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Master Thesis

Treatment of Polymer Containing Oilfield Water for Re-injection – Field Tests with a Pilot Plant

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AFFIDAVIT

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Abstract

Treatment of Polymer Containing Oilfield Water for Re-injection

Field Tests with a Pilot Plant

Formation water that is co-produced with the production of petroleum needs to be collected and treated prior to re-injection into the reservoirs. The treatment of the produced water is important in order to keep the injection pressure as low as possible. A new water treatment plant is under construction at the moment and will start operating by 2014. Since 2012 OMV Austria Exploration & Production GmbH operates a polymer flooding pilot in order to increase the recovery factor of their mature oil fields. As a result polymer will also be back-produced and could therefore enter the new water treatment plant within the feed. This would lead to a decreased separation efficiency in single processing steps and to a reduced injection water quality.

The water treatment process under the influence of the polymer was simulated with a water treatment pilot plant, which works with the same process steps than the future new water treatment plant. Chemical sets of flocculants were tested regarding the achievable hydrocarbon content and filterability of the water after dissolved gas flotation. In a second set of tests, the separation efficiency and the operating behavior of the final filtration process with nutshell granules were tested as well.

The application of polyaluminum chloride for flocculation and subsequent flotation has proven to be promising at low polymer concentrations. In the tests with the nutshell filter the required water quality for re-injection could be achieved. However the operating behavior of the nutshell filter was influenced by residual polymer. The long-term impact of the polymer on the nutshell granules' capacity for oil separation and on the operational behavior of the nutshell filter needs to be investigated in further tests.

Kurzfassung

Aufbereitung von Polymer-haltigem Erdölbegleitwasser für die Rückverpressung

Feldversuche mit einer Pilotanlage

Formationswasser, das bei der Erdölförderung mitproduziert wird, muss gesammelt und für die Rückverpressung aufbereitet werden. Die Aufbereitung des produzierten Wassers ist notwendig, um den Einpressdruck in die Lagerstätte möglichst gering zu halten. Eine neue Wasserflutanlage befindet sich derzeit in Bau und wird 2014 in Betrieb gehen. Die OMV Austria Exploration & Produktion GmbH betreibt seit 2012 einen Pilotversuch zur Steigerung der Ausbeute ihrer bereits lang produzierenden Ölfelder mit Hilfe von Polymerfluten. Daher wird auch Polymer rückproduziert werden und könnte in Zukunft im Zulauf der neuen Wasserflutanlage enthalten sein. Daraus würden eine Verringerung der Abscheideleistung in einzelnen Prozessschritten und eine Verschlechterung der Einpresswasserqualität resultieren.

Der Wasseraufbereitungsprozess unter dem Einfluss von Polymer wurde zu Testzwecken mit einer zur neuen Wasserflutanlage verfahrensgleichen Pilotanlage nachgestellt. Ziel war die Erprobung flokkulationsfördernder Chemikaliensets hinsichtlich des erreichbaren Kohlenwasserstoffgehalts und der möglichen Filtrierbarkeit des Wassers nach Entspannungsflotation. Ebenso untersucht wurden die Abscheideleistung und das Betriebsverhalten der abschließenden Filtration mittels Nussschalengranulat.

Die Anwendung von Polyaluminiumchlorid für die Flockung und die anschließende Flotation hat sich bei niedrigen Polymerkonzentrationen als vielversprechend erwiesen. In den Versuchen mit dem Nussschalenfilter konnte die erforderliche Wasserqualität für die Rückverpressung in die Lagerstätte erreicht werden. Allerdings zeigte sich das Betriebsverhalten des Nussschalenfilters von Restpolymer beeinflusst. Langzeitauswirkungen des Polymers auf die Ölabscheidefähigkeit des Nussschalengranulats und auf das Betriebsverhalten des Nussschalenfilters sind in weiteren Untersuchungen abzuklären.

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APPENDIX I

1 Introduction

1.1 About the Subject Matter of this Thesis

The subject of this thesis is an investigation to the treatment of water that is coproduced with crude oil. This water is a mixture of formation water, some condensed water and injection water from water flooding operations, but partly also from a polymer flooding pilot operation. Formation water is associated with petroleum in a reservoir. Originally, due to its higher density, it is found beneath the petroleum. In the exploitation of mature fields the produced water is re-injected. This way it is used to sweep the petroleum out of the reservoir. To be suitable for re-injection, the produced water has to be treated.

1.1.1 Enhanced Oil Recovery by means of Polymer Flooding

Polymer flooding is a specific type of tertiary oil recovery methods summarized under enhanced oil recovery (EOR). EOR methods are used when primary (e.g. water or gas cap drive) and secondary (injection of water) recovery methods are becoming uneconomic.

Polymer flooding belongs to the group of chemical EOR methods. Basically this method consists of mixing a suitable polymer with the injection water. The result is an augmented water viscosity which leads to a more efficient displacement of the oil in place (see **Figure 1-1**).

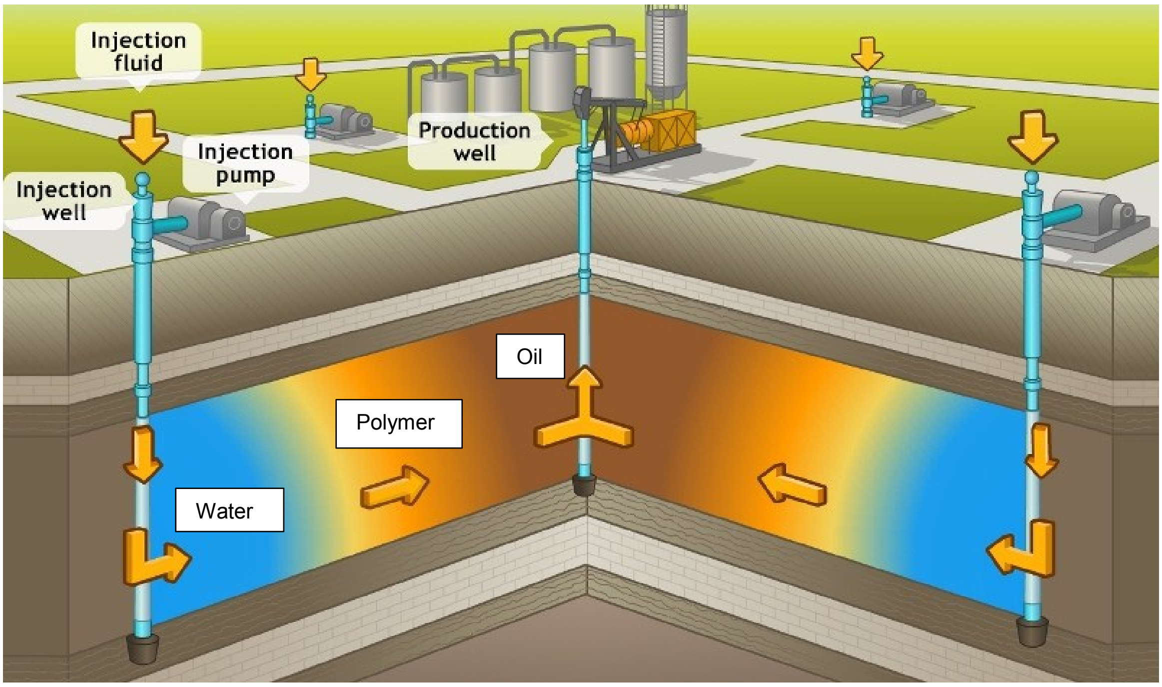

Figure 1-1: Enhanced oil recovery (EOR) by polymer flooding (SNF S.A.S.)

1.1.2 Petroleum Production in the Matzen Oil Field

Oil and gas is produced from the Matzen field by OMV Austria Exploration & Production GmbH (OMV AUT), situated in the Vienna Basin. 820 000 tons of oil are produced per year which amounts approximately to 10 % of the Austrian demand for oil (OMV Austria Exploration & Production GmbH, 2012). The field is under water flood to increase the hydrocarbon recovery and thereby the economic lifetime of the field. The percentage of produced water compared to oil (water cut) is 93% (OMV Austria Exploration & Production GmbH, 2012). Based on the expertise in adequate produced water treatment an excellent injection water quality is provided and helps to maintain production still profitable (Radauer, 2007 p. 2).

The produced volumes of water and crude oil from the production wells are transferred to gathering stations where the produced fluid is separated in oil, gas and water. Separated oil is routed to the tank farm Auersthal where it is stored for the transfer to the refinery Schwechat while separated gas is sent to the compressor station Auersthal. Produced water is pumped to the water treatment plant (WTP) Schönkirchen, where remaining oil is removed and treatment for re-injection takes place.

OMV AUT operates a polymer flooding pilot in the Matzen field. Part of the polymer research is the water treatment pilot investigating influences of polymer on the water treatment process.

1.1.3 Reasons and Importance for Produced Water Treatment

For a successful and profitable recovery of oil by means of processes that involve fluid injection, it is most important to inject the fluid at the lowest possible pressure (Ostroff, 1979 p. 302). Therefore the purpose of water treatment is, to achieve the lowest necessary content of substances with reservoir blocking potential. Within the treatment process remaining oil and suspended solids have to be removed. All of those substances could lead to plugging of injection wells or they could plug the pore spaces of the formation. Furthermore bacterial activity leading to corrosion and fouling problems has to be prevented.

The required quality of injection water for water flooding purposes is determined by the pore size and the porosity of the reservoir rock. The bigger the pore size and the higher the porosity are, the less the necessary quality of injection water has to be. (Ostroff, 1979 p. 311)

Using polymer flooding instead of water flooding, an even higher quality of injection water is required, because polymers can interact with substances contained in the water leading to the generation of unwanted and disturbing products. Another important issue is the control of microbes in the injection water. Due to the long residence time of produced polymer solution in maturation tanks, microbes have time to grow and generate biomass.

1.1.4 Water Treatment Plants Schönkirchen

Since the 1960s the water treatment plant Schönkirchen, named existing water treatment plant (existing WTP) in this thesis, treats the water that is coproduced with crude oil for re-injection into the reservoirs. OMV intends continuing the recovery of oil and gas in the Vienna Basin for another 30 years. The existing water treatment plant will in future not comply with the legal and environmental regulations anymore. The optimization of the plant is not possible under economic aspects. That is why OMV AUT planned the construction of a new water treatment plant (new WTP) according to the state of the art (Ramler, 2008 p. 2). At the moment the new WTP is being constructed and should start operating in 2014. Until then the produced water is going to be treated at the existing WTP.

Following, the consecutive process units of the existing and the new water treatment plant are listed.

Existing water treatment plant:

- First sedimentation basin
- Combined flocculation and flotation
- Activated-sludge basin
- Second sedimentation basin
- Sand filter

New water treatment plant:

- Corrugated plate interceptor (CPI)
- Combined flocculation and flotation
- Nutshell filter (NSF)

The new WTP is a closed system. All processing units are blanketed with a nitrogen atmosphere. This allows an anaerobic process, which prevents the formation of oxygen containing corrosion products and suppresses the activity of aerobic microbes. Further there are no emissions of CO_2, H_2S and VOC (especially CH_4) due to the closed system. Operating security is enhanced this way, because the formation of explosive atmospheres is prevented. Also environmental odor nuisance can be avoided. Another benefit is, that only a fifth of the space of the existing WTP is needed. (OMV Austria Exploration & Production GmbH, 2012)

1.2 Project Challenges and Expectations

In 2012 OMV AUT started a polymer flooding pilot operation. Therefore, injection water is mixed with a polymer solution and injected into the 8th Tortonian Horizon (8. TH) of the Matzen field. The goal of this project is to increase the recovery factor of the mature reservoir. The used polymer is a medium charged anionic copolymer of acrylamide and sodium acrylate monomers with an ultra-high molecular mass. Due to its polyelectrolyte nature it is soluble in water. The trade name of the polymer is Flopaam 3630 S. As a result of the polymer flooding operation, polymer will also be back-produced and could therefore enter the new WTP within the feed.

However, neither the existing WTP, nor the new WTP are designed for this case. Eventually all process stages could be affected. With respect to the future new WTP the following problems are expected and of importance:

- Decreased hydrocarbon separation efficiency of the combined flocculation and flotation unit
- Plugging of the NSF due to the very large size of polymer molecules, leading to a reduction of the operating period before regenerative back-washing is necessary

At the moment, back-produced polymer would concern the existing WTP. In future, after completion and startup, the new WTP would be concerned and the negative impacts mentioned above could disturb the water treatment process. A change of the designed process is not possible, as the new WTP is already in construction. Hence the following questions arose:

- What is the impact on separation efficiencies regarding oil and suspended solids with Flopaam 3630 S in the feed?
- At which limits could be operated with polymer-containing produced water?
- To which extend of polymer in the feed an acceptable and stable quality of injection water can be achieved after treatment?
- How could the different separation units be affected?

The amount of Flopaam 3630 S in the feed of the new WTP is hard to predict. When back-produced, a maximum content of 12 ppm of polymer is expected under current operating conditions (May, 2013), though a concentration of 8 or only 6 ppm is more likely. In section 3.4.4 underlying assumptions for this estimation are presented.

In order to achieve the required water quality for re-injection specified water qualities must be met after each process step of the new WTP. The same qualities also must be reached with produced water containing polymer from the polymer flooding pilot operation. For specifications of water qualities after each process step see section 3.3.

A technical solution to compensate the impact of Flopaam 3630 S on the water treatment process of the new WTP is the application of adequate chemical agents for an optimum efficiency of the dissolved gas flotation.

1.3 Tasks and Scope

When designing the process of the new WTP, a pilot plant was built, which has been used to operate the water treatment process of the new WTP on a small scale in order to gather information for the future full scale operation. The application of chemical flocculation agents prior to flotation was part of the testing at this stage. Within the scope of the water treatment pilot project which was started as a consequence of the polymer flooding pilot operation, those formerly tested flocculation agents were supposed to be tested again under the influence of Flopaam 3630 S. Therefore, stock solution of Flopaam 3630 S was added to the feed of the pilot plant and the performance of the combined flocculation and flotation unit was tested *in a first stage of testing* (pilot plant experiment 1 to 4). The selected chemical agents were added single or in combination prior to flotation in order to test their efficacy for removing emulsified oil and suspended solids under the influence of the polymer. The result should point out the set of chemicals that performs best and leads to the lowest hydrocarbon contents after flotation.

Four of such distinguished chemical sets of flocculating agents were supposed to be tested. Three of them have already been successfully tested with regular water from water flooding operations only as it was mentioned above, whereas the forth chemical agent (Floquat FL 2949) was specially recommended by the manufacturer for the flocculation of Flopaam 3630 S and was tested in a previous laboratory test as mentioned later on. The selected chemicals are described and listed in section 3.5.

In a second stage of testing (pilot plant experiment 5), a performance test was also conducted for the nutshell filter with the assumption of back-produced polymer. Therefore, oilfield water containing Flopaam 3630 S was treated with the best performing set of chemical agents, evaluated in the first stage, and then fed to the nutshell filter to observe its impact.

During the tests the hydrocarbon separation performance of the CPI under the influence of Flopaam 3630 S was observed as well. A strong impact was not expected, because the raise in viscosity due to the added polymer is assumed to be too little. Contamination by flocked or precipitated cross-linked polymer could be possible.

The parameters observed and analyzed for a thorough evaluation of the tests described above are:

- Hydrocarbon contents at inlet and outlet of all separation units inclusive the efficiency calculations;
- Filterability of the treated water after the flotation, which is an important characteristic for the successful subsequent filtration;

- Filterability of the treated water after the nutshell filter, which is an important characteristic for a successful re-injection and a successful production of polymer solution for the polymer flooding operation;

- Concentration of suspended solids, because they contribute to filterability of treated water;

- Concentration of iron (solid and dissolved);

- Turbidity (as supplementary parameter which is used for information but is not evaluated, see 3.7.5);

- Operating period and plugging behavior of the nutshell filter;

- Ratio of consumed back-washing to filtered water for regeneration of the nutshell filter.

Additionally it was observed if

- flocs were present in the treated water after flotation as a sign of prolonged floc formation or insufficient separation of the flocs in the flotation process;

- jellylike precipitates from flocked or cross-linked polymer contaminated the CPI.

It was not possible to visually investigate the flocs after the flocculation of the added chemicals, nor could the flotation process be observed itself. The vision panel in the flotation reactor was not transparent any more due to adhering ferrous sulfide.

2 Theory of Precipitation and Flocculation

Since precipitation and flocculation are crucial mechanisms for the separation of impurities from water, the most important mechanisms are described in the following sections.

2.1 Definitions

Precipitation, in a simplified way, is the formation of a solid phase from two or more dissolved (usually ionic) components. In contrast flocculation is a process without phase transition. With flocculation small suspended solids form bigger collectives. (Hahn, 1987 p. 19) Both processes play an important role in water treatment. Referring to the concepts described in 2.3.1 and 2.3.2 flocculation is also called coagulation.

2.2 Stability of Suspended Particles

Almost all suspended particles have negative surface charges at usual conditions. For that reason they repel each other which contributes to the stability of a suspension. On the other hand there are attracting forces between particles, the so called Van-der-Waals forces. They result from dipole-dipole interactions, when particles come very close to each other. Considering the two effects particle attraction or repulsion is mainly a function of the distance between them. (Hahn, 1987 pp. 33-35)

2.3 Destabilization of Suspended Particles

There are two concepts explaining the destabilization of a suspension leading to coagulation of suspended particles. They are explained in 2.3.1 and 2.3.2. Another way to explain the destabilization of a suspension is the concept of flocculation with organic flocculants. Suspended particles can also be included into precipitating inorganic flocculants. Last coagulation and flocculation can be combined in subsequent steps to generate stable macroflocs.

2.3.1 Coagulation by Double Layer Compression

Suspended particles are surrounded by a double layer of water (see **Figure 2-1**). The layers contain ions of the opposite charge of the particles surface charge (counter ions). The inner layer, called Stern layer, is bound to the particle and moves with it. It is densely charged with counter ions. The outer layer, called diffuse layer, is free and moves with the bulk phase. (Quantachrome Instruments, 2013) Counter ions compensate the surface charge of a particle. The more counter-ions in the double layer and the higher their charge (e.g. divalent or trivalent), the less space is needed to compensate the charges and the thinner the layers are, especially the outer one. As a result with dosage of counter ions the double layer gets compressed and the particle destabilizes, which eventually leads to floc formation, when the particles approach each other close enough. (Hahn, 1987 pp. 36-38)

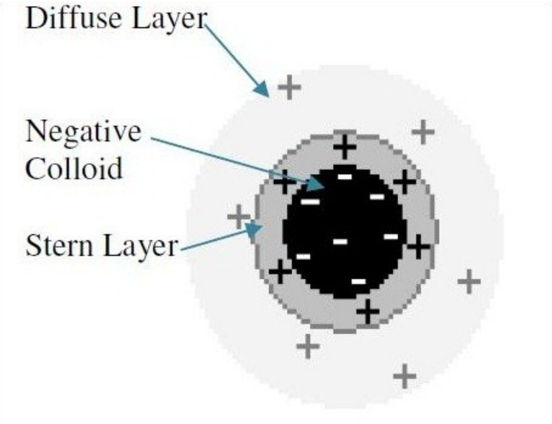

Figure 2-1: Schematic sketch of the double layer surrounding a charged particle (Quantachrome Instruments, 2013)

2.3.2 Coagulation by Change of Surface Charge

The surface charge of particles can be changed by chemical adsorption of cationic ions. The adsorption happens according to isotherms (Freundlich or Langmuir). With increasing amount of adsorbed cationic ions the surface charge changes to more positive values. To induce floc formation, the surface charge of particles has to be neutralized to the isoelectric point. In this point particles can easily approach each other and form bigger compounds, the flocs. But it is important, that the concentration of the neutralizing species is not too high, because the overall surface charge of the particles can even get positive and the particles stabilize again.

Especially hydroxide complexes of multivalent metal ions are very effective in changing the surface charge of particles by chemical adsorption. The hydroxide complexes of aluminum for example can have the following molecular formula:

Monoaluminum hydroxide complex: $Al(OH)_n^{+(3-n)}$

Polyaluminum hydroxide complex: $Al_m(OH)_n^{+(3m-n)}$

The dosage of charge changing agents is proportional to the specific surface charge and the size of the particles surface. The pH of the suspension is very important in this process of destabilization, because it contributes to the surface charge of the particles. An overdose of surface charge changing agents has to be avoided, because it can lead to recurring stabilization of the suspension, as it was stated above.

Usually in water treatment the dosage of an inorganic flocculant is constant, but the concentration of suspended particles in the feed varies. This leads to a fluctuating efficiency of the coagulation process. It is advantageous, that flocs forming by this mechanism, are dense and their water content is low. (Hahn, 1987 pp. 38-40).

2.3.3 Destabilization of Suspended Particles by Flocculation

Flocculation is also a concept to describe the destabilization of suspended particles. There are two mechanisms:

One is the formation of a permanent bridges between suspended particles by adsorption to the flocculant. The mechanism is called polymer bridging. The efficiency of flocculation depends on the concentration of the flocculant and on the places available for adsorption on the surface of the particles.

The other is the flat adsorption of the flocculant onto the particles' surface forming a polymer patch. This way the surface charge is changed in the places of adsorption and the destabilized particles finally coagulate. The mechanism is called polymer charge patching.

Flocculants are mostly organic polymers of a specific molecular mass with or without charge. There are cationic (positively charged) and anionic (negatively charged) polymers, but also nonionic polymers.

The surface charge of suspended particles and their concentration in suspension are important for the dosage of flocculants. The pH of the suspension plays an important role with flocculation. Recurring stabilization of the suspended particles can occur after overdosing.

