Conditioning of aggressive water in Suriname

4 April 2008

Anushka Salmin

Department of Water Management
Sanitary Engineering Section

Faculty of Civil Engineering and Geosciences

Delft University of Technology

Conditioning of aggressive water in Suriname

Master of Science Thesis

Anushka Salmin

Delft, April 2008

Committee:

Prof. Ir. J. C. van Dijk	Delft University of Technology Department of Water Management Section of Sanitary Engineering Chair of Drinking Water
Dr. Ir. J. Q. J. C. Verberk	Delft University of Technology Department of Water Management Section of Sanitary Engineering Chair of Drinking Water
Prof. Dr. Ir. T. N. Olsthoorn	Delft University of Technology Department of Water Management Section of Water Resources Chair of Hydrology

Preface

This report is written within the framework of the Master Thesis Research at the Section of Sanitary Engineering at the Delft University of Technology. The subject of this research is the conditioning of aggressive water in Suriname. Currently aggressive water is treated in Suriname by means of shell filtration. Due to the multi purpose use of shells among which water treatment and soap production, the shells provision is threatened to run out in the long term. Therefore in time the shells will need to be replaced by an alternative conditioning material. Currently at pumping stations of the SWM, Surinaamsche Waterleiding Maatschappij, certain treatment processes are applied for the treatment of aggressive groundwater. However, based on water quality data of the raw water of several of these pumping stations it is found that the necessary treatment steps for the conditioning of the aggressive groundwater is not applied at the pumping stations.

This report is the final project of my study at the faculty of Civil Engineering and Geosciences at the Delft University of Technology. There are some people who have helped and supported me throughout this project and in my study in the past years. To these persons I would like to address a few words of gratitude.

First of all I would like to thank my supervisors professor Hans van Dijk, Jasper Verberk and Professor Theo Olsthoorn for the advice, time, patience and guidance throughout my research. I would also like to thank Luuk Rietveld and Eric Baars for the advice and guidance throughout my Internship and my Master thesis.

My special thanks go to Patrick Andeweg and Tonny Schuit for the advice and assistance during my laboratory experiments. I would like to thank the persons of SWM, GMD, Aqua Jura Perle, Waternet, DZH, Oasen who provided me with the information necessary for this research.

I would like to thank my dear parents and family de Boer- Pawirodimedjo for the love, care and support in difficult times. My sincere gratitude goes to family Kartopawiro for granting me the opportunity to study in Delft. I would also like to thank my dear friends Anoeshka, Ryanto, Raheena, Maya and Fatma for the love, support and precious times we spent together.

Executive summary

Introduction

In Suriname groundwater is mostly used for drinking water production. Depending on the ground layers from which groundwater is extracted, groundwater is characterized as aggressive water. The disadvantage of aggressive water is its ability to cause corrosion of metal pipelines and cement bound materials. In drinking water practice this water type is conditioned by means of air stripping, dosing of hydroxides or filtration through carbonate rich media. Currently the drinking water company SWM in Suriname suffers from water quality problems regarding low pH and occasionally low hardness and low alkalinity. These water quality problems are observed at pumping stations with aggressive raw water. Despite the conditioning of the aggressive groundwater by means of shell filtration, the drinking water quality does not satisfy the National Drinking Water Standards and VEWIN recommendations. It is noticed that in Suriname there are no strict guidelines for the water quality of drinking water and for the treatment of aggressive groundwater.

Due to the fact that shells are also used for many other purposes such as the improvement and neutralization of acidic agricultural grounds, the shell provision is threatened to run out in the long term. Therefore it is important that alternative materials are found for shells.

Objective

The objective of this research is to determine:

- Operational guidelines for several SWM pumping stations regarding necessary filter bed height and refilling frequency of shell filters
- Necessary treatment processes for several SWM pumping stations with water quality problems, based on water quality data of the raw water of the pumping stations

Method

In order to reach the objective, the behaviour of shell filters is studied by performing jar tests and column experiments. For the purpose of finding alternative filter materials for shells, the jar tests and column experiments were also performed with crushed limestone and softening pellets. Furthermore the operation of the shell filters and the applied treatment processes of several SWM pumping stations were closely analyzed. In Suriname the WHO guidelines are applied by SWM for safe and clean drinking water. However, the WHO guidelines do not give strict guidelines for conditioning parameters concerning pH, calcium and bicarbonate. For this research the National Drinking Water Standards (Waterleidingbesluit) and VEWIN guidelines are used to assess the water quality and of several SWM pumping stations and the treatment processes that are applied at these pumping stations.

Results and conclusions

By combining theory and practice of conditioning with the raw water quality data of several SWM pumping stations, the necessary treatment processes were determined for the pumping stations. It was found that for most of the SWM pumping stations shell filtration is not even necessary. Shell filtration is only necessary for La Vigilantia and Republiek. The raw water of most pumping stations can be sufficiently conditioned by applying air stripping. One of the problems which have led to this research was that shells are threatened to run out in the long term and that alternative materials have to be found for shells for the conditioning of aggressive groundwater. Another problem which led to this research was the fact that currently shell filtration is not applied at pumping stations where aggressive groundwater is present because of the high consumption of shells and thus high costs for the conditioning of aggressive water. If most of the pumping stations only needs conditioning by air stripping, than the problems with shells and the high costs for the conditioning of aggressive water are perfectly solved.

The goal of the column experiments was to study the behavior of shell filters. Among other parameters, the influence of filtration rate on contact time was analyzed. From the column experiments with shells and varying filtration rates it was noticed that the filtration rate influences contact time. The contact time decreases with increasing filtration rate. The necessary contact time to reach a pH of 9 was reach after 1 minute at a filtration rate of 10 m/h and after 7 minutes at a filtration rate of 3 m/h.

The online computer programme Stimela was used to model the conditioning process. The results showed that Stimela can be used to model the conditioning process. By fitting the results of the column experiments with the results of the model, the reaction rates of shells, softening pellets, crushed shells and crushed limestone were estimated. It was found that for whole shells, crushed shells and for crushed limestone the reaction rate is 1.9 h^{-1}. For softening pellets the reaction rate is 4.5 h^{-1}.

By using the reaction rate, it is possible to calculate operational parameters such as contact time and refilling frequency of the filter bed. A calculation was done for the pumping station La Vigilantia with the most aggressive water. It was found that for La Vigilantia the necessary contact time to reach the desirable pH of 8.1 is 2 minutes at a filtration rate of 5 m/h, which means that the desirable pH is reached after the first 17 cm of the filter bed. A safety margin is chosen of 3 minutes, which means that the contact time is 5 minutes with a corresponding filter bed height of 0.42 m. If a filter bed height is chosen of 0.8 m, the refilling frequency for La Vigilantia is 6 months. This is the pumping station with the most aggressive water. When the same filtration is applied, the contact time and the filter bed height increases if the water is less aggressive. For less aggressive water the filter bed height is larger than 0.8 m.

Table of Contents

List of Figures

List of Tables

Nomenclature

1. Alkalinity : Bicarbonate concentration [mol/l]
2. Ca^{2+} : Calcium ion [mol/l]
3. $CaCO_3$: Calcium Carbonate [mol/l]
4. CH_4 : Methane [mol/l]
5. CO_3^{2-} : Carbonate ion [mol/l]
6. Conductivity : measure for the ability of a solution to carry an electric current [µS/cm]
7. EBCT : Empty Bed Contact time [min]
8. Effluent : Outgoing water of the filter
9. Fe^{3+} : Trivalent iron ion [mol/l]
10. H_3O^+ : Hydronium ion [mol/l]
11. H_2S : Hydrogen sulphide [mol/l]
12. Hardness : Total sum of calcium and magnesium ions concentration [mol/l]
13. Influent : Ingoing water of the filter
14. SI : Saturation Index [-]
15. Mg^{2+} : Magnesium ion [mol/l]
16. Mn^{2+} : Manganese ion [mol/l]
17. m- number : Ion balance which is defined as the sum of bicarbonate, 2 x carbonate and hydroxide ions minus hydronium ions [mol/l]
18. Conditioning : Treatment process at which pH, hardness and alkalinity are changed until the desirable values are reached
19. NH_4^+ : Ammonium ion [mol/l]
20. NWTP : New Water Treatment Plant
21. OH^- : Hydroxide ion [mol/l]
22. pH : measure for acidity [-]
23. p- number : Ion balance which is defined as the sum of carbonate and hydroxide ions minus hydronium and carbonic acid ions [mol/l]
24. P.S. : Pumping station
25. Shell filtration : Water treatment process at which the water is flown through a bed of shells with a filter bed height of 1.5 - 2 m.
26. Aggressive water : Water with a pH such that it causes corrosion of metals and cement bound materials
27. SWM : Surinaamsche Waterleiding Maatschappij
28. VEWIN : the association of drinking water companies in the Netherlands
29. WHO : World Health Organisation

1 Introduction

In drinking water practice groundwater is mostly used for drinking water production. Depending on the ground layers of abstraction, the groundwater is sometimes characterized as aggressive water. However, in drinking water practice aggressive water is considered an undesirable water type. The term aggressive is explained by the fact that aggressive water can cause corrosion of metal pipelines and cement bound materials during treatment, transport and distribution of drinking water. This is caused by the character of the aggressive water in which the pH, a measure for the acidity, plays an important role [1,2]. Aggressive water is usually also characterized by a low bicarbonate concentration and a low hardness. These characteristics are considered undesirable in drinking water practice. In order to prevent corrosion of metal pipelines and cement bound materials, the pH of the drinking water needs to be such that metal pipelines and cement bound materials are not dissolved in the water. Due to processes of micro-organisms in drinking water networks the pH of the water can be decreased such that it causes corrosion. Bicarbonate has the property of buffering pH fluctuations. If the concentration of bicarbonate is not sufficient, these pH fluctuations cannot be neutralized. The fact that a low hardness is considered an undesirable property for drinking water is based on studies done by researchers who have shown that there might be a relation between a low hardness of drinking water and the occurrence of cardiovascular diseases [3,4,5].

It is clear that aggressive water must be treated before it is supplied to the customer. The aggressive water is treated in such way that pH, bicarbonate and calcium concentration are changed to the desirable values as given for drinking water in the National Drinking Water standards. In technical terms the treatment of aggressive water is called conditioning of aggressive water.

In Suriname groundwater is mostly used for the production of drinking water. The groundwater is often characterized as aggressive water. In Surinam aggressive water is currently conditioned by shell filtration in which the water flows through a bed of shells. Water quality data of several pumping stations such as Republiek, van Hattemweg and Flora have shown that after treatment by means of shell filtration the water quality of the effluent concerning pH, hardness and alkalinity are below the standards. It is noticed that in Suriname there are no strict guidelines for the water quality of drinking water and for the treatment of aggressive groundwater.
In Suriname the WHO guidelines are applied by drinking water company SWM, Surinaamsche Waterleiding Maatschappij, as a measure for safe and clean drinking water. In the Netherlands the National Drinking Water standards and the VEWIN recommendations are applied. The National Drinking Water standards may under no circumstance be exceeded. In the WHO guidelines there are no strict guidelines for pH, bicarbonate and calcium concentration. For this research the National Drinking Water standards and the VEWIN recommendations will be used for the analysis of the water quality data of the SWM pumping stations. The National drinking water standards for pH, bicarbonate, calcium concentration and SI are: $7.5 < pH < 9$, bicarbonate > 1 mmol/l, 0.5 mmol/l $<$ calcium $<$ 2 mmol/l and $-0.2 < SI < 0.3$. The VEWIN recommendations for pH, bicarbonate, calcium concentration and SI are $7.8 < pH < 8.3$, bicarbonate > 1 mmol/l, 3.74 mmol/l and $-0.2 < SI < 0.3$.

Next to water treatment the shells in Suriname are also used for other purposes such as soap production and improvement and neutralization of acidic agricultural grounds [6,7]. According to SWM the shell provision, as a result of the multi purpose use of the shells, is threatened to run out in the long term. It is also said that the problem of salt intrusion in the northern coast may be caused by the continuous excavation of shells.

Currently there are no strict guidelines in Suriname for the operation of shell filtration. In order to know how the current conditioning situation can be optimized, it important that the operation of shell filtration and the processes involved are understood. Therefore this research will be focused on the study into several aspects of shell filtration and the parameters that influence the conditioning process. For the purpose of the long term replacement of shells as filter medium, the experiments that will be carried out with shells will also be done with crushed limestone and softening pellets.

1.1 Problem definition

Currently there are no strict guidelines for the water quality concerning pH, bicarbonate and calcium. There are also no strict guidelines for the operation of shell filters and the assessment of necessary treatment processes for the pumping stations with water quality problems. In order to optimize the water quality of the pumping stations with water quality problems, it is important that the guidelines are implemented.

1.2 Objective

The objective of this research is to determine:

- Operational guidelines for SWM pumping stations with regard to necessary height and regeneration of the shell filters
- Necessary treatment processes for several SWM pumping stations with water quality problems, based on water quality data of the raw water of the pumping stations

1.3 Method

In order to reach the objectives several aspects need to be focused on. The chemical processes that take place during the conditioning of aggressive water need to be understood. Therefore theory and practice of the conditioning of aggressive water are studied first. The behaviour and operation of shell filter also need to be understood. Therefore jar tests and column experiments will be carried out at which the aggressive water of Suriname is simulated. For the purpose of the replacement of shells as filter medium, the experiments will also be carried out with crushed limestone and softening pellets. For the optimization of the water quality of pumping stations with water quality problems, the treatment of the pumping stations are assessed by using the theory of the application of necessary treatment processes for the conditioning of different types of aggressive water. Within this research it is also aimed to see whether the minimum contact time, which is needed to reach sufficient conditioning of the aggressive water, can be predicted. This is done by modelling the course of the conditioning process during filtration by using the online modelling computer programme Stimela in combination with the kinetics of the conditioning of aggressive water through filtration. The modelling is done for all materials that are used during the column experiments. As a result the reaction rates of the filter media are determined. With the reaction rate an advice can be given for the minimum contact time. The minimum contact time is necessary to reach the desirable water quality.

1.4 Overview

The structure of this report is as follows:
In chapter 2 a description is given of the current drinking water situation in Suriname at SWM pumping stations regarding the conditioning of aggressive water. The water quality concerning pH, bicarbonate and calcium concentration is also presented in this chapter. Also a short description and the design data of the pumping stations Republiek, van Hattemweg and Flora are given in chapter 2. In chapter 3 the theory and practice of the conditioning of aggressive water is presented and discussed. The conventional treatment methods for the conditioning processes for the conditioning of aggressive water are also given in this chapter. In chapter 4 the description of the jar tests and the column experiments are given along with a list of the materials, the apparatus and the methods that are used. In chapter 5 the results of the experiments are presented and discussed. In chapter 6 the mathematical model is given of the conditioning of aggressive water through filtration at which the online modelling computer programme Stimela is used in combination with and calculations are given. In chapter 7 the evaluation and design is given of the pumping stations that are analyzed for this. The conclusions and recommendations are presented in chapter 8.

2 Current situation in Suriname

In Suriname aggressive water is conditioned by shell filtration. Because of the persistent problems with corrosion of installations and metal pipelines and the threat of limited availability of the shells in the long term, conditioning of aggressive water is a topic of discussion at SWM, Surinaamsche Waterleiding Maatschappij, in Suriname. Sometimes water quality problems occur because knowledge of the conditioning of aggressive water is not sufficient with as result that the shell filters are not correctly operated. In order to assess the operation process, information is gathered regarding management of the shell filters at the pumping stations Republiek, van Hattemweg and Flora. Furthermore water quality data of some pumping stations is gathered. Currently several SWM pumping stations are rehabilitated in cooperation with Vitens, the largest drinking water company in the Netherlands. The rehabilitated pumping stations will all be upgraded in the following configuration of treatment processes: plate aeration, sand filtration, tower aeration, sometimes shell filtration, storage. Based on the water quality data of the rehabilitated pumping stations it is found that the applied treatment processes are not always necessary or suitable for every pumping station. It is important that the water quality of each rehabilitated pumping station is closely analyzed and that the right treatment steps are chosen and applied.

In paragraph 2.1 a short description is given of Suriname and its geographical location, population and language. Also a short description is given of SWM in paragraph 2.2. In paragraph 2.3 a list is given of the pumping stations that are administered by SWM. In paragraph 2.4 the water quality data is given of several SWM pumping stations among which the pumping stations that are rehabilitated in cooperation with Vitens. The pumping stations Republiek, van Hattemweg and Flora are closely analyzed in paragraph 2.5. The operational information and backwashing and the application of shell filters in Suriname are given in paragraph 2.6.

2.1 Suriname

Suriname (figure 2.2) lies on the northeast coast of South America (figure 2.1). In the west it is bordered by Guyana (formerly British Guyana), in the east by French Guyana, in the north by the Atlantic Ocean and in the south by Brazil. The capital is Paramaribo. Because of the border disputes between Suriname and the neighbouring countries Guyana and French Guyana there are some obscurities regarding the area of Suriname. Including the disputed area Suriname has a surface[1] of 163,820 km^2. The number of inhabitants is 492,829[2] of which 75% lives in the northern coast in the districts Paramaribo, Wanica and Nickerie. The population exists of a mix of ethnic groups among which Hindustani's, Creoles, Marrons, Javanese, Chinese, Native Americans, Jews and nowadays also Brazilians. The official language is Dutch. The language that is spoken by everyone is called Sranantongo which literally means "Surinamese language".

---

[1] http://www.suriname.nu/101alg/statis02.html (Last visit on: march 13 2008)

[2] http://www.evd.nl/zoeken/showbouwsteen.asp?bstnum=88779 (Last visit on: march 13 2008)

Figure 2.1 Map of South America

Figure 2.2 Map of Suriname[3]

2.2 Drinking water Company SWM

The drinking water company SWM, de Surinaamsche Waterleiding Maatschappij, is responsible for the drinking water supply in the coastal plain of Suriname. The Dienst Watervoorziening of the Ministry of Natural Resources is responsible for the drinking water supply in the inlands of Suriname. However, currently some of the water treatment plants in the coastal plain e.g. pumping station Wageningen in the district of Nickerie are still administered by the Dienst Watervoorziening. SWM is in the process of taking over these treatment plants, because the objective of SWM is to be responsible for the drinking water supply in the total coast plain where as many as possible inhabitants should have access to sufficient, safe and clean drinking water.

In order for SWM to supply drinking water to customers, SWM has to be granted legislation by the government. The legislation must be established for protection and management of groundwater. SWM aims for a durable extraction of groundwater because of the reliability of the groundwater and the lower investment and operational costs for the treatment of groundwater compared to surface water. Thereby SWM prefers proven conventional groundwater treatment methods. In this way the risk of operational and water quality problems is minimized.

2.3 SWM pumping stations

The pumping stations that are administered by SWM are categorized in the divisions West, Central and East. The establishments cover the pumping stations in the western, central and eastern part of the coastal plain of Suriname. In this paragraph the divisions are given along with the accompanying pumping stations and the districts in which the pumping stations are located (table 2.1). The pumping stations that are administered by the SWM are:

---

[3] http://www.select4you.be/images/suriname/kaart.gif

- Establishment West: Nickerie (Nickerie)

- Establishment Central
    - Blauwgrond (Paramaribo)
    - Flora (Paramaribo)
    - Helena Christina (Paramaribo)
    - Koewarasan (Wanica)
    - Leiding 9A (Wanica)
    - La Vigilantia (Wanica)
    - Leysweg (Paramaribo)
    - Livorno (Paramaribo)
    - Meerzorg (Commewijne)
    - Pontbuiten (Paramaribo)
    - Republiek (Para)
    - Sidoredjo (Paramaribo)
    - Tourtonne (Paramaribo)
    - Uitkijk (Wanica)
    - Van Hattemweg (Wanica)
    - William Kraan plein (Paramaribo)

- Establishment East
    - Albina (Marowijne)
    - Moengo (Marowijne)
    - Wonoredjo (Marowijne)

Table 2.1 Districts of Suriname

Number	District	Capital	Map of Suriname
1	Brokopondo	Brokopondo	
2	Commewijne	Nieuw- Amsterdam	
3	Coronie	Totness	
4	Marowijne	Albina	
5	Nickerie	Nieuw- Nickerie	
6	Para	Onverwacht	
7	Paramaribo	Paramaribo	
8	Saramacca	Groningen	
9	Sipaliwini	None	
10	Wanica	Lelydorp	

Rehabilitation SWM pumping stations by Vitens

SWM is in the process of taking over the in the coastal plain of Suriname which are still under the administration of the Ministry of Natural Resources. Due to lack of finances these pumping stations have been neglected. The pumping stations are old and in bad state. The pumping stations are rehabilitated by SWM in cooperation with Vitens. Vitens is the largest drinking water company in the Netherlands and supplies 5.4 million people and companies in the provinces Flevoland, Friesland, Gelderland, Utrecht, Overijssel and several municipalities in Drenthe and Noord-Holland. At the beginning of 2005 Vitens signed a contract for technical support to SWM. Vitens helps SWM at public tenders and supervision of building projects. These activities are the result of the short term investment programme for which the Dutch government has made 16 million euros available. The goal of the short term investment programme is to improve the production, the quality and the availability of drinking water in Suriname. The pumping stations that are rehabilitated by Vitens are:

- Koewarasan
- La Vigilantia
- Koewarasan
- La Vigilantia
- Leiding 9A
- Leysweg
- Meerzorg
- Pontbuiten
- Tourtonne
- Uitkijk

These pumping stations will successively be operated once in every 3 months starting with Uitkijk and followed by Koewarasan. Uitkijk will be operated at the end of April 2008. All these pumping stations will be rehabilitated or built with the following configuration: plate aeration, sand filtration, tower aeration, shell filtration (if necessary), storage.

Districts without drinking water

Currently in the districts Coronie and Saramacca and certain parts of the district Commewijne, the households are not supplied with drinking water. In these areas drinking water is obtained in two ways. The first is by collecting rain water in so called Duro tanks. The collected rainwater is used for consumption purposes such as cooking and drinking. The second is by collecting groundwater from water wells by using bucket and rope. These water wells are usually situated in the gardens of the households. The collected water from the water wells is mostly used for household purposes such as, washing, bathing and gardening.

2.4 Water quality data

For this research the water quality data of the SWM pumping stations were gathered. In this paragraph the water quality data of several pumping stations are given. The water quality data were obtained from Vitens and the SWM laboratory.

2.4.1 Guidelines

In the introduction the guidelines and standards which are applied in Suriname and in the Netherlands are given. For the convenience of comparing the given water quality data of the SWM pumping stations to the guidelines and standards, the guidelines and standards are given in this paragraph.

WHO guidelines (Suriname)
pH : no strict guideline
Bicarbonate : no strict guideline
Calcium : no strict guideline
SI : no strict guideline

National Drinking Water standards (Netherlands)
pH : 7.5 > pH > 9
Bicarbonate : > 60 mg/l (=1 mmol/l)
Calcium : 20 mg/l < calcium < 80 mg/l (0.5 mmol/l < calcium < 2 mmol/l)
SI : -0.2 < SI < 0.3

VEWIN recommendations (Netherlands)
pH : 7.8 > pH > 8.3
Bicarbonate : > 1 mmol/l
Calcium : 150 mg/l (= 3.75 mmol/l)
SI : -0.2 < SI < 0.3

In the WHO guidelines there are no strict guidelines for pH, bicarbonate and calcium. Therefore for this research the National Drinking Water standards and the VEWIN recommendations will be used for the analysis of the water quality data of the SWM pumping stations.

2.4.2 Measured water quality data

The water quality data of the SWM laboratory are based on measurements which are carried out twice a month throughout the whole year. The water quality data from the SWM laboratory which are used for this research are based on measurements taken in the period January 2005 to July 2006. The water quality data from Vitens are based on samples that were taken once in September 2004.

Water quality data

In table 2.2 a list is given of the water quality data obtained from Vitens and the SWM laboratory. The water quality data obtained form Vitens were measured by the laboratory of Vitens. The parameters that are currently measured by the SWM laboratory differ from the parameters that were measured once by Vitens. In table 2.2 the measured parameters are given and the periods in which these parameters were measured. In table 2.3 the average values of the water quality data are given regarding pH, CO_2, calcium, bicarbonate, iron and manganese. For more water quality data see appendix I.

Currently the SWM laboratory does not measure calcium and magnesium. The calcium and magnesium measurements were done on request for 2006. For the purpose of the analysis of the water quality data concerning the conditioning of aggressive groundwater it is important that calcium and magnesium measurement are included in the measuring programme. It is observed that manganese and methane are also not measured by the SWM laboratory. For the purpose of determining the configuration of necessary treatment steps, it is important that the manganese and methane concentrations are measured. If the manganese and methane concentrations in the raw water exceed the standards, aeration and sand filtration must be implemented as first step in the treatment. The difference in parameters measured by SWM and by Vitens is explained by the fact that Vitens assigned to measure all parameters which are of interest for drinking water.

The water quality data of Vitens were only done for the raw water of the pumping stations. The water quality data of SWM are done before and after every treatment step.

Table 2.2 Water Quality data Vitens and SWM

Source: SWM laboratory Measuring period: January 2005 – December 2006			Source: Vitens Measuring period: September 2004		
Pumping station	Measured Parameters	Measuring locations	Measured parameters	Measured parameters	Measuring locations
- Blauwgrond - Flora - Helena Christina - Livorno - Moengo - Nickerie - Republiek - Sidoredjo - Tourtonne - Van Hattemweg - WK- plein	- pH - CO_2 - Total hardness - Bicarbonate - Iron - Chloride	After every treatment step	- Koewarasan - La Vigilantia - Leiding 9A - Leysweg - Meerzorg - Pontbuiten - Tourtonne - Uitkijk	- pH - Conductivity - Calcium - Magnesium - Total hardness - Bicarbonate - Iron - Manganese - Methane - Ammonium - Chloride - DOC - Nitrate - Oxygen - Sulphate	Raw water

Table 2.3 Raw water quality data SWM pumping stations

Source	Pumping station	pH [-]	CO_2 calculated [mg/l]	Calcium [mg/l]	Bicarbonate [mg/l]	Iron [mg/l]	Manganese [mg/l]
Vitens	Koewarasan	6	NA	22	88	8	0.5
	La Vigilantia	3.9	NA	2	< 1	0.28	0.23
	Leiding 9A	6.2	NA	32	153	9.9	1
	Leysweg	5.7	NA	25	110	4	0.8
	Meerzorg	6.25	NA	5	93	3.6	0.16
	Pontbuiten	6	NA	76	80	5.4	0.22
	Tourtonne	6.55	NA	10	161	0.01	0.07
	Uitkijk	6.25	NA	8	63	5.5	0.3
SWM	Flora	5.90	104.50	11	84	5.79	NA
	Helena Christina	5.81	167.64	13	69	8.31	NA
	Republiek	4.92	111	1	10	2.48	NA
	Van Hattemweg	5.94	90.78	7	82	4.67	NA

NA = Not Available

Missing data

The water quality data regarding manganese are not available in the water quality data obtained from SWM because manganese is not measured by SWM.

2.5 Description of pumping stations Republiek, van Hattemweg and Flora

At pumping stations Republiek, van Hattemweg and Flora shell filtration is applied. At these pumping stations the water quality data show that the values for pH, bicarbonate concentration and hardness do not satisfy the National Drinking Water standards after treatment with shell filtration. These pumping stations are therefore chosen for detailed analysis. For the study on the operation of the shell filters the station chiefs and operators of the concerning pumping stations were asked questions regarding configuration and operation (e.g. backwashing, refilling of filter bed) of the filters, because there are no manuals on how the filters should be operated. All the information that was gathered by questioning the station chiefs and the operators is processed in this paragraph.

In this paragraph a description is given of the pumping stations Republiek, van Hattemweg and Flora, along with the configuration, water quality and operational data of these pumping stations.

Pumping station Republiek

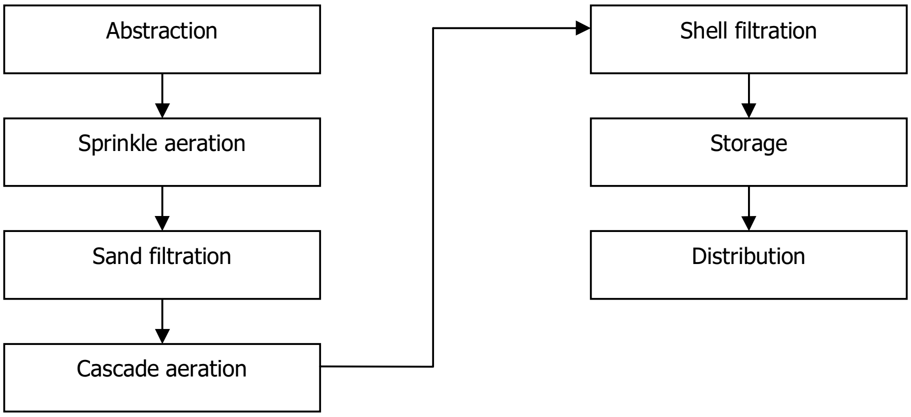
Pumping station Republiek (figure 2.3) is located in the district of Para. It is the oldest pumping station of the SWM. This can be seen by the old steam engines which are no longer in use (figure 2.4). The following treatment processes are applied: abstraction, sprinkle aeration, sand filtration, cascade aeration, shell filtration, storage. Sand filtration takes place in pressurised vessels and shell filtration in open rectangular concrete tanks.

Figure 2.3 Pumping station Republiek

Figure 2.4 Steam engines p.s. Republiek

Process scheme Republiek

The process scheme of pumping station Republiek is as follows:



Design data Republiek

The design data of pumping station Republiek is given in table 2.4.

