THERMOGRAVIMETRY: A METHOD TO EVALUATE THE REGENERABILITY OF ACTIVATED CARBON

by

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INDEX

SYNOPSIS

A method was developed to evaluate solid phase adsorbate distribution and implied regenerability of activated carbon used in water reclamation. The method is based on thermal analysis principles and consists of heating the activated carbon in a nitrogen atmosphere to 850 °C.

From the wide range of thermoanalytical techniques currently in use, thermogravimetry and evolved gas analysis were selected as the most appropriate techniques. The physical properties measured with these techniques were mass loss and moisture content.

The different adsorbate fractions which influence regenerability, were characterised with respect to temperature intervals, based on first derivative minima. A specific advantage of adsorbate characterisation is the possibility of quantifying the highly volatile adsorbate fraction (desorbing at temperatures below 230 °C). This quantification was done by distinguishing between moisture and total mass loss in this temperature range.

In this study the emphasis lay in the development of a test method for the evaluation of spent activated carbons from a regenerability point of view and also on the practical evaluation of this test method. The activated carbons studied were evaluated for the influence liquid phase oxidative pretreatment has on regenerability. The overall tendency was that, of the pretreatments used, preozonation had a more favourable influence on regenerability than preoxygenation and prechlorination. The test method was also used to study carbons used to reclaim secondary treated wastewater for paper production. With the developed test method it was possible to advise the user on the reusability and regenerability of the carbons in question.

This practical application of the developed test method helped to prove that substantial cost savings can be obtained by proper regeneration of spent activated carbons.

SAMEVATTING

'n Metode is ontwikkel om soliedefase-adsorbaatverdeling te evalueer, asook die gepaardgaande regenereerbaarheid. Hierdie metode is gebaseer op termoanalitiese beginsels en bestaan uit die verhitting van geaktiveerde koolstof, in 'n stikstofatmosfeer, tot 850 °C.

Van die wye verskeidenheid van termoanalitiese tegnieke in gebruik, is termogravimetrie en ontwikkeldegasanalise as die mees geskikte tegnieke geselekteer. Die fisiese eienskappe met hierdie tegnieke gemeet, is massaverlies en voginhoud onderskeidelik.

Die verskillende adsorbaatfraksies, wat regenereerbaarheid beïnvloed, is gekarakteriseer met verwysing na temperatuurintervalle wat op eerste afgeleide minima gebaseer is. 'n Spesifieke voordeel in die kwantifisering van adsorbate is die moontlikheid om die hoogsvlugtige adsorbaatfraksie (wat onder 230 °C desorbeer) te kwantifiseer. Die kwantifisering is gedoen deur die verskil tussen totale massaverlies en voginhoud in dié temperatuurgebied te onderskei.

Die klem het in hierdie studie gelê op die ontwikkeling van 'n toetsmetode vir die evaluering van gebruikte geaktiveerde koolstowwe vanuit 'n regenerasieoogpunt asook op die praktiese toepassing van hierdie toetsmetode. Die geaktiveerde koolstowwe is bestudeer om die invloed van vloeistoffasevooroksidering op adsorbaatverdeling na te gaan. Die algemene tendens is dat, van die verskillende vooroksiderings gebruik, voorosonering 'n gunstiger invloed het op regenereerbaarheid as voorchlorering en vooroksigenering. Die toetsmetode ontwikkel is verder gebruik om koolstowwe te bestudeer wat gebruik is vir die herwinning van water uit sekondêre uitvloeisel vir papierproduksie. Met die ontwikkelde tegniek was dit moontlik om die gebruiker te adviseer aangaande

die hergebruik en regenereerbaarheid van die toepaslike koolstowwe.

Die praktiese toepassing van die toetsmetode het ook help bewys dat doeltreffende heraktivering van gebruikte koolstof kan lei tot aansienlike kostebesparings.

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GLOSSARY

{1} Thermogravimetry (TG). A technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled-temperature program (ASTM E473-82).

{2} Evolved gas analysis (EGA). A technique in which the evolution of amount of volatile product(s) released by a substance is measured as a function of temperature while the substance is subjected to a controlled-temperature program (McAdie, 1972; ASTM E473-82).

{3} Porosimetry. A technique in which the porosity of a substance is measured by means of mercury intrusion under high pressure and in which the pore sizes are proportional to the pressure.

{4} Derivative. Pertaining to the first derivate (mathematical) of any curve.

{5} Thermal analysis (TA). A group of techniques in which a physical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature program (ASTM E473-82).

{6} Standardisation. The selection and fixing of the most appropriate experimental conditions, taking in account the possible experimental conditions (Paulik and Paulik, 1981).

{7} Normalisation. The adaptation of experimental conditions in the development of new measuring techniques to approach the ideal isothermal, isobaric and equilibrium conditions prescribed by rules of physical chemistry (Paulik and Paulik, 1981).

TABLES

FIGURES

1. INTRODUCTION

Rapid industrialization and the population explosion in South Africa have led to a progressive deterioration in the quality of its surface water supplies. Limited available water and low rainfall, coupled with frequent periods of drought, make South Africa particularly vulnerable. In order to produce water of high quality to satisfy the ever increasing demand, water treatment methodology must be continuously upgraded.

The technologies involved, such as activated carbon adsorption and desalination processes, are costly. In South Africa, activated carbon has been applied in a number of plants with Sasol, Mondi Merebank, Iscor Newcastle (and Windhoek) being relatively large users. However, process optimization is essential to reduce the high cost of activated carbon adsorption and regeneration.

For example, an average mass loss of 7% is experienced per adsorption/regeneration cycle (Hutchins, 1975; Suzuki *et al.*, 1978; van Vliet, 1978). The make-up costs caused by this loss can account for as much as 50% of the total water treatment costs for processes which include activated carbon adsorption. Cairo *et al.* (1982) report that 80% of the annual costs of an adsorption plant can be ascribed to regeneration related aspects. These figures illustrate that the regeneration process is the main cost determining factor in the operation of an adsorption plant. During regeneration the adsorbates saturating the adsorption capacity of the activated carbon are removed.

Knowledge about the behaviour, during heating, of the adsorbates present on the activated carbon may be beneficial in formulating the required regeneration conditions. In this way it may be possible to limit regeneration losses.

The most widely used regeneration process is selective oxidative thermal regeneration (von Dreusche, 1975; Gomella, 1982). During thermal regeneration, adsorbed compounds pass through the following successive steps:

- drying
- volatilization
- cracking
- pyrolysis
- oxidation with steam or carbon dioxide.

The last step is used to remove the carbonaceous residual formed during pyrolysis (Gomella, 1982; Jones and Gwinn, 1983).

Activated carbon regenerability and thus also the regeneration conditions are determined mainly by such adsorbate characteristics as quantity, mineral content and carbonaceous residual formation potential, as well as the characteristics of the carbonaceous residual (Suzuki *et al.*, 1978). The main characteristics are the form under which the residual is deposited, either graphitic or amorphous (Jones and Gwinn, 1983 and Takeuchi, 1979), the base material of the activated carbon as well as the pyrolysis temperature (Jones and Gwinn, 1983).

Besides having an influence on the regeneration conditions, carbonaceous residual characteristics also have an influence on activated carbon losses (Jones and Gwinn, 1983). It would therefore be advantageous if some of the carbonaceous residual characteristics could be controlled. Organic products are always present in waste waters and as these are removed during adsorption it would be an advantage to be able to change the structure of these organics so as to improve spent activated carbon regenerability (i.e. reduce carbonaceous residual formation).

Van Leeuwen *et al* (1983) studied the influence liquid phase oxidative pretreatment has on the removal of organic substances in a water reclamation plant and on biological activity on biological activated carbon. It is also known that pre-oxidation has an influence on the structure of organic substances (Benedek, 1974) and on their adsorbability onto activated carbon. It was therefore decided to investigate the influence liquid phase oxidative pretreatment has on spent activated carbon regenerability, based on adsorbate distribution patterns.

For this investigation it was necessary to develop a specific test method to evaluate the influence of liquid phase oxidative pretreatment on adsorbate distribution in spent activated carbon and on spent activated carbon regenerability. The method had to be developed in such way that it could be used for the evaluation of the regenerability of any spent activated carbon.

The test method is based on the following analytical techniques, (the figures given in brackets refer to the glossary where a full definition is given):

- Thermogravimetry (TG) {1}
- Evolved gas analysis (EGA) {2}
- Porosimetry {3} and
- Derivative {4} thermogravimetry (DTG)

This thesis deals with the development and evaluation of a test method for the evaluation of spent activated carbon regenerability, and is presented as follows:

- Background to familiarize the reader with thermal analysis and an overview of related literature. (Section 2)

- Method development in which the influence of three variables is studied and formulation of a standardized test procedure based on the observed influence o these variables. (Section 4)

- Evaluation of the method using spent activated carbons derived from pilot scale adsorption plants as well as from a full scale plant. (Section 5)

- Discussion and cost calculation which support the feasibility of the test method developed for the evaluation of spent activated carbon regenerability (Section 5)

2. BACKGROUND

In this section, a concise background is given for readers who are not familiar with thermal analysis (TA{5}), especially with TG. The basic principles of TA (particularly TG) are dealt with, since TG forms the basis of the developed test method.

An overview of the applications of TG and also EGA for the evaluation of activated carbon and related substances will also be presented.

2.1. Historical evolution

Thermal analysis finds its roots as far back in history as the 17th century. In 1659 the Bohemian philosopher and teacher J.A. Comenius stated: "To observe clearly the effect of heat or cold, a visible object should be subjected to heating and subsequent cooling, and the sensible changes made by heat or cold will then be visible to the eye" (Sestak, 1984).

Modern TA is not only the continuation of the above but also of the original experiments of Le Chatelier (1887) and Robert-Austin (1889) who used TA for phase analysis. In the 20th century, Czechoslovakia and Hungary took the lead in the field of TA. This group of analytical techniques entered a new development phase in the 1950's, when sensitive thermocouples became available and electronics emerged. However, errors of as much as 20% still occurred, owing to overlapping thermal events (Paulik and Paulik, 1981). This shortcoming led to the introduction of derivative and simultaneous methods (Paulik and Paulik, 1981), in order to:

- increase the information obtained
- increase the resolution between the thermal events
- standardise {6} the experimental conditions
- increase the selectivity of the measurements
- normalise {7} the experimental conditions.

The first attempt to achieve these aims was to change the type of sample holder (Paulik and Paulik, 1981) because some of the equipment in use is insensitive, thus necessitating large samples. Samples as large as 600 mg (Paulik et al, 1983) were and still are not uncommon and accurate analyses are only possible by using a so called multiplate sample holder (i.e. different small sample holders are stacked on top of each other and supported on a central shaft using spacers to separate the different sample holders from each other).

With the evolution of electronics, more sensitive analytical equipment became available and currently, thermobalances with a sensitivity of 0,1 μg are available, requiring samples of between 5 and 10 mg. In spite of this, the multiplate sample holder is still very popular with East European researchers because they have to rely on insensitive equipment, while in the West the newer type of high sensitivity equipment is mainly used. The equipment used in this study belongs to the latter category. The use of such sensitive equipment results in the collection of very accurate experimental data.

Paulik (1954) developed a combined technique that could produce TG as well as DTG curves simultaneously by using a derivative thermobalance. Nowadays, the TG signal generated by the thermal events taking place in the sample, is derivated electronically, making the older, complicated equipment and techniques obsolete. The very accurate first derivative curve generated in this way is called the "derivative thermogravimetric curve".

As a single thermoanalytical technique is seldom sufficient to obtain all the required information on a sample, a combination of techniques must be used. However, as a combination of techniques has never been used before for the study of activated carbon, their necessity is illustrated using analysis of bauxite samples as an example. During the analysis of bauxite it was found that insufficient information could be obtained from the TG-curve alone. However, the DTG-curve revealed much more information. The final elucidation of bauxite decomposition, however, was only possible when EGA was used in combination with TG and DTG (Paulik, 1981).

This example shows that the combination of different thermoanalytical techniques is sometimes necessary to obtain complete information about the thermal events taking place in a sample and thus also about the sample itself. When more than one analytical technique is used, it is of utmost importance that all analyses are performed under the same conditions in order to avoid experimental and analytical errors. This requirement must also be met to ensure repeatability of results (Sestak, 1984).

2.2 Equipment requirements

As TG is a very sensitive technique it is evident that the equipment used must be of very high quality and comply with very high standards. These standards and requirements are described in the following subsections.

2.2.1 Thermobalance

The major component in a TG system is the thermobalance. This type of balance differs from an ordinary analytical balance in that it is highly accurate (sensitivity = 0,1 µg) and that it can be used in environments where a controlled temperature change occurs. During analysis the position of a thermobalance will only change when the thermal event taking place in the sample releases entrapped gas or when volatile compounds are desorbed. As the position of the sample relative to the furnace is very important in obtaining accurate and reproducible results, special attention must be given to the design and selection of the thermobalance (Daniels, 1973).

Thermobalances can be divided into two types, namely deflection balances and null balances. The latter type of balance is preferred over a deflection balance because deflection balances have disadvantages, for example the position of the sample (sample holder) changes relative to the furnace during the course of the analysis. This change in position results in an uncontrolled change in thermal environment during analysis, which may have an influence on the analytical results. A second disadvantage is that the deflection as result of a change in sample mass is only linear for very small displacements. These factors influence accuracy and reproducibility, especially when small samples (5-10 mg) undergo large mass changes as is the case of some of the activated carbon samples studied.

Figure 1 depicts different thermobalance mechanisms. Of these, the beam balance is best suited as null balance. In a null balance, as is depicted in detail in Figure 2 (Cahn balance), the balance displacement, as result of a change in sample mass, is continuously counteracted by the nul mechanism. The balance displacement is measured and a restoration (counteracting) force proportional to the displacement is applied to the balance beam. This counteraction keeps the sample in its original position and thus ensures a controllable thermal environment. The magnitude of the counter action is measured and displayed as a change in sample mass (mass loss).

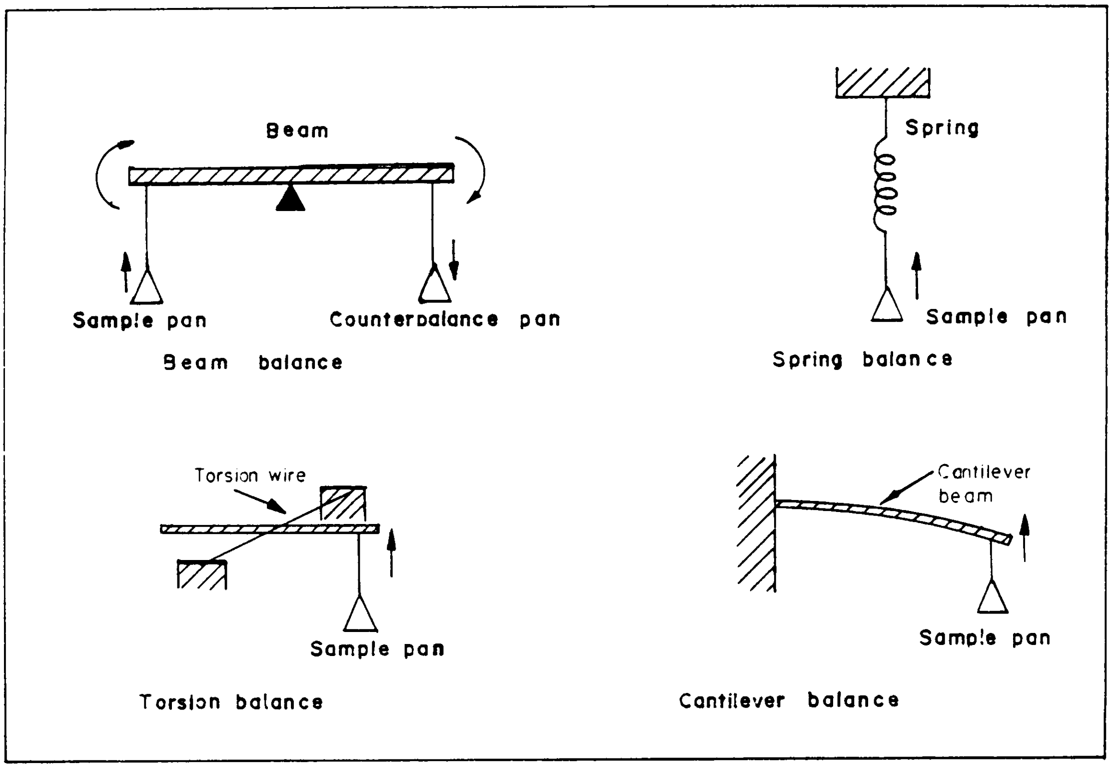


Figure 1: Thermobalance mechanisms

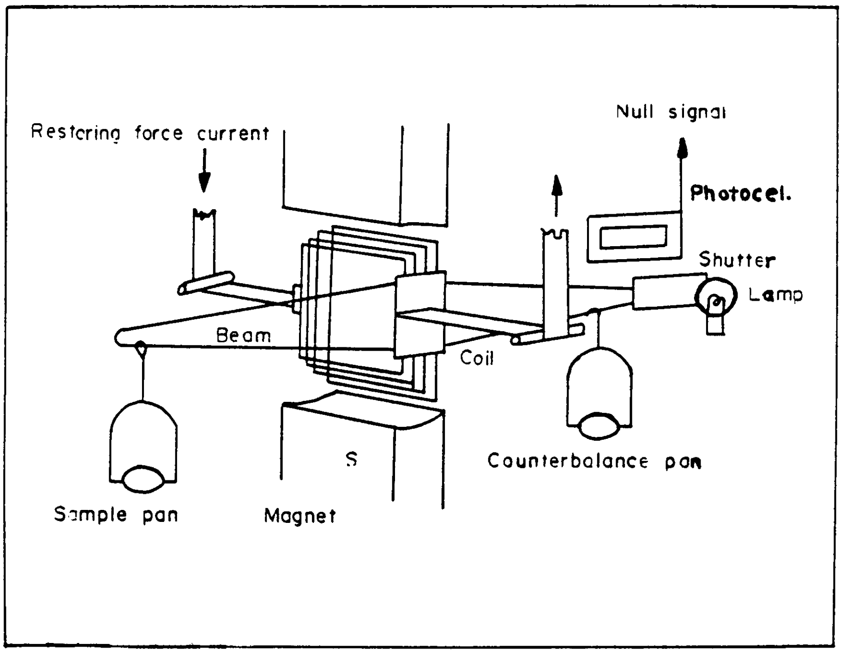


Figure 2: Cahn balance

2.2.2 Microfurnace

Apart from the balance, a TG-system also needs a heat source in the form of a microfurnace (Figure 3 depicts two different furnaces).