The flocs formed due to polymer bridging form three dimensional nets. The flocs are big and light and usually incase a lot of water. (Hahn, 1987 pp. 40-43)

2.3.4 Inclusion of Suspended Particles by Precipitating Flocculant

At medium pH of a suspension and the dosing of metal ions as flocculant to a suspension, metal hydroxides form and precipitate including small suspended particles. In most practical applications the generation of metal hydroxide flocs cannot be avoided, but very small suspended and persistent particles can effectively be included this way. If this effect is desired, the dosage of the flocculant has to be high enough. An intermediate pH of suspension is crucial for the formation of metal hydroxides. The effectiveness of inclusion increases with increasing dosage of flocculant. There is no recurring stabilization with an overdose of metal ions. The resulting flocs are fragile and contain a lot of water, which can cause problems in phase separation (e.g. flotation). (Hahn, 1987 pp. 43-45)

2.3.5 The Concept of Combined Coagulation and Flocculation

Organic flocculants are often used as flocculation aids in water treatment. The basic concept is the following: First an inorganic flocculant is added to coagulate the suspended solids to microflocs. Then an organic flocculant is added to promote the formation of macroflocs. (Hahn, 1987 p. 36) The flocculant leading to coagulation of the suspended particles can also be called coagulant in this case.

2.4 Zeta Potential Measurement

As it was described above suspended particles are surrounded by a double layer of water containing ions compensating the surface charge of the suspended particles (Ostroff, 1979 pp. 36-37). There is a potential difference between the Stern layer and the solvent. This potential difference is called zeta potential. It can be measured by means of electrophoresis of suspended particles in an electric field. In fresh or waste water treatment zeta potential measurement is used to determine the required dosage of flocculant. Commonly it is not used in produced water treatment. Highly saline water like produced water has a very high permittivity leading to very small values of the zeta potential with questionable significance. (Ostroff, 1979 p. 230), (Quantachrome Instruments, 2013)

2.5 Process of Floc Formation

Flocculation of suspended particles is the result of two subsequent steps:

- Destabilization
- Transport for collision and coagulation

The concepts of destabilization of suspended particles were described above. The reaction time for the destabilization is determined by the time for activation of the destabilizer (hydrolysis[1]) and the time for adsorption onto the particles' surface.

The transport of suspended particles towards each other for collision happens in two ways: by diffusion, caused by Brownian motion and by dispersion, caused by velocity gradients. The collision results in coagulation of the particles. The particle number decreases with ongoing coagulation. The speed of coagulation is determined by the number of collisions in time. In reality not every collision leads to coagulation. The reasons therefore are: incomplete particle destabilization and the fact that the coagulation speed decreases with increasing particle size. These considerations lead to the definition of the collision efficiency. Chemists are challenged to find the right flocculant and their application in the right concentration in order to optimize the collision efficiency. In case that the transport step determines the coagulation speed, process engineers need to optimize this step providing sufficient collision frequency. The collision frequency is influenced by physical parameters. If the destabilization step is slower than the transport step, chemical parameters are of greater significance. (Hahn, 1987 pp. 46-52)

2.5.1 The Transport Step Described by a Kinetic Model

There is a kinetic model describing the step of transport. It is assumed that the destabilization of the particles happens quickly compared to the transport step. So the transport step determines the coagulation speed. In technical applications transport by

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[1] Hydrolysis is the reaction of polyvalent metal ions with water leading to the formation of hydroxylated, soluble compounds like e.g. $Al(OH)^{+2}$, $Al(OH)_2^{+1}$, $Al(OH)_4^{-1}$.

dispersion is dominant over transport by diffusion. The kinetic model shows that coagulation speed increases with energy input (by mechanical or hydraulic mixing) and/or increasing residence time. The comparison of real coagulation behavior with the results from the kinetic model shows, that adaptions have to be made to account for the influences of the reactor geometry, of the geometry of the used mixer and even of the mixing speed. In order to compensate a short residence time, the energy input can be increased so that sufficient coagulation is reached. Limiting is the fact that at some point flocs are destroyed again by too much energy dissipation.

The kinetic model is exactly valid for solid particles of spherical shape, laminar current, monodisperse suspensions, uniform energy dissipation and uniform retention time distribution. In reality particles are of different shape, the current is turbulent, suspensions are polydisperse and energy dissipation as well as residence time distribution is not uniform. But with some constraints the kinetic model is still valid for real systems. (Hahn, 1987 pp. 62-82)

2.5.2 Phases of Floc Formation

The floc formation can be divided in three phases according to the type of flow that is prevailing:

1.) Mixing in of the flocculant

2.) Coagulation of suspended particles to flocs

3.) Growth of Flocs

In the first phase the flocculant has to be rapidly dissolved. That’s why a very turbulent flow is needed generated by violent mixing.

In the second phase the destabilized particles have to get in contact in order to grow to microflocs. Therefore intermediate mixing at lower speed is necessary.

In the third phase flocs have to build up. Therefore slow movement is important. The agitation should be sufficient for collision and ongoing coagulation to macroflocs, but not too vigorous to break up the flocs again. (Ostroff, 1979 pp. 210,219,220)

2.5.3 Influences on Reaction Time of Floc Formation

The period of time needed to complete the formation of large impurity charged flocs comprises the time for coagulation and for flocculation. The reaction time for coagulation is dependent on the concentration of the coagulant; the higher its concentration the faster the reaction. Furthermore it is important that the pH of the treated water is in the right range for the efficient use of the selected flocculant. Each flocculant has an optimum range of pH in which it works best. Temperature is also an important factor. The time for coagulation is chiefly influenced by temperature. Coagulation works better at higher temperatures. (Ostroff, 1979 pp. 219-220)

2.6 Chemical Agents for Floc Formation

2.6.1 Inorganic Flocculants

The most important inorganic flocculants are metal salts. They usually are acidic in nature (Ostroff, 1979 p. 219). Examples are ferrous/ferric salts and aluminum salts or calcium salts. Other inorganic substances used as flocculants are activated aluminum, kaolinite (aluminum silicate) and bentonite (colloidal clay). They do not dissolve in water. Their most important function is the adsorption of dissolved substances that usually cannot be flocked.

Ferric and aluminum salts exist in different forms depending upon the pH of the suspension. At low pH iron and aluminum exist as hydrated ions so called aquo complexes. They lead to coagulation by double layer compression of suspended particles. According to the rule of Schulze-Hardy due to their higher charge density they are more effective than bivalent cations, like calcium ions, or monovalent cations, like sodium ions. At medium pH of a suspension iron/aluminum hydroxide complexes exist. They are strongly adsorptive and change the surface charge of suspended particles. They are more effective in destabilizing suspended particles than hydrated ferric or aluminum ions. Polymerized aluminum salts, e.g., polyaluminum chloride (PAC) are even more effective than the mono-aluminum hydroxide complexes caused by their even higher density in charge. At neutral pH and high dosage of iron or aluminum metal hydroxide flocs form. During the precipitation they include suspended particles as it also was described above. (Hahn, 1987 pp. 85-91, 96)

Summarizing, the destabilization mechanism of aluminum or iron salts depends on pH of suspension and their concentration. At low pH they lead to destabilization by double layer compression of suspended particles. At middle pH and low concentration they lead to destabilization by change of surface charge of suspended particles. At middle pH and high concentration they lead to precipitation and simultaneous inclusion of finely dispersed suspended particles. The mechanisms of destabilization discussed above, can be explained with the knowledge of thermodynamic behavior of the metal salts in solution. There are thermodynamic diagrams describing the configuration of a dissolved metal salt depending on concentration and pH of the suspension. **Figure 2-2** shows such a diagram for ionic aluminum in water.

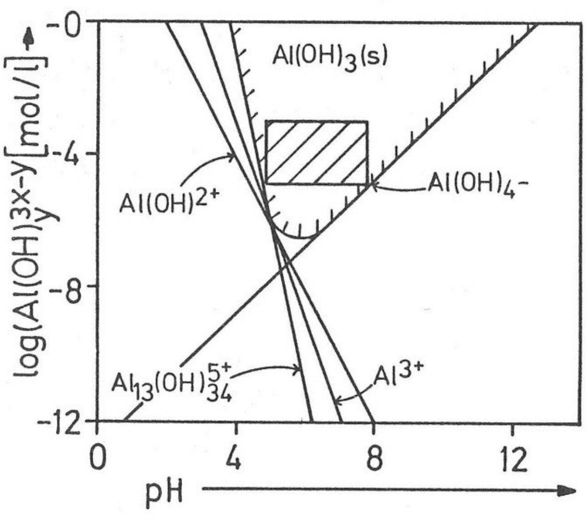

Figure 2-2: Formation of aluminum hydroxide complexes in dependency of the pH of solution (Hahn, 1987 p. 94)

Changes of inlet concentrations of suspended particles in a treatment process with constant dosage of flocculant are no problem with coagulation by double layer compression of suspended particles and with inclusion of suspended particles by precipitation. Coagulation from the change of surface charge of suspended particles is sensitive on changes of inlet concentrations of suspended particles. If the concentration of suspended particles in this case decreases, unchanged dosing of flocculant can lead to recurring stabilization of the suspension. The reason therefore, is the change of surface charges to even positive values by the adsorbed flocculant.

Multinuclear aluminum hydroxide complexes were discovered dosing acidic solutions of mononuclear hydrolyzed aluminum ions to suspensions with higher pH. The mononuclear aluminum is exposed to a change in pH and concentration by dilution. During this process the mentioned multinuclear complexes probably form as an intermediate substance. They are very effective flocculants as mentioned above due to their high density in charge. They destabilize suspended particles by efficiently changing their surface charge at already low concentrations.

Multinuclear hydroxide complexes are industrially produced and are available in the form of polyaluminum slats in aqueous solution ready for dosing. (Hahn, 1987 pp. 43, 97, 98)

2.6.2 Organic Flocculants

Organic flocculants are natural or synthetic polymers. There are no thermodynamic data to describe the interaction of organic polymers and suspended particles. The data that exist about the effectiveness of organic polymers in reducing the concentration of suspended particles are empirically gained. The destabilization of suspended particles is explained by the model of polymer bridging or by polymer charge patching.

Very little amounts of organic polymers are needed for flocculation (in the magnitude of 0.1 ppm). It is not easy to dose such little amounts. With overdosing a recurring stabilization of suspended particles can be expected because of steric hindrance. Resulting flocs are of low specific density and can cause problems in a following dewatering process. (Hahn, 1987 pp. 98-100)

The most important properties of organic polymers are:

- Ionic character
- Molecular mass
- Charge density

An organic polymer is classified as being of high, medium or low molecular mass and of being cationic, nonionic or anionic. Especially the molecular mass determines the prevailing mechanism of destabilization. With organic polymers of low to medium molecular mass charge patching is dominant. With organic polymers of high molecular mass polymer bridging is dominant. Therefore polymers with a molecular mass of 10 to 20 million Dalton are the most effective flocculants. (Burkert, et al., 2005 p. 6) This is easy to explain for cationic polymers with negatively charged suspended particles. It is not so easy to explain for anionic polymers. Here, the assistance of dissolved substances like calcium or magnesium is assumed. Furthermore, the adsorption of cationic and nonionic polymers is strongly affected by the concentration of hydrogen ions, whereas their effect on anionic polymers is low. (Hahn, 1987 p. 90)

3 Description of Test Setting

3.1 The Pilot Plant

With the pilot plant, situated on the site of the existing WTP, the future treatment process of the new WTP is simulated. There are the following process steps:

- Mixing of stock solution of Flopaam 3630 S with the feed of the pilot plant;
- Separation of oil by ascension and suspended solids by sedimentation;
- Flocculation of oil and suspended solids and separation of the loaded flocs by dissolved gas flotation;
- Separation of residual oil by filtration.

According to the process steps there are the following process units with the corresponding main equipment:

1. Polymer storage and dosing unit: storage tank and dosing equipment;
2. Gravity separation unit: corrugated plate interceptor (CPI);
3. Combined flocculation and flotation unit: coagulator and flocculator, flotation reactor, gas dissolving reactor (GDR);
4. Filtration unit: Nutshell filter (NSF).

In **Figure 3-1** and **Figure 3-2** the process units are shown in process flow diagrams (PFD). The units and the corresponding equipment are lined up along the flow of the water to be treated from the left to the right hand side. Pumps as well as dosing and sampling points are named by capital letters (P for pump, DP for dosing point and SP for sampling point) followed by a first digit describing the process unit it belongs to and a second digit describing the order in the flow line of the water.

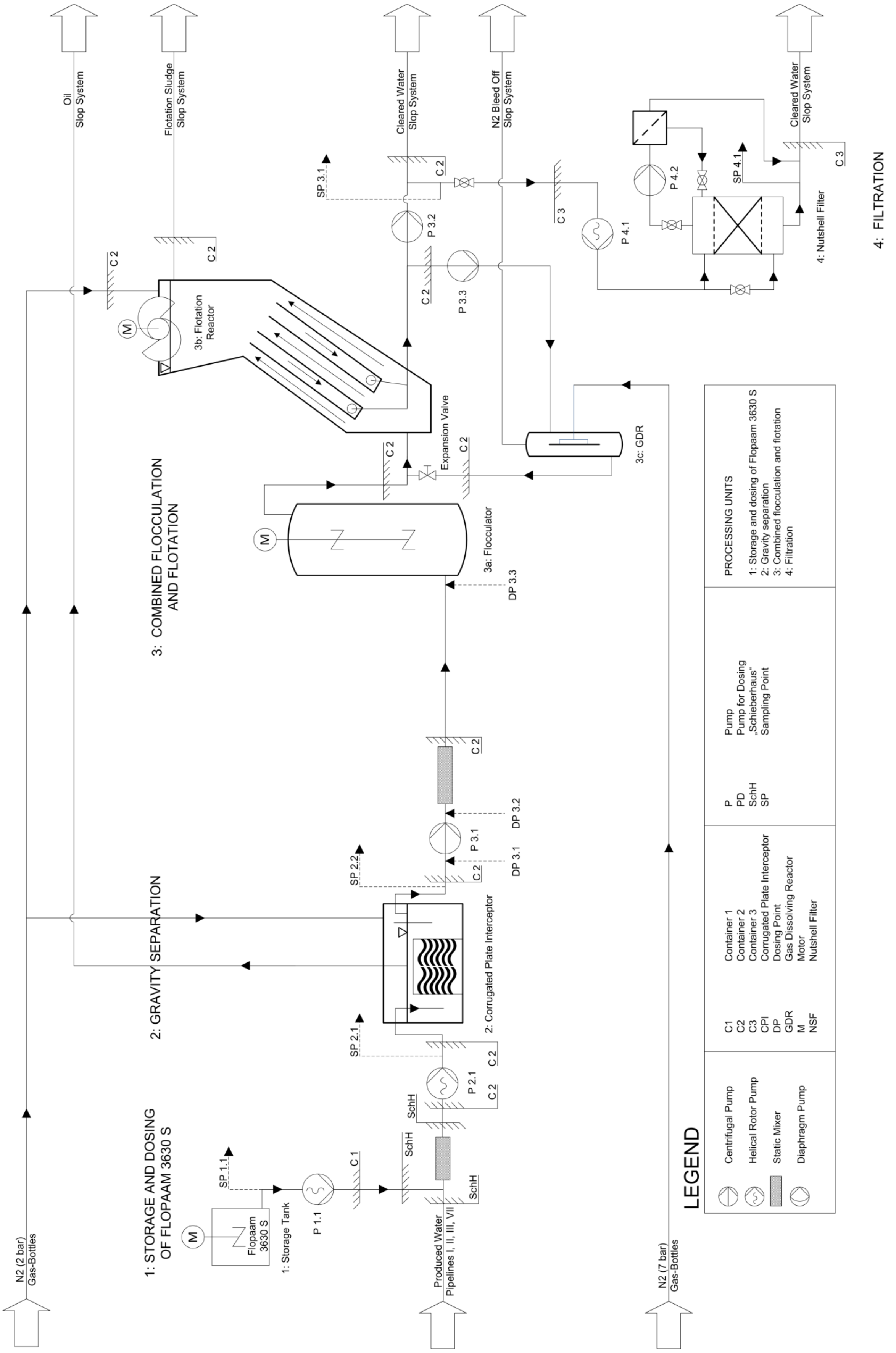

Figure 3-1 Process flow diagram (PFD) of the water treatment pilot plant in pilot plant experiments 1

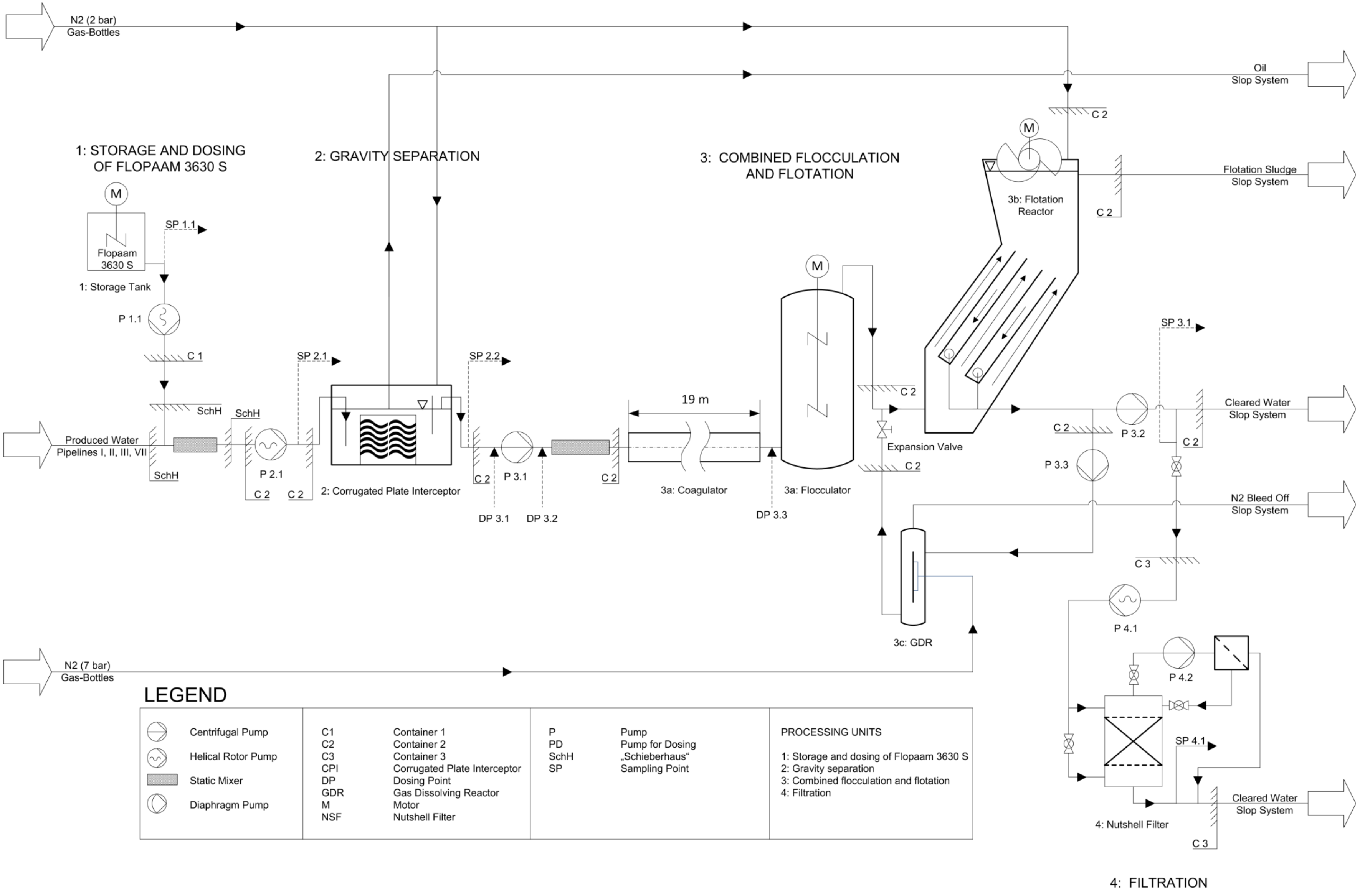

Figure 3-2: Process flow diagram (PFD) of the water treatment pilot plant in the pilot plant experiments 2, 3, 4 and 5

The CPI as well as the flotation reactor is blanketed with nitrogen gas to avoid oxygen entrance as it is provisioned for the new WTP. All pipes situated outdoor are electrically heated and isolated to avoid temperature loss and freezing of the water in case of a temporary shutdown of the pilot plant. Most of the equipment is housed inside containers except the CPI, the coagulator, the flocculator and the equipment for the nitrogen saturation of the flotation water (GDR). The third process unit (combined flocculation and flotation) is operated at 50 % load as it is planned for the new WTP (VTU Engineering GmbH, 2012 p. 5).

Pilot plant experiments 2 - 5 were performed with the plant configuration as it is shown in **Figure 3-2**. In pilot plant experiment 1 the pilot plant was operated without coagulator (see **Figure 3-1**).

3.1.1 Process Description

The water treatment process is described following the process steps that were presented in 3.1.

1. Storage and Dosing Unit for Flopaam 3630 S

The pilot plant was operated with produced water from the feed of the existing WTP within the “Schieberhaus”. The “Schieberhaus” is a small building on the site of the existing WTP where the different pipes with produced water from the production facilities are united to one stream entering the existing WTP. The water is a mixture of all produced waters in the field. Right after the branch off of the inlet water stream for the pilot plant, the dosage point for the stock solution of Flopaam 3630 S was installed as it is shown in the PFD. Right after the dosage point a static mixer is installed to fairly mix in the added stock solution to the water stream for the dissolution of Flopaam 3630 S.