Table 2.4 Design data pumping station Republiek

Parameter	Unity	Sand filters	Shell filters
Filter type	-	Pressurised vessels	Open rectangular tanks
Flow	m^3/h	300	300
Number of filters	-	6 (4 of type A in operation)	2
Length	m	-	6
Width	m	-	3
Height	m	4.3	5
Diameter	m	Filter type A: 3.0	-
		Filter type B: 2.5	-
Volume	m^3	Filter type A: 4 filters; 30.3	90
		Filter type B: 2 filters; 22	
Filter bed height	m	1.8	1.5 – 1.8
Grain size	mm	1 – 2	2 – 12
Porosity	%	NA	NA
Velocity	m/s	7.9	8.3
EBCT	min	13.7	13

Pumping station van Hattemweg

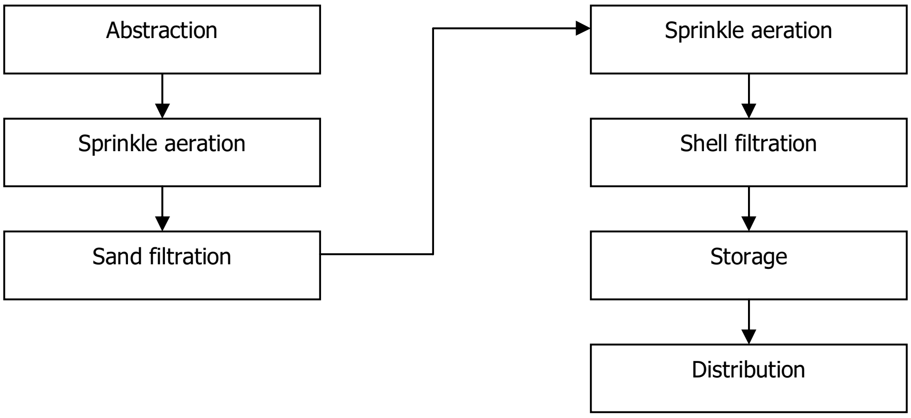
Pumping station van Hattemweg (figure 2.5) lies also in the district of Para. The following treatment processes are applied: abstraction, sprinkle aeration, sand filtration, sprinkle aeration, shell filtration (figure 2.6), storage. Both sand filtration and shell filtration are carried out in open concrete tanks.

Figure 2.5 Pumping station van Hattemweg

Figure 2.6 Shell filtration at van Hattemweg

Process scheme van Hattemweg

The process scheme of pumping station van Hattemweg is as follows:



Design data van Hattemweg

The design data of pumping station van Hattemweg is given in table 2.5

Table 2.5 Design data pumping station van Hattemweg

Parameter	Unity	Sand filter	Shell filter
Filter type	-	Open rectangular tank	Open rectangular tank
Flow	m^3/h	1100	1100
Number of filters	-	5	2
Length	m	11.3	11.3
Width	m	4.8	4.8
Height	m	8.2	6.1
Volume	m^3	444.8	330.9
Filter bed height	m	1.5	2
Grain size	mm	1 – 2	2 – 12
Porosity	%	NA	NA
Velocity	m/h	4.1	10.1
EBCT	min	22	12

Pumping station Flora

Pumping station Flora (figure 2.7) is located in the quarter Flora (figure 2.8) within the district of Paramaribo. The configuration of the treatment is as follows: abstraction, tower aeration, sand filtration, shell filtration, storage. Sand filtration and shell filtration are performed in pressure vessels.

Figure 2.7 Pumping station Flora

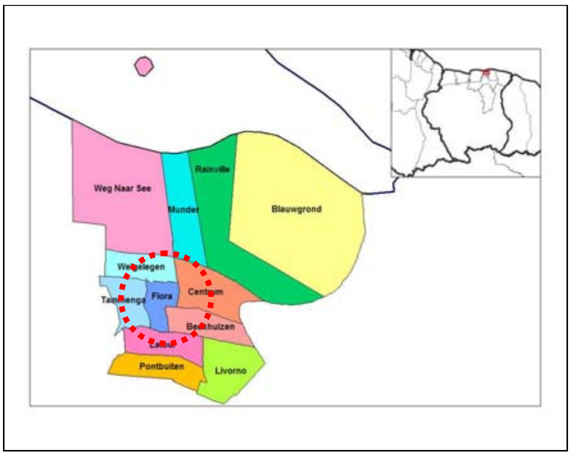
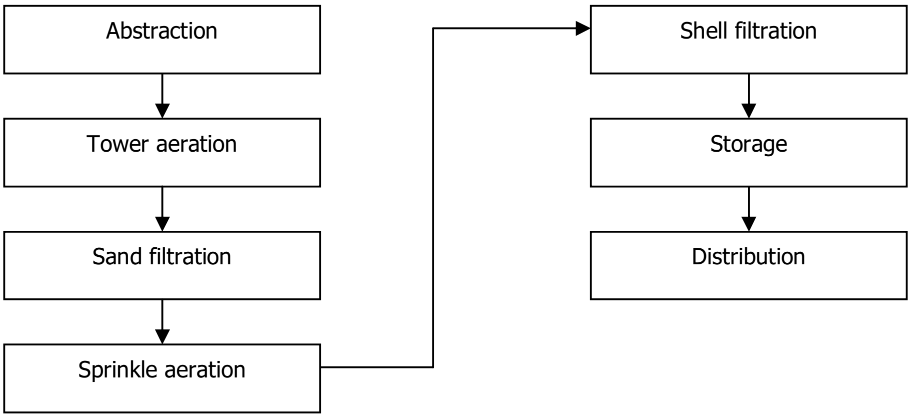


Figure 2.8 District of Paramaribo

<u>Process scheme Flora</u>

The process scheme of the pumping station Flora is as follows:



<u>Design data Flora</u>

The design data of pumping station Flora is given in table 2.6

Table 2.6 Design data pumping station Flora

Parameter	Unity	Sand filter	Shell filter
Filter type		Pressurised vessels	Pressurised vessels
Flow	m^3/h	126	126
Number of filters	-	3	3
Diameter	m	3.0	3.0
Height	m	4.3	4.3
Volume	m^3	30.3	30.3
Filter bed height	m	1.8	1.8
Grain size	mm	1 – 2	2 – 6
Porosity	%	NA	NA
Velocity	m/h	6	6
EBCT	min	18	18

2.6 Operation and application of shell filters

In Suriname the shell filters are operated similar to limestone filters. There are however some differences. In this paragraph a description is given of how the shell filters of the pumping stations Republiek, van Hattemweg and Flora are operated with regard to backwashing and refilling. This is given in table 2.7. The description of the operation is followed by a discussion. The shell filters of Republiek are e.g. refilled once in 4 months with 80 m^3. According to the operators the shell filters are refilled on a basis of 2 to 4 months and not by checking the height of the shell bed. It has been noticed that the operators lacked the knowledge of purpose of a minimum filter bed.

Table 2.7 Operation of the shell filters regarding backwashing and refilling

Pumping station	Backwashing			Refilling	
	Frequency weeks	Method	Duration [min]	Frequency months	Quantity m^3 per filter unit
Republiek	Once in 4 weeks	- Air (ca. 60 m/h) - Water (ca. 10 m/h) + air (ca. 60 m/h) - Water (ca. 30 m/h)	- 5 - 5 - 5	Once in 2 months	60
Van Hattemweg	Once in 3 weeks	- Air - Water + air - Water	- 5 - 5 - 5	Once in 3 months	80
Flora	Once in 2 weeks	- Air - Water + air - Water	- 5 - 5 - 5	Once in 2 months	10

The difference in backwash frequency is explained by the iron content of the raw water which is 2.60, 4.62 and 5.79 for respectively Republiek, van Hattemweg and Flora.

In the Netherlands refilling of the filter bed takes place when the bed has reduced with 10%. By assuming that the given filter bed height is constant and by using the dimensions of the shell filter, the refilling frequency, and the refilling volumes, it is determined when the shell filter of the pumping stations Republiek, van Hattemweg and Flora are refilled. The results are given in table 2.8. The consumption rate is also calculated and given in table 2.8.

Table 2.8 Refilling of filter bed and consumption rate of shells

Pumping station	**Reduction of filter bed [%]**	**Shell consumption rate [cm/day]**
Republiek	6	0.2
Van Hattemweg	25	0.6
Flora	22	0.7

During visits to some pumping stations such as Leiding 9A, where conditioning is needed, it was observed that shell filtration was however not applied. According to the operators of those pumping stations shell filtration was not applied because of the extremely high consumption of shells. Recently the shell filters of pumping station Tourtonne were also taken out of operation.

3 Theory and practice of conditioning

In this chapter the theory and practice of neutralization will be discussed. First the standards and guidelines are listed for the parameters concerning conditioning. Since in Suriname the WHO guidelines for drinking water are applied, these will be listed below. The standards and guidelines that are applied in the Netherlands are also listed. In order to know how the conditioning process works the theory of conditioning of aggressive water will be discussed in this chapter. Furthermore it is important to know which previous studies have been done in this field and to know to which extent these studies have been done. Among other researchers previous studies on conditioning of aggressive water were done by van Dijk et al. [8,9,10], Reijnen [11,12,13], Tillmans [14] and Anderlohr [15]. In practice several methods are applied for the neutralization of aggressive water.

In paragraph 3.1 a list is given of the WHO guidelines which are applied in Suriname. The standards and guidelines which are applied in the Netherlands are also discussed in this paragraph. In paragraph 3.2 the theory of conditioning will be discussed. The previous studies on neutralization done by Tillmans, Anderlohr, van Dijk and Reijnen are considered significant for this research. Therefore these studies will be discussed in paragraph 3.3. Furthermore, the conventional treatment methods for neutralization of soft water are given and discussed in paragraph 3.4. In paragraph 3.5 the kinetics of limestone filtration are given.

3.1 Standards and guidelines

As a result of conditioning some water quality parameters such as pH, bicarbonate and calcium are influenced. For these parameters certain standards apply. In Suriname the WHO guidelines for drinking water, determined by the World Health Organization, are applied for clean and safe drinking water. These guidelines are based on public health. In the WHO guidelines the pH, hardness and alkalinity are considered parameters that do not influence the human health directly. Therefore there are no strict WHO guidelines for these parameters.

In the Netherlands the standards for pH, bicarbonate and hardness are given in the National Drinking Water standards (Waterleidingbesluit). According to the National Drinking Water standards drinking water is never allowed to contain micro-organisms, parasites or substances in such a way that it forms a threat on the public health. The National drinking water standards may under no circumstance be exceeded. Beside the National drinking water standards there are recommendations by the VEWIN. The VEWIN recommendations are apprehended by the drinking water companies as goals and may be exceeded. For this research it is chosen to use the National Drinking Water standards and the VEWIN guidelines for the analysis of water quality data of the SWM pumping stations.

The water quality parameters that influence the conditioning process:

- **pH:**

  The pH is defined as the negative logarithm of the H_3O^+ ions and is considered a measure for the acidity of the water. The acidity increases with decreasing pH. The standards and guidelines for the pH are:

WHO guidelines (3rd edition)	: no guideline (WHO guidelines: paragraph 12.100)
National Drinking Water standards	: $7.5 < pH < 9.0$ (WLB: Appendix A, table III a)
VEWIN recommendations	: $7.8 < pH < 8.3$

- **Calcium:**

WHO guideline (3rd edition)	: no guideline
National Drinking Water standard	: 20 mg/l < calcium < 80 mg/l (0.5 mmol/l < calcium < 2 mmol/l)
VEWIN recommendations	: 150 mg/l (= 3.74 mmol/l)

- **Hardness: Total of calcium and magnesium ions; $[Ca^{2+}] + [Mg^{2+}]$**

  Hardness is defined as the sum of calcium and magnesium ions. The hardness decreases with decreasing concentration of calcium and magnesium. The standards and guidelines for hardness are:

WHO guideline (3rd edition)	: no guideline (WHO guidelines: paragraph 12.67)
National Drinking Water standards	: 1.0 < total hardness < 2.5 mmol/l (WLB: Appendix A, table III a)
VEWIN recommendations	: 1.0 < total hardness < 2.5 mmol/l

- **Bicarbonate concentration: $[HCO_3^-]$**

  The bicarbonate concentration, which is also called the alkalinity, is a measure for the buffering capacity of the water in case of pH fluctuations in the water. The buffering capacity decreases with decreasing bicarbonate concentration. The standards and guidelines for the bicarbonate concentration are:

WHO- guideline (3rd edition)	: no guideline
National Drinking Water standards	: > 60 mg/l (= 1.0 mmol/l) (WLB: Appendix A, table III a)
VEWIN recommendations	: > 60 mg/l (=1.0 mmol/l)

- **SI**

  The Saturation Index (SI) is defined as the difference between the measured pH and the equilibrium pH.

WHO- guideline (3rd edition)	: no guideline
National Drinking Water standards	: $-0.2 < SI < 0.3$
VEWIN recommendations	: $-0.2 < SI < 0.3$

3.2 Theory of conditioning

The equilibrium reactions that are of concern for conditioning are:

$$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^- \qquad K_1 = \frac{(H_3O^+)\left(HCO_3^-\right)}{\left(CO_2\right)} \qquad (3.1)$$

$$HCO_3^- + H_2O \rightleftarrows H_3O^+ + CO_3^{2-} \qquad K_2 = \frac{(H_3O^+)\left(CO_3^{2-}\right)}{\left(HCO_3^-\right)} \qquad (3.2)$$

$$H_3O^+ + OH^- \rightleftarrows 2H_2O \qquad K_w = \left(H_3O^+\right)\left(OH^-\right) \qquad (3.3)$$

$$Ca^{2+} + CO_3^{2-} \rightleftarrows CaCO_3 \qquad K_s = \left(Ca^{2+}\right)\left(CO_3^{2-}\right) \qquad (3.4)$$

$$CaCO_3 + CO_2 + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^- \qquad K = \frac{\left(Ca^{2+}\right)\left(HCO_3^-\right)^2}{\left(CO_2\right)} = \frac{K_s * K_1}{K_2} \qquad (3.5)$$

$$H^+ + CaCO_3 \rightleftarrows Ca^{2+} + HCO_3^- \qquad (3.6)$$

p-number and m-number

The p-number and m-number include an ion balance as well as a mass balance. Because of this the effect of dosing acids, bases or water types can be determined. The p-number and m-number are independent of the temperature and ion strength. Due to the shift of the equilibrium of the reactions 3.1, 3.2 and 3.3, the temperature and the ion strength have an influence on the concentrations of CO_2, HCO_3^-, CO_3^{2-}, OH^- en H_3O^+, but not on the value of p-number and m-number itself. The p-number and m-number are defined by the following relation:

$$m = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H_3O^+] \qquad (3.7)$$

$$p = -[CO_2] + [CO_3^{2-}] + [OH^-] - [H_3O^+] \qquad (3.8)$$

$$C_T = m - p = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \qquad (3.9)$$

Saturation Index

The Saturation Index (SI) is defined as the difference between the measured pH and the equilibrium pH.

The SI can be written in the following formula:

$$SI = \log\left[\frac{\left[Ca^{2+}\right]\left[CO_3^{\ 2-}\right]}{K_s}\right] = pH - pH_s \tag{3.10}$$

$$pH_s = \log K_s - \log K_2 - \log\left[Ca^{2+}\right]\left[HCO_3^{\ -}\right] \tag{3.11}$$

In this case pH_s is the pH that the water would have if it would be in equilibrium at the same as $[Ca^{2+}]$ and $[CO_3^{2-}]$. In the equilibrium phase the following applies: $pH = pH_s$

Each concentration of Ca^{2+} and HCO_3^- belongs to a certain concentration of CO_2. Water with more CO_2 than the equilibrium concentration of CO_2 has an SI smaller than 0. In this case one speaks of aggressive water. Water with aggressive CO_2 means an undersaturation to $CaCO_3$ as a result of which the water is corrosive for metal piping and cement bound materials. The opposite applies for water with less CO_2 than the equilibrium concentration of CO_2 the SI is larger than 0. This means an over-saturation to $CaCO_3$ as a result of which scaling can take place.

3.3 Previous studies into the carbonic acid equilibrium

The purpose of this paragraph is to discuss the previous studies that have been done into the carbonic acid equilibrium among which the studies done by van Dijk et al. [8,9,10], Reijnen [11,12,13], Tillmans [14], Anderlohr [15], Houtepen [16] and Bakker [17].

Tillmans et al. [14]

Tillmans et al. [14] investigated conditioning of aggressive water by filtering demineralised water with CO_2 through a bottle with crushed limestone with a diameter of 0.5 – 1.0 mm. The demineralised water contained a concentration of 10 – 100 mg CO_2/l. The results of the experiments are presented in figure 3.1.

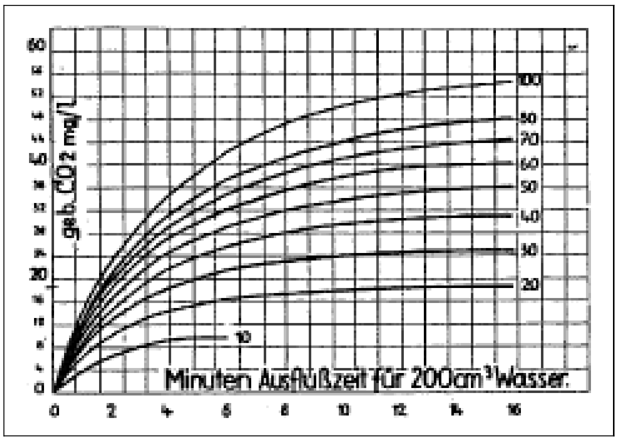


Figure 3.1 Tillmans, CO_2 concentration as function of contact time

As a result Tillmans generated the Tillmans curve which reflects the position of the equilibrium at a certain temperature and ion strength for a solution for which applies: $m = 2 [Ca^{2+}]$.

In figure 3.2 the Tillmans curve is reflected for a temperature of 10 °C. In the area under the curve one speaks of scaling water where scaling in transports and distribution pipes and in boilers, geysers and other heating elements with as a result important economic damage. In the area above the curve one speaks of aggressive water where corrosion of pipe material occurs.

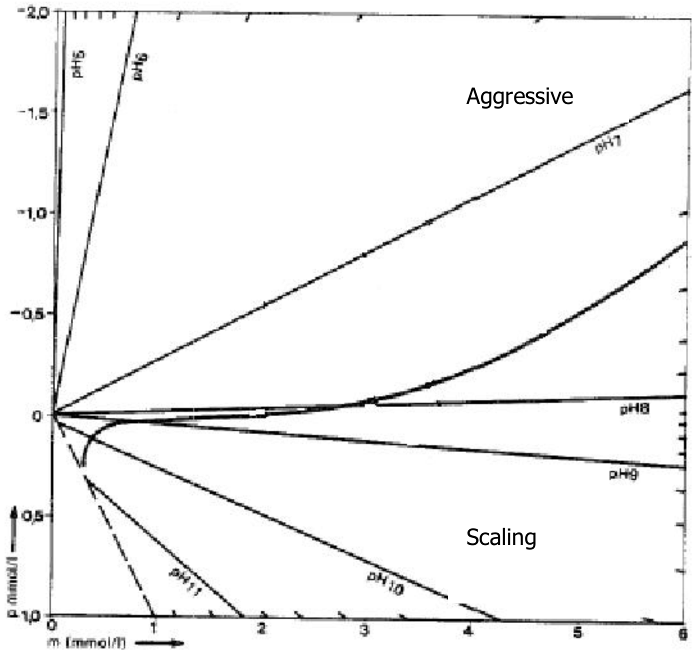


Figure 3.2 Tillmans curve at 10 °C

The disadvantage of the Tillmans curve is that it is presented in p-number and m-number. However, p-number is rather difficult to measure as a certain amount of CO_2 that is present in the water is bound to escape into air directly after sample taking. Calcium and pH can also be used to determine the water type (de Moel) as presented in figure 3.3. Water with a chemical property above the equilibrium curve has a scaling character and thus the property to deposit calcium. Water with a chemical property below the equilibrium curve has an aggressive character and thus the property to dissolve iron and cement bound materials.

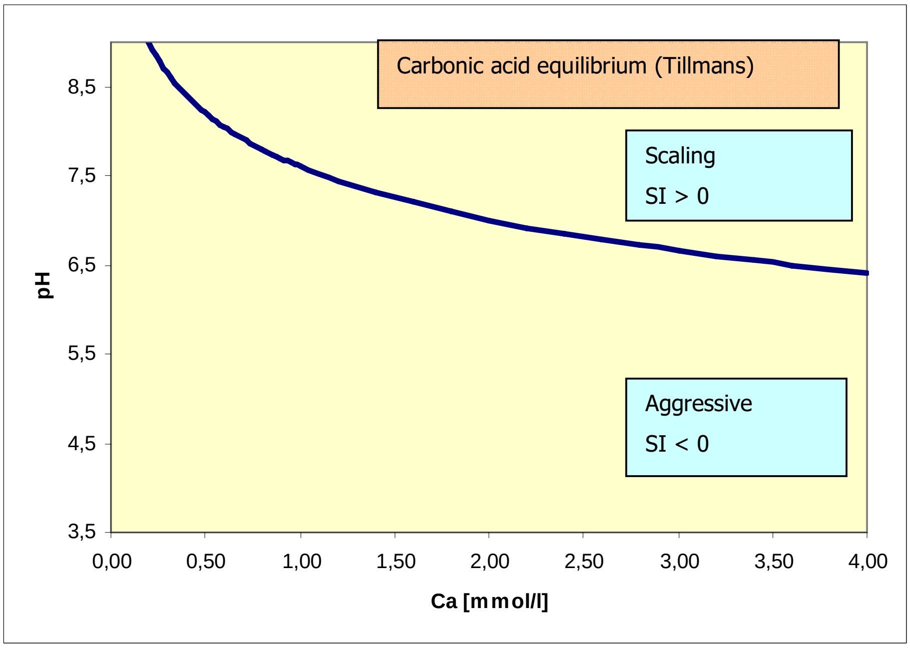


Figure 3.3 Tillmans curve at 25 °C (Source: P. J. de Moel)

In paragraph 3.1 the standards and guidelines for drinking water are given. By using the Tillmans curve and the National Drinking Water standard the area of optimal consumption is determined in figure 3.4. This is also done for the VEWIN recommendations in figure 3.5.

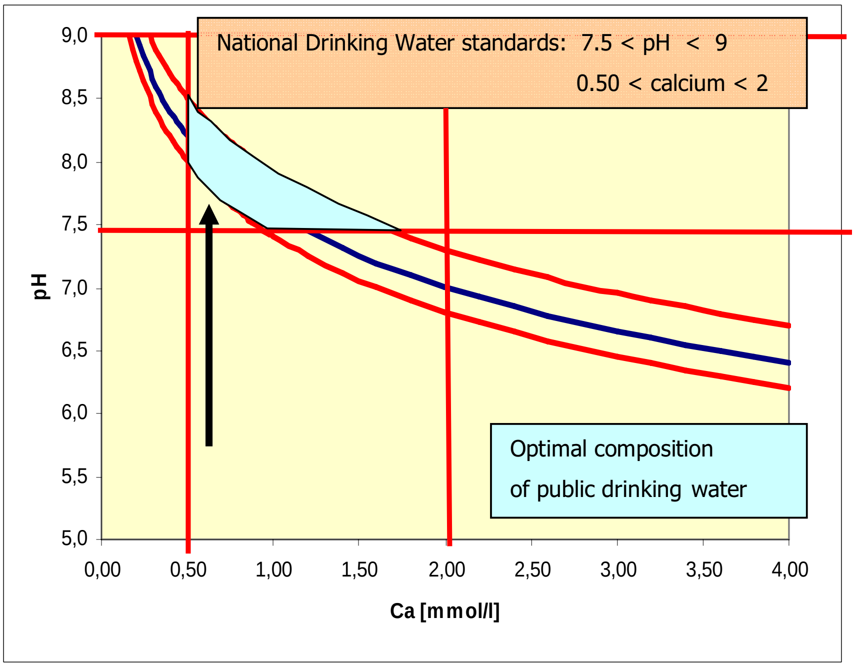


Figure 3.4 Optimal water quality for public drinking water according to the National Drinking Water standards (Source: P. J. de Moel)

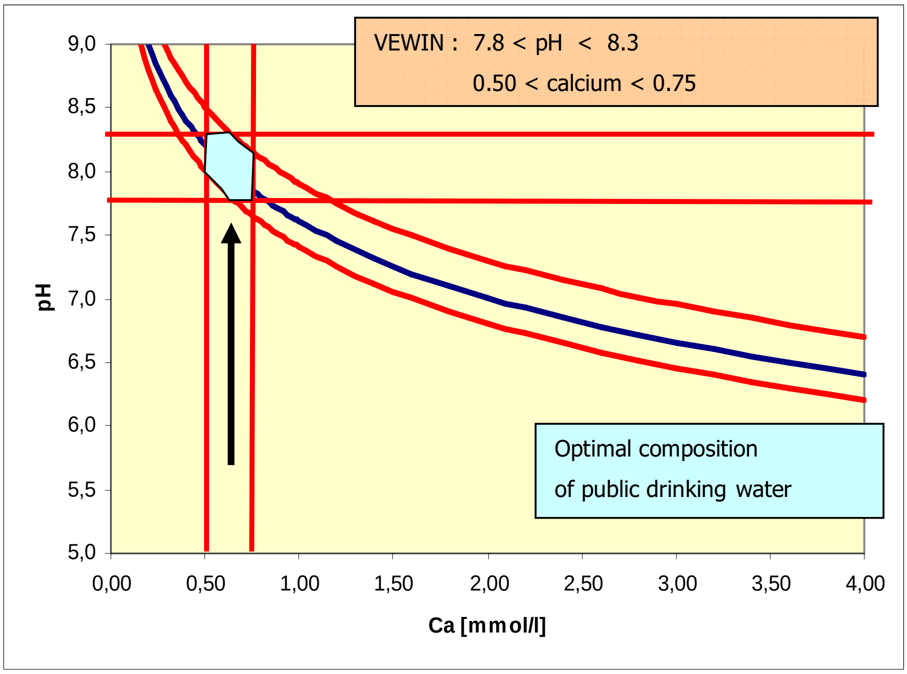


Figure 3.5 Optimal water quality for public drinking water according to the VEWIN recommendations (Source: P. J. de Moel)

From the figures 3.4 and 3.5 it is clear that the area for optimal composition of drinking water is larger when the National Drinking Water standards are applied. The National Drinking Water standards include the VEWIN recommendations.

Tillmans found that the contact time necessary to reach equilibrium:

- Increased with an increasing CO_2 content of the water
- Decreased with decreasing diameter of crushed limestone
- Was not influenced by the filtration rate
- Decreased when the temperature of the water was increased

3.4 Conventional treatment methods for the neutralization of soft water

Depending on the pH and calcium concentration the following processes can be applied as shown in figure 3.4:

- Processes for the increase of the pH
- Processes for the increase of the hardness

The primary effect of these processes is removing the total amount of CO_2. After removal of the total CO_2, the soft water types can still have corrosive properties. This is caused by the low buffering capacity and the low m-number. For the practice it is therefore important that with conditioning also the hardness and the m- number are increased. The processes which are applied with as goal removal of the total amount of CO_2 are:

1. Aeration (removal of CO_2)
2. Dosing of alkaline reagents
    - $Na(OH)$
    - $Ca(OH)_2$
    - Na_2CO_3
3. Filtration through alkaline media
    - $CaCO_3.MgO$ (dolomite)
    - $CaCO_3$ (shells, crushed limestone)

With many aggressive water types the equilibrium is already reached at points where the hardness and the m-number have not reached the desired values yet. In order to reach the desired pH and at the same time the desired hardness and m- number, the following processes are also applied in combination with the earlier mentioned treatment processes:

4. Dosing of bicarbonates
    - $NaHCO_3$ of $Ca(HCO_3)_2$
    - $CO_2 + NaOH$
    - $CO_2 + Ca_2(OH)_2$

Aeration

With aeration water is brought in contact with air. As a result the concentrations of dissolved gases in the water are removed. With aeration of groundwater it concerns raising the oxygen concentration en removing the concentrations of carbonic acid, methane, hydrogen sulphide en other volatile organic compounds. The existing methods for aeration are e.g. sprinkler, cascade- or waterfall aeration, bubble aeration, compressor aeration and tower aeration.

Dosing of alkaline reagents

Alkaline reagents are well soluble solid substance and is therefore dosed as a solution.

Filtration through alkaline media

$CaCO_3.MgO$ en $CaCO_3$ are relatively bad soluble solid substances and are therefore run through by the aggressive water in order to achieve sufficient contact time (limestone or shell filtration).

Limestone filtration

With limestone filtration the aggressive water flows through the bed of limestone grains. The filters are operated the same way as with rapid filters. The height of the supernatant water can be kept constant by the valve in the filter exit or can be raised as a function of the resistance in the filter bed. The last one has the advantage for the management that it is directly visible when the bed needs to be backwashed. During the flow of the aggressive water through the filter the grains get smaller with as a result that the height of the bed reduces. The bed must be refilled regularly. Generally the filter is refilled if 10% of the filter bed height has dissolved. Refilling is done with a hydraulic system by means of which the limestone is transported from the storage silo to the filter. This takes an average time of an hour. The backwashing of the filters varies from once a day in case of high concentrations of iron to once a month in case of low concentrations of iron and dissolved substances in the water.

Applied process

Depending on the property of the water the above mentioned processes can be applied to reach the optimal water quality as shown in figure 3.6.

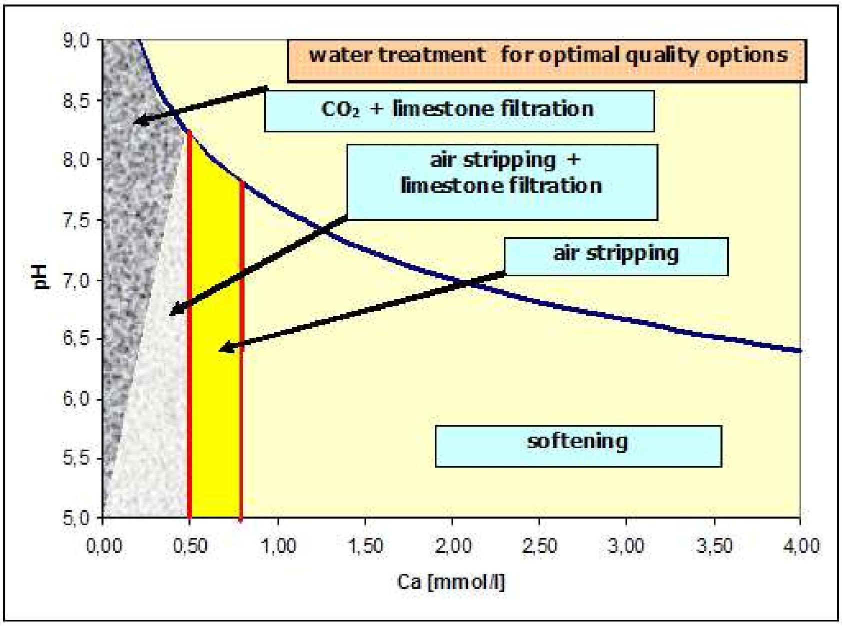


Figure 3.6 Tillmans curve, treatment processes for optimal water quality (Source: P. J. de Moel)

3.5 Kinetics of limestone filtration

It would seem logical to describe the kinetics of conditioning by the amount of aggressive CO_2. It can be assumed that the conditioning reaction follows the first order law:

$$c = c_0 * e^{-kt} \tag{3.12}$$

In which:

c = the concentration of aggressive CO_2 at time t
c_0 = the concentration of aggressive CO_2 at time 0
k = reaction constant

In order to test the assumption, the supplier of crushed limestone, Aqua-Techniek carried out experiments with crushed limestone as presented in table 3.1. Anderlohr also carried out experiments with crushed limestone and at varying filtration rates as presented in table 3.2.

