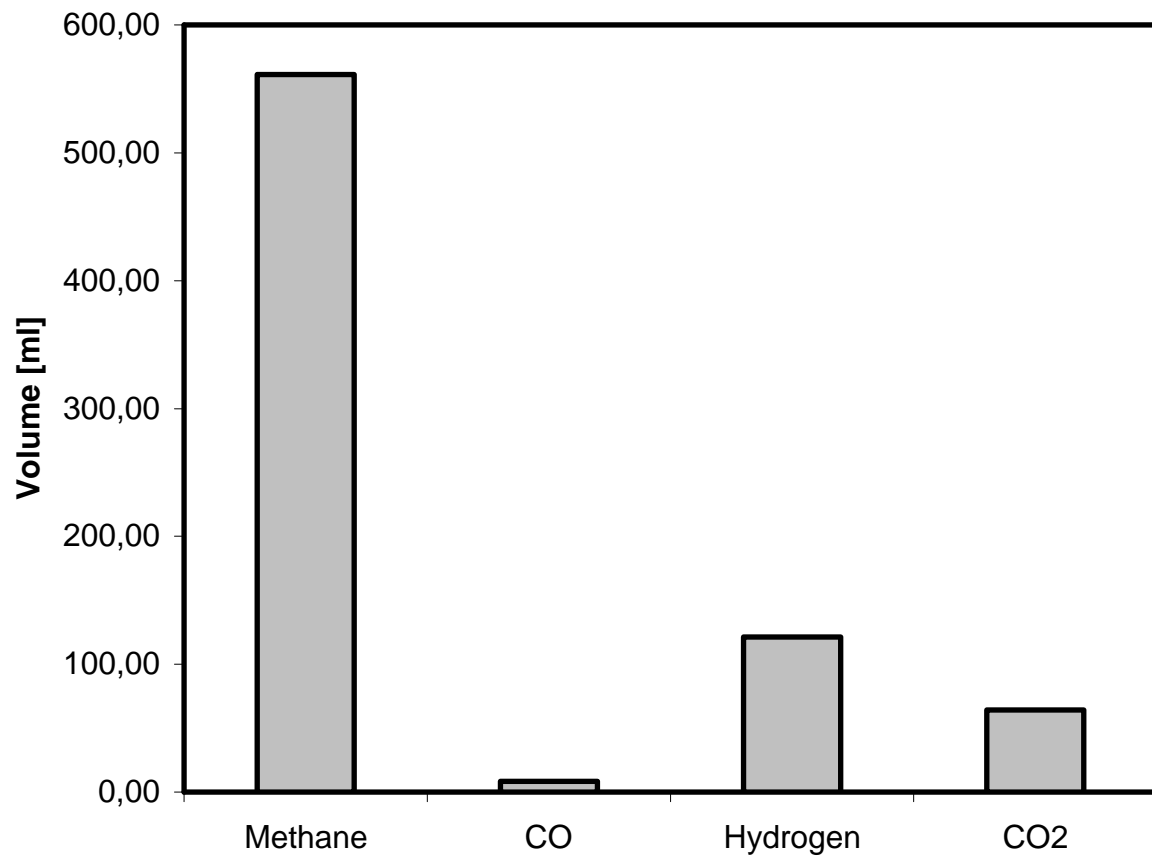
| Components  | Test 1 | Test 2 | Test 3 | Test 4 | Test 5 | Test 6 | mean         |
|-------------|--------|--------|--------|--------|--------|--------|--------------|
| Methane     | 86,1%  | 51,7%  | 73,8%  | 82,3%  | 80,4%  | 71,7%  | <b>74,3%</b> |
| CO          | 2,3%   | 2,3%   | 0,00%  | 0,00%  | 0,00%  | 1,9%   | <b>1,1%</b>  |
| Hydrogen    | 4,7%   | 33,3%  | 18%    | 8,3%   | 14,3%  | 17,9%  | <b>16,1%</b> |
| CO2         | 7%     | 12,6%  | 8,2%   | 9,4%   | 5,4%   | 8,5%   | <b>8,5%</b>  |
| Time [days] | 1      | 2      | 3      | 4      | 6      | 7      |              |
| Volume      | 105    | 125    | 110    | 70     | 75     | 75     |              |

**Table 11:** composition of the measured biogas

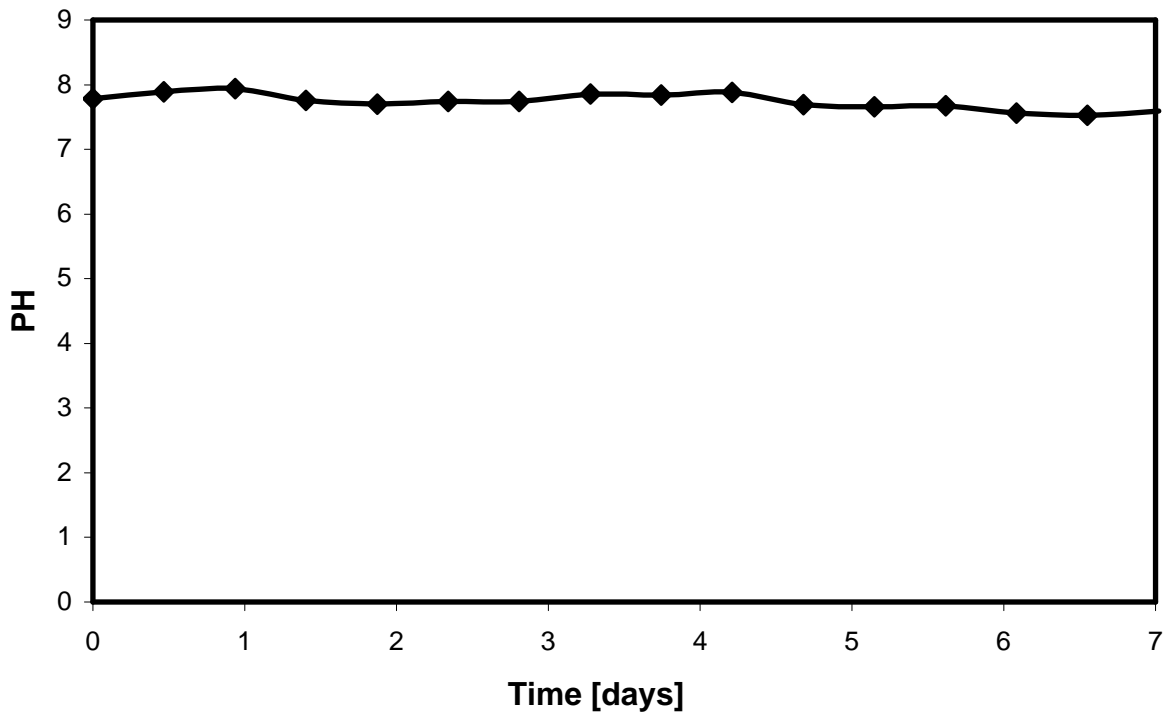


**Diagram 29:** composition of the biogas minus the oxygen and the nitrogen

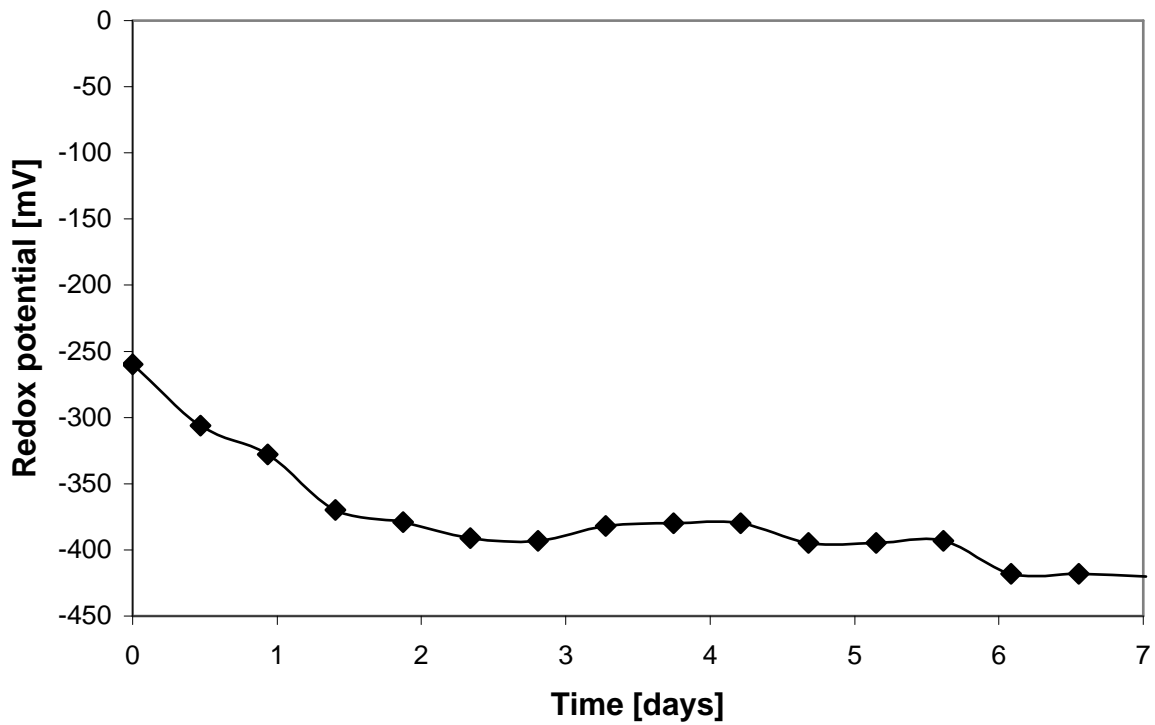
In **diagram 30** one can see the composition of the biogas in ml.



**Diagram 30:** composition of the biogas in ml



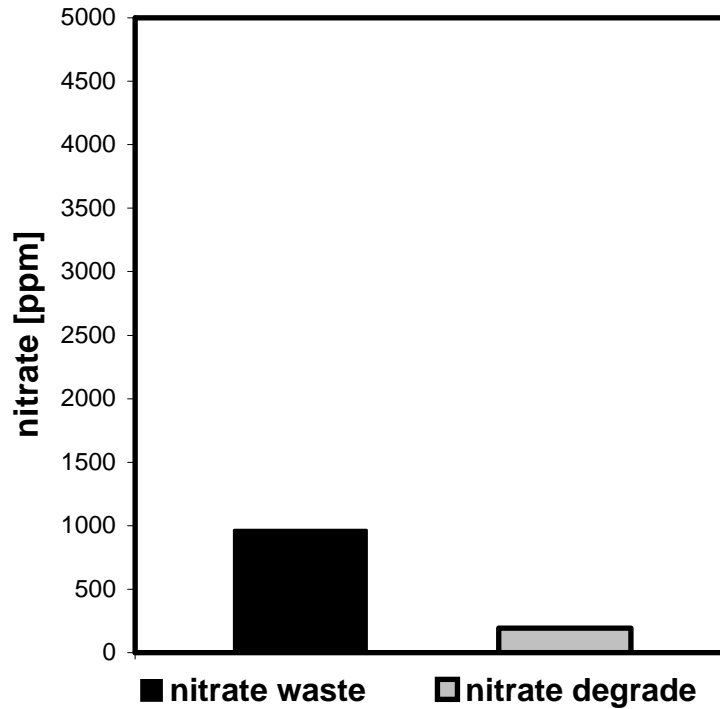
**Diagram 31:** PH value during the testing



**Diagram 32:** redox potential during the testing

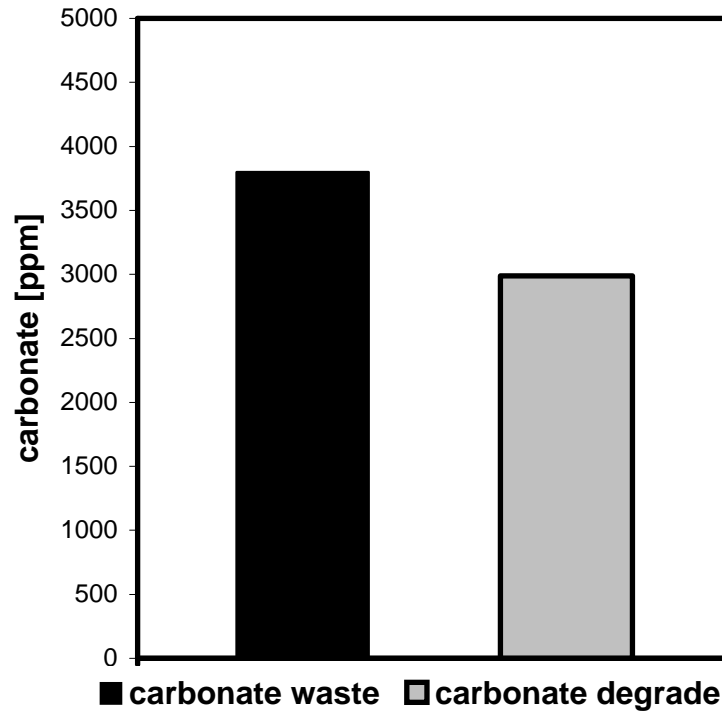
### 6.3.2 Waste water

In this part the values of the waste water before and after the test. Following nitrate, ammonium, carbonate and sulphide. These ions are building the nutrient for the bacteria. In **diagram 33** one can see the nitrate. Before the testing the value of the nitrate is **965 ppm** and after the testing the value is **192 ppm**.



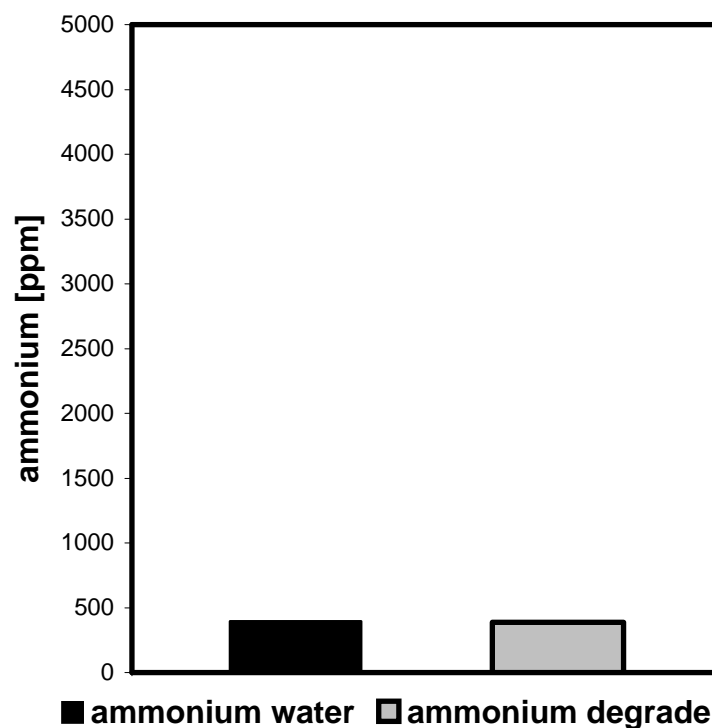
**Diagram 33:** comparing the carbonate in solution before and after the testing

In **diagram 34** one can see the amount of carbonate in ppm before and after the testing. The amount before the test is **3800 ppm** and after the test the amount is **2990 ppm**.



**Diagram 34:** comparing the carbonate in solution before and after the testing

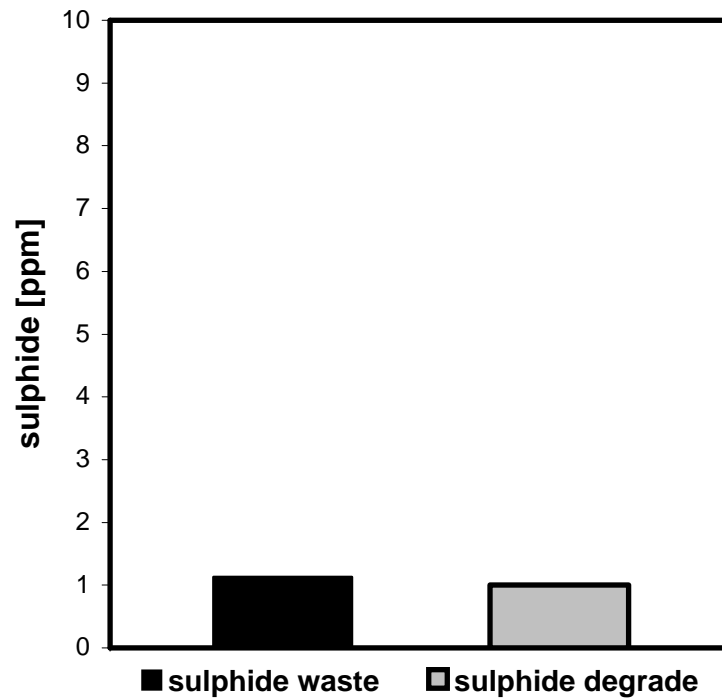
In **diagram 35** one can see the amount of ammonium in ppm before and after the testing. The amount before the test is **397 ppm** and after the test the amount is **388 ppm**.



**Diagram 35:** comparing the ammonium in solution before and after the testing

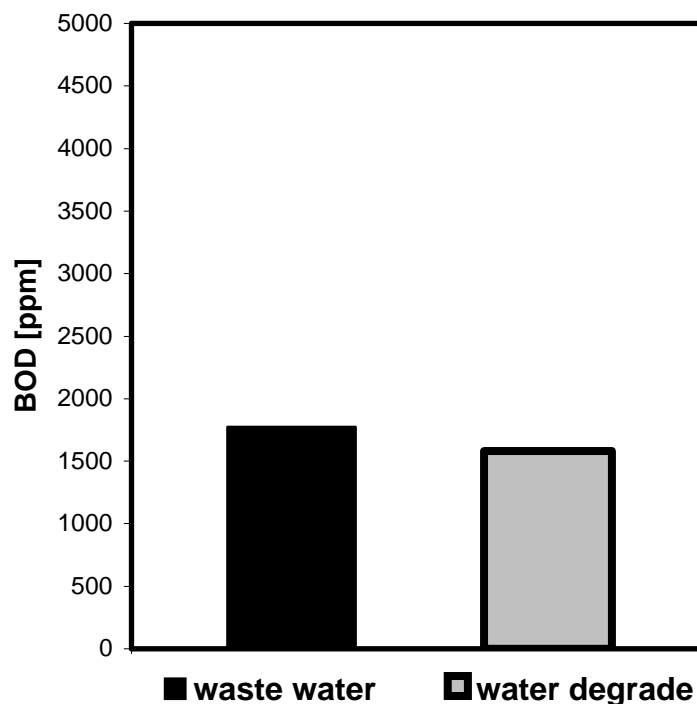


In **diagram 36** one can see the amount of sulphide before and after the testing. In this case the scale has been changed because the value of the sulphide is too small for the other scale. The amount before the test is **1,128 ppm** and after the test the amount is **1,005 ppm**.