The helical rotor pump P 2.1, situated in the container housing the flotation reactor, transports the water to the gravity separation unit. The pump allows a gentle transport of the water, avoiding further emulsification of the oil as it would take place with a centrifugal pump.

2. Gravity Separation Unit

Gravity separation is a first stage process in produced water treatment (Janka, 2007 p. 13). The driving force of separation is gravity. In the pipe after the helical rotor pump P 2.1 the volume flow and the inlet pressure are measured. Next the water enters the CPI, which is situated right outside of the container hosting the flotation reactor. In the CPI the biggest part of the oil and of the suspended solids is separated. The centrifugal pump P 3.1 is located after the CPI and controls its fluid level in combination with a level metering. The water is forced to flow through the combined flocculation and flotation unit by P 3.1.

Oxygen is excluded by nitrogen blanketing. The hydrocarbon content after the CPI should normally be ≤ 100 ppm (see section 3.3) independently of the hydrocarbon content at the inlet if 500 ppm are not exceeded.

3. Combined Flocculation and Flotation Unit

Flotation with preceding flocculation is a second stage process in produced water treatment (Janka, 2007 p. 13). Chemical agents are added to the water stream prior to flotation in order to react with dispersed oil and suspended solids that passed the CPI. Dosing points for the continuous addition of chemical agents are installed. Depending on the kind of chemical agent a diaphragm pump or a helical rotor pump is used. In the dosing point DP 3.1 or DP 3.2 the first flocculant can be added. Pump P 3.1 and the static mixer provide quick mixing in. In the following coagulator the formation of flocs takes place. Then follows dosing point 3.3 for the continuous addition of the second flocculant. The water then enters flocculator and flows upwards. The flocs grow on their way up. The floc loaded water finally leaves the flocculator on top of the reactor, flows down a pipeline until it enters the flotation reactor.

The coagulator was not installed during the first pilot plant experiment because only one flocculant, chemical set III, was tested. The flocculant was added in dosing point DP 3.3 right in front of the flocculator. In pilot plant experiment 4 only one flocculant was tested as well, but a longer residence time was afforded for reaction. The coagulator was used to extend the possible reaction time and was added in dosing point DP 3.1.

In the flotation reactor the loaded flocs are separated from the water. The flocs adhere to the nitrogen bubbles and are lifted then by buoyancy forces. The hydrocarbon content after the combined flocculation and flotation should be ≤ 20 ppm (see section 3.3).

Oxygen is excluded by nitrogen blanketing. The resulting flotation sludge is removed periodically by a skimmer and leaves the pilot plant to the slop system. The fluid level in the flotation reactor is measured and controlled by the centrifugal pump P 3.2 at the outlet of the flotation reactor. The cleared water either entirely leaves the flotation reactor to the slop system or is partly branched off to the filtration unit in case the NSF is operated.

20 % of the cleared water (1 m^3/h during all pilot plant experiments) is recirculated by the centrifugal pump P 3.3. It is pressurized and saturated with nitrogen gas in the gas dissolving reactor (GDR). The saturated flotation water flows back to the flotation reactor and is expanded into the inlet stream of the reactor.

4. Filtration Unit

In a last step the treated water is filtered. Filtration is a third stage process in produced water treatment (Janka, 2007 p. 13).

Pump P 4.1 conveys the water to the inlet of the NSF. The water enters the NSF on top and passes the filter bed downwards. The cleared water leaves the filter at the bottom and goes to the slop system.

For back-washing of the filter bed the direction of water flow is changed and reversely passes the filter bed from bottom to top. The filter bed is lifted and loosened. Then the centrifugal pump P 4.2 is activated and forces the water to circulate with the loosened nutshells in an external recycled loop. The filtered oil is separated from the nutshells by abrasive wear and leaves the water stream through a sieve towards the slop system.

After filtration the hydrocarbon content of the water should be ≤ 2 ppm (see section 3.3).

3.1.2 Operational Description

The pilot plant was operated with a volume flow of 5 m^3/h of produced water in all pilot plant experiments. After each sampling the volume flow was inspected and reset. The pressure after the inlet pump P 2.1 is around 0.2 bar gauge. The inlet temperature of the water is in the range of 25 to 35°C. The pH of the water is around 7.2.

In this section the setup and the functioning of the main equipment is explained.

1. Storage Tank and Dosing Equipment for Flopaam 3630 S

To imitate produced polymer containing water in the feed of the pilot plant, a storage tank (IBC) for the stock solution of Flopaam 3630 S and two dosing pumps were installed in a container next to the “Schieberhaus”. The storage tank is connected to the inlet pipe of the pilot plant. The container is provided with heating and aeration to keep the stock solution at ambient temperature. A removable mechanical mixer (1400 rpm) on top of the IBC is installed to provide a homogenous stock solution for dosing. Two helical rotor pumps are installed in parallel setting. The pumps are continuously controllable from 0 to 100 %. The first pump conveys a maximum volume flow of maximum 25 l/h and the second pump conveys a maximum volume flow of 3 l/h. For the dosing only the first pump was used in all pilot plant experiments. The pumps and the mechanical mixer are electrically connected to the EC&I of the pilot plant. In case of an automatic shutdown of the pilot plant the dosing of Flopaam 3630 S is stopped as well. The stock solution is not blanketed with nitrogen gas. This was because the storage tank, a simple IBC, is not gastight. Being located in a closed container nitrogen blanketing would impose a security risk for operators. So oxygen entrance to the stock solution is presumed to a certain amount.

2. Corrugated Plate Interceptor (CPI)

The CPI is a reactor of rectangular shape containing four bundles of horizontal parallel corrugated plates that are placed in the middle of the CPI. The water is forced to flow through the plates. Suspended solids settle and oil droplets coalesce on the plates’ surface and rise through holes due to their lower density compared to produced water. In **Figure 3-3** the flow of the oil and the water is shown. A weir hinders the separated oil from flowing towards the outlet. Produced water, being the heavy phase, flows underneath the weir to the outlet of the CPI. The separated suspended particles accumulate between the corrugated plates in the CPI and are removed periodically by washing the bundles of plates outside of the CPI (Note: The bundles were cleaned before every pilot plant experiment). Accumulated surface oil is drained by gravity into overflow pipes twice a day for half an hour at a volume flow of about

2 m³/h. The CPI is covered with a lid and the water is protected from oxygen uptake by nitrogen blanketing.

The separation process follows Stocks' Law. As a condition the rising flow of the oil droplets has to be laminar. The rising velocity v is described by the following equation:

$$v = \frac{d^2 \Delta\rho\, g}{18\,\eta}, \qquad Re < 0.5$$

Equation 3-1: Stokes' Law (Robel, 1985 p. 80)

The rising velocity is directly proportional to the square of the oil droplets diameter d and inversely proportional to the viscosity η of the surrounding fluid. The smaller the diameter and the higher the viscosity of the water the slower an oil droplet rises. Gravity in Equation 3-1 is represented by the letter g and Δρ represents the difference in the densities of water and oil.

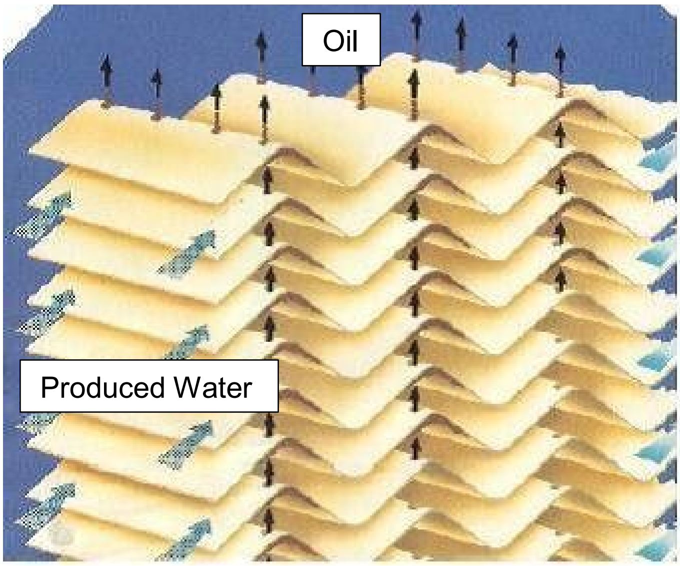

Figure 3-3: Flow of produced water and oil through the bundles of parallel plates in the corrugated plate interceptor (FREYLIT Umwelttechnik GmbH)

3a. Coagulator and Flocculator

The function of the coagulator and the flocculator is to provide residence time for the added chemicals to react with the oil and suspended solids after gravity separation.

The coagulator consists of pipes that can easily be coupled to form a pipeline of desired length. The pipes were designed by a company named "Bauer" and therefore the pipeline is called "Bauerrohr" in German. The coagulator has a length of 19 meters. Its inner diameter (10 cm) is bigger than the inner diameter of the preceding pipeline (5 cm). As a result the hydraulic flow velocity of the water is reduced from approximately 58 to 18 cm/s and the flow is less turbulent. This enhances the formation of flocs.

The second flocculator is a cylindrical reactor with an inner diameter of 63 cm and a height of 2 meter. The hydraulic flow velocity of the water is reduced again from approximately 18 to 0.5 cm/s due to the bigger diameter of the reactor which results in an even lower level of turbulence. With the added flocculation aid the entering flocs grow on their way up through the reactor. A mechanical mixer provides gentle mixing (20 – 30 rpm). The mixing speed can be controlled via frequency converter.

The hydraulic residence times of the coagulator and the flocculator are 1.8 and 7.5 minutes. This gives an idea of the time that is provided for the reaction of the added chemicals.

In the future new WTP the coagulator and the flocculator prior to flotation are both designed as continuous stirred-tank reactors. The coagulator of the pilot plant was originally also planned to be designed as continuous stirred-tank reactor, but it was closer to assemble the quick coupling pipes to build the first flocculator because they were easily available.

The advantage of this solution is, that due to the smaller diameter compared to the flocculator the water flows faster than in a continuous stirred-tank reactor naturally resulting in a higher turbulence which promotes the quick formation of flocs by increased collision of reactants.

3b. Flotation Reactor

The flotation reactor consists of inclined parallel compartments where the water flows co-currently upwards with the lifted flocs. Intensive collision of nitrogen bubbles and flocs is provided. The cleared water turns back downwards and leaves the flotation reactor. A rotating skimmer on top of the reactor periodically removes the flotation sludge.

3c. Gas Dissolving Reactor (GDR)

The GDR is of cylindrical shape. Cleared water from the flotation reactor is pressurized up to 6 bar by a centrifugal pump and enters the GDR on top. Inside the reactor, close to the wall, a membrane is mounted. It is fed with nitrogen gas at a pressure of 7 bars which is supplied by gas bottles. The nitrogen gas transits the membrane and quickly dissolves in the pressurized water until saturation. The saturated water leaves the reactor on the bottom.

4. Nutshell Filter

The NSF is a deep-bed downflow filter with an oil coalescing surface (Steinbrugger, 2009 p. 6). Remaining oil droplets coalesce to bigger ones and adhere to the nutshell granules. The nutshells are held back by a sieve. The nutshell filter is operated in filtration cycles. Once the nutshell granules have reached their capacity to separate residual oil from the water regenerative back-washing is started.

For the filtration tests in the second stage of testing (pilot plant experiment 5) nutshells of the black walnut with mesh 20/30 were used (equals a grading of 0.59 – 0.84 mm). The NSF was operated as recommended with a flux of 15 m/h (that equals 0.42 cm/s) (compare Steinbrugger, 2009 p. 60). For the calculation of the flux see Equation 3-2. The filter bed depth was around 40 cm.

The operating time of a filtration cycle should reach 24 hours before regenerative back-washing is necessary. Any longer operation would lead then to excess loading of the nutshells and to an augmented consumption of water for back-washing. (Steinbrugger, 2009 p. 5)

At a maximum differential pressure of 1 bar (Steinbrugger, 2009 p. 60) or at a hydrocarbon break through (augmented hydrocarbon content after the NSF; (Steinbrugger, 2009 p. 17)) the filtration is stopped and back-washing is started.

Full regeneration of the filter bed by back-washing lasts 20 to 30 minutes.

3.2 Testing Procedure of the Pilot Plant Experiments

To perform the experiments the pilot plant was operated 24 hours from Monday to Friday. The chemicals were continuously added during all week to provide a constant treatment process. Sampling was done during working hours from 07:00 to 16:00. In the first stage of testing all process units except the nutshell filter were operated (pilot plant experiments 1 – 4). In the second stage of testing (pilot plant experiment 5) also the nutshell filter was operated to additionally test its performance.

3.2.1 Operating Modes of the Pilot Plant

There are two operating modes of the pilot plant. The first is the "Normal Operating Mode". In this mode the pilot plant is fully operating. The second is the "Reduced Operating Mode". In this mode the pilot plant is operated without chemicals and without flotation water. The purpose was to avoid freezing of pilot equipment that was not insulated (e.g. flocculator). Note: The GDR can be completely separated from the flotation reactor and is emptied in reduced operating mode.

Over the weekend the pilot plant was either operated in reduced mode or it was shut down and emptied.

3.2.2 Preparatory procedure

In order to start the testing the following steps have to be proceeded (compare (VTU Engineering GmbH, 2012))

1.) Start of the Pilot Plant

For safety reasons the level monitoring switch is always set to the position "A" (automatic mode). In this mode all sensors for an automatic shutdown are activated. All equipment that is switched on during startup of the pilot plant has to be set to automatic mode.

Startup to Reduced Operating Mode

For the complete start up all valves in the flow line of the pilot plant are opened (except the valves that connect the flotation water loop to the flotation reactor). The inlet pump of the pilot plant (P 2.1) is switched on and the system starts filling with water. Next the centrifugal pump after the CPI (P 3.1) is activated as well as the level control of the CPI and the outlet pump (P 3.2) of the flotation reactor. Finally the mechanical mixer of the flocculator and the skimmer of the flotation reactor are switched on as well. The filling of the pilot plant lasts about 1 hour. When a stable flow of water is established, the startup can be continued to operate the pilot plant in Normal Operating Mode.

Startup to Normal Operating Mode

The valves in the flotation water loop are opened. The circulating pump (P 3.3) is then started and simultaneously vented. The gas bottles are further opened. The nitrogen gas pressure supplying the GDR is set to 7 bars and the nitrogen gas flow to 3 l/min. The nitrogen gas bleed off valve on top of the gas dissolving reactor is slightly opened. For the nitrogen blanketing of the CPI and the flotation reactor the nitrogen flow is set to 3 to 4 l/min (nitrogen atmosphere is exchanged approximately every 2 to 3 hours). The set values of the pilot plant are adjusted: the volume flow of the inlet pump (P 2.1) via frequency converter and the volume flow of the circulating pump of flotation water with throttle control via hand valve. Further the operating parameters are inspected: the inlet pressure gauge after the inlet pump P 2.1, the level of the CPI and the level of the flotation reactor. After some minutes time the quality of the nitrogen saturated flotation water is checked (milky color).

The stock solution supply of Flopaam 3630 S is organized. The chemical agents are prepared and the dosing is finally started (setting and adjusting of the volume flow). These steps are described below.

For pilot plant experiment 5 the NSF was also activated. Therefore all valves in the flow line of the water are opened. The inlet pump of the NSF (P 4.1) is switched on and the required volume flow is set via frequency converter. The volume flow has to be checked by measuring the volume in time.

It is very important to set the right volume flow. The volume flow determines the filtration velocity, also called flux. The flux is a very important parameter. It strongly influences the separation efficiency of the NSF. It is calculated with the following formula:

$$\mathrm{Flux} = \frac{\mathrm{Volume\ Flow}}{\mathrm{Cross\ Section\ of\ Filter\ Bed}}$$

Equation 3-2: Calculation of the flux in the NSF (Steinbrugger, 2009 p. 17)

2.) Supply of Flopaam 3630 S

The necessary volume of stock solution for dosing to the inlet stream of the pilot plant was calculated beforehand for the tests that were planned for the week. The usual content of Flopaam 3630 S in the stock solution was in the range of 2150 – 3600 ppm. The stock solution was taken from the polymer mixing plant, situated in the field next to the two injection wells used for polymer flooding of the 8. TH. The polymer solution was filled into an IBC and transported to the site of the pilot plant where it was placed in the provisioned container and connected to the dosing pump. Finally the mechanical mixer was started in order to provide a homogenous solution.

3.) Preparation and Dosing of the Chemical Agents

In order to add a chemical agent in the right concentration a convenient dilution had to be prepared. The degree of dilution was chosen with respect to the range of volume flow that is possible with the dosing pump.

Preparation of Flocculating Agents

The chemical solutions were usually prepared once a day in the morning at a volume needed in 24 hours. Note: Solution stability is guaranteed for one day for most agents. Preparation procedures were adapted to suit the properties of the different chemical agents.

Preparation of the Solution of Flopaam 3630 S

The polymer solution was automatically prepared in the mixing plant situated in the field next to the two injection wells used for polymer flooding of the 8. TH. In this plant polymer powder is violently mixed under exclusion of oxygen (nitrogen blanketing) with injection water coming from the treatment process of the existing WTP. The polymer content is determined by weighting of the masses of polymer and water. The content is calculated with a half width error of about 30 to 50 ppm. This is reported by the operator of the polymer mixing plant. According to information of the OMV LEP, the powder of Flopaam 3630 S is hygroscopic. Its water content is about 10 % by weight. This fact has not been considered in the calculation of the content of Flopaam 3630 S in the prepared solution.

Dosing Points

All dosing points are placed in the combined flocculation and flotation unit. That’s why their numbering always starts with a 3. With the following digit they are numbered according to their order in the flow line of the water.

DP 3.1: The dosing point is located right in front of the centrifugal pump (P 3.1) conveying the water through the flocculation and flotation unit. Dosing in this point allows a very intense mixing in of the chemical agent. The point was used in pilot plant experiment 4 for the mixing in of Flopam FL 2949.

DP 3.2: The dosing point is located right after the centrifugal pump (P 3.1) conveying the water through the flocculation and flotation unit. Dosing in this point allows intense mixing in of the chemical agent induced by the following static mixer. The point was used to mix in Flopam SFC 60, Chimec 5762 and Alustar 1010 L in the pilot plant experiments1, 2 and 3.

DP 3.3: The dosing point is located right in front of the flocculator. Dosing in this point allows mixing in of the chemical agent induced by the following turbulence due to the narrowed cross area. The point was used to mix in the flocculation aids in the pilot plant experiments 2, 3 and 5. Note: A possible destructive effect on the generated flocs affected by the turbulence - especially due to the curvature of the pipe in this place - cannot be excluded.

4.) Adjusting of the Dosing Volume Flow

The dosing volume flow of all chemicals, including Flopaam 3630 S, has been adjusted by measuring the volume conveyed per unit of time in test runs with each solution.

5.) Sampling

During the tests water samples before and after a processing step were taken to analyze their hydrocarbon content. The samples were taken every one or one and a half hour during working hours from 7:00 to 16:00. Thus 6 to 7 sets of samples were taken and analyzed a day.

It was noticed that the skimming has an influence on the hydrocarbon content of the samples in the outlet of the flotation (SP 4.1). To avoid that influence an Excel-file was made predicting the times of skimming. Samples were only taken before skimming or at least 15 minutes after. On Monday mornings and after every stop of the pilot plant the calculation had to be updated.

In the pilot plant experiments 2, 3, 4 and 5 additionally to the samples for hydrocarbon content determination, samples for additional testing of the water quality (filterability, suspended solids, iron, turbidity) were taken. The sampling procedure is described in section 3.7.3.

Right before each sampling the operating parameters of the pilot plant were recorded and transferred to an Excel-file in the field lab.

Procedure

The valve of a sample point was completely opened. So it was rinsed at the highest possible velocity for 15 to 30 seconds. (The water was caught in a bucket and poured away afterwards.) Then the water was filled in a glass bottle of 500 or 1000 ml depending on expected concentration level of hydrocarbons. The bottle was filled up to the half with the sample to leave space for adding the solvent. Then the bottle was closed with a lid. All operating parameters were adjusted after sample taking. The samples were immediately taken to the field laboratory for analysis.

Sampling Points

There were 5 different sampling points (see PFD, **Figure 3-2**). They are numbered with two digits separated by a point. The first digit describes the process unit it belongs to and the second digit describes the order of the sampling point in the flow line of the water.

SP 1.1: Allows to take a sample of the polymer (Flopaam 3630 S) solution from the storage tank.

SP 2.1: The sampling point is inside the second container. It is placed between the inlet pump (P 2.1) and the CPI. The sampling point is also described as “Inlet CPI”.

SP 2.2: The sampling point is inside the second container. It is placed between the CPI and the following centrifugal pump (P 3.1). The sampling point is also described as “Outlet CPI” which is the same as “Inlet Flotation”.

SP 4.1: The sampling point is inside the second container. It is placed after the outlet pump of the flotation reactor in the pipeline that branches of to the NSF. The sampling point is also described as “Outlet Flotation”.

SP 5.1: The sampling point is inside the third container. It is placed after the outlet of the NSF. The sampling point is also described as “Outlet NSF”.

3.2.3 Cleaning work

At the end of every pilot plant experiment (or in case of necessity) the following equipment of the pilot plant was cleaned with water from a nearby fireplug:

- coagulator, flocculator, flotation reactor and GDR.

Some movable parts were cleaned with hot water (approx. 80°C):

- bundles of corrugated plates of the CPI, polymer storage tank (IBC), mechanical mixer of the polymer storage tank.

The dosing pumps and hoses were run with distilled water for their cleaning.