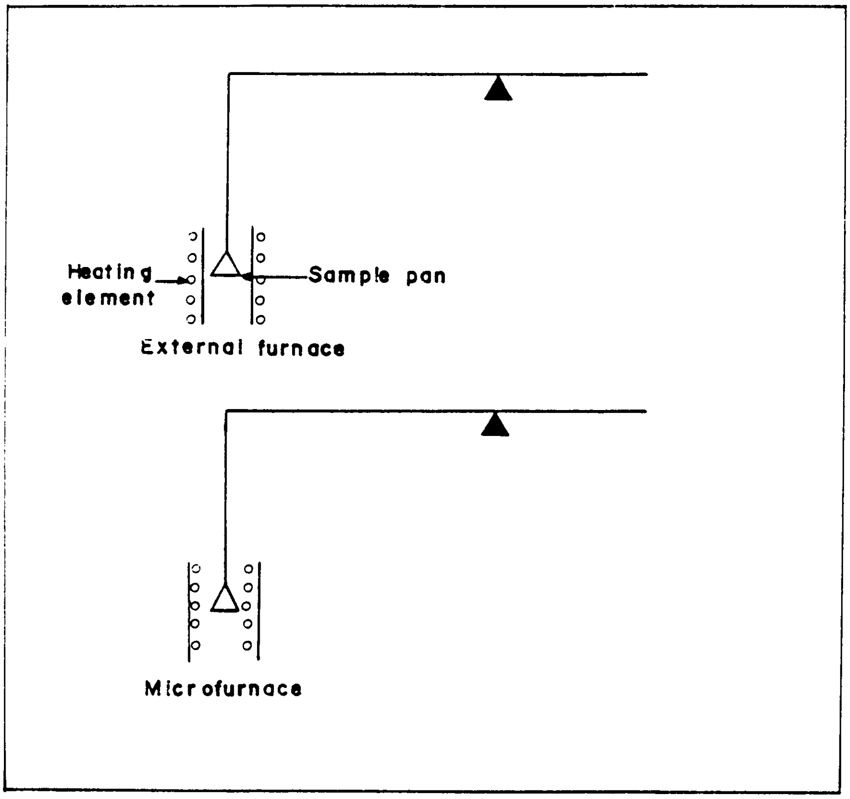


Figure 3: Microfurnaces

The ideal microfurnace has a very low thermal mass so that high heating rates (up to 200 °C) can be used. This low mass is mainly found in the so called internal microfurnace. This type of furnace allows performance of high temperature studies because here the sample can be heated very quickly to the required commencing temperature. This is advantageous when a controlled atmosphere is used and when the furnace cannot be opened to insert a sample at the isothermal temperature because this can disturb the atmosphere. Other advantages offered by an internal microfurnace are (Daniels, 1973) -

- reduced heat transfer path length
- minimisation of atmospheric effects

- small samples may be used
- "Curie point" calibration may be used

2.3 Thermogravimetric data generation

Modern TG is based on the very accurate observation of small mass changes, which can only be measured using high sensitivity systems. These systems need careful protection of the electronic weighing mechanism against corrosive gases and vapours. This is usually done by passing an inert gas, at a slight overpressure, through the compartment housing the balance electronics and by introducing the reactive gas(es) directly in the furnace compartment. This technique, in which a gas passes continuously over the sample, is known as dynamic atmosphere analysis. The advantage of this method is that vaporous and gaseous decomposition products are immediately evacuated from the system, which helps to protect the electronics of the thermobalance. A dynamic atmosphere also offers two other advantages over a static one, namely -

- the occurrence of secondary reactions is reduced
- the partial pressure of the gaseous and vaporous decomposition products is lowered.

TG is applicable only to systems that liberate vapours or gases upon heating, with a concomitant mass loss. The ideal case, if more than one volatile product is liberated upon heating, would be that every volatile product, or group of products, is released in a specific well defined temperature interval, where the temperature intervals do not overlap. The resulting TG curve will then be of the same form as the curve shown in Figure 4 (stepped curve). This TG-curve, illustrating the decomposition of $CaSO_4.2H_2O$ (Figure 4) shows very distinctive steps separated by plateaus, with each step corresponding with a specific reaction or volatile product release. This example is used, as there are no such curves for activated carbon.

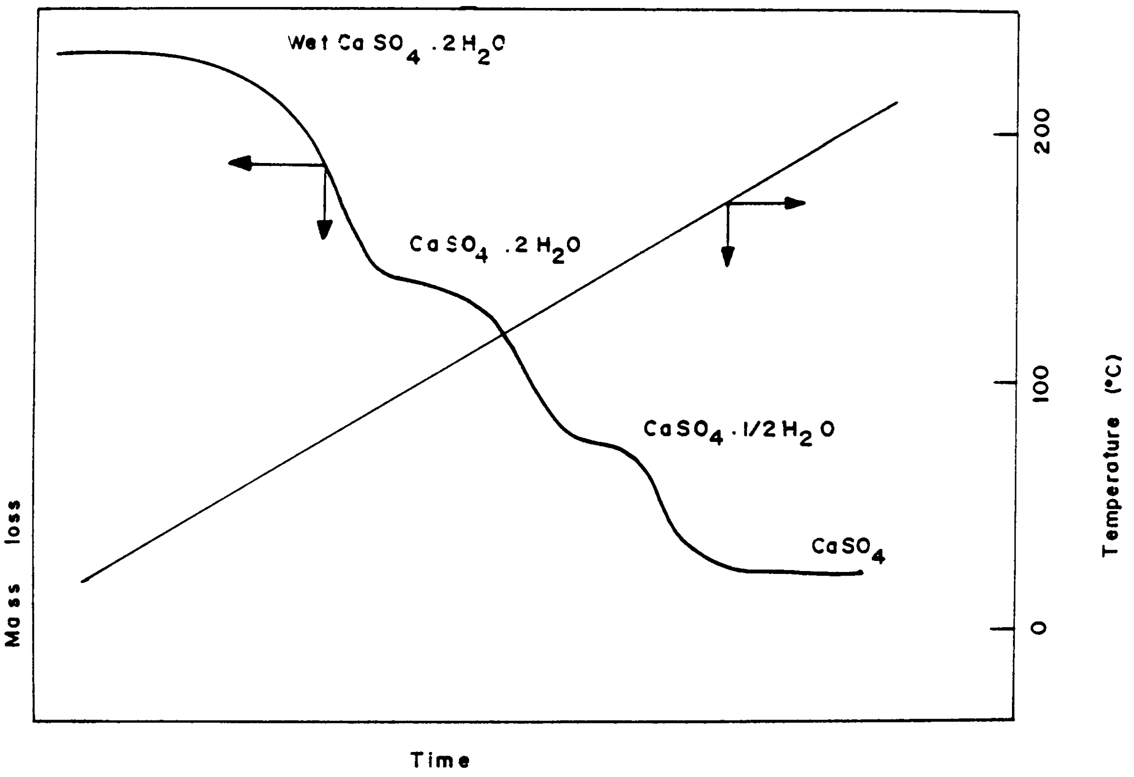
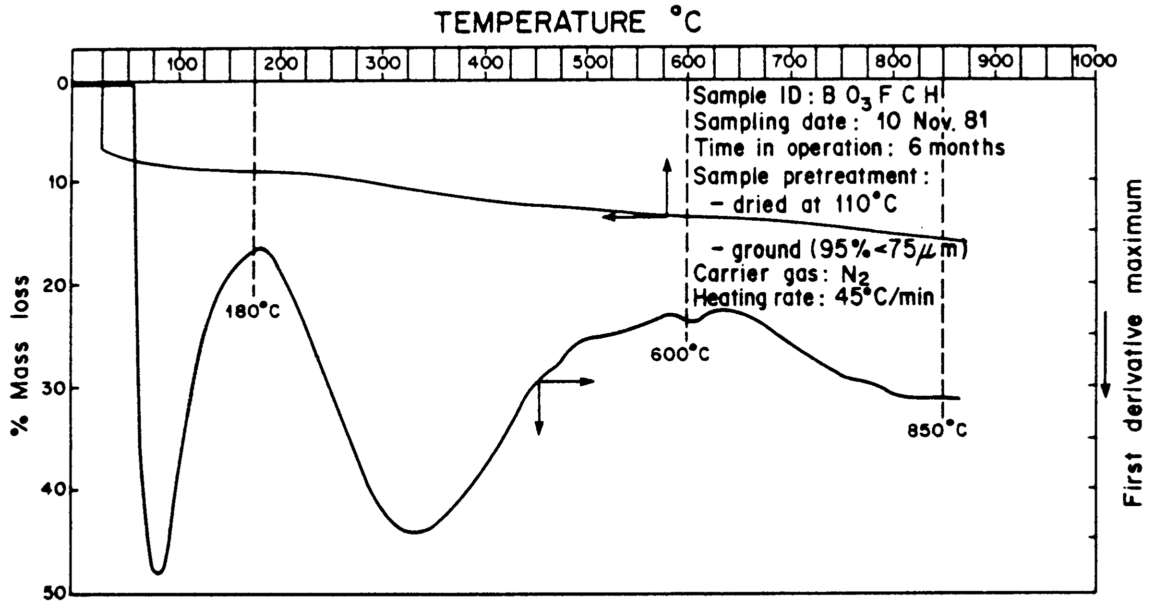


Figure 4: Stepped curve

Since chemical reactions are influenced by temperature, the main mass losses in a dynamic (scanning) TG analysis, however, usually occur in specific temperature ranges which generally overlap, resulting in the disappearance of the plateaus. This phenomenon finally results in a smoothed (multiple reaction) curve, which shows no clearly defined steps (Figure 5, top curve).

In an ideal (stepped) curve, the initial deviation from the horizontal line (onset) is not very reliable as reference point for the determination of the beginning of a reaction and for the comparison of reaction temperatures. This becomes totally impossible in a multiple reaction curve with overlapping thermal events. To facilitate the interpretation of TG-curves, DTG is used to obtain additional information. The DTG-curve (Figure 5, bottom curve) consists



Sample ID: B O_3 F C H
Sampling date: 10 Nov. 81
Time in operation: 6 months
Sample pretreatment:
- dried at 110°C
- ground (95% < 75 μm)
Carrier gas: N_2
Heating rate: 45°C/min

Figure 5: Smooth curve

of a series of peaks, each corresponding with a specific reaction step or thermal phenomenon. The peak maximum corresponds with the point on the TG-curve where the highest reaction rate (mass loss rate) occurs, while the area under the curve is proportional to the fractional mass loss at each particular stage of the analysis. A return of the DTG-curve to the baseline corresponds with a plateau in the TG-curve. In the case of overlapping reactions or thermal events, however, the DTG-curve will only show a minimum and it is usually very difficult to increase peak resolution due to the complex nature of the reactions causing this problem.

In order to derive better information from TG-curves, knowledge of how these curves can be influenced during analysis is required. The shape of the curve (separation of thermal events) is influenced by both operational and apparatus related variables. The apparatus related variables are determined by the equipment used, the following being the most important:

- Shape of the sample holder
- Dimensions of the furnace
- Place of the sample in the furnace.

These variables, except perhaps the shape of the sample holder, are determined by the manufacturer, and very little can thus be done to change them. The main operational variables that can be changed by the operator are -

- heating rate
- sample form (particle size)
- sample mass
- purge gas flow
- purge gas composition.

If all these variables are optimised and a smoothed curve is still obtained then DTG curve minima, instead of DTG curve zeros, have to be used for the determination of the different reaction temperature intervals.

The influence of some of these variables (when applicable) will be discussed in greater detail further on in the thesis (section 4). Once the influence of the governing variables is established and a standardized test procedure formulated (based on the knowledge of how the operational variables influence the results), TG-curves can be compared and reliable information can then be derived from these curves.

2.4 The application of TG for the analysis of activated carbon and related substances

As the activated carbon regeneration process is accompanied by mass loss and volatile product evolution, TG and EGA are the most appropriate methods from the wide range of thermoanalytical techniques to use for the study of regeneration processes. The use of TG for the study of activated carbon regenerability and the study of related materials is reported on in only a limited number of publications. The subject of these publications can be divided into three categories, namely -

- general regeneration processes
- analysis of coal and coke
- activated carbon regeneration.

Before each of these categories is dealt with, the influence of adsorption on pore size distribution is discussed.

2.4.1 Influence of adsorption on pore size distribution

The pores of activated carbon play a very important role in the adsorption process. Three pore types can be discerned (van Vliet, 1978), namely -

- Macropores (60 to 10000 nm)
- Mesopores (3 to 60 nm)
- Micropores (< 3 nm).

The meso- and macropores serve primarily as conduits connecting the external liquid phase with the adsorption sites, but can also provide adsorption sites for relatively large molecules. During adsorption the volume of the micropores, which contain a preponderance of adsorption sites, decreases dramatically with time. This indicates that these pores play an important role in the adsorption of pollutants (Calgon Corporation).

The reduction in micropore volume results in a progressive decrease of the initial adsorption capacity. When the adsorption capacity has been reduced to the extent that effective removal of pollutants is no longer possible, it may be restored by means of regeneration. During regeneration the congested micro-, meso- and macropores are recovered optimally, where virgin carbon levels for these pore types are approached. However, if the regeneration operation continues beyond this point, structural degradation follows as meso- and macropore volumes increase rapidly at the expence of micropore volume, which is lost concomitantly (van Vliet, 1978).

2.4.2 General regeneration processes

The basic processes taking place during regeneration (von Dreusche, 1975; Gomella, 1982) are -

- drying
- volatilisation
- cracking
- pyrolysis
- final regeneration.

During pyrolysis, part of the adsorbate is deposited on the activated carbon matrix in the form of a carbonaceous residual. This residual must be removed during regeneration by means of selective oxidation. Previous studies have been rather vague about te mechanisms of regeneration and are based on generalised reactions (C-Steam, C-CO_2 and C-O_2) without really questioning whether these generalised reactions are always valid.

Von Dreusche (1975) bases his designs solely on past experience and the generalised reactions. Generalisation is insufficient because, according to Jones and Gwinn (1983) and Umehara *et al* (1983), the origin of the carbonaceous residual influences regenerability; e.g. the carbonaceous residual from sodium dodecylbenzene sulphonate is more difficult to remove than the residual formed during the pyrolysis of sucrose. This illustrates that it is difficult and even rash to use generalized reactions for the design of regeneration equipment. To optimise the regeneration process, each case must be studied on its own merits. It is at this stage that TA becomes important.

The TG methods presented by Jones and Gwinn (1983) and Sontheimer and Hoelzel (1979) are useful as initial studies but have the disadvantage of using relatively large samples (between 50 and 100 mg). This is also found in the works of Clifford *et al.* (1983); (300 mg), Hashimoto *et al* (1982); (80 mg)and Skowronski (1979); (500 mg). Chihara *et al.* (1981), on the other hand, used a 2 mg sample, with excellent results, showing that large samples are not a necessity.

When large samples are used it is possible that intraparticle diffusion becomes the reaction rate controlling process. This means that the actual reactions or processes controlling the regeneration reaction(s) pass unnoticed, which can result in the interpretation of false data. Another disadvantage of using large samples is that low analytical sensitivities and long analysis times are required. It is only when processes are studied where intraparticle diffusion will not become rate determining (in general isothermal studies where the reaction is of the "contracting area" type) that large samples can be used, but certainly not in non-isothermal studies.

2.4.3 Analysis of coal and coke

The use of thermoanalytical methods for the analysis of activated carbon is an uncommon application and therefore no references are made by TA equipment suppliers to this application.

The only "application notes" (Perkin-Elmer Corporation and Du Pont Company) that relate to the study of activated carbon are the use of TG for the proximate analysis of coal and coke. Fyans (1977), Hassel (1978) and Smith (1981) report on this subject (Figure 6). By using N_2 and O_2 as purge gases the following components of coal can be determined: Water, volatiles, fixed carbon and ash. Hassel (1978) also reports on the use of a moisture evolution analyser for the determination of the moisture content of coal.

All these applications are accepted by ASTM as a replacement for ASTM D-3172 and ASTM D-3173. Use of the moisture evolution analyser, in particular (which falls in the group of EGA equipment), may be useful for the study of spent activated carbons.