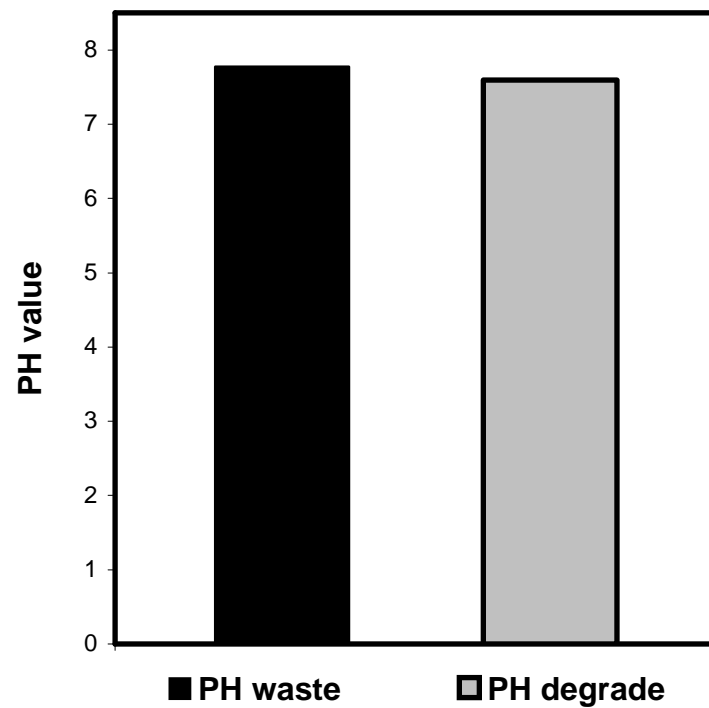
**Diagram 36:** comparing the sulphide in solution before and after the testing

In **diagram 37** one can see the amount the biological oxygen demand ( BOD ) that gives information about the amount of the biodegradable substances in the wastewater before and after the test. The amount before the test is **1773 ppm** and after the test the amount is **1582 ppm**.



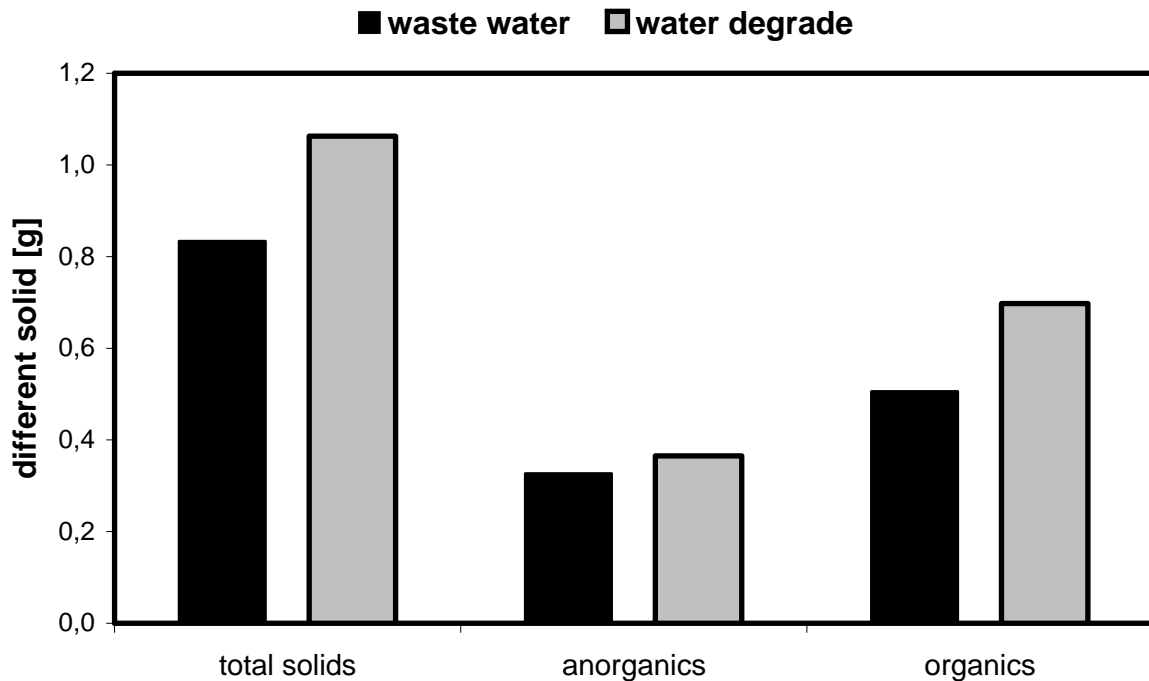
**Diagram 37:** comparing the BOD before and after the testing

In **diagram 38** one can see the value of the PH before and after the testing. The PH before the test is **7,78** and after the test the amount is **7,59**.



**Diagram 38:** comparing the PH before and after the testing

In **diagram 39** one can see the amount of the solids in g. For the test 25ml wastewater have been taken. The amount of the total solids before the test is **0,903 g** and after the test it is **0,998 g**. The amount of the inorganics before the test is **0,347 g** and after the test it is **0,366 g**. The amount of the organics before the test is **0,556 g** and after the test it is **0,632 g**. The percentage of the total solids before the test is **3,6%** and after the test it is **3,99%**.



**Diagram 39:** comparing total solids, inorganics and organics before and after the testing

### 6.3.3 Discussion

In this part some analyse about the data shown in chapter 5.3. In **diagram 27** one can see the amount of gas produced every day divided with the amount of gas produced during the whole test. One can see that at the first day the amount of gas produced is higher than at the following days. Also one can see the tests which have been done and on what day the tests have been done. In **table 9** one can see the 6 Tests which have been done with the corresponding composition. Also one can see at what day the tests were made and the volume of each of the tests in ml. The compositions of the tests are all quite the same. In **diagram 28** one can see the mean of the data in **table 10**. To make the analyse of the biogas it is better to use the following **table 11** and **diagram 29**. In **diagram 28** and **table 10** there is still an error because of the air, which came into the apparatus during the tests. The tests have been corrected with the composition of the air ( 78% nitrogen and 21% oxygen). In **table 11** one can see the composition of the biogas corrected. In the tests one can see the composition of the gas is in all the tests quite the same. Only the hydrogen in the 2<sup>nd</sup> test is much higher than in the other tests and in the first test the percentage of the hydrogen is very low. The fact is, it have been took 2 tests on the first day but the quality of the first test was not satisfying. Test 1 was the second test on the first day. This differences result of, how I did the test, which is explained at the beginning of chapter 6 and out of the different density of the gases. Hydrogen is the lightest gas so it is more located on the top of the tube. CO<sub>2</sub> is the heaviest gas and more located on the bottom of the tube. In the tests one can see this fact. Also there are every time fluctuation in the tests because of the different time left between the tests, the different amount and composition of the biogas produced during the test. In **diagram 29** one can see the percentage of biogas without the air. One can see the amount of hydrogen is quite high. If the time of staying is longer, the degradation is better <sup>[22]</sup>. At a later point of the degradation when the CO<sub>2</sub> emitting hydrolyses is nearly over, a lot of methane is produced and so on a Biogas with a higher energy amount. In my case the waste water is already degraded more than in the test before but one can see the composition is quite the same than in the test before. Also when the initial material is quite fluid more CO<sub>2</sub> is soluted in the water and the amount of CO<sub>2</sub> is lower <sup>[23]</sup>. The amount of CO<sub>2</sub> is quite low and as a consequence the amount of hydrogen is higher. In **diagram 30** one can see the composition of the biogas in ml. In all tests an amount of **755 ml** of biogas is produced. To use the waste water for industrial energy production the amount is not enough but for the own consumption of the waste water treatment plant it is every time useful.

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In **diagram 33,34,35 and 36** one can see the amount of nitrate, sulphide, carbonate and ammonium before and after the testing. The amounts are quite the same as in the test shown in chapter 6.1. With 1.13 ppm sulphide and 397 ppm ammonium the components are not inhibitant for the process. For further information's look up chapter 6.

The BOD **diagram 25** is also higher before the test then afterwards like expected because of previous test. For further information look up chapter 6.1.

The PH **diagram 38** is during the whole test a little bit high when one compares it with the theory. In the theory they say the optimum is between 7 up to 7,5<sup>[24]</sup>. In my case the PH starts at 7,78 and ends at the 7,59.

The optimum of the redox potential **diagram 32** normally in the theory is between  $-300$  and  $-330$ <sup>[25]</sup> but the process works also at higher levels. In my case the redoxpotential starts at  $-260$  mV and ends at  $-418$  mV. The increasing of the redoxpotential effects, because at the beginning there is oxygen in the reactor. Oxygen is an oxidant like sulphide and nitrate. When there is oxygen in the system the redoxpotential increase. It is not possible in a discontinues process to eliminate all the oxygen. I tried to fill up the reactor totally with wastewater to minimize the amount of oxygen but still there is oxygen. This oxygen one can see in the diagram.

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## 7 Conclusion

The objective was to build up an apparatus with existing components to test the production of biogas out of waste water. Afterwards tests should be done and the gas and the water should be characterized. With the data of the water and the gas together the process should be analysed.

The result of the work was an apparatus with a simple test set-up. The apparatus captivate through fast testing with sufficient exact results to analyse the gas. With the additional measured parameter of the waste water interesting conclusion about the process could be done. To measure the gas no computer or complicated computer programs are necessary. The costs for the tests are low but results are practical.

The apparatus consists out of a 2.5 litre gas chamber which is the reactor where the gas is produced. To measure the volume a glass tube is used. The principle is that the gas displaces the water in the tube chapter 3.3. The gas is measured with an apparatus for complete gas analyses. The apparatus use the absorption to characterize the gas. With the corresponding chemical every component in the gas is absorbed and the difference of the amount is measured and ground off 100%. Only nitrogen is not absorbed because it is inert and stays in the apparatus. The  $\text{CH}_4$  is oxidized to  $\text{CO}_2$  and afterwards absorbed.

The three tests are all made at a temperature of 35 degrees. The results out of the three tests are that at the beginning of the process the amount of the produced gas is higher. At the beginning it needs a little time till the number of the bacteria arise and process starts. The tests are showing a small amount of  $\text{CO}_2$  in the biogas compared with the literature. The amount of  $\text{H}_2$  in the gas is quite high when one compares it with the literature. The amount of methane is also quite high like it is desired. The difference to the literature comes because the waste water I got from a water treatment plant neat Valencia is already degraded till an unknown state. The other measured parameters like nitrate, sulphide, ammonium and carbonate are like expected. The amount is less after the process because these components are working more or less as nutrient for the bacterium. The  $\text{BOD}_{\text{which}}$  was also measured gives information how many biodegradable components are in the water. The biodegradable components are less after the process than before the test. That's normal because the anaerobe fermentation is a process where certain components of the water are degraded in biological way without air like in the anaerobe fermentation. The redox potential and the PH are measured during the process. The redox potential gives information about how anaerobe the process is and the PH gives information about if the process is stable or not. In the tests one can see that the PH and the redox are linked in a certain way. In the process the redox potential is at the beginning higher than at the end because the process uses the oxygen to produce gas and so the process gets more anaerobe. There is a light acidification in the process one can see at the PH value. Also the total solids, the organics and the inorganics were measured. The solids are more after the process because the number of bacteria increases during the process.

In the future a mass balance of the reactor should be performed. That's to check how far the reality is away from the theory. Also the problematic with the air which comes into the reactor is still not solved perfectly. It could be favourably to change into continuous testing to eliminate the air which is in the reactor at the beginning of the testing but than it is not possible anymore to make a balance. For the measuring of the PH and the redox potential it would be favourable to afford a recording with the computer. When a process needs 7 days like in my case it would be much easier to control the process. Also the process factors like the temperature could be varied in further testing. The using of different waters would also be interesting.

## 8 Annex

### 8.1 Water before Test 1

| Solids water waste   |               |               |               |              |              |              |               |        |
|----------------------|---------------|---------------|---------------|--------------|--------------|--------------|---------------|--------|
| Water waste 06.05.07 | 1             | 2             | 3             | 4            | Total solid  | Inorganics   | Organics      | Humid  |
|                      | 36,275        | 61,087        | 36,9876       | 36,547       | 0,712        | 0,272        | 0,440         | 24,812 |
|                      | 37,512        | 62,216        | 38,2355       | 37,798       | 0,724        | 0,286        | 0,438         | 24,704 |
|                      | 30,909        | 55,752        | 31,638        | 31,192       | 0,730        | 0,283        | 0,446         | 24,844 |
|                      | Mean          |               |               |              |              |              |               |        |
| <b>34,898</b>        | <b>59,685</b> | <b>35,620</b> | <b>35,179</b> | <b>0,722</b> | <b>0,281</b> | <b>0,441</b> | <b>24,787</b> |        |

**Table 11:** solids in the wastewater before the test

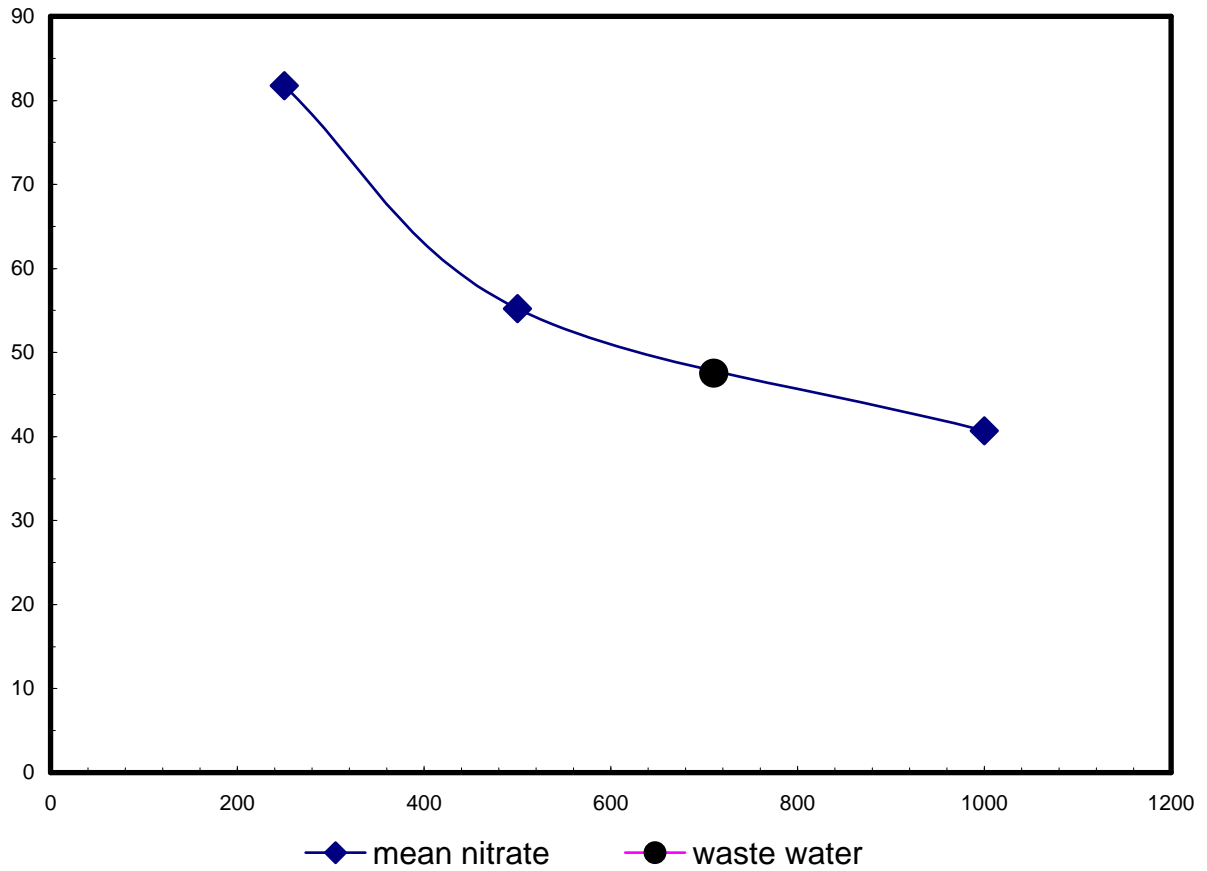
| PH            |       |       |       |       |               |
|---------------|-------|-------|-------|-------|---------------|
| Measured data |       |       |       |       | Mean          |
| 7,945         | 7,951 | 7,967 | 7,964 | 7,979 | <b>7,9611</b> |

**Table 12:** PH of the wastewater before the test

| Nitrate          |               |      |      |      |      |             |
|------------------|---------------|------|------|------|------|-------------|
| ppm              | Measured data |      |      |      |      | Mean [mV]   |
| <b>1000</b>      | 42,6          | 41,9 | 43,6 | 37,1 | 38,1 | <b>40,7</b> |
| <b>500</b>       | 52,4          | 58   | 52,5 | 57,4 | 55,7 | <b>55,2</b> |
| <b>250</b>       | 74,3          | 80,4 | 83,5 | 84,1 | 86,6 | <b>81,8</b> |
| Nitrate degraded |               |      |      |      |      |             |
| <b>315</b>       | 54,9          | 45,5 | 54,9 | 45,5 | 36,9 | <b>47,5</b> |

**Table 13:** calibration and amount of nitrate before the test

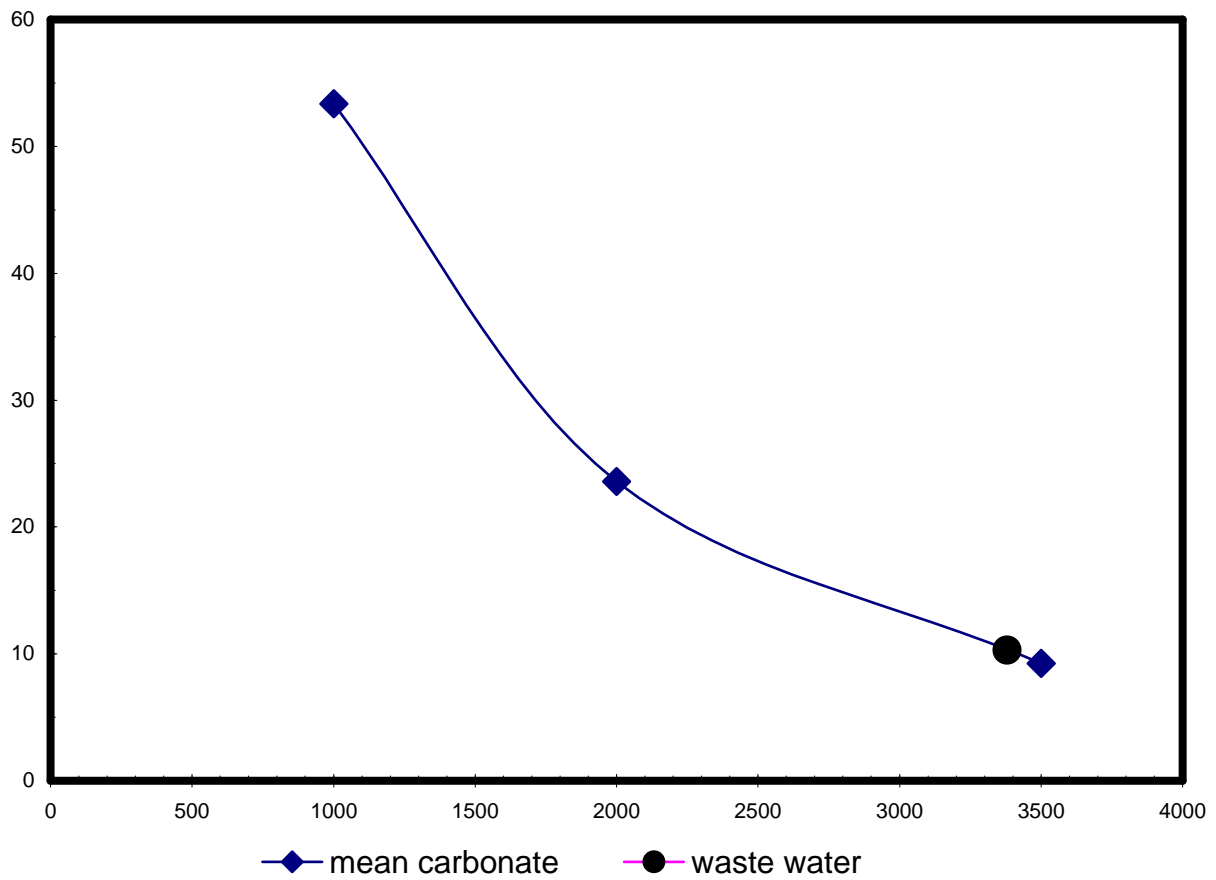




**Diagram 40:** calibration curve and determination of the ppm

| Carbonate         |               |      |      |      |      |           |
|-------------------|---------------|------|------|------|------|-----------|
| ppm               | Measured data |      |      |      |      | Mean [mv] |
| 1000              | 59,3          | 56,9 | 52,7 | 50   | 47,8 | 53,3      |
| 2000              | 23,5          | 21,3 | 23,8 | 24,1 | 25,2 | 23,6      |
| 3500              | 3,9           | 6,1  | 8,6  | 10,2 | 17,5 | 9,3       |
| Carbonate degrade |               |      |      |      |      |           |
| 3380              | 10,6          | 14,4 | 9,4  | 10,4 | 6,8  | 10,3      |