Exceeding volumes of chemical solutions were disposed in a special reservoir on-site.

3.3 Specification of Water Quality for the Pilot Plant Experiments

In order to achieve the required water quality for re-injection specific qualities have to be obtained after each process unit.

The following values were specified as target values for the pilot plant experiments (compare: VTU Engineering GmbH, 2013 p. 3)

Feed of the pilot plant:

- 300 and 500 ppm of hydrocarbons
- A maximum of 30 ppm of suspended solids[1]

Water after gravity separation:

- ≤ 100 ppm of hydrocarbons

Water after combined flocculation and flotation:

- ≤ 20 ppm of hydrocarbons

Water after filtration:

- ≤ 2 ppm of hydrocarbons
- ≤ 1 ppm of suspended solids[2]
- WBF (3 µm) < 0.7 min^{-1}

A required WBF (8 µm) after flotation is not specified. But a WBF (8 µm) of about 2 to 3 min^{-1} could be acceptable for further filtration of the water in the nutshell filter.

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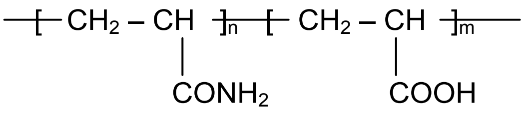
[1] Equals the content of suspended solids after filtration over a 3 µm membrane filter

[2] as explained in footnote 1

3.4 Flopaam 3630 S – the Polymer used in the Polymer Flooding Pilot

3.4.1 Description of Flopaam 3630 S

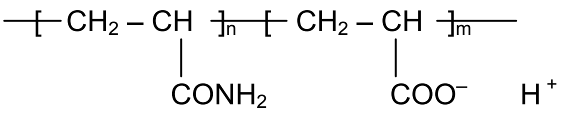
Flopaam 3630 S is the brand name of the polymer that is used for polymer flooding in the current pilot project (8. TH). It is produced by the company SNF. The physical form of Flopaam 3630 S is a powder, which is indicated by the S for solid. The powder consists of hydrolyzed polyacrylamide (HPAM) molecules. HPAM is a copolymer of acrylamide and acrylic acid (or sodium acrylate in the case of Flopaam 3630 S). The chemical structure of HPAM looks as shown in **Figure 3-4**:



$$-\left[CH_2 - \underset{CONH_2}{\underset{|}{CH}} \right]_n - \left[CH_2 - \underset{COOH}{\underset{|}{CH}} \right]_m -$$

Figure 3-4: Chemical structure of HPAM (Zheng, et al., 2011)

The functional groups of acrylic acid (or sodium acrylate) dissociate in aqueous solution to a certain degree in dependency of the pH. This dissociation leaves negative charges with the molecule. The charged anionic molecule is illustrated as shown in **Figure 3-5**:



$$-\left[CH_2 - \underset{CONH_2}{\underset{|}{CH}} \right]_n - \left[CH_2 - \underset{COO^-}{\underset{|}{CH}} \right]_m - \quad H^+$$

Figure 3-5: Dissociation of the carboxylic group in HPAM

The resulting overall negative charge of the molecule is called anionicity and the molecule is characterized to be anionic. The degree of anionicity is determined by the percentage of acrylic acid (or sodium acrylate) monomers in the molecule. Flopaam 3630 S has a medium charge density. This refers to an anionicity of 30 % at a pH > 6.5 (Gil, 2013).

The molecular mass of Flopaam 3630 S is ultra-high (20 million Dalton).

Flopaam 3630 S is a straight chain polymer with a flexible structure that can coil up especially in solutions with divalent ions. It forms so-called random coils. In solution with water, HPAM is a polyelectrolyte.

To get the solution ready for injection into the reservoir, the delivered powder has to be mixed with injection water. This happens on-site in a specially designed mixing plant. The stability of the polymer solution is 1 day.

(Compare: SNF SAS, 2004 and Zheng, et al., 2011 p. 2)

3.4.2 Degradation of Flopaam 3630 S

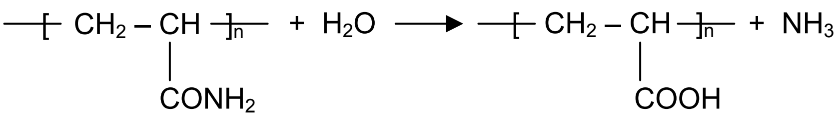
The HPAM molecules are subject to degradation when they pass the reservoir, process lines and equipment. The degradation is caused by many physical and chemical effects; amongst them: mechanical shearing, free radical degradation and hydrolysis reaction. As a result of the degradation processes the produced HPAM has

- lower molecular mass and
- higher degree of hydrolysis (augmented anionicity)

than the injected HPAM. With a higher degree of hydrolysis the anionic charge density is augmented. This means that HPAM is stronger negatively charged. (Zheng, et al., 2011 p. 2)

Hydrolysis Reaction

When HPAM is subjected to hydrolysis, the amide groups of the polymer react with water converting to carboxylic groups and ammonia. In **Figure 3-6** the hydrolysis reaction is illustrated. The rate of hydrolysis depends on temperature and pH.



$$-\!\left[CH_2 - \underset{\substack{|\\ CONH_2}}{CH} \right]_n\!- + H_2O \longrightarrow -\!\left[CH_2 - \underset{\substack{|\\ COOH}}{CH} \right]_n\!- + NH_3$$

Figure 3-6: Hydrolysis of the amide group in HPAM (Zheng, et al., 2011 p. 2)

Free Radical Degradation

Besides mechanical shearing, free radical degradation leads to a reduction in the molecular mass of the polymer. In reactions between oxidizing and reducing agents (redox reactions) free radicals are generated. They are very reactive and can break up polymer chains. Oxidizing agents are for instance: oxygen, ferric ions (Fe^{3+}). Reducing agents are for instance: hydrogen sulfide (H_2S), oxygen scavengers, sulfate-reducing bacteria, ferrous ions (Fe^{2+}). (SNF S.A.S., 2004)

Polymers of higher molecular mass are more sensitive to lose molecular mass than polymers of lower molecular mass. (SNF S.A.S., 2004)

3.4.3 Influence of Multivalent Cations on Flopaam 3630 S

Curling and Crosslinking

In distilled water the negative charges along the backbone of HPAM keep the molecule stretched. At the presence of cations the HPAM chain tends to curl. The reason therefore is the compensation of the negative charges of the oxygen. (Littmann, 1988 pp. 25-26) Multivalent cations like Ca^{2+}, Al^{3+}, Fe^{3+} can interact with the carboxylic functional groups of different HPAM polymer chains. Ionic crosslinking is the result (Zheng, et al., 2011 p. 5).

Flocculation

HPAM can act as flocculant with cationic molecules. It can also floc anionic molecules by a mechanism called cationic bridging. Thereby the HPAM molecule and anionic molecules get connected by multivalent cations as explained above for the ionic crosslinking. (Zheng, et al., 2011 p. 3)

Polymer Cloudiness

Polymer cloudiness describes a solution of HPAM that has turned cloudy by water hardness cations. The cloudiness is dependent on temperature, pH, the concentration and types of cations, the concentration of HPAM and its degree of hydrolysis. (Zheng, et al., 2011 p. 2)

3.4.4 Estimation of the Possible Future Content of Flopaam 3630 S in the Feed of the New Water Treatment Plant

The possible future content of Flopaam 3630 S in the feed of the existing or new WTP is not easy to estimate. It depends on many factors. Amongst them are:

- Amount of injected polymer
- Amount of produced water from other production wells that dilute the produced polymer containing water
- Adsorption in the reservoir (SNF S.A.S., 2007)
- Dilution by formation water (SNF S.A.S., 2007)

By beginning of May 2013 120 tons of Flopaam 3630 S were injected into the reservoir from the start of the polymer flooding pilot operation, which was about a year before. It is known that the amount of yearly treated oilfield water is about 10 million m³. In a scenario with all injected polymer breaking through, the content of polymer in the feed of the WTP can easily be calculated dividing the amount of injected polymer by the amount of water in which it is diluted. This calculation results in a polymer content of 12 ppm. With the assumption that about 30 percent of the polymer gets lost on its way from injection to production well, the possible polymer content in the feed of the water treatment plant reduces to about 8 ppm. (Jour fix, May 2nd, 2013)

According to the information given by the company SNF polymer concentration in produced water very often reaches only 50 % of the injection concentration (SNF S.A.S., 2007). In this case only 60 tons of polymer would reach the production well and the resulting polymer content in the feed of the WTP would be 6 ppm.

3.4.5 Possible Influences on Separation Processes by Degraded Flopaam 3630 S in the Water Treatment Process of the New Water Treatment Plant

Due to degradation processes in the reservoir and in production equipment Flopaam 3630 S is expected to enter the WTP with a lower molecular mass and a higher anionicity.

Polymers of high molecular mass (with 20 million Dalton, like Flopaam 3630 S) can lose 50 to 70 % of their molecular mass (SNF S.A.S., 2007). The decrease in molecular mass could have a **positive impact on the filterability** of the treated water after flotation. The plugging of the NSF pores would probably be reduced and a longer operating period could be possible.

HPAM is subject to hydrolysis of the amide groups due to elevated temperature > 50 to 60°C. An increase in anionicity by hydrolysis is expected during residence in the reservoir. It is reported that with an anionicity higher than 35 to 40 % the polymer can precipitate with bivalent ions in formation water. But it is stated that an anionicity of 35 to 40 % is not reached though. (SNF S.A.S., 2007) Anyhow, the increase in anionicity could lead to a **higher necessary dosage of PAC** in the flocculation unit of the WTP. But it also seems possible that due to the increased anionicity and the presence of divalent ions (e.g. Ca^{2+}) in the formation water polymer precipitates already in the reservoir or in production equipment. This effect would cause a lowered concentration of Flopaam 3630 S in the feed of the WTP.

3.4.6 Solution of Flopaam 3630 S used for Dosing in the Pilot Plant Experiments

Due to degradation processes in the reservoir and in production equipment Flopaam 3630 S is expected to enter the WTP with a lower molecular mass and a higher anionicity.

In the pilot plant experiments which are described in this thesis fresh stock solution of Flopaam 3630 S was used for dosing to the feed of the pilot plant. Therefore, the hydrocarbon separation behavior of the pilot plant with degraded Flopaam 3630 S in the feed is not known. In section 3.4.5 it was tried to predict possible changes.

Concerning the actual content of Flopaam 3630 S that could enter the new WTP probably a lower content can be presumed than that which has been estimated in 3.4.4. It is likely that part of the polymer already deposits in production facilities ahead of the new WTP which has been reported in literature (Zheng, et al., 2011 p. 5).

To perform experiments which are closer to reality the use of produced water that already contains back-produced polymer would be ideal.

After pilot plant experiment 5 the pilot plant was moved to another place on the site of the existing WTP. This was necessary, because the constructing of the new WTP moved on to the former spot the pilot plant was located. When the pilot plant was started again for further testing mid-April 2013, the hydrocarbon contents in the feed of the pilot plant were constantly >> 500 ppm. That is why it was decided to stop testing and to install a buffering tank. In future, Flopaam 3630 S will be dosed to the inlet stream of this tank. At a volume flow of 5 m³/h and a capacity of 10 m³ the hydraulic residence time of Flopaam 3630 S would be 2 hours. During this time it is possible that Flopaam 3630 S degrades and deposits to a certain degree before entering the water treatment pilot plant.

Degradation of Flopaam 3630 S in the polymer stock solution could also be promoted by heating to the temperature of the reservoir (40 to 50°C) and exposing to shear forces by violent mechanical mixing before dosing.

3.4.7 Possible Degradation of Flopaam 3630 S during the Pilot Plant Experiments

Molecular Mass

The stock solution of Flopaam 3630 S, that was stored for the dosing into the feed of the pilot plant, was continuously mixed with 1400 rpm to homogenize the fluid. The storage vessel (a simple IBC) was not blanketed with nitrogen gas for operator safety reasons. So the stock solution was exposed to air. As a result degradation of the solution by free radicals and mechanical shearing could have occurred at the same time resulting in a reduction of the molecular mass of the polymer chains. However, it has to be stated that this is a presumption that has not been proved by examination so far.

Actual Content of Flopaam 3630 S

The solution of Flopaam 3630 S was slightly turbid in all pilot plant experiments like it is shown in **Figure 3-7**, especially the solution used in pilot plant experiment 5. This could be due to reaction with divalent ions in the injection water that was used to dissolve the solid polymer. This effect is called polymer cloudiness (Zheng, et al., 2011 p. 2). The actual polymer content in the feed of the pilot plant could have been slightly reduced by this effect which has not been proved however.

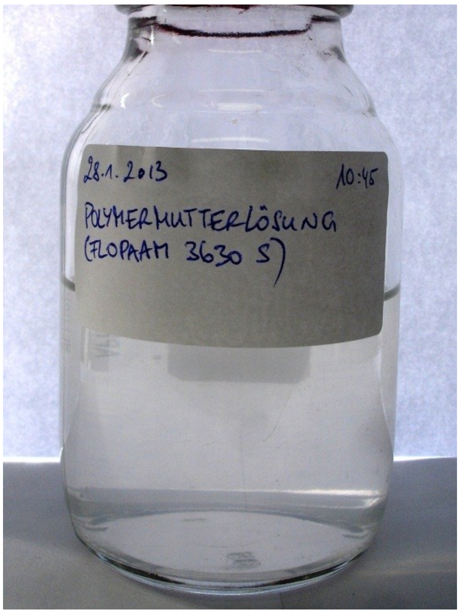


Figure 3-7: Sample of the stock solution of Flopaam 3630 S used for dosing to the feed of the pilot plant in pilot plant experiment 2 (Content of Flopaam 3630 S: 3400 ppm)

Jellylike agglomerates like shown in **Figure 3-8** floating in the separated oil phase of the CPI were observed a lot of times during the pilot plant experiments. It is assumed that these are agglomerates of flocculated or cross-linked polymer. This effect could also slightly have lowered the actual polymer content after the CPI. To prove the presumption chemical analysis of the agglomerates would be necessary.

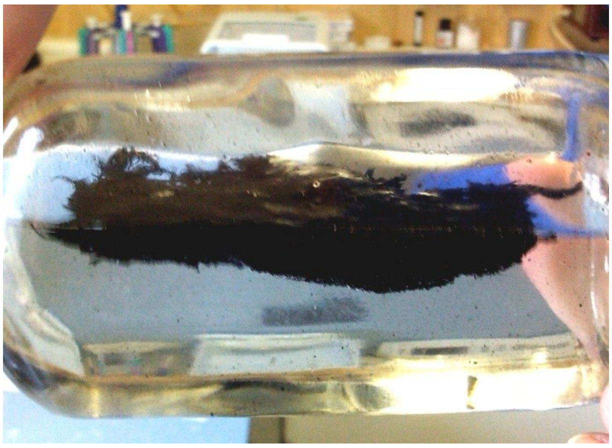


Figure 3-8: Jellylike agglomerate from the CPI during pilot plant experiment 1; most of adhering oil has been removed with an organic solvent

3.5 Preselected Chemicals for Flocculation - Description

Four chemical sets were preselected in earlier investigations for testing purposes in the combined flocculation and flotation unit of the water treatment pilot plant. An overview of these chemicals is given in **Table 3-1**.

Table 3-1: Overview of preselected chemical agents for flocculation

Brand Name	Active Ingredient	Used as	Company
CHEMICAL SET I			
Alustar 1010 L	Inorganic Polymer	Coagulant	ACAT
Drewfloc 285	Organic Polymer	Flocculation Aid	Ashland
CHEMICAL SET II			
Chimec 5762	Inorganic Polymer	Coagulant	Chimec
Chimec 5498	Organic Polymer	Flocculation Aid	Chimec
CHEMICAL SET III			
Flopam SFC 60	Organic Polymer	Flocculant	SNF
CHEMICAL SET IV			
Floquat FL 2949	Organic Polymer	Flocculant for Flopaam 3630 S	SNF

The general properties and mechanisms of efficacy are explained in section 2.6. The characteristic properties and the chemistry of the flocculants are shown in **Table 3-2**.

3.5.1 Alustar 1010 L and Drewfloc 285 (Chemical Set I)

Alustar 1010 L

Alustar 1010 L is an aqueous solution of polyaluminum chloride. Polyaluminum is a **cationic** inorganic coagulant. Due to its polymeric structure it can effectively be used in a wide range of pH and at low temperatures. The hydroxide ions in Alustar 1010 L let the pH drop less dramatically when dosing, but due to the high alkalinity of the produced water and the low added concentrations no significant drop in pH is assumed anyway.

Alustar 1010 L can be diluted with water in any desired ratio. The dosing is recommended with an acid-proof diaphragm pump because the pH of the pure solution is < 1. The content of PAC, the active ingredient, is between 30 and 40 %. The basicity of Alustar 1010 L is approximately 43 %.

Alustar 1010 L is not explicitly recommended for the flocculation of hydrocarbons in produced water. According to information on the website of the company, Alustar 1010 L has been designed for the use in drinking water production, sewage- and waste water treatment and cleaning of industrial water (ACAT, 2013).

Compare technical and safety data sheets (ACAT, 2008) and (ACAT, 2010).

Drewfloc 285

Drewfloc 285 is a copolymer of acrylamide and acrylic acid. The physical state of the preparation is solid. It is delivered as powder. The powder needs to be dissolved in clean water prior to dosing. The solution of Drewfloc 285 that was used in pilot plant experiment 3 was prepared in a special mixing plant onsite of the existing WTP.

Drewfloc 285 is an **anionic** polyelectrolyte with **medium molecular mass** and **high charge density** (Mueller, 2013). The optimum pH for maximum efficacy of Drewfloc 285 is in between pH 6 to 10 (Mueller, 2013).

Drewfloc 285 was used as flocculation aid in combination with Alustar 1010 L in pilot plant experiment 3. It is very similar to Flopaam 3630 S, the polymer used in the polymer flooding pilot operation.

Compare technical and safety data sheets (Ashland, 2013) and (Ashland, 2009).

3.5.2 Chimec 5762 and Chimec 5498 (Chemical Set II)

Chimec 5762

Chimec 5762 is an aqueous solution of PAC (15 to 20 % active content). It acts as a **cationic** flocculant over a wide range of pH. It is recommended to be used as flocculation aid following coagulation with Chimec 5762. The dosing is recommended with a metering pump. The pH of 1 % of Chimec 5762 in solution is 3.5 ± 1.

Compare technical and safety data sheets (Chimec S.p.A., 2009) and (Chimec S.p.A., 2011).

Chimec 5498

Chimec 5498 is an emulsion of a colloidal aqueous phase containing the active polymer dispersed in a hydrocarbon phase as carrier phase.

The active polymer in Chimec 5498 has a **cationic character** and is of **high molecular mass**. Its charge density was not specified. It was used as flocculation aid in combination with Chimec 5762 in the pilot plant experiments 2 and 5.

Compare technical and safety data sheets (Chimec S.p.A., 2009) and (Chimec S.p.A., 2013).

3.5.3 Flopam SFC 60 (Chemical Set III)

Flopam SFC 60 is a chemical preparation which consists of two phases: a carrier phase which is brine and a colloidal polymer stabilized water phase containing the active polymer. **Figure 3-9** shows the dispersion on a microscopic scale.

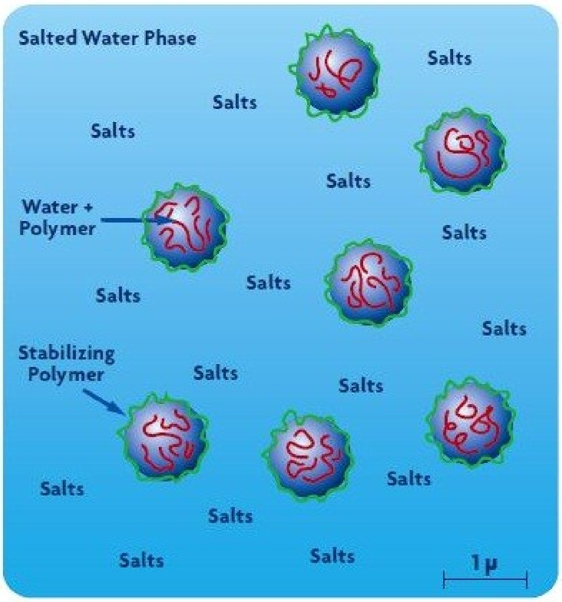


Figure 3-9: Microscopic appearance of Flopam SFC 60 (SNF Floerger, 2002)

The active polymer contained in Flopam SFC 60 is a **cationic** organic polymer of **very high charge density** with a **medium molecular mass**. It is a copolymer on the basis of polyacrylamide. It is water soluble.

Flopam SFC 60 contains no solvent other than brine nor any surfactant for stabilization of the dispersion. Flopam SFC 60 is easy to dissolve in water. High shear forces for activation are not necessary. It simply needs to be diluted in water. Thus there is no risk of a reduction in the molecular mass of the polymer. Flopam SFC 60 is applicable in a wide range of pH. It is recommended for the flocculation of oil, grease and hydrocarbons. The phase separation is indicated by flotation.

The advantage of the easy dosing due to the prepared dispersion goes along with lower active content, lower molecular mass and a short shelf life. The stability of a dilute solution of Flopam SFC 60 is limited to one day only.

Compare technical and safety data sheets (SNF S.A.S., 2013) and (SNF Floerger, 2002).

3.5.4 Floquat FL 2949 (Chemical Set IV)

Floquat FL 2949 is a solution of **cationic** organic polymers of **very high charge density**. The molecular mass is not specified. It is soluble in water, but the solvent in Floquat FL 2949 is not specified either.