Table 3.1 Data experiments by Aqua-Techniek

Raw water quality				
Parameter	Unity	Water type 1	Water type 2	Water type 3
Calcium	mmol/l	0.20	0.31	0.51
m-number	mmol/l	0.15	0.34	0.70
p-number	mmol/l	(-0.45) – (-0.80)	(-0.34) – (-0.68)	(-0.22) – (-0.62)
pH	--	5.7 – 5.9	6.1 – 6.4	6.5 - 6.9

SI	--	(-4.0) – (-4.2)	(-3.0) – (-3.3)	(-2.0) – (-2.4)
Temperature	°C	10	10	10
Product water quality				
Parameter	Unity	Water type 1	Water type 2	Water type 3
Calcium	mmol/l	0.66 – 0.94	0.65 – 0.93	0.74 – 1.03
m-number	mmol/l	1.08 – 1.64	0.98 – 1.57	1.15 – 1.72
p-number	mmol/l	(-0.01) – (-0.04)	(-0.01) – (-0.05)	(-0.01) – (-0.05)
pH	--	8.0 – 8.3	7.9 – 8.2	7.6 – 8.1
SI	--	(-0.25) – (-0.30)	(-0.3) – (-0.4)	(-0.3) – (-0.4)
Temperature	°C	10	10	10
Contact time				
Apparent contact time: 5.8 – 55.5 minutes				
Crushed limestone				
Commercial grade Jura Perle, grain size “000”(1.2 – 1.8 mm)				

Table 3.2 Data experiments by Anderlohr

Experiment number	CO_2 concentration [mmol/l]	Filtration rate [m/h]
1	0.01	10
2	0.25	10
3	0.50	10
4	1.18	5
5	1.18	10
6	1.18	15
7	1.68	10
8	1.88	5
9	1.88	10
10	2.26	5
11	2.26	10
12	2.26	10
13	2.26	15
14	3.25	5
15	3.25	5
16	3.25	10
17	3.25	15
18	3.50	10
19	4.95	5
20	4.95	10
21	4.95	15
22	4.95	15
23	5.90	10
24	1.50 With additional 3.5 mmol/l $NaHCO_3$	5
Crushed limestone (supplier: E. Schwenk/Herrlingen)		
Grain diameter 0.90 – 1.00		

For the results reference is made to van Dijk et al. [8,9] and Anderlohr [15]. Anderlohr found that the reaction constant (k) was 3.6 h^{-1}. From the results it appeared that the removal of CO_2 as function of time followed a straight line on logarithmic scale only during the first minutes. This was probably caused by the fact that the aggressive CO_2 became extremely small after a relatively short contact time of approximately 10 minutes.
For longer contact times van Dijk et al. assumed that the kinetics of conditioning can be described by the amount of CO_3^{2-} formed.

The second part of the conditioning process is assumed to follow the first order law:

$$c = c^{\sim} * (1 - e^{-kt}) \qquad (3.13)$$

In which

c = the concentration of CO_3^{2-} at time t

$c^{\sim}$ = the concentration of CO_3^{2-} at time ~

Van Dijk et al. found that the log(c/$c^{\sim}$) against contact time did not show a very good conformity for results and theory. It was assumed that the reaction does not reach the theoretical solubility product but the value that is measured with the Heyer test. The water composition after the Heyer test is such that the SI is -0.25. Van Dijk et al. checked the log(c/ $c^{\sim}_{\text{Heyer test}}$) against contact time on the log-graph for the Aqua-Techniek and Anderlohr experiments as presented in figure 3.7 and 3.8. Van Dijk et al. found that the reaction constant for the Aqua-Techniek experiments was 2.76 h^{-1}.

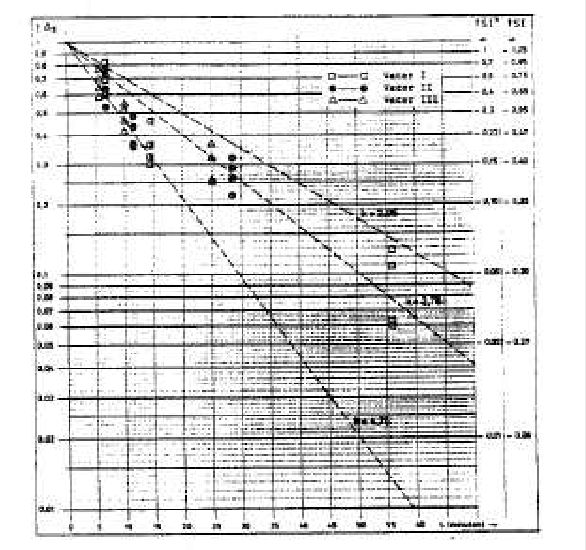


Figure 3.7 Yield CO_3^{2-} as function of contact time, Jura Perle, calculated in relation to Heyer test)

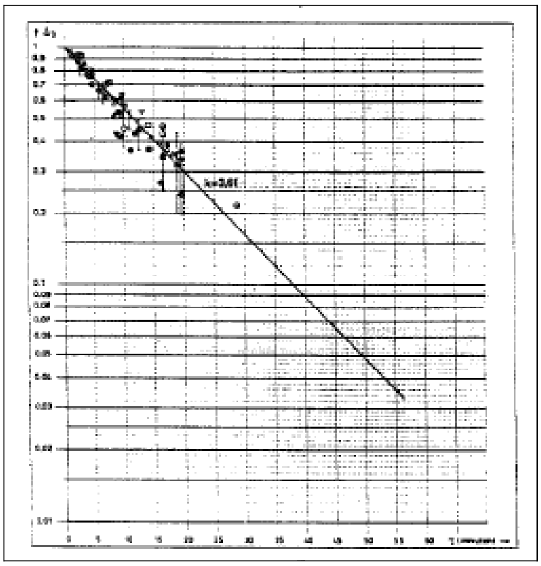


Figure 3.8 Yield CO_3^{2-} as function of contact time, Anderlohr, calculated in relation to Heyer test)

Van Dijk et al. concluded that the removal of CO_2 and the formation of CO_3^{2-} can be used to describe the conditioning process. The removal of CO_2 can be used for short contact times and the formation of CO_3^{2-} for longer contact times. For the influence of temperature and grain diameter on the reaction constant, reference was made to the experiments of Anderlohr [15] who found the following relation:

$$k = (3.80 / d) \exp 0.05(T - 20) \tag{3.14}$$

In which

k = reaction constant
d = grain diameter
T = temperature

Reijnen [12,13,14] investigated the difference between different types of limestone by filtering two different water types through glass filters with a diameter of 0.05 m and filled with 400 ml of crushed limestone. Reijnen also investigated if softening can be used for conditioning. The results of the experiments were such that the reaction constants of the different types of limestone and the softening pellets are comparable. The two water types that were used for the experiments were raw water from the pumping stations Wezep and Leersum. The raw water quality of the two water types is presented in table 3.3. The materials that were used are presented in table 3.4.

Table 3.3 Raw water quality experiments by Reijnen

Parameter	Unity	Raw water Wezep	Raw water Leersum
pH	--	6.1	6.9 - 7.1
Bicarbonate	mgl	27	32 – 35
Calcium	mg/l	11	15
CO_2	mg/l	44 (calculated)	6 – 9 (calculated)

Table 3.4 Materials experiments by Reijnen

Material	Diameter [mm]	Origin	Supplier
Juraperle 000	1.2 – 1.8	Valley of river Bau Ulm, South-Germany	Aqua-Techniek
Juraperle 0000	0.7 – 1.2	Valley of river Blau Ulm, South-Germany	Aqua-Techniek
Juraweiss 000	1.2 – 1.8	Ulmer Weisskalkwerke	Dutch Benzol company
Sauerland Kristall	1 - 2	Brilon Sauerländische Kalkindustrie	Akdolit-Werk/Wessem
Hydrokarbonat	1.2 – 1.8	NA	Akdolit-Werk
Softening pellets	1.0 – 1.7	Pumping station Weesperkarspel	Pumping station weesperkarspel

For all experiments the Juraperle 000 were used as comparing material. The following conclusions were drawn:

- The applied experimental set up can be used as a quick method to show the differences in reaction rate between two types of limestone
- The reaction rate of the softening pellets and Sauerland Kristall is equal to the reaction rate of Juraperle 000
- Hydrokarbonat and Juraweiss have a higher reaction rate than Juraperle 000, which can expectantly be explained by the difference in the distribution of the grain diameters
- The samples of Hydrokarbonat and Juraweiss have, according to the sieve analysis, a high content of material that is smaller than the given minimum grain diameter of 0.5 mm and do not satisfy the specifications of the supplier

4 Materials and Methods

Based on the water quality data of the pumping stations Republiek, Flora and van Hattemweg, research was done into the effects of shell filtration on the water quality with respect to pH, calcium concentration, m-number and conductivity. The research existed of jar tests and column experiments.

The goal of the experiments is to determine the behavior of the parameters that are characteristic for the conditioning process during filtration with different materials: whole shells, crushed shells, crushed limestone and softening pellets.

The goal of the jar tests was to determine which filter materials will be used for the column experiments. The goal of the column experiments is to study the behavior of the filter media in columns.

4.1 Jar tests

The jar tests were done to determine which materials were going to be used with the column experiments. But first the standard stirring speed and material weight had to be determined for all jar tests. Therefore the first set of jar tests were done with shells and at the following stirring speeds 75, 100, 140, 170 and 180 rpm. The second set of jar tests were done with the following material weights: 10, 40, 60, 80 and 100 gram.

The choice for stirring speed and amount of material is based on the time it took to do the calcium and m-number analysis for every beaker. There were 6 beakers. For every beaker a calcium and m-number analysis had to be done directly after stirring. It took 15 minutes to do the calcium and m-number analysis. The choice for stirring speed and material weight had to be such that the increase of the calcium, pH and m-number could be clearly observed. The pH measurements were continuous online measurements. The increase in pH could be seen instantly. The stirring speed and amount of material had to be chosen such that the time between initial and end pH of 8 was 15 minutes or more. After having done this, the stirring speed and material weight that were chosen are 75 rpm and 10 gram. Subsequently the jar tests were continued by the actual jar tests. These tests were done with the following materials:

1. Shells:
    a. Whole shells : Grain size ; 2 – 12 mm
    b. Crushed shells : Grain size ; 1 – 6 mm
2. Crushed limestone:
    a. Grain size : 1.0 – 1.8 mm
    b. Grain size : 1.8 – 2.5 mm
    c. Grain size : 2.5 – 4.0 mm
3. Softening pellets of the following pumping stations:
    a. Waternet ; 1.0 - 1.7 mm
    b. Oasen ; 1.0 – 1.7 mm
    c. DZH ; 1.0 – 1.7 mm

The technical data of these materials are presented in table 4.2. Detailed information concerning the composition of the filter media can be found in appendix II.

Table 4.1 Technical data of filter materials used for experiments

Material	Diameter [mm]	Density [kg/m^3]	Mass percentage $CaCO_3$ [%]
Whole shells	2.0 – 12.0	2751	98.0
Crushed shells	0.5 – 3.0	2727	98.0
Crushed limestone (small)	1.0 – 1.8	2700	99.1
Crushed limestone (medium)	1.8 – 2.5	2700	99.1
Crushed limestone (large)	2.5 – 4.0	2700	99.1
Softening pellets	1.0 – 1.7	2685	97.8

Next to the different materials, the column experiments were done with two different water types called water type 1 and water type 2. The jar tests were done with water type 1. The main purpose of working with these two water types was to simulate the raw water of the pumping stations mentioned in chapter 2. Looking closely at the raw water quality of the pumping stations mentioned in chapter 2 one can see that some of the raw waters have little to no bicarbonate in the water. Other raw waters have a slight to reasonable amount of bicarbonate. The purpose of making two types of water for the experiment was to simulate these two kinds of water.

The water types that were used for the jar tests were demineralised water with hydrochloric acid (water type 1) and demineralised water with hydrochloric acid and sodium carbonate (water type 2). The concentration of the hydrochloric acid solution is 1M. The molar weight of the sodium carbonate is 105.99 g/mol. The water quality of the water types is presented in table 4.2.

Table 4.2 Water quality of the water types

Water type	Composition [per litre]	pH [-]	p-number [mmol/l]	Calcium [mmol/l]	m-number [mmol/l]	Conductivity [µS/cm]	SI [-]
1	- Demineralised water - 0.15 mmol 1M HCl-solution	3.8	-0.15	0	-0.15	9	- 5.7
2	- Demineralised water - 6.65 mmol 1M HCl-solution - 4 mmol Na_2CO_3 (105.99 g/mol)	6.1	-2.65	0	1.35	485	- 1.1

Experimental procedure

The jar tests consisted of a beaker apparatus with a capacity of 6 beakers of 1.8 litres (fig. 4.1 and 4.2). For the first set of jar tests all beakers were filled with 1 litre of demineralised water. Subsequently 0.16 ml of the 1M HCl- solution was added to the demineralised water. The 10 g of whole shells is added to the water. The test was repeated for crushed shells, softening pellets and for every grain size of the softening pellets. For the second set of jar tests all beakers were filled with demineralised water. Subsequently 6.65 ml of the 1M HCl- solution and

0.42 g sodium carbonate (105.99 g/mol) was added to the demineralised water. The 10 g of whole shells is added to the water. The test was repeated for crushed shells, crushed limestone and softening pellets.

For every jar test pH, conductivity, m-number and calcium concentration were measured. For a detailed description of the jar tests see appendix III A.

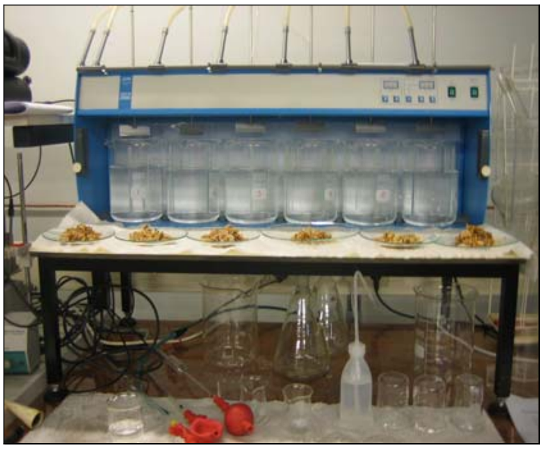


Figure 4.1 Jar test apparatus

Figure 4.2 Jar tests with shells

For an overview of the jar tests in table 4.3 the order is given in which the jar tests were done.

Table 4.3 Overview of jar tests

Order	Material	Water type	Constant parameter	Variable parameter	Measured parameters
1	Whole shells	1	Material weight: 10 g	Stirring speed: 75, 100, 140, 170, 180 rpm	pH
2	Whole shells	1	Stirring speed: 150 rpm	Material weight: 10, 40, 60, 80, 100 gram	pH
3	Whole shells	1	Stirring speed : 75 rpm Material weight: 10 g	Material: shells	- pH - conductivity - calcium - m-number - temperature
4	Crushed shells	1	Stirring speed : 75 rpm Material weight: 10 g	Material: crushed shells	
5	Crushed limestone	1	Stirring speed : 75 rpm Material weight: 10 g	Material: crushed limestone Grain size: 1.0 – 1.8 mm	
6	Crushed limestone	1	Stirring speed : 75 rpm Material weight: 10 g	Material: crushed limestone Grain size: 1.8 – 2.5 mm	
7	Crushed Limestone 2.5-4.0 mm	1	Stirring speed : 75 rpm Material weight: 10 g	Material: crushed limestone Grain size: 2.5 – 4.0 mm	
8	Softening pellets Waternet	1	Stirring speed : 75 rpm Material weight: 10 g	Material: softening pellets Waternet	
9	Softening pellets Oasen	1	Stirring speed : 75 rpm Material weight: 10 g	Material: softening pellets Oasen	
10	Softening pellets DZH	1	Stirring speed : 75 rpm Material weight: 10 g	Material: softening pellets DZH	

4.2 Column experiments

The experimental set up of the column experiments (fig. 4.3) consisted of a perspex column and two dosing tanks with an HCl-solution and a dosing tank with a Na_2CO_3 solution (fig. 4.4). The column had a diameter of 90 mm. The filter bed consisted of whole shells, crushed shells, crushed limestone and softening pellets and the height varied from 0.90 – 1.00 m. The filtration rate was regulated by a valve downstream of the filter. The flow rate was read from the flow meter. The filter column had 6 sample points. The first set of column experiments was carried out with water type 1, and shells at filtration rates of 3, 5, 7 and 10 m/h. The second set of column experiments was carried out with water type 1 and shells at a filtration rate of 5 m/h. The second set of experiments was followed by the column experiments with water type 2 and shells at a filtration rate of 5 m/h. The following sets of column experiments were carried out similar to the second set of column experiments but then with the other materials. For every sample pH, conductivity, calcium concentration and m-number were measured. In table 4.4 the filter bed heights and the used amount of materials are given for the column experiments. In table 4.5 the order is given in which the column experiments were done

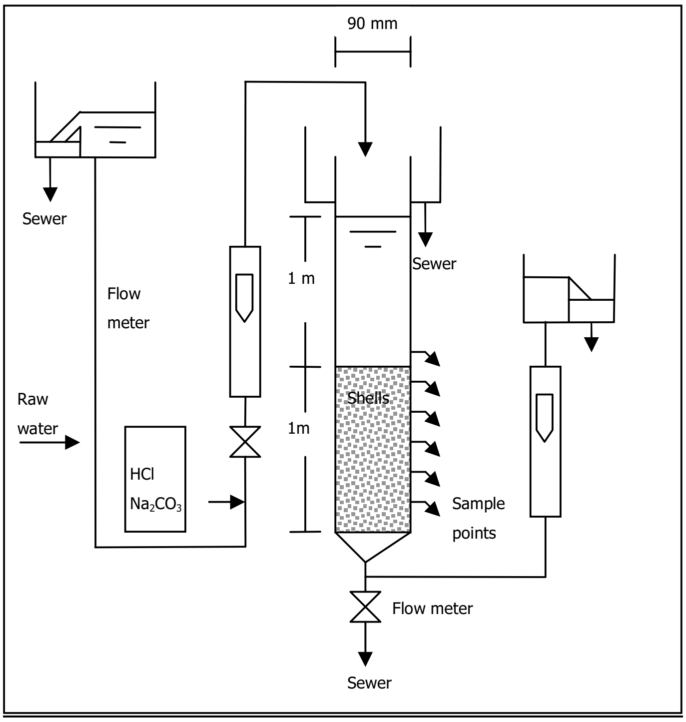


Figure 4.3 Experimental set up of column experiments

Figure 4.4 Dosage tanks with Na_2CO_3 solution (left) and HCl solution (right)

Figure 4.5 Column experiments

Table 4.4 Data materials used for column experiments

Order of experiment	Material	Height filter bed [m]	Volume Filter bed [cm^3]	Weight material [g]	Density material [kg/m^3]	Volume pores [cm^3]	Porosity [%]
1	Whole shells	0.92	5852.79	5480	2751	3860.78	66
2	Crushed limestone (1.8–2.5 mm)	0.97	6170.87	8414.6	2700	3054.36	49.5
3	Softening pellets	0.93	5884.60	10355.4	2685	2027.84	34.5
4	Crushed shells	0.91	5789.17	5091.4	2727	3922.14	67

Table 4.5 Order of column experiments

Order	Material	Water type	Constant parameter	Variable parameter	Measured parameters
1	Whole shells	1	--	Velocity: 3, 5, 7 and 10 m/h	- pH - conductivity - calcium - m-number - temperature
2	Whole shells	2	Velocity: 5 m/h	--	
3	Crushed shells	1	Velocity: 5 m/h	--	
4	Crushed shells	2	Velocity: 5 m/h	--	
5	Crushed limestone 1.8–2.5 mm	1	Velocity: 5 m/h	--	
6	Crushed limestone 1.8-2.5 mm	2	Velocity: 5 m/h	--	
7	Softening pellets Waternet	1	Velocity: 5 m/h	--	
8	Softening pellets Waternet	2	Velocity: 5 m/h	--	

5 Results and Discussion

The experiments for this research consist of jar tests and column experiments. The goal of the jar tests was to determine which filter materials will be used for the column experiments. The goal of the column experiments is to study the behavior of the filter media in columns.

In this chapter the results of the experiments are presented and discussed. The results of the jar tests are given in paragraph 5.1. The results of the column experiments are given in paragraph 5.2. In paragraph 5.3 the general conclusions of the experiments are given.

5.1 Results jar tests

In this paragraph the results of the different jar tests are presented and discussed.

5.1.1 Default parameters

In order to determine the default stirring speed and the amount of material that will be used for every jar test, two jar tests are done of which the first is done at stirring speeds of 75, 100, 140, 170 and 180 rpm and a constant amount of whole shells of 10g. The second jar test is done at a constant stirring speed of and 10, 30, 50, 80 and 100 g of whole shells. Both jar tests were done with shells. The results are presented in figure 5.1 and 5.2.

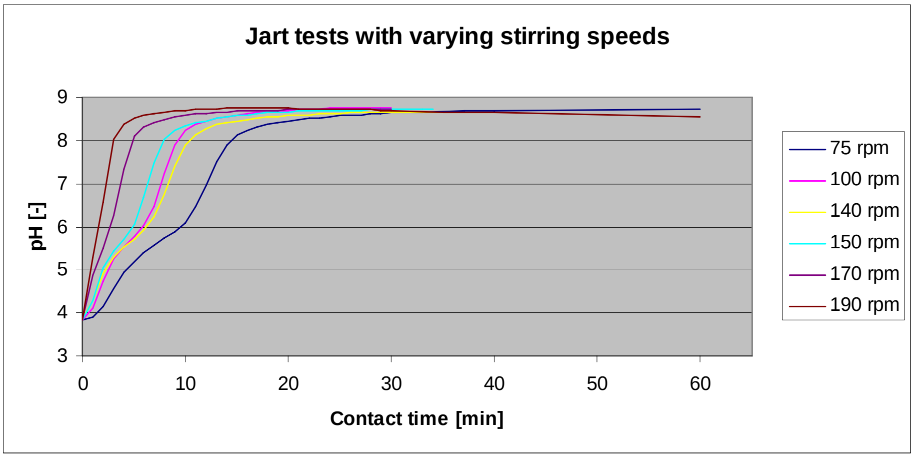


Figure 5.1 Jar tests, pH as function of contact time with varying stirring speeds, water type 1 and 10 g whole shells

The equilibrium-pH for water type 1 is 8.8 (fig. 5.1). It is seen that the pH curve does not show a straight line. This is explained by the buffering process during the conditioning process. The buffering is caused by the bicarbonate ions formed during the conditioning process.

Figure 5.1 shows that the conditioning process depends on the stirring speed. The necessary contact time to reach the equilibrium pH decreases with increasing stirring speed. At a stirring speed of 170 rpm the equilibrium pH is reached after a contact time of 11 minutes. At stirring speeds higher than 170 rpm the contact time increases negligibly.

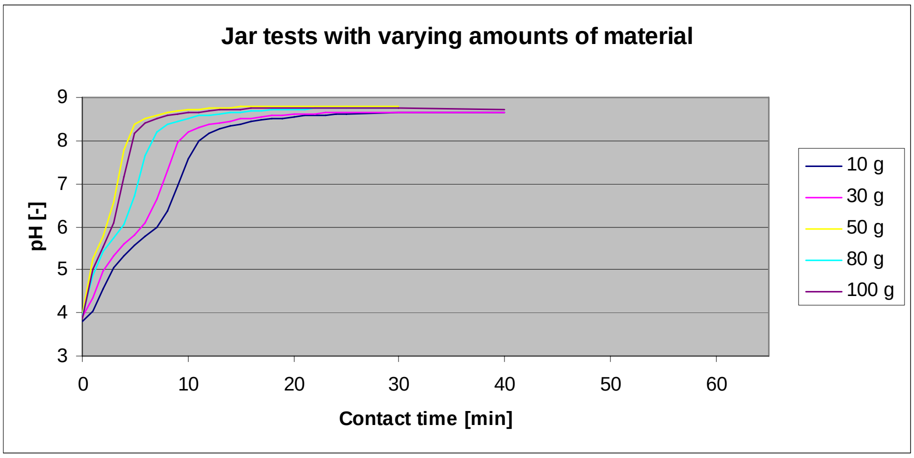


Figure 5.2 Jar tests, pH as function of contact time with varying amounts of material, water type 1 and 150 rpm

Next to the stirring speed the conditioning rate also depends on the amount of shells. The necessary contact time to reach the equilibrium decreases with increasing amount of material. This is explained by the increasing contact surface at increasing amount of material.

The choice for stirring speed and amount of material is based on the time it took to do the calcium and m-number analysis for every beaker. There were 6 beakers. For every beaker a calcium and m-number analysis had to be done directly after stirring. It took 15 minutes to do the calcium and m-number analysis for every beaker. The choice for stirring speed and material weight had to be such that the increase of the calcium, pH and m-number could be clearly observed. For the purpose of the calcium and m-number analysis a default stirring speed and amount of material of 75 rpm and 10 g are chosen.

5.1.2 Variation in materials

In this paragraph the results are presented of the jar tests with a variation in materials.

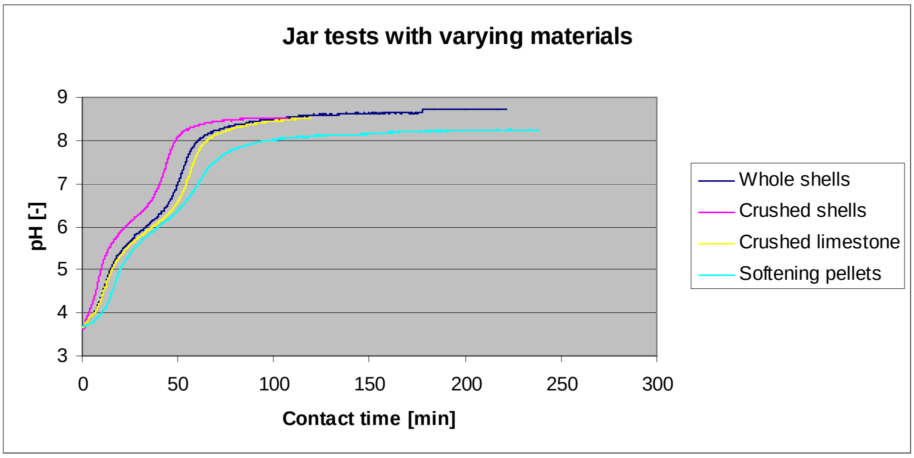


Figure 5.3 Jar tests, pH as function of contact time with varying materials, water type 1, 10g material and 75 rpm

Figure 5.3 shows that the crushed shells, whole shells and crushed limestone reach an equilibrium of 8.7, whereas the softening pellets reach a lower equilibrium of 8.3. In theory a water type with a high pH (e.g. a pH of 6) reaches a lower equilibrium-pH than a water type with a low pH (e.g. a pH of 5). Since the measuring environment regarding stirring speed, amount of material and temperature were kept constant for all materials, explanation for the lower equilibrium that is reached by the softening pellets lies in an error in the dosing of the hydrochloric acid solution to the demineralised water.

In figure 5.3 to 5.6 it is seen that the crushed shells give the shortest contact time of 70 minutes and thus the best result with regard to conditioning of the water. The difference in contact time for the different materials is mainly caused by the difference in grain diameter. The contact time decreases with decreasing grain diameter.

In figure 5.4 and 5.5 it is seen that the in crease of calcium concentration and m-number is higher for crushed shells than the other materials. The explanation is found in figure 5.6 which shows that the initial conductivity of the test with crushed shells is higher than for the tests with the other materials. This means that the initial hydrochloric acid concentration of the test with crushed shells is higher than for the tests with the other materials. As a result more hydrochloric acid is consumed and more calcium and bicarbonate are formed, which also explains the shorter contact time for the crushed shells. The higher the initial hydrochloric acid concentration, the higher the driving force for the conditioning process and thus the shorter the contact time.