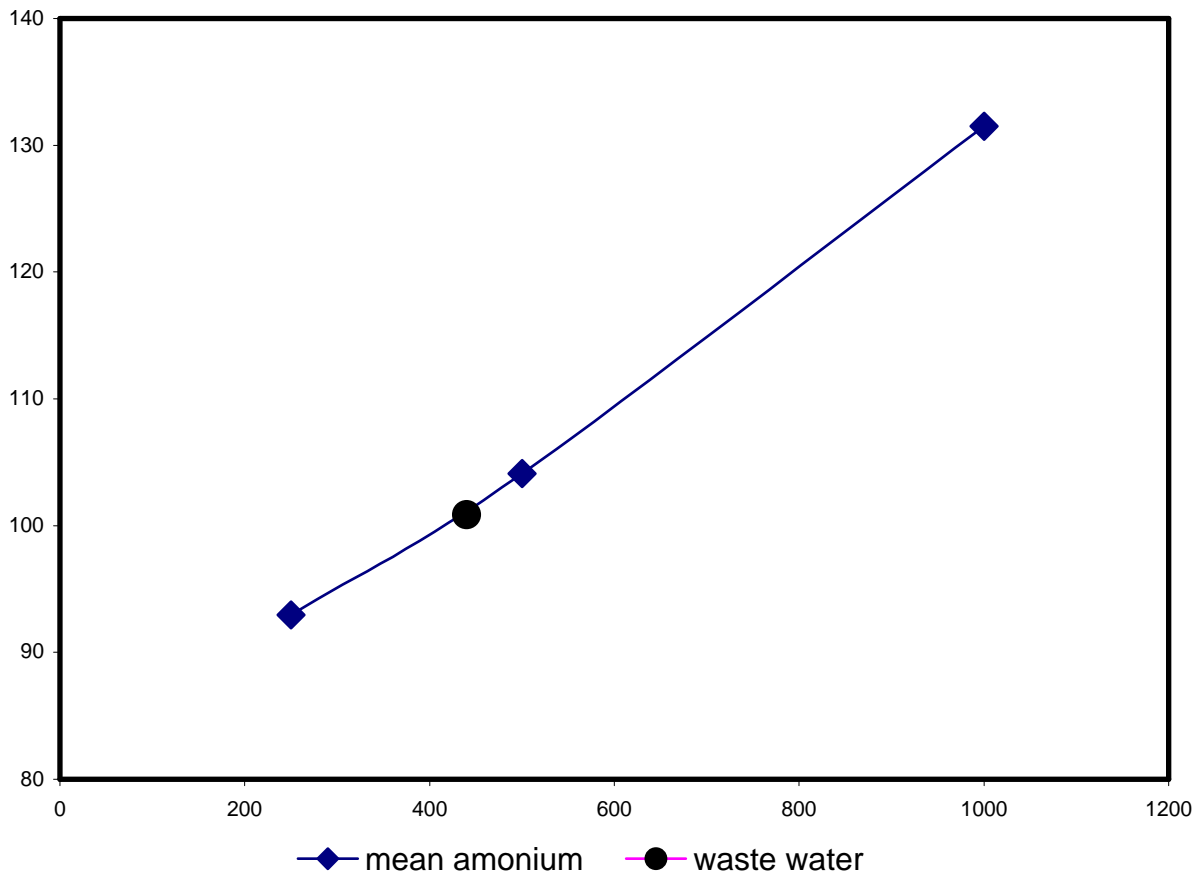
**Table 14:** calibration and amount of carbonate before the test



**Diagram 41:** calibration curve and determination of the ppm

| Ammonium         |               |       |       |       |       |           |
|------------------|---------------|-------|-------|-------|-------|-----------|
| ppm              | Measured data |       |       |       |       | Mean [mV] |
| 1000             | 133,2         | 132,8 | 131,1 | 130,5 | 129,8 | 131,5     |
| 500              | 102,2         | 103,3 | 104,1 | 105,2 | 105,7 | 104,1     |
| 250              | 92,1          | 92,2  | 93,1  | 93,7  | 93,8  | 93        |
| Ammonium degrade |               |       |       |       |       |           |
| 440              | 108,1         | 101,3 | 100,1 | 97,9  | 97    | 100,9     |

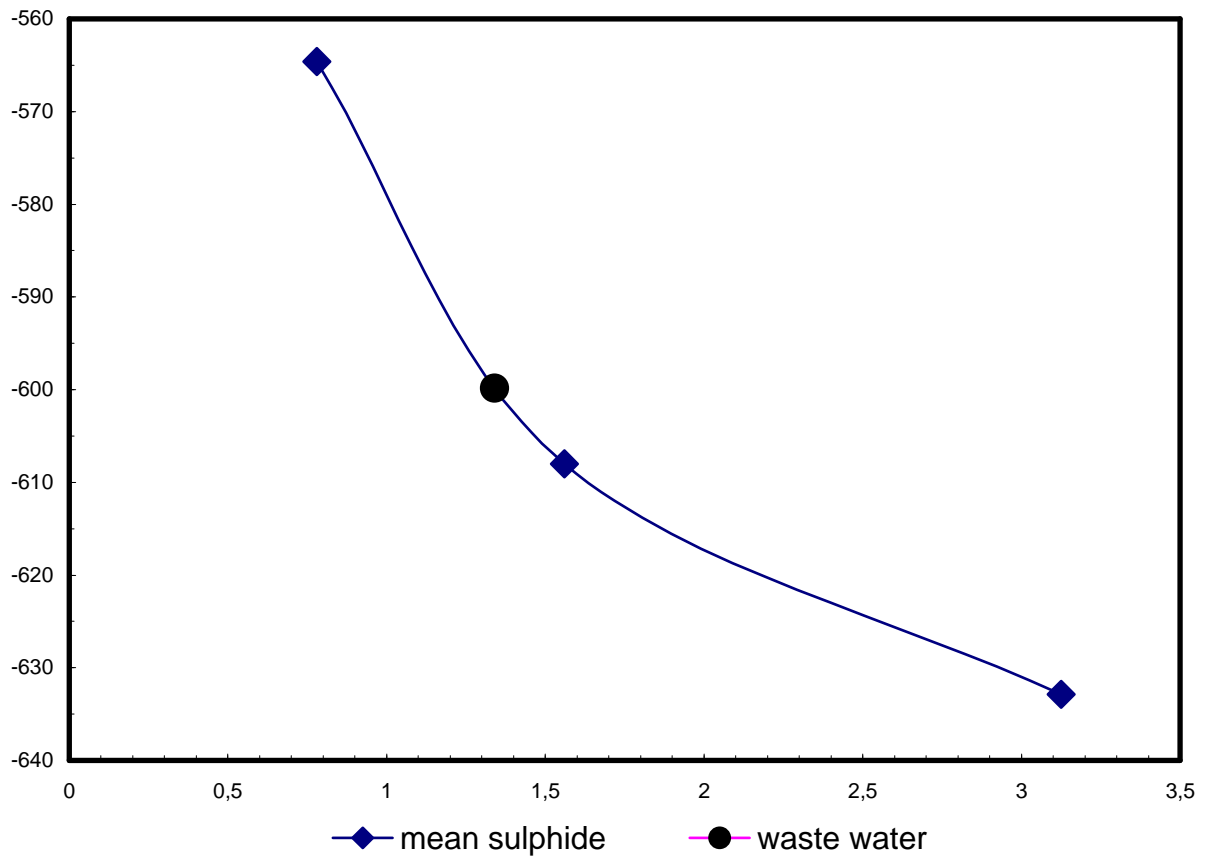
**Table 15:** calibration and amount of ammonium before the test



**Diagram 42:** calibration curve and determination of the ppm

| Sulphide          |               |        |        |        |        |           |
|-------------------|---------------|--------|--------|--------|--------|-----------|
| ppm               | Measured data |        |        |        |        | Mean [mV] |
| 3,1               | -620,1        | -629,6 | -637   | -638,3 | -639,4 | -632,8    |
| 1,7               | -604,2        | -610,8 | -609,6 | -611,1 | -604,4 | -608,0    |
| 0,8               | -560          | -559,7 | -565,3 | -568,6 | -569,4 | -564,6    |
| Sulphide degraded |               |        |        |        |        |           |
| 1,3               | -604,7        | -600,3 | -592,9 | -594,7 | -606,6 | -599,8    |

**Table 16:** calibration and amount of sulphide before the test



**Diagram 43:** calibration curve and determination of the ppm

|                    |      |      |                    |      |      |
|--------------------|------|------|--------------------|------|------|
| <b>50 07.05.07</b> |      |      | <b>20 07.05.07</b> |      |      |
| 4,9                | 4,9  | 4,63 | 3,38               | 2,93 | 2,55 |
| 0,61               | 0,74 | 0,45 | 0,2                | 0,04 | 0,09 |
| <b>50 12.05.07</b> |      |      | <b>20 12.05.07</b> |      |      |

|                     |      |      |                     |      |      |                     |      |      |
|---------------------|------|------|---------------------|------|------|---------------------|------|------|
| <b>100 07.05.07</b> |      |      | <b>200 07.05.07</b> |      |      | <b>500 07.05.07</b> |      |      |
| 5,19                | 5,11 | 5,19 | 5,79                | 5,46 | 5,71 | 5,34                | 5,57 | 5,55 |
| 0,47                | 0,54 | 0,83 | 0,73                | 1,13 | 2,01 | 2,61                | 3,56 | 3,57 |
| <b>100 12.05.07</b> |      |      | <b>200 12.05.07</b> |      |      | <b>500 12.05.07</b> |      |      |

**Table 17:** measured data BOD

| <b>F</b>   | <b>Mean before</b> | <b>Mean after</b> | <b>Difference</b> | <b>Result</b>  | <b>C1/3</b> | <b>(2*C1)/3</b> |
|------------|--------------------|-------------------|-------------------|----------------|-------------|-----------------|
| 100        | 5,16               | 0,61              | 4,55              | 455,00         | 1,72        | 3,44            |
| 200        | 5,65               | 1,29              | 4,36              | 45,6           | 1,88        | 3,77            |
| <b>500</b> | <b>5,49</b>        | <b>3,25</b>       | <b>2,24</b>       | <b>1120,00</b> | <b>1,83</b> | <b>3,66</b>     |
| 50         | 4,81               | 0,60              | 4,21              | 210,50         | 1,60        | 3,21            |
| 20         | 2,95               | 0,11              | 2,84              | 56,87          | 0,98        | 1,97            |

**Table 18:** determination of the BOD

## 8.2 Water after Test 1

| <b>Solid degrade</b>        |               |               |               |              |                    |                |                  |              |
|-----------------------------|---------------|---------------|---------------|--------------|--------------------|----------------|------------------|--------------|
| <b>Water degr. 26.04.07</b> | <b>1</b>      | <b>2</b>      | <b>3</b>      | <b>4</b>     | <b>Total solid</b> | <b>Organic</b> | <b>Inorganic</b> | <b>Humid</b> |
|                             | 54,407        | 79,304        | 55,467        | 54,743       | 1,060              | 0,336          | 0,723            | 24,897       |
|                             | 35,132        | 60,063        | 35,906        | 35,441       | 0,774              | 0,310          | 0,465            | 24,931       |
|                             | 31,122        | 55,900        | 31,877        | 31,431       | 0,755              | 0,310          | 0,446            | 24,778       |
|                             | <b>Mean</b>   |               |               |              |                    |                |                  |              |
| <b>34,898</b>               | <b>59,685</b> | <b>35,620</b> | <b>35,179</b> | <b>0,722</b> | <b>0,281</b>       | <b>0,441</b>   | <b>24,787</b>    |              |

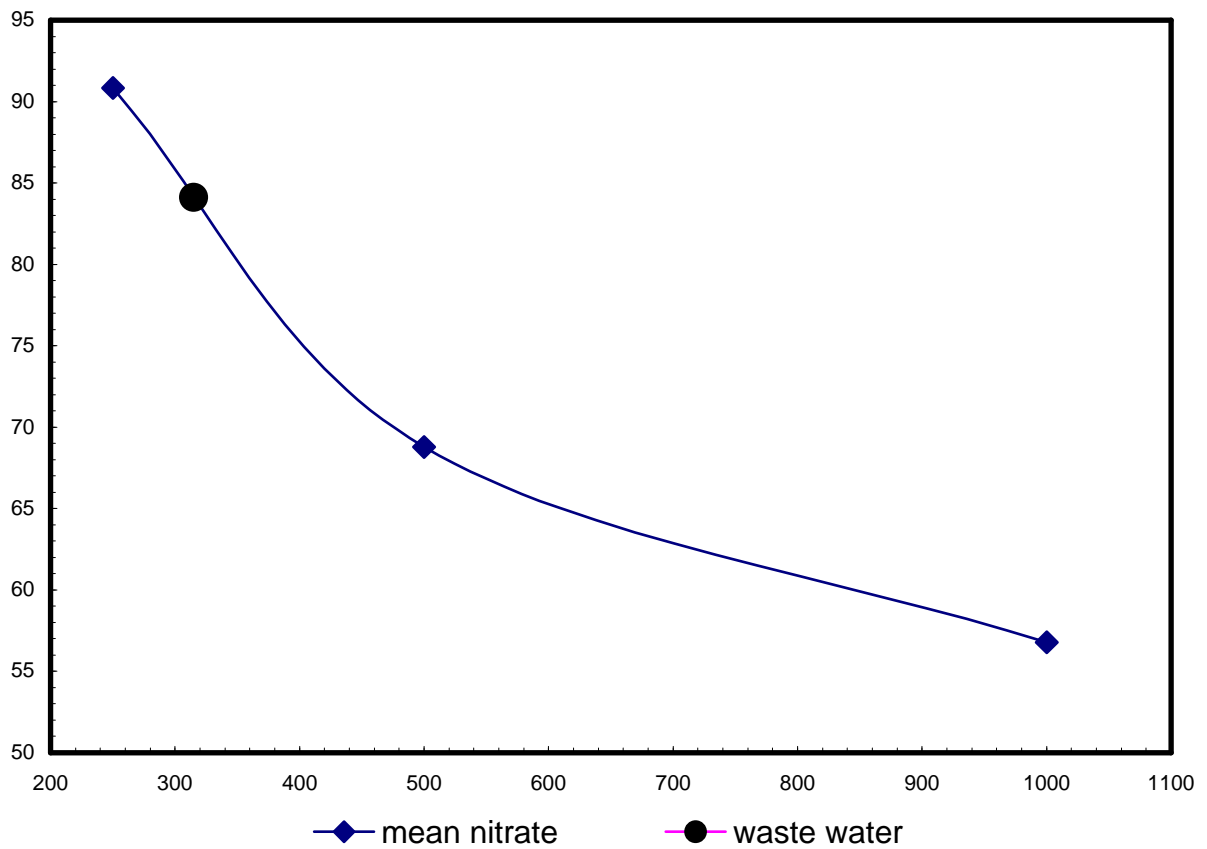
**Table 19:** solids in the wastewater after the test

| <b>PH</b>            |       |       |       |       |              |
|----------------------|-------|-------|-------|-------|--------------|
| <b>Measured data</b> |       |       |       |       | <b>Mean</b>  |
| 7,518                | 7,512 | 7,526 | 7,532 | 7,558 | <b>7,529</b> |

**Table 20:** PH of the wastewater after the test

| <b>Nitrate</b>          |                      |      |      |      |      |                  |
|-------------------------|----------------------|------|------|------|------|------------------|
| <b>ppm</b>              | <b>Measured data</b> |      |      |      |      | <b>Mean [mV]</b> |
| <b>1000</b>             | 56,6                 | 56,7 | 57   | 56,9 | 56,7 | <b>56,8</b>      |
| <b>500</b>              | 68,8                 | 68,8 | 68,8 | 69   | 68,5 | <b>68,8</b>      |
| <b>250</b>              | 90,6                 | 90,1 | 91,4 | 91,1 | 91   | <b>90,8</b>      |
| <b>Nitrate degraded</b> |                      |      |      |      |      |                  |
| <b>310</b>              | 105                  | 99,9 | 78   | 74,3 | 63,4 | <b>84,1</b>      |

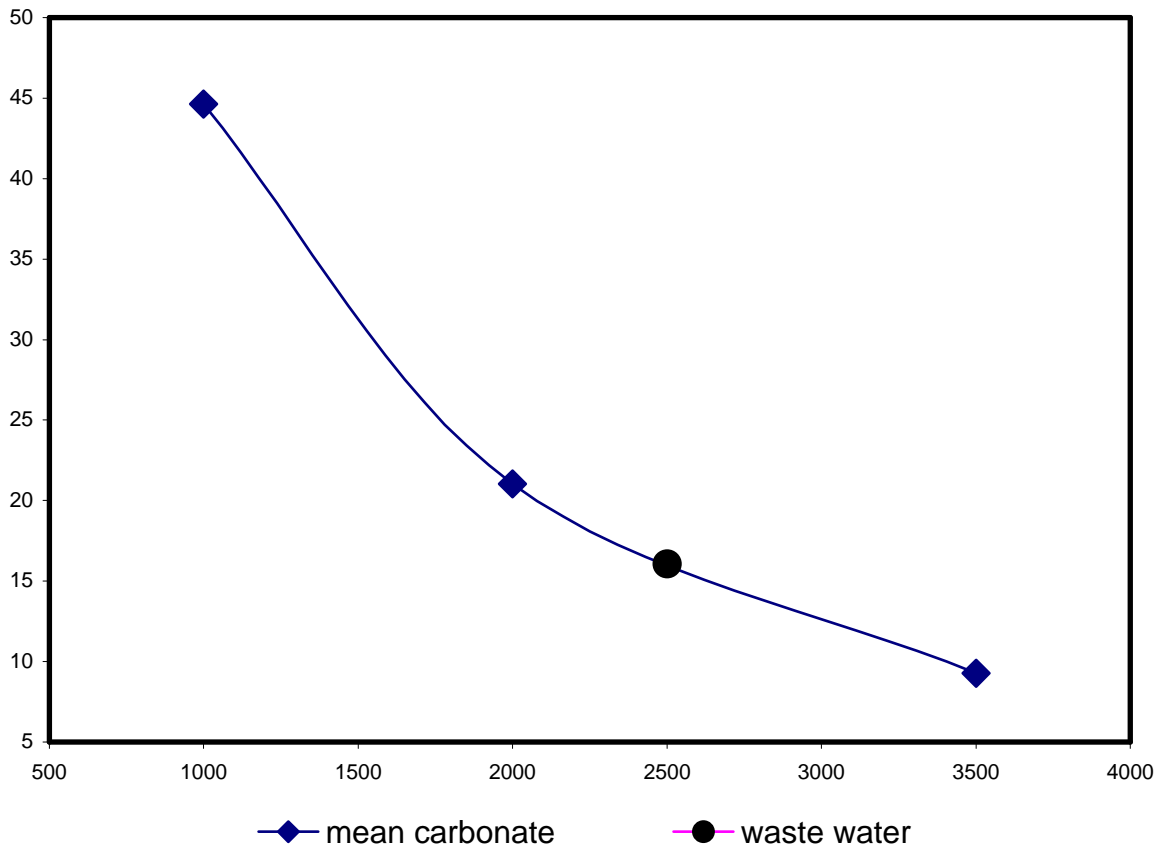
**Table 21:** calibration and amount of nitrate after the test