2.4.4 Activated carbon regeneration

Suzuki *et al.* (1978) showed that the nature of the adsorbates associated with spent activated carbon can be suitably characterised through TG studies. Their study was performed in an inert, nitrogen, dynamic atmosphere. They

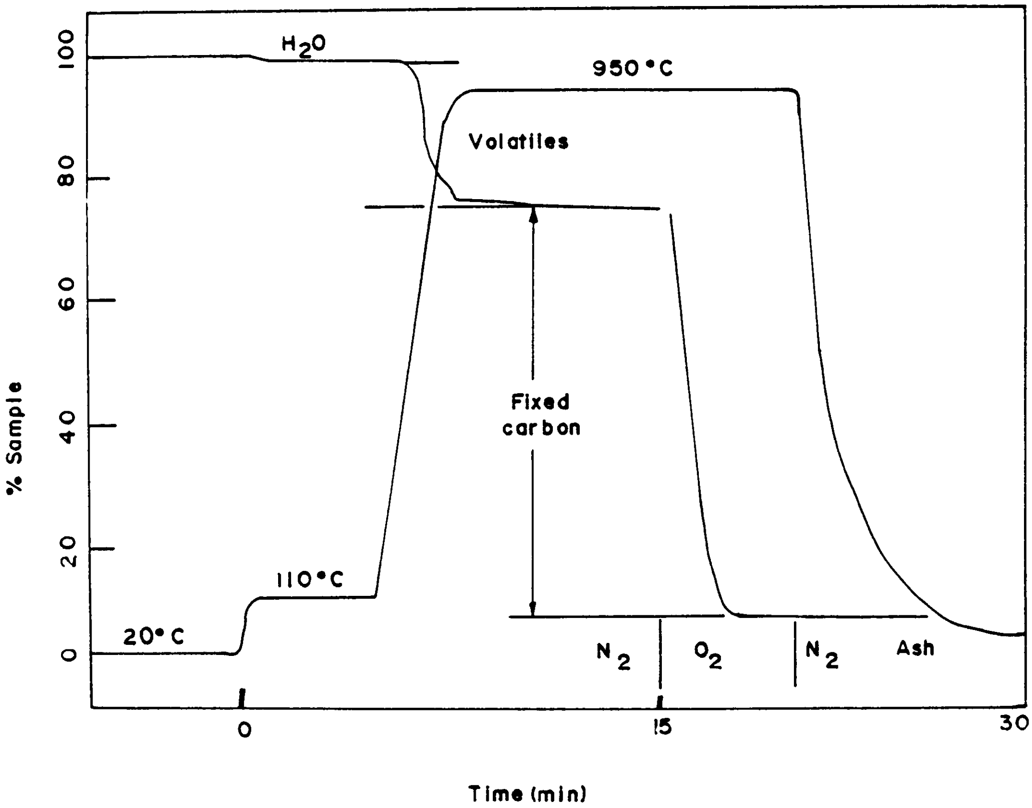


Figure 6 Proximate analysis

categorized the various types of reactions taking place as temperature progressively increased in an inert atmosphere as follows:

Type I thermal desorption of volatile organic compounds initially adsorbed on the activated carbon, but not irreversibly bound to active surface sites

Type II thermal decomposition (cracking) of organic compounds which are not sufficiently volatile for thermal desorption and/or which are tenaceously bound to the surface sites, forming volatile fragments

Type III carbonization or pyrolysis of remaining organic compounds, with the concomitant deposition of a carbonaceous residual, at 800 °C for example.

Compounds which partake in the latter type of reaction are most critical to regeneration considerations, insofar as the carbonaceous residual has to be removed selectively. In practice this is done by means of endothermic steam or carbon dioxide oxidation at comparatively high temperatures (>800 °C). This regeneration temperature domain is best avoided, since energy losses increase significantly, equipment specifications become more stringent (and costly), and base activated carbon losses invariably occur concurrently with the oxidation of carbonized adsorbate residuals.

Suzuki *et al.* (1978) considered the possible influence of various adsorbate properties such as boiling point, aromaticity, oxygen content, molecular mass and chemical functional groups on thermal treatment response (Table 1). Boiling point and aromaticity (i.e. the ratio of aromatic to total carbon atoms in a molecule) appear to most significantly characterize the behaviour of an adsorbate during (inert) thermal treatment, in particular the extent to which carbonaceous residuals will be deposited upon heating to 800 °C. Organic compounds with high boiling points and of appreciable aromatic content, would be most likely to exhibit Type III behaviour, with concomitant excessive carbonaceous residual formation at 800 °C. These residuals have to be endothermically and selectively oxidized (normally with steam) at temperatures in excess of 800 °C, thus posing the greatest difficulty in thermal regeneration.

Prime examples of such intractable substances are humic acids (which act as precursors for the formation of organohalogen compounds upon chlorination), lignin, phenol and substituted phenols. If liquid phase oxidative pretreatment could have the ultimate effect of shifting the adsorbate thermal treatment response pattern and of reducing or eliminating Type III behaviour, much benefit would be derived from such pretreatment. The relative intensity of the regeneration conditions could then also be reduced. In reality, however, the situation is much more complex in that most organic adsorbates will display combinations of Type I and Type III behaviour.

Urano *et al.* (1982) analysed thermogravimetric curves for various pure (single component) adsorbates on activated carbon and classified them as shown in Table 2. They added two further reactions, namely thermal decomposition of activated carbon and the oxidizing decomposition of activated carbon with steam. This work is very similar to the work of Suzuki *et al.* (1978).

Thermal analysis offers a versatile method for the evaluation of different materials on condition the test conditions can be standardized. As activated carbon regeneration is a difficult and very costly process, a better understanding of this process or any improvement to the process will result in a better operation and can lead to considerable cost savings.

For this reason the development of an appropriate test method for the evaluation of spent activated carbon regenerability was necessary because this is a major influencing factor. The motivation for the development of this method and the development and evaluation of it will be discussed in the following sections.

3. MOTIVATION FOR THE STUDY AND FORMULATION OF RESEARCH OBJECTIVES

Activated carbon regeneration is a very difficult process which is not completely understood. Adsorbate characteristics have an influence on regenerability (carbonaceous residual formation) as can be seen from the study of pure components loaded on activated carbon.

Design of activated carbon regeneration systems is based on generalised reactions without taking into account the influence adsorbates have on regenerability. The actual regeneration process, as well as the equipment used, is thus based mainly on past experience and generalisations.

Various authors have tried to shed some light on the activated carbon regeneration process. However, they used pure components loaded on activated carbon under laboratory conditions. Although this procedure shows very little similarity with actual practice, it gave an insight into the influence adsorbate characteristics can have on regenerability. All previous studies have one shortcoming in common, namely all samples were predried at temperatures between 105 and 120 °C. This predrying results in the volatilisation of highly volatile adsorbates, which can be of importance in water activated carbon regeneration technology.

In studies on activated carbon regeneration and regenerability, TG techniques were sometimes used. Most of these techniques had the disadvantage that relatively large samples were required. Large samples may have an adverse effect on accuracy, and it was therefore decided that small samples, the feasibility of which was proved by Suzuki *et al.* (1978), should be used.

The above observations made it clear that a test method for the evaluation of spent activated carbon regenerability needed to be developed. This test method should have the following characteristics:

- Distinction between the different adsorbate fractions present, including distinction between highly volatile adsorbate and moisture
- Use of small samples (maximum 10 mg), yet having a very high accuracy
- Ability to determine carbonaceous residual formation
- Application for the evaluation of activated carbon samples derived from pilot as well as full scale adsorption plants treating secondary effluent.

After careful thought a conceptual test method was formulated that complied with the above requirements. The method combines TG and EGA techniques and is supported by pore size distribution analysis.

The research objectives were formulated as follows:

- Development of a standardized test method for the evaluation of spent activated carbon regenerability using TG and EGA

- Application and proof of the validity of the developed test method using activated carbon samples derived from pilot and full scale adsorption plants.

During the development of the test method the following variables had to be evaluated for their influence on the test results:

- Heating rate

- Adsorbent particle size

- Carrier gas flow rate.

4. DEVELOPMENT OF TEST METHOD

As most of the activated carbon regenerability research work reported on to date has certain shortcomings, an improved, practical, applicable test method was developed. In the following description of the test method, the experimental arrangement and operating modes are discussed. The influence of heating rate, particle size and carrier gas flow rate are also evaluated in order to be able to formulate a standardized test method.

4.1. Experimental arrangement

Figure 7 shows the TG and EGA equipment arrangement used in all experimental work.

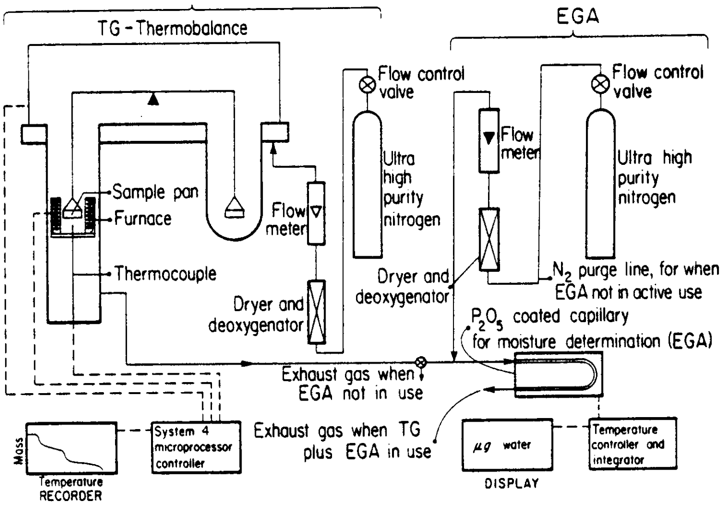


Figure 7: TG-EGA experimental arrangement

The TG section consisted of a Perkin-Elmer model TGS-2 thermobalance (Perkin-Elmer Corporation, Norwalk, Connecticut) with its control unit and a microfurnace with heater control unit. A Perkin-Elmer System 4 temperature controller enables comprehensive temperature programming capabilities (e.g. starting temperatures, heating rates, with four sequential program stages). The Perkin-Elmer first derivative computer (FDC) determines the rate of mass loss of the sample in the microfurnace. The outputs of the balance (mass change) and the FDC (rate of mass loss) are simultaneously recorded on a X-Y-Y' recorder. High purity nitrogen gas is passed through a molecular sieve cartridge filter which removes oxygen and moisture to below 0,5 ppm and is then used as microfurnace dynamic atmosphere and as carrier gas.

The EGA section comprised a Du Pont 903 moisture evolution analyser (Du Pont Company, Wilmington, Delaware) which, when not in use for analysis, was kept under a constant flow of purified nitrogen in order to keep a stable baseline.

All gas connections were teflon and stainless steel tubing, with brass couplings. In order to avoid water condensation in the stainless steel tubings or the stainless steel valve (used for the switch-over between the two operational modes used), all connections between the TG and EGA sections were heated with heating tape to 50 °C and the valve was heated to 85 °C.

The experimental arrangement used could be operated in two different modes, namely the "TG only" mode and the "TG plus EGA" mode. In the "TG only" mode no information on highly volatile adsorbate and moisture content was collected. When this information was required, the "TG plus EGA" mode was used.

4.1.1 "TG only" mode of operation

This operational mode, in which only the TG section is operative, was used to characterise the thermal treatment response of all adsorbate fractions with exception of the highly volatile adsorbate fraction. The carrier gas emerging from the microfurnace was vented to the atmosphere.

In the following study, reference is made to different adsorbate fractions which correspond with well defined temperature intervals. The specific temperatures defining every temperature interval were determined using DTG-curve minima. As seen in section 2.3, every DTG-curve minimum corresponds with a minimum mass loss rate, which thus signals that a certain series of reactions ends and that the following series becomes more important. In this way four adsorbate fractions were identified, namely:

- highly volatile adsorbate (hv) fraction, excluding moisture
- medium volatile adsorbate (mv) fraction
- low volatile adsorbate (lv) fraction
- non-volatile adsorbate (nv) fraction

The temperature intervals used for the different studies show some variation depending on the activated carbon samples used. The respective temperature intervals used in the different studies and the corresponding adsorbate fractions are listed in Appendix I.

4.1.2 "TG plus EGA" mode of operation

All the methods discussed in section 2 have one disadvantage in common, namely, none of them can determine the adsorbate fraction desorbing below 110 °C. After centrifugation, the moisture content of activated carbon can be as high as 40%. In order to be able to report all data on a dry mass basis, the carbon is predried at temperatures between 105 °C (Clifford *et al.*, 1983) and 120 °C (Urano *et al.*, 1982). In this process, not only moisture, but also highly volatile adsorbates (such as chloroform and bromoform) are removed.

A method was developed at the National Institute for Water Research (NIWR) enabling distinction between moisture and highly volatile adsorbates (Vennekens and van Vliet, 1985). With this method it was possible to obtain more information on adsorbate distribution and adsorbate loading, because the adsorbate fraction usually lost during sample predrying can be determined.

In the "TG plus EGA" mode of operation the TG and EGA instruments are thus used in series for the simultaneous determination of both total mass loss and moisture content (desorbed below 230 °C). The highly volatile adsorbate fraction is calculated as the difference between total mass loss and moisture content.

If the highly volatile adsorbate loading is required, the nitrogen carrier gas which has passed over the heated sample is routed to the moisture evolution analyser where the cumulative moisture content is measured. In this way moisture content and total mass loss (between 25 and 230 °C) are measured simultaneously.

In the evolved gas analysis detector the nitrogen is passed through an electrolytical cell. In this cell a thin film of phosphorous pentoxide is precipitated between two helically wound electrodes. The moisture in the nitrogen gas is absorbed by the P_2O_5 which, in this way, is rendered electrically conductive. The absorbed water is promptly electrolysed by a current flowing between the two electrodes. The water is converted to hydrogen and oxygen gas which are discharged through the vent with the nitrogen carrier gas. In this way the cell is regenerated coulometrically and the charge required to regenerate the cell is integrated and displayed as total moisture content (0-99999,9 µg water).

The EGA equipment has to be calibrated regularly, using an AR grade disodium tartrate standard, which has a water content of 15,66% (<180 °C). A pronounced drift in the calibration performance usually signals the need to regenerate or replace the electrolytical cell.

4.1.3 Activated carbon samples used

The spent carbon samples used for studying the influence of the variables were collected from a pilot experiment (Figure 8; discussed in greater detail by van Leeuwen *et al.*,1983), designed to study the influence of liquid phase oxidative pretreatment (ozonation at different levels, oxygenation and chlorination) on adsorber performance, adsorber service time, water quality, solute biodegradability and adsorbability. The pilot plant treated activated sludge plant (Bardenpho) effluent, and had been in operation for 6 months at

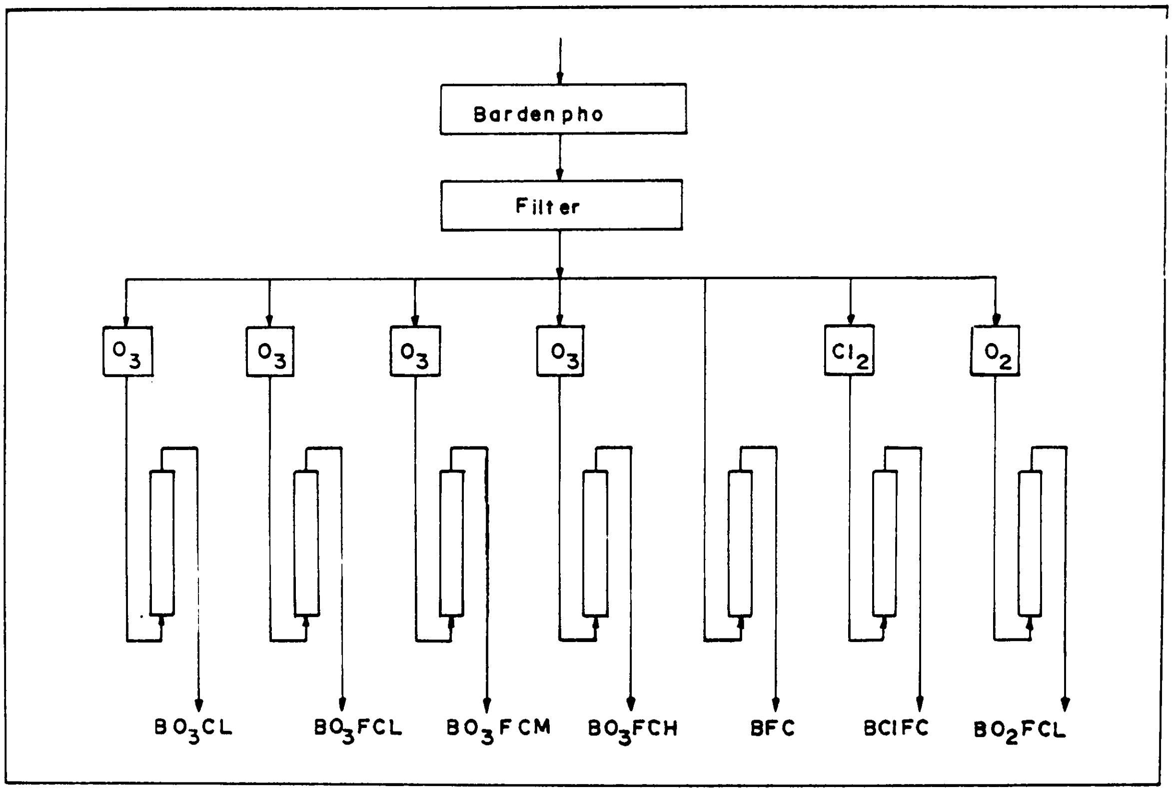


Figure 8: POBAC I, experimental arrangement

the time of spent carbon sampling. The adsorber columns were operated in an upflow mode, had an empty bed contact time of·16 minutes and were sampled (250 ml each) near the process inlet. Each adsorber contained 19 l of 8x13 mesh bituminous coal based activated carbon, and was immediately preceded by a dual medium filter.

Table 3 summarizes the different liquid phase oxidative pretreatments and gives the corresponding spent activated carbon sample codes. A part (20 ml) of each spent carbon sample was centrifuged and immediately deep frozen in order to arrest possible loss of highly volatile adsorbate, biological activity or other biological adsorbate conversions. This was done with a view to subsequent determination of the highly volatile (desorbed below 230 °C) adsorbate fraction, and to afford extended storage possibility. The remainder of each sample was pre-dried at 110 °C for 24 h, and stored in sealed containers.

The TG curves determined during the study of the influence of variables, using spent activated carbon sample BO_3CL, were divided into the following temperature intervals: 30 to 215 °C and 215 to 800 °C, based on the first derivative curve minima (at 215 and 800 °C).

4.2 Influence of variables

Before a test method can be generally applied, the influence the different operator controlled variables have on the test results have to be investigated. In order to be able to use the "t-test" (Spiegel, 1972) for the statistical evaluation of the test results, a minimum of three analyses was performed on every sample and for every analysis.