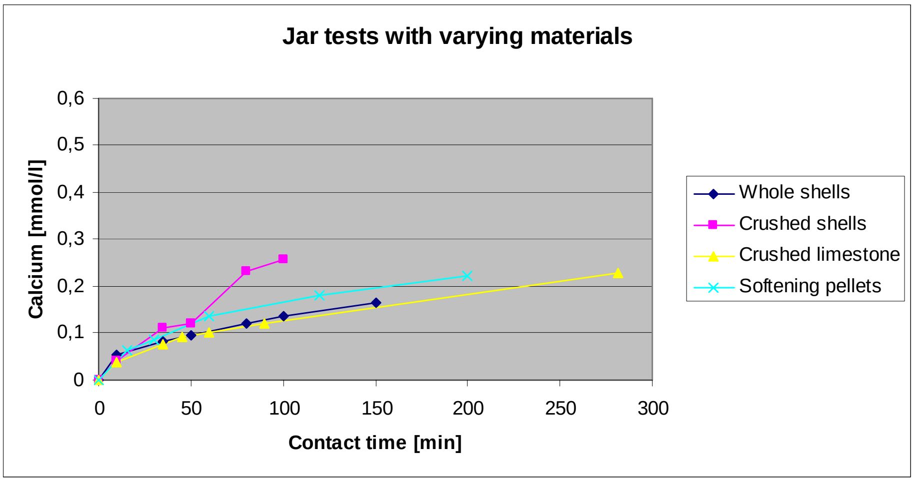


Figure 5.4 Jar tests, calcium as function of contact time with varying materials, water type 1, 10g material and 75 rpm

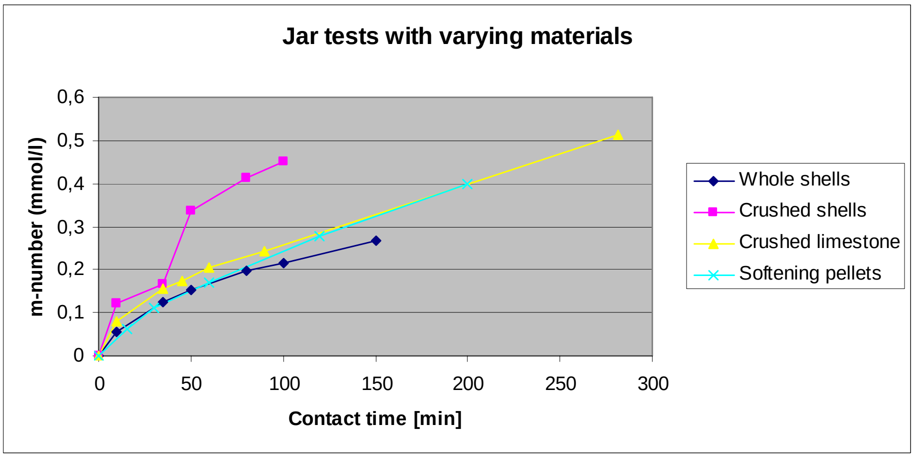


Figure 5.5 Jar tests, m-number as function of contact time with varying materials, water type 1, 10g material and 75 rpm

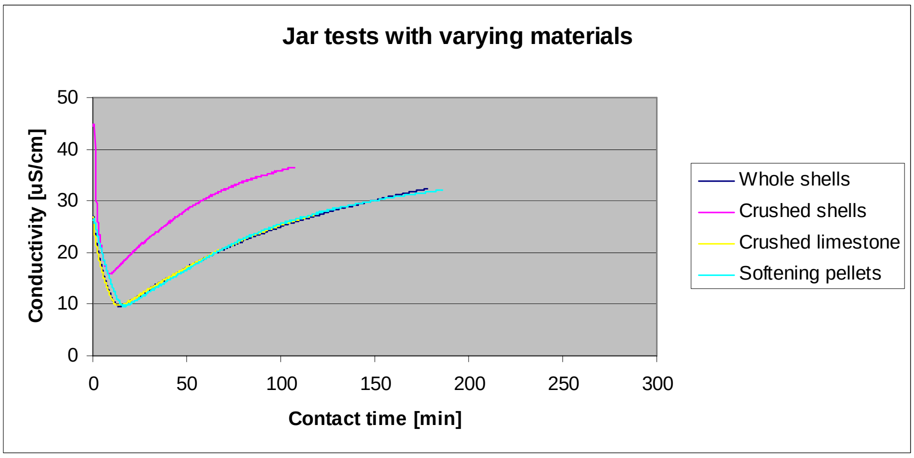


Figure 5.6 Jar tests, conductivity as function of contact time with varying materials, water type 1, 10g material and 75 rpm

In the figures 5.4 and 5.5 it can be seen that the calcium concentration and the m-number do not reach equilibrium. In theory the reaction reaches equilibrium according to equation 3.6. At a certain point nearly all acid has been consumed, as a result of which the reaction is ended. Because of the fact that the beakers were not closed during the tests, the water was in contact with the open air in which approximately 1 mg/l CO_2 is present. Due to contact with open air, CO was able to enter into the water. As a result the conditioning process was continued according to reaction 3.5. In contrary to the calcium concentration and m-number, the pH reaches equilibrium and stays in equilibrium. This is caused by the fact that pH changes are buffered by the bicarbonate that is formed.

The increase of calcium in relation to the increase of m-number is 1:2. This in contrary to equation 3.6 in which the relation is 1:1. Due to the fact that after consumption of the hydrochloric acid, CO_2 enters from open air into the water the conditioning process follows the conditioning reaction according to equation 3.5 in which the relation is 1:2.

The conductivity curves in figure 5.6 show a steep descend during the first 20 minutes. This is explained by the removal of the H_3O^+ ions which in relation to calcium and bicarbonate ions add a larger contribution to the conductivity. After the minimum the H_3O^+ - concentration is negligibly small and the Ca^{2+}, HCO_3^- and CO_3^{2-} - ions add the largest contribution to the conductivity.

5.1.3 Variation in softening pellets

In this paragraph the results of the jar tests with softening pellets from the drinking water companies Waternet, Oasen and DZH are presented. The experiments were carried out with 10 gram material and a stirring speed of 75 rpm.

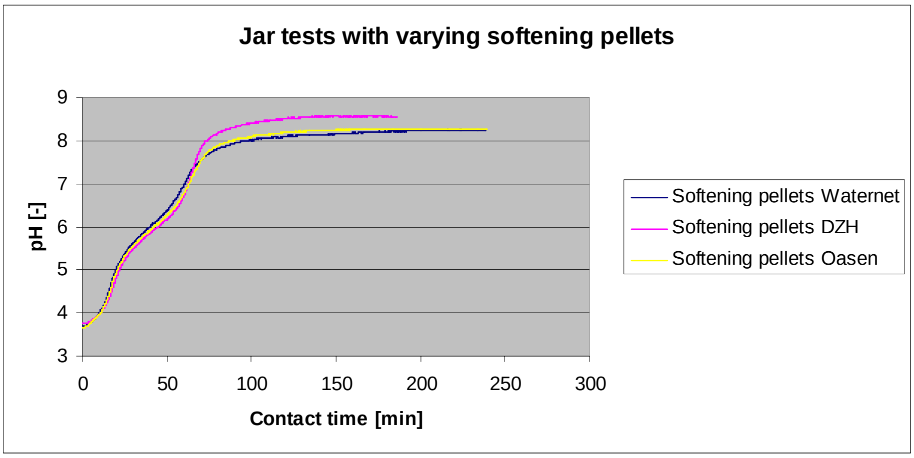


Figure 5.7 Jar tests, pH as function of contact time with varying softening pellets, water type 1, 10g material and 75 rpm

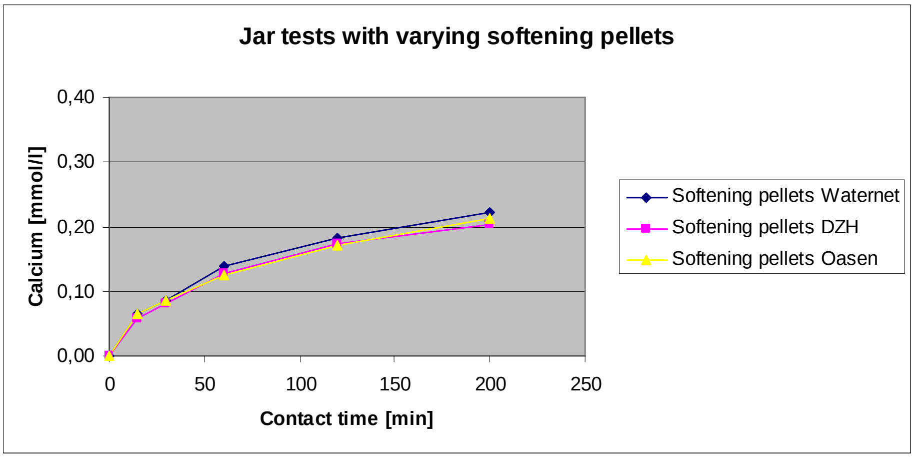


Figure 5.8 Jar tests, calcium as function of contact time with varying softening pellets, water type 1, 10g material and 75 rpm

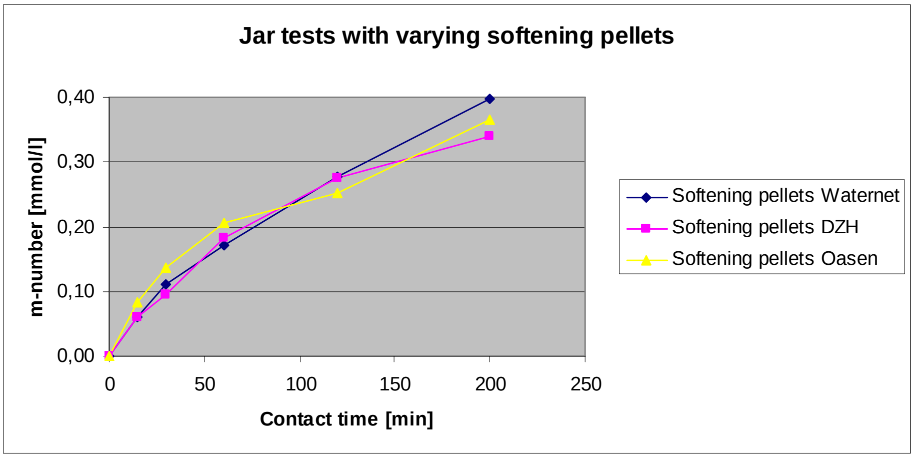


Figure 5.9 Jar tests, m-number as function of contact time with varying softening pellets, water type 1, 10g material and 75 rpm

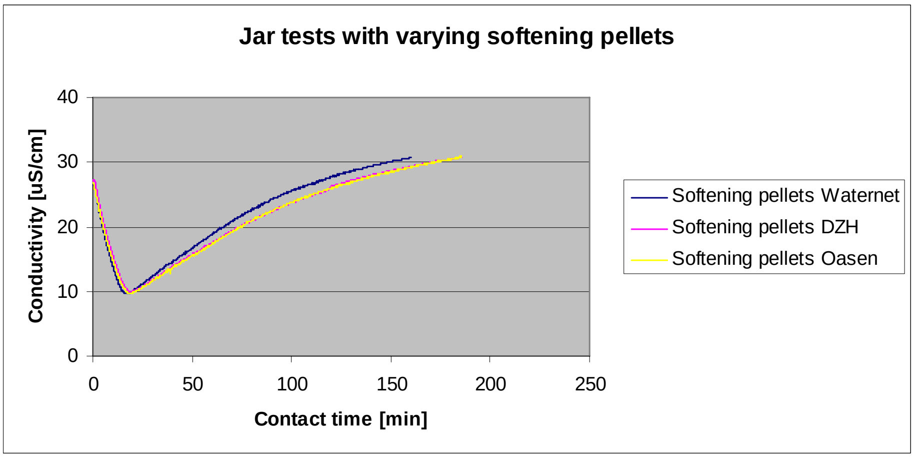


Figure 5.10 Jar tests, conductivity as function of contact time with varying softening pellets, water type 1, 10g material and 75 rpm

From the figures 5.7 to 5.10 it is seen that the contact time is nearly equal for all softening pellets. It was decided that the Waternet softening pellets were used for the column experiments as they were easily available.

5.1.4 Variation in grain sizes

In this sub paragraph the results of the jar tests with varying grain sizes of crushed limestone are presented. The tests are done with 3 different grain sizes: small (1.0 – 1.8 mm), medium (1.8 – 2.5 mm) and large (2.5 – 4.0 mm). It was decided to choose the crushed limestone for these tests and not softening pellets mainly because the difference in grain diameters of the different softening pellets were not significantly large.

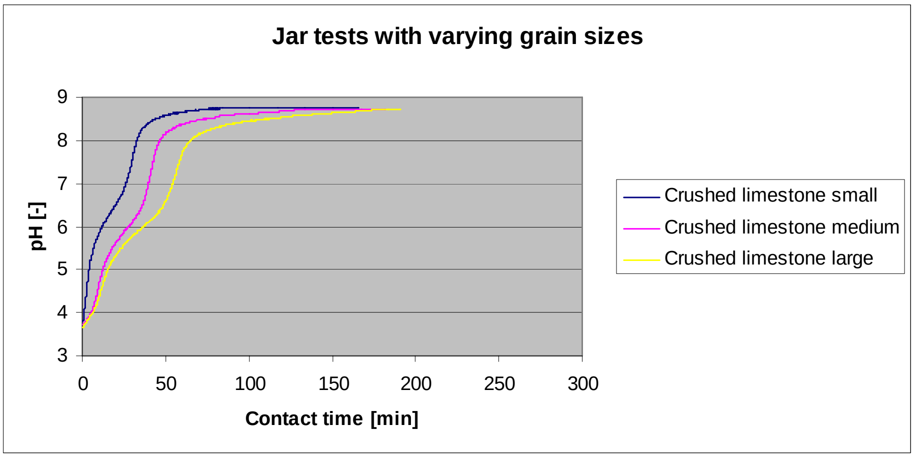


Figure 5.11 Jar tests, pH as function of contact time with varying grain sizes, water type 1, 10g crushed limestone and 75 rpm

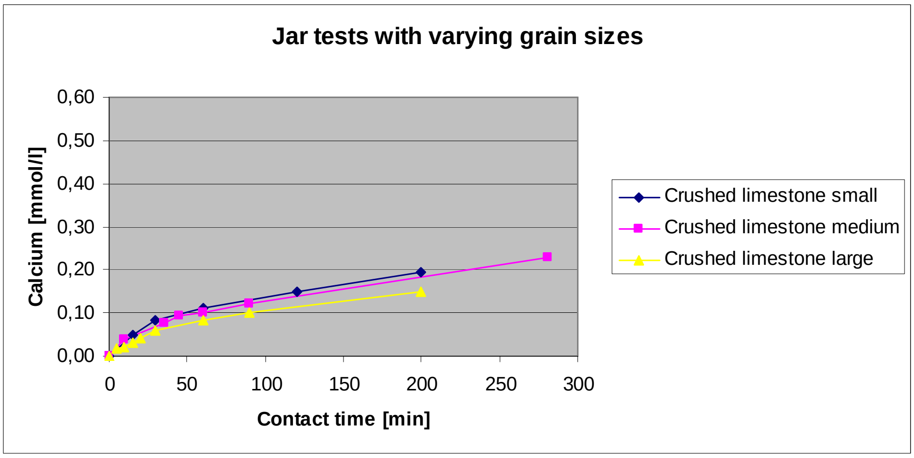


Figure 5.12 Jar tests, calcium as function of contact time with varying grain sizes, water type 1, 10 g crushed limestone and 75 rpm

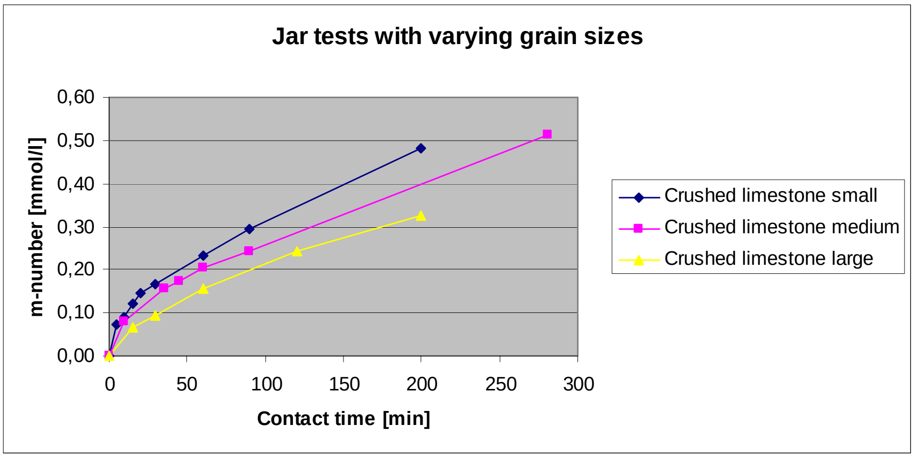


Figure 5.13 Jar tests, m-number as function of contact time with varying grain sizes, water type 1, 10g crushed limestone and 75 rpm

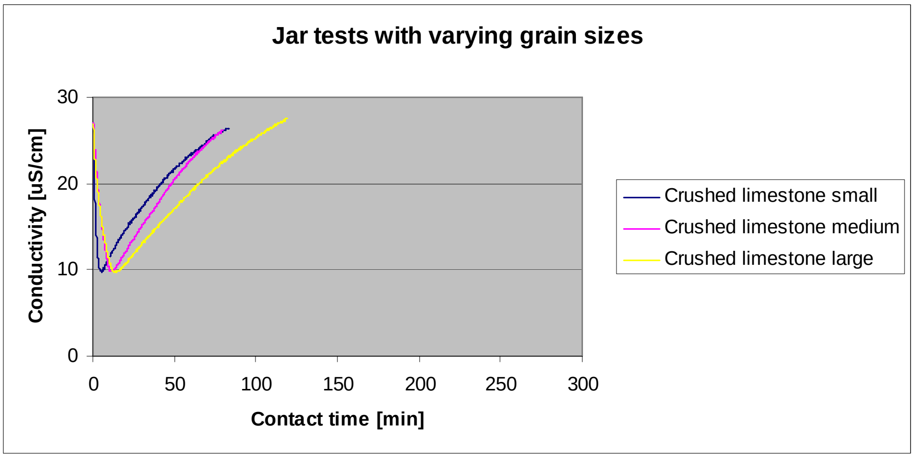


Figure 5.14 Jar tests, conductivity as function of contact time with varying grain sizes, water type 1, 10g crushed limestone and 75 rpm

In figure 5.11 to 5.14 it can be seen that the conditioning rate depends on the grain size. The conditioning rate increases with decreasing diameter. This is in accordance to what was found by Tillmans [14] i.e. the necessary contact time to reach equilibrium decreased with decreasing diameter of crushed limestone.

It was decided that the crushed limestone with grain diameter 1.8 – 2.5 mm were used for the column experiments as they were easily available.

5.2 Column experiments

In this paragraph the result of the column experiments are presented and discussed.

5.2.1 Variation in materials

In this part the results are given of the column experiments with varying materials. The results are given as function of EBCT (empty bed contact time):

$$EBCT = H / v \tag{5.1}$$

In which:

EBCT	= Empty Bed Contact Time	[min]
H	= Height filter bed	[m]
v	= Filtration rate	[m/min]

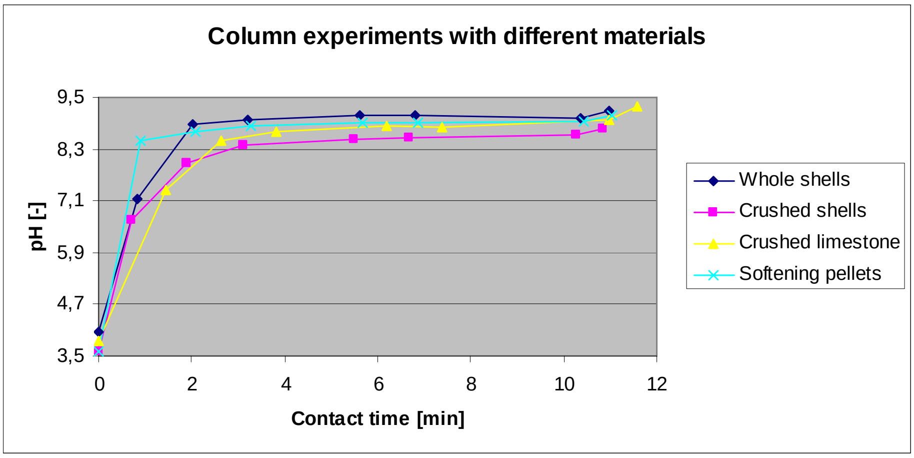


Figure 5.15 Column experiments, pH as function of contact time with varying materials and filtration of 5 m/h

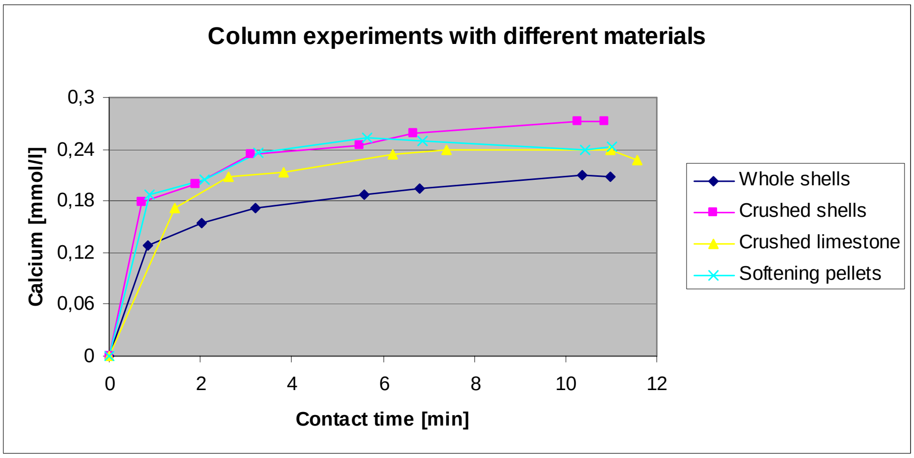


Figure 5.16 Column experiments, calcium as function of contact time with varying materials and filtration rate of 5 m/h

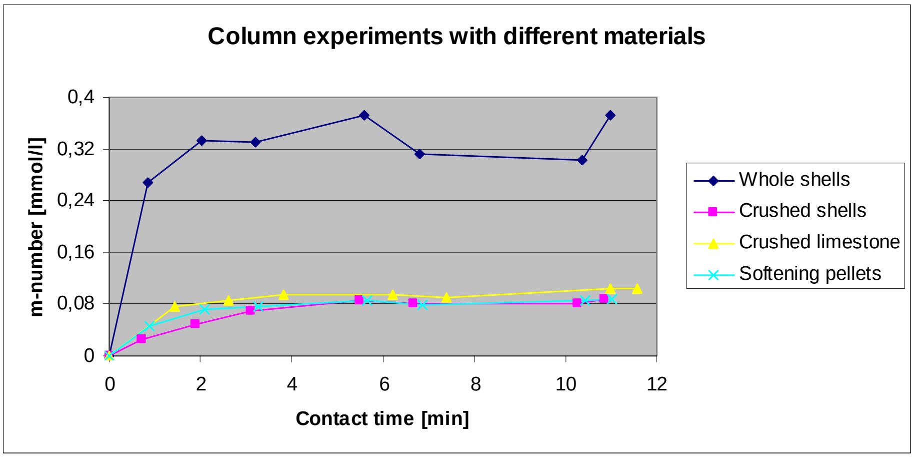


Figure 5.17 Column experiments, m-number as function of contact time with varying materials and filtration rate of 5 m/h

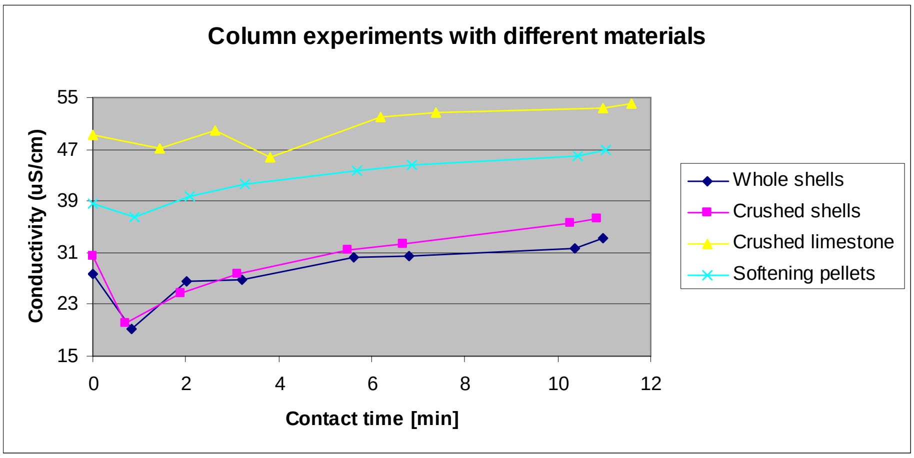


Figure 5.18 Column experiments, conductivity as function of contact time with varying materials and filtration rate of 5 m/h

From figure 5.15 it is seen that the necessary contact time to reach equilibrium is 7 minutes. This is in accordance with experiments by Anderlohr for which the contact time varied from 5.8 to 55.5 minutes.

In figure 5.16 and 5.17 strange results are observed. For the crushed shells, crushed limestone and softening pellets the relation between the increase of calcium concentration and m-number is 3:1. The fact that the increase of calcium is higher than the increase of bicarbonate is according to equation 3.6 and 3.5 not possible. The increase of bicarbonate should at least be equal to the increase of calcium. The explanation for these findings can unfortunately not be found. According to equation 3.6 the relation between the increase of calcium and m-number should be 1:1. For the whole shells the relation of calcium: m-number is 1:2. This can be partly explained by the fact that the upper part of the filter column was open and the water was in contact with open air. As a result CO_2 could enter into the water and the conditioning process was continued followed the reaction according to equation 3.5. The relation 1:2 can also partly be explained by the definition of the m-number in which the m-number is the sum of bicarbonate and 2x carbonate ions as a result of which the increase of the m-number is higher than the increase of calcium.

In figure 5.19 the SI is plotted as function of contact time. This is only done for the column experiments with shells, because the outcome of the column experiments with the other materials is not a reliable outcome. The standards and guidelines for SI are -0.2 < SI < 0.3. Figure shows that the water reaches the desirable SI of -0.2.

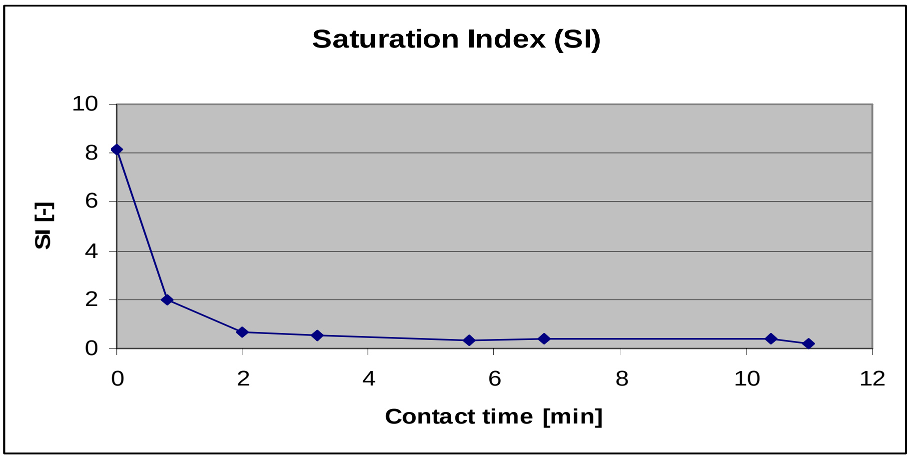


Figure 5.19 SI as function of contact time, results of the column experiments with shells

5.2.2 Variation in filtration rate

In this sub paragraph the results are given of the column experiments at filtration rates of 3, 5, 7 and 10 m/h. The experiments are done with whole shells.

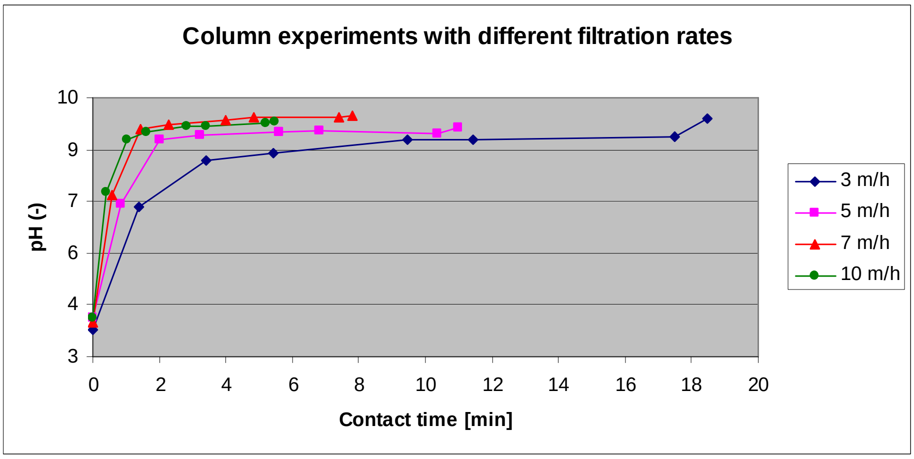


Figure 5.20 Column experiments, pH as function of contact time with varying filtration rates, water type 1 and whole shells

In figure 5.20 it is clear that filtration rate influences the contact time necessary to reach equilibrium. This is contrary to what was found by Tillmans [14]. Tillmans found that filtration rate has no influence on the contact time necessary to reach equilibrium. This is also in contrary to relation 3.14 found by Anderlohr [15] in which the reaction rate is only influenced by grain diameter and temperature. The contact time necessary to reach equilibrium is influenced by the filtration rate due to the fact that the turbulence of the flow increases with increasing filtration rate. Turbulence is determined by the Reynolds number. The Reynolds number is inversely proportional with the kinematic viscosity and porosity of the filter bed and proportional with the filtration rate and grain diameter [24]:

$$\mathrm{Re} = \frac{1}{p_0} \frac{v * d_0}{\upsilon} \tag{5.2}$$

In which:

Re = Reynolds number [-]
P_0 = porosity = 0.66 for shells (table 4.4) [%]
v = filtration rate [m/s]
d_0 = grain diameter [m]
υ = kinematic viscosity = $1.011*10^{-6}$ at 20 °C [m^2/s]

When the Reynolds numbers is smaller than 2000, the flow is laminar. In table 5.1 the Reynolds number is calculated for the different filtration rates. From table 5.1 it is seen that the Reynolds number increases with increasing filtration rate. This can also be seen from the jar tests with varying stirring speeds in figure 5.1. An increasing stirring speed causes more turbulence of the flow with as result that the transfer of substances is accelerated. An acceleration of the transfer of substances results in a shorter contact time.

Table 5.1 Reynolds number for varying filtrations rates with an average diameter of 7 mm

Filtration rate [m/h]	Reynolds number [-]
3	9
5	15
7	20
10	29

If the necessary contact time to reach equilibrium decreases with increasing filtration rate, it would seem logical to choose for filtration through a thin column with a high filtration rate than for filtration through a thick column with a low filtration rate. However, the advantage of a thin column is the high pressure drop.