**Diagram 44:** calibration curve and determination of the ppm

| Carbonate         |               |      |      |      |      |           |
|-------------------|---------------|------|------|------|------|-----------|
| ppm               | Measured data |      |      |      |      | Mean [mV] |
| 1000              | 46,1          | 45,6 | 46,1 | 46,9 | 38,4 | 44,6      |
| 2000              | 14,7          | 17,6 | 19,3 | 28,6 | 25   | 21,0      |
| 3500              | 3,9           | 6,1  | 8,6  | 10,2 | 17,5 | 9,3       |
| Carbonate degrade |               |      |      |      |      |           |
| 2500              | 26,6          | 19,5 | 13,3 | 10,8 | 10,1 | 16,1      |

**Table 22:** calibration and amount of carbonate after the test

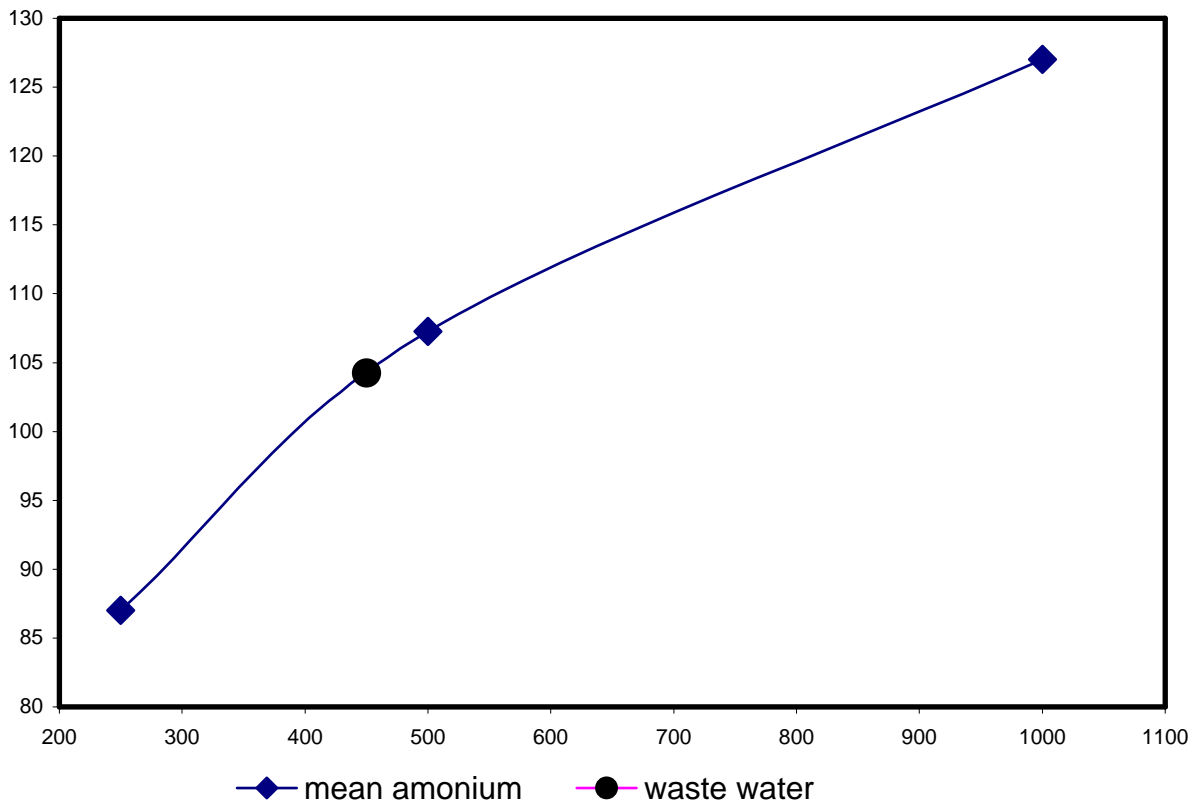


**Diagram 45:** calibration curve and determination of the ppm



| Ammonium         |               |       |       |       |      |           |
|------------------|---------------|-------|-------|-------|------|-----------|
| ppm              | Measured data |       |       |       |      | Mean [mV] |
| 1000             | 123,2         | 129,6 | 128,1 | 127,1 | 127  | 127       |
| 500              | 103,8         | 110,9 | 107,3 | 107,3 | 107  | 107,3     |
| 250              | 83,5          | 86,3  | 87,7  | 88,6  | 89   | 87        |
| Ammonium degrade |               |       |       |       |      |           |
| 450              | 110,6         | 106,9 | 102,5 | 101,4 | 99,9 | 104,3     |

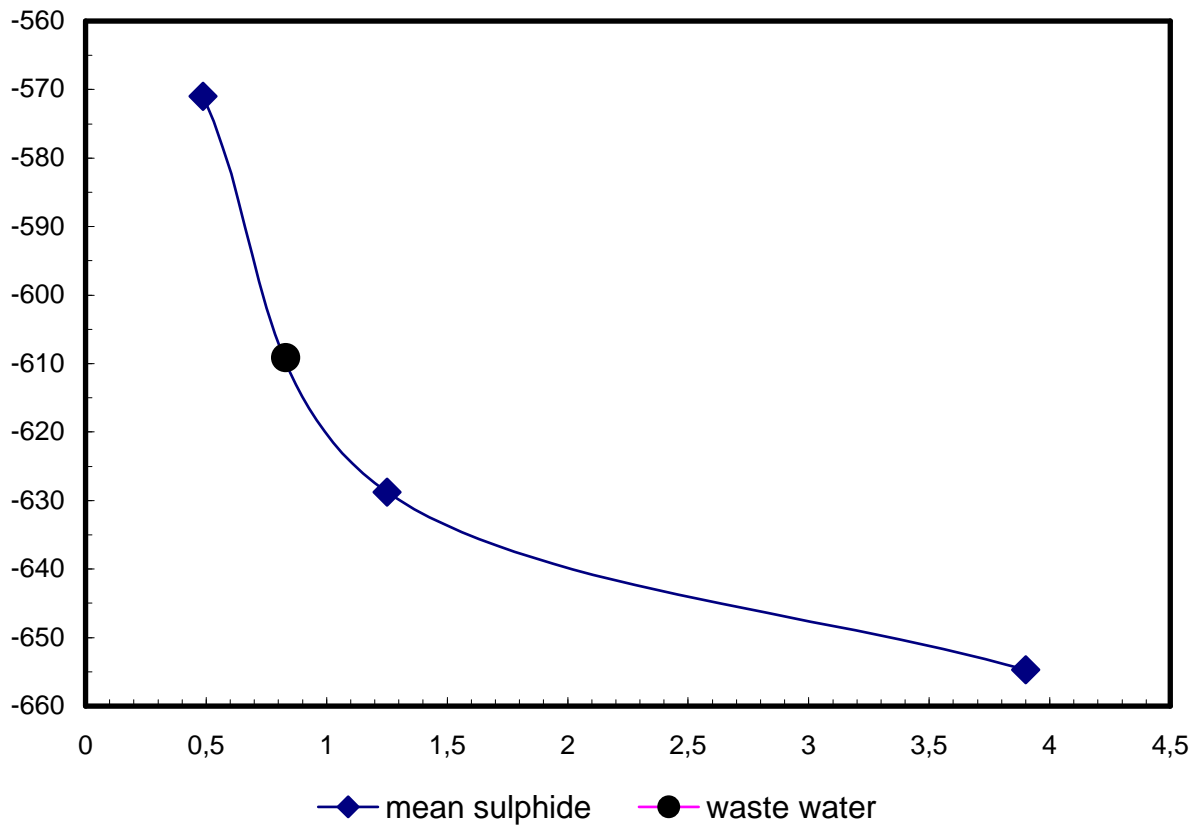
**Table 23:** calibration and amount of ammonium after the test



**Diagram 46:** calibration curve and determination of the ppm

| Sulphide         |               |       |       |       |       |           |
|------------------|---------------|-------|-------|-------|-------|-----------|
| ppm              | Measured data |       |       |       |       | Mean [mV] |
| 3,9              | 646,6         | 654,4 | 654,7 | 656,5 | 661,2 | 654,7     |
| 1,3              | 624,1         | 629,4 | 625,8 | 633,4 | 631,3 | 628,8     |
| 0,5              | 561,9         | 571,9 | 573,6 | 569,4 | 578,3 | 571       |
| Sulphide degrade |               |       |       |       |       |           |
| 0,8              | 609,6         | 610,7 | 606,2 | 612,6 | 606,6 | 609,1     |

**Table 24:** calibration and amount of sulphide after the test



**Diagram 47:** calibration curve and determination of the ppm

|                    |      |      |                    |      |      |
|--------------------|------|------|--------------------|------|------|
| <b>50 04.05.07</b> |      |      | <b>20 04.05.07</b> |      |      |
| 4,97               | 4,98 | 5,01 | 4,81               | 4,32 | 4,39 |
| 0,25               | 0,44 | 0,68 | 0,12               | 0,3  | 0,31 |
| <b>50 09.05.07</b> |      |      | <b>20 09.05.07</b> |      |      |

|                     |      |      |                     |      |      |                     |      |      |
|---------------------|------|------|---------------------|------|------|---------------------|------|------|
| <b>100 04.05.07</b> |      |      | <b>200 04.05.07</b> |      |      | <b>500 12.02.07</b> |      |      |
| 5,18                | 5,16 | 5,19 | 5,11                | 5,17 | 5,13 | 5,36                | 5,71 | 5,39 |
| 0,75                | 0,73 | 0,38 | 1,64                | 1,36 | 1,21 | 3,63                | 3,56 | 3,32 |
| <b>100 09.05.07</b> |      |      | <b>200 08.11.06</b> |      |      | <b>500 08.11.06</b> |      |      |

**Table 25:** measured data BOD

| <b>F</b> | <b>Mean before</b> | <b>Mean after</b> | <b>Difference</b> | <b>Result</b> | <b>C1/3</b> | <b>(2*C1)/3</b> |
|----------|--------------------|-------------------|-------------------|---------------|-------------|-----------------|
| 100      | 5,18               | 0,62              | 4,56              | 455,67        | 1,73        | 3,45            |
| 200      | 5,14               | 1,40              | 3,73              | 45,6          | 1,71        | 3,42            |
| 500      | 5,49               | 3,50              | 1,98              | 991,67        | 1,83        | 3,66            |
| 50       | 4,99               | 0,46              | 4,53              | 226,50        | 1,66        | 3,32            |
| 20       | 4,51               | 0,24              | 4,26              | 85,27         | 1,50        | 3,00            |

**Table 26:** determination of the BOD

### 8.3 Water before Test 2

| Solid waste          |        |        |        |        |             |            |          |        |
|----------------------|--------|--------|--------|--------|-------------|------------|----------|--------|
| Water waste 10.05.07 | 1      | 2      | 3      | 4      | total solid | Inorganics | Organics | Humid  |
|                      | 37,513 | 62,333 | 38,596 | 37,856 | 1,083       | 0,343      | 0,740    | 24,820 |
|                      | 31,122 | 55,872 | 31,939 | 31,482 | 0,817       | 0,360      | 0,457    | 24,750 |
|                      | 54,409 | 79,196 | 55,216 | 54,746 | 0,807       | 0,337      | 0,470    | 24,788 |
|                      | Mean   |        |        |        |             |            |          |        |
| 41,014               | 65,800 | 41,917 | 41,361 | 0,903  | 0,347       | 0,556      | 24,786   |        |

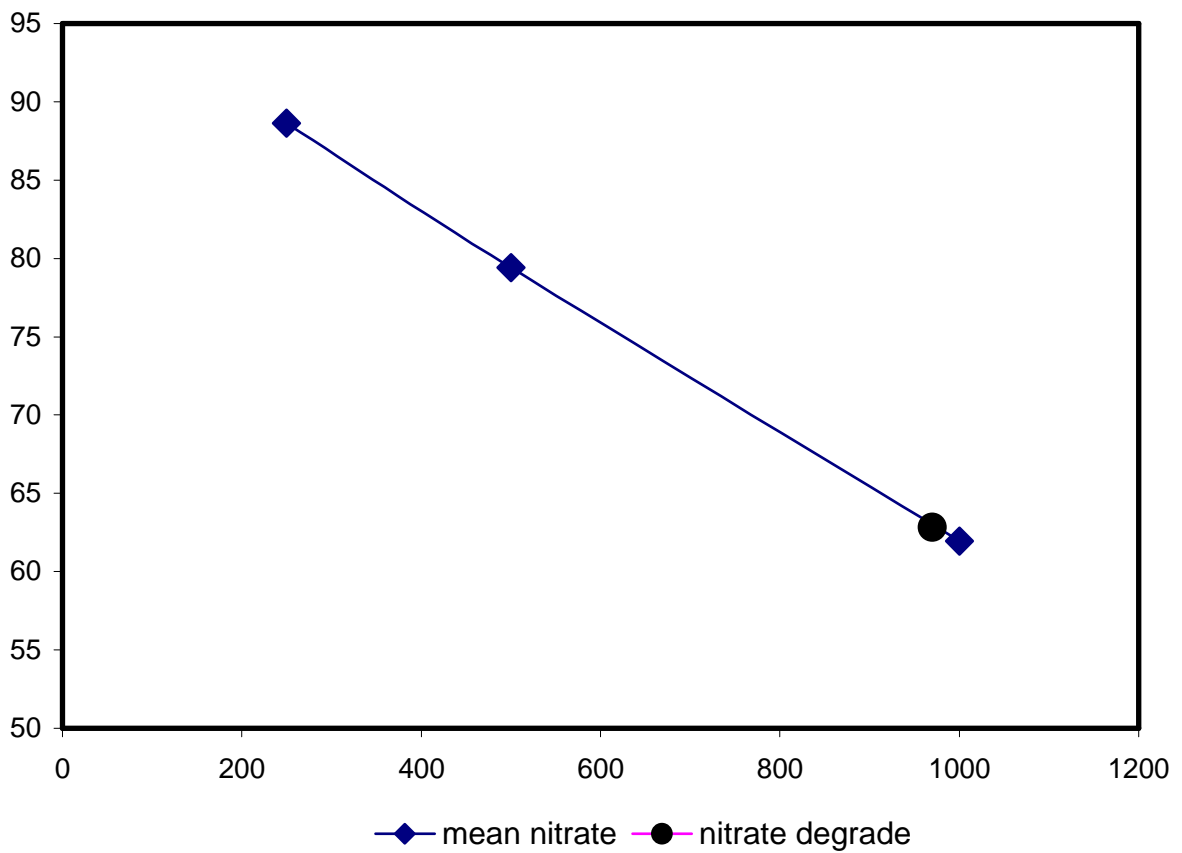
**Table 27:** solids in the wastewater before the test

| PH            |      |       |       |       |       |
|---------------|------|-------|-------|-------|-------|
| Measured data |      |       |       |       | Mean  |
| 7,535         | 7,53 | 7,537 | 7,521 | 7,563 | 7,537 |

**Table 28:** PH of the wastewater before the test

| Nitrate         |               |      |      |      |      |           |
|-----------------|---------------|------|------|------|------|-----------|
| ppm             | Measured data |      |      |      |      | Mean [mV] |
| 1000            | 62            | 62,6 | 61,7 | 61,8 | 61,6 | 61,9      |
| 250             | 79            | 79,2 | 79,6 | 79,6 | 79,7 | 79,4      |
| 62,5            | 84,9          | 87,9 | 89,9 | 89,6 | 90,9 | 88,6      |
| Nitrate Degrade |               |      |      |      |      |           |
| 970             | 89,9          | 64,5 | 73,6 | 48,2 | 38   | 62,8      |

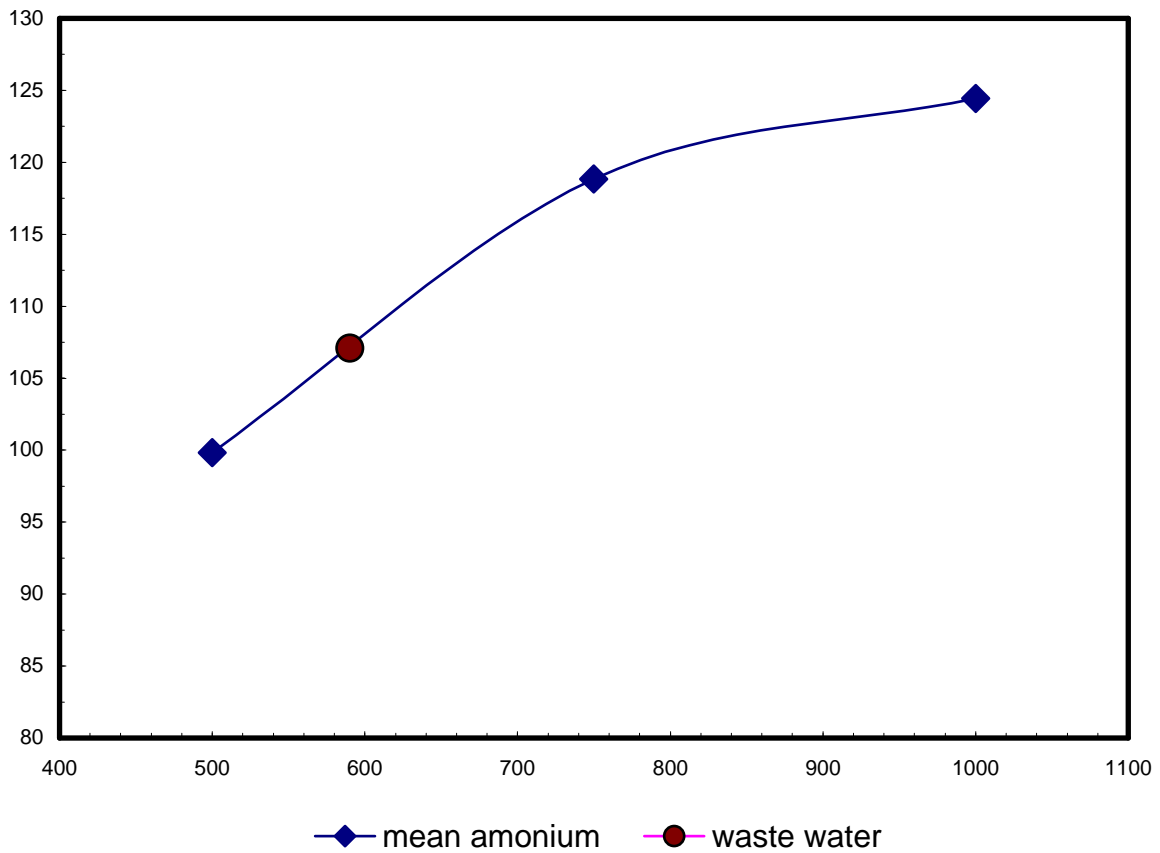
**Table 29:** calibration and amount of nitrate before the test