Three variables were identified and their influence on the test results evaluated, namely heating rate, carrier gas flow rate and particle size.

Table 3 : POBAC I, liquid phase oxidative pretreatments and corresponding spent activated carbon sample codes

Liquid phase pretreatment	Spent activated carbon sample code
No oxidative pretreatment, filtration, carbon (control)	BFC
Low (3 mg/1) ozone dosage, carbon	BO_3CL
Low (3 mg/1) ozone dosage, filtration, carbon	BO_3FCL
Medium (5,2 mg/1) ozone dosage, filtration, carbon	BO_3FCM
High (8 mg/1) ozone dosage, filtration, carbon	BO_3FCH
Chlorination (0,5 mg/1 free residual), filtration, carbon	BClFC
Oxygenation (3 mg/1), filtration, carbon	BO_2FC

4.2.1 Heating rate

Before the influence of the heating rate on the test results is evaluated, the temperature accuracy of the equipment used must be determined.

Accurate, meaningful TG-measurements can only be done when the actual sample temperature can be measured accurately over the entire temperature range used. It is therefore necessary that the thermocouple measuring the sample temperature has a maximum temperature deviation of 5 °C (Sestak, 1984) over the entire range. In order to determine the temperature accuracy of the TG system, the so called "Curie point" calibration method is used. This method is based on the fact that ferromagnetic materials lose their magnetic properties at a well defined temperature (transition temperature), the Curie point. For Curie point calibration, different ferromagnetic metals are placed in the balance, while a permanent magnet is placed around the sample on the outside of the balance (Figure 9). The downward force exerted on the sample is the sum of the sample mass and the magnetic force. As the sample is heated a sudden decrease in mass is noticed as one of the ferromagnetic materials reaches its Curie point temperature. This sudden mass loss is the result of the disappearance of the magnetic force. The use of different ferromagnetic materials results in a multipoint temperature calibration curve (Figure 10) from which the accuracy of the system can be assessed and adjusted.

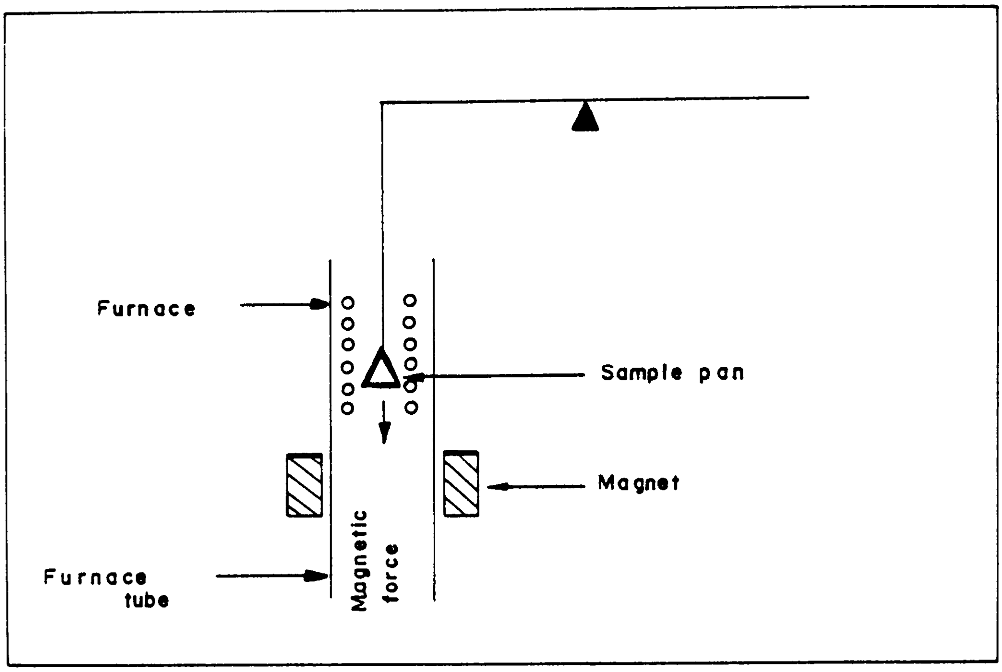


Figure 9: Apparatus for Curie point calibration

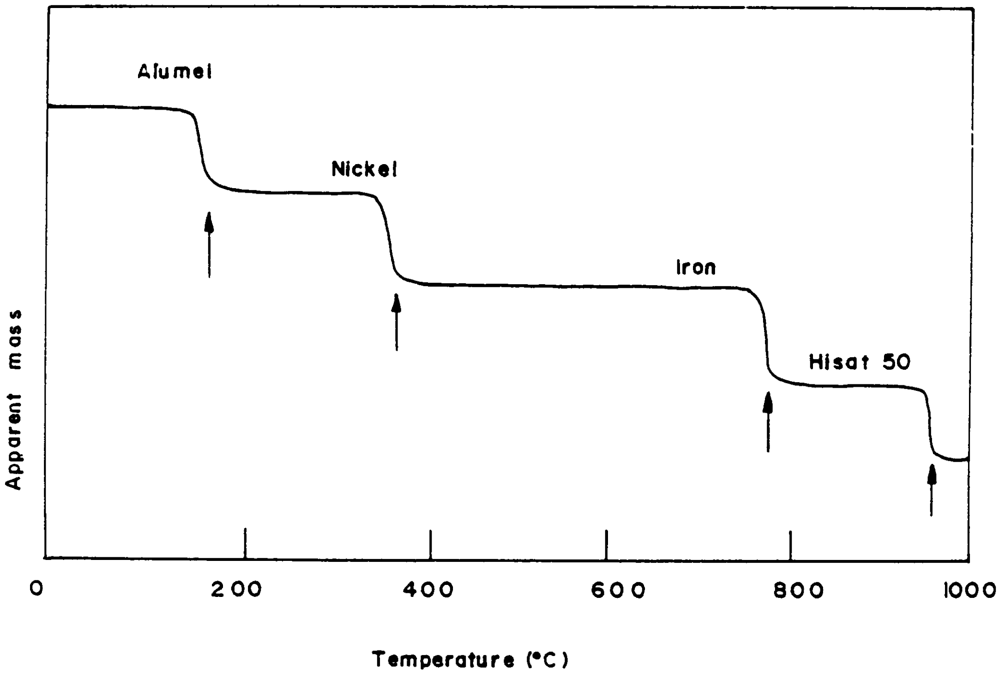


Figure 10: Multipoint calibration curve

Table 4 compares the experimental transition temperatures, as obtained with the apparatus used for my experimental work, with the theoretical transition temperatures (Daniels, 1973).

Table 4 : Curie point calibration data

Material	Theoretic* transition temperature(°C)	Measured transition temperature(°C)	Deviation (°C)
Alumel	163	164	1
Nickel	354	353,5	-0,5
Perkalloy	596	595	-1
Iron	780	782,5	2,5
Hisat 50	1000	999	-1

* Daniels (1973)

The maximum deviation of the measured transition temperatures from the theoretical transition temperatures was 2,5 °C. This is remarkably small for a 850 °C temperature interval and this deviation is also well within the limits set for good data collection (max 5 °C) (Sestak, 1984).

For the evaluation of the influence this variable has on the test data, the 1 700-2 000 µm fraction of the BO_3CL sample was selected and the heating rates investigated varied between 10 and 200 °C/min.

Figure 11 shows the influence heating rate has on mass loss for the temperature intervals 30 to 215 °C and 215 to 800 °C using the equipment in the "TG only" mode. By and large, mass loss is relatively insensitive to heating rate over a wide range. At heating rates above 160 °C/min, the 30 to 215 °C fraction increases, with a pronounced decrease of the 215 to 800 °C fraction. It is likely that equilibrium desorption conditions are not attained in this rapid heating rate range.

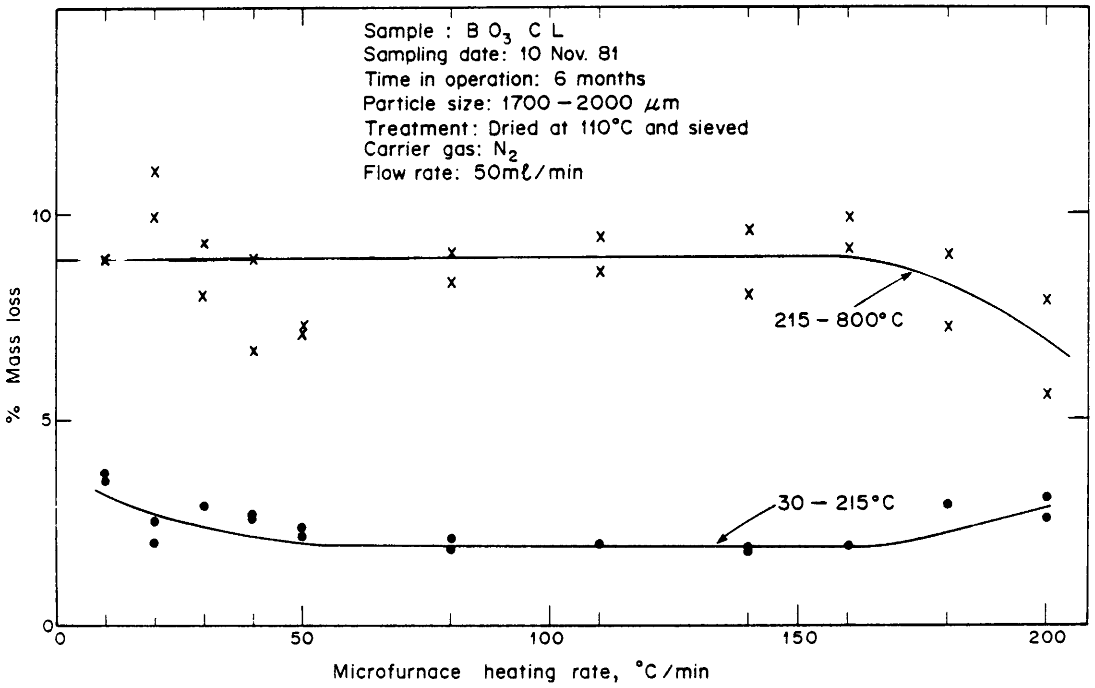


Figure 11: Influence of heating rate

If the heating rate exceeds the volatilisation and intraparticle diffusion rate of adsorbates in the 215 to 800 °C interval, for example, then adsorbates could be partially carbonised prior to escape from the particle. The result will be a smaller amount of mass loss in this temperature interval, with more carbonaceous residual to deal with at higher temperature. A heating rate of 45 °C/min, which is the average heating rate in a multiple hearth furnace used for activated carbon regeneration (van Vliet, 1978), has been selected for all the subsequent TG work, with the exception of the highly volatile adsorbate determinations.

When the equipment was used in the "TG plus EGA" mode of operation a more complex heating programme was required due to equipment (EGA) restrictions. When the electrolytical cell of the moisture evolution analyser (in the unmodified form) is overloaded, the purge gas flow over the sample is interrupted by means of a solenoid valve which is triggered by the electrolysis current passing through the cell. In this way moisture cannot pass through the cell without being absorbed onto the P_2O_5 layer. However, in the modified form, this bypass action is no longer possible and therefore the heating rate had to be decreased to such an extent that no triggering of the solenoid valve occurred. The triggering of the solenoid valve occurred at a heating rate of 3 °C/min for the first temperature interval up to 110 °C. Between 110 and 230 °C the maximum heating rate was determined as being 14 °C/min.

In order to obtain complete equilibrium at 110 or 230 °C an isothermal period was included in the heating programme. An equilibrium can be detected on a TG-curve when mass loss, as a function of time, is zero at a constant temperature. At both temperatures (110 and 230 °C) equilibrium was reached in 2 min but a 5 min isothermal temperature interval was selected in order to reach absolute equilibrium.

Based on the above observations the following temperature programme was formulated: The sample is heated at 2,5 °C/min up to 110 °C and kept isothermal at this temperature for 5 min. The heating rate is then increased to 14 °C/min and the sample is heated to the final analysis temperature of 230 °C. The sample is again kept isothermal at this final temperature for 5 min in order to establish equilibrium. A typical TG curve obtained with this temperature program, is shown in Figure 12.

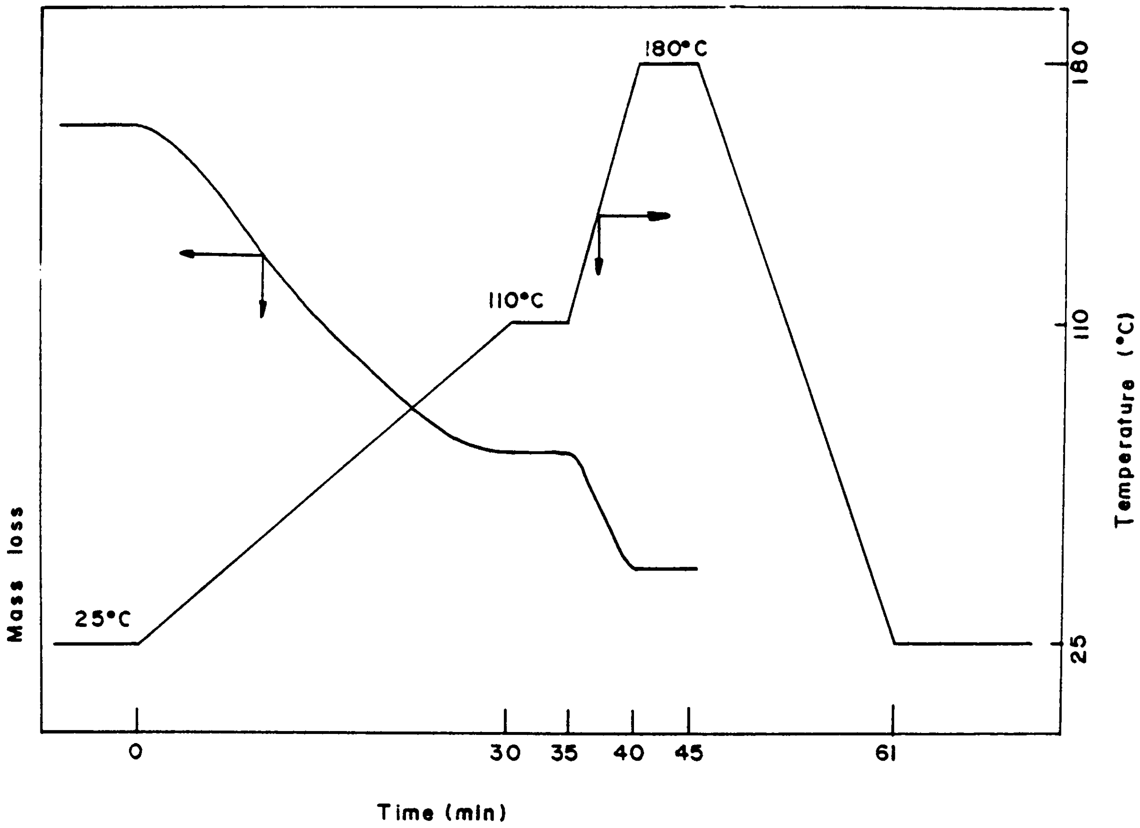


Figure 12: TG curve for highly volatile adsorbate determination

4.2.2 Carrier gas flow rate

TG analyses were performed at carrier gas flow rates varying between 30 and 60 ml/min using a fixed particle size fraction (1 700 to 2 000 µm) and a fixed heating rate (80 °C/min). The 30 to 215 °C fraction, consisting of highly volatile adsorbate after drying at 110 °C plus traces of water vapour adsorbed during handling, was insensitive to carrier gas flow rate, as shown in Figure 13. The 215 to 800 °C fraction increased gradually with gas flow rate, although it seemed to level off somewhat at higher flow rates. Carrier gas flow rate is constrained at the lower and upper levels by the need to remove desorption/reaction products, and by onset of physical disruption of the sample pan, respectively.

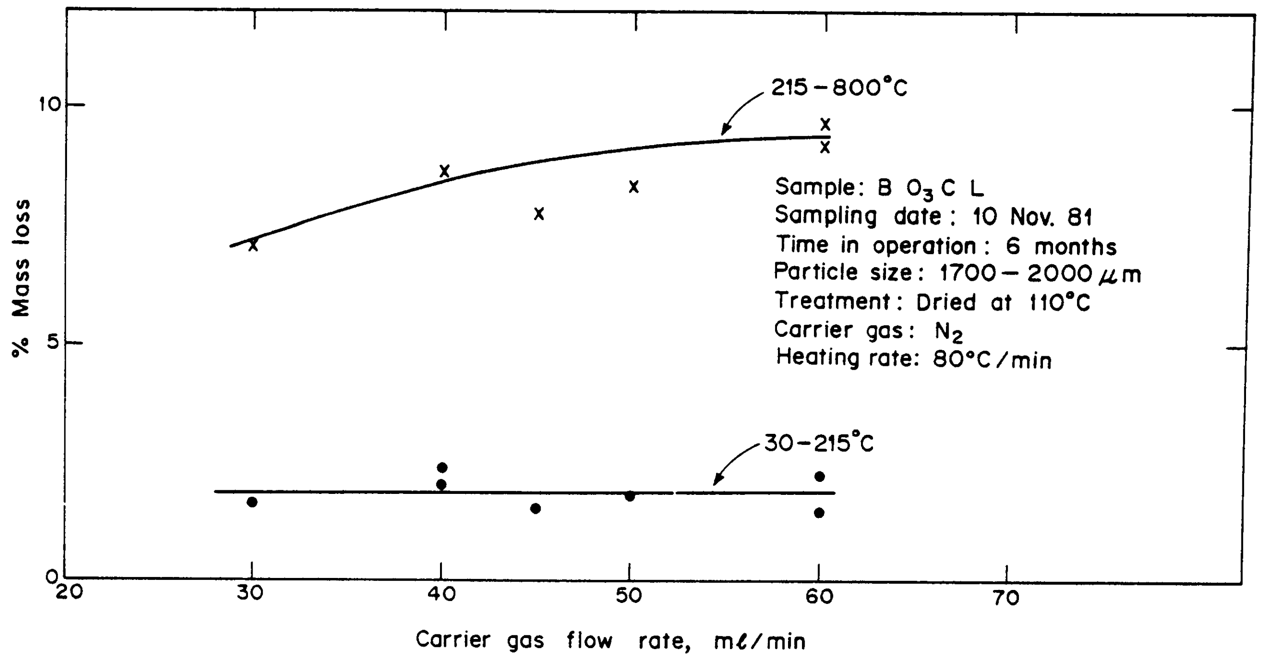


Figure 13: Influence of gas flow rate

Due to the relatively small influence carrier gas flow rate has on mass loss a 50 ml/min flow rate was selected, which is the rate recommended by the manufacturer.