Floquat FL 2949 is a copolymer of epichlorhydrin and dimethylamine (EPI-DMA). It belongs to the chemical product group of polyamines. It is supposed to react with Flopaam 3630 S forming a gel. David Owen (expert on chemical water treatment, Co.Treatchem Ltd) talked of so-called coacervation in this case (Workshop on March 21, 2013).

Compare technical and safety data sheets (SNF S.A.S., 2012) and (SNF S.A.S., 2013).

Table 3-2: Chemistry and characteristic properties of the preselected flocculants

Brand Name	Chemistry	Characteristic Properties (*)
CHEMICAL SET I		
Alustar 1010 L	PAC	Cationic/ High CD
Drewfloc 285	Copolymer of Acrylamide/ Acrylic acid	Anionic/ Medium MM/ High CD
CHEMICAL SET II		
Chimec 5762	PAC	Cationic/ High CD
Chimec 5498	n.s.	Cationic/ High MM/ CD n.s.
CHEMICAL SET III		
Flopam SFC 60	Based on Polyacrylamide	Cationic/ Medium MM/ Very High CD
CHEMICAL SET IV		
Floquat FL 2949	EPI-DMA	Cationic/ MM n.s./ Very High CD

(*) MM…Molecular Mass, CD…Charge Density, n.s. … not specified

3.6 Preceding Tests with the Pre-selected Chemical Sets

3.6.1 Alustar 1010 L and Drewfloc 285 (Chemical Set I)

Chemical set I was first tested with the pilot plant from April to Mai 2008 (Epp, 2010 p. 34). Further it was tested in the months of March and April 2010 (Epp, 2010 pp. 34-37). Latest tests were performed in the months of September and October 2010 (Cané, 2011 pp. 64-65).

The testing conditions in the precedent tests were slightly different than the ones for the tests in this thesis (e.g. dosage points, equipment of flocculation unit, origin of produced water inlet stream). The concentrations of Alustar 1010 L and Drewfloc 285 were about 55 ppm and 0.30 – 0.35 ppm.

The tests show that a hydrocarbon content of < 20 ppm after flotation can be reached. A strong influence of the hydrocarbon content in the inlet of the flotation can be noticed, but not in every case. Over some periods the hydrocarbon content after flotation even increased up to 40 and even 60 ppm. A constant water treatment process in terms of hydrocarbon separation seems hard to perform.

Latest tests on the pilot plant were performed in the time from March 2012 until July 2012.

3.6.2 Chimec 5762 and Chimec 5498 (Chemical Set II)

Chemical set II was first tested on the pilot plant in July 2010 (Epp, 2010 pp. 55-57). The testing conditions were slightly different than the ones for the tests in this thesis (e.g. dosage points, equipment of flocculation unit, origin of produced water inlet stream). The tests show that a hydrocarbon content of < 10 ppm after flotation can be reached. The optimum concentrations of Chimec 5762 and of Chimec 5498 in these tests were 14.8 ppm and 0.32 ppm with a volume flow of 6.3 m³/h.

Chemical set II was further tested in the month of November 2010 (Cané, 2011 pp. 66-68). The testing conditions were already similar to the ones in the experiments described in this thesis, except for: the dosage point of Chimec 5498, slightly different setting of the flotation equipment and the origin of the produced water. The best resulting hydrocarbon contents after flotation were around 20 ppm with a concentration of Chimec 5762 of 26 ppm and concentration of Chimec 5498 of 0.32 ppm. The volume flow was 5 m³/h. The influence of the hydrocarbon content in the inlet was not so strong. A constant water treatment process in terms of hydrocarbon separation seemed to be possible.

Latest tests on the pilot plant were performed in the time from March 2012 until July 2012.

3.6.3 Flopam SFC 60 (Chemical Set III)

Chemical set III was tested on the pilot plant from August 2012 until the start of the pilot plant experiments described in this thesis in December 2012.

3.6.4 Floquat FL 2949 (Chemical Set IV)

With chemical set IV only laboratory testing was done before the first testing with the pilot plant which is described in this thesis. The laboratory test was performed in April 2012. A quick description of the test is given in section 4.3.5.

3.7 Description of Analytical Methods

3.7.1 Determination of Hydrocarbons

Background

The hydrocarbon content was formerly determined with FTIR spectroscopy after liquid-liquid extraction of the hydrocarbons with trichlorotrifluoroethane (CFC 113 ® or Freon 113 ®) from water samples. Trichlorotrifluoroethane is a very expensive and ozone depleting substance. These facts led to the introduction of a new recently developed measuring method based on Quantum Cascade Laser Infrared (QCL-IR) Technology. According to this method hydrocarbons are extracted with cyclohexane as a solvent and measured with an analyzing device called Eracheck. The sample preparation procedure is similar to the procedure described in DIN 38409, part H 18. The method allows a hydrocarbon recovery rate of nearly 100 % (depending on the calibration substance) and precise and quick measuring over a range of 0.5 to 2000 ppm (Eralytics GmbH p. 6).

The term hydrocarbon content in this thesis refers to the content of “Total Petroleum Hydrocarbons” (TPH) and is given in ppm (parts per million) referring to the mass of the sample.

Procedure

The testing procedure is standardized in the OMV LEP working procedure instruction AA D CHE 708, “Bestimmung von Mineralöl-Kohlenwasserstoffen”.

Samples were filled on-site in glass bottles of 500 or 1000 ml depending on the expected concentration level of hydrocarbons. The bottles were filled up to the half with the sample to leave space for adding the solvent. The mass of the sample was determined. Then 5 ml of diluted sulfuric acid was added for acidification promoting the dissolution of contained particles. Then 25 or 50 ml respectively of cyclohexane was added as a solvent for the hydrocarbons. The bottle with the two liquid phases was then shaken for 10 minutes to extract the hydrocarbons from the water samples. If necessary the cyclohexane phase was diluted to stay within the measuring range of the Eracheck analyzer. After extraction a clean-up step followed by filtering the extract with sodium sulfate to remove remaining water and with aluminum oxide to remove polar substances (e.g. humins). Then the measuring step with the Eracheck analyzer followed. As a result the analyzer displayed the units of infrared light absorption (mAU) caused by the sample depending on its hydrocarbon content. In a last step the hydrocarbon content was calculated according to a linear calibration curve gained from hexadecane in consideration of the sample mass and the hydrocarbon enrichment of the solvent.

$$\text{hydrocarbon content} = \frac{\text{Oil in Solvent}}{\text{Enrichment}}$$

Equation 3-3: Calculation of the hydrocarbon content of the taken samples with the results from equation 3-3 and 3-4

$$\text{Oil in Solvent} = \text{k (mAU)} + \text{d}$$

Equation 3-4: Calculation of the hydrocarbon content in cyclohexane with the measuring result of the Eracheck analyzer

$$\text{Enrichment} = \frac{\text{Sample volume}}{\text{Solvent volume}}$$

Equation 3-5: Calculation of the enrichment

3.7.2 Determination of Iron

Background

Produced water contains iron in solid and dissolved form (in total about 2.5 mg/l; most of it in dissolved form). Dissolved iron (Fe^{+2} and Fe^{+3}) can deposit to solid iron due to the presence of sulfide ions, carbonate ions and dissolved oxygen. The deposition depends on the pH and the oxidation-reduction balance of the water. The resulting products can be: ferrous sulfide (FeS), ferrous carbonate ($FeCO_3$), ferrous hydroxide ($Fe(OH)_2$), ferric hydroxide ($Fe(OH)_3$) and ferric oxide (Fe_2O_3). (Ostroff, p.73)

There are two sources for iron compounds in produced water:

1. The formation water itself can contain dissolved iron, or
2. corrosion processes of metal equipment (e.g. pipes) can generate dissolved iron that can form solid corrosion products (Ostroff, 1979 p. 72). Conditioning circumstances for the deposition are mentioned above.

A corrosion mechanism for the generation of sulfide ions for instance, is the reduction of sulfate (about 16 mg/l in the feed of the WTP) by sulfate reducing bacteria (SRB) in anaerobe environment. The mechanism is very complex, but can be summarized in the following reaction equation:

$$4Fe + SO_4^{2-} + 4\,H_2O \xrightarrow{SRB} FeS + 3\,Fe(OH)_2 + 2\,OH^-$$

Equation 3-6: General reaction equation of the reduction of sulfate ions by SRB

(Kunze, 2001 S. 2748-2749)

As SRB are anaerobic microbes they especially cause problems in anaerobic systems (like the new WTP).

Iron containing corrosion products contribute to plugging of injection wells (Ostroff, 1979 p. 311).

For this thesis iron was determined for the inlet and outlet of the NSF. Therefore, a taken water sample was split. Out of one part, the total iron concentration in water was determined as described below. The other part is filtered over a 0,45 µm filter mounted on a syringe. The filtrates iron content is considered as dissolved iron. The difference in total and dissolved iron is separable solid iron.

A crucial step in the determination of the iron content of the water samples is the right sampling. It is important to avoid the exposure of sample water to air. If so, ferrous ions together with bicarbonate ions can form ferric hydroxide according to the following formula (Ostroff, 1979 p. 73):

$$2\,Fe^{2+} + 4\,HCO_3^- + H_2O + \frac{1}{2}\,O_2 \rightleftharpoons 2\,Fe(OH)_3 + 4\,CO_2$$

Equation 3-7: Oxidation of dissolved iron by bicarbonate ions due to exposure to air

This process reduces the amount of dissolved iron and the determined iron content is lower than the original one. As a consequence in sampling, sample bottles should be filled up to the very top, letting the water gently stream into it.

Procedure

The testing procedure is standardized in the OMV LEP working procedure instruction AA D CHE 419, “Photometrische Bestimmung von Eisen in Wasser mittels Testkit”.

One way to determine the iron content in produced water is a photometric method using test kits from Merck. The advantage of this method is, that it can also be applied in the filed lab. With this method only free ions can be determined. Therefore all iron has to be dissolved in advance. To do so, a crack set was used for sample preparation (Spectroquant® Crack Set 10C, Co. Merck KgaA, Cat. No. 1.14688.0001). A sample volume of 10 ml was pipetted into a digestion cell. A reagent was added and dissolved by shaking. Further all prepared samples were heated simultaneously in a thermo-reactor for 1 hour at 120°C. Finally the preparation of the samples for the photometric measurements was accomplished with a Spectroquant® test kit for iron (Cat. No. 1.14761.0001). A coloring reagent was added. After three minutes time, the intensity of the samples color correlates to its iron content. With a photometer (Spectroquant® NOVA 400) the total iron contents of the samples in milligram per liter were determined. (Manual of Crack Set 10C and Spectroquant test kit)

3.7.3 Determination of Filterability – Water Blocking Factor

Background

As the pretreated water after flotation has to pass the NSF, and as the purpose of produced water treatment is the reuse of the water as injection water, it is of most importance how easy the treated water can be filtered. The filterability of the water has to be good enough, in order not to lead to an unacceptable rise in pressure drop over the NSF or over the injection well respectively.

Membrane filtration is a common laboratory analyzing technique in water treatment to estimate the potential of water to block a filter like the NSF or to damage the formation rock. Therefore membranes with pore sizes of 8 µm (similar to the pore sizes of a NSF), 3 µm (similar to the pore sizes of a formation rock) and 0,45 µm (smaller than the significant pores in a formation rock (Ostroff, 1979 p. 312)) are used.

The membranes are of about five centimeters in diameter. They are flat and are made of cellulose nitrate. The water passes the filter at constant pressure in the test (1.4 bar). The outcome of a membrane filtration test is a curve representing the volume or, because easier to measure, the mass of filtrate passing the filter over time. Performed with pure water the filtration rate does not change and the filtration curve would ideally be linear. With water, containing oil and suspended solids, the filtration rate decreases with time and the curve is digressively shaped and even bends after a certain time, depending on the amount, type, size and shape of the suspended particles.

To evaluate filtration curves, in order to be able to say which filtration works best, a lot of knowledge and experience is necessary. Even then it is hard to rank the curves. This works better, if the ease of a filtration is characterized by only one figure. Therefore a characteristic function was needed, that represents the filtration behavior of water and that can be parameterized. The filtered volume of water in dependency of time as exponential function was chosen to be suitable:

$$V = \frac{R_{(\text{initial})}}{\lambda}\left(1\text{-}e^{-\lambda t}\right), \qquad \lambda > 0$$

Equation 3-8: Calculation of the filtered volume after a certain time t in a filtration test

The presented approach was developed by OMV LEP. $R_{(\text{initial})}$ is the initial flow rate of pure water (or treated water in best quality) depending on the filter (pore size and area) and the applied pressure. The initial flow rate has to be determined individually. The factor λ is an exponential factor that determines the decrease of the initial flow rate. $R_{(\text{initial})}/\lambda$ is the volume that is filtered after infinite time. If Equation 3-8 is differentiated with respect to time, the instantaneous flow rate can be calculated:

$$\frac{\mathrm{dV}}{\mathrm{dt}} = R_{(initial)}\, e^{-\lambda t}$$

Equation 3-9: Equation for the calculation of the instantaneous flow rate in a filtration test (λ = WBF)

As it is obvious in Equation 3-9, λ being 0 means, that there is no decrease in flow rate. This would be the ideal case. In reality λ is always > 0. So the actual flow rate during a filtration decreases with time depending on λ. The bigger λ the quicker the flow rate decreases. This is correlated to the blocking of the pores in a filter medium during filtration. That's why λ is described as water blocking factor (WBF).

Figure 3-10 shows the influence of the WBF on a filtration curve.

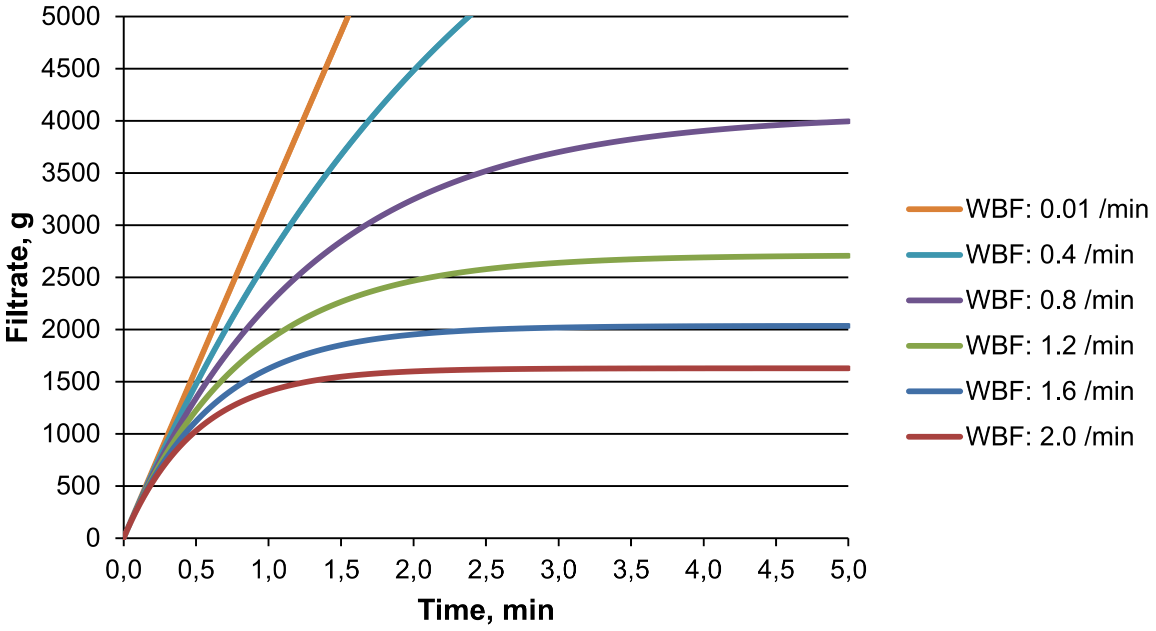


Figure 3-10: Filtration curves resulting from different water blocking factors (WBF); the curves were calculated with Equation 3-8.

Procedure

The testing procedure is standardized in the OMV LEP working procedure instruction AA D CHE 430, "Filtrierbarkeit von Wässern".

For a filtration test 6 liters of sample is necessary. For the 8 µm filtration test, pretreated water after flotation was taken. For the 3 and 0,45 µm filtration test, a sample of the treated water after NSF was taken. The filtration test could be performed as single filtration or cascade filtration. Cascade filtration means that a sample is filtered over an 8 and subsequently over a 3 µm filter (or over a 3 and 0,45 µm filter respectively).

For the sampling a metal vessel, that can be sealed and pressurized, was used. In preparation, the vessel was thoroughly rinsed with nitrogen gas and sealed. This way the sampling could be performed excluding oxygen. The sampling point has fairly been rinsed as well. Then the vessel was entirely filled and brought to the field lab in order to immediately start the filtration test. Otherwise processes that could change the result of the test, have time to occur. In the field lab the vessel was installed into the pressurizing system, where it was constantly stirred by a magnetic mixer to guarantee homogeneity of the sample. The magnetic mixer was placed in the vessel before sampling. Beforehand the filter (of 8 or 3 µm pore size) has been built into a holding device. This was done under water, so that all air bubbles were expelled. Finally the filter was mounted as it is shown in **Figure 3-11**. To catch the filtrate and measure its increasing mass with time, it was caught in a vessel placed on a scale below the filter. In case of a single filtration an open vessel was used. In case of a cascade filtration a closed vessel was used. The scale was connected to a computer, which runs a data logging software. With the generated data the WBF was calculated by means of MS Excel using the formulas, described above. The experimental setup is shown in **Figure 3-11**.

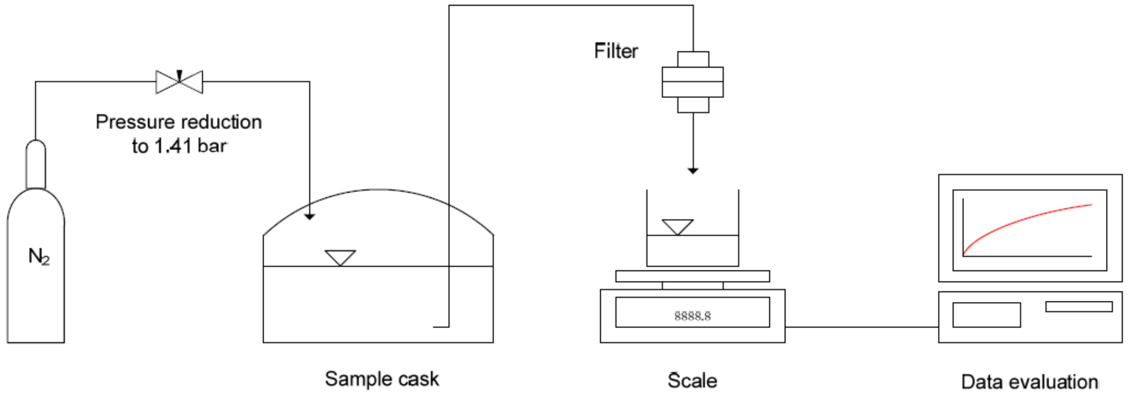


Figure 3-11: Experimental setup for the determination of a filtration curve (Radauer, 2007 p. 19)

3.7.4 Determination of Suspended Solids (de-oiled)

Background

Suspended solids in produced water may consist of sand, corrosion products, scale products and biomass (Ostroff, 1979 p. 311). Together with the oil contained in a sample, they lead to the blocking of a filter during filtration test. The amount of suspended solids, next to the amount of oil and iron is important to know for the interpretation of filtration curves or asking for the origin of a high WBF.

Procedure

The testing procedure is standardized in the OMV LEP working procedure instruction AA D CHE 432, “Bestimmung der abfiltrierbaren Stoffe durch Memranfiltration”.

For the determination of the suspended solids in a sample, the mass of suspended solids on the filter after a filtration test is divided by the volume that was filtered over it. The result is the concentration of suspended solids in milligram per liter. The mass of suspended solids is determined by the difference in weight of the loaded filter and the filter itself. Before weighing the filter after the filtration test, it has to be treated. The sodium chloride, the oil and the water have to be removed. This is done by rinsing the filter with distilled water, isopropanol, and solvent naphtha on a ceramic drip mounted on an evacuated flask. Finally the filter is dried at 105°C for at least one hour in a drying cabinet.

3.7.5 Determination of Turbidity

Background

Undissolved particles in a liquid can scatter light. This effect makes the liquid turbid. Turbidity is an optical property of the liquid. The aim of turbidity measurement is to correlate turbidity with the content of suspended particles (In the case of produced water: oil and suspended solids). But turbidity is influenced by the nature of the particles as well as dependent on the refractive index of the liquid, the particles are dissolved in. Therefore no general correlation is possible. Correlations between turbidity and the concentration of suspended particles can only be made for specific waters which contain a given quantity and size distribution of suspended particles. Knowing this specific correlation, the quantity of suspended particles or their size distribution can be correlated with the amount of scattered light according to a given function. One has to be aware too, that measurements of the same water with different turbidimeters may not agree. (Patton, 1995 pp. 46-49)

Procedure

The testing procedure is standardized in the OMV LEP working procedure instruction AA D CHE 431, “Bestimmung der Trübung von Wasserproben mittels Trübungsmessgerät”.

A nephelometer was used for turbidity measurements (Turbiquant 1000 IR, Co. Merck, Cat. No. 1.18334.0001). The result is given in NTU (Nephelometer Turbidity Units). The cuvette was flushed with the sample before filling it in entirely and measuring.

The correlation of turbidity measuring results presented in this thesis and the concentration of suspended particles is questionable. The reason therefore is the very different composition of the samples containing different amounts of oil, different kinds and amounts of suspended solids, dissolved polymeric molecules, remained flocs and bacteria.