**Diagram 48:** calibration curve and determination of the ppm

| Ammonium         |               |       |       |       |       |           |
|------------------|---------------|-------|-------|-------|-------|-----------|
| ppm              | Measured data |       |       |       |       | Mean [mV] |
| 1000             | 125           | 124,2 | 124,6 | 124,3 | 124,1 | 124,4     |
| 750              | 118,5         | 118,9 | 118,5 | 119,2 | 119,1 | 118,8     |
| 500              | 98,2          | 99,8  | 100,2 | 100,4 | 100,6 | 99,8      |
| Ammonium degrade |               |       |       |       |       |           |
| 590              | 114,2         | 106,8 | 105,6 | 104,8 | 104,1 | 107,1     |

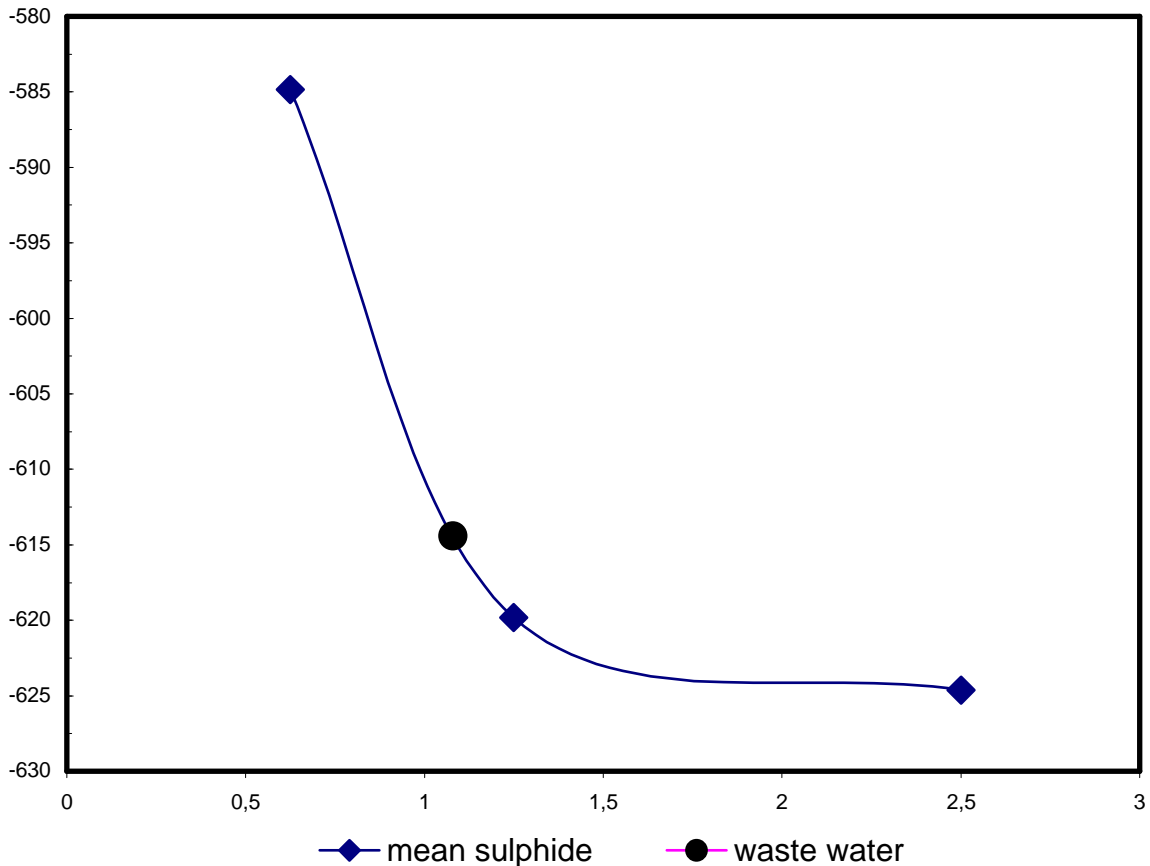
**Table 30:** calibration and amount of ammonium before the test



**Diagram 49:** calibration curve and determination of the ammonium

| Sulphide         |               |        |        |        |        |           |
|------------------|---------------|--------|--------|--------|--------|-----------|
| ppm              | Measured data |        |        |        |        | Mean [mV] |
| 2,5              | -590,4        | -624,7 | -632,2 | -635,9 | -639,9 | -624,6    |
| 1,25             | -616,9        | -619,7 | -620,4 | -623,3 | -618,7 | -619,8    |
| 0,63             | -591,8        | -584,7 | -581,9 | -584   | -581,9 | -584,8    |
| Sulphide degrade |               |        |        |        |        |           |
| 1,08             | -621,4        | -608,7 | -610,8 | -610,6 | -620,6 | -614,4    |

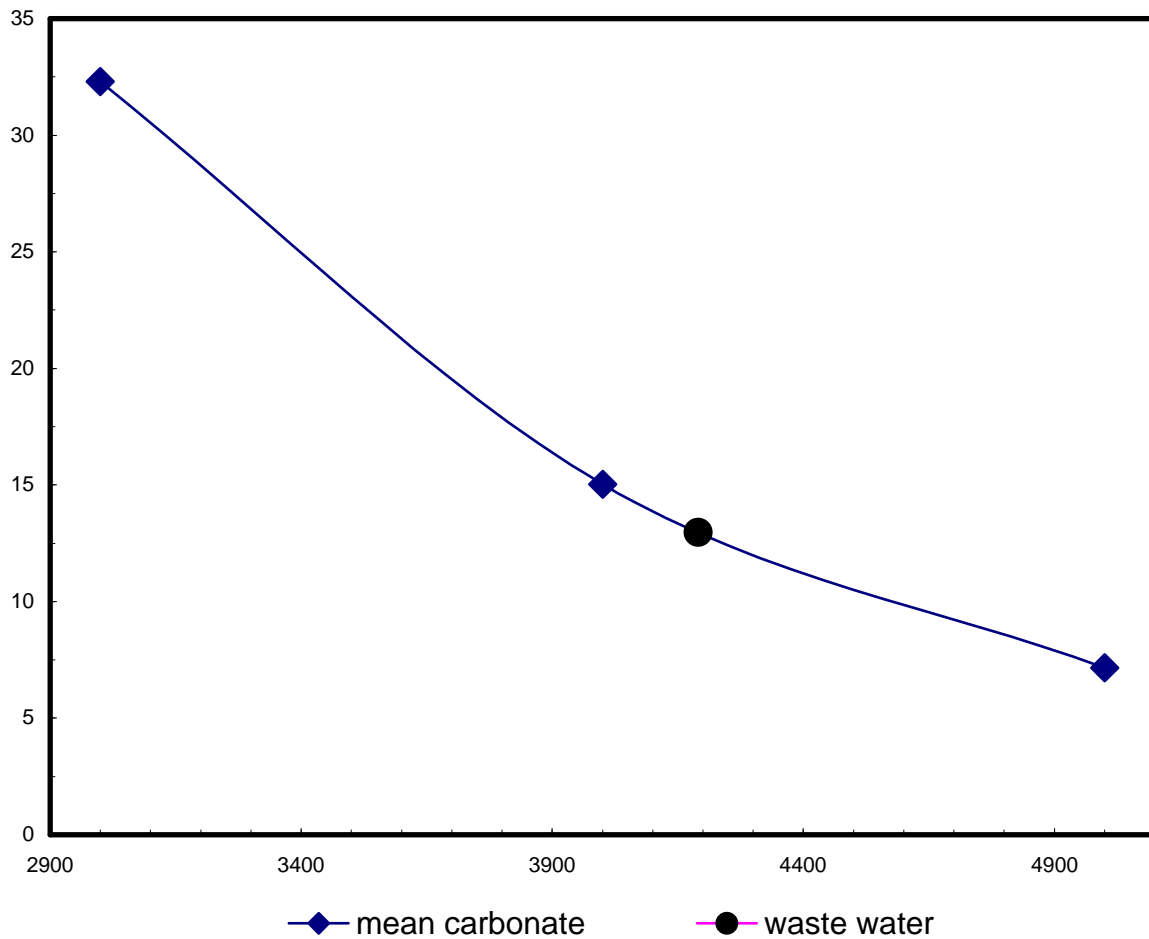
**Table 31:** calibration and amount of sulphide before the test



**Diagram 50:** calibration and determination of the ppm

| Carbonate       |               |      |      |      |      |           |
|-----------------|---------------|------|------|------|------|-----------|
| ppm             | Measured data |      |      |      |      | Mean [mV] |
| 3000            | 35,1          | 33,5 | 32,6 | 31,6 | 28,7 | 32,3      |
| 4000            | 7,3           | 11,9 | 17   | 17,8 | 21,1 | 15        |
| 5000            | 1,4           | 5,8  | 7,1  | 9,6  | 11,9 | 7,2       |
| Nitrate degrade |               |      |      |      |      |           |
| 4190            | 16,5          | 15,1 | 13,8 | 14,1 | 5,4  | 13        |

**Table 32:** calibration and amount of carbonate before the test



**Diagram 51:** calibration and determination of the ppm



|                    |      |      |                    |      |      |
|--------------------|------|------|--------------------|------|------|
| <b>50 10.05.07</b> |      |      | <b>20 10.05.07</b> |      |      |
| 4,97               | 5    | 5,14 | 4,41               | 4,02 | 4,16 |
| 0,66               | 0,36 | 0,81 | 0,2                | 0,05 | 0,03 |
| <b>50 15.05.07</b> |      |      | <b>20 15.05.07</b> |      |      |

|                     |      |      |                     |      |      |                     |      |      |
|---------------------|------|------|---------------------|------|------|---------------------|------|------|
| <b>100 10.05.07</b> |      |      | <b>200 10.05.07</b> |      |      | <b>500 10.05.07</b> |      |      |
| 5,59                | 5,51 | 5,45 | 5,23                | 5,36 | 5,79 | 5,53                | 5,8  | 5,72 |
| 1,18                | 0,61 | 0,84 | 0,56                | 0,72 | 1,66 | 2,44                | 3,02 | 3,65 |
| <b>100 15.05.07</b> |      |      | <b>200 15.05.07</b> |      |      | <b>500 15.05.07</b> |      |      |

**Table 33:** measured data BOD

| <b>F</b> | <b>Mean before</b> | <b>Mean after</b> | <b>Difference</b> | <b>Result</b> | <b>C1/3</b> | <b>(2*C1)/3</b> |
|----------|--------------------|-------------------|-------------------|---------------|-------------|-----------------|
| 100      | 5,52               | 0,88              | 4,64              | 464,00        | 1,84        | 3,68            |
| 200      | 5,46               | 0,98              | 4,48              | 45,6          | 1,82        | 3,64            |
| 500      | 5,68               | 3,04              | 2,65              | 1323,33       | 1,89        | 3,79            |
| 50       | 5,04               | 0,61              | 4,43              | 221,33        | 1,68        | 3,36            |
| 20       | 4,20               | 0,09              | 4,10              | 82,07         | 1,40        | 2,80            |

**Table 34:** determination of the BOD

## 8.4 Water after Test 2

| Solid waste          |        |        |        |        |             |           |         |        |
|----------------------|--------|--------|--------|--------|-------------|-----------|---------|--------|
| Water degr. 15.05.07 | 1      | 2      | 3      | 4      | Total solid | Inorganic | Organic | Humid  |
|                      | 31,141 | 55,863 | 31,956 | 31,502 | 0,815       | 0,361     | 0,454   | 24,722 |
|                      | 35,135 | 60,393 | 36,064 | 35,479 | 0,929       | 0,344     | 0,585   | 25,257 |
|                      | 30,926 | 56,048 | 32,177 | 31,319 | 1,250       | 0,393     | 0,858   | 25,121 |
|                      | Mean   |        |        |        |             |           |         |        |
| 32,401               | 57,434 | 33,399 | 32,767 | 0,998  | 0,366       | 0,632     | 25,034  |        |

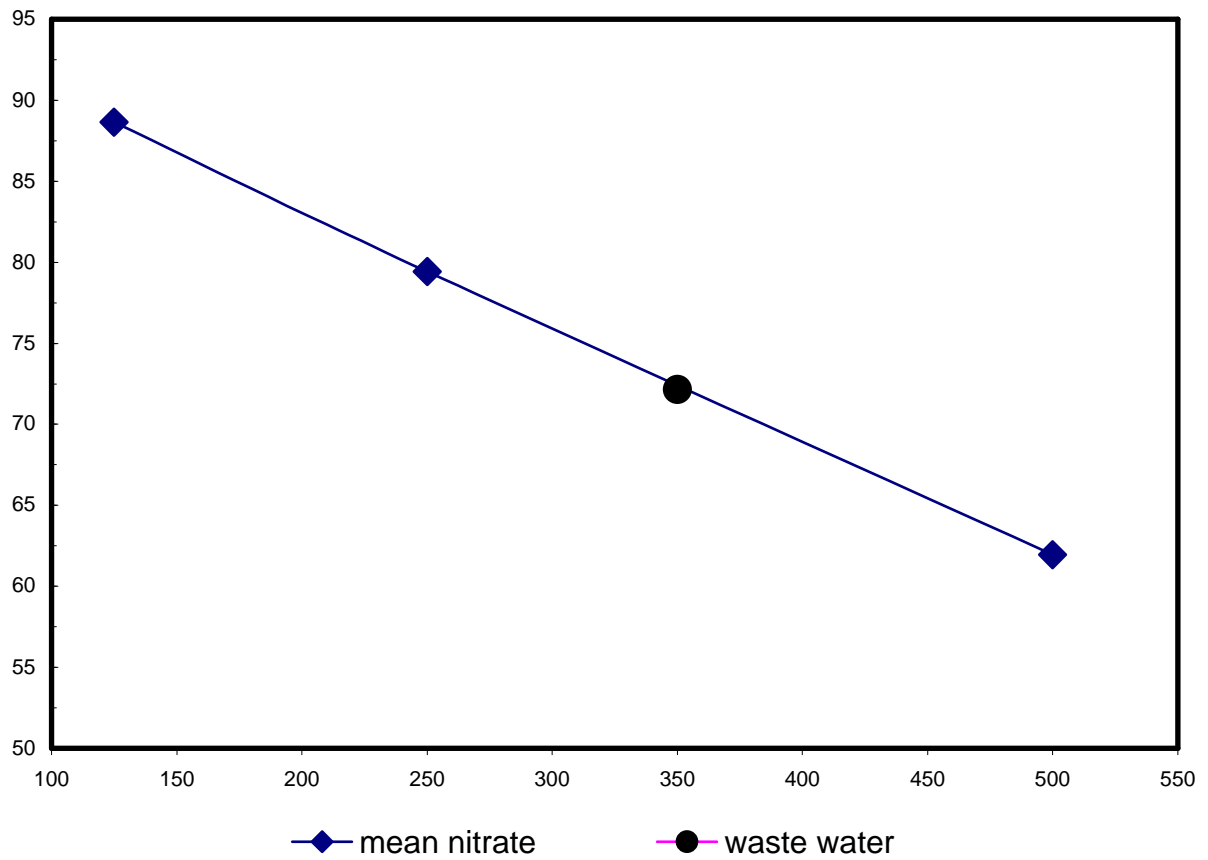
**Table 35:** solids in the wastewater after the test

| PH            |      |       |       |       |       |
|---------------|------|-------|-------|-------|-------|
| Measured data |      |       |       |       | Mean  |
| 7,386         | 7,38 | 7,369 | 7,382 | 7,376 | 7,379 |

**Table 36:** PH of the wastewater after the test

| Nitrate       |               |      |      |      |      |           |
|---------------|---------------|------|------|------|------|-----------|
| ppm           | Measured data |      |      |      |      | Mean [mV] |
| 500           | 62            | 62,6 | 61,7 | 61,8 | 61,6 | 61,9      |
| 250           | 79            | 79,2 | 79,6 | 79,6 | 79,7 | 79,4      |
| 125           | 84,9          | 87,9 | 89,9 | 89,6 | 90,9 | 88,6      |
| Nitrate waste |               |      |      |      |      |           |
| 370           | 97,6          | 75,2 | 68,1 | 61,6 | 58,2 | 72,1      |

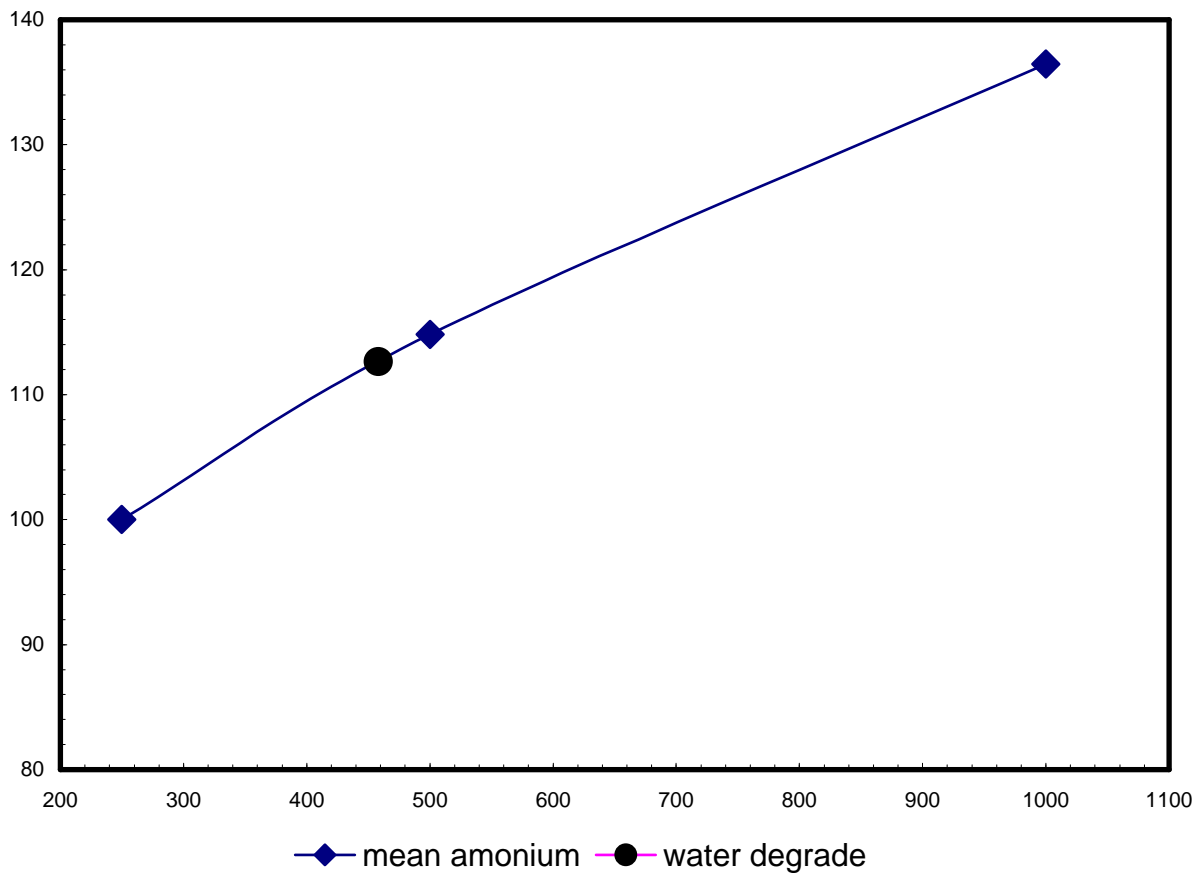
**Table 37:** calibration and amount of nitrate after the test