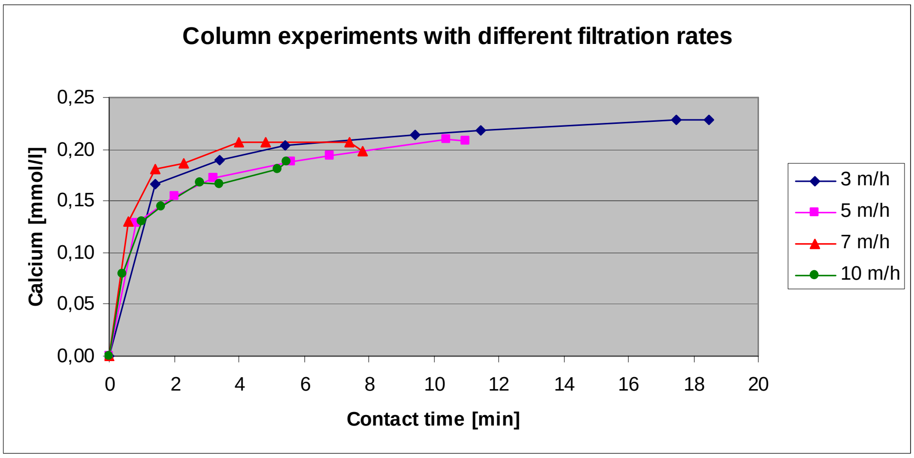


Figure 5.21 Column experiments, calcium as function of contact time with varying filtration rates, water type 1 and whole shells

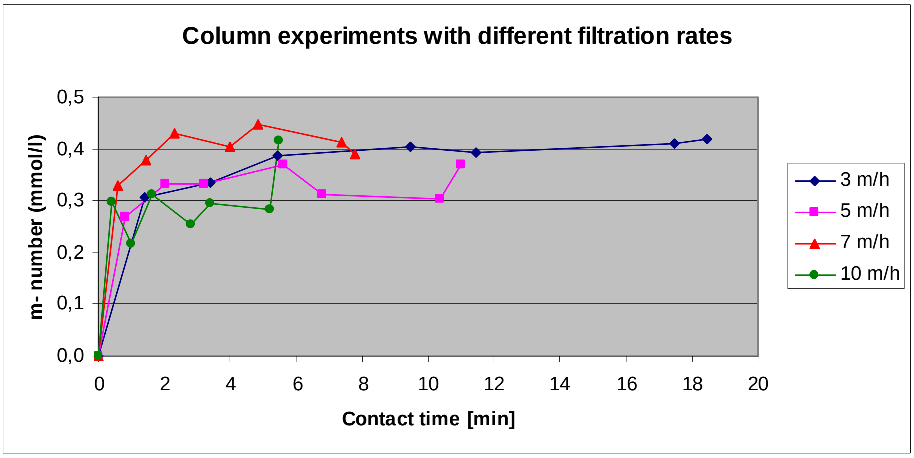


Figure 5.22 Column experiments, m-number as function of contact time with varying filtration rates, water type 1 and whole shells

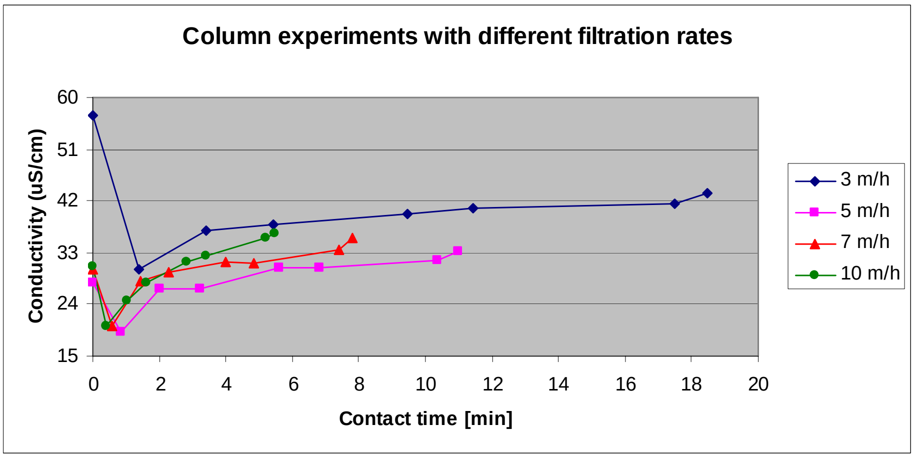


Figure 5.23 Column experiments, conductivity as function of contact time with varying filtration rates, water type 1 and whole shells

It was mentioned that the necessary contact time to reach equilibrium decreases with increasing filtration rate. It would seem logical to choose the highest filtration rate as default parameter for the column experiments. However for the purpose of reliability a filtration rate is chosen of 5 m/h as default for the all column experiments.

5.3 Conclusion experiments

- For the replacement of whole shells for the conditioning of aggressive water, both crushed limestone and softening pellets can be used. This is proven by the jar tests and the column tests with varying materials
- The necessary contact time to reach equilibrium is increased with decreasing diameter. This is proven by the jar tests with varying grain diameters of crushed limestone. This is also in accordance to what is found by Tillmans.
- The conditioning rate is not influenced by the type of softening pellets.
- The necessary contact time to reach equilibrium is influenced by filtration rate. This is proven by the column experiments with varying filtration rates. This is in contrary to what was found by Tillmans and Anderlohr.

6 Mathematical model for conditioning

In order to maintain sufficient conditioning of aggressive water it is important to maintain the desired contact time. The desired contact time is, depending on the filtration rate, related to a certain height of the filter bed. When the filter bed has reached a critical filter bed height the filter bed must be refilled. To determine the refilling frequency, the conditioning rate must be calculated first. This can be done by modelling the conditioning process and by determining the reaction constant k. In order to model the conditioning process from the beginning until the point of equilibrium, a mathematical model can be used for the calculation of pH, calcium concentration, m-number, carbonate concentration and conductivity.

The objective of using the mathematical model is:

1. To calculate the effluent water quality based on the water quality data as given in chapter 2
2. To determine operational parameters with regard to contact time and refilling frequency

To achieve the objectives the reaction rate k should be determined. The determined reaction rates are compared with literature.

In paragraph 6.1 the mathematical model is discussed and the graphs of the modelled parameters are presented. Subsequently the reaction rate is determined by fitting the curve of the measured parameters in the model. This is discussed in paragraph 6.2. The reaction rate is determined by estimating an approximate value from the graph.

6.1 Modelling of measured parameters

During the experiments the following parameters were measured:

- pH
- Calcium
- m-number
- Conductivity

In this chapter these parameters will be modelled by using by using the online modelling programme Stimela and the kinetics of limestone filtration.

Stimela

Stimela is an environment for standardized mathematical models of drinking water treatment processes. Stimela is developed by Delft University of Technology, Kiwa and DHV and is especially designed for water quality modeling.

With the use of Stimela the carbonic acid equilibrium can be calculated. Once a few parameters are known, the remaining parameters can be calculated. For the calculation of the water composition the ionic strength in mmol/l, which is defined as 0.0165 * EGV (μS/cm), the temperature in ^{o}C and at least two of the following parameters need to be known:

- CO_2 concentration [mmol/l]
- Calcium concentration [mmol/l]
- Carbonate concentration [mmol/l]
- pH [-]
- m-number [mmol/l]
- p-number [mmol/l]

pH, calcium and m-number

For the conditioning process the assumption is made that the reduction of the H^+- concentration takes place according to a 1st order reaction, which is as follows:

$$\frac{dc}{dt} = -k(c - c_e) \tag{6.1}$$

Of which the general solution is:

$$\frac{c - c_e}{c_0 - c_e} = e^{-kt} \tag{6.2}$$

In which:

c = actual concentration H^+ (mmol/l)
c_0 = concentration of H^+ at t = 0 (mmol/l)
c_e = equilibrium concentration of H^+ (mmol/l)
k = reaction constant (h^{-1})
t = contact time (h)

The actual H^+ concentration is calculated with the formula for the kinetics of conditioning. The pH, calcium and bicarbonate are calculated according to reaction 3.6. In order to check the assumption that the conditioning process takes place according to a 1st order reaction, the reaction constant is calculated and subsequently compared to the results of the experiments.

In order to simulate the raw water of Suriname HCl was added to demineralised water. The HCl dissolves in the water according to the following reaction:

$$HCl \rightarrow H^+ + Cl^- \tag{6.3}$$

During the conditioning process the H^+ reacts with the $CaCO_3$ according to reaction 3.6:

$$H^+ + CaCO_3 \rightleftarrows Ca^{2+} + HCO_3^-$$

According to the stoichiometry of reaction 3.6 a reaction with 1 mol H^+ gives 1 mol Ca^{2+} en 1 mol HCO_3^- .

The procedure for determination of the effluent water quality and the reaction rate k is as follows:

1. Determine c_0: the H_3O^+- concentration in the water at t=0
2. Select the Online Carbonic acid Equilibrium option on www.stimela.com
3. Fill in pH=7 and m- number=0 in Stimela
4. Fill in the H_3O^+- concentration in the HCl window of the dosing section in Stimela
5. Fill in the equal concentration of $CaCO_3$ in the $CaCO_3$ window of the dosing section in Stimela
6. The equilibrium concentration of CO_2 is equal to c_e
7. Assume a certain reaction rate
8. Take time steps of 0.20 minutes
9. Calculate c_0 - c_e
10. Calculate c - c_e with equation 5.2
11. Calculate c: the actual H_3O^+ concentration
12. The decrease of the H_3O^+ concentration per time step is equal to the increase of HCO_3^- ions
13. Fill in the actual H_3O^+ concentration in the CO_2 window and the actual HCO_3^- and let Stimela calculate the pH, CO_3^{2-} concentration and the m- number.
14. The calcium concentration is the sum of the HCO_3^- and CO_3^{2-} ions
15. The conductivity can be calculated by filling the concentrations of the H_3O^+, HCO_3^- , CO_3^2 and Ca^{2+} ions in equation 5.4 and 5.4

Conductivity

In an ideal situation the increase of unknown parameters such as calcium and m-number can be followed by measuring the conductivity. The main condition is that all other parameters must be known. For this research the substances that are left or formed in the water are known. The conductivity was modelled to see if it is possible to follow the conditioning process by measuring the conductivity. For the purpose of modelling the conductivity, the carbonate ions were also modelled.

At infinite dilution the mutual attraction between the ions becomes zero and the molar conductivity of the electrolyte solution is the sum of the molar conductivities of the ions which the electrolyte consists of. In formula form this can be written as follows:

$$\Lambda_m^\infty = v_+\lambda_+^\infty + v_-\lambda_-^\infty \qquad (6.4)$$

In which:

$\lambda_+^\infty, \lambda_-^\infty$ = limiting molar conductivity of positive and negative ion of the electrolyte at infinite dilution

v_+, v_- = the numbers of cations and anions per formula unit of electrolyte

Table 6.1 gives the molar conductivity for the ions at infinite dilution.

Table 6.1 Limiting ionic conductance in aqueous solutions at 25 °C

Cations	λ_+ (S.cm^2/mol)	Anions	λ_- (S.cm^2/mol)
H_3O^+	350	HCO_3^-	45
Ca^{2+}	60	CO_3^{2-}	72
Na^+	50	Cl^-	76

Source: J.A. Dean, Ed., Lange's Handbook of chemistry, 12th ed., table 6-7, p. 6-34, McGraw-Hill Book Company, New York, 1979)

The molar conductivity Λ_m is defined as follows:

$$\Lambda_m^\infty = \frac{\gamma}{c} \qquad \text{(S.cm}^2\text{/mol)} \qquad (6.6)$$

In which:

γ = conductivity (S/cm)
c = concentration of the ions (mol/l)

Modelling of column experiment with water type 1

The concentration c_0 of the raw water for H^+, calcium and m-number of water type 1 0.16, 0 and 0 mmol/l at t=0 respectively. By using the programme Stimela the equilibrium concentrations are calculated. For a dosing of 0.16 mmol/l HCl and an excess of $CaCO_3$ in demineralised water Stimela gives the equilibrium concentrations as presented in table 6.2.

Table 6.2 Equilibrium concentrations for water type 1 with 0.16 mmol/l HCl

Ca^{2+} (mmol/l)	HCO_3^- (mmol/l)	CO_3^{2-} (mmol/l)	CO_2 (mmol/l)	pH (-)	Ionic strength (mmol/l)	m- number (mmol/l)	p- number (mmol/l)
0.21	0.18	0.02	0.000143435	9.47	0.64	0.25	0.05

For CO_2, Ca^{2+} and HCO_3^- Stimela gives a c_e of respectively 0, 0.21 and 0.18 mmol/l. According to equation 6.4 the equilibrium concentration of HCO_3^- should be 0.16 mmol/l. However the Tillmans-curve shows that this is not the case. Every water type reaches its own equilibrium.

After the equilibrium is reached 0.02 mmol/l CO_3^{2-} is formed. As a result of this the c_e for Ca^{2+} is the sum of $[HCO_3^-]$ and $[CO_3^{2-}]$ namely 0.21 mmol/l.

Input of the known parameters in the 1st order equation gives the conditioning process as function of time as shown in figure 6.1. Thereby the k-value is calculated by using the Anderlohr relation with an average grain diameter of 3.25 mm.

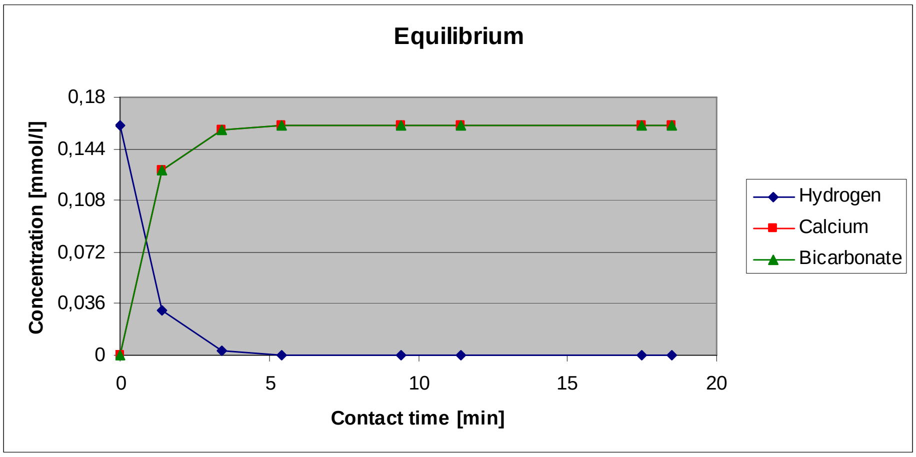


Figure 6.1. Result model, H^+, Ca^{2+} and HCO_3^- - concentrations as function of contact time

In figure 6.1 the c_e for CO_2, Ca^{2+} and HCO_3^- is 0, 0.16 and 0.16 mmol/l. However, Stimela gives for CO_2, Ca^{2+} and m-number a c_e of 0, 0.21 and 0.25 mmol/l. The measuring results show a c_e of approximately 0.21 and 0.41 mmol/l Ca^{2+} and m-number respectively as given in fig. 5.20 and 5.21. The calculated c_e- values and the simulated c_e- values do not correspond with the measured c_e- values.

The explanation for the difference between the HCO_3^- concentration and the m-number is explained by the fact that at a certain pH the CO_2, HCO_3^- en CO_3^{2-} ions are present in a certain proportion. At high pH values the CO_2- concentration is negligibly small and at low pH the CO_3^{2-} concentration is negligibly small.
The m- number is defined as:

$$m - number = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H_3O^+]$$

Thus at high pH (in this case a pH of 9.4) the m-number is different from bicarbonate because at high pH both bicarbonate and carbonate add a contribution to the m-number.

Table 6.1 shows that the concentrations of Ca^{2+} and HCO_3^- are different from what is expected according to the stochiometry. In order to see if this is also the case with other dosages, a few more calculations are made in Stimela with different dosages. The results of these calculations are presented in table 6.2.

Table 6.3 and 6.4 show that solutions with a concentration lower than 0.90 mmol/l HCl and an excess of calcium carbonate reach an equilibrium with calcium and bicarbonate concentrations that are higher than the given HCl dosing. At a HCl dosing higher than 0.90 mmol/l the opposite applies. This is explained by the Tillmans- curve.

Table 6.3 Equilibrium for several water types, calculated with Stimela at 20^{o}C

HCl	mmol/l		0.16		0.16		0.80	
$CaCO_3$	mmol/l		0.16		0.25		0.80	
Calcium	mmol/l		0		0		0	
		Demineralized water	After mixing	Equilibrium after precipitation	After mixing	Equilibrium after precipitation	After mixing	Equilibrium after precipitation
CO_2	mmol/l	7.54042e-6	0.00229755	0.000143437	8.4111e-5	0.000143436	0.00167761	0.00906576
HCO_3^-	mmol/l	3.13e-005	0.16	0.18	0.20	0.18	0.81	0.78
CO_3^{2-}	mmol/l	1.32e-008	0.00113761	0.0244158	0.0508978	0.0244162	0.0437058	0.00763682
m-number	mmol/l	0	0.16	0.25	0.34	0.25	0.9	0.80
p-number	mmol/l	-3.89e-5	3.89e-5	0.05	0.09	0.05	0.05	-4.95e-6
pH	-	7	8.20	9.47	9.74	9.47	9.04	8.30
Calcium	mmol/l	0	0.16	0.21	0.25	0.21	0.85	0.80
SI	-	-	-1.43	0	0.39	0	0.78	0

Table 6.4 Equilibrium for several water types, calculated with Stimela at 20^{o}C

HCl	mmol/l	1.00		2.00		3.00	
$CaCO_3$	mmol/l	1.00		2.00		3.00	
Calcium	mmol/l	0		0		0	
		After mixing	Equilibrium after precipitation	After mixing	Equilibrium after precipitation	After mixing	Equilibrium after precipitation
CO_2	mmol/l	0.0112242	0.0165799	0.0221363	0.0980504	0.0333216	0.249932
HCO_3^-	mmol/l	0.98	0.97	1.96	1.80	2.94	2.50
CO_3^{2-}	mmol/l	0.00974779	0.00644539	0.0206404	0.00394539	0.0318316	0.00305742
m-number	mmol/l	1	0.98	2	1.81	3	2.51
p-number	mmol/l	-3.89e-5	-0.01	-3.89e-5	-0.09	-3.89e-5	-0.25
pH	-	8.30	8.12	8.29	7.61	8.29	7.34
Calcium	mmol/l	1	0.99	2	1.91	3	2.75
SI	-	0.18	0	0.73	0	1.04	0

6.2 Determination of reaction rate

6.2.1 Reaction rate for shells

In this sub paragraph the reaction constant (k) is determined for shells.

The pH, calcium, m-number and conductivity are modelled for different k-values. In order to model the conductivity the concentrations of the CO_3^{2-} ions are required. These are calculated by using stimela. The results of the model are presented in figure 6.2 to 6.4.

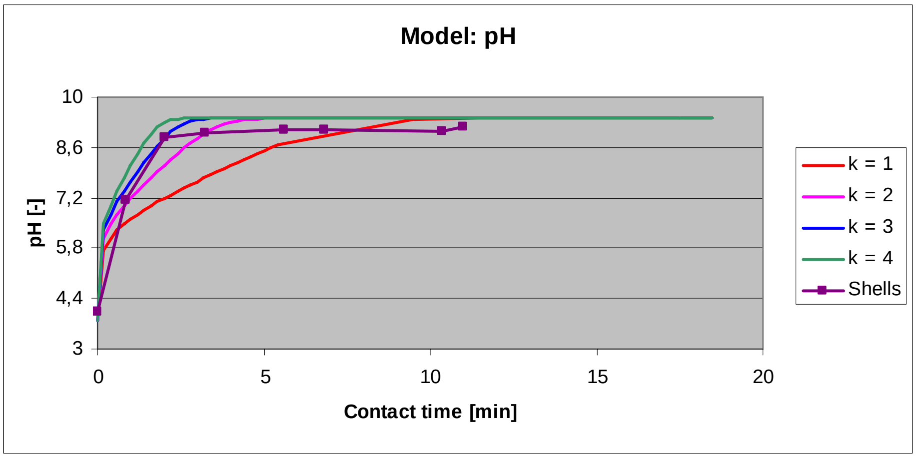


Figure 6.2 Result model, pH as function of contact time

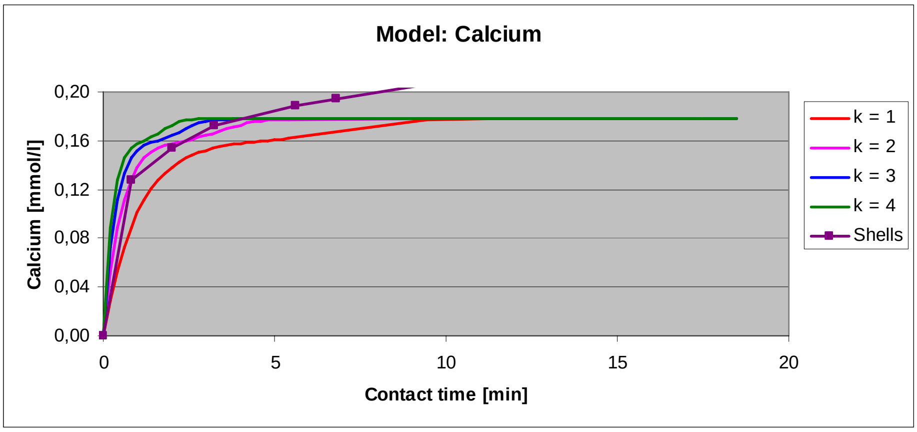


Figure 6.3 Result model, Calcium as function of contact time

The reaction rate is estimated by fitting the measured values of pH and calcium with the modelled values of pH and calcium. The curve of the shells lies between the curve for k=2 and k= 3. As the results of the experiments are fairly inaccurate the k-value is determined by estimating the k-value from the graph. The k-value is estimated at 1.9 h^{-1} for whole shells.

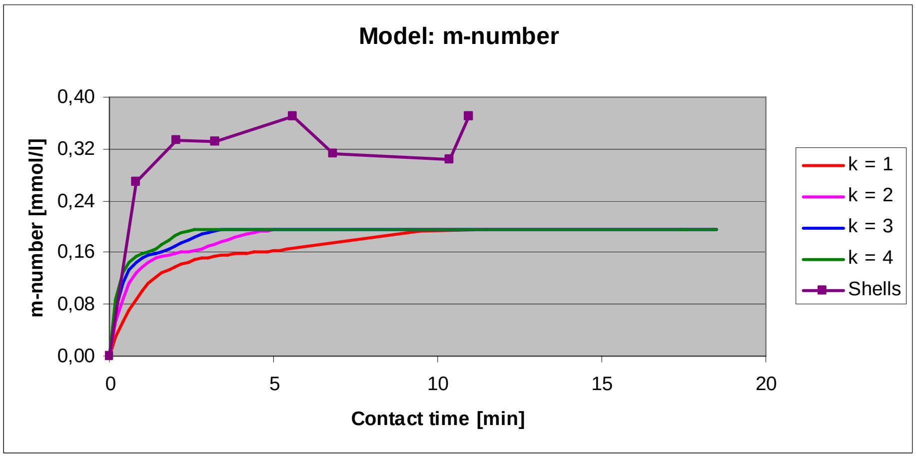


Figure 6.4 Result model, m-number as function of contact time

From figure 6.4 it is noticed that the modelled values for m-number do not fit the measured values. This is in line with the discussion in sub paragraph 5.2.1 in which is stated that the m-number increases twice as much as calcium. That the increase of the m-number is double the increase of calcium can be explained by the possibility of intrusion of CO_2 from the air into the water which caused 2 mol increase of the m-number in relation to 1 mol increase of calcium.

In order to model the conductivity the concentrations of all ions that are present in the water, must be known. After conditioning the following parameters are left or formed:

- Hydrogen
- Chloride
- Bicarbonate
- Calcium
- Carbonate

Next to pH, calcium and m-number carbonate is also modelled for the purpose of modelling the conductivity. In table 6.5 the results of the modelled carbonate are presented. The carbonate concentration of the experiments is calculated by means of the online modelling computer programme Stimela with pH and bicarbonate as fixed parameters.

Once the concentrations of all present ions are determined the conductivity of the solution can be calculated. The results of the modelled conductivity are presented in figure 6.6.

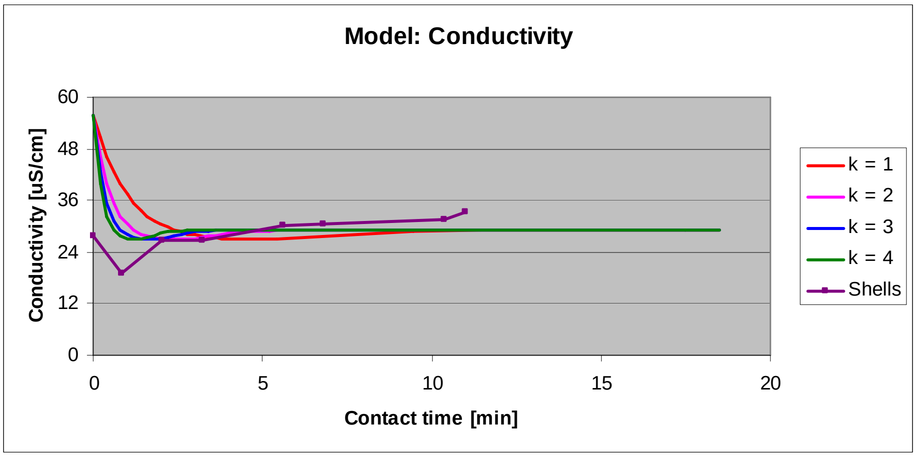


Figure 6.5 Result model, conductivity as function of contact time

Figure 6.5 shows that the measured conductivity does not fit the modelled conductivity. It is decided not to investigate this problem, mainly because the results of the experiments were not always very accurate e.g the test for which the increase of calcium is 3x the increase of bicarbonate (fig. 5.16 and 5.17).

6.2.2 Reaction constant other filter media

The reaction constant is also determined for crushed limestone and softening pellets. This is done by fitting the values for measured pH with modelled values for pH in a graph. The reaction rate is subsequently estimated from the graph. In figure 6.6 the modelled pH is presented at different reaction rates. In figure 6.6 to 6.7 the measured pH for crushed shells, crushed limestone and softening pellets are also presented. Subsequently the reaction constants are determined by estimating a value that lies nearest to the modelled pH.

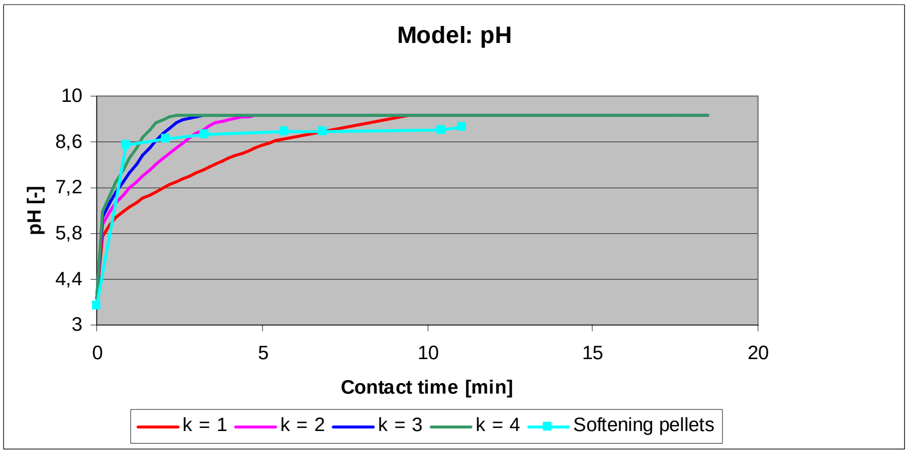


Figure 6.6 Result model, pH as function of contact time, softening pellets

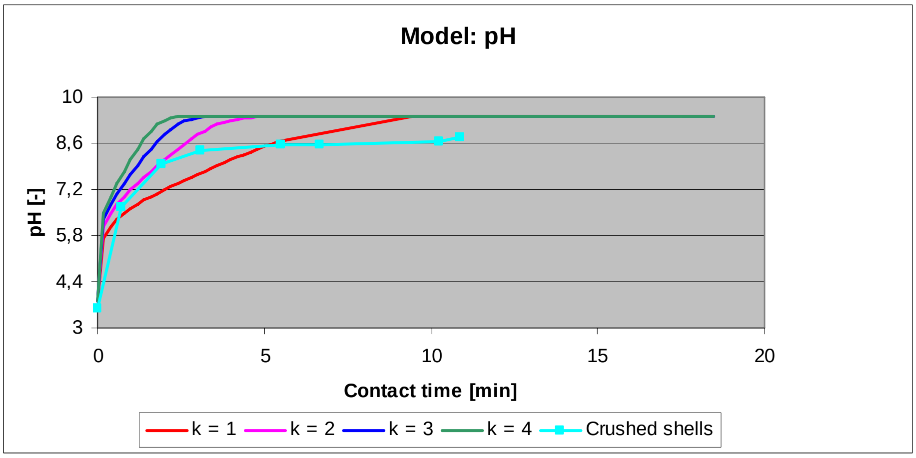


Figure 6.7 Result model, pH as function contact time, crushed shells

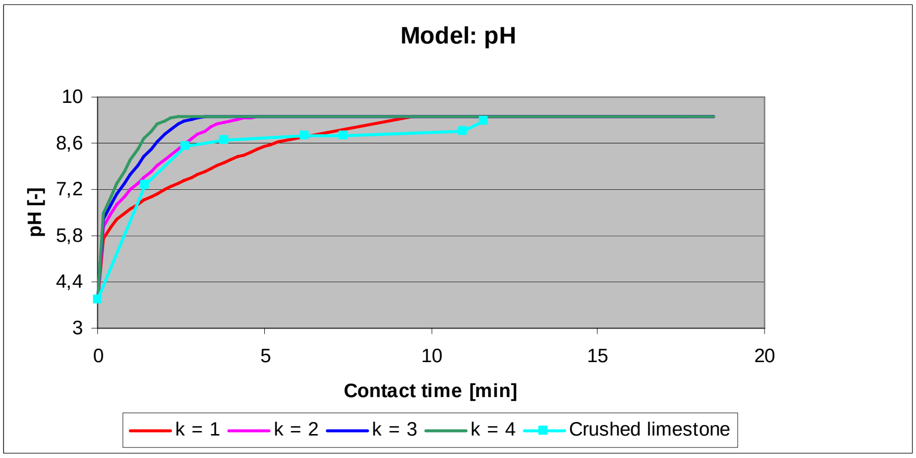


Figure 6.8 Result model, pH as function of contact time, crushed limestone

From figure 6.6 it is seen that the reaction constant for softening pellets is higher larger than 4. The reaction rate for softening pellets is estimated at 4.5 h^{-1}. From figure 6.7 and 6.8 it is seen that the reaction constants for crushed shells and crushed limestone are practically the same as for whole shells. The reaction constants for crushed shells and crushed limestone are estimated at 1.9 h^{-1}.