3.7.6 Determination of Flopaam 3630 S – Methods, Applications and Problems

The determination of the content of Flopaam 3630 S before and after each process step would help to investigate where the polymer is separated in the process. Unfortunately there are no laboratory methods delivering reliable quantitative analyzing results in low concentration ranges of about 2 to 10 ppm. The three methods for the determination of polymer concentration that are performed in the OMV Laboratory for Exploration and Production are:

- Qualitative analysis of polyacrylamide in oilfield waters with kaolinite (AA CHE D 664); Determined by: Accelerated settling after coagulation; Application: Field test; Result: There may be polymer/ there is no polymer.

- Quantitative analysis of polyacrylamide in produced water with cadmium iodide (AA CHE D 665); Determined by: Extinction of UV-VIS after modifying amide-groups; Application: Laboratory test; Result: Polymer content from > 10 to < 300 ppm, 10% variability.

- Quantification of polyacrylamide in aqueous samples by means of SEC (Size Exclusion Chromatography, also named gel permeation chromatography) (AA CHE D 666); Determined by: UV-detection after SEC of disturbing matrix components; Application: Laboratory test; Result: The polymer content (down to a content of about 5 ppm (not verified yet)) and the determination of the average molecular mass significant up to maximum 6 million Dalton.

The third method was used to verify the polymer content of the stock solution, which was added to the feed of the pilot plant during the pilot plant experiments described in this thesis. The concentration of the polymer stock solution was calculated by the operator of the polymer mixing plant. The results of the verifying should allow to adjust the dosing of polymer solution during testing. Due to the very time consuming analyzing procedure the results could only serve as information. The adjustment of the dosing did not make sense anymore, because by the time the results were available the tests were over.

In future testing, the analysis could be used to evaluate the quality of the polymer solution. This could help in interpreting the results of the tests because degraded polymer with reduced molecular mass due to free radical degradation most probably has a different impact on the water treatment process then fresh polymer solution. Furthermore the determination of the degree of anionicity would also help in the interpretation of the testing results.

With the method of SEC the content of Flopaam 3630 S in the water before and after gravity separation, flotation and filtration was tried to be determined. The results have to be carefully interpreted, because the expected contents are out of the range that can be quantified. Therefore the results were not considered in this thesis.

4 Experimental Part

4.1 Introduction

In this chapter the pilot plant experiments that were performed and the laboratory experiments with Floquat FL 2949 (chemical set IV) are described and their results are presented and discussed.

The testing was divided in two stages as described in 1.3:

- First stage of testing: Pilot plant experiments 1, 2, 3 and 4; testing of all pre-selected chemical sets with polymer containing oilfield water for flocculation and separation of the flocs by flotation

- Second stage of testing: Pilot plant experiment 5; testing of the nutshell filter with originally polymer containing oilfield water that has been treated with the best performing chemical set evaluated in the first stage of testing.

4.1.1 General Remarks

In all pilot plant experiments the content of Flopaam 3630 S in the feed of the pilot plant was varied. In pilot plant experiment 1 and 4 additionally the content of the used chemical flocculation agent was varied. Every test within a pilot plant experiment with different dosing concentrations of chemicals is identified with a capital letter (e.g. test A, B and so on). In the diagrams showing the hydrocarbon separation results of all tests performed within a pilot plant experiment (e.g. **Figure 4-3**, p. 64) three lines below the x-axis are shown. The first line shows the test identification letter, the second line shows the sampling number and the third line shows the feed concentration of Flopaam 3630 S. In pilot plant experiment 1 and 4 the diagrams showing the hydrocarbon separation results of the combined flocculation and flotation unit (e.g. **Figure 4-4**, p. 67) also show a fourth line beneath the x-axis. This line shows the concentration of flocculant that was added in the flocculation stage.

In the pilot plant experiments 2 – 5 the hydrocarbon separation performance was also tested without Flopaam 3630 S in the feed of the pilot plant in order to have a reference for the tests with Flopaam 3630 S. For reasons mentioned below, this was not done in pilot plant experiment 1. This is the reason why in this case the testing period right before starting with pilot plant experiment 1 was taken as a reference (see section 4.3).

Each section describing a pilot plant experiment contains a summary of the testing data and a process flow diagram providing a quick understanding of the plant setting. The analyzing results of all samples of a pilot plant experiment are listed in tables in the appendix.

Chemical Set IV was also tested beforehand on a laboratory scale imitating the flocculation and flotation process of the new WTP. The results are presented and discussed in section 4.2.

4.1.2 Evaluation of the Hydrocarbon Separation Performance and of the Filterability by Additional Testing

To evaluate the performance of each processing step, the median outlet hydrocarbon contents were compared to limit values which were specified for the New WTP.

If the median hydrocarbon content after flotation in the first stage of testing (pilot plant experiment 1 – 4) was ≤ 20 ppm at a given content of Flopaam 3630 S in the feed of the pilot plant additional testing of the water quality was done. Additional testing means the performance of filtration tests (single or cascade filtrations), the determination of suspended solids, of solid and dissolved iron and also the determination of the turbidity. The additional testing was performed with samples after flotation. With the results of the additional testing it was possible to evaluate whether the required water quality for the filtration with the NSF was achieved.

In the second stage of testing (pilot plant experiment 5) additional testing was performed with samples after flotation with the same purpose described above and with samples after the NSF to evaluate whether the required water quality for re-injection was achieved.

The background of the parameters and the analyzing methods are explained in section 3.7.

Another important parameter to evaluate the hydrocarbon separation performance of a process step is the separation efficiency. The HC separation efficiency η (%) was calculated with the analyzed inlet and outlet HC contents (ppm) of a sampling using the following formula:

$$\eta = \left(1 - \frac{\text{HC Content Outlet}}{\text{HC Content Inlet}}\right) 100\ \%$$

Equation 4-1: Calculation of the hydrocarbon (HC) separation efficiency η of a process step in water treatment

4.1.3 Statistical Evaluation of the Hydrocarbon Contents before and after a Process Step – The Median

The determined hydrocarbon contents of each test in a pilot plant experiment and the hydrocarbon separation efficiencies were statistically evaluated by the median. The median of measured single values is the value that separates the higher half from the lower half. The median is preferred to the mean if the measured values do not follow a Gauss distribution, but are more or less random values. Furthermore, the median is not so sensitive to outliers as the mean. The hydrocarbon separation results often are very erratic which makes it impossible to identify a value being an outlier. This is not a problem when using the median. In the diagrams showing the hydrocarbon separation performances of the process units in each pilot plant experiment the median value of a test sequence is presented after all single values of the test sequence and can be identified by the letter M in the second row below the x-coordinate (e.g. **Figure 4-3**).

Evaluating the HC separation performance in a test the median values together with the single values have to be considered.

4.1.4 Actual Content of Flopaam 3630 S

The actual contents of Flopaam 3630 S in all pilot plant experiments are 10 % less than the stated contents. The reason is that Flopaam 3630 S is a hygroscopic powder and contains about 10 % of water. This fact was not considered in the calculations of the content of Flopaam 3630 S in the feed of the pilot plant in the pilot plant experiments. However, it was considered in the laboratory tests.

4.1.5 Influences on hydrocarbon Separation Performance

Analyzing the hydrocarbon separation performance of the CPI it is important to keep in mind that its performance also depends on the degree of stabilization of the emulsified oil. The smaller the oil droplets are and the more similar their size, the more stable is the emulsion (Ullmann, et al., 1975 p. 452) and the harder their separation in the CPI can be achieved (see also Equation 3-1). As a result with very stable emulsions, more oil droplets break through the CPI and have to be separated in the next treatment step. Chemicals that are used in the production of crude oil like e.g. corrosion inhibitors can stabilize oil in water.

Oil droplets may also break through if the load of oil in the feed of the CPI exceeds its capacity. Usually in these cases the content of stably emulsified oil in the feed is about the same as always, but the content of less stably emulsified oil (which may be called “free oil”) is augmented. It is presumed that free oil breaking through the CPI does not strongly affect the hydrocarbon separation in the following flocculation and flotation unit. The reason is that the droplets are big enough to rise on their own passing the flotation reactor due to the difference of their density to water. So the hydrocarbon content after CPI may exceed the desired 100 ppm, but the outlet hydrocarbon content of the flotation may hardly be affected. For an example see pilot plant experiment 5, sampling D54 (**Figure 4-20**, **Figure 4-21**). However, if the overloading of the CPI lasts on, the hydrocarbon separation performance of the following units is certainly affected. For an example see pilot plant experiment 5 F78-80 after CPI and F80-83 after flotation (**Figure 4-20**, **Figure 4-21**).

Also the presence of ligroin (very light hydrocarbons) in the produced water stream strongly influences the hydrocarbon separation efficiency. It can hardly be separated neither in the CPI nor the flotation. For an example see pilot plant experiment 3, sampling A7 and A12 after flotation (**Figure 4-13**).

It has to be emphasized that the statements given above are working hypotheses and have not been proven.

4.2 Laboratory Experiments with Chemical Set IV (Floquat FL 2949)

4.2.1 Goal and Purpose

Before testing Floquat FL 2949 in the flocculation unit of the pilot plant, it was tested on a laboratory scale for its capacity to remove hydrocarbons and Flopaam 3630 S by flocculation. The purpose was to find out the relevance of the reaction time and the reachable WBF (8 µm) and hydrocarbon content after flotation.

4.2.2 Performance

For each experiment treated water after gravity separation (PFD: SP 2.2, see **Figure 3-2**) was used. The vessel used for the flocculation and flotation processes was a cylindrical plastic bin of 20 liter with a bottom side outlet valve. For each test the bin has been filled with water to a volume of 18 liters. For the flotation process 20 % of the volume was taken and saturated with nitrogen gas up to a pressure of 5 bar. The saturated flotation water then was induced with a metal lance to the bottom of the plastic bin. The gas expanded again and the flocs that were generated in the preceding flocculation process were separated by flotation.

The reference sample (treated water after gravity separation only) was mixed for 7 minutes on a medium turbulence level with a mechanical mixer and then treated by flotation.

In the samples 1 and 2 the dissolved Flopaam 3630 S was vigorously mixed in, then Floquat FL 2949 was added (except sample 1 in test batch 1: no Floquat FL 2949 was added) and mixed on a medium turbulence level for 7 or 14 minutes. Finally the samples were treated by flotation as described above.

In all experiments samples for the determination of the hydrocarbon content and the filtration test were taken from the bottom side valve of the plastic bin. The samples were taken 2 minutes after flotation to make sure that all bubbles have risen.

4.2.3 Results and Discussion

Table 4-1 shows the results of the laboratory experiments 1, 2 and 3 which are discussed in this section.

No matter if the reaction time was 7 or 14 minutes, prolonged floc formation could be observed in the samples 2 in experiments 1 and 2. Doubling of the reaction time from 7 to 14 minutes did not lead to any significant difference in the resulting WBFs (8 µm) and the resulting hydrocarbon content after flotation (see results of test batch 3 in **Table 4-1**).

The flotation sludge was very sticky in each case.

The WBFs (8 µm) of the samples treated with Floquat FL 2949 were in the high range of 6 to 8 min^{-1}.

In experiment 1 a cascade filtration test was performed with the reference sample and with sample 2. The resulting WBF (3 µm) of the reference sample is augmented by not separated suspended solids and oil. The WBF (3 µm) of sample 2 is quite good compared to the afforded WBF (3 µm) of 0.7 min^{-1} for the re-injection. The augmented WBF (8 µm) of 6.33 min^{-1} is a sign for the buildup of a filter cake that filtered most of the suspended solids < 3 µm as well. That's probably the reason for the good WBF (3 µm).

The hydrocarbon separation efficiency cannot be judged because the original hydrocarbon content of the treated water after gravity separation was not determined. However the hydrocarbon content after flocculation with Floquat FL 2949 and following flotation was very low (< 10 ppm) except in sample 2 of experiment 2.

Table 4-1: Results of the laboratory experiments with Floquat FL 2949

Expe-riment	**Sample**	**Flopaam 3630 S**	**Floquat FL 2949**	**Reaction Time**	**HC content**	**WBF (8 µm)**	**WBF (8 → 3 µm)**
#		ppm	ppm	min	ppm	1/min	1/min
1	**Reference**	0	0	7	15	-	1.46 → 2.21
	1	10	0	7	30	19.71	-
	2 (*)	10	75	7	1.9	-	6.33 → 1.00
2	**Reference**	0	0	7	46	1.66	-
	1	-	-	-	-	-	-
	2 (*)	10	75	14	34.0	7.97	-
3	**Reference**	0	0	7	28	1	-
	1 (**)	10	75	7	9.2	6.2	-
	2 (**)	10	75	14	7.8	6.5	-

(*) Very sticky flotation sludge and ongoing flocculation after sampling
(**) Sticky flotation sludge

In sample 1 of experiment 1 the water containing Flopaam 3630 S was not treated with Floquat FL 2949. In comparison to the hydrocarbon content of the reference sample it can be observed that Flopaam 3630 S has a direct worsening influence on the flotation process itself. The very high WBF (8 µm) of 19.71 min^{-1} proves that hardly any (or none) Flopaam 3630 S can be separated by flotation alone.

4.3 First Stage of Testing

4.3.1 Testing of Flopam SFC 60 (Chemical Set III) before Pilot Plant Experiment 1

4.3.1.1 General Remarks

Before starting pilot plant experiment 1 Flopam SFC 60 was tested over a long period of time without the dosing of Flopaam 3630 S to the feed of the pilot plant. This testing period was from August 6 until December 7, 2012.

The goals were:

1. To find out the range of dosing for best hydrocarbon separation results
2. To collect flotation sludge for an experiment on the treatability of the flotation sludge with a tricanter centrifuge

The hydrocarbon separation performance was satisfactory, but at the end of the testing period the hydrocarbon contents after flotation showed a trend to higher values. It was assumed that this was due to fouling of the pilot plant equipment. It was decided to clean the following parts:

- Inlet of the CPI (pressure was at about 0.6 bar instead of 0.2 to 0.3 bar)
- GDR (it was supposed that the nitrogen saturation was diminished because of fouling of the membrane by residues of Flopam SFC 60 – that may not have been sufficiently separated in the flotation process – and oil)
- Flotation reactor (fouling of the skimmer and the walls inside the reactor was supposed)

None of the cleaning led back to the earlier lower hydrocarbon contents after flotation.

4.3.1.2 Reference Testing Period

To be able to compare the performance of Flopam SFC 60 without and with Flopaam 3630 S (pilot plant experiment 1) in the feed of the pilot plant, the testing period directly before pilot plant experiment 1 was chosen as reference testing period.

The results of the reference testing period are shown in **Figure 4-1**.

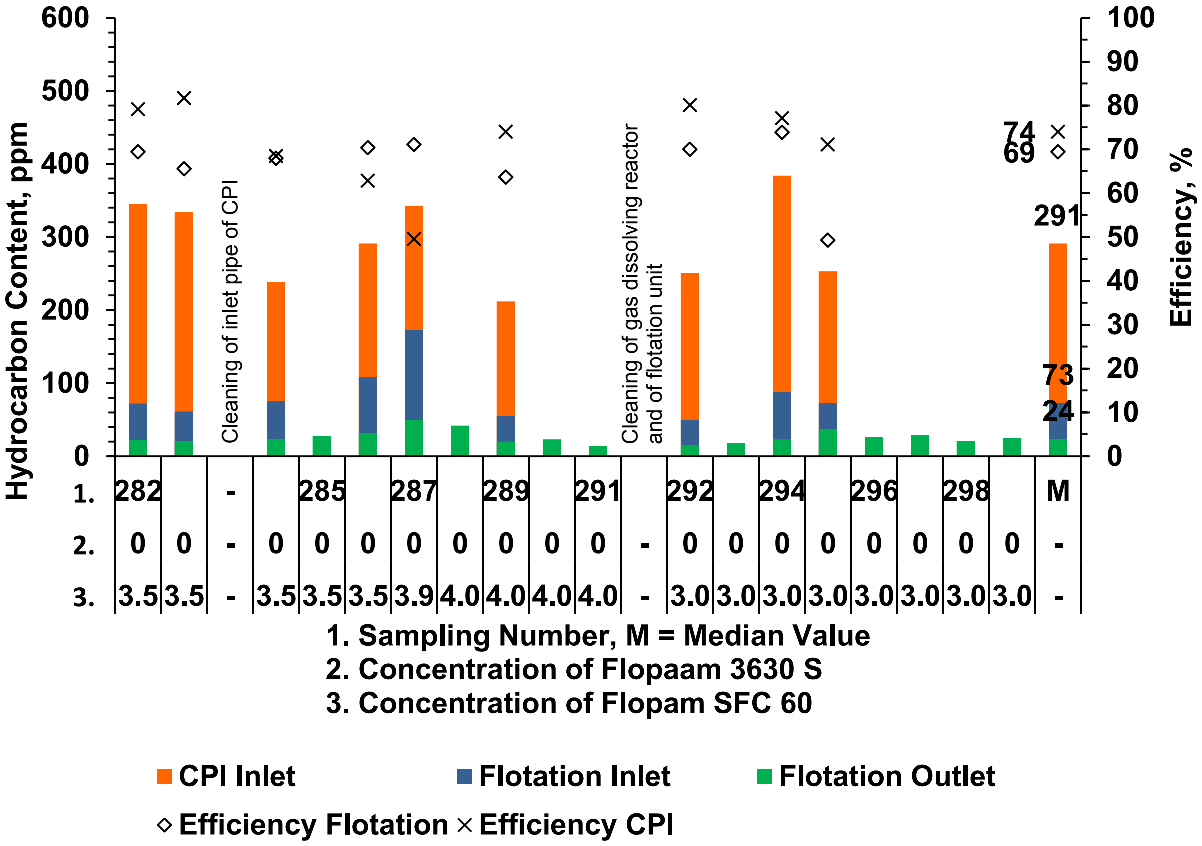


Figure 4-1: Hydrocarbon separation results of the CPI and the combined flocculation and flotation during the reference testing period, as well as the resulting separation efficiencies

The median hydrocarbon content in the inlet of the CPI was 291 ppm. That is below the specified range of hydrocarbon content the pilot plant was designed for (300 to 500 ppm). Despite this very low median hydrocarbon content, the median outlet content of 73 ppm is rather high. The median hydrocarbon separation efficiency of the CPI in this period was 74 % only. The median hydrocarbon content of 24 ppm after flotation is unusual high as it was already discussed above. The median hydrocarbon separation efficiency of the flotation in this period was 69 % only. It has to be noticed that many single hydrocarbon values after flotation were well above 20 ppm. The hydrocarbon content after flotation in sampling 287 was even 50 ppm.

4.3.2 Pilot Plant Experiment 1 – Flopam SFC 60 (Chemical Set III)

4.3.2.1 Goal and Approach

In pilot plant experiment 1 the hydrocarbon separation performance of the pilot plant was intended to be tested with a content of 10 ppm of Flopaam 3630 S in the feed of the pilot plant and a varying dosage of Flopam SFC 60 in the flocculation unit.

The goal was to find the concentration of Flopam SFC 60 leading to the lowest possible hydrocarbon content after flotation. The limit value for the hydrocarbon contents after flotation in this case was ≤ 24 ppm (see reference testing period in section 4.3.1.2).

Due to unsatisfying hydrocarbon separation results after flotation during the pilot plant experiment it was decided to reduce the dosing of Flopaam 3630 S (Jour fixe on December 13, 2012). So 5 and 2 ppm of Flopaam 3630 S were tested as well.

4.3.2.2 Testing Data

Testing Period: December 10 – 20, 2012 (CW 50 and 51)

Dosage of Chemical Set III: 3.5, 6.0, 9.9, 0.0 ppm

Corresponding Volume Flow: 2.9, 5.0, 8.2, 0.0 l/h

Dosing Point: DP 3.2 (see **Figure 4-2**)

Hydraulic Residence Time: 7.9 min (dosing → inlet flotation reactor)

Percentage of Reagent in Distilled Water in Prepared Solution: 0.5 % (by volume)

Lot Number: C18/1326

Dosing Pump: Helical rotor pump

Dosage of Flopaam 3630 S: 10, 5 and 2 ppm in the feed of the pilot plant

Note: Flopam SFC 60 was tested first because the installation of the coagulator (quick coupling pipes, co. Bauer) was only necessary testing the other chemical sets (I, II and IV).

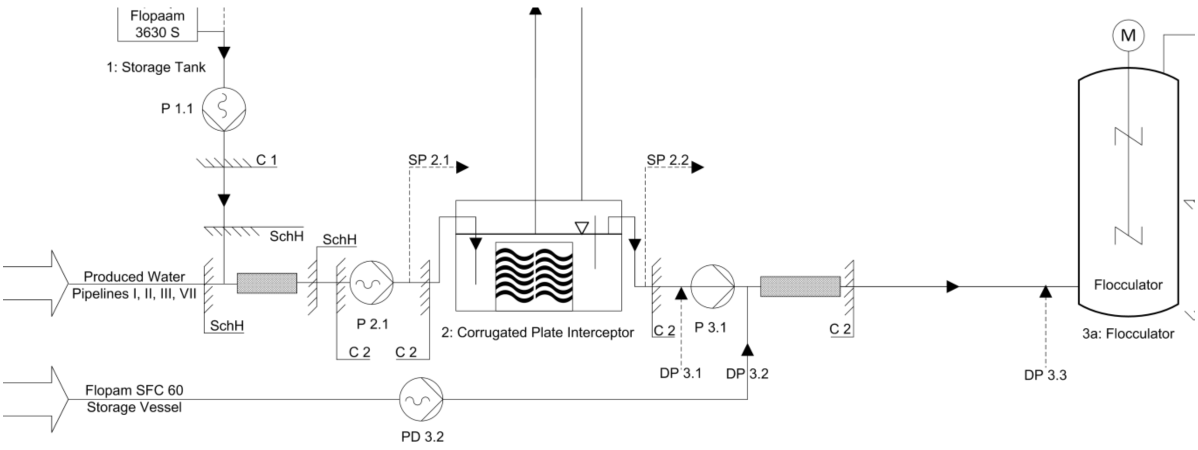


Figure 4-2: Detail of PFD in pilot plant experiment 1 with dosing location of Flopam SFC 60

4.3.2.3 Hydrocarbon Separation Results of the Corrugated Plate Interceptor

The following description refers to the results of the hydrocarbon separation performance of the CPI shown in **Figure 4-3** on page 64. The figure shows the hydrocarbon contents before and after the CPI in pilot plant experiment 1, as well as the correlating hydrocarbon separation efficiencies. Note: The dosing of the flocculant Flopam SFC 60 was after the CPI, so the potentially influencing parameter was Flopaam 3630 S.