**Diagram 52:** calibration curve and determination of the ppm

| Ammonium        |               |       |       |       |       |           |
|-----------------|---------------|-------|-------|-------|-------|-----------|
| ppm             | Measured data |       |       |       |       | Mean [mV] |
| 1000            | 136,9         | 136,9 | 136,9 | 135,8 | 135,8 | 136,5     |
| 500             | 115,3         | 115,7 | 114,6 | 114,2 | 114,3 | 114,8     |
| 250             | 99,8          | 99,8  | 99,8  | 100,1 | 100,6 | 100       |
| Nitrate degrade |               |       |       |       |       |           |
| 458             | 120,4         | 112,8 | 111,2 | 109,6 | 109,3 | 112,7     |

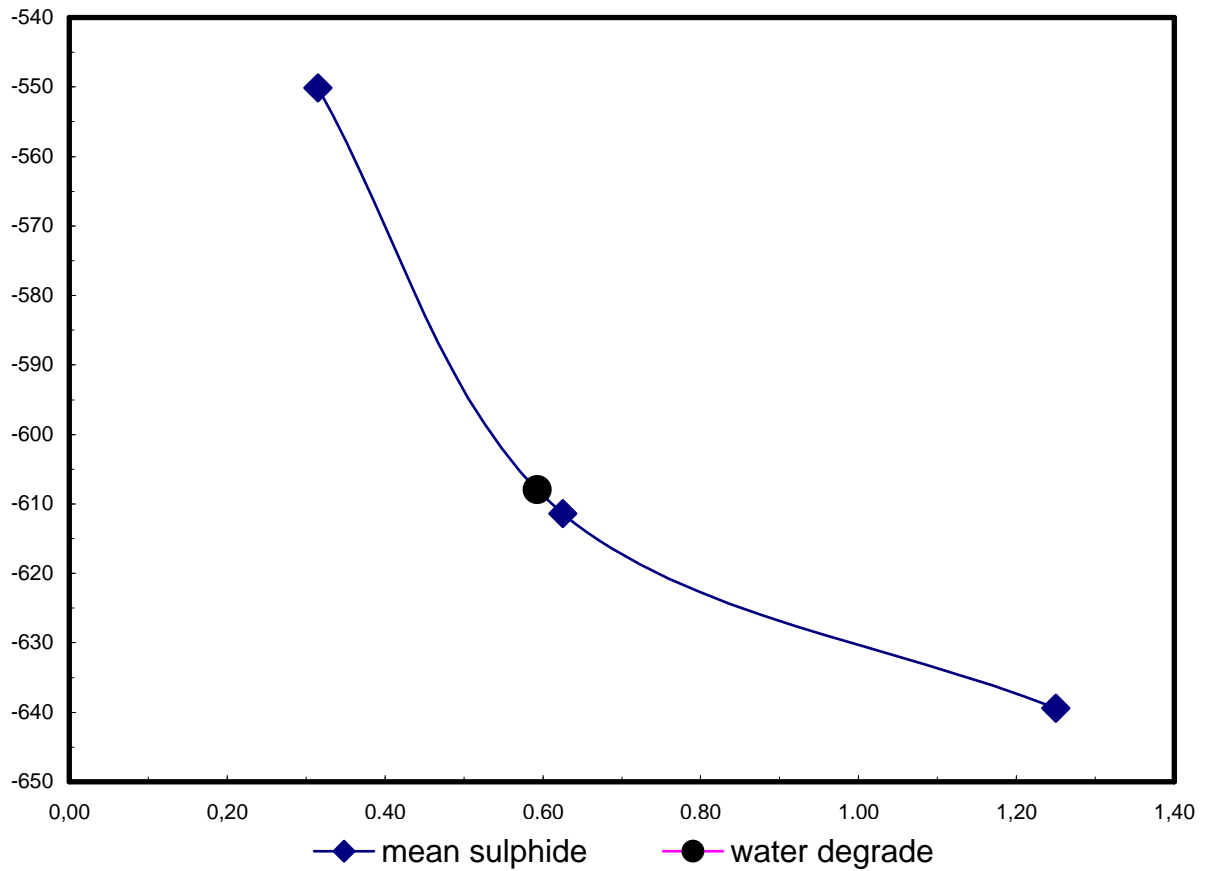
**Table 38:** calibration and amount of ammonium after the test



**Diagram 53:** calibration curve and determination of the ppm

| Sulphide      |               |        |        |        |        |           |
|---------------|---------------|--------|--------|--------|--------|-----------|
| ppm           | Measured data |        |        |        |        | Mean [mV] |
| 1,3           | -633          | -638,7 | -643,2 | -640,3 | -641,7 | -639,4    |
| 0,6           | -613,4        | -609,8 | -608,2 | -615,4 | -610   | -611,4    |
| 0,3           | -568,9        | -545,3 | -550,3 | -535,1 | -550,9 | -550,1    |
| Water degrade |               |        |        |        |        |           |
| 0,6           | -596,7        | -621,9 | -606,9 | -599,9 | -614,3 | -607,9    |

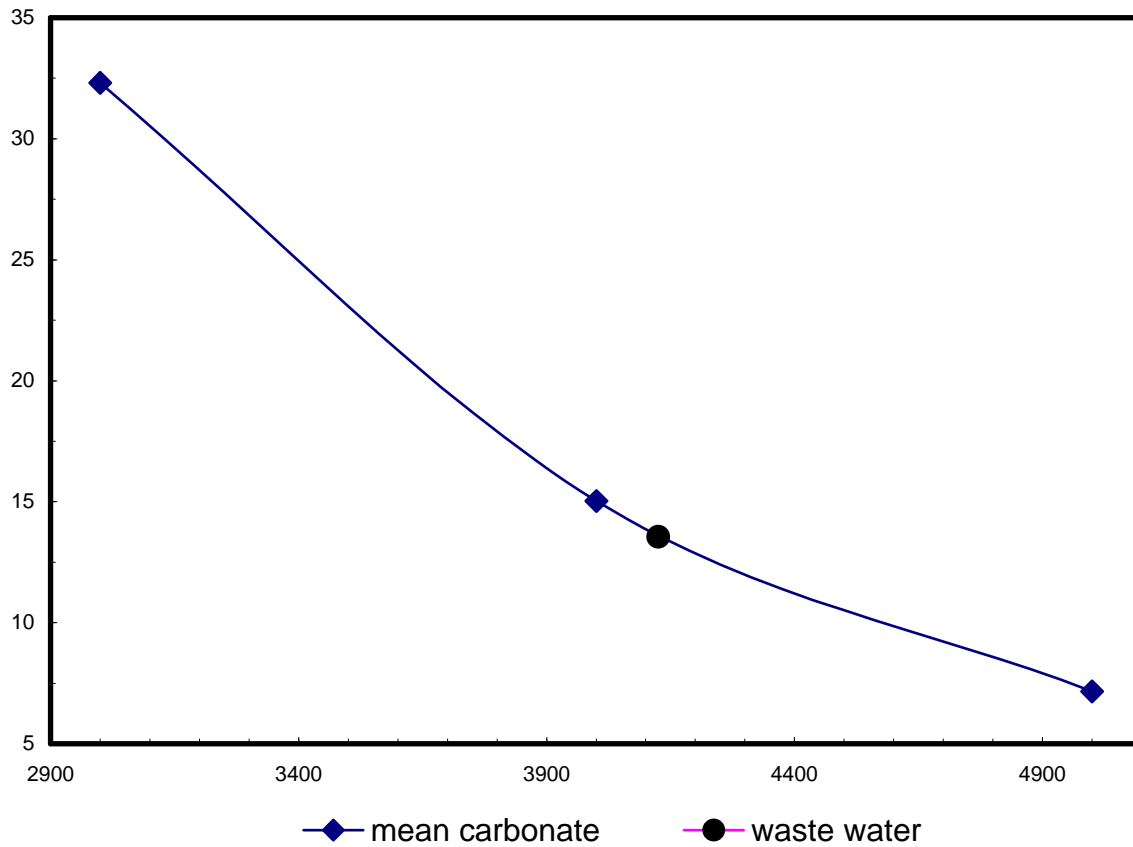
**Table 39:** calibration and amount of sulphide after the test



**Diagram 54:** calibration curve and determination of the ppm

| Carbonate       |               |      |      |      |      |           |
|-----------------|---------------|------|------|------|------|-----------|
| ppm             | Measured data |      |      |      |      | Mean [mV] |
| 3000            | 17,1          | 17,4 | 19,3 | 18,4 | 17,4 | 17,9      |
| 4000            | 15,1          | 13,9 | 17,3 | 14,5 | 13,1 | 14,8      |
| 5000            | 2,9           | 5,8  | 6,6  | 8,6  | 6,9  | 6,2       |
| Nitrate degrade |               |      |      |      |      |           |
| 4570            | 14,8          | 6,1  | 6,4  | 8,9  | 14,8 | 10,2      |

**Table 40:** calibration and amount of carbonate after the test



**Diagram 55:** calibration curve and determination of the ppm

|                    |      |      |                    |      |      |
|--------------------|------|------|--------------------|------|------|
| <b>50 15.05.07</b> |      |      | <b>20 15.05.07</b> |      |      |
| 4,97               | 5    | 5,14 | 4,41               | 4,02 | 4,16 |
| 0,66               | 0,36 | 0,81 | 0,2                | 0,05 | 0,03 |
| <b>50 22.05.07</b> |      |      | <b>20 22.05.07</b> |      |      |

|                     |      |      |                     |      |      |                     |      |      |
|---------------------|------|------|---------------------|------|------|---------------------|------|------|
| <b>100 15.05.07</b> |      |      | <b>200 10.05.07</b> |      |      | <b>500 10.05.07</b> |      |      |
| 5,59                | 5,51 | 5,45 | 5,23                | 5,36 | 5,79 | 5,53                | 5,8  | 5,72 |
| 1,18                | 0,61 | 0,84 | 0,56                | 0,72 | 1,66 | 2,44                | 3,02 | 3,65 |
| <b>100 22.05.07</b> |      |      | <b>200 08.11.07</b> |      |      | <b>500 08.11.06</b> |      |      |

**Table 41:** measured date BOD

| F   | Mean before | Mean after | Difference | Result         | C1/3 | (2*C1)/3 |
|-----|-------------|------------|------------|----------------|------|----------|
| 100 | 5,56        | 0,94       | 4,62       | 461,67         | 1,85 | 3,71     |
| 200 | 5,74        | 1,10       | 4,64       | 45,6           | 1,91 | 3,83     |
| 500 | 5,59        | 3,54       | 2,04       | <b>1021,67</b> | 1,86 | 3,72     |
| 50  | 4,72        | 0,44       | 4,29       | 214,33         | 1,57 | 3,15     |
| 20  | 4,41        | 0,17       | 4,24       | 84,73          | 1,47 | 2,94     |

**Table 42:** determination of the BOD

## 8.5 Water before Test 3

| Solid waste          |               |               |               |              |              |              |               |        |
|----------------------|---------------|---------------|---------------|--------------|--------------|--------------|---------------|--------|
| Water waste 22.05.07 | 1             | 2             | 3             | 4            | total solid  | Inorganics   | Organics      | Humid  |
|                      | 30,917        | 54,966        | 31,723        | 31,264       | 0,806        | 0,347        | 0,459         | 24,049 |
|                      | 35,155        | 59,551        | 35,977        | 35,475       | 0,822        | 0,320        | 0,502         | 24,395 |
|                      | 36,296        | 61,077        | 37,167        | 36,610       | 0,871        | 0,314        | 0,557         | 24,781 |
|                      | Mean          |               |               |              |              |              |               |        |
| <b>34,123</b>        | <b>58,531</b> | <b>34,956</b> | <b>34,450</b> | <b>0,833</b> | <b>0,327</b> | <b>0,506</b> | <b>24,408</b> |        |

**Table 43:** solids in the wastewater before the test

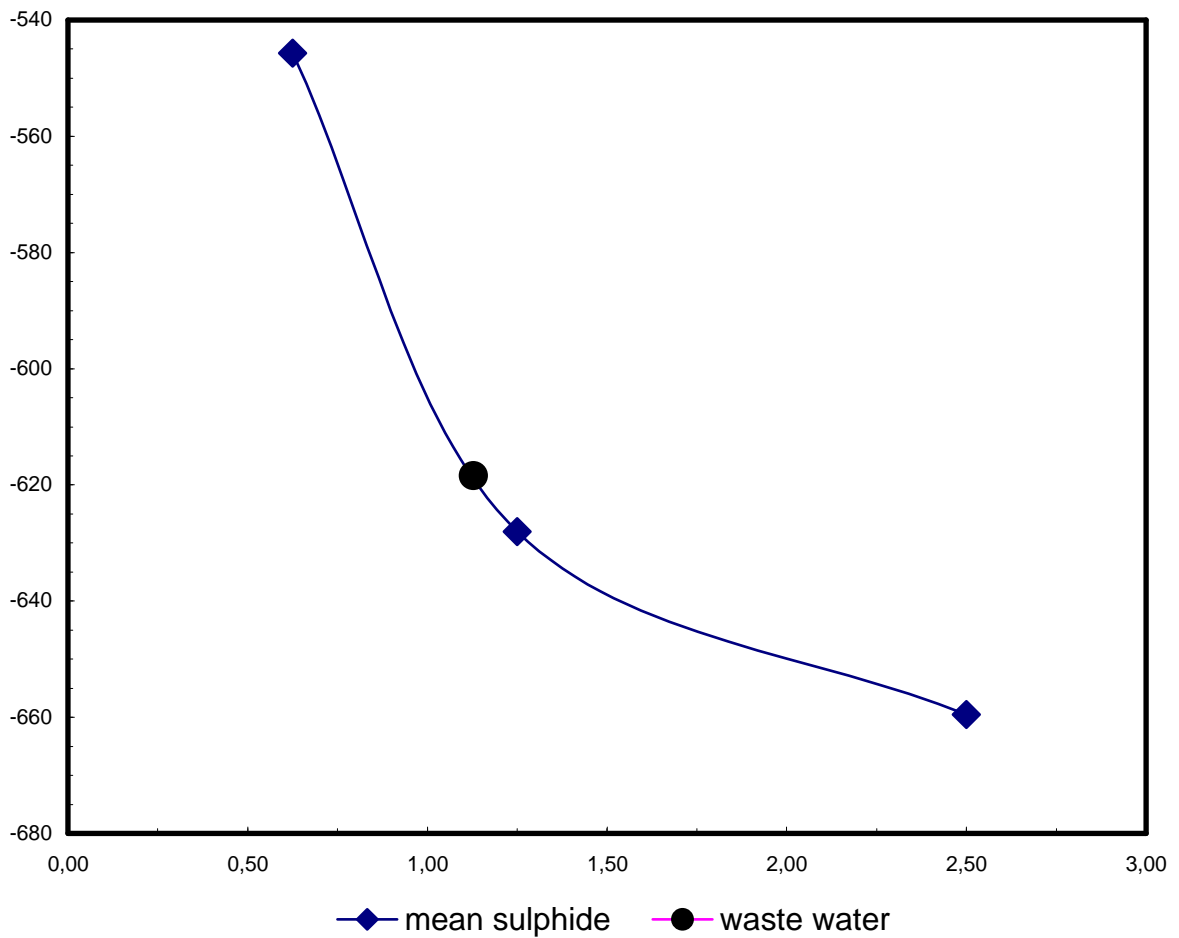
| PH            |       |       |       |       |              |
|---------------|-------|-------|-------|-------|--------------|
| Measured data |       |       |       |       | Mean         |
| 7,787         | 7,781 | 7,757 | 7,781 | 7,786 | <b>7,778</b> |

**Table 44:** PH in the wastewater before the test

| Sulphide       |               |        |        |        |        |               |
|----------------|---------------|--------|--------|--------|--------|---------------|
| ppm            | Measured data |        |        |        |        | Mean [mV]     |
| <b>2,5</b>     | -656,1        | -657,8 | -660,2 | -658,6 | -665,1 | <b>-659,6</b> |
| <b>1,3</b>     | -627,1        | -627,8 | -628,2 | -628,9 | -628,2 | <b>-628</b>   |
| <b>0,6</b>     | -541,8        | -546,6 | -541,4 | -546,2 | -552,4 | <b>-545,7</b> |
| Sulphide waste |               |        |        |        |        |               |
| <b>1,1</b>     | -609,7        | -611,9 | -610,4 | -629,6 | -630,3 | <b>-618,4</b> |

**Table 45:** calibration and amount of sulphide before the test

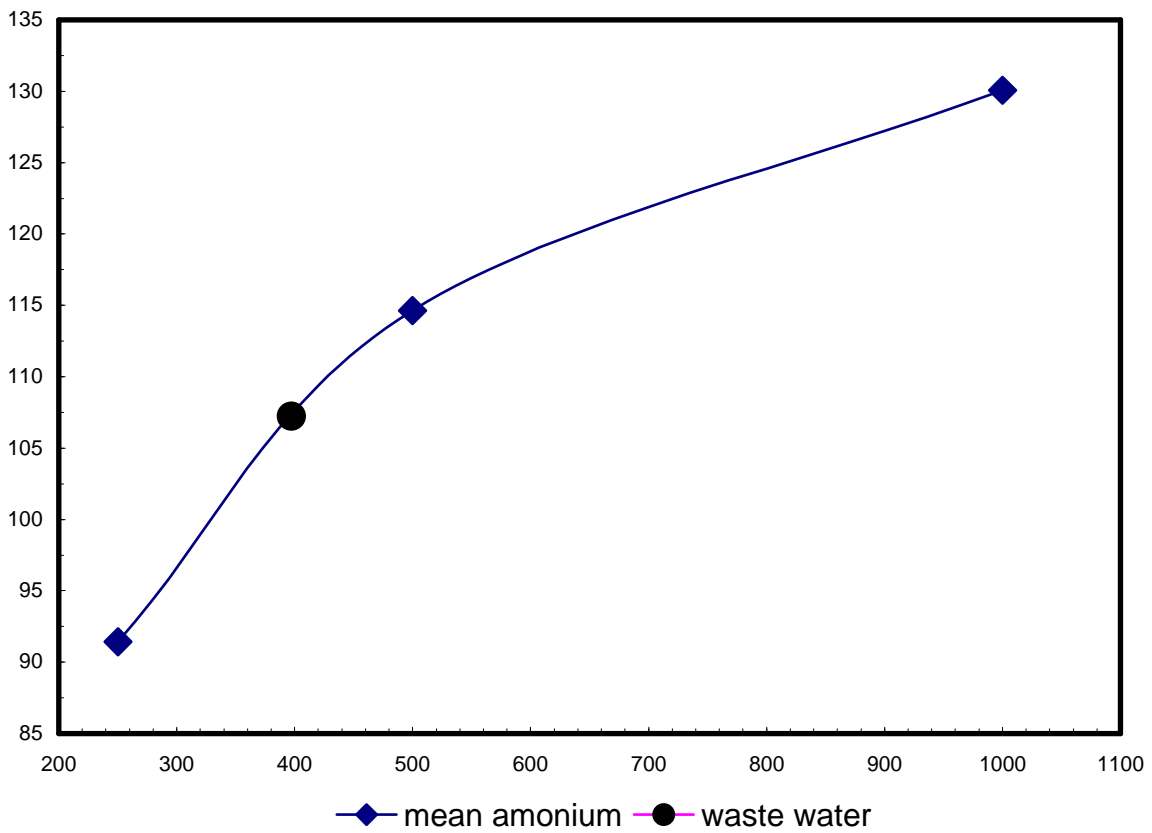




**Diagram 56:** calibration curve and determination of the ppm

| Ammonium       |               |       |       |       |       |           |
|----------------|---------------|-------|-------|-------|-------|-----------|
| ppm            | Measured data |       |       |       |       | Mean [mV] |
| 1000           | 131,6         | 130,9 | 129,4 | 129,3 | 129,1 | 130,1     |
| 500            | 115,4         | 115   | 114,6 | 114,3 | 113,9 | 114,6     |
| 250            | 87,4          | 91    | 92,4  | 93    | 93,4  | 91,4      |
| Ammonium waste |               |       |       |       |       |           |
| 397            | 109,1         | 107,3 | 105,9 | 105,8 | 108,1 | 107,2     |