4.2.3 Adsorbent particle size

The third and last influencing variable evaluated was the adsorbent particle size. Sontheimer and Hoelzel (1979) found that stratification occurs in adsorbers that are regularly backwashed. They also observed that the smaller carbon particles, which collect at the top of an adsorber, have an higher adsorption capacity than the larger particles further down. This higher adsorption capacity can be explained by the fact that the ratio of active to inactive material is larger in a small particle than in a large particle. This phenomenon is caused by the nature of the activation process that uses a reaction which progresses linearly with time. In order to evaluate the influence of particle size on mass loss levels in spent activated carbon the following approach was adopted using dry BO_3CL carbon:

- Evaluation of different particle size fractions
- Manual grinding and selection of the 150-250 µm particle size fraction
- Manual grinding to 95%<150 µm
- Mechanical grinding to 95%< 75 µm
- Mechanical grinding to 95%< 45 µm

A cooled grinding method was also developed in order to be able to grind wet carbon samples required for the determination of the highly volatile adsorbate fraction.

The results shown in Figure 14 show the marked effect of carbon particle size on TG mass loss levels. Mass loss for both the 30 to 215 °C and the 215 to 800 °C temperature intervals increases sharply for the small particle sizes (<1 200 µm), indicating that adsorption activity increases inversely with particle size. This heterogeneity of adsorbate loading with respect to particle size posed a serious problem when 3 to 7 mg samples, typically a few particles, had to be analysed by TG. Therefore different pretreatment (grinding) procedures were evaluated.

The results of all sample pretreatment procedures are analysed statistically in Table 5. The first column shows the analysis of the results as presented in Figure 14. The second column presents the statistical analysis results using manual grinding in a mortar with the selection of the 150-250 µm size fraction. The following step (third column) was to use the same manual grinding method but this time the sample was ground to 95%<150 µm. The statistical analysis (coefficient of variation, CV) of all these approaches was unsatisfactory (CV<23%) and the manual grinding procedure was replaced by mechanical grinding using a blender type mill (Janke & Kunkel, Ika Werke, Staufen, West Germany).

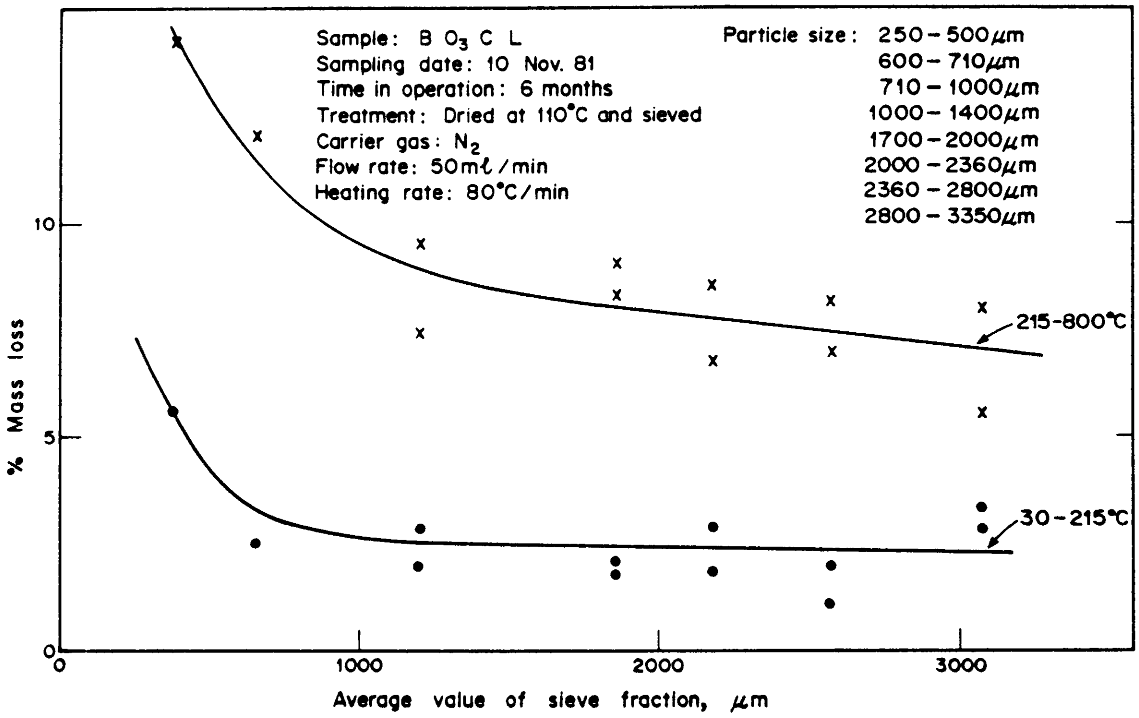


Figure 14: Influence of adsorbent particle size

The carbon sample was ground to 95%<75 μm. This grinding procedure yielded a CV of 5%, which is acceptable. After this approach a further refinement was introduced; i.e. the use of a centrifugal ball mill (Model S2, Retsch KG, Duesseldorf), with two 50 ml grinding jars (each containing three 20 mm grinding balls). This refinement of the procedure enabled us to use a powder with a particle size of 95%<45 μm. This particle size is recommended in most activated carbon analysis methods when ground samples are used (AWWA, B604-74 and ASTM,D2355-70). The statistical analysis of the mass loss results using a carbon sample pretreated in the last way gave a CV of 2%, which is well below the 5% generally used in data analysis.

Another remarkable feature of the different pretreatment methods is that both mechanical grinding procedures gave average mass loss figures that were closest to the average of all mass losses from all pretreatments. The average for all pretreatment procedures is 7,52%. The values of 7,7 and 7,58% are much closer to the average than the 8,8; 7,0 and 6,5% of the other pretreatment methods.

For the determination of the highly volatile adsorbate fraction a wet (20-40% moisture) ground sample is required. When a ball mill is used for the grinding of wet carbon, the carbon is heated due to frictional heat generated in the grinding process. Therefore a centrifuged and frozen spent activated carbon sample was ground manually in a low temperature room (4 °C) to minimize the loss of highly volatile adsorbate as result of frictional heat. The ground sample is kept in a freezer until required for analysis. Because this manual grinding is very time consuming (~20 min/sample) and also very inconvenient (working in a 4 °C room) a different approach was evaluated. An icewater-glycol mixture cooled blender type mill (Janke & Kunkel, Ika Werke, Staufen, BRD) was selected for the mechanical grinding of the frozen activated carbon sample. Using this mill the sample temperature rose to only 16 °C, which is well below room temperature (the room temperature is also the start temperature). Storage and sample handling were as previously described.

4.3 Standardized test method

Using the knowledge of how the different variables influence the test results, a standardized test procedure was formulated for both operational modes, as shown in Table 6 and 7.

Table 6 "TG only" mode of operation

Predrying	depending on reference point 110, 180 or 230 °C
Grinding	centrifugal ball mill
Sample particle size	95%<45 µm
Sample storage	room temperature
Temperature range	25 to 850 °C
Heating rate	45 °C/min
Carrier gas flow rate	50 ml/min

Table 7 "TG plus EGA" mode of operation

Predrying	none
Grinding	cooled blender type mill
Sample particle size	95%<45 µm
Sample storage	-18 °C
Temperature range	25 to 230 °C
Temperature program	2,5 °C/min to 110 °C
	5 min isothermal
	14 °C/min up to 230 °C
	5 min isothermal
Carrier gas flow rate	50 ml/min

The study of activated carbon regenerability involves, in addition to TG, the calculation of adsorbates loadings. For this purpose specific formulas were developed. All are based on TG mass loss and particle density. More information on these formulas and on particle density (pore size distribution) can be found in Appendices II and III.

4.4 Summary

A standardized test procedure for the evaluation of spent activated carbon regenerability was developed using TG and EGA. In common with other test methods, this one is influenced by a number of variables. Three influencing variables were identified, namely -

- Heating rate
- Adsorbent particle size
- Carrier gas flow rate.

The heating rate influences the mass loss at rates of 160 °C/min and higher. For the analysis of all adsorbate fractions, except the highly volatile adsorbate fraction, a rate of 45 °C/min was selected. For the analysis of the highly volatile adsorbate fraction a special heating programme was developed. Carrier gas flow rate has a very limited influence on TG mass loss and a carrier gas flow rate of 50 ml/min, as recommended by the supplier, was selected.

Adsorbent particle size was found to be the main influencing variable. It was observed that different particle size fractions have different TG mass losses. This observation shows that it is impossible to use the carbon sample on an as received basis. The influence of particle size could only be nullified by grinding and blending the carbon sample. Different grinding procedures were evaluated and the final method selected for the grinding of a dry carbon sample to 95%<45 µm was to use a centrifugal ball mill. For the grinding of wet carbon samples an icewater-glycol mixture cooled blender type mill was selected in order to avoid heating of the carbon sample during the grinding process.

The final formulation of the standardized test method was based on the influences the different variables have on the test results. This test method comprises two separate sets of procedures, namely a first set for the determination of the highly volatile adsorbate fraction and a second set for the determination of all other adsorbate fractions.

5. APPLICATION

This part focuses on the evaluation of the test method developed. For this purpose different activated carbon samples, from both research and practical applications are used.

Activated carbon samples derived from two pilot scale research adsorption plants (POBAC I and POBAC II) were evaluated. These pilot plants were originally designed to study the influence of liquid phase oxidative pretreatment on adsorption related factors and the solid phase (activated carbon) was used for the evaluation of the developed test method.

The POBAC I samples were evaluated for the influence of liquid phase oxidative pretreatment on adsorbate distribution and regenerability in a specific section of an adsorber (bottom section). The POBAC II samples were used to study the influence of liquid phase oxidative pretreatment on overall adsorber regenerability as well as to study the influence of carbon position in the adsorber on adsorbate distribution and regenerability.

Besides these two research applications, activated carbon samples from the full scale adsorption plant at Mondi Paper Company, Merebank, were evaluated for regenerability as well as for the effectiveness of the on-site regeneration process.

5.1 Research applications - POBAC I

The samples used in this part of the study were evaluated for the influence of liquid phase oxidative pretreatment on adsobate distribution and regenerability in the bottom section of the adsorber.

5.1.1. Process description

The spent carbon samples used for this application example were collected from the same pilot plant described in section 4.1.3.

5.1.2 Results

All results were analysed statistically, using the "t-test", in order to be able to determine the significance of the differences observed. The Chi-square test could not be used for this purpose because the number of data points was insufficient and the data were not in the required form (Spiegel, 1972).

A. Effect of type of liquid phase pretreatment. The effect of type of liquid phase oxidative pretreatment, as described in Table 3, is shown in Figure 15 and Table 8. Between 3 and 5 analyses were performed in respect of each pretreatment alternative. None of the pretreatment alternatives was capable of eliminating the non-volatile adsorbate fraction ($q_{>850}$), which would have been most desirable from a regeneration point of view. Oxygenation had very little effect on the adsorbate distribution, except for a moderate increase in the highly volatile adsorbate fraction (q_{25-180}). The direction of change, however, was for the fractions below 600 °C to increase, and those above 600 °C to decrease. This trend again has a favourable influence on regenerability. The total adsorbate loading was somewhat higher when compared with the control (BFC) adsorber.

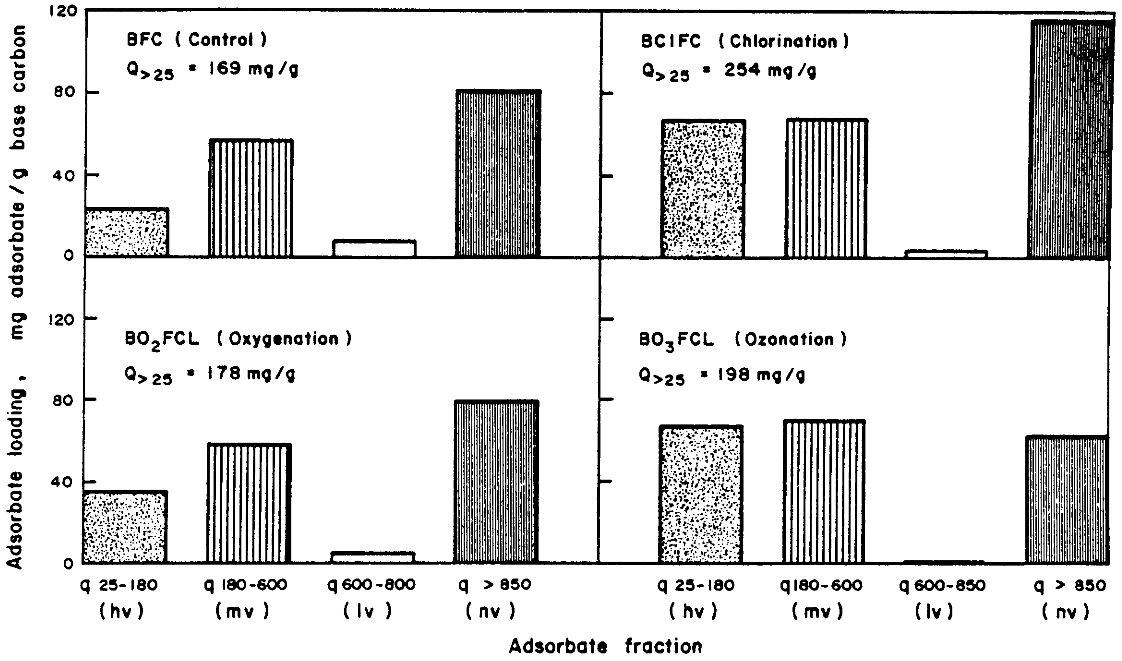


Figure 15: Influence of liquid phase oxidative pretreatment

The direction of change for all adsorbate fractions, in the case of a low ozone dosage, was identical to that for oxygenation and therefore favourable from a regeneration perspective. Moreover, the extent of change was considerable greater for all fractions, and the low ozone dosage actually resulted in the most favourable adsorbate distribution for all the pretreatment possibilities in this study. The total adsorbate loading further increased, relative to preoxygenation.

Prechlorination further increased the total adsorbate loading, to a high level ($Q_{>25}$ = 254 mg adsorbate/ g base carbon). With the exception of a slight decrease in the low volatile adsorbate fraction ($q_{600-850}$), the dominant tendency was for the resultant adsorbate loadings to increase as a result of prechlorination.

B. Effect of preozonation dosage level. Preozonation at various dosage levels had a non-linear effect on the thermal treatment response patterns for the various adsorbate fractions (Figure 16) and the total adsorbate loading increased with increasing ozone dosage.

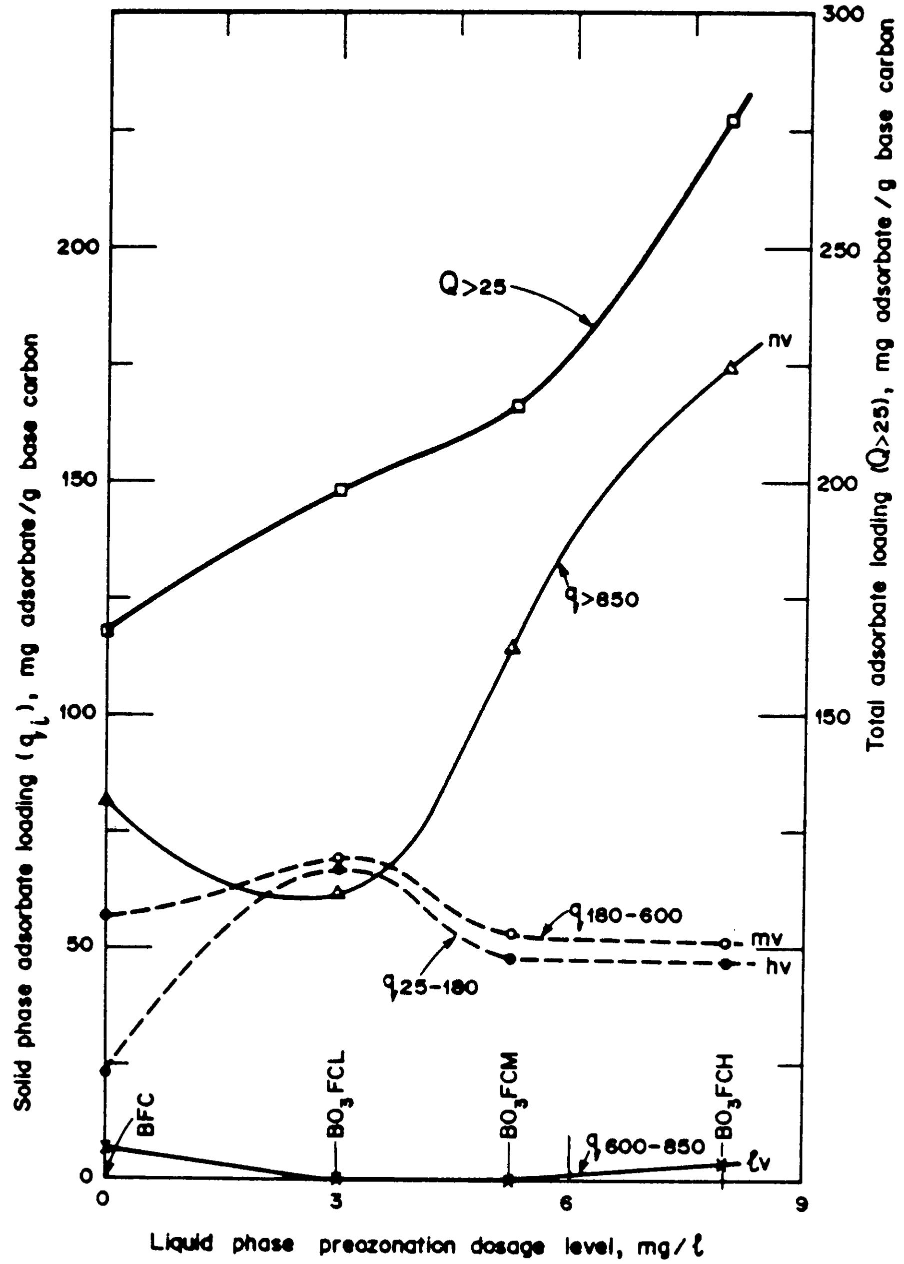


Figure 16: Influence of ozone dosage level

From Figure 16 it can be seen that the nv adsorbate fraction is the main regenerability influencing factor (this fraction increases with increasing ozone dosage) and is lowest for the low ozone (3 mg/l) dosage level.