During the tests A to E the inlet hydrocarbon contents were scattered within the required range of 300 to 500 ppm. The median inlet hydrocarbon contents varied from 319 ppm up to even 446 ppm. The median outlet hydrocarbon contents were higher than the limit value of 100 ppm. They rose during the tests from 110 to 134 ppm. The hydrocarbon separation efficiencies popped up and down. Their median values show a decreasing tendency mainly due to the constant rise of the outlet hydrocarbon contents. In test A the median hydrocarbon separation efficiency was 73 %, which is close to the one of the reference period (74 %). In test E the median value of the hydrocarbon separation efficiency was reduced to only 66 %.

During Test F there was an automatic pilot plant shutdown. The pneumatic valve of the pilot plant inlet (normally closed function) closed because pressurized air supply stopped due to a fail of the compressor. The pilot plant was shut down for about 12 hours. The outlet hydrocarbon contents of sampling 27 to 34 were significantly raised. In test G their median value was 182 ppm. Also the inlet hydrocarbon contents were augmented. Their median value resulted in 493 ppm. The median hydrocarbon separation efficiency in test G (62 %) was the lowest of the pilot plant experiment. The efficacy of the CPI seems to be affected by the shutdown.

The median hydrocarbon contents and the separation efficiency were not calculated for test F due to the shutdown of the pilot plant.

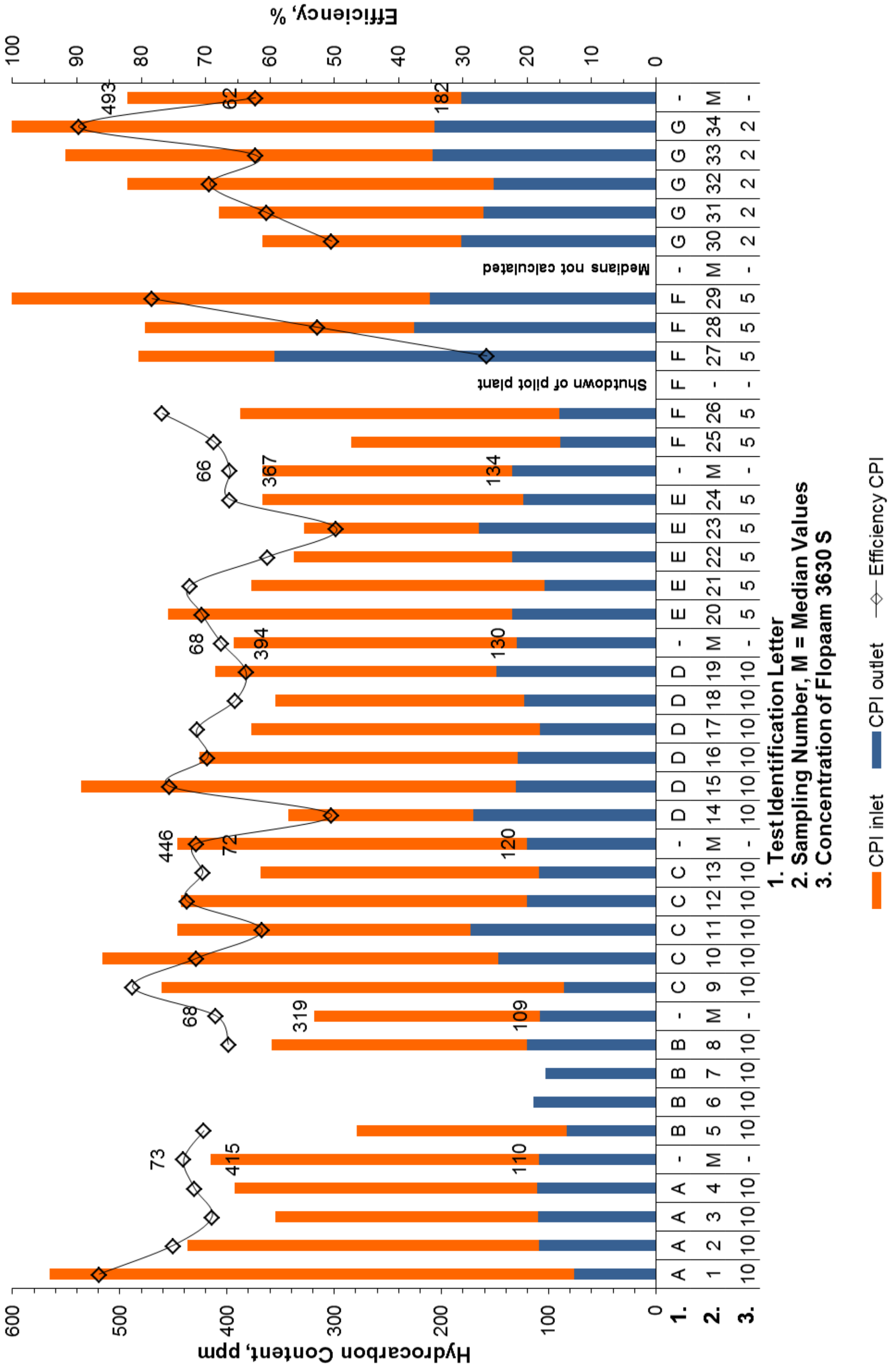


Figure 4-3: Pilot plant experiment 1 - Hydrocarbon separation results of the CPI at 10, 5 and 2 ppm of Flopaam 3630 S in the feed of the pilot plant, as well as the resulting separation efficiencies (Inlet hydrocarbon values exceeding the y-axis: 974 ppm in F29 and 2021 ppm in G34)

4.3.2.4 Results of the Combined Flocculation and Flotation

The following description refers to the results of the hydrocarbon separation performance of the combined flocculation and flotation unit shown in **Figure 4-4**, on page 67. The figure shows the hydrocarbon contents before and after flotation in pilot plant experiment 1 as well as the corresponding hydrocarbon separation efficiencies.

Test A - 10 ppm of Flopaam 3630 S

In test A 3.5 ppm Flopam SFC 60 were added to the water stream. This content was successfully used in treating produced water from water flooding only (without Flopaam 3630 S in the feed of the pilot plant). The median inlet hydrocarbon content of the flocculation unit was 110 ppm. This is slightly higher than the limit value of 100 ppm after gravity separation. The inlet contents were quite stable. The median hydrocarbon content after flotation was 58 ppm. The minimum value was 41 and the highest value was 87 ppm. The hydrocarbon separation efficiency was therefore rather erratic. Its median value was 45 %.

Test B - 10 ppm of Flopaam 3630 S

Trying to improve the hydrocarbon separation performance with a higher content of Flopam SFC 60 the dosing was raised to 6.0 ppm. The median inlet hydrocarbon content (109 ppm) was similar to the one in test A, but varying a bit more now. The hydrocarbon contents after flotation were less erratic. With a median value of 47 ppm they were generally lower than in Test A. The separation efficiency was higher and more stable now. Its median value was 53 %.

Test C - 10 ppm of Flopaam 3630 S

The dosing content of Flopam SFC 60 was raised again. It was 9.9 ppm. The inlet contents were significantly risen for the first time in sampling C10 and C11 (147 and 173 ppm), but turned back to lower values in sampling C12 and C13 (120 and 109 ppm). The median inlet content was higher than in Test A and B (120 ppm). The hydrocarbon contents after flotation went along with the inlet hydrocarbon contents. Their median outlet hydrocarbon content was 75 ppm which was significantly increased. Considering the efficiency of 46 % the performance is similar to test A where the efficiency was 45 %. In test C the efficiency values were relatively constant, which is a sign for a more stable treatment process.

The outlet hydrocarbon content of sampling C9 was not considered in the calculation of the median value in test C, because of its differing dosing of Flopam SFC 60.

Test D - 10 ppm of Flopaam 3630 S

To see if the hydrocarbon separation performance without Flopam SFC 60 becomes worse, its dosing was stopped in test D. The median inlet hydrocarbon content of 130 ppm was again higher than the ones in the tests A, B and C. The single values were between 108 ppm (minimum) and 170 ppm (maximum). As a surprise the median outlet hydrocarbon content was similar to the one in test C with a dosing of 9.9 ppm. The median separation efficiency of 44 % was also only a little bit lower.

Test E - 5 ppm of Flopaam 3630 S

Flopam SFC 60 has still been left away and the content of Flopaam 3630 S in the feed of the pilot plant was reduced to 5 ppm. The median inlet hydrocarbon content was again augmented (134 ppm) in comparison to the preceding tests. The outlet hydrocarbon contents again went up and down following the inlet contents. This results of course in a relatively stable hydrocarbon separation efficiency which is a sign for a stable separation process. The median outlet hydrocarbon content was 72 ppm which is very close to the one of test D. The median efficiency was 46 %. The reduction of Flopaam 3630 S to half of the concentration of test D had no significant impact on the hydrocarbon separation performance.

Test F - 5 ppm of Flopaam 3630 S

Flopam SFC 60 was added again with a dosage of 3.5 ppm. The content of Flopaam 3630 S in the feed of the pilot plant was still 5 ppm. Unfortunately there was an automatic shutdown of the pilot plant in the night following sampling number 26. Test F is therefore not considered for analyzing; the median hydrocarbon contents are not calculated.

Test G - 2 ppm of Flopaam 3630 S

Finally the content of Flopaam 3630 S was reduced to 2 ppm. The content of Flopam SFC 60 was kept constant at 3.5 ppm. The median hydrocarbon inlet content of 182 ppm was significantly augmented. In the outlet the median hydrocarbon content was 82 ppm. This results in a median hydrocarbon separation efficiency of 54 % which is the highest median separation efficiency in the pilot plant experiment even though the outlet hydrocarbon content (82 ppm) was the highest of all tests.

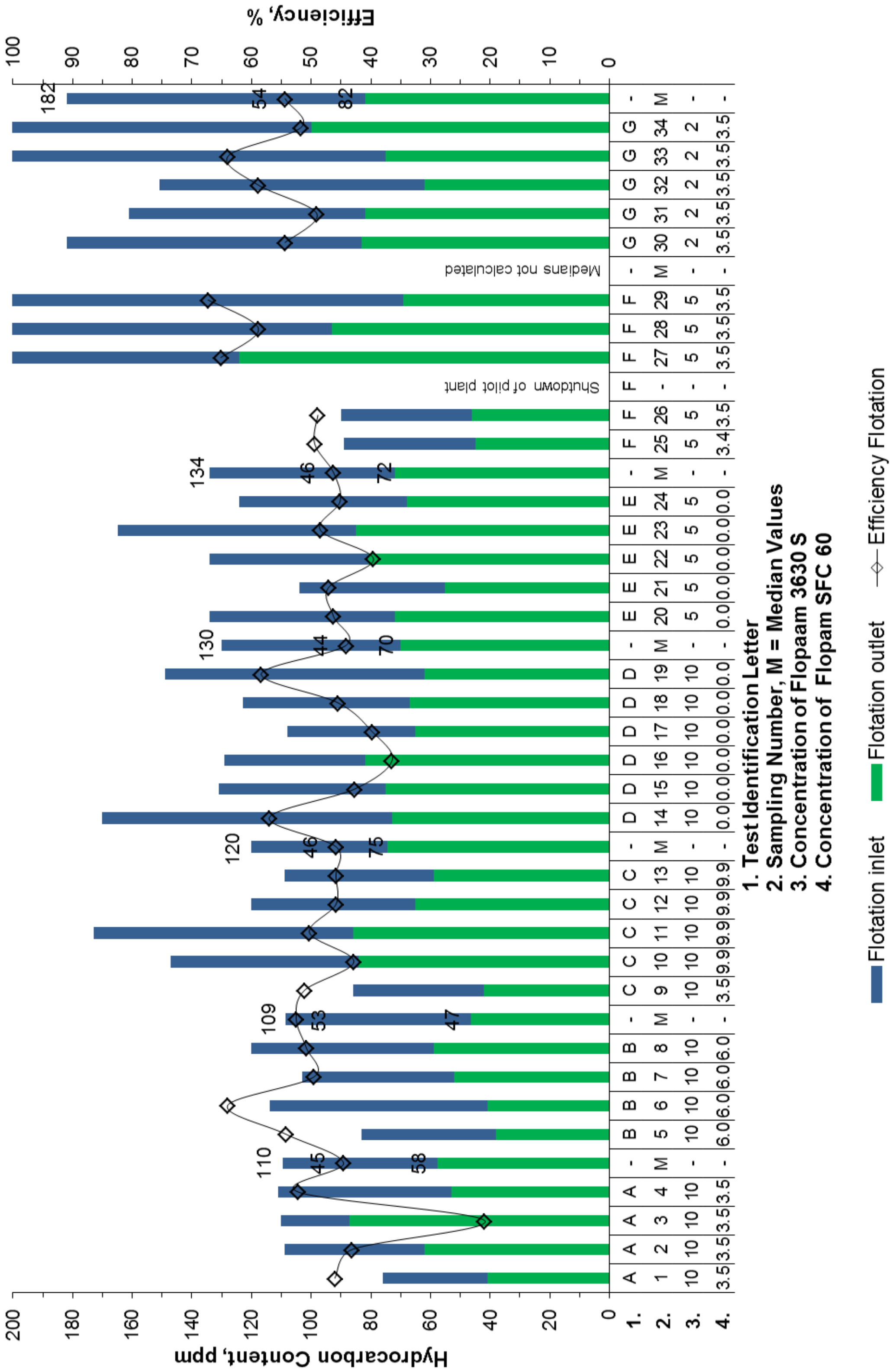


Figure 4-4: Pilot plant experiment 1 - hydrocarbon separation results of the combined flocculation and flotation unit at 10, 5 and 2 ppm of Flopaam 3630 S in the feed of the pilot plant and different concentrations of Flopam SFC 60, as well as the resulting separation efficiencies (Inlet hydrocarbon contents exceeding the y-axis: 356, 226, 211 ppm in F27, F28, F29; 208 and 207 ppm in G33 and G34.)

4.3.2.5 Discussion and Conclusion

The median test results of pilot plant experiment 1 are summarized in **Table 4-2**.

Table 4-2: Pilot plant experiment 1 – Summary of the median hydrocarbon (HC) contents and separation efficiencies of each test with correlating content of Flopaam 3630 S in the feed of the pilot plant (all hydrocarbon contents and separation efficiencies are median values)

		Corrugated Plate Interceptor		**Combined Flocculation & Flotation**		
Test ID	**Flopaam 3630 S**	**HC content Inlet → Outlet**	**Separation Efficiency**	**Chemical Set III**	**HC content Inlet → Outlet**	**Separation Efficiency**
-	ppm	ppm	%	ppm	ppm	%
Ref.	0	291 → 73	74	3.5	73 → 24	69
G	2	493 → 182	62	3.5	182 → 82	54
F (*)	5	-	-	3.5	-	-
E	5	367 → 134	66	0.0	134 → 72	46
D	10	394 → 130	68	0.0	130 → 70	44
C	10	446 → 120	72	9.9	120 → 75	46
B	10	319 → 109	68	6.0	109 → 47	53
A	10	415 → 110	73	3.5	110 → 58	45

(*) Median values not calculated due to failure of the pilot plant during the test

Corrugated Plate Interceptor

The hydrocarbon separation performance of the CPI started about the same level then in the reference period. Considering the separation efficiencies of the CPI during the whole pilot plant experiment, a general decline can be noticed. Jellylike agglomerates were observed floating in the separated oil phase and also between the corrugated plates when they were taken out for cleaning. It seems possible that the decreasing separation efficiency is due to contamination of the corrugated plates of the CPI. The origin of the agglomerates is not known. Their generation may have been promoted or induced by Flopaam 3630 S. But they could also just be contaminants that come with the water from production side. Unfortunately the degree of contamination of the separated oil phase in the CPI was not investigated before pilot plant experiment 1, so a comparison is not possible.

A correlation of the hydrocarbon separation efficiency and the content of Flopaam 3630 S in the feed of the pilot plant could assumingly not be detected. The contents of Flopaam 3630 S were too low to significantly affect the viscosity. Other influences are more dominant.

It can be noticed in **Figure 4-3** that sometimes the hydrocarbon contents after the CPI do not go along with the hydrocarbon inlet content. That could depend upon the degree of emulsification of the oil. The better it is emulsified, the smaller the oil droplets are and the easier they can break through the CPI.

Due to remodeling of the piping between the production facilities and the existing WTP, the water quality changed a lot. This could also have been a reason for the reduced hydrocarbon separation performance of the CPI during the pilot plant experiment.

Combined Flocculation and Flotation

First it has to be stated that even before pilot plant experiment 1 the hydrocarbon separation process did not work well with Flopam SFC 60, beginning with November 20, 2012. Before that date the hydrocarbon separation process was satisfactory. The hydrocarbon contents after flotation were mostly << 20 ppm.

In pilot plant experiment 1 generally all hydrocarbon contents after flotation were way beyond the limit value of 24 ppm specified based on the results of the reference period. Variation of the dosing of Flopam SFC 60 led to no satisfying result. The best hydrocarbon separation performance could be reached in test B (with 6 ppm of Flopam SFC 60). The median separation efficiency (53 %) was almost as high as in test G and the median hydrocarbon content after flotation was the lowest throughout all tests (47 ppm). But still this is no acceptable result for the future operation of the new WTP.

The testing of the filterability of the water after flotation was not performed in pilot plant experiment 1, because in any of the tests the median hydrocarbon content after flotation was below 24 ppm. Afterwards it can be stated, that the testing of the filterability would have been interesting in order to find out if the WBF of produced water containing Flopaam 3630 S could be improved by adding Flopam SFC 60. However, a low hydrocarbon content after flotation is usually a sign for a low WBF and all hydrocarbon contents were comparably high.

The actual content of Flopaam 3630 S in test E (5 ppm) and in test G (2 ppm) as well as the actual content of Flopam SFC 60 in test D (0.0 ppm) could be higher than the content achieved with dosing. It is possible that the chemicals that were added before in a higher concentration accumulated in zones of poor current and were slowly swept out by the water stream. Thus, a higher actual concentration could have been the result.

4.3.3 Pilot Plant Experiment 2 – Chimec 5762 and Chimec 5498 (Chemical Set II)

For the following pilot plant experiments a prolongation of the residence time in the flocculation stage was needed to gain reaction time for the formation of flocs with Chimec 5762. Therefore a pipeline of quick coupling pipes of 19 m length was installed in the combined flocculation and flotation unit. The pipe has an inner diameter of about 10 cm. This is about twice the diameter of the preceding pipeline. It leads to a slow-down of the water stream (less turbulence) which is favorable for the desired formation of flocs after the mixing in of the first flocculant. The reactor is described as coagulator in this thesis.

The coagulator was installed outside of the containers due to its length. To avoid temperature loss or even freezing of the transported water (in case of a pilot plant shutdown) the pipeline was equipped with an electric trace heating and was insulated. The pipeline was also installed with a slight downward slope for drainage purposes for the case it was necessary to empty the pilot plant.

4.3.3.1 Goal and Approach

In pilot plant experiment 2 the hydrocarbon separation performance of the pilot plant was intended to be tested with 0, 10, 5 and 2 ppm of Flopaam 3630 S in the feed of the pilot plant and at constant dosage of Chimec 5762 and Chimec 5498. Chimec 5762 acts as coagulating agent and Chimec 5498 acts as flocculation aid.

In order to avoid that polymer that accumulated in zones with reduced flow during preceding tests with a higher polymer concentration finally influences the actual polymer concentration at lower testing concentrations it would have been better in this pilot plant experiment to start with 2 ppm of polymer and switch to higher contents afterwards. The reason for selected approach was to stick to the same testing procedure than performed in pilot plant experiment 1 in order to obtain comparable results and presuming that the effect would not be significant.

As a result of the satisfying hydrocarbon separation performance with 2 ppm of Flopaam 3630 S in the feed of the pilot plant in test D the content of the polymer was raised to 3 ppm in the last test of the pilot plant experiment.

4.3.3.2 Testing Data

Testing Period: January 8 – 17, 2013 (CW 02 and 03)

Dosage of Chemical Set II: 20 ppm (Chimec 5762) and 0.15 ppm of (Chimec 5498)

Corresponding Volume Flow: 1.9 l/h (Chimec 5762) and 1.5 l/h (Chimec 5498)

Dosing Points: DP 3.2 (Chimec 5762) and DP 3.3 (Chimec 5498) (see **Figure 4-5**)

Hydrodynamic Detention Time: 9.7 min (Chimec 5762) and 7.8 min (Chimec 5498) (dosing → inlet flotation reactor)

Percentage of Reagent in Distilled Water in Prepared Solution: 4.0 % (Chimec 5762) and 0.05 % (Chimec 5498)

Lot Number: 121366 (Chimec 5762) and 121367 (Chimec 5498)

Dosing Pump: Diaphragm pump (Chimec 5762) and helical rotor pump (Chimec 5498)

Dosage of Flopaam 3630 S: 10, 5, 2 and 3 ppm in the feed of the pilot plant

Note: The coagulator (quick coupling pipes, co. Bauer) was installed right before the pilot plant experiment.