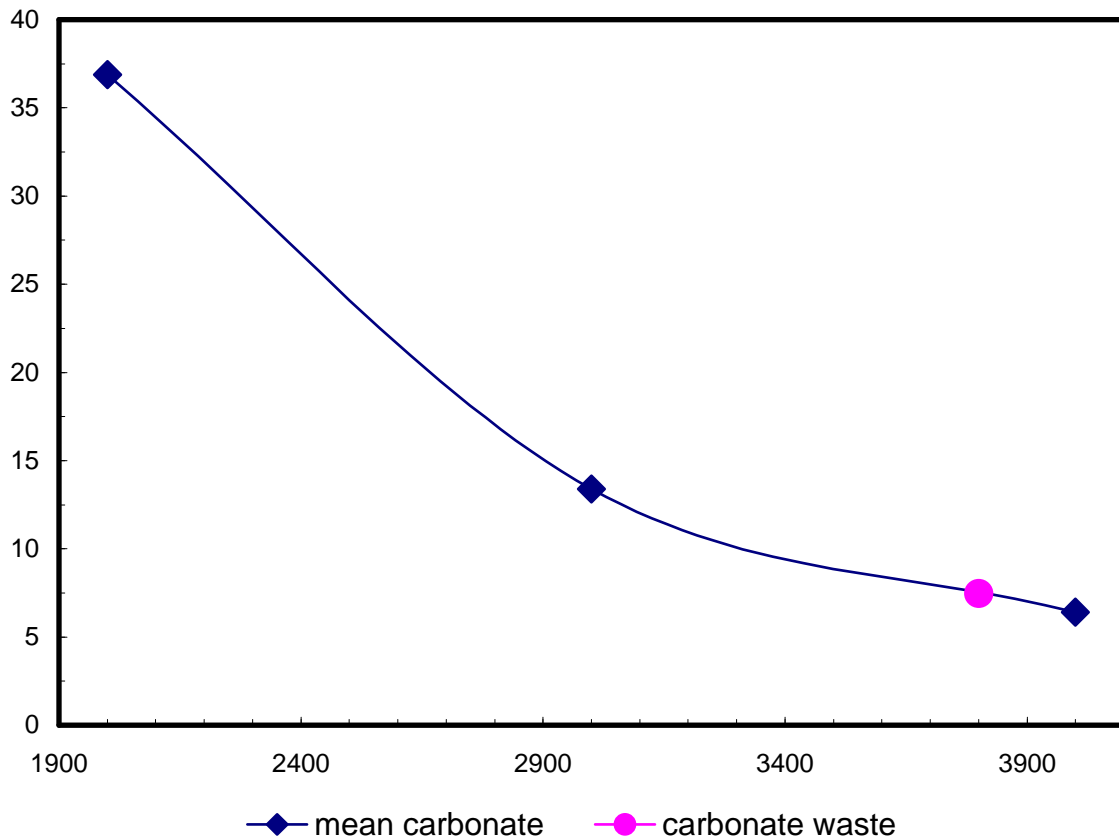
**Table 46:** calibration and amount of the ammonium before the test



**Diagram 57:** calibration curve and determination of the ppm

| Carbonate       |               |      |      |      |      |           |
|-----------------|---------------|------|------|------|------|-----------|
| ppm             | Measured data |      |      |      |      | Mean [mV] |
| 2000            | 46,6          | 39,1 | 35,8 | 32,9 | 30,1 | 36,9      |
| 3000            | 9,1           | 14,9 | 14,9 | 13,3 | 14,8 | 13,4      |
| 4000            | 9,6           | 7    | 4,4  | 5,9  | 5,2  | 6,4       |
| Carbonate waste |               |      |      |      |      |           |
| 3800            | 8,4           | 8,2  | 7,6  | 6,4  | 6,8  | 7,5       |

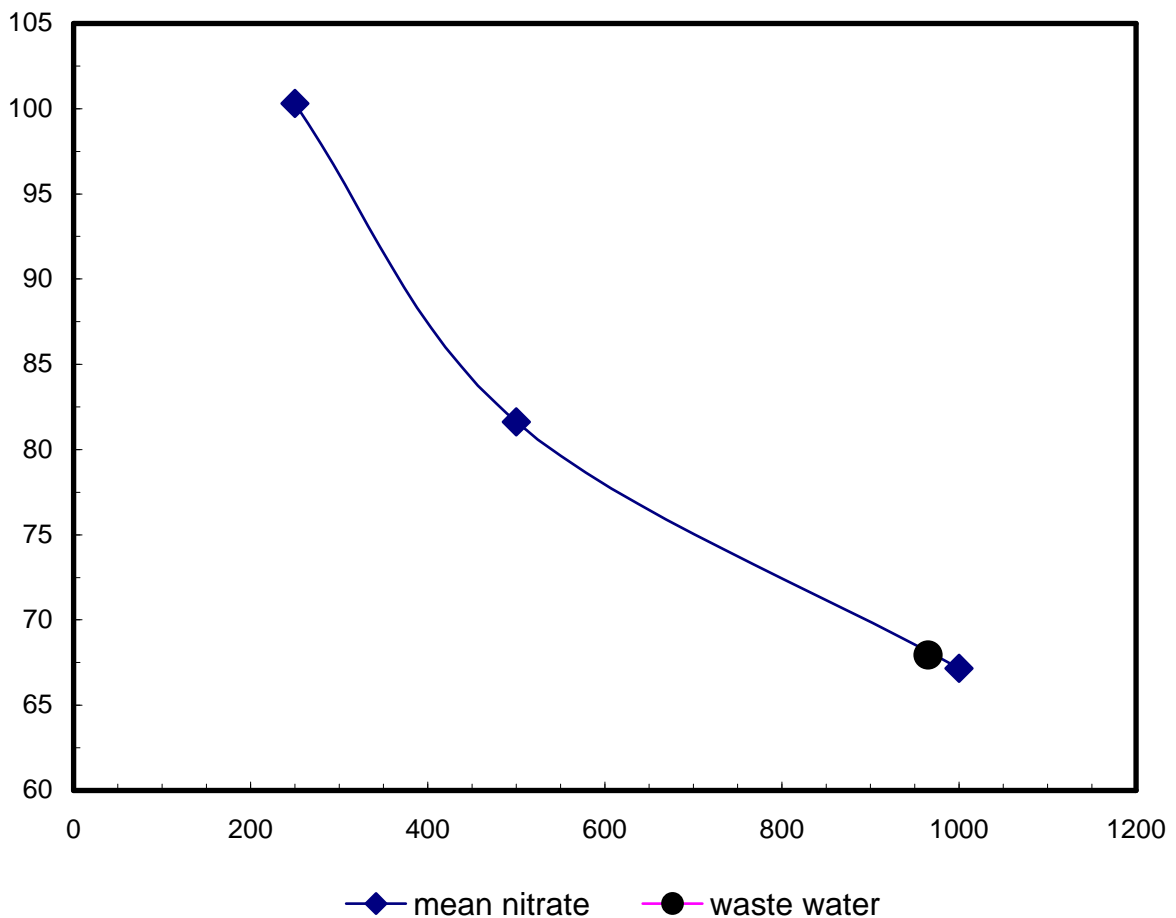
**Table 47:** calibration and amount of carbonate before the test



**Diagram 58:** calibration curve and determination of the ppm

| Nitrate       |               |      |       |       |       |           |
|---------------|---------------|------|-------|-------|-------|-----------|
| ppm           | Measured data |      |       |       |       | Mean [mV] |
| 1000          | 68,4          | 67,7 | 66,9  | 67,9  | 64,9  | 67,2      |
| 500           | 83,9          | 81,9 | 81,1  | 80,1  | 81,1  | 81,6      |
| 250           | 97,3          | 97,1 | 100,2 | 103,9 | 103,1 | 100,3     |
| Nitrate waste |               |      |       |       |       |           |
| 965           | 70,9          | 69,4 | 62,5  | 68,1  | 68,9  | 68        |

**Table 48:** calibration and amount of nitrate before the test



**Diagram 59:** calibration curve and determination of the ppm

|                    |      |      |                    |      |      |
|--------------------|------|------|--------------------|------|------|
| <b>50 21.05.07</b> |      |      | <b>20 21.05.07</b> |      |      |
| 5,34               | 5,4  | 5,54 | 4,66               | 4,61 | 4,5  |
| 0,69               | 0,27 | 0,63 | 0,24               | 0,11 | 0,12 |
| <b>50 26.02.07</b> |      |      | <b>20 26.02.07</b> |      |      |

|                     |      |      |                     |      |      |                     |      |      |
|---------------------|------|------|---------------------|------|------|---------------------|------|------|
| <b>100 21.05.07</b> |      |      | <b>200 21.05.07</b> |      |      | <b>500 21.05.07</b> |      |      |
| 5,7                 | 5,68 | 5,9  | 5,56                | 5,76 | 5,93 | 5,8                 | 5,82 | 6,05 |
| 0,69                | 0,38 | 0,47 | 0,76                | 1,37 | 0,98 | 2,31                | 2,21 | 2,36 |
| <b>100 26.05.07</b> |      |      | <b>200 26.05.07</b> |      |      | <b>500 26.05.07</b> |      |      |

**Table 49:** measured data BOD

| <b>(C1-C2)*F</b> | <b>Mean before</b> | <b>Mean after</b> | <b>Difference</b> | <b>Result</b>  | <b>C1/3</b> | <b>(2*C1)/3</b> |
|------------------|--------------------|-------------------|-------------------|----------------|-------------|-----------------|
| 100              | 5,76               | 0,51              | 5,25              | 524,67         | 1,92        | 3,84            |
| 200              | 5,75               | 1,04              | 4,71              | 45,6           | 1,92        | 3,83            |
| 500              | 5,84               | 2,29              | 3,55              | <b>1773,33</b> | 1,95        | 3,89            |
| 50               | 5,43               | 0,53              | 4,90              | 244,83         | 1,81        | 3,62            |
| 20               | 4,59               | 0,16              | 4,43              | 88,67          | 1,53        | 3,06            |

**Table 50:** determination of the BOD

## 8.6 Water after Test 3

| Solid degrade     |               |               |               |              |              |              |               |        |
|-------------------|---------------|---------------|---------------|--------------|--------------|--------------|---------------|--------|
| Water degr. 20.05 | 1             | 2             | 3             | 4            | Total solid  | Inorganic    | Organics      | Humid  |
|                   | 36,481        | 61,444        | 37,678        | 36,842       | 1,197        | 0,361        | 0,836         | 24,962 |
|                   | 33,622        | 58,347        | 34,688        | 33,990       | 1,065        | 0,367        | 0,698         | 24,724 |
|                   | 32,638        | 57,534        | 33,564        | 33,005       | 0,926        | 0,367        | 0,559         | 24,896 |
|                   | Mean          |               |               |              |              |              |               |        |
| <b>34,247</b>     | <b>59,108</b> | <b>35,310</b> | <b>34,612</b> | <b>1,063</b> | <b>0,365</b> | <b>0,698</b> | <b>24,861</b> |        |

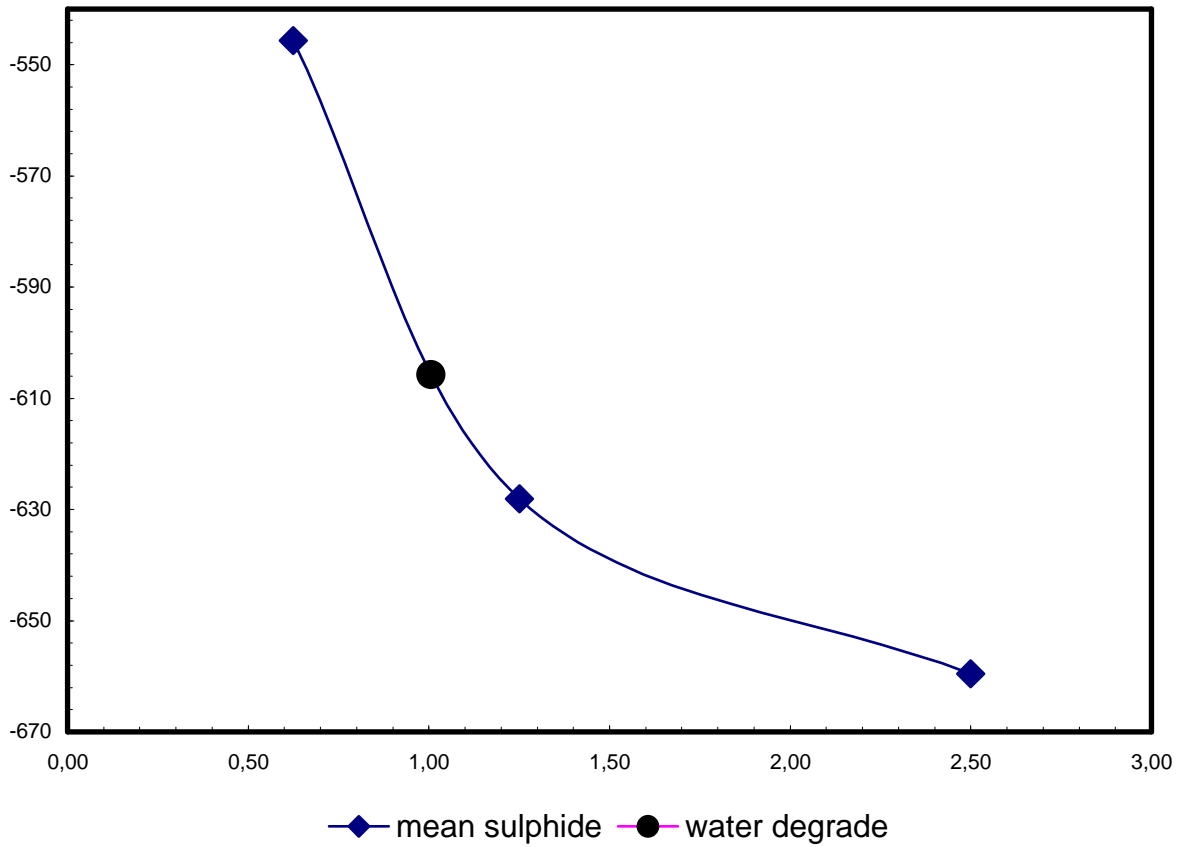
**Table 51:** solids in the wastewater after the test

| PH            |       |       |       |       |              |
|---------------|-------|-------|-------|-------|--------------|
| Measured data |       |       |       |       | Mean         |
| 7,596         | 7,598 | 7,588 | 7,588 | 7,598 | <b>7,594</b> |

**Table 52:** PH of the wastewater after the test

| Sulphide      |               |        |        |        |        |           |
|---------------|---------------|--------|--------|--------|--------|-----------|
| ppm           | Measured data |        |        |        |        | Mean [mV] |
| 2,5           | -656,1        | -657,8 | -660,2 | -658,6 | -665,1 | -659,6    |
| 1,3           | -627,1        | -627,8 | -628,2 | -628,9 | -628,2 | -628,0    |
| 0,6           | -541,8        | -546,6 | -541,4 | -546,2 | -552,4 | -545,7    |
| Water degrade |               |        |        |        |        |           |
| 1             | -614,1        | -598,9 | -599,4 | -616,6 | -599,4 | -605,7    |

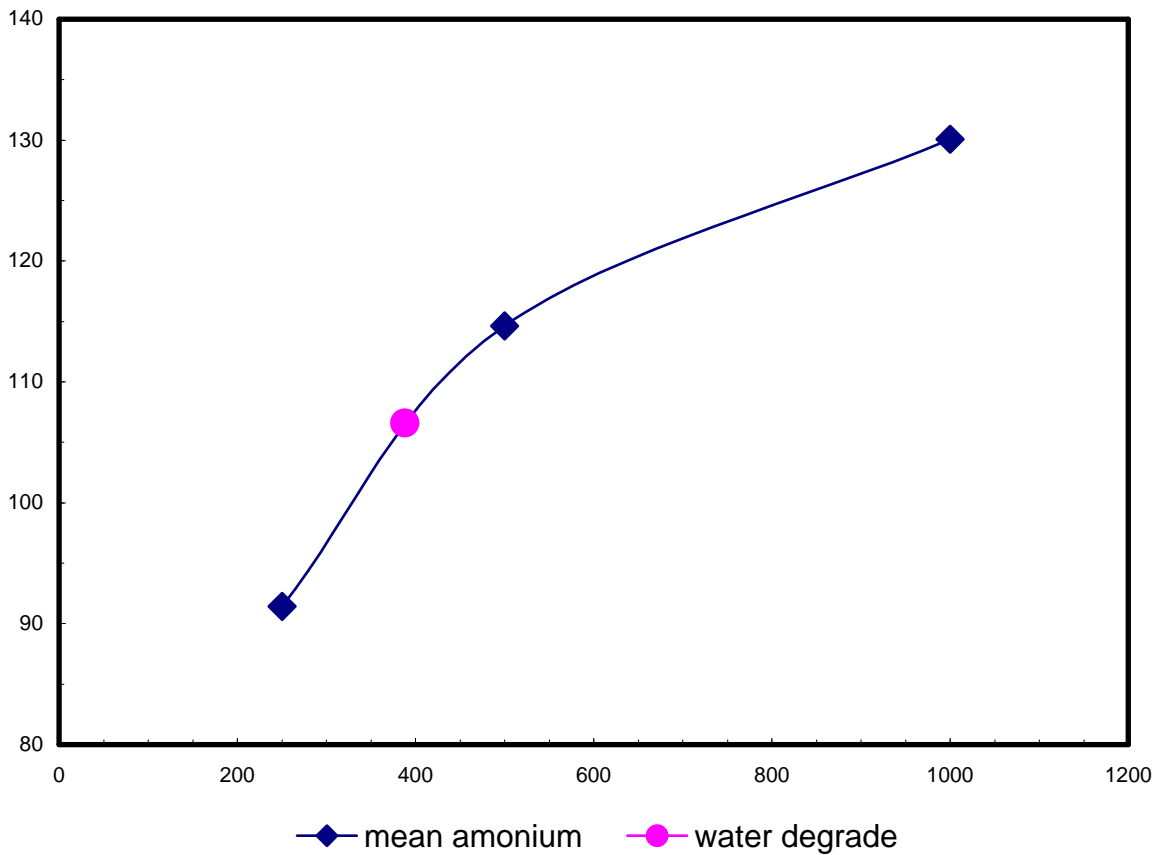
**Table 53:** calibration and amount of sulphide after the test



**Diagram 60:** calibration curve and determination of the ppm

| Ammonium         |               |       |       |       |       |           |
|------------------|---------------|-------|-------|-------|-------|-----------|
| ppm              | Measured data |       |       |       |       | Mean [mV] |
| 1000             | 131,6         | 130,9 | 129,4 | 129,3 | 129,1 | 130,06    |
| 500              | 115,4         | 115   | 114,6 | 114,3 | 113,9 | 114,64    |
| 250              | 87,4          | 91    | 92,4  | 93    | 93,4  | 91,44     |
| Ammonium degrade |               |       |       |       |       |           |
| 388              | 108,9         | 106,3 | 105,2 | 106,2 | 106,4 | 106,6     |