5.2 Research Applictions - POBAC II

In this part of the study the influence of liquid phase oxidative pretreatment on overall adsorber regenerability as well as the influence of carbon position in an adsorber on regenerability is evaluated.

5.2.2 Process description

The spent activated carbon samples used in this example were collected from a modified pilot plant (Figure 17) designed to study the effects of liquid phase oxidative pretreatment (oxygenation, chlorination, and especially ozonation) on adsorber performance, adsorber life, water quality, solute biodegradability and adsorbability.

In this study special attention was paid to the effect of preozonation. The pilot plant therefore comprised two ozonated wastewater receiving adsorber trains as well as a prechlorinated, a preoxygenated and an unpretreated wastewater receiving adsorber train. Each adsorber train consisted of two adsorbers in series. After 18 weeks the first experimental run was ended and the carbon of the first adsorber of every train was regenerated. For the second run the second adsorber of the first run was used as first adsorber and the adsorber containing regenerated carbon was used as second adsorber (Figure 18).

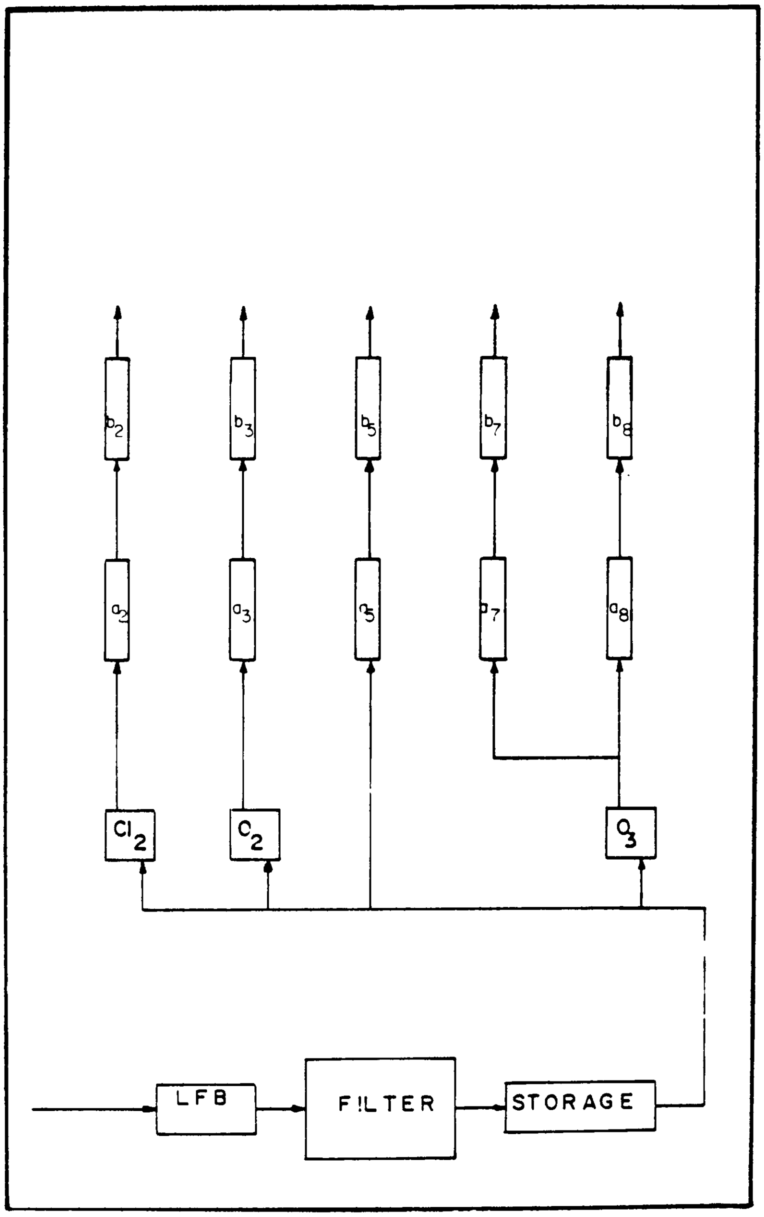


Figure 17 POBAC II, experimental arrangement: First run

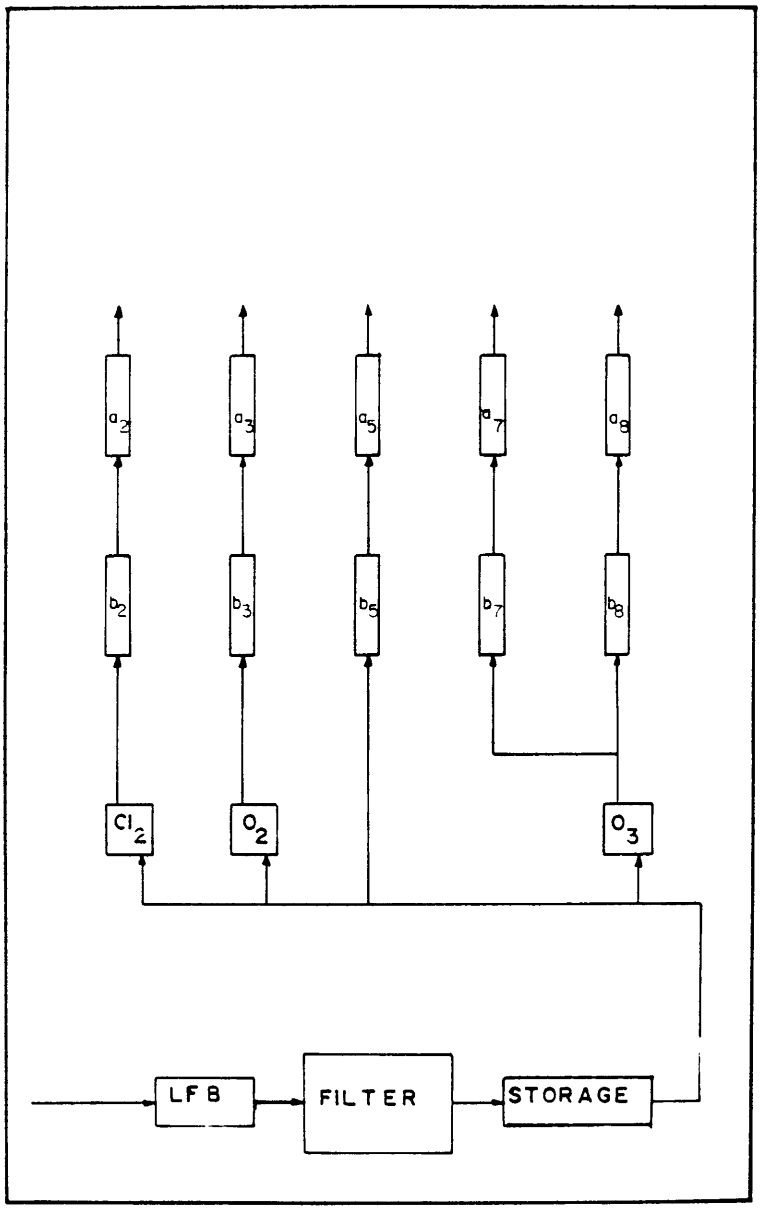


Figure 18: POBAC II, experimental arrangement: Second run

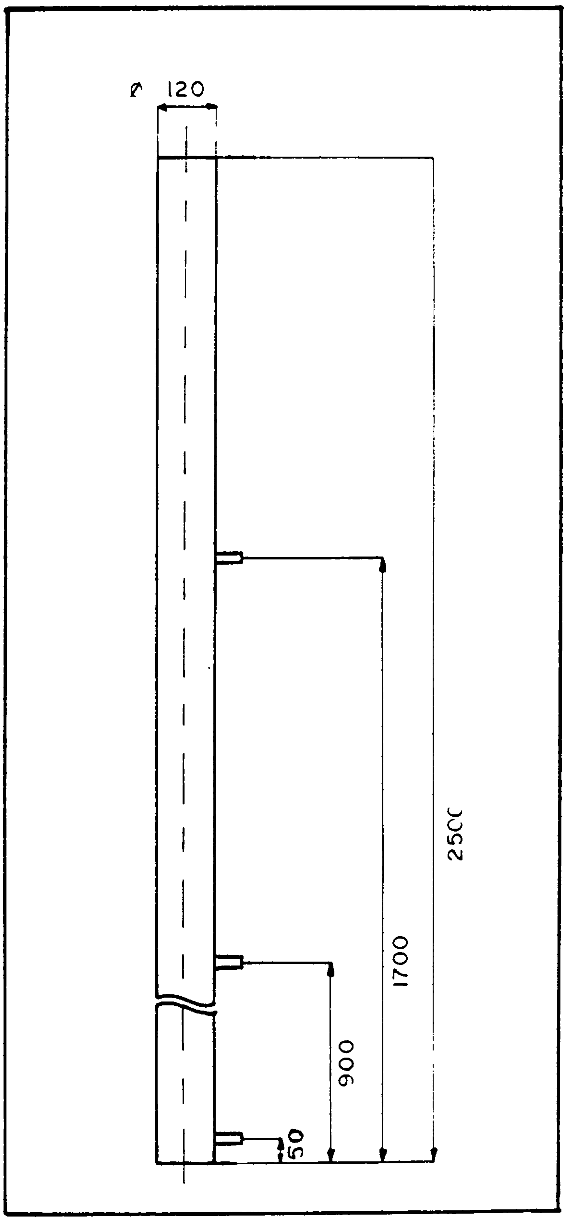


Figure 19: Sample port location

Every pilot plant upflow adsorber train (each containing 2x19 l of 8x13 mesh bituminous coal based activated carbon) was fed with secondary treated wastewater (LFB) and had been in operation for 37 weeks at the time of sampling. The samples were taken from the bottom, middle and top of the carbon bed in the first adsorber (sample ports; Figure 19). Table 9 summarises the different pretreatments used and the corresponding adsorber codes. The values reported for the ozonated wastewater receiving adsorber are in fact the average of the two ozonated wastewater receiving adsorbers. This was done in order to facilitate data interpretation.

Table 9: POBAC II, liquid phase oxidative pretreatment and according spent activated carbon sample codes

Liquid phase pretreatment	Adsorber code
No oxidative pretreatment,	Z5
Chlorination (0,9 mg/l free residual),	Z2
Oxygenation (10,8 mg/l),	Z3
Ozonation (4,1 mg/l),	Z7/Z8

5.2.2 Results

A. Effect of liquid phase oxidative pretreatment. None of the pretreatment alternatives in this study were capable of reducing the non-volatile adsorbate fraction, which is most desirable from a regenerability point of view.

The total adsorbate loadings ($Q_{>25}$) are shown in Table 10 for each adsorber and sample port. From this Table it is evident that there is a considerable difference between the $Q_{>25}$ values obtained for the bottom and middle sample ports of each adsorber and the top sample ports. This is due to the increase of adsorption capacity with decreasing particle size. As mentioned previously (section 4.2.3), stratification occurs during adsorber backwash with the particle size decreasing from the bottom to the top of the adsorber. This, together with the fact that adsorption capacity increases with decreasing particle size, explains why the top samples have very high total adsorbate loadings.

Table 10: Total adsorbate loading ($Q_{>25}$) values

Adsorber code	Total adsorbate loading* Sample port			Weighted average
	Bottom	Middle	Top	
Z2 (Cl_2)	188	144	362	204
Z3 (O_2)	137	135	306	176
Z5 (none)	106	94	276	140
Z7/Z8 (O_3)	169	155	322	197

* All total adsorbate loading values are in mg adsorbate/g carbon matrix

In order to be able to compare the effect of liquid phase oxidative pretreatment on an entire adsorber, weighted average adsorbate loadings were calculated for each adsorber for the total adsorbate loading and also for every adsorbate fraction.

The weighting factors used for the calculation of the weighted averages were derived from the results of sieve analyses, according to AWWA B604-74, of five spent activated carbon samples obtained from the adsorbers studied. The sieve fractions used and the weighting factors (they express the contribution of a certain sieve fraction to the entire sample) for every fraction are shown in Table 11. The sieve fractions used were chosen arbitrarily, taking into account that the bottom and the middle of an adsorber contain the major part of the activated carbon (~75%) and that the carbon particles at the top are relatively small (visual inspection).

Table 11: Sieve fractions and weighting factors

Sieve fraction	Weighting factor
>850 µm (Top)	0,24
850 - 1700 µm (Middle)	0,59
>1700 µm (Bottom)	0,17

Table 12 presents all the adsorbate distribution data per adsorbate fraction and per adsorber sample port. The weighted averages for every adsorbate fraction for the entire adsorber are also shown and are marked as follows: $Z2_{wt}$

Figure 20 shows the weighted average adsorbate loadings grouped according to total volatile (hv+mv+lv fractions = tv) and non-volatile (nv fraction) adsorbate fractions. This grouping was decided upon in order to facilitate data interpretation and also because these are the two adsorbate groups encountered during actual regeneration of spent activated carbon. The total volatile adsorbate corresponds with the part of the adsorbate that is readily removed during regeneration (Type I and II reactions) while the non-volatile adsorbate corresponds with that part of the adsorbate that has to be removed by means of selective oxidation (Type III reactions).

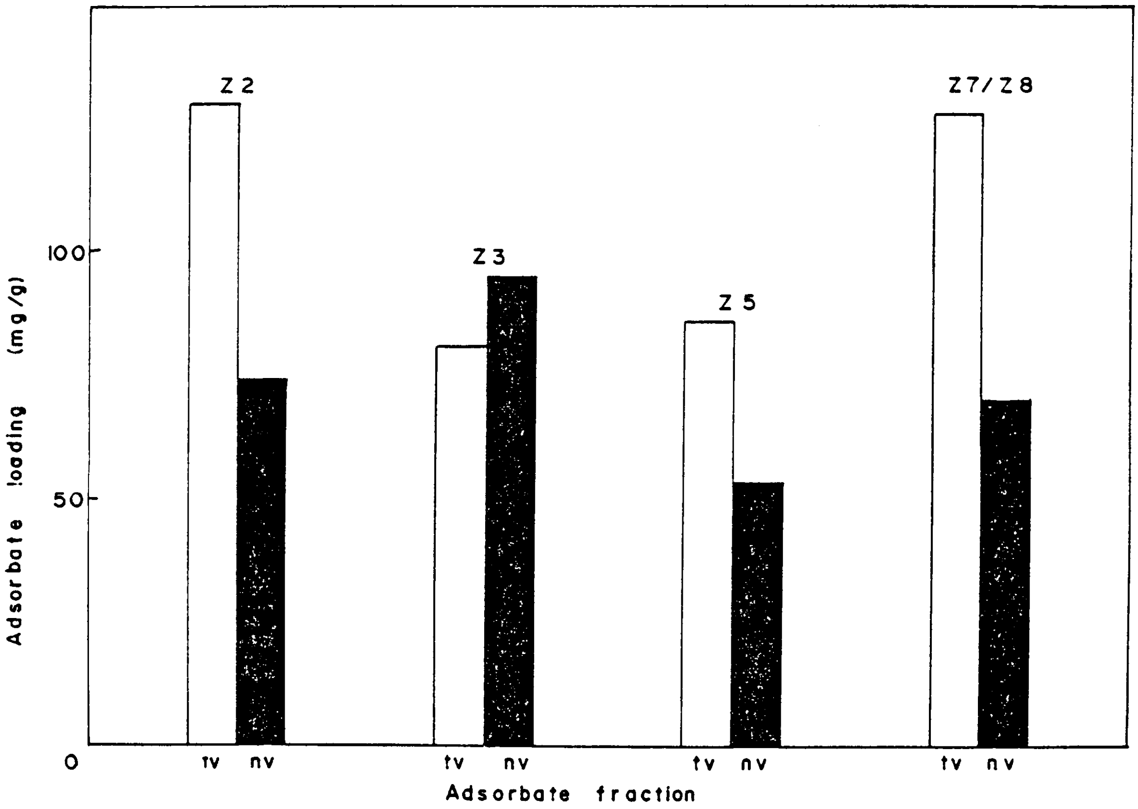


Figure 20: Weighted average values (grouped)

Table 12: Adsorbate loadings per fraction

Sample port	q_{tm}	$Q_{>25}$	hv	mv	lv	tv	nv
Z2 bottom	144	188	45	53	12	110	79
Z2 middle	80	144	68	38	7	113	31
Z2 top	258	362	104	74	7	185	176
$Z2_{wt}$	134	204	73	49	8	130	74
Z3 bottom	93	137	44	27	1	72	65
Z3 middle	86	135	49	22	2	73	62
Z3 top	235	306	71	32	3	106	199
$Z3_{wt}$	123	176	53	25	2	81	95
Z5 bottom	90	106	16	49	9	74	33
Z5 middle	65	94	29	43	5	77	17
Z5 top	240	276	36	73	8	117	156
$Z5_{wt}$	111	140	28	51	6	86	53
Z7/Z8 bottom	112	169	55	37	4	96	71
Z7/Z8 middle	71	155	85	32	4	120	36
Z7/Z8 top	226	322	98	64	7	169	153
$Z7/Z8_{wt}$	115	197	83	41	5	128	70

* All adsorbate values are in mg adsorbate/g base carbon

The highest nv adsorbate loading was found in the adsorbers receiving oxygenated and chlorinated wastewater. The ozonated wastewater receiving adsorber and the unpretreated wastewater receiving adsorber had lower nv adsorbate loadings in comparison with the two other adsorbers.