6.2.3 Comparison of determined reaction rate with literature

In this paragraph the reaction constant of the column experiment will be compared to literature. This is only done for crushed limestone because the experiments by Anderlohr and Jura Perle, for which the reaction rates were determined, were done with crushed limestone. The reaction constant of the column experiments is compared with the work of Anderlohr and Jura Perle. In table 6.5 the rates of the column experiments by Anderlohr and Jura Perle are given. From the experiments with Jura-Perle it was found that the reaction constant for crushed limestone is 2.76 h^{-1}. The experiments of Jura-Perle were done with crushed limestone diameter 1.2 – 1.8 mm. From the experiments with Anderlohr a reaction constant was found of 3.6 h^{-1}, determined with relation 3.14. The experiments of Anderlohr were done with crushed limestone diameter 0.9 – 1.0 mm, at a temperature of 20 °C and with demineralised water with 0.01 – 5.90 mmol/l CO_2.

The experiments of this research were carried out with crushed limestone diameter 1.8 – 2.5 mm at an average temperature of 19 °C and with demineralised water with 0.16 mmol/l HCl. The difference in reaction constant between the experiments of this research and the experiments of Anderlohr is that the experiments of Anderlohr were done with a crushed limestone with a smaller diameter. It seems acceptable that the smaller reaction rate of the experiments in comparison with the Anderlohr and Jura Perle experiments is explained by the fact that for the experiments of this research larger diameters were used.

Table 6.5 Reaction rate (k) crushed limestone; column experiments, Anderlohr and Jura Perle

Filter medium	Reaction constant k $[h^{-1}]$		
	Column experiments	Anderlohr	Jura-Perle
Crushed limestone	1.9	3.6	2.76

6.3 Calculation operational parameters

Now that the k-value for shells is known, the contact time can be calculated for all pumping stations. This is done by submitting the water quality of the raw water into the model. Once the contact time is calculated, the critical filter bed height can be calculated for each pumping station. An example is given for pumping station La Vigilantia. The raw water quality data of La Vigilantia is nearly equal to the raw water quality used for the column experiments with water type 1. The results of the modelling will be used to demonstrate the determination of contact time:

1. Calculate the effluent water quality data as function of time by using the reaction constant for the filter medium that is used. For pumping station La Vigilantia shells are used. The reaction constant is 1.9 h^{-1}
2. Plot the pH as function of contact time.
3. Determine the SI of the raw water quality: $SI = pH - pH_s$
   Determine which desirable pH. The desirable pH is reached when the minimum standard for SI is reached. The standard for SI is $-0.2 < SI < 0.3$. The minimum necessary pH is: $(pH_{raw\ water} - SI_{raw\ water}) - 0.2$. For La Vigilantia the SI of the raw water is -2.3. The minimum necessary pH is 8.1. The necessary contact time to reach a pH of 8.1 is 1.8 minutes. A safety margin is taken into account. A contact time is chosen of 5 minutes.
4. Determine the necessary filter bed height. The necessary filter bed height is calculated according to reaction 5.1. For La Vigilantia the design data are not known. It is assumed that for La Vigilantia the flow (Q) is 130 m^3/h with and the filtration rate (v) is 5 m/h. The necessary filter bed height for La Vigilantia is: EBCT * v = (5/60) * 5 = 0.42 m. It is decided that the filter bed must be refilled when a filter bed height of 0.5 is reached. A filter bed is chosen of 0.8 m. Assuming a total filter area of 20 m^2, the volume of the filter bed is 40 m^3
5. Determine the refilling frequency by calculating the $CaCO_3$ consumption (c). For La Vigilantia the $CaCO_3$ consumption is 0.24 mmol/l (fig. 5.16). The daily consumption is 130 *24 * 0.24 * 1.10^3 = 748800 mmol $CaCO_3$ = (748800/1000) * 100 g = 74880 g = 74.88 kg = 74.88 / 2751 m^3 = 0.03 m^3 = 0.03 / 20 m = 0.0015 m $CaCO_3$.. The filter bed will need refilling after (0.8 – 0.5) / 0.0015 = 200 days = 6 months.

The method for the determination of the k-value can also be applied for the other filter media. In case SWM decides to replace the shells for another filter medium, the critical filter bed height for every pumping station can be calculated by first determining the k-value for particular filter medium. After the k-value is determined, the needed contact time to reach the desired pH can be read from the graph. Subsequently the filter bed height is calculated at the chosen filtration rate.

6.4 Conclusion modelling

The conclusions that can be drawn from the modelling are:

- The amount of CO_2 can be used to describe the kinetics of conditioning
- The computer programme Stimela combined with the kinetics of conditioning, can be used to model the conditioning process and calculate the values of water quality parameters
- The water quality data combined with Stimela and the reaction rate enables the calculation of operational parameters like necessary contact time to reach equilibrium and refilling frequency
- For shells the reaction rate of the whole shells, crushed shells and crushed limestone is approximately 1.9 h^{-1}. For the softening pellets the reaction rate is 4.5 h^{-1}.

7 Evaluation and Design

In chapter 2 a description is given of the current situation of conditioning in Suriname. Based on the theory and practice of the carbonic acid equilibrium and the conditioning of aggressive water, this chapter will elaborate on each aspect given in chapter 2.

7.1 Elaboration water quality pumping stations

By using the Tillmans curve of figure 3.2 the raw water of the pumping stations, which are mentioned in chapter 2, can be categorized: aggressive, scaling or in equilibrium. The results are given in table 7.1. The pH and the calcium concentrations of the raw water are also listed in table 7.1.

Table 7.1 Analysis raw water quality SWM pumping stations

Pumping station	**pH [-]**	**Calcium concentration**		**Bicarbonate**		**Iron**	**Manganese**	**SI**	**pH_s (=pH-SI)**
		[mg/l]	**[mmol/l]**	**[mg/l]**	**[mmol/l]**	**[mg/l]**	**[mg/l]**	**[-]**	**[-]**
Koewarasan	6	22	0.55	88	1.44	8	0.5	- 2.3	8.3
La Vigilantia	3.9	2	0.05	< 1	< 0.02	0.28	0.23	- 7.3	11.2
Leiding 9A	6.2	32	0.8	153	2.51	9.9	1	- 1.7	7.9
Leysweg	5.7	25	0.63	110	1.80	4	0.8	- 2.4	8.1
Meerzorg	6.25	5	0.13	93	1.52	3.6	0.16	- 2.7	8.95
Pontbuiten	6	76	1.9	80	1.31	5.4	0.22	- 1.8	7.8
Tourtonne	6.55	10	0.25	161	2.64	0.01	0.07	- 1.8	8.35
Uitkijk	6.25	8	0.2	63	1.0	5.5	0.3	- 2.7	8.95
Flora	5.99	10.91	0.27	86.90	1.42	5.79	NA	- 2.6	8.59
Helena Christina	5.81	12.46	0.31	69.04	1.13	8.31	NA	- 2.8	8.61
Republiek	4.98	0.79	0.02	10.58	0.17	2.60	NA	- 5.7	10.68
Van Hattemweg	6.10	8.64	0.22	84.50	1.39	4.62	NA	- 2.6	8.7

By plotting the pH and the calcium concentration in a graph the property of the feed water (scaling or aggressive) can easily be determined. This is done for all pumping stations in figure 7.1. With figure 7.1 the necessary processes to apply can be determined for every pumping station. The choice for the necessary processes is based on the pH and bicarbonate concentration.

Table 7.2 Analysis raw water quality SWM pumping stations

Pumping station	pH [-]	CO_2 (calculated)		Calcium	Bicarbonate	Necessary treatment process
		[mg/l]	[mmol/l]	[mmol/l]	[mmol/l]	
Koewarasan	6	137.72	3.13	0.55	1.44	Aeration
La Vigilantia	3.9	--	--	0.05	< 0.02	CO_2 + limestone filtration
Leiding 9A	6.2	151.80	3.45	0.8	2.51	Aeration
Leysweg	5.7	344.08	7.82	0.63	1.80	Aeration
Meerzorg	6.25	81.84	1.86	0.13	1.52	Aeration
Pontbuiten	6	125.40	2.85	1.9	1.31	Aeration
Tourtonne	6.55	71.28	1.62	0.25	2.64	Aeration
Uitkijk	6.25	55.44	1.26	0.2	1.0	Aeration
Flora	5.99	104.50	2.38	0.27	1.42	Aeration
Helena Christina	5.81	167.64	3.81	0.31	1.13	Aeration
Republiek	4.98	111	2.52	0.02	0.17	Limestone filtration
Van Hattemweg	6.10	90.78	2.06	0.22	1.39	Aeration

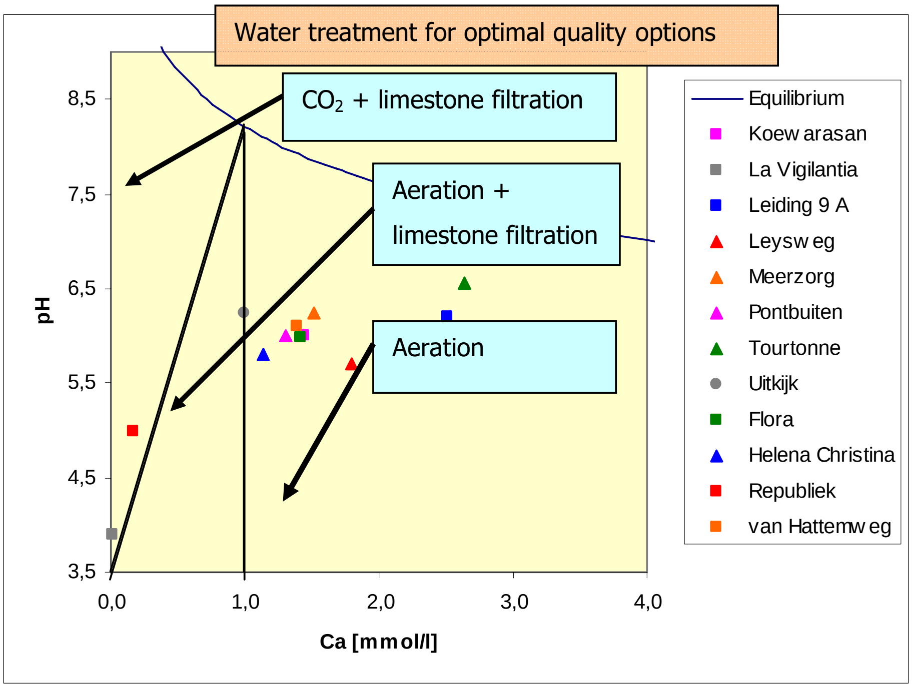


Figure 7.1 Raw water quality of SWM pumping stations and necessary treatment processes

From table 7.2 and figure 7.1 it can be concluded that for most of the pumping stations shell filtration is not even necessary. Shell filtration is only necessary for La Vigilantia and Republiek. The raw water of most of the pumping stations can be sufficiently conditioned by applying air stripping. One of the problems which have led to this research was that alternative materials had to be found for shells for the conditioning of aggressive groundwater. Another problem was the fact that shell filtration is not applied at pumping stations where aggressive groundwater is present because of the high consumption of shells and thus high costs. If at most of the pumping stations the raw water only needs conditioning by air stripping, than the problems with the use of shells and high conditioning costs are solved.

The water quality data of the pumping stations Republiek, van Hattemweg and Flora regarding pH, alkalinity and hardness are presented again in table 7.3 to 7.5. These data are analysed and discussed by calculating the expected values for HCO_3^- and the pH of the effluent of the sand filter and the shell filter. The calculations for the expected value of HCO_3^- are based on the assumption that the amount of H^+ that is produced by the oxidation of Fe^{2+}, is totally absorbed by HCO_3^-. The calculations for the expected value of the pH are done with the online modelling programme Stimela (www.stimela.com). The expected data for the shell filter are calculated with Stimela. The expected data are calculated in the following order:

1. Calculation CO_2 concentration of raw water with Stimela with HCO_3 and pH as fixed parameters. Exception is made for Republiek for which the raw water quality concerning bicarbonate is measured by using pH and CO_2 as fixed parameters. This is done because the first method gives a CO_2 concentration of 4.19 mmol/l which differs 1.67 mmol/l from the measured value. This deviation is considered too large.
2. Calculation removed CO_2 by aeration and escape in into open air. The assumption is made that with cascade aeration 15% CO_2 is removed per aeration step (there are 4 aeration steps) and with sprinkler aeration 45% [ref. 3]. Thus with cascade aeration 60% CO_2 is removed. The amount of CO_2 that escapes into open air depends on the type of filter: closed or open. The assumption is made that with an open filter 20% of the CO_2 escapes into open air and with a closed filter 10%. Based on the measured values for CO_2, the assumption is made that the removal of CO_2 with tower aeration is 70%.
3. Calculation water quality of the filtrate of the shell filter in case of equilibrium.

Table 7.3 Elaboration raw water quality data of pumping station Republiek (Source: laboratory SWM)

Parameter	Unity	Pumping station Republiek							
		Raw water		Sprinkler aeration	After sand filter		After cascade aearation	After shell filter	
		Meas.	Calc.	Calc.	Meas.	Calc.	Calc.	Meas.	Calculated equilibrium
pH	-	▨ 4.92			4.93	4.54	4.94	6.42	8.48
Calcium	mmol/l	0.02			0.02			0.07	0.54
Magnesium	mmol/l	0.03			0.09			0.04	
Bicarbonate	mmol/l	0.16	0.10		0.07	0.02		0.18	1.02
Iron	mg/l	2.48			0.07			0.05	
	mmol/l	0.04			0.00			0.00	
Carbon dioxide	mg/l	111			87.25			37.84	
	mmol/l	▨ 2.52		1.39	1.98	1.25	0.50	0.86	0.01

Meas. = measured

Calc. = calculated

▨ = fixed parameters for the calculation of the water quality concerning parameters in the column marked as calc.

Table 7.4 Elaboration raw water quality data of pumping station van Hattemweg (Source: laboratory SWM)

Parameter	Unity	Pumping station van Hattemweg							
		Raw water		After sprinkler aeration	After sand filter		After sprinkler aeration	After shell filter	
		Meas.	Calc.	Calc.	Meas.	Calc.	Calc.	Meas.	Calc. equilibrium
pH	-	5.94		6.20	6.24	6.20	6.46	6.77	7.82
Calcium	mmol/l	0.18			0.19			0.43	0.95
Magnesium	mmol/l	0.37			0.40			0.39	
Bicarbonate	mmol/l	1.34			1.05	1.18	1.18	1.46	2.72
Iron	mg/l	4.67			0.17			0.15	
	mmol/l	0.08			0.00			0.00	
Carbon dioxide	mg/l	90.78			25.77			6.51	
	mmol/l	2.06	3.17	1.74	0.59	1.55	0.85	0.15	0.08

Meas. = measured

Calc. = calculated

▨ = fixed parameters for the calculation of the water quality concerning the parameters in the column marked as calc.

Table 7.5 Elaboration raw water quality data of pumping station Flora (Source: laboratory SWM)

Parameter	Unity	Flora						
		Raw water		After sprinkler aeration	Filtrate sand filter		Filtrate shell filter	
		Measured	Calculated	Calculated	Measured	Calculated	Measured	Measured equilibrium
pH	-	5.90		6.42	6.58	6.43	7.08	7.71
Calcium	mmol/l	0.27			0.27		1.05	1.12
Magnesium	mmol/l	0.86			0.90		0.92	
Bicarbonate	mmol/l	1.38			1.16	1.20	2.72	2.88
Iron	mg/l	5.79			0.65		0.25	
	mmol/l	0.10			0.01		0.00	
Carbon dioxide	mg/l	104.50			33.46		28.28	
	mmol/l	2.48	3.57	1.07	0.76	0.96	0.64	0.12

Meas. = measured

Calc. = calculated

▨ = fixed parameters for the calculation of the water quality concerning the parameters in the column marked as calc.

Discussion

In groundwater filters several chemical and biological processes concerning the oxidation of dissolved groundwater components take place [10]. Table 7.4 gives an overview of these processes. Per mol oxidized Fe^{2+} 2 mol H^+ is produced. If there is enough HCO_3^- present in the water, the produced H^+ is consumed by the HCO_3^-. In table 2.5 it is noticed that 0.04 mmol/l Fe has oxidized and 0.08 mmol/l HCO_3^- is consumed. It can also be noticed that there is a difference of 0.30 between the measured and the calculated pH of the effluent of the sand filter. This is explained by the large difference in CO_2 concentration. The decrease of the pH of the effluent of the sand filter is a combination the escape of CO_2 and the oxidation of Fe^{2+}. In table 7.1 the Ca of the effluent of the shell filter increases with 0.90 mmol/l and the HCO_3^- with 0.18 mmol/l.

In table 7.4 the pH of the effluent of the sand filter increases from 5.94 to 6.24. This is explained by a combination of aeration, the oxidation of Fe^{2+} and the escape of CO_2 into open air. The HCO_3^- of the effluent of the sand filter decreases from 1.34 to 1.05 mmol/l. This gives a decrease of 0.29 mmol/l of which 0.16 mmol/l is consumed by 0.16 mmol/l H^+ which is produced by the oxidation of 0.08 mmol/l Fe. The remaining 0.13 mmol/l decrease of HCO_3^- may be caused by the consumption by acids that are produced as a result of other oxidation processes. At this point the decrease of HCO_3^- that is caused by other oxidation processes cannot be calculated because except from Fe the groundwater components that are oxidized are not known. The Ca concentration of the effluent of the shell filter increases with 0.24 and HCO_3^- with 0.41. This is almost in accordance with equation 3.5 according to which 2 mol HCO_3^- is produced per mol produced Ca.

In table 7.5 the pH of the effluent of the sand filter increases from 5.90 to 6.58. As mentioned above this cannot be caused by the oxidation processes and so the increase of the pH is most probably caused by the aeration of the water at which CO_2 is removed from the water. The Ca of the effluent of the shell filter increases from 0.27 to 1.05 mmol/l. This should result in an increase of the HCO_3^- from 1.16 to 2.72 mmol/l. The HCO_3^- of the effluent of the sand filter decreases from 1.38 to 1.16 mmol/l. This gives a difference of 0.22 mmol/l of which 0.18 mmol/l decrease is caused by the consumption by the 0.10 mmol/l acid that is produced as a result of the oxidation of 0.10 mmol/l Fe. The remaining 0.12 mmol/l decrease of HCO_3^- may be caused by the consumption by acids that are produced as a result of other oxidation processes.

Table 7.6 Groundwater filtration processes [10]

Process	Mechanism	Reaction
Oxidation and hydrolysis of Fe^{3+}	Chemical	$4\ Fe^{2+} + O_2 + 10\ H_2O \rightarrow 4\ Fe(OH)_3\ (s) + 8\ H^+$
Oxidation of CH_4	Biological	$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$
Oxidation of H_2S	Biological	$H_2S + 2\ O_2 \rightarrow SO_4^{2-} + 2\ H^+$
Oxidation of NH_4^+	Biological	$2\ NH_4^+ + 3\ O_2 \rightarrow 2\ NO_3^- + 8\ H^+$
Oxidation of Mn^{2+}	Chemical (catalytic)	$Mn^{2+} + MnO_2\ (s) \rightarrow Mn^{2+}.MnO_2\ (s)$

Table 7.3 shows that the pH, alkalinity and hardness of the raw water of pumping station Republiek is extremely low. The raw water quality of pumping stations van Hattemweg and Flora are higher compared to that of Republiek. The raw water of Republiek will therefore demand a higher extent of neutralization than the raw water of the other two pumping stations.

As mentioned before the water quality data show that for the pumping stations Republiek and van Hattemweg the pH, alkalinity and hardness of the effluent (product water) of the shell filter do not satisfy the Dutch/WHO standards for drinking water. The data also show that for pumping station Republiek the values are still extremely low compared to that of the other two stations. Compared to pumping stations Republiek and van Hattemweg, pumping station Flora has the best water quality.

Based on the water quality data it can be said that pumping station Republiek has little to none performance. A possible explanation for this is that the samples for the measurements that belong to these results were collected at the time that the height of the shell bed was too low in order to get enough neutralization of the water.

7.2 Discussion process scheme

During aeration the excess CO_2 is removed from the water and oxygen is added to the water. However, CO_2 is an important parameter for the neutralization process according to equation 3.5. It is important to consider whether it is better to place the shell filtration step before the aeration step. By doing this the problem of soft water at the end of the whole treatment might be solved. However, before doing this the manganese and methane concentration have to be measured first in order to see what the effects will be on the shell filters and rest of the treatment. This assessment process can be applied to every pumping station to theoretically predict if the water quality is reached.

7.3 Discussion on backwashing

The backwashing of the shell filters is done once in 1 to 3 weeks. Daily backwashing is evidently not necessary because the removal of iron, methane, manganese and other substances has already taken place in the sand filters. The substances that are removed in the shell filters are the remaining substances that may have passed the sand filters.
In 2007 Suzan Bakker, student at the faculty of Civil engineering at the Delft University of Technology, carried out a study into the backwashing effects of shell filters [21]. The conclusion that was drawn from this study was that backwashing of the shell filters is hardly possible due to the fact that during backwashing of the shell bed packages of shells start floating (figure 7.2). This is due to the fact that during backwashing the shells cling together in packages because of the shape of the shells. As a result of this a certain amount of the substances that must be removed stay remained in the filter bed. With regard to backwashing the conclusion can be drawn that shells are a less suitable material for filtration. However it must be noted here that the backwashing was performed with water only.

(a)

(b)

(c)

Figure 7.2 (a), (b) and (c) Backwashing shell filter (Source: S. A. Bakker)

In practice marble filters are refilled if the filter bed has reduced with 10%. In Suriname this is done once in 2 to 4 months. In order to say whether this method of refilling is right or wrong it is required to know the reduction rate of the filter bed. The reduction rate is dependent of the water quality of the influent. The higher the acidity of the water is, the higher the neutralization rate. Pumping stations with softer water and thus a higher neutralization rate need a higher frequency of refilling. In chapter 6 calculations will be made for the refilling frequency of these three pumping stations.

7.4 Study into alternative materials and use of shells in Suriname

Apart from the study into the functioning of the shell filters also a study into the use of the shells has been done. This research has been subdivided in a study into:

- Origin and costs of the shells
- Use of the shells
- Alternatives for neutralization
- Operation of the shell filters

Origin and costs of the shells

In Suriname concessions are required in order to be able to excavate shells from regions where the shells are to be found. The SWM is the concession holder of certain shell regions. These regions are however not exploited because of the high costs for the required excavation equipment. The shells that are used for neutralization at the moment are from the district Coronie. These shells are called the JORO JORO shells. The shells are bought from concession holder Zandvliet for an amount of 85 SRD per m^3 (approx. 24 euro's). After washing and sieving the costs for the shells are 165 SRD (approx. 47 euro's) per m^3. The shells which remain after washing and sieving are called waste shells. These shells are sold for 24 SRD (approx. 7 euro's) per m^3 to SWM employees (figure 7.6). Formerly the shells were also bought from concession holders in Saramacca. However the shells of Saramacca appeared to have a grain diameter that was smaller than that of the Coronie shells. For the shell filtration the SWM uses shells with a grain diameter of 2-6 mm. After sieving of the Coronie shells a percentage of 20% waste shells is retrieved, whereas with the Saramacca shells a percentage of 40% waste shells is retrieved. So when purchasing the shells, the SWM has to order 40% more Saramacca shells and 20% more Coronie shells than required. However the advantage of the Saramacca shells over the Coronie shells is the distance between the Saramacca/ Coronie and Paramaribo where the shells are needed. The distance between Coronie and Paramaribo is 100 km and between Saramacca and Paramaribo this is 45 km. Since in Suriname the world market price for petrol is maintained, this difference in distance contributes on the decision whether to buy the shells in from concession holders in Coronie or Saramacca. At the moment the price for 1 liter petrol is 3.65 SRD (1.04 euro's).

Due to the uncontrolled excavation of shells the danger of salt intrusion threatens inland of Suriname. Except for water treatment purposes the shells are also used for agriculture, the cattle fodder industry, the construction sector and other aims, as a result of which the danger of exhaustion of the shell stock occurs.

Use of shells

The shells are transported by truck to the shell laundry at a location in Paramaribo called Saramacca Doorsteek, where the shells are washed and sieved at a grain diameter of 2-6 mm (figure 7.3). After washing and sieving the shells are stored at the same location (figure 7.4). Once a shell filter at a certain pumping station needs refilling, the shells are then transported by truck to the concerning pump station. The shells are temporarily stored at the pumping station in the open air (figure 7.5). Afterwards the shell filters are refilled. The shell bed is subsequently disinfected with chlorine. Samples of the effluent of the shell filters are taken by the SWM laboratory and analyzed on E-coli. Once the E-coli concentration satisfies the WHO standards for drinking water, the shell filters are taken in operation.

Figure 7.3 Washing and sieving of shells

Figure 7.4 Storage of shells

Figure 7.5 Storage of shells at p.s. Republiek

Figure 7.6 Waste shells

Alternatives for neutralization

For this research an interview was held with the Mr. Paansa of Geologische Mijnbouw Dienst (GMD) , the Geological Mining industry Service of the ministry of Natural Resources.

Limestone has a marine origin. However, Suriname has no marine origin as a result of which the presence of magnesium and calcium carbonates in Suriname are highly improbable. Suriname exists mainly from metamorphosed area. This means that Suriname is rich of minerals with a granite composition. These minerals are rich to siliciumoxides and silicates. The only calcium carbonate resources that are known so far in Suriname are shells.

Availability limestone

The nearest provider of limestone is the Mining Company Curacao. In case of exhaustion of the shells the SWM has the option of buying limestone grains from the mining company Curacao. The transport charges may be higher than the total costs for shells because of the purchase costs and shipping costs.

Other alternatives

Another alternative for shells are the softening pellets from water treatment plants in the Netherlands. These pellets contain calcium carbonate and these are the end product of the softening processes that are applied in the treatment plants in the Netherlands. As with the crushed limestone from the mining company Curacao the total costs for the pellets may be higher than the costs for shells because of the shipping costs. These costs will be calculated further on in the report. In order to get an indication of the shipping costs the price list of the shipping company Jos Steeman Shipping was obtained. Jos Steeman carries out shipping from the Netherlands to Suriname as well as from Curacao to Suriname. The costs for shipping are divided in:

• shipping:	80	euro's per m^3
• loading:	15	euro's per m^3
• pick up:	35	euro's per m^3
• bill or loading:	25	euro's
• administration:	12.50	euro's
• import document:	25	euros

Availability of chemicals for neutralization

The chemical company Bergwijn is the provider of chemicals in Suriname. The chemical company was asked for information concerning the availability of the following chemicals:

- $NaOH$
- $Ca(OH)_2$
- Na_2CO_3
- $CaCO_3$
- Calcium
- Magnesium
- CO_2

The chemical company has only NaOH in store. It is delivered granular by bags of 25 kilograms with a volume percentage of 98%. The costs are 93 SRD (approx. 27 euros) per bag. All other chemicals must be imported. For the cost analysis of the use of these chemicals the costs for the chemicals in the Netherlands will be used.

Choice for certain neutralization alternatives

Based on the fact that the solution on finding an alternative for shell filtration should be robust, cheap and durable it is decided that in this research the focus will be on neutralization by means of filtration. Since at this moment shell filtration is applied at the pumping stations where neutralization is needed, it is considered cheaper to look for alternative filter materials. The filter constructions already exist so there are no costs for the realization of filter constructions. The disadvantage of chemical dosing is that the dosing should be done with accuracy in order to avoid overdosing of the chemicals.

8 Conclusions and Recommendations

The general research consisted of 4 parts:

- Information concerning shell filtration and theory and practice of conditioning
- Experiments
- Modelling
- Evaluation and design

Based on the findings and results of the 4 parts conclusions are drawn and recommendations are given regarding aspects that need to be focused on in further research.

8.1 Conclusions

By combining the theory and practice of conditioning with the raw water quality of the SWM pumping stations, the necessary treatment processes were determined for every pumping station. It was found that for most of the SWM pumping stations shell filtration is not even necessary. Shell filtration is only necessary for La Vigilantia and Republiek. The raw water of most pumping stations can be sufficiently conditioned by applying air stripping. One of the problems which have led to this research was that shells are threatened to run out in the long term and that alternative materials have to be found for shells for the conditioning of aggressive groundwater. Another problem which led to this research was the fact that currently shell filtration is not applied at pumping stations where aggressive groundwater is present because of the high consumption of shells and thus high costs for the conditioning of aggressive water. If most of the pumping stations only needs conditioning by air stripping, than the problems with shells and the high costs for the conditioning of aggressive water are perfectly solved.

The goal of the column experiments was to study the behavior of shell filters. Among other parameters, the influence of filtration rate on contact time was analyzed. From the column experiments with shells and varying filtration rates it was noticed that the filtration rate influences contact time. The contact time decreases with increasing filtration rate. The necessary contact time to reach a pH of 9 was reach after 1 minute at a filtration rate of 10 m/h and after 7 minutes at a filtration rate of 3 m/h.

The online computer programme Stimela was used to model the conditioning process. The results showed that Stimela can be used to model the conditioning process. By fitting the results of the column experiments with the results of the model, the reaction rates of shells, softening pellets, crushed shells and crushed limestone were estimated. It was found that for whole shells, crushed shells and for crushed limestone the reaction rate is 1.9 h^{-1}. For softening pellets the reaction rate is 4.5 h^{-1}.