**Table 54:** calibration and amount of ammonium after test

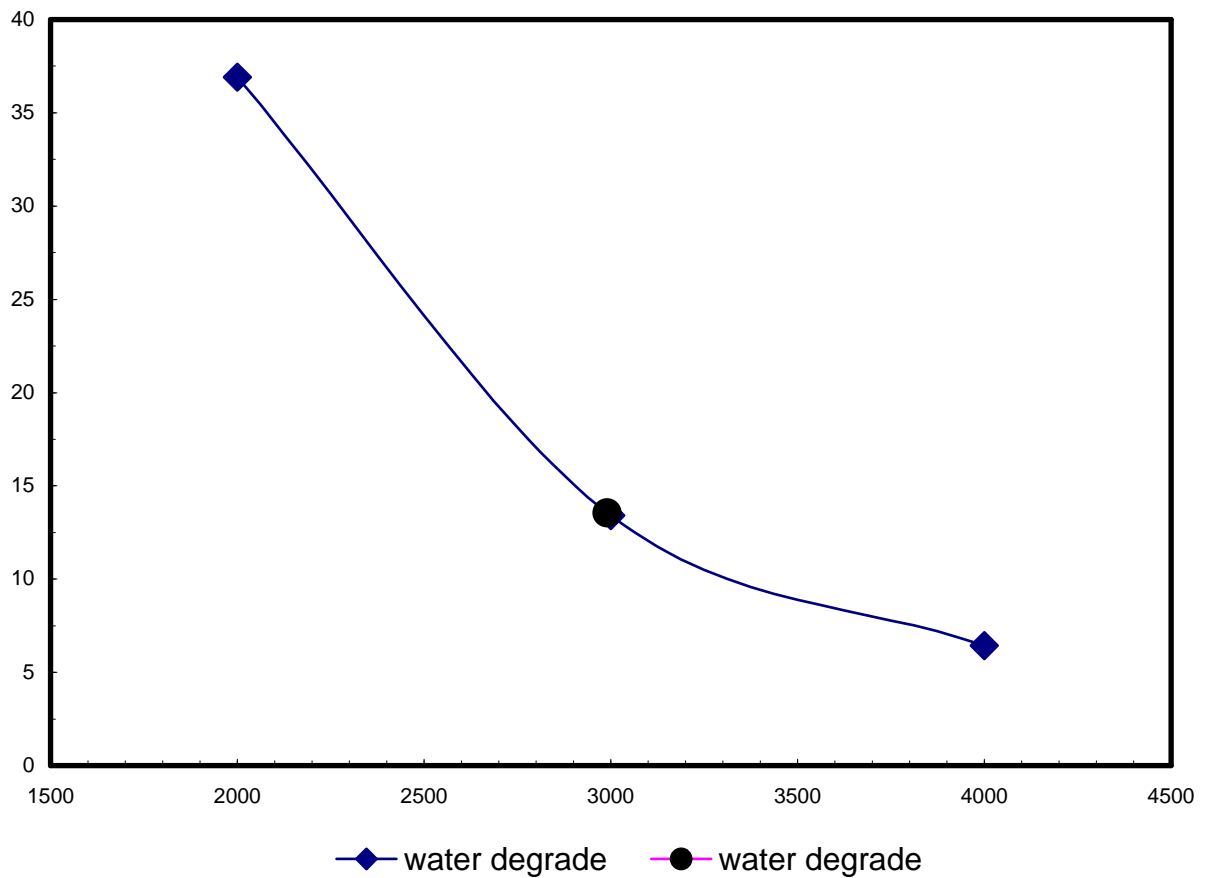


**Diagram 61:** calibration curve and determination of the ppm



| Carbonate         |               |      |      |      |      |           |
|-------------------|---------------|------|------|------|------|-----------|
| ppm               | Measured data |      |      |      |      | Mean [mV] |
| 2000              | 46,6          | 39,1 | 35,8 | 32,9 | 30,1 | 36,9      |
| 3000              | 9,1           | 14,9 | 14,9 | 13,3 | 14,8 | 13,4      |
| 4000              | 9,6           | 7    | 4,4  | 5,9  | 5,2  | 6,4       |
| Carbonate degrade |               |      |      |      |      |           |
| 2500              | 28,8          | 18,9 | 12,7 | 3,8  | 3,6  | 13,6      |

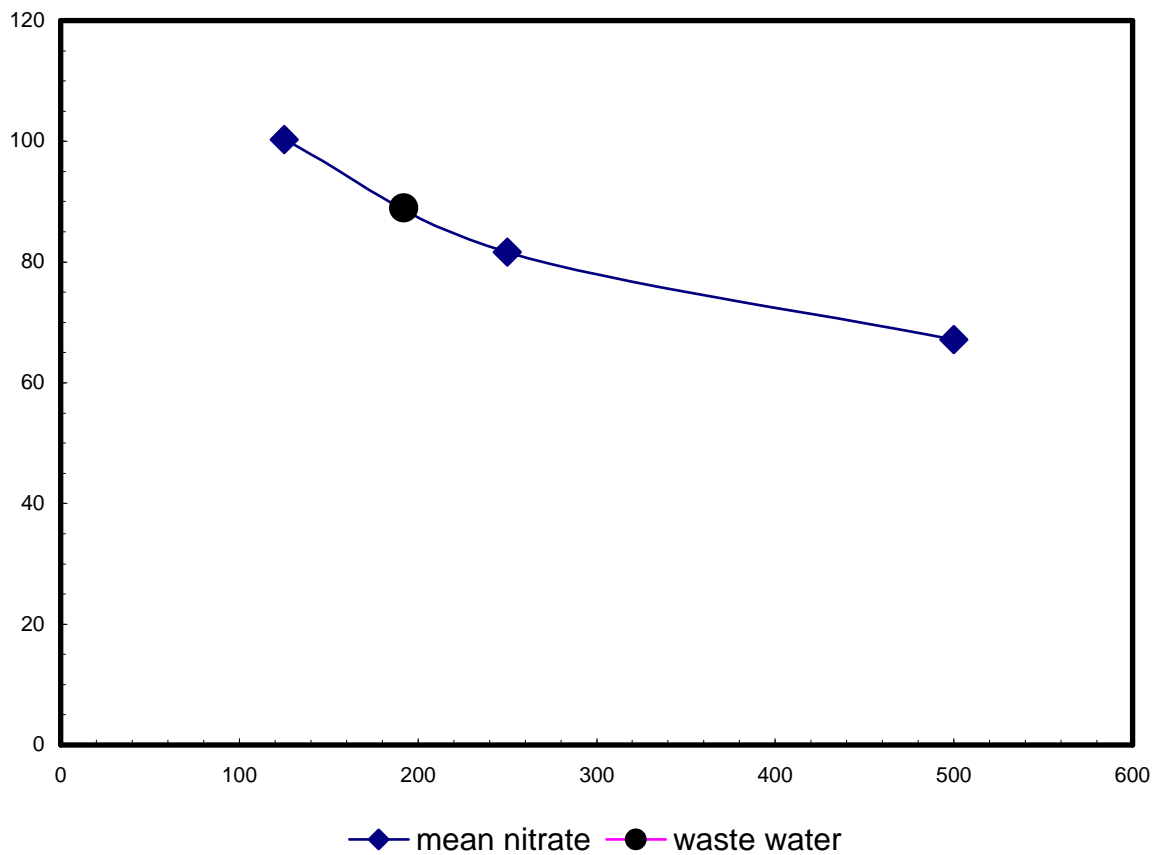
**Table 55:** calibration and amount of carbonate after the test



**Diagram 62:** calibration curve and determination of the ppm

| Nitrate         |               |      |       |       |       |           |
|-----------------|---------------|------|-------|-------|-------|-----------|
| ppm             | Measured data |      |       |       |       | Mean [mV] |
| 500             | 68,4          | 67,7 | 66,9  | 67,9  | 64,9  | 67,2      |
| 250             | 83,9          | 81,9 | 81,1  | 80,1  | 81,1  | 81,6      |
| 125             | 97,3          | 97,1 | 100,2 | 103,9 | 103,1 | 100,3     |
| Nitrate degrade |               |      |       |       |       |           |
| 192             | 104,9         | 98,4 | 86,1  | 84,3  | 71    | 88,9      |

**Table 57:** calibration and amount of nitrate after the test



**Diagram 63:** calibration curve and determination of the ppm

|                    |      |      |                    |      |      |
|--------------------|------|------|--------------------|------|------|
| <b>50 20.05.07</b> |      |      | <b>20 20.05.07</b> |      |      |
| 5,22               | 5,4  | 4,98 | 4,45               | 3,75 | 4,38 |
| 0,51               | 1,04 | 0,88 | 0,34               | 0,2  | 0,37 |
| <b>50 25.05.07</b> |      |      | <b>20 25.02.07</b> |      |      |

|                     |      |      |                     |      |      |                     |      |      |
|---------------------|------|------|---------------------|------|------|---------------------|------|------|
| <b>100 20.05.07</b> |      |      | <b>200 20.05.07</b> |      |      | <b>500 20.05.07</b> |      |      |
| 6,12                | 5,36 | 5,61 | 5,68                | 6,11 | 5,99 | 5,76                | 6,12 | 5,95 |
| 0,33                | 0,63 | 0,73 | 0,75                | 0,62 | 0,72 | 2,54                | 2,77 | 2,69 |
| <b>100 25.05.07</b> |      |      | <b>200 25.05.07</b> |      |      | <b>500 25.05.07</b> |      |      |

**Table 58:** measured data BOD

| <b>(C1-C2)*F</b> | <b>Mean before</b> | <b>Mean after</b> | <b>Difference</b> | <b>Result</b> | <b>C1/3</b> | <b>(2*C1)/3</b> |
|------------------|--------------------|-------------------|-------------------|---------------|-------------|-----------------|
| 100              | 5,70               | 0,56              | 5,13              | 513,33        | 1,90        | 3,80            |
| 200              | 5,93               | 0,70              | 5,23              | 45,6          | 1,98        | 3,95            |
| 500              | 5,83               | 2,67              | 3,16              | 1581,67       | 1,94        | 3,89            |
| 50               | 5,20               | 0,81              | 4,39              | 219,50        | 1,73        | 3,47            |
| 20               | 4,19               | 0,30              | 3,89              | 77,80         | 1,40        | 2,80            |

**Table 59:** determination of the BOD

## **8.7 Instrument specifications Ion Meter**

### **Model 3345**

#### **pH:**

|            |                   |
|------------|-------------------|
| Range      | -2 to 19.999 pH   |
| Resolution | 0.1/0.01/0.001 pH |
| Accuracy   | ±0.003 pH         |

#### **mV:**

|            |                     |
|------------|---------------------|
| Range      | -1999.9 to 1999.9mV |
| Resolution | 0.1mV               |
| Accuracy   | ±0.mV               |

#### **Concentration:**

|            |  |
|------------|--|
| Range      | $1 \times 10^{-9}$ to $9.99 \times 10^9$ |
| Units      | Activity, ppm, %, mg/l, M or none        |
| Resolution | 3 significant digits                     |
| Accuracy   | ±0.003pX for monovalent ions             |

**Input Impedance** >10<sup>13</sup> Ohms

**Number of Electrodes Inputs** 2

#### **Temperature:**

|                          |                             |
|--------------------------|-----------------------------|
| Range                    | - 10 to 105°C / 14 to 221°C |
| Resolution               | 0.1°C / 1°F                 |
| Accuracy                 | ±0.5°C / ±1°F               |
| ATC Range                | 0 to 100°C / 32 to 212°F    |
| Manual Temp. Comp. Range | 0 to 100°C / 32 to 212°F    |

## **8.8 Instrument specification Crison OXI 45**

|  |   |
|--|---|
| <b>Scale of the measurement unit<br/>,with the electrode Cellox 325:</b> | 0.0...199.9% x 200...600% of the saturation<br>0.00..19.99mg/l y 20.0...60,0 mg/l of the<br>concentration |
| <b>Temperature:</b>  | 0.0....50.0°C   |
| <b>Measurement error:</b>  | ≤ 0,5% of the measurement<br>temperature: ≤ 0,2°C   |
| <b>Reproducibility:</b>  | ≤ 0,2% of the measurement<br>temperature: ≤ 0,1°C   |
| <b>Correction of the salinity and<br/>atmospheric pressure:</b>          | automatically, with manual entrance of data   |
| <b>automatically compensation of<br/>the temperature:</b>                | of the sample<br>of the sensorial permeability of the membrane<br>type<br>sensors type NTC                |
| <b>Calibration:</b>  | To 100% of saturation of the OD   |
| <b>Screen:</b>   | Fluid crystal, with pictograms  |
| <b>Keyboard:</b>   | Of membrane<br>Pulsations per keypress: > 6 millions<br>Material: PET, with protective treatment          |
| <b>Connector:</b>  | DIN, protection IP67  |
| <b>Feeding:</b>  | two batteries of 1,5V, type AA,   |
| <b>Electrical security:</b>  | Follows UNE-EN 61010, UNE-EN 61010-1/A2   |
| <b>Electromagnetically compatibility:</b>                                | Follows CE,UNE-EN 61326, EN61010-1/A2   |

|                                      |   |
|--------------------------------------|---|
| <b>Protection class:</b>             | IP 65   |
| <b>Permitted ambient conditions:</b> | working temperature 0...50°C<br>Temperature of storage and transport -15...65°C |
| <b>Container:</b>                    | body material ABS   |
| <b>Physical parameters:</b>          | Weight approximately 200g, Dimension 160 x 75<br>x 50mm                         |

## 8.9 Instrument Specifications PH-Redoxmeter

|  |  |
|--|--|
| <b>Measurement scales:</b>                     | PH 0...14.00,<br>MV -1999....1999  |
| <b>Resolution:</b>                             | PH 0,01<br>MV 1  |
| <b>Manuel compensation of the temperature:</b> | -20...125°C  |
| <b>Criteria of the metering stability:</b>     | Variation maximum at 0,1mV in 5 sec  |
| <b>Display:</b>                                | Fluorescent 3 ½ digit for measurement,<br>3 ½ for temperature  |
| <b>Initial impedance:</b>                      | 1012 Ohms  |
| <b>Thermal driftage:</b>                       | 0,002 pH/°C  |
| <b>Inlets:</b>                                 | Indicative electrode or combined<br>Reference electrode  |
| <b>Outlets:</b>                                | current of polarization for Karl Fischer<br>analogical signal to record (to follow potential<br>electrode)               |
| <b>Autocalibration:</b>                        | tampon recognizes the solutions  |
| <b>Potential of asymmetry:</b>                 | Except 0...+- 20mV<br>Except with "AVISO" +-20...70mV/pH<br>Rejected > +-70mV  |
| <b>Slope:</b>                                  | Except 53....65mV/pH<br>Except with "AVISO" 48...53mV/pH.<br>65...70mV/pH<br>Rejected < 48mV/pH<br>Rejected > +- 70mV/pH |
| <b>Working conditions:</b>                     | room temperature 0-50°C<br>relative humidity 90%, not condensed  |
| <b>Feeding:</b>                                | 220V. 50/60Hz, 110V under order  |
| <b>Dimensions:</b>                             | 305 x 80 x 220 mm  |
| <b>Weight:</b>                                 | 2,5k   |

## **8.10 Accomplishment of a complete analysis**

The series of operations to assure, for a complete analysis of a gas mixture contains all the components previously mentioned. Which are in execution order, the following ones.

- Introduction of the gas in the apparatus
- Absorption of the carbon dioxide
- Absorption of the heavy hydro carbons
- Absorption of oxygen
- Absorption of the carbon monoxide
- Combustion of the hydrogenate
- Combustion of the methane
- Absorption of the formed carbonic dioxide
- Measurement of the remainder
- Calculations

### **Introduction of the gas in the apparatus:**

In this part it is explained what steps are necessary to introduce the gas into the apparatus to get good results with this measurement. Initially key A is closed and connected with the surrounding and J. A is a three way valve. So one can connect the apparatus with the surrounding the gas collecting tube and close it. The keys K, F, E, D, C, and B are closed. Afterwards the key A gets opened. Fill so much water in the bottle M that it shows 0 at the measuring tube. Now rise bottle M till the measuring tube shows hundred. Close key A and open key B. Now the water level rises in the chamber 1a. It should rise until the blue mark like it is shown in **Figure7**. If there is not enough force at the first time repeat the same procedure again. Repeat the explained process also with the other chambers. Then the apparatus gets filled with biogas. Pump first al the air with the bottle M out of the apparatus. If there is enough pressure it should be no problem to fill the tube with the gas.



### **Absorption of the carbon dioxide:**

Key B is driven that it communicates H with the first chamber. At the beginning the solution reaches the marker. The bottle M is to afford a circulation of the biogas in the measurement. Circulation means the gas gets in contact with the absorbent. When one move the bottle on a higher level the water in the clamp follows to the same in this case higher level. With this up and down movements one creates a circulation and thus there is a communication between the gas and the fluid. At the interface between the gas and the fluid the adsorption is taking place. Take the bottle M and bring the solution back to the blue marker close B and put the bottle back in the device. R1 is the number of CO<sub>2</sub>, which got absorbed.

$$\% \text{ CO}_2 = R1$$

### **Absorption of oxygen:**

For this operation the same procedure than above was repeated. Nevertheless, the absorption of oxygen with the pirogalat is slower and therefore it is necessary that the gas pass through the adsorbent 4 or 5 times.

$$\% \text{ O}_2 = R1 - R2$$

### **Absorption of Oxide of carbon:**

For this operation the same procedure than above with the CO<sub>2</sub> was repeated.

$$\% \text{ CO} = R2 - R3$$

### **Combustion of the hydrogen**

This part explains how to combust the hydrogen in details and how to measure the contraction. The furnace is put on, after it is necessary placing the regulation in the position 10% of **Tension**. Place the key G that chamber 6 communicates with the left part of the furnace. Open key K. Bottle M rises and 6a makes it possible that the gas slowly pass through the tube of quartz S through key K until the chamber. The temperature arises so high that the H<sub>2</sub> changes into water, which stays in chamber 6a. The gas which leads to the measuring burette H without passing through the quartz tube is given back; it is enough to turn key G back and to lower bottle M. The contraction, which minimizes the volume, is the percentage of hydrogenate that is in the mixture.

$$\% \text{ H}_2 = R3 - R4$$

### **Combustion of the methane:**

This part shows how to combust the methane in details. Next the combustion of the methane takes place. Beginning with adjusts the regulating R in the point 60% ( it takes about 20 minutes to arrive at this temperature ). If a pyrometer is available it is possible to introduce it in the furnace, between S and T ). Till now it is quite the same as in the case of the combustion of the hydrogenate explained in 6a. (oxidize of copper of the interior of the quartz tube should be renewed each 4 or 5 determinations according to the class of gas that is analysed). The next step is the combustion of carbonic anhydride to carbon dioxide. In the combustion of the methane with oxidize of copper a contraction of the volume does not take place because there is only a changing of the molecules between the solid and the gaseous condition. If the operation has been carried out satisfactorily, the volume of gas that becomes back to the burette has to be just the same like before burning the hydrogenate. The volume of methane becomes quantitative carbonic anhydride. The determination of the percentage function the same way like the percentage of CO<sub>2</sub> is determined.

$$\% \text{ CH}_4 = \text{R}_4 - \text{R}_5$$

### **Measurement of the remainder:**

The remainder that has been left after the last operation consists only up of the inert gases that continues in the mixture, considering it self into the percentage of nitrogen.

$$\% \text{ N}_2 = \text{R}_5$$

### **9° Calculations Summary of the found percentage:**

$$\% \text{ CO}_2 = \text{R}_1$$

$$\% \text{ O}_2 = \text{R}_1 - \text{R}_2$$

$$\% \text{ CO} = \text{R}_2 - \text{R}_3$$

$$\% \text{ H}_2 = \text{R}_3 - \text{R}_4$$

$$\% \text{ CH}_4 = \text{R}_4 - \text{R}_5$$

$$\% \text{ N}_2 = 100\% - \text{R}_5$$

## 9 List of literature

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