The tv adsorbate fraction was maximized in the ozonated wastewater receiving adsorber as well as in the chlorinated wastewater receiving adsorber. Because this fraction can readily be removed, as seen before, it does not affect regenerability to the same extent as does the nv adsorbate fraction. For this reason our attention will only focus on the nv-adsorbate fraction. The nv adsorbate fraction accounted for between 35 and 55% of the total adsorbate loadings ($Q_{>25}$) in the adsorbers studied.

B. **Effect of carbon position in an adsorber on regenerability.** As already seen before (Table 10), large differences in adsorbate loading exist between the sample ports in an adsorber. These differences show that the position of the carbon in an adsorber has an influence on adsorbate distribution.

Figure 21 shows this adsorbate distribution as function of carbon position. It is difficult to establish a definite and general adsorbate distribution pattern for all the adsorbers and therefore the adsorbates are again grouped as tv and nv adsorbate fractions. Figure 22 shows these grouped adsorbate fractions. The tv adsorbate fraction increased from the bottom to the top of all adsorbers, while the nv adsorbate fraction was highest for the top sample and lowest for the sample derived at the middle of the adsorbers.

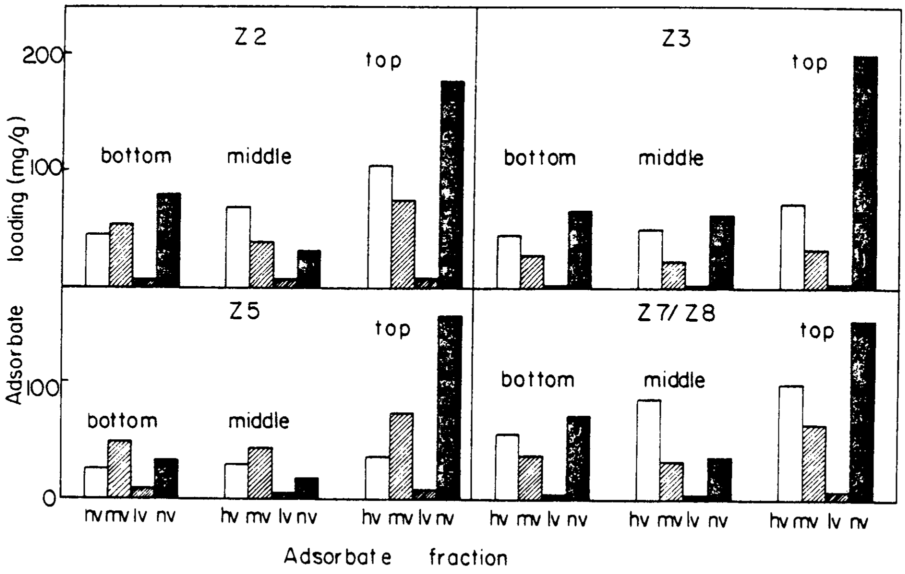


Figure 21: Adsorbate fractions per sample port

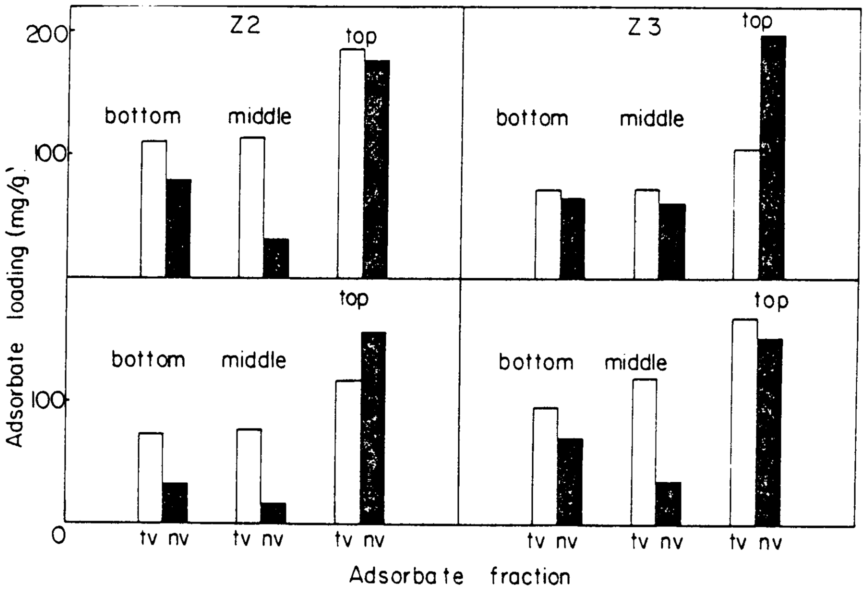


Figure 22: Grouped adsorbate fractions per sample port

The weighting factor of 0,24 and the highest nv adsorbate fraction for the carbon at the top of all adsorbers shows that the top of every adsorber made a considerable contribution towards the nv adsorbate loading of the entire adsorber. The top of the adsorbers contributed between 50 and 70% approximately to the cumulative nv adsorbate load of the entire adsorber. This observation can be very important from a regeneration point of view because the different sections of the adsorber have a different influence on overall adsorber regenerability. The percentages are calculated by multiplying the top nv adsorbate loading with the weighting factor and then dividing this result by the weighted total adsorbate loading of the adsorber in question.

5.3 Practical application : Mondi Paper Company Limited, Merebank, Durban

This section deals with the use of the test method developed for evaluataion of the regenerability of spent activated carbons derived from the adsorption plant at Mondi Paper Company, Merebank. The test method is also used to evaluate the effectiveness of the regeneration process at this plant.

The results presented in this example are intended to illustrate that the method developed can also be applied to activated carbons used in industry and that the method is not only developed for research applications.

5.3.1 Process description

Activated carbon adsorption is used by Mondi Paper Company, Merebank, Durban, as a final step in the process to reclaim water from secondary treated sewage for paper production. This process (Figure 23) consists of coagulation with alum and polyelectrolyte, clarification, prechlorination, high pressure filtration, activated carbon adsorption and post chlorination.

The activated carbon adsorption is used to remove residual textile dyes from the secondary treated sewage. The dye residuals have an adverse effect on bleached pulp brightness. The use of activated carbon implies that it will become saturated and thermal regeneration performed under the right conditions is, as seen before (section 2.4.2), a popular and effective method to restore the adsorptive capacity of activated carbon. A series of thermogravimetric analyses and pore size distributions were done by the NIWR, at the request of Mondi Paper, Merebank, in order to evaluate the regenerability of the carbons used as well as the regenration process.

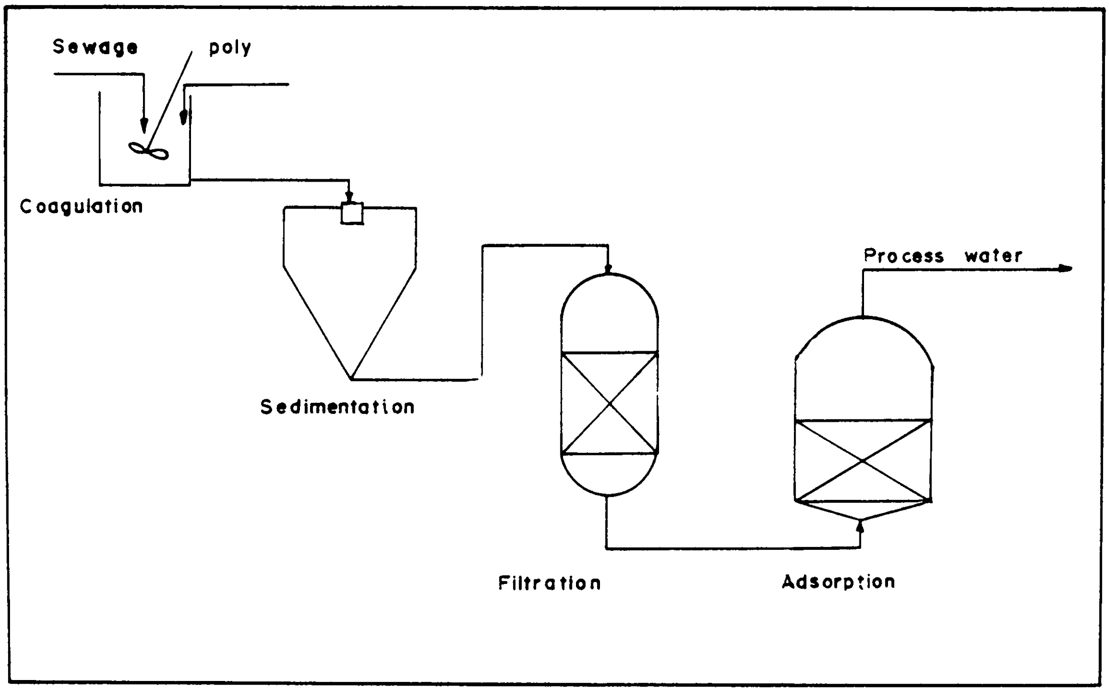


Figure 23: Mondi, Merebank, schematic layout of treatment plant

5.3.2 Results

The tests performed consisted of thermogravimetric analysis as well as pore size distribution of virgin, spent and regenerated carbons as supplied by Mondi Paper, Merebank. The pore size distribution analyses are necessary to be able to fully evaluate the activated carbons submitted. Table 13 presents the sample designation used by Mondi, Merebank, with the corresponding NIWR sample codes.

Table 13 Sample designation

NIWR sample code	Mondi
411	Virgin carbon, F300
419	Old spent carbon, No. 2 CT., 84/10/04
420	New spent carbon, No. 4 CT., 84/10/04
421	New regenerated carbon, No. 4 CT., 84/10/04

A. **Thermogravimetric analyses.** Three predried (110 °C) spent activated carbon samples were used for TG analysis, namely old spent, new spent and new regenerated carbon. The adsorbate fractions were determined using DTG minima and because they do not correspond with the adsorbate fractions in the POBAC studies, these adsorbate fractions will be identified by their temperature intervals.

All samples were analysed in triplicate in order to obtain representative analytical results. The results shown in Table 14 are the mass losses for each adsorbate fraction as a percentage of the total mass at 180 °C. Table 15 presents the same mass losses as mg adsorbate/g base activated carbon matrix as well as the total adsorbate loadings and the adsorbate fraction not removed ($q_{>950}$ °C).

Table 14 Percentage mass loss

NIWR sample number	$M_{110-180}$	$\%M_{180-390}$	$\%M_{390-695}$	$\%M_{695-950}$
419	0,91	2,54	2,45	0,95
420	1,06	2,95	3,23	1,47
421	0,95	0,69	0,80	1,92

Table 15 Adsorbate losses

NIWR sample number	$q_{tm\ 180}$	$q_{110-180}$	$q_{180-390}$	$q_{390-695}$	$q_{695-950}$	$q_{>950}$	$\%q_{tm}$
419	210	11	31	30	12	137	65
420	195	13	35	39	17	104	53
421	149	12	8	9	16	116	78

$q_{tm\ 180}$: mg adsorbate/g carbon matrix (pre-dried at 180·C)

$q_{180-390}$: mg adsorbate/ g carbon matrix removed between 180 and 390 °C

$q_{390-695}$: mg adsorbate/ g carbon matrix removed between 390 and 695 °C

$q_{695-950}$: mg adsorbate/ g carbon matrix removed between 695 and 950 °C

$q_{>950}$: $q_{tm180} - q_{180-390} - q_{390-695} - q_{696-950}$

$\%q_{tm}$: $q_{>950}$ expressed as percentage of $q_{tm\ 180}$

The thermal analysis results show that the "new regenerated" activated carbon is incompletely regenerated. From a comparison of the "new spent" and "new regenerated" carbon results it is clear that the major part of the adsorbate, up to 695 °C, has been removed. The fractions above 695 °C have not been influenced much during regeneration. It is precisely these fractions that cannot readily be removed by simple volatilisation or thermal cracking, but which normally have to be removed by means of selective oxidation with steam.

The "old spent" carbon shows an adsorbate distribution pattern that is similar to the pattern found in the "new spent" carbon. For the "old spent" carbon the adsorbate fractions desorbing below 950 °C are somewhat lower than for the "spent" carbon, while the nv adsorbate fraction ($q_{>950}$) is higher in the "old spent" carbon than in the "new spent" carbon. These results show that the "old spent" carbon has undergone several adsorption-regeneration cycles without proper regeneration. Incomplete regeneration leaves part of nv-adsorbate fraction on the carbon and this fraction increases with every cycle. This residual nv adsorbate fraction explains why the "old spent' carbon has undergone several adsorption-regeneration cycles.

B. Pore size distribution.

Particle density but also pore size distribution plays an important role in the evaluation of spent activated carbon regenerability. It was therefore necessary to include this part to complement the TG results and in order to be able to fully evaluate the regenerability of the carbons tested.

Table 16 shows the pore size distribution and particle density analysis results of the different carbons evaluated.

Table 16 Pore size distributions and particle densities

NIWR sample number	ρ_s	ρ_p	V_{mi}	V_{me}	V_{ma}	V_{tot}
411	2,166	0,8313	0,237	0,188	0,192	0,616
419	2,047	1,0062	0,142	0,155	0,212	0,508
420	2,027	0,9934	0,152	0,172	0,187	0,510
421	2,088	0,9953	0,161	0,186	0,195	0,542

ρ_s = skeletal density, g/cm^3 skeleton (helium density)

ρ_p = particle density, g/cm^3 particle

V_{mi} = micropore volume, cm^3 pore volume/cm^3 particle

V_{me} = mesopore volume, cm^3 pore volume/cm^3 particle

V_{ma} = macropore volume, cm^3 pore volume/cm^3 particle

V_{tot} = total pore volume, cm^3 pore volume/cm^3 particle

5.4. Discussion

The overview presented in section 2.4. showed that very little information is available on the use of TG for the evaluation of spent activated carbon regenerability. Due to the fact that limited information is found in literature on regenerability, the observed differences for the POBAC I samples are explained using basic organic chemistry.

5.4.1 POBAC I

The aim of the analysis of the POBAC I samples was to evaluate the influence of liquid phase oxidative pretreatment on adsorbate distribution and spent activated carbon regenerability. Regenerability is mainly reflected in the nv adsorbate fraction or the carbonaceous residual. All the other adsorbate fractions are readily removed during regeneration and have only a very limited influence on regenerability. This influence is thus as good as negligible in comparison with the influence the nv adsorbate fraction has on regenerability.

Table 17 presents the statistical analysis of the experimental data from section 5.1. Every adsorbate fraction of every sample is compared with the respective adsorbate fraction of the control sample (BFC). The values presented in Table 17 are the percentage confidence levels of the t-test.

All confidence limits of 99,95% and higher are accepted as pointing to a significant difference between the evaluated adsorbate fraction and the reference.

Table 17 POBACI, t-test results of the influence of liquid phase oxidative pretreatment on adsorbate distribution

Sample	Adsorbate fraction				
	hv	mv	lv	nv	$Q_{>25}$
BClFC	99,995	99,995	99,700	99,995	99,995
BO$_2$FCL	99,995	99,750	99,750	99,700	99,995
BO$_3$FCL	99,995	99,990	99,925	99,995	99,995
BO$_3$FCM	99,995	99,975	99,900	99,995	99,995
BO$_3$FCH	99,995	99,995	99,800	99,995	99,995

The statistical results show that most of the differences between the adsorbate fraction are significant. The only exceptions are all the lv adsorbate fractions as well as the mv and nv adsorbate fractions in the preoxygenated wastewater receiving adsorber. As the lv fraction makes a virtually inconsequential contribution to the total adsorbate distribution, the insignificance of these differences is not of primary concern. The reference adsorber and the oxygenated wastewater receiving adsorber have the same amount of nv-adsorbate loading and have thus the same regenerability. Based on the statistical results for the nv adsorbate fraction and Figure 15, the different pretreatment alternatives can be ranked, with regenerability decreasing from left to right, as follows: BO$_3$FCL > BFC = BO$_2$FCL > BClFC.

Ozonation thus shows the most favourable regenerability with chlorination having the poorest regeneration characteristics. Preoxygenation and no pretreatment have a similar influence on regenerability and can be placed between preozonation and prechlorination.

When the different preozonation dosage levels are compared statistically with the control adsorber, then the ranking based on the extent of the nv adsorbate fraction and Figure 16, with regenerability decreasing from left to right, can be done as follows: $BO_3FCL > BFC > BO_3FCM > BO_3FCH$. This ranking shows that a low ozone dosage (3 mg/l) yields the most favourable adsorbate distribution and thus also the best regenerability. This is because the nv adsorbate fraction is the smallest for this pretreatment.

As mentioned in section 5.2.2, the carbonaceous residual increases with increasing ozone dosage while prechlorination also results in very high nv adsorbate loading. In the case of prechlorination the increase in carbonaceous residual is most probably due to the formation of halogenated components which have a higher boiling point than the unchlorinated base component (e.g. benzene: b.p. 80 °C and chlorobenzene: b.p. 179 °C). This increase in boiling point results in a slower desorption of the adsorbate upon heating and thus a larger fraction is pyrolysed and this is accompanied with carbonaceous residual deposition.