By using the reaction rate, it is possible to calculate operational parameters such as contact time and refilling frequency of the filter bed. A calculation was done for the pumping station La Vigilantia with the most aggressive water. It was found that for La Vigilantia the necessary contact time to reach the desirable pH of 8.1 is 2 minutes at a filtration rate of 5 m/h, which means that the desirable pH is reached after the first 17 cm of the filter bed. A safety margin is chosen of 3 minutes, which means that the contact time is 5 minutes with a corresponding filter bed height of 0.42 m. If a filter bed height is chosen of 0.8 m, the refilling frequency for La Vigilantia is 6 months. This is the pumping station with the most aggressive water. When the same filtration is applied, the contact time and the filter bed height increases if the water is less aggressive. For less aggressive water the filter bed height is larger than 0.8 m.

8.2 Recommendations

In the mathematical model only the CO_2 concentration is used to model the conditioning process. For longer contact times the CO_3^{2-} concentration must be used to model the conditioning process. It is recommended that in further research the CO_3^{2-} concentration is included in the mathematical model.

When the necessary processes for the pumping stations are determined, it is recommended to also analyze the iron, manganese and methane content. If these concentrations are above the given standards according to the WHO guidelines, National Drinking Water standards or VEWIN recommendations, it is recommended to apply aeration and sand filtration as first step in the treatment in order to e.g. avoid clogging of the shell filters. Currently manganese and methane are not measured by SWM. It is recommended that the measurement of these parameters is included in the routine measuring programme.

References

1. L.L. Shreir, R.A. Jarman, G.T. Burstein;
   Corrosion
   Oxford, 1994, Butterworth/Heinemann

2. D. Talbot, J. Talbot;
   Corrosion Science and technology
   Boca Raton, CRC Press, 1998

3. S. J. Pocock, A. G. Shaper, R. F. Packham;
   STUDIES OF WATER QUALITY AND CARDIOVASCULAR DISEASE IN THE UNITED KINGDOM
   Science of the Total Environment, Volume 18, April 1981, Pages 25-34

4. Margaret D. Crawford, D. G. Clayton, Fiona Stanley and A. G. Shaper;
   AN EPIDEMIOLOGICAL STUDY OF SUDDEN DEATH IN HARD AND SOFT WATER AREAS
   Journal of Chronic Diseases, Volume 30, Issue 2, February 1977, Pages 69-80

5. Margaret D. Crawford, M. J. Gardner and J. N. Morris;
   MORTALITY AND HARDNESS OF LOCAL WATER- SUPPLIES
   The Lancet, Volume 298, Issue 7720, 14 August 1971, Pages 327-329

6. F. Graanoogst;
   Schelpen: een kwalitatieve analyse van enkele Surinaamse schelpenvoorkomens
   Paramaribo, 1993, Anton de Kom Universiteit - Faculteit der Technologische wetenschappen, Sectie Geologie

7. C. E. Ligeon;
   Het ontstaan van schelpen en hun toepassingsmogelijkheden in Suriname
   Anton de Kom Universiteit – Faculteit der Technologische Wetenschappen, Sectie Geologie

8. DHV Raadgevend Ingenieursbureau BV;
   Het kalk-koolzuurevenwicht opnieuw bezien
   Internal DHV publication, 1982

9. J.C. van Dijk, P.J. de Moel, J.H.C.M. Oomen;
   Crushed limestone filtration; the comeback of a forerunner
   Paper submitted for publication in journal JAWWA

10. J.C. van Dijk, P.J. de Moel, J.H.C.M. Oomen;
    Marmerfiltratie van ijzerhoudend agressief grondwater
    H_2O, 1983

11. G. K. Reijnen, J. A. M van Paassen;
    Het vergelijken van ontzuringssnelheid van enige kalksteensoorten en onthardingspellets
    Nieuwegein, 1981, KIWA Research

12. Ir. G. K. Reijnen;
    Marmerontzuring, een oud proces met nieuwe perspectieven
    H_2O, nr. 13, 1979

13. G. K. Reijnen;
    Ontzuren van grondwater
    Nieuwegein, 1988, Kiwa mededeling 101

14. J. Tillmans;
    Über die Geschwindigkeit der Entsärung kohlensäurehaltiger Wässer beim Marmorrieselungsverfahren
    Vom Wasser, 1932

15. A. Anderlohr;
    Experimentelle Untersuchungen zur Auflösung von Calciumkarbonat durch Kohlensäurehaltige Wässer in Schüttungen
    In: Veroffentlichungen des Bereichs und des Lehrstuhl für Wasserchemie
    Karlsruhe, 1976, Engler-Bunte –Institut der Universität Karlsruhe

16. F. Houtepen;
    pH/ verhoging mengwater door marmerfiltratie
    Pompstation Bergen op Zoom, 1995

17. S. A. Bakker;
    Guidelines for backwashing Shell filter, BSc- thesis in Civil Engineering
    Delft, 2007, Department of Sanitairy Engineering , Faculty of Civil engineering, TUDelft

18. P.J. de Moel, J.Q.J.C. Verberk, J.C. van Dijk;
    Drinkwater principes en praktijk
    Den Haag, 2004, Sdu Uitgevers

19. J.C. van Dijk, L.C. Rietveld, J.Q.J.C. Verberk;
    Drinkwater technologie 1
    Delft, 2001, Delft university of Technology

20. L.Huisman;
Rapid Filtration (CT4470)
Delft, 2004, Delft University of Technology, Department of Sanitary Engineering

21. L.S.Clesceri, et. al.;
Standard Methods for the Examination of Water and Wastewater. 20th Edition
Washington DC, American Public Health Association, 1998

22. S. Alberga;
Verlaging kalkagressiviteit en ijzergehalte van het aan de van Hattemweg geproduceerde water
Delft, TU Delft, Faculty of Civiel Engineering and Geosciences, Department of Watermanagement, Sectie of Sanitairy Engineering, 2003

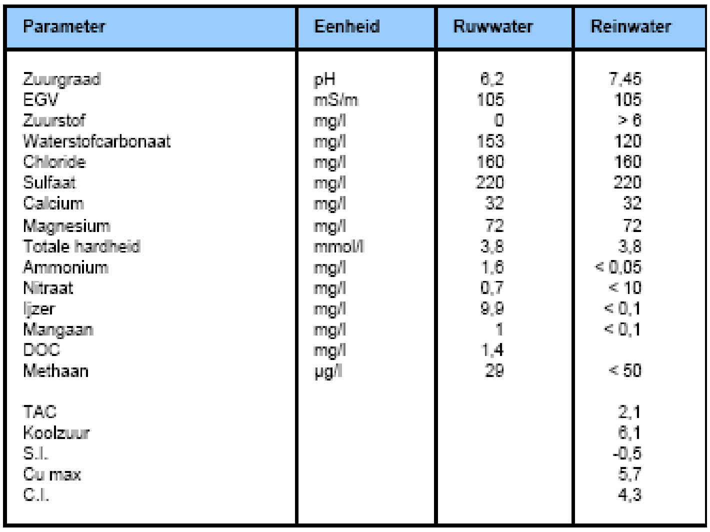
23. N. Tilborg;
Schelpenonderzoek
Paramaribo, 1999, Natuurtechnisch Instituut (NATIN)

24. H. H. Willard; L. L. Merritt, JR.; J. A. Dean; F. A. Settle, JR.
Instrumental Methods of Analysis, Sixth Edition
Belmont California, Wadsworth Publishing Company, 1981

Appendices

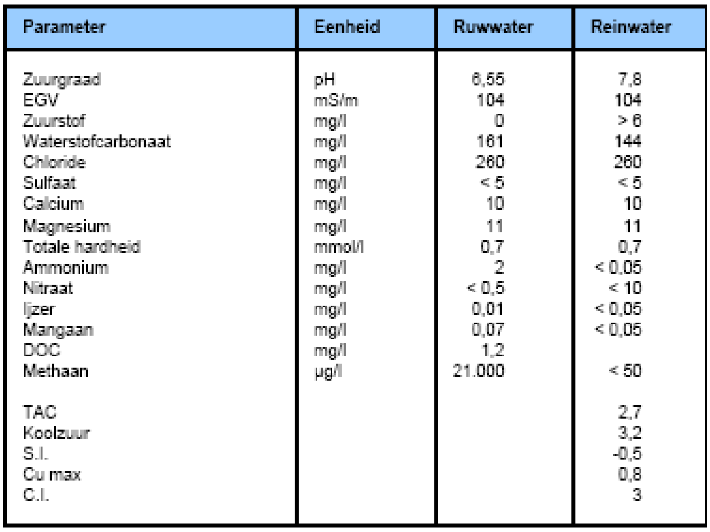
Appendix I A: Water quality data Vitens

P.S. Leiding 9A (Source: Vitens)



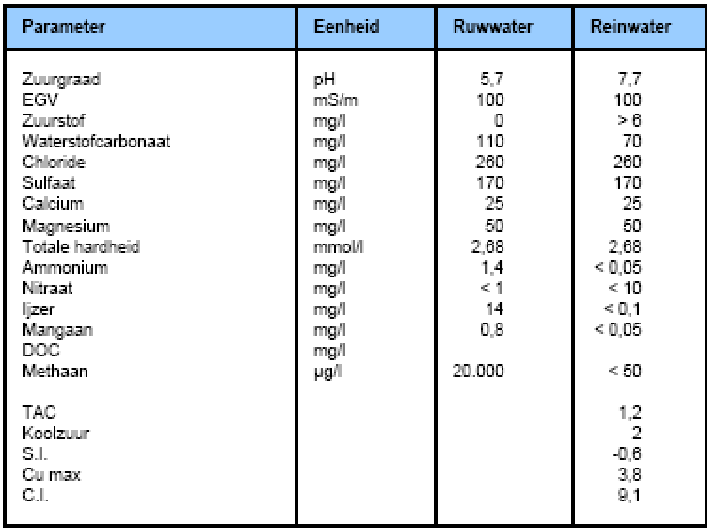
Parameter	Eenheid	Ruwwater	Reinwater
Zuurgraad	pH	6,2	7,45
EGV	mS/m	105	105
Zuurstof	mg/l	0	> 6
Waterstofcarbonaat	mg/l	153	120
Chloride	mg/l	160	160
Sulfaat	mg/l	220	220
Calcium	mg/l	32	32
Magnesium	mg/l	72	72
Totale hardheid	mmol/l	3,8	3,8
Ammonium	mg/l	1,6	< 0,05
Nitraat	mg/l	0,7	< 10
Ijzer	mg/l	9,9	< 0,1
Mangaan	mg/l	1	< 0,1
DOC	mg/l	1,4	
Methaan	µg/l	29	< 50
TAC			2,1
Koolzuur			6,1
S.I.			-0,5
Cu max			5,7
C.I.			4,3

P.S. Tourtonne (Source: Vitens)



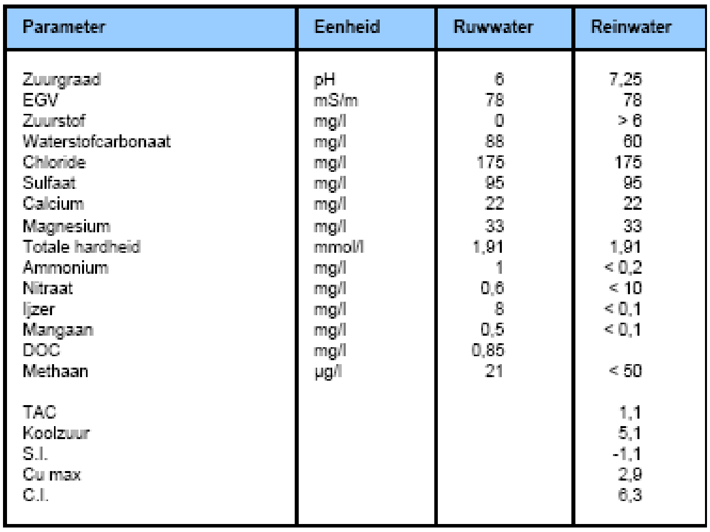
Parameter	Eenheid	Ruwwater	Reinwater
Zuurgraad	pH	6,55	7,8
EGV	mS/m	104	104
Zuurstof	mg/l	0	> 6
Waterstofcarbonaat	mg/l	161	144
Chloride	mg/l	260	260
Sulfaat	mg/l	< 5	< 5
Calcium	mg/l	10	10
Magnesium	mg/l	11	11
Totale hardheid	mmol/l	0,7	0,7
Ammonium	mg/l	2	< 0,05
Nitraat	mg/l	< 0,5	< 10
Ijzer	mg/l	0,01	< 0,05
Mangaan	mg/l	0,07	< 0,05
DOC	mg/l	1,2	
Methaan	µg/l	21.000	< 50
TAC			2,7
Koolzuur			3,2
S.I.			-0,5
Cu max			0,8
C.I.			3

P.S. Leysweg (Source: Vitens)



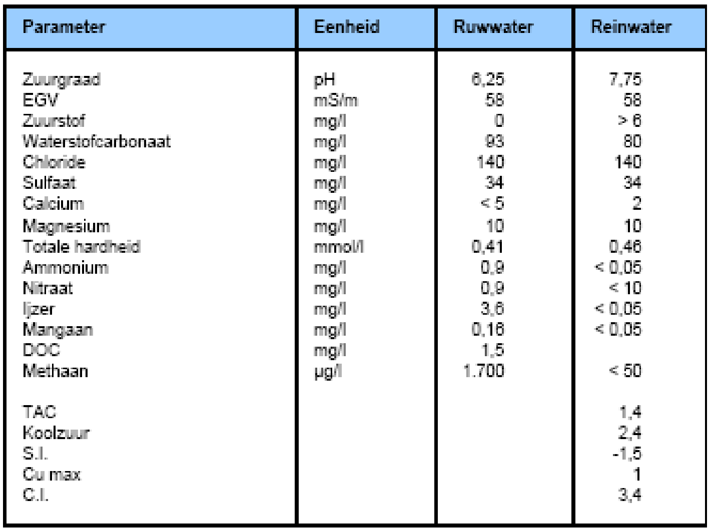
Parameter	Eenheid	Ruwwater	Reinwater
Zuurgraad	pH	5,7	7,7
EGV	mS/m	100	100
Zuurstof	mg/l	0	> 6
Waterstofcarbonaat	mg/l	110	70
Chloride	mg/l	260	260
Sulfaat	mg/l	170	170
Calcium	mg/l	25	25
Magnesium	mg/l	50	50
Totale hardheid	mmol/l	2,68	2,68
Ammonium	mg/l	1,4	< 0,05
Nitraat	mg/l	< 1	< 10
Ijzer	mg/l	14	< 0,1
Mangaan	mg/l	0,8	< 0,05
DOC	mg/l		
Methaan	µg/l	20.000	< 50
TAC			1,2
Koolzuur			2
S.I.			-0,6
Cu max			3,8
C.I.			9,1

P.S. Koewarasan (Source: Vitens)



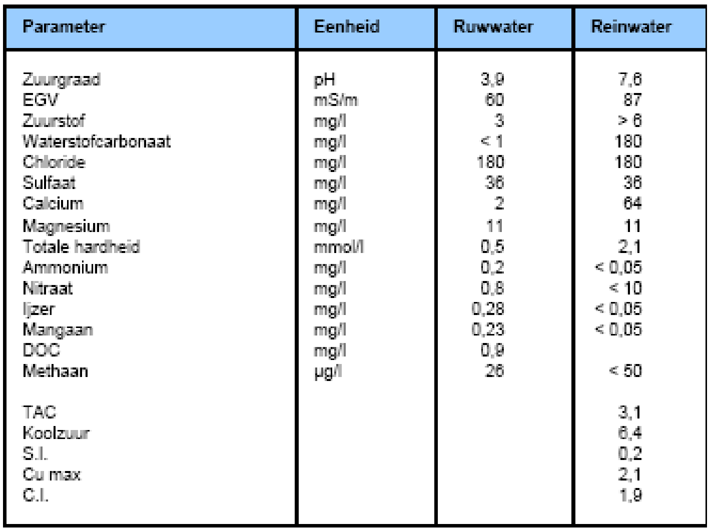
Parameter	Eenheid	Ruwwater	Reinwater
Zuurgraad	pH	6	7,25
EGV	mS/m	78	78
Zuurstof	mg/l	0	> 6
Waterstofcarbonaat	mg/l	88	60
Chloride	mg/l	175	175
Sulfaat	mg/l	95	95
Calcium	mg/l	22	22
Magnesium	mg/l	33	33
Totale hardheid	mmol/l	1,91	1,91
Ammonium	mg/l	1	< 0,2
Nitraat	mg/l	0,6	< 10
Ijzer	mg/l	8	< 0,1
Mangaan	mg/l	0,5	< 0,1
DOC	mg/l	0,85	
Methaan	µg/l	21	< 50
TAC			1,1
Koolzuur			5,1
S.I.			-1,1
Cu max			2,9
C.I.			6,3

P.S. Meerzorg (Source: Vitens)



Parameter	Eenheid	Ruwwater	Reinwater
Zuurgraad	pH	6,25	7,75
EGV	mS/m	58	58
Zuurstof	mg/l	0	> 6
Waterstofcarbonaat	mg/l	93	80
Chloride	mg/l	140	140
Sulfaat	mg/l	34	34
Calcium	mg/l	< 5	2
Magnesium	mg/l	10	10
Totale hardheid	mmol/l	0,41	0,46
Ammonium	mg/l	0,9	< 0,05
Nitraat	mg/l	0,9	< 10
Ijzer	mg/l	3,6	< 0,05
Mangaan	mg/l	0,16	< 0,05
DOC	mg/l	1,5	
Methaan	µg/l	1.700	< 50
TAC			1,4
Koolzuur			2,4
S.I.			-1,5
Cu max			1
C.I.			3,4

P.S. La Vigilantia (Source: Vitens)



Parameter	Eenheid	Ruwwater	Reinwater
Zuurgraad	pH	3,9	7,6
EGV	mS/m	60	87
Zuurstof	mg/l	3	> 6
Waterstofcarbonaat	mg/l	< 1	180
Chloride	mg/l	180	180
Sulfaat	mg/l	36	36
Calcium	mg/l	2	64
Magnesium	mg/l	11	11
Totale hardheid	mmol/l	0,5	2,1
Ammonium	mg/l	0,2	< 0,05
Nitraat	mg/l	0,8	< 10
Ijzer	mg/l	0,28	< 0,05
Mangaan	mg/l	0,23	< 0,05
DOC	mg/l	0,9	
Methaan	µg/l	26	< 50
TAC			3,1
Koolzuur			6,4
S.I.			0,2
Cu max			2,1
C.I.			1,9

Appendix I B: Water quality data SWM

In this chapter the water quality data of SWM pumping stations are presented.

Missing data

The calcium and magnesium data are missing in some of the data because these parameters are usually not measured by SWM. The hardness is measured in terms of total hardness. Manganese is also a parameter which is generally not measured by the SWM.

Table IB.1 Water quality data pumping station Flora (Source: SWM)

Parameter	Unit	Pumping station Flora			
		Raw water	After sand filter	After shell filter	Clear water
pH	-	5.99	6.22	6.61	7.62
Calcium	mg/l	10.91	11.02	12.44	NA
Magnesium	mg/l	20.64	21.76	20.79	NA
Total hardness	mg/l	112.28	116.99	140.26	198.61
Bicarbonate	mg/l	86.90	74.27	96.6	116.20
Iron	mg/l	5.79	0.62	0.23	0.02
Carbondioxide	mg/l	110.20	33.71	26	2.80
Chloride	mg/l	241.05	NA	233.4	249.79

NA = Not available

Table IB.2 Water quality data pumping stations Helena Christina

Parameter	Unit	Pumping station Tourtonne				
		Raw water	After aeration	After sand Filter	After shell filter	Clear water
pH	[-]	5.81	6.03	5.75	6.31	6.38
Calcium	m/l	12.46	10.64	NA	NA	NA
Magnesium	m/l	12.50	18.52	NA	NA	NA
Total hardness	mg/l	82.5	102.78	NA	NA	119.92
Bicarbonate	mg/l	69.04	49.68	50.78	80.44	80.40
Iron	mg/l	8.31	0.09	0.11	0.04	0.03
Carbondioxide	mg/l	124.16	42.68	80.88	31.52	27.36
Chloride	mg/l	98.51	NA	NA	NA	100.80

Table IB.3 Water quality data pumping station Republiek

Parameter	Unit	Pumping station Republiek				
		Raw water	After aeration	After sand filter	After shell filter	Clear water
pH	-	4.98	4.75	4.75	5.85	6.08
Calcium	mg/l	0.79	44.29	NA	NA	NA
Magnesium	mg/l	1.04	0.19	NA	NA	NA
Total hardness	m/l	6.24	111.20	NA	59.90	60.66
Bicarbonate	mg/l	10.58	5.25	4.74	79.54	93.25
Iron	mg/l	2.60	0.31	0.22	0.14	0.25
Carbondioxide	mg/l	106.38	64.87	80.75	36.78	33.38
Chloride	mg/l	9.48	NA	NA	NA	8.70

Table IB.4 Water quality data pumping station van Hattemweg

Parameter	Unit	Pumping station van Hattemweg			
		Raw water	After sand filter	After shell filter	Clear water
pH	-	6.10	6.42	7.13	6.77
Calcium	mg/l	8.64	8.90	18.19	11.62
Magnesium	mg/l	9.37	9.39	7.36	10.39
Total hardness	m/l	58	59.54	77.12	77.88
Bicarbonate	mg/l	84.50	70.80	102.53	94.53
Iron	mg/l	4.62	0.17	0.14	0.17
Carbondioxide	mg/l	89.80	25.62	6.78	12.56
Chloride	mg/l	28.70	NA	NA	28.37

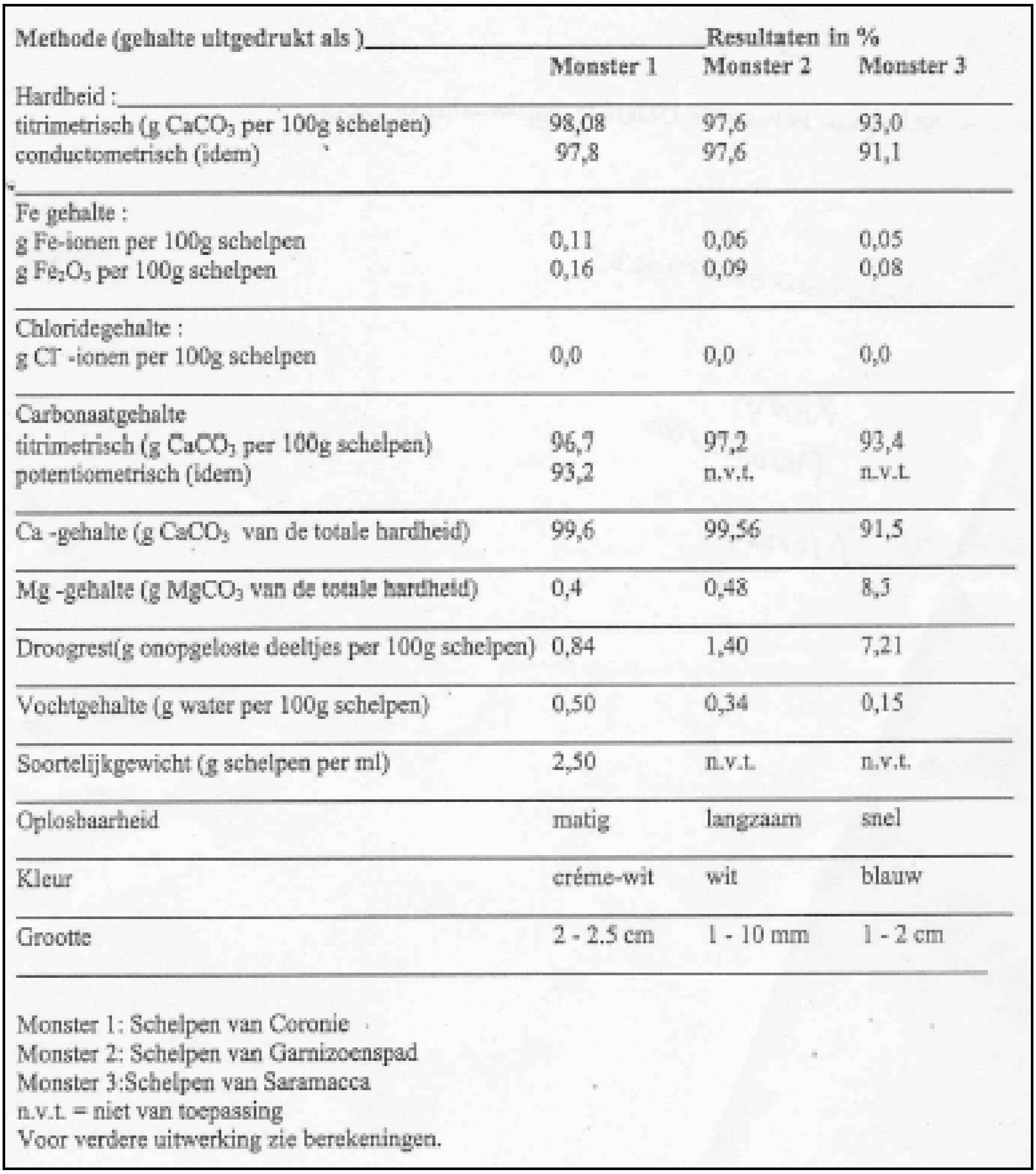
Table IB.5 Water quality data pumping station Tourtonne (Source: SWM)

Parameter	Unit	P.S. Tourtonne				
		Raw water	After aeration	After sand Filter	After shell filter	Clear water
pH	[-]	6.47	7.15	7.04	7.29	7.34
Total hardness	mg/l	NA	NA	NA	77.63	81.28
Bicarbonate	mg/l	167.46	10.33	152.77	152.62	145.91
Iron	mg/l	0.02	160.33	0.02	0.03	0.02
Carbondioxide	mg/l	62.17	62.17	11.54	6.98	6.45
Chloride	mg/l	226.57	0.03	NA	222.04	210.63

Appendix II: Technical data materials

In this appendix available information concerning the composition of the filter media is given.

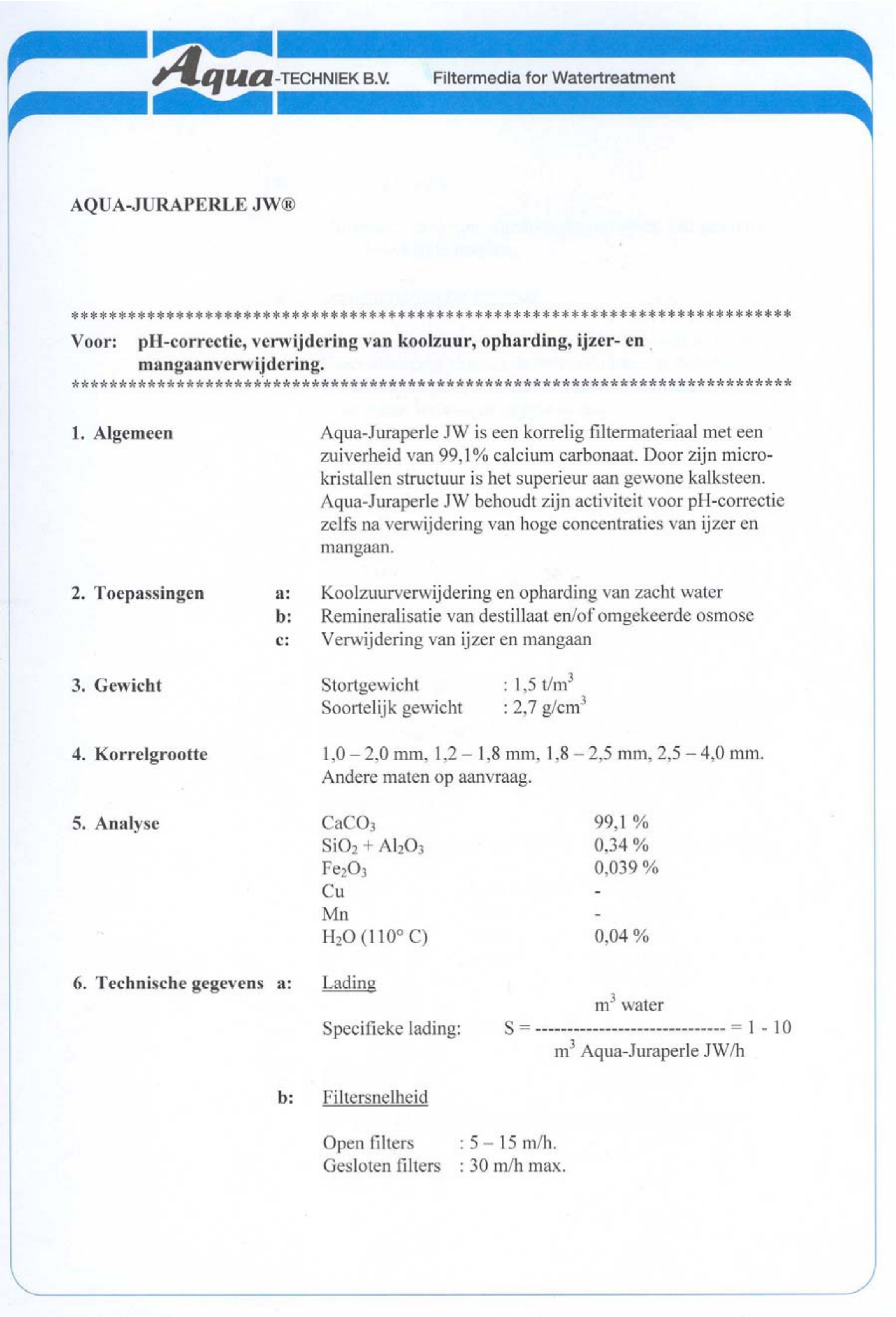
Shells (Source: N. Tilborg [ref. 22])



Methode (gehalte uitgedrukt als)	Resultaten in %		
	Monster 1	Monster 2	Monster 3
Hardheid :			
titrimetrisch (g $CaCO_3$ per 100g schelpen)	98,08	97,6	93,0
conductometrisch (idem)	97,8	97,6	91,1
Fe gehalte :			
g Fe-ionen per 100g schelpen	0,11	0,06	0,05
g Fe_2O_3 per 100g schelpen	0,16	0,09	0,08
Chloridegehalte :			
g Cl^- -ionen per 100g schelpen	0,0	0,0	0,0
Carbonaatgehalte			
titrimetrisch (g $CaCO_3$ per 100g schelpen)	96,7	97,2	93,4
potentiometrisch (idem)	93,2	n.v.t.	n.v.t.
Ca -gehalte (g $CaCO_3$ van de totale hardheid)	99,6	99,56	91,5
Mg -gehalte (g $MgCO_3$ van de totale hardheid)	0,4	0,48	8,5
Droogrest(g onopgeloste deeltjes per 100g schelpen)	0,84	1,40	7,21
Vochtgehalte (g water per 100g schelpen)	0,50	0,34	0,15
Soortelijkgewicht (g schelpen per ml)	2,50	n.v.t.	n.v.t.
Oplosbaarheid	matig	langzaam	snel
Kleur	créme-wit	wit	blauw
Grootte	2 - 2.5 cm	1 - 10 mm	1 - 2 cm

Monster 1: Schelpen van Coronie
Monster 2: Schelpen van Garnizoenspad
Monster 3:Schelpen van Saramacca
n.v.t. = niet van toepassing
Voor verdere uitwerking zie berekeningen.