The increase in carbonaceous residual with increasing ozone dosage is not readily explicable. It is known that ozone tends to attack double binding [electrophylic(1,3,-bipolar)addition] (Peter Sykes, 1972). This attack causes the molecules to break up in smaller fractions, which may be more readily adsorbable than the larger molecules. It might hovever be that an increase in ozone dosage cuases the smaller molecules to recombine (dimerisation; Peter Sykes, 1972) or that the high ozone dosage alters the stucture of the organic components in such a way that they are more difficult to desorb from the carbon surface.

The study of the POBAC I samples shows that, for the samples derived at the bottom of an adsorber and receiving Bardenpho effluent, preozonation at 3mg/l is the best pretreatment alternative. Prechlorination and high dosage (8 mg/l) preozonation are the least favourable pretreatment strategies.

5.4.2. POBAC II

This section deals with the influence liquid phase oxidative pretreatment has on overall regenerability as well as with the influence of carbon position in an adsorber on regenerability. Tables 18, 19 and 20 present the statistical analysis results (t-test) for the tv and nv adsorbate fractions. The unpretreated wastewater receiving adsorber is again taken as reference. The statistical results in Table 18 are for overall adsorber regenerability while these in Tables 19 and 20 are the results for the influence of carbon position on regenerability. A confidence limit of 99,95% and higher is accepted as showing a significant difference.

Table 18 POBAC II, t-test results of weighted average adsorbate loadings (overall adsorber regenerability)

Adsorber	Adsorbate fraction	
	tv	nv
Z2	99,995	99,995
Z3	99,900	99,995
Z7/Z8	99,995	99,995

Table 19 POBAC II, t-test results of tv-adsorbate fraction

Adsorber	Sample port		
	Bottom	Middle	Top
Z2	99,995	99,995	99,995
Z3	99,550	99,800	99,950
Z7/Z8	99,995	99,995	99,995

Table 20 POBAC II, t-test results for the nv-adsorbate fraction

Adsorber	Sample port		
	Bottom	Middle	Top
Z2	99,995	99,990	99,990
Z3	99,995	99,995	99,995
Z7/Z8	99,995	99,995	99,925

As mentioned before, the tv adsorbate fraction has only a very limited influence on regenerability because the adsorbates in this fraction undergo Type I and II reactions and do not form carbonaceous residuals. If there is a significant difference between the adsorber evaluated and the reference adsorber then this difference will only have an influence on the energy required for the volatilisation of these adsorbates, which is very small in comparison with the energy required for regeneration. Since it has only a very limited influence on regenerability, this fraction will not be discussed and our attention will focus on the nv adsorbate fraction.

The data in Table 18 must be evaluated together with Figure 20, while these of Tables 19 and 20 are to be evaluated together with Figure 22.

When overall adsorber regenerability is evaluated it can be seen that the tv adsorbate fraction is significant larger in the chlorinated and ozonated wastewater receiving adsorbers than it is in the adsorber receiving preoxygenated wastewater.

For all the adsorbers the nv adsorbate fraction is larger than in the reference and it is largest in the adsorber receiving preoxygenated wastewater. These results show that none of the pretreatments has a positive influence on regenerability because the nv adsorbate fraction increases relative to the reference adsorber. Of all the pretreatments, preoxygenation is the least favorable, followed by prechlorination and then preozonation. Thus when overall adsorber regenerability is evaluated, liquid phase oxidative pretreatment does not improve activated carbon regenerability.

The results in Table 19 show significant differences for the tv adsorbate fraction in the prechlorinated and preozonated wastewater receiving adsorber. For the preoxygenated wastewater receiving adsorber the difference is only significant for the top sample port. Because the tv adsorbate fraction has only a limited influence on regenerability it will not be discussed further.

The nv adsorbate fraction for all samples shows a significant difference from that of the reference adsorber, the only exception being the top of the ozonated wastwater receiving adsorber. All the nv adsorbate fractions that show a significant difference from the reference are larger than the nv adsorbate fraction in the reference adsorber. From Figure 22 it can also be seen, even without statistical analysis, that the top of every adsorber has the highest tv and nv adsorbate loadings of all the samples. This shows that the adsorbate loading of the top samples is quite different from the other samples. This high adsorbate loading of the top samples and especially the high nv adsorbate loading means that when this is combined with the weighting factor for the top (0,24), the top of an adsorber contributes a minimum of 50% to the cumulative nv-adsorbate loading of the entire adsorber.

The finding that at least 50% of the cumulative nv adsorbate loading of an entire adsorber is found in the top section is very important. This means that when overall adsorber regenerability is evaluated, the influence or contribution of the top fraction is mainly observed.

These results show that when regeneration conditions are determined on overall adsorber regenerability, the carbon with a lower loading than average adsorbate loading will be over-regenerated and part of the adsorption capacity will then be lost. The carbon with a higher than average adsorbate loading will be under-regenerated; a part of the adsorption capacity will also be lost due to incomplete regeneration.

Based on these findings a strategy for better regeneration can be developed. A possibility is that the activated carbon can be split in two fraction, namely a fraction containing particles smaller than 1 000 µm and a fraction that contains the larger particles. These fractions can then be loaded in different adsorbers. In this way the high and low adsorption capacity carbons are separated and they can then also be regenerated separately under more optimal conditions. Another possibility would be to use activated carbon of a more uniform particle size. This alternative, however, might be more difficult to attain because the the activated carbon supplier has to supply a more uniform material, which might be less cost effective for him.

The study of the POBAC II samples showed that any of the pretreatments improved overall adsorber regenerability and that the top fraction of an adsorber has an enormous influence on regenerability, demanding more specific regeneration strategies.

5.4.3 Mondi Paper Company, Merebank

The pore size distribution was analysed first and then combined with the TG results in order to completely evaluate the carbon samples. The effectiveness of the regeneration process used at Mondi was evaluated by comparing the "new spent" and the "new regenerated" carbons.

The results presented in Table 15 show that the spent carbons have very high adsorbate loadings, (i.e. approx. 20% m/m), which is proportional to the increase in particle density and the decrease in micropore volume (Table 16).

The "old spent" carbon, which is assumed to have undergone several saturation-regeneration cycles, appears to have been consistently under-regenerated, in view of the fact that the meso- and macropore volumes are not markedly greater than virgin values. The pore volume distribution for the "old spent" carbon therefore suggests that this carbon should be recoverable through optimum regeneration operations.

If the "new spent" carbon and the "new regenerated" carbons are compared, it is evident that the partially congested meso- and macropore volumes were extremely well restored during regeneration operations. Micropore volume, which displayed a dramatic decrease in the "new spent" carbon, was restored to only a small degree during regeneration. Only 10% of the possible degree of micropore restoration took place. This leaves 90% of the micropore volume to be restored. Significantly shorter useful operation cycles can be expected if the "new regenerated" carbon is put into practice. It should also be noted that irreversible over-regeneration had not taken place in the case of "new regenerated" carbon (no increase in V_{me} and V_{ma}), and that subsequent optimum regeneration operations are therefore likely to further recover adsorptive properties.

The TG results were analysed statistically in the same way as all the other TG results. Table 21 shows the statistical analysis data for the comparison of samples number 420 (new spent) and 421 (new regenerated) with sample 419 (old spent). Sample 421 was also compared with sample 420 in order to evaluate the effectiveness of regeneration operations.

Table 21 Mondi, Merebank, t-test results of adsorbate loadings

Sample number	$q_{110-180}$	$q_{180-390}$	$q_{390-695}$	$q_{695-950}$	$q_{>950}$
420*	99,600	99,990	99,990	99,975	99,995
421*	99,500	99,995	99,995	99,900	99,990
421**	99,650	99,995	99,995	99,800	99,995

* t-test results using sample 419 as reference

** t-test results using sample no. 420 as reference

When the $q_{110-180}$ and $q_{695-950}$ adsorbate fractions for samples 420 and 421 are compared with the "old spent" carbon, no significant differences can be observed. All the other fractions show significant differences. When we compare the nv adsorbate fraction of the "new spent" carbon with the "old spent" carbon, the "new spent" carbon has a much lower adsorbate loading than the "old spent" carbon. Because the "old spent" carbon has undergone several saturation-regeneration cycles with improper regeneration after every cycle. This leaves progressively more of the nv adsorbate in the carbon pores after every cycle.

When both "new" carbons are compared, the $q_{110-180}$ and $q_{695-950}$ fractions do not really differ from each other. The other fractions, however, show significant differences and from these the $q_{180-390}$ and $q_{390-695}$ fractions are fairly well removed during regeneration (they are lower in sample 421 than in sample 420). The $q_{695-950}$ fraction remained virtually unchanged after regeneration while the nv adsorbate fraction increased after regeneration. The increase of the nv adsorbate fraction is most probably due to the deposition of inorganic salts in the carbon pores, which can be formed upon heating of certain organic components (e.g. sodium dodecylbenzene sulphonate). The increased nv adsorbate loading and the unchanged $q_{695-950}$ adsorbate fraction show that the carbon is not completely regenerated and that the actual regeneration temperature reached was probably around 700 - 750 °C. This conclusion can be drawn because if the regeneration temperature had been higher then the $q_{695-950}$ fraction would have been smaller or completely absent in the "new regenerated" carbon.

When we combine the pore size distribution and the TG results it can be said that the "old spent' carbon, although having a high nv adsorbate loading, can probably be completely regenerated and this carbon is thus reusable. The "new regenerated" carbon is incompletely regenerated and the regeneration temperature was most probably around 700 - 750 °C. All these results show that the

Table 22 Cost comparison between Mondi's current and an optimised regeneration process

Parameter	Regeneration process	
	Actual	Optimal
Iodine number increase	458 to 632	458 to 900
% adsorbate capacity recovery	70	100
Carbon regenerated (t/year)**	320	225
Make-up carbon at 5% loss/cycle (t/a	16	11,25
Make-up cost/year (R 7/kg)	120 000	78 750
Regeneration costs (R/year)	171 200	120 373
Carbon replacement time * (years)	2	3
Operating costs (R/year)	283 200	199 123
Total operating costs over 6 years (R) (including complete carbon replacement)	3 379 200	1 834 750
Total operating costs/year (R)**	563 200	305 792
Difference in operating costs (R/year)	257 408	

* van Vliet (1978)

** Is calculated in such a way that an identical total adsorption capacity is used per year, based on iodine number regeneration process used at Mondi can be improved and that considerable cost savings can be achieved with proper regeneration, as will been seen it the next section.

5.4.4 Cost calculation

A brief cost comparison (Table 20) will now be made between the regeneration process as currently used by Mondi and between an optimised regeneration process, basing on the observations in sections 5.3. and 5.4.

The following data are used in the cost comparison

Average volume wastewater treated (Ml)	8
Number of adsorbers	4
Carbon per adsorber (t)	20
Total carbon inventory (t)	80
Regeneration frequency/adsorber (times/year)	4
Regeneration cost (dry carbon)* (c/kg)	53.5
Iodine number of virgin carbon	900
Average iodine number of spent carbon	458

\+ Time carbon can be used until regeneration can no longer restore the adsorption capacity (based on iodine number)

++ linear discounting over 6 years

The above cost calculation shows that proper regeneration results in considerable cost savings. When these are compared with the total costs of this study (equipment plus labour, which amounts to approx. R 450 000), the savings which can be effected at a single factory completely cover the cost of the study in less than two years. This shows that the development of the new test method is more than justified.

6. CONCLUSIONS

* The newly developed combined thermoanalytic test method using thermogravimetry and evolved gas analysis is very useful for the evaluation of spent activated carbon regenerability. This method enables us to investigate the influence of adsorber plant operational conditions on adsorbate distribution, which is coupled to regenerability through the carbonaceous residual or the nv adsorbate fraction. When combined with pore size distribution regeneration performance of full scale regeneration facilities can also be evaluated.

* Of the various influencing variables evaluated, particle size (and sample preparation) is the most important variable, while heating rate and carrier ga flow rate are negligble.

* The test method developed offers the advantage that the hv-adsorbate fraction can be determined, which was impossible up to now. For research purposes thi is an enormeous step forward and it is also a completely new technique.

* Application of this test method showed that when the bottom sample of adsorber receiving oxidative pretreated Bardenpho effluent are compared, preozonation a 3 mg/l is the most favourable alternative while prechlorination and preozonation at 8 mg/l are the least favourable alternatives.

* When overall adsorber regenerability is evaluated as function of liquid phase oxidative pretreatment of LFB effluent, no pretreatment is the best propositio

- The top sample of all the adsorbers receiving LFB effluent contributed more than 50% of the cumulative nv adsorbate loading of an adsorber.

- The method is thus considered to be a significant contribution to water utilisation science and engineering.

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APPENDIX I

Adsorbate fractions

As the POBAC I and POBAC II pilot plants were fed with different types of effluent it is not abnormal that the different adsorbate fractions for the two sets of samples are characterized by different temperature intervals. The adsorbate fractions with their corresponding temperature intervals are listed below for both POBAC I and POBAC II.

POBAC I samples

----

25 to 180 °C (excluding moisture) : highly volatile adsorbate (hv)
180 to 600 °C : medium volatile adsorbate (mv)
600 to 850 °C : low volatile adsorbate (lv)
> 850 °C : non-volatile adsorbate (nv)
> 25 °C : total adsorbate loading ($Q_{>25}$)

POBAC II samples

----

25 to 230 °C (excluding moisture) : highly volatile adsorbate (hv)
230 to 680 °C : medium volatile adsorbate (mv)
680 to 840 °C : low volatile adsorbate (lv)
25 to 840 °C : total volatile adsorbate (tv)
> 840 °C : non-volatile adsorbate (nv)
> 25 °C : total adsorbate loading ($Q_{>25}$)

APPENDIX II

Formulas used and supporting analyses

$$q_{TM\ 180} = \frac{1000(\rho_{pa\ 180} - \rho_{pv\ 180})}{\rho_{pv180}} \text{ mg adsorbate/g base activated carbon}$$

Adsorbate loss (hv) between 25 and 180 °C is calculated as

$$q_{25-180} = \frac{(\%M_{25-180} - \%H_2O\ _{25-180}) \times 100 \times 10 \times \rho_{pa\ 180}}{(100 - \%M_{25-180}) \times \rho_{pv\ 180}}$$

Adsorbate loss (mv) between 180 and 600 °C is calculated as

$$q_{180-600} = \frac{(\%M_{180-600}) \times 100 \times 10 \times \rho_{pa\ 180}}{(100 - \%M_{25-180}) \times \rho_{pv\ 180}}$$

Adsorbate loss (lv) between 600 and 850 °C is calculated as

$$q_{600-850} = \frac{(\%M_{600-850}) \times 100 \times 10 \times \rho_{pa\ 180}}{(100 - \%M_{25-180}) \times \rho_{pv\ 180}}$$

The non volatile residual (nv), (>850 °C) is calculated as

$$q_{>850} = q_{TM\ 180} - (q_{180-600}) - (q_{600-850})$$

The total adsorbate loading is calculated as

$$Q_{>25} = q_{25-180} + q_{180-600} + q_{600-850} + q_{>850}$$

where : $\rho_{ps\ 180}$ = particle density, spent carbon dried at 180 °C, g/cm^3

$\rho_{pv\ 180}$ = particle density, virgin carbon dried at 180 °C, g/cm^3

$\%H_2O_{\ 25-180}$ = percentage water loss between 25 and 180 °C

$\%M_{25-180}$ = mass loss between 25 and 180 °C, in percent

$\%M_{180-600}$ = mass loss between 180 and 600 °C, in percent

$\%M_{600-850}$ = mass loss between 600 and 850 °C, in percent

All "q" and "Q" values are in units of mg adsorbate/ g of base (virgin) activated carbon.

Adsorbate loadings calculations were based on particle densities and TG mass losses. The particle densities were determined on predried carbons (180 or 230 °C). The actual particle densities were determined by means of mercury intrusion (Autopore 9200, Micromeritics Inc., Georgia).

Pore size distributions were determined by using the mercury intrusion results as well as helium densities (Auto Pycnometer 1320, Micromeritics, Inc., Georgia).

APPENDIX III

Pore size distribution - pressure relationship

Mercury porosimetry is based on the capillary law governing liquid penetration into small pores. This law, in the case of a non-wetting liquid like mercury and cylindrical pores, is expressed by

$$D= -(1/P)4\gamma\cos\Theta \qquad (1)$$

Where D is the pore diameter, P the applied pressure, γ the surface tension and Θ the contact angle, all in consistent units. The volume of mercury penetrating the pores is measured directly as a function of applied pressure. This D-V information serves as a unique characterisation of pore structure.

Pores are rarely cylindrical, hence eq. 1 constitutes a special model. Such a model may not best represent pores in actual materials, but its use is generally accepted as the practical means for treating what, otherwise, would be a most complex problem.

The surface tension of mercury varies with purity; its usually accepted value and the value here recommended is 484 dynes/cm. The contact angle between mercury and the solid containing the pores varies somewhat with solid composition. A value of 130° is recommended in the absence of specific information to the contrary.

Mercury extruding from pores upon reduction of pressure is in general accord with eq. 1, but indicated pore diameters are always offset toward larger diameters. This results from the equivalent volumes of mercury extruding at pressures lower than those at which the pores were intruded. It is also commonly observed that actual pores always trap mercury. The first phenomenon is usually attributed to receding contact angles being less than advancing ones.

The second is likely due to pore irregularities giving rise to hysteresis phenomena, i.e., distinct intrusion and extrusion P-V curves.

Pore surface is calculated from P-V work expended in forcing mercury into the pores. The work dW required to immerse area dA of pore wall is expressed by

$$dW = \gamma\cos\Theta dA = -PdV \qquad (2)$$

The total pore area is then

$$A = \frac{-1}{\gamma\cos\Theta}\ {}_{V_{min}}^{V_{max}} PdV \qquad (3)$$

where V_{max} and V_{min} correspond, respectively, to the volume of mercury when pores of maximum size were first penetrated and when pores of minimum size were filled.