Crushed limestone (Source: Aqua-Techniek B.V.)



Aqua-TECHNIEK B.V. Filtermedia for Watertreatment

AQUA-JURAPERLE JW®

****

Voor: pH-correctie, verwijdering van koolzuur, opharding, ijzer- en mangaanverwijdering.

****

1. Algemeen

Aqua-Juraperle JW is een korrelig filtermateriaal met een zuiverheid van 99,1% calcium carbonaat. Door zijn microkristallen structuur is het superieur aan gewone kalksteen. Aqua-Juraperle JW behoudt zijn activiteit voor pH-correctie zelfs na verwijdering van hoge concentraties van ijzer en mangaan.

2. Toepassingen

a: Koolzuurverwijdering en opharding van zacht water
b: Remineralisatie van destillaat en/of omgekeerde osmose
c: Verwijdering van ijzer en mangaan

3. Gewicht

Stortgewicht : 1,5 t/m^3
Soortelijk gewicht : 2,7 g/cm^3

4. Korrelgrootte

1,0 – 2,0 mm, 1,2 – 1,8 mm, 1,8 – 2,5 mm, 2,5 – 4,0 mm. Andere maten op aanvraag.

5. Analyse

$CaCO_3$	99,1 %
$SiO_2 + Al_2O_3$	0,34 %
Fe_2O_3	0,039 %
Cu	-
Mn	-
H_2O (110° C)	0,04 %

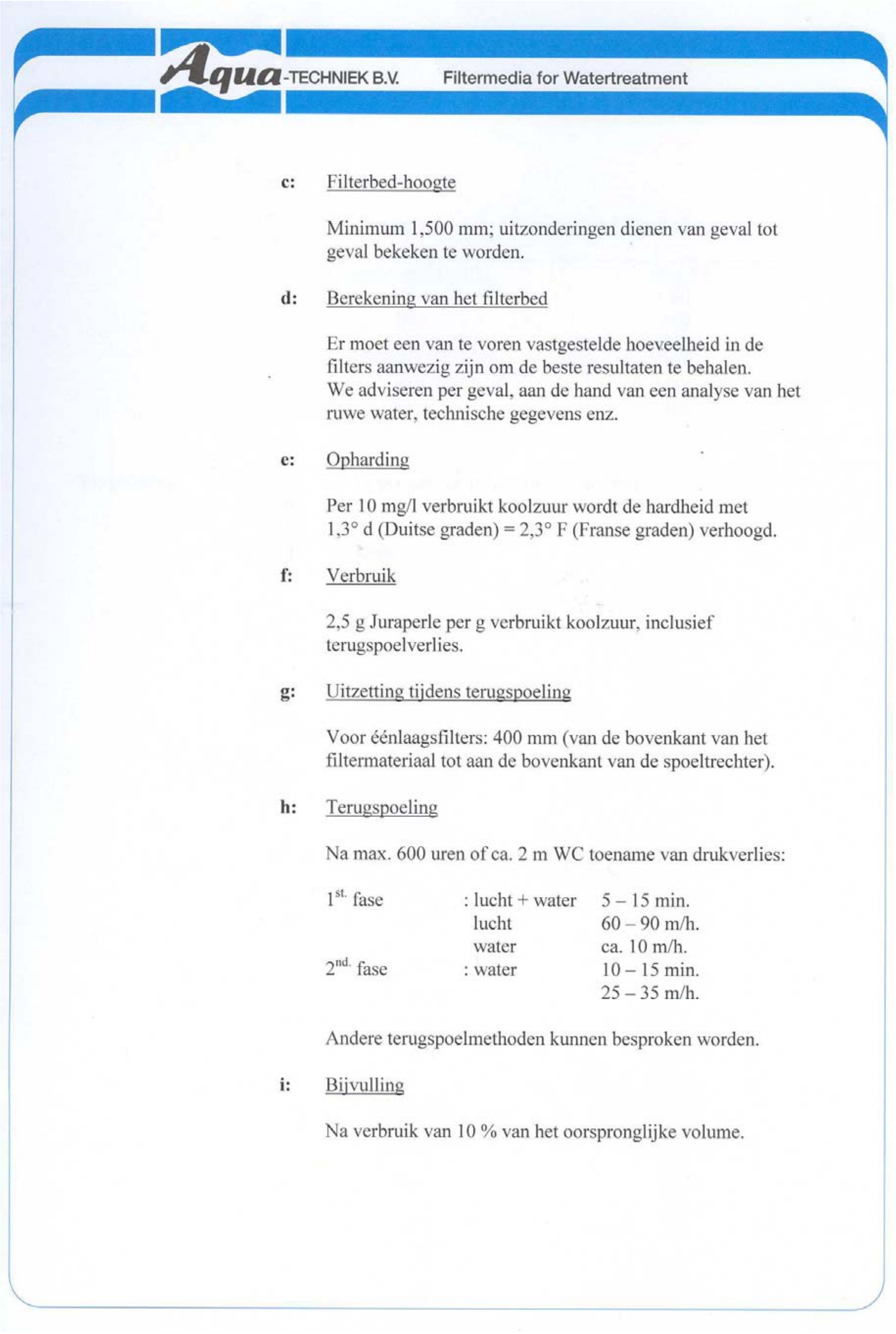
6. Technische gegevens

a: Lading

Specifieke lading: $S = \dfrac{m^3 \text{ water}}{m^3 \text{ Aqua-Juraperle JW/h}} = 1 - 10$

b: Filtersnelheid

Open filters : 5 – 15 m/h.
Gesloten filters : 30 m/h max.



c: Filterbed-hoogte

Minimum 1,500 mm; uitzonderingen dienen van geval tot geval bekeken te worden.

d: Berekening van het filterbed

Er moet een van te voren vastgestelde hoeveelheid in de filters aanwezig zijn om de beste resultaten te behalen. We adviseren per geval, aan de hand van een analyse van het ruwe water, technische gegevens enz.

e: Opharding

Per 10 mg/l verbruikt koolzuur wordt de hardheid met 1,3° d (Duitse graden) = 2,3° F (Franse graden) verhoogd.

f: Verbruik

2,5 g Juraperle per g verbruikt koolzuur, inclusief terugspoelverlies.

g: Uitzetting tijdens terugspoeling

Voor éénlaagsfilters: 400 mm (van de bovenkant van het filtermateriaal tot aan de bovenkant van de spoeltrechter).

h: Terugspoeling

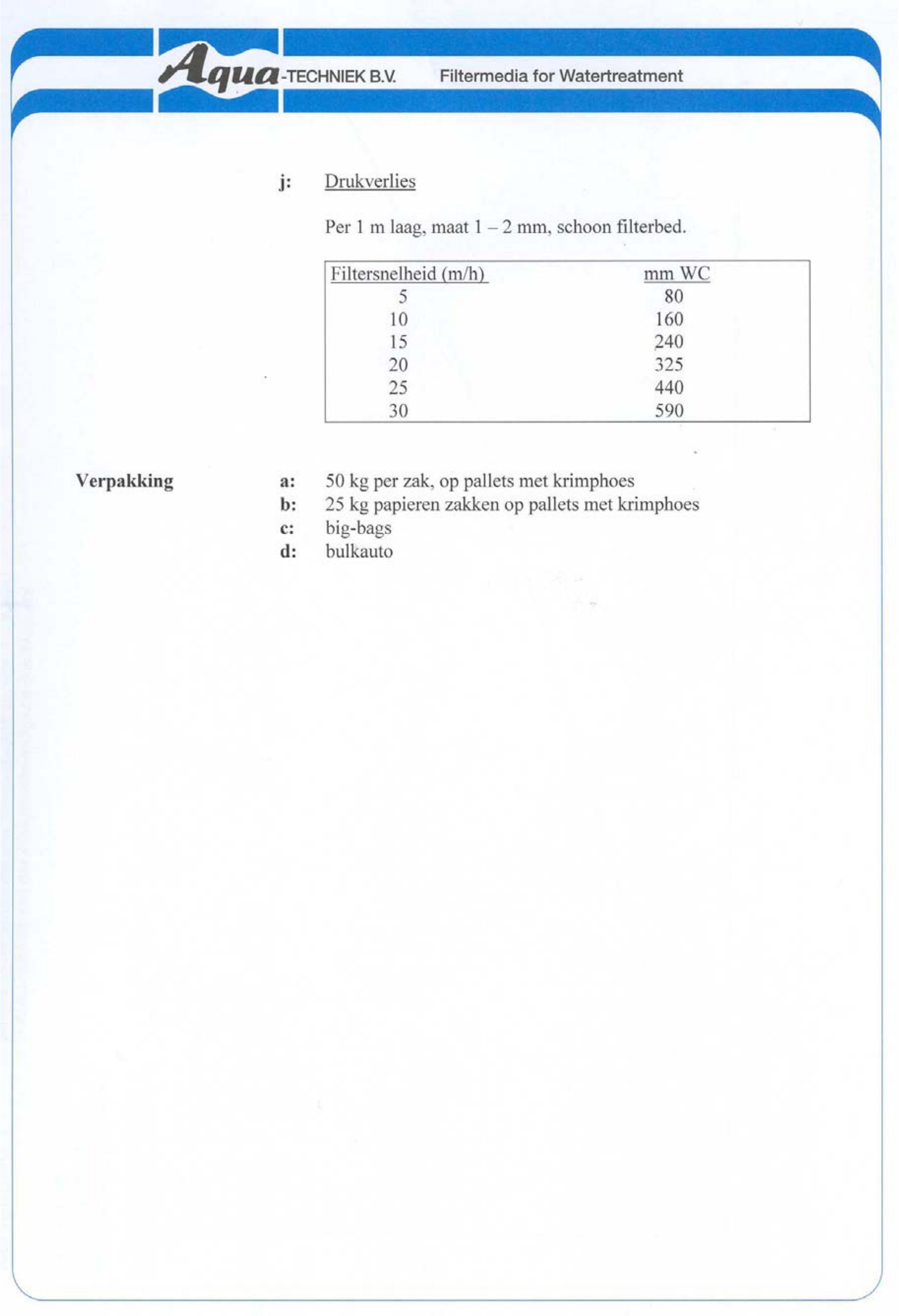
Na max. 600 uren of ca. 2 m WC toename van drukverlies:

1st. fase	: lucht + water	5 – 15 min.
	lucht	60 – 90 m/h.
	water	ca. 10 m/h.
2nd. fase	: water	10 – 15 min.
		25 – 35 m/h.

Andere terugspoelmethoden kunnen besproken worden.

i: Bijvulling

Na verbruik van 10 % van het oorspronglijke volume.



j: Drukverlies

Per 1 m laag, maat 1 – 2 mm, schoon filterbed.

Filtersnelheid (m/h)	mm WC
5	80
10	160
15	240
20	325
25	440
30	590

Verpakking

a: 50 kg per zak, op pallets met krimphoes
b: 25 kg papieren zakken op pallets met krimphoes
c: big-bags
d: bulkauto

Softening pellets

Source:

Sector Water en Natuur / Afdeling Productie / Team Centraalbureau Productie
Waterleidingbedrijf Amsterdam Vestiging Weesperkarspel
Internet: http://www.wlb.amsterdam.nl

Composition nucleus			
Source: Website Aqua-Techniek			
		EN 12910	
Constituent	Chemical analysis	Lower limit	Upper limit
	[mass%]	[mass%]	[mass%]
SiO_2	36.10%	32.00%	42.00%
FeO	29.80%	20.00%	40.00%
$Al6O_3$	20.40%	15.00%	25.00%
Fe2O3	1.70%	0.00%	15.00%
TiO_2	1.80%	0.00%	5.00%
MnO	1.10%	0.00%	5.00%
CaO	1.60%	0.00%	5.00%
MgO	5.50%	0.00%	15.00%
	98.00%		
Ilmeniet	1.50%		
Zironium	0.25%		
Quartz	0.25%		
	100.00%		

Composition nucleus					
Source: Report Internship Stemvers 1981					
Constituent	Component	With sand		Without sand	Without sand
		[mass%]		[mass%]	[mass%]
Cations	Ca^{2+}	25.50%		25.50%	38.46%
	Mg^{2+}	0.21%		0.21%	0.32%
	Fe(2+/3+)	0.01%		0.01%	0.01%
Anions	SO_4^{2-}	0.42%		0.42%	0.63%
	PO_4^{3-}	0.04%		0.04%	0.05%
	CO_3^{2-}	38.49%		38.49%	58.05%
Other	Sand	33.70%			
	Rest	1.64%		1.64%	2.47%
		100.00%		66.30%	100.00%

Bepaling dichtheid pellet-water mengsel					
Primaire invoergegevens	Versie:	2,00			
Volume pellet-water mengsel	V_{pw} =	10	[m³]		
Secundaire invoergegevens					
Gemiddelde korreldiameter afgetapte kalkpellets	d_p =	1,0	[mm]		
Watertemperatuur	T =	12	[ºC]		
Gegevens					
Soortelijke massa granaatkorrels	ρ_g =	4114	[kg/m³]		
Soortelijke massa kalk ($CaCO_3$)	ρ_k =	2671	[kg/m³]		
Gravitatie constante	g =	9,81	[m/s²]		
Porositeit fixed bed (fictief)	ε_0 =	0,38	[m³/m³]		
Berekeningen					
Geschatte watertemperatuur (jaargemiddelde WPK 1991-2003)	T =	9	[ºC]		
Soortelijke massa water	ρ_w =	999	[kg/m³]		
Soortelijke massa kalkpellets	ρ_p =	2685	[kg/m³]	$\rho_{pw} = \rho_p(1-\varepsilon_0)+\rho_w\varepsilon_0$	
Soortelijke massa kalkpellets-water mengsel	ρ_{pw} =	2044	[kg/m³]		
Massa pellet-water mengsel	m_{pw} =	**20444**	[kg]		

Appendix III A: Description jar tests

In this appendix a detailed description is given of the procedures of the jar tests

Procedure 1: Determination stirring speed

The goal of this procedure is to determine which stirring speed will be applied to the jartests. Since the sample taking, the measurements and the analysis of the samples are performed by one person, the choice for the stirring speed is based on the criteria that the change in the increase of the pH is such that there is enough time between the analysis of two samples. This means that the stirring speed must not be too high.

- Place the stirrer and 1 litre distilled water in the 6 beakers
- Set the stirring speed at 70 rpm
- Place the pH electrode in beaker 1 and initiate the online measurement of the pH and the temperature
- Place the conductivity electrode in beaker 2 and initiate the online measurement of the conductivity
- Add 10 gram of whole shells to the water
- Take after 5, 10, 15, 20, 30 and 60 minutes a 50 ml and 100 ml sample from respectively beaker 1, 2, 3, 4, 5 and 6 for the determination of the calcium concentration and the m- number
- Measure the calcium concentration and the m- number
- Repeat the test at 100, 130, 160 en 190 rpm
- Put the calcium and bicarbonate concentrations against the contacttime for the different stirring speed

Procedure 2: Determination material weight

The goal of this procedure is to determine the amount of filter material that will be used to do the jartests. The choice for the weight of the material is made by looking at which weight the process the process speed is not influenced anymore.

- Place the stirrer and 1 litre distilled water in the 6 beakers
- Set the stirring speed at 70 rpm
- Place the pH electrode in beaker 1 and initiate the online measurement of the pH and the temperature
- Place the conductivity electrode in beaker 2 and initiate the online measurement of the conductivity
- Add 40 gram of whole shells to the water
- Take after 5, 10, 15, 20, 30 and 60 minutes a 50 ml and 100 ml sample from respectively beaker 1, 2, 3, 4, 5 and 6 for the determination of the calcium concentration and the m- number
- Measure the calcium concentration and the m- number
- Put the calcium and bicarbonate concentrations against the contacttime for the different stirring speed
- Repeat the jartest with 60, 80 and 100 g whole shells

Procedure 3: Jartests with watertype 1 and all materials

The goal of this procedure is to determine the difference in the effect between the different materials on the neutralization process.

- Place the stirrer and 1 litre distilled water in the 6 beakers
- Add 0.16 ml of the 1M HCl solution to the water

- Set the stirring speed at 70 rpm
- Place the pH electrode in beaker 1 and initiate the online measurement of the pH and the temperature
- Place the conductivity electrode in beaker 2 and initiate the online measurement of the conductivity
- Add 10 gram of the whole shells in every beaker
- Measure every 5, 10, 15, 20, 30, and 60 minutes the pH, the temperature and the conductivity of the effluent en simultaneously take 50 ml sample and a 100 ml sample of the effluent for the determination of the calcium concentration and the m- number
- Repeat the jartest with crushed shells, crushed limestone and softening pellets

Procedure 4: jartests with watertype 2 and all materials

The goal of this procedure is to determine the behaviour of the neutralization process at different watertypes.

- Place the stirrer and 1 litre distilled water in the 6 beakers
- Add 6.65 ml of the 1M HCl solution and 0.42 g of the Sodium carbonate (105.99 g/mol) to the water
- Set the stirring speed at 70 rpm
- Place the pH electrode in beaker 1 and initiate the online measurement of the pH and the temperature
- Place the conductivity electrode in beaker 2 and initiate the online measurement of the conductivity
- Add 10 gram of the whole shells in every beaker
- Measure every 5, 10, 15, 20, 30, and 60 minutes the pH, the temperature and the conductivity of the effluent en simultaneously take 50 ml sample and a 100 ml sample of the effluent for the determination of the calcium concentration and the m- number
- Repeat the jartest with crushed shells, crushed limestone and softening pellets

Appendix III B: Description column experiments

In this appendix a detailed description is given of the different procedures column experiment

Procedure 1

The goal of this procedure is to determine whether the filtration rate is of any influence on the neutralization process

- Fill the column to a height between 0.90 and 1.00 m with shells
- Measure the filterbed height
- Set the flow meter of the effluent, which is demineralized water at 120 l/h
- Set the flow of the HCl solution (0.26 mol/l) at 0.07 l/h
- Set the flow of the effluent at 19 l/h
- Wait for 20 minutes
- Measure the temperature T [^oC], the conductivity [μS/cm] and the pH of the influent
- Take a 50 ml and 100 ml sample from every sample point and determine the calcium concentration and the m-number
- Take a 50 ml sample from every sample point and measure the temperature T [^oC], the conductivity [μS/cm] and the pH
- Keep checking the flow of the influent
- Keep checking the flow of the effluent
- Repeat the whole test for the following filtration rates: 32, 45 and 64 l/h

Procedure 2

The goal of this procedure is to determine the effect of the different materials and water types on the neutralization process

- Set the flow of the of the influent, which is demineralized water, at 120 l/h
- Set the flow of the HCl solution (0.26 mol/l), which is in dosage tank 1, at 0.07 l/h
- Set the flow of the effluent at 19 l/h
- Wait for 20 minutes
- Measure the temperature T [^oC], the conductivity [μS/cm] and the pH of the influent
- Take a 50 ml and 100 ml sample from every sample point and determine the calcium concentration and the m-number
- Take a 50 ml sample from every sample point and measure the temperature T [^oC], the conductivity [μS/cm] and the pH
- Keep checking the flow of the influent
- Keep checking the flow of the effluent
- Set the flow of the HCl solution (1.60 mol/l) at 0.5 l/h
- Set the flow of the Na_2CO_3 solution (0.49 mol/l) at 1 l/h
- Set the flow of the effluent at 32 l/h
- Wait for 20 minutes
- Measure the temperature T [^oC], the conductivity [μS/cm] and the pH of the influent

- Take a 50 ml and 100 ml sample from every sample point and determine the calcium concentration and the m-number
- Take a 50 ml sample from every sample point and measure the temperature T [^{o}C], the conductivity [µS/cm] and the pH
- Repeat the whole procedure for crushed shells, crushed limestone and softening pellets

Determination Bicarbonate concentration [HCO_3^-]

For the determination of the following equipment is used:

- Apparatus; Titrator (fig. 4.4 (a))
- Brand; Metrohm
- Brand Type; 702 SM Tirtrino
- Electrode; 6.0253.100
- Solution; HCl- solution (0.02 M)

The determination of the bicarbonate concentration takes place by dosing HCl to the water until all HCO_3^- ions are transformed into CO_2. At a pH of 4.4 practically all HCO_3^- is transformed into CO_2. At a pH between 4.4 and 8.3 the amount of dosed HCl is equal to the amount of transformed HCO_3^- . After a certain pH the amount of transformed HCO_3^- is equal to the m- number, which is defined as follows:

m- number = $2[CO_3^{2-}] + [HCO_3^-] + [OH^-] + [H_3O^+]$

The determination of the m- number is carried out with a titration apparatus at which the titration curve is drawn. The endpoint at which all HCO_3^- is transformed into CO_2 is and the accompanying pH with the amount of dosed HCl is shown.

The determination of the m- number is done as follows:

- Fill the burette of the titration apparatus with the HCl solution
- Pipette a 100 ml of the sample in a 250 ml beaker
- Put a magnetic stirrer in the sample, place the beaker in the titration apparatus under constant stirring
- Rinse the electrode and syringe of the burette with demineralized water and place the electrode and the syringe in the sample without touching the glass or the stirrer
- Initiate the titration
- If the titration has reached the endpoint the titration can be stopped

Determination of the calcium concentration

For the determination of the calcium concentration the following equipment is used:

- Apparatus; Digital buret (fig. 4.4. (b))
- Brand; Rudolf Brand
- Brand Type; Bürette digital
- Solution;
  - KOH- solution (1M)
  - EDTA- solution (0.01 M)
- Indicator; murexide/KCl (mass proportion 1:500)

The calcium concentration is determined by means of titration with an EDTA solution.

- Pipette 50 ml of the sample or a smaller sample which is diluted until 50 ml to reach 2 – 6 mg
- Put a magnetic stirrer in the beakerglass
- Add 2 ml potassium hydroxide and start stirring
- Add 100 mg murexide and keep stirring
- Attach the beakerglass to the standard. Adjust the height in such a way that the tip of the buret is immersed in the sample
- Titrate with the EDTA solution (0.01 M = t_e) until a colour change occurs from pink to purple. The equivalent point is reached if extra dosing of EDTA does not give more colour change. The amount of dosed EDTA is equal to V_e

The calcium concentration is calculated as follows:

$$[Ca^{2+}] = \frac{V_e * t_e * 1000}{V_m} \text{ mmol/l}$$

In which:

V_e = amount of dosed EDTA [ml]
t_e = EDTA concentration= 0,01 M = 0,01 mol/l
V_m = volume sample

Figure 4.4. (a) Apparatus for m- number analysis (b) Apparatus for calcium analysis

Conductivity

The conductivity is measured with a conductivity meter. The specifications of the meter are the following:

- Brand; WTW
- Type; Cond 197i
- Serial number; 03490007
- Electrode; Tetracon 325

pH

The pH is measured with a pH meter. The specifications of the pH meter are the following:

- Brand; WTW
- Type; pH 197i
- Serial number; 05240069
- Electrode; senTix 41-3

Temperature

De temperature is measured with the pH- meter.

The pH- and conductivity- measurements of the jartests are continuous online measurements. These measurements take place by keeping the electrodes in the beakers throughout the experiment. The apparatus is connected to a personal computer. By means of the programme Multilab the measurements are directly on the computer.

With the columntest online measurements are not possible. The pH and conductivity measurements of the columntests are discrete measurements. These measurements take place by collecting a sample at a certain time and then measuring the pH, the conductivity and the temperature by submerging the electrode in the sample

Appendix IV: Results column experiments with water type 2

In this part the results are given of the column experiments with water type 2 and varying materials.

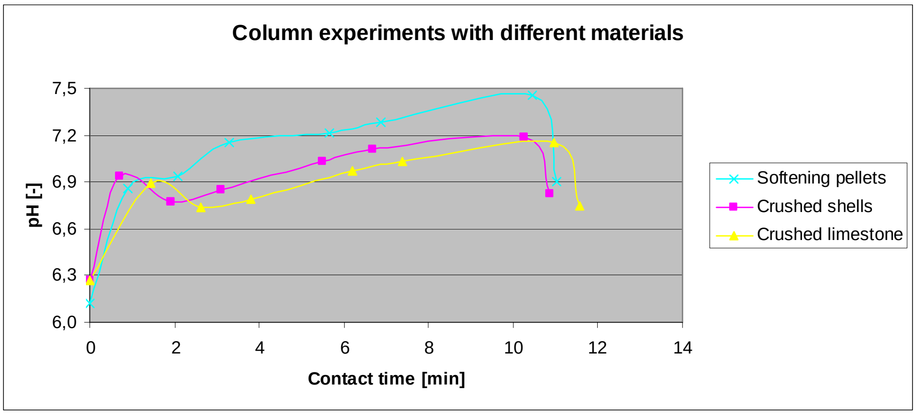


Figure 5.23 Increase of pH in time at varying materials and with water type 2

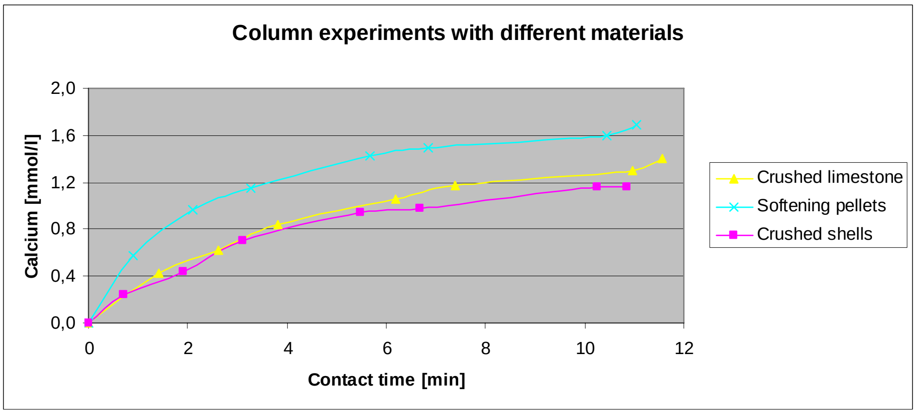


Figure 5.24 Increase of calcium in time at varying materials and with water type 2

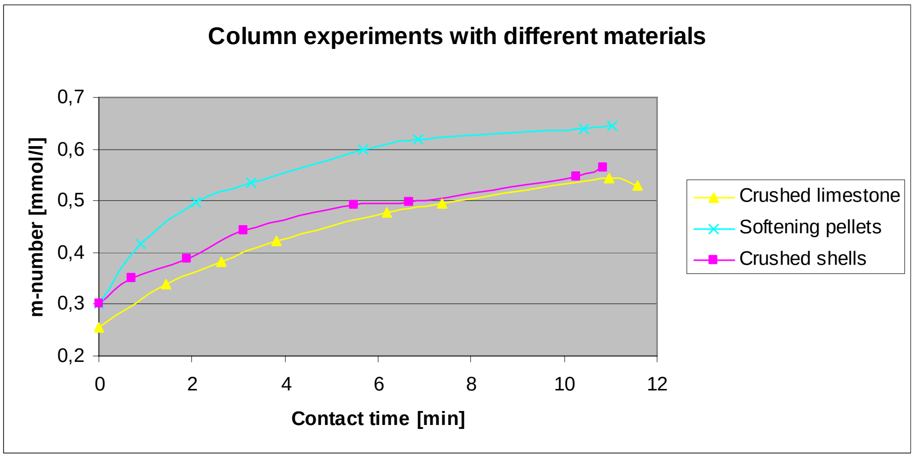


Figure 5.25 Increase of m-number in time at varying materials and with water type 2

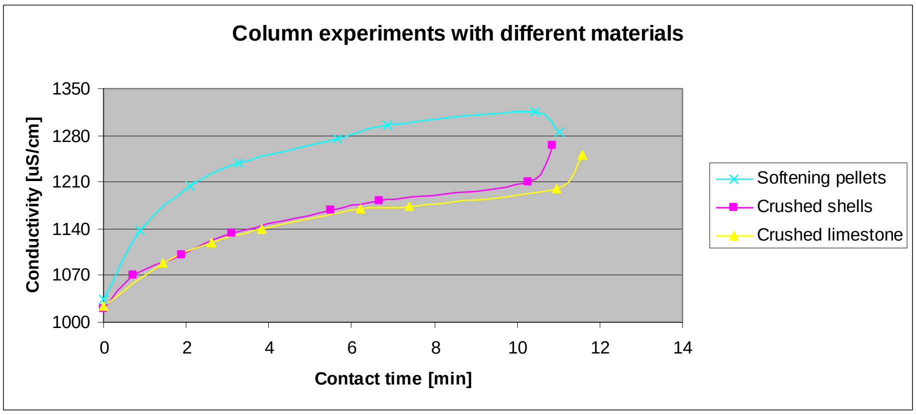


Figure 5.26 Course of conductivity in time at varying materials and with water type 2

With water type 1 the necessary contact time to reach the equilibrium-pH is shorter than for water type 2. With water type 1 the equilibrium-pH of 9 is reached after 6 minutes and with water type 2 after longer than 12 minutes. This is on the one hand explained by the SI of the water. The SI of water type 1 is -5.7 and -1.1 for water type 2. The conditioning rate increases with decreasing SI. On the other hand the difference in conditioning rate between water type 1 and water type 2 is caused by the presence of bicarbonate in water type 2. Due to the presence of bicarbonate, buffering takes place during the conditioning process. As a result the conditioning rate is decreased.