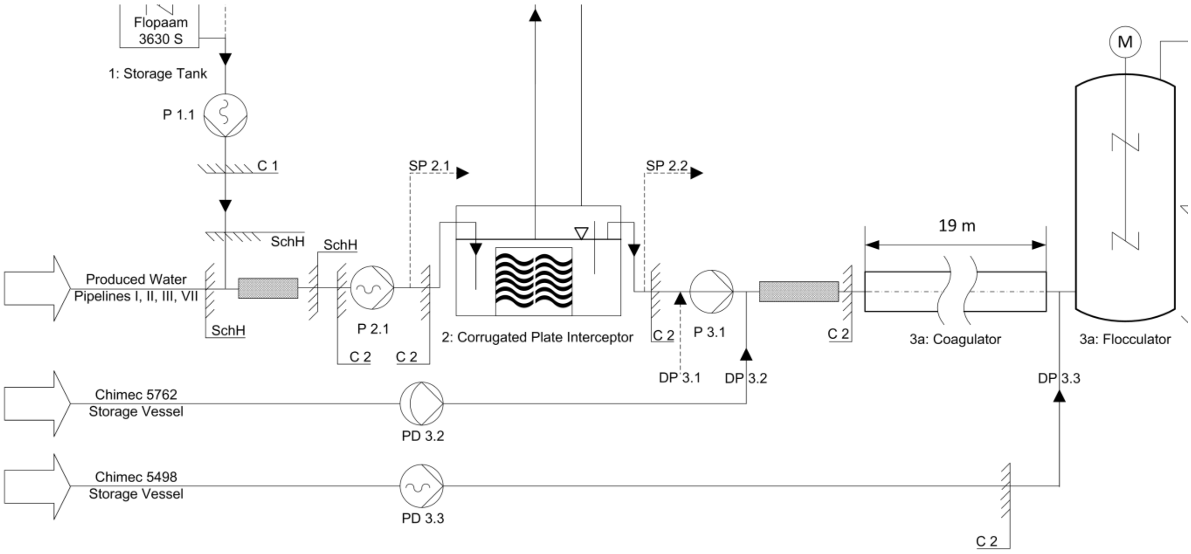


Figure 4-5: Detail of PFD in pilot plant experiment 2 and in pilot plant experiment 5 with dosing location of Chimec 5762 and Chimec 5498

4.3.3.3 Hydrocarbon Separation Results of the Corrugated Plate Interceptor

The following description refers to the results of the hydrocarbon separation performance of the CPI shown in **Figure 4-6**, on page 74. The figure shows the hydrocarbon contents before and after the CPI in pilot plant experiment 2, as well as the correlating hydrocarbon separation efficiencies. Note: The dosing of chemical set II was after the CPI, so the potentially influencing parameter was Flopaam 3630 S.

The inlet hydrocarbon contents in all tests were within the required range of 300 to 500 ppm. The outlet hydrocarbon contents also were all below the limit value of 100 ppm in all tests. In test A, B, D and E their median values were between 55 and 58 % of the limit value. Only in test C the median hydrocarbon content was 94 ppm. That are 94 % of the limit value. The hydrocarbon separation performance of the CPI was excellent throughout all tests. The median separation efficiencies ranged from 77 to 84 %. Most efficiency values were between 80 and 90 %. This is a clear sign for a very stable separation process.

The results of the tests A, B, D and E prove that the CPI is far from its limits with the inlet hydrocarbon content of approximately 350 ppm.

4.3.3.4 Hydrocarbon Separation Results of the Combined Flocculation and Flotation

The following description refers to the results of the hydrocarbon separation performance of the combined flocculation and flotation unit shown in **Figure 4-7**, on page 75. The figure shows the hydrocarbon contents before and after the combined flocculation and flotation unit in pilot plant experiment 2, as well as the correlating hydrocarbon separation efficiencies. The dosing of chemical set II was kept constant in all tests sequences.

As it was expected the influence of Flopaam 3630 S became obvious.

Test A - 0 ppm of Flopaam 3630 S

In test A no Flopaam 3630 S was added to determine the hydrocarbon separation performance of the pilot plant without its influence. The median inlet hydrocarbon content of only 58 ppm was rather low. The outlet hydrocarbon content is < 10 ppm as it was expected due to previous testing results. The median hydrocarbon separation efficiency was 87 % which is a proof for an excellent performance of the flocculation and flotation processes.

Test B - 10 ppm of Flopaam 3630 S

In test B the median inlet hydrocarbon content is the same as in test A (58 ppm). So the resulting outlet hydrocarbon contents of the two tests can directly be compared to each other. With a content of 10 ppm of Flopaam 3630 S in the feed of the pilot plant the outlet hydrocarbon content was significantly augmented to a median value of 35 ppm (7.4 ppm in test A). The resulting median hydrocarbon separation efficiency was only 36 %.

Test C - 5 ppm of Flopaam 3630 S

In test C the content of Flopaam 3630 S was reduced to 5 ppm. Nevertheless, the median outlet hydrocarbon content rose to 45 ppm. Calculating the median hydrocarbon separation efficiency with the also augmented median inlet hydrocarbon content (94 ppm) shows that the hydrocarbon separation process performs assumingly better than in test B. The median hydrocarbon separation efficiency was 54 %.

Test D - 2 ppm of Flopaam 3630 S

The separation efficiency keeps on improving with lower contents of Flopaam 3630 S in the feed of the pilot plant. With 2 ppm of Flopaam 3630 S it was 77 %. This is 10 % lower than in test A without Flopaam 3630 S. The median outlet hydrocarbon content was 14 ppm. The median inlet hydrocarbon content of 58 ppm was very low compared to the one in test A.

Test E - 2 ppm of Flopaam 3630 S

Due to the good hydrocarbon separation results in test D the content of Flopaam 3630 S was raised to 3 ppm. The median outlet hydrocarbon content was 16 ppm now. The median hydrocarbon separation efficiency was reduced to 70 %.

Especially in test B, C and E with 10, 5 and 2 ppm of Flopaam 3630 S in the feed of the pilot plant fluctuations of the hydrocarbon separation efficiency are noticeable. With increasing content of Flopaam 3630 S the separation process seems to become more and more unstable.

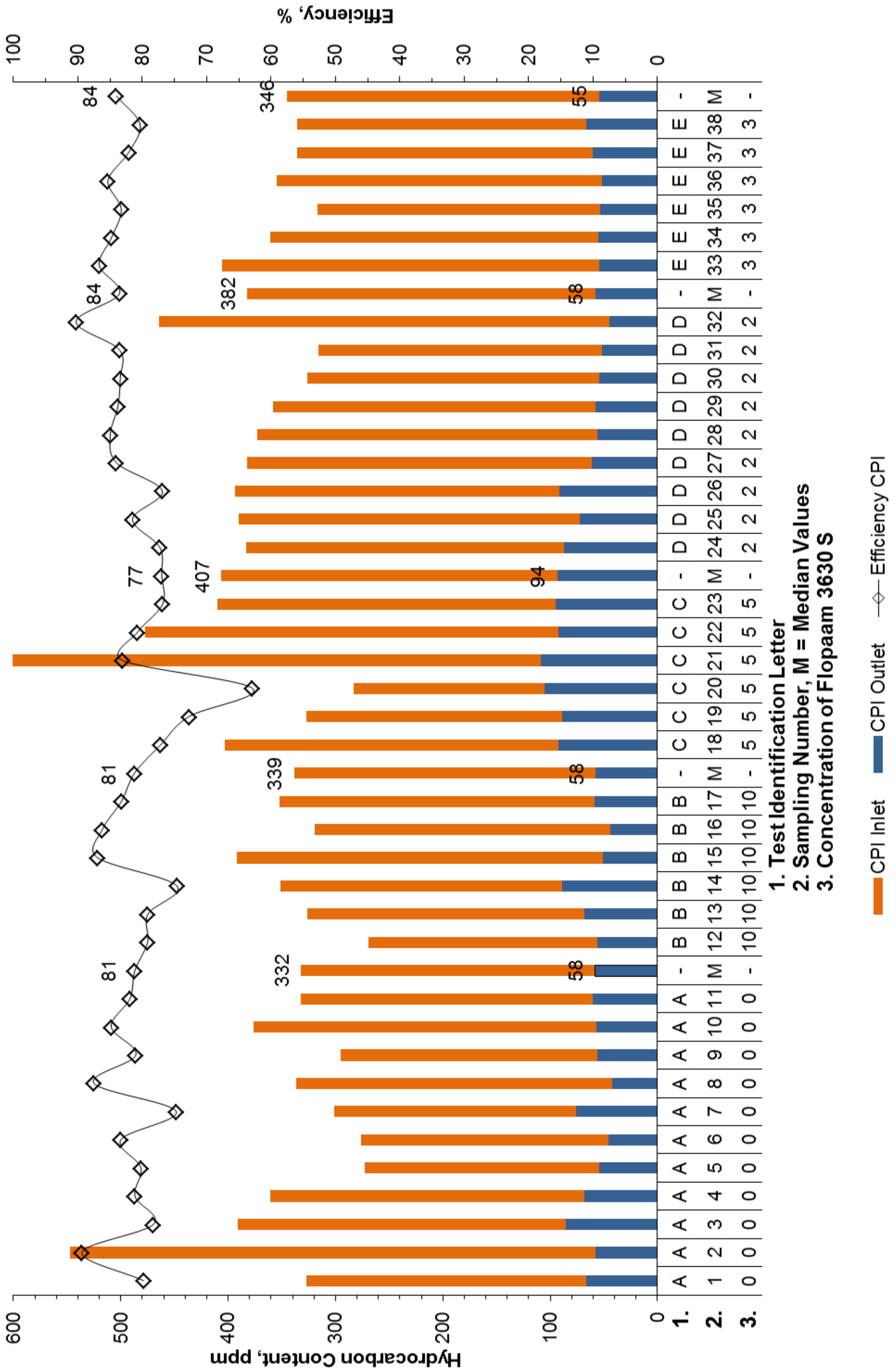


Figure 4-6: Pilot plant experiment 2 - Hydrocarbon separation results of the CPI at 0, 10, 5, 2 and 3 ppm of Flopaam 3630 S in the feed of the pilot plant, as well as the resulting separation efficiencies (Inlet hydrocarbon values exceeding the y-axis: 646 ppm in C21)

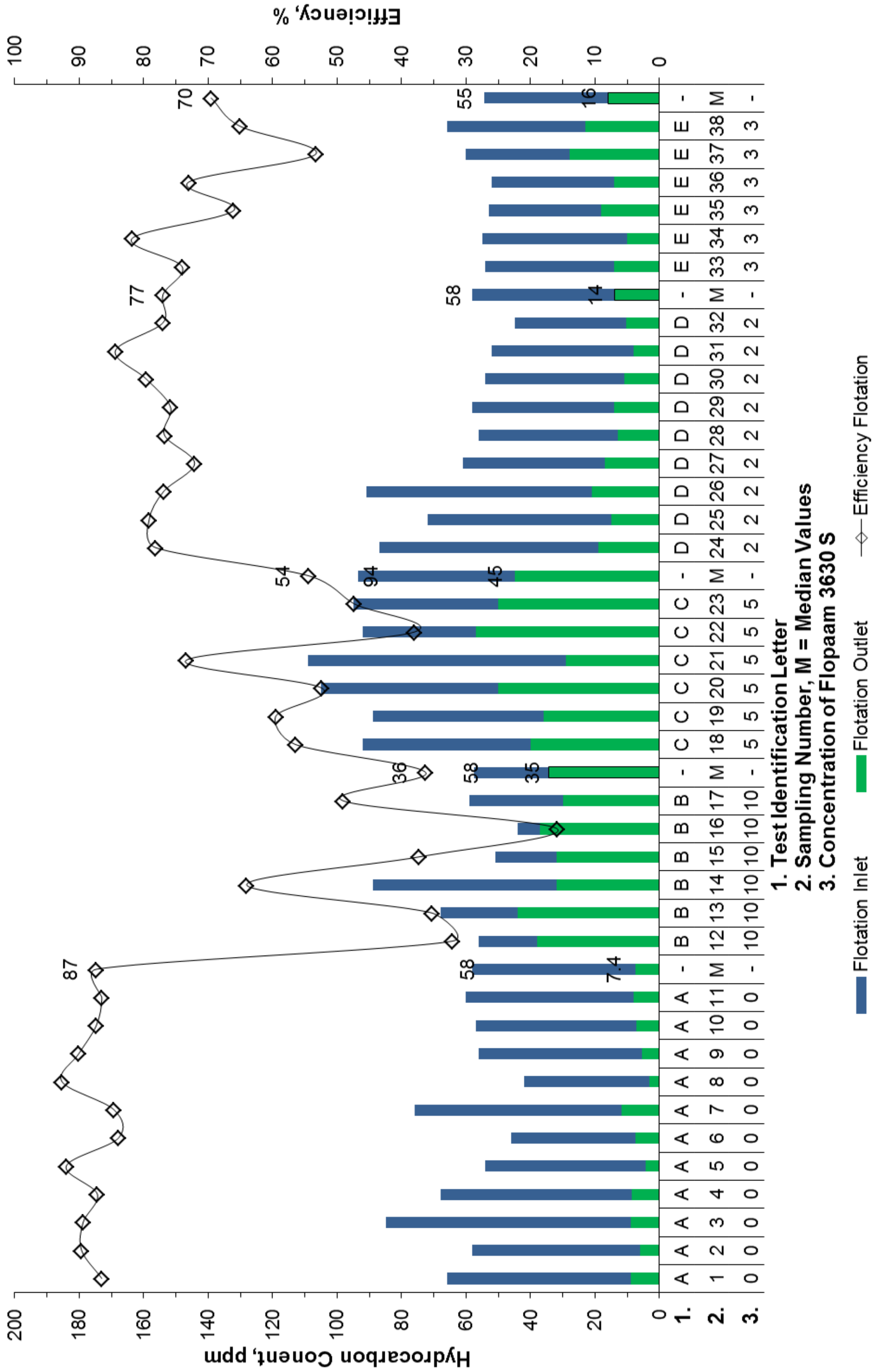


Figure 4-7: Pilot plant experiment 2 - Hydrocarbon separation results of the combined flocculation and flotation unit at 0, 10, 5 and 2 ppm of Flopaam 3630 S in the feed of the pilot plant, but constant dosing of chemical set II, as well as the resulting separation efficiencies

4.3.3.5 Results of Additional Testing after Flotation

In Test D and E the median hydrocarbon contents after flotation were below the limit value of 20 ppm. To investigate if the quality of the treated water after flotation would also be sufficient for further treatment with the NSF additional samples were taken after flotation to determine the WBF (8 µm), the WBF (3 µm), the concentration of suspended solids, the concentrations of solid and dissolved iron and the turbidity. In order to be able to compare the results with the quality of treated oilfield water without Flopaam 3630 S, the mentioned parameters were as well determined from a sample after flotation in test A (0 ppm Flopaam 3630 S). In **Table 4-3** the results of the testing is listed.

Table 4-3. Results of additional testing after flotation in pilot plant experiment 2

SAMPLES: Flotation Outlet					
Test ID			**A**	**D**	**E**
Sampling No.		#	**5**	**28**	**35**
Flopaam 3630 S		ppm	0	2	3
HC Content (feed of pilot plant)		ppm	4.3	13	18
Turbidity		NTU	13	-	-
CASCADE FILTRATION	**WBF (8 µm → 3 µm)**	1/min	1.76 → 0.12	2.29 → 0.10	2.36 → 0.08
	SS, de-oiled (> 8 µm → > 3 µm)	mg/l	3.7 → 0.7	4.5 → 0.9	4.7 → 0.4
	Total Iron	mg/l	2.34	2.09	2.16
	Iron (< 8 µm → < 3 µm)	mg/l	1.96 → 1.84	1.59 → 1.46	2.00 → 1.93
	Dissolved Iron (< 0.45 µm)	mg/l	1.78	1.37	1.77
	Calculated Iron (> 0.45 µm)	mg/l	0.56	0.72	0.39

The WBFs (8 µm) of the samples after flotation from sampling D28 and E35 are slightly augmented compared to the one of sampling A5. It is known that long chained organic polymers, especially the ones of high molecular weight, easily block the pores of filtering media. So it can be assumed that the WBFs (8 µm) are augmented due to the presence of Flopaam 3630 S in the water. The WBFs (8 µm) are still low enough to allow the testing of the filtration unit (NSF) in a second testing stage.

4.3.3.6 Discussion and Conclusion

The median test results of pilot plant experiment 2 are summarized in **Table 4-4**.

Table 4-4: Pilot plant experiment 2 – Summary of the median hydrocarbon (HC) contents and separation efficiencies of each test with correlating content of Flopaam 3630 S in the feed of the pilot plant (all hydrocarbon contents and separation efficiencies are median values)

		Corrugated Plate Interceptor		**Combined Flocculation & Flotation**		
Test ID	**Flopaam 3630 S**	**HC Contents Inlet → Outlet**	**Separation Efficiency**	**Chemical Set II**	**HC Contents Inlet → Outlet**	**Separation Efficiency**
-	ppm	ppm	%	ppm	ppm	%
A	0	332 → 58	81	20/0.15	58 → 7.4	87
D	2	382 → 58	84	20/0.15	58 → 14	77
E	3	346 → 55	84	20/0.15	55 → 16	70
C	5	407 → 94	77	20/0.15	94 → 45	54
B	10	339 → 58	81	20/0.15	58 → 35	36

Corrugated Plate Interceptor

The separation performance of the CPI in pilot plant experiment 2 was excellent. Even with a Flopaam 3630 S content of 10 ppm in test B, the separation efficiency stayed the same as in test A where no Flopaam 3630 S was added. The augmented median outlet hydrocarbon content in test C cannot be explained. Contamination of the CPI as a reason can be excluded, because in this case the outlet hydrocarbon content would not go back to lower levels any more. This was the case though in test D and E. In test D and E the hydrocarbon separation efficiency was even better than without Flopaam 3630 S in produced water in test A.

A correlation between the hydrocarbon separation performance and the content of Flopaam 3630 S could assumingly not be observed. The gravity separation of the oil in the feed of the pilot plant is not affected by Flopaam 3630 S. The dosages were obviously too little to lead to a significant rise in viscosity, which would influence the rising velocity of oil droplets according to Stokes' Law.

Combined Flocculation and Flotation

In pilot plant experiment 2 the hydrocarbon separation performance was decreasing with increasing content of Flopaam 3630 S. The summarized results in **Table 4-4** clearly show it. The best hydrocarbon separation performance could be reached in test D (2 ppm of Flopaam 3630 S in the feed of the pilot plant). The median outlet hydrocarbon content was 14 ppm. Only 1 value of 9 exceeded the limit value of 20 ppm. The hydrocarbon separation efficiencies were very stable. The best acceptable hydrocarbon separation performance with the highest content of Flopaam 3630 S (3 ppm of Flopaam 3630 S) was reached in test E.

The median outlet hydrocarbon content was 16 ppm. 2 of 6 values exceeded the limit value of 20 ppm. The hydrocarbon separation efficiencies were unstable but a stable water treatment process seems to be possible. The tested WBF of 2.36 min^{-1} (sampling E35) was also low enough to expect a good performance of the NSF in future tests.

The median inlet hydrocarbon contents in test D and E were very low (58 and 55 ppm). The inlet hydrocarbon contents of the combined flocculation and flotation unit in this pilot plant experiment were generally very low. Investigating the separation performance with higher inlet hydrocarbon contents of 100 ppm, as specified for the outlet of the CPI, in combination with different contents of Flopaam 3630 S would be of strong interest.

The enormous up and down of the single hydrocarbon separation efficiency values in test B and C (10 and 5 ppm of Flopaam 3630 S) cannot be explained.

The produced flocs seem to be resistant to mechanical shear and very well separable in the flotation process. This can be stated because no flocs were observed in any samples after flotation.

4.3.4 Pilot plant experiment 3 – Alustar 1010 L and Drewfloc 285 (Chemical Set I)

4.3.4.1 Goal and Approach

In pilot plant experiment 3, like in pilot plant experiment 2, the hydrocarbon separation performance of the pilot plant was intended to be tested with 0, 10, 5 and 2 ppm of Flopaam 3630 S in the feed of the pilot plant and at constant dosage of Alustar 1010 L and Drewfloc 285 in the flocculation stage. The testing procedure was the same than in the pilot plant experiments 1 and 2. Alustar 1010 L was used as coagulating agent and Drewfloc 285 as flocculation aid.

In test A the performance of chemical set I was tested without Flopaam 3630 S in the feed. In the Tests B to E different contents of Flopaam 3630 S were added to the feed of the pilot plant. The dosing of Alustar 1010 L and Drewfloc 285 in the flocculation unit was kept constant. In test D the treatment performance should have been tested with 2 ppm of Flopaam 3630 S. Due to the occurrence of flocs and an ongoing worsening of the hydrocarbon content in the samples after flotation, the dosing of Flopaam 3630 S was stopped and the pilot plant was cleaned. Thereby many settled flocs were found accumulated in the bottom part of the flocculator. After the restart of the pilot plant it was expected that the good performance of the treatment process without Flopaam 3630 S in the feed will be reestablished again, but this was not the case. The median separation efficiency was much lower than in test A without Flopaam 3630 S in the feed, but at least there were no more flocs in the samples after flotation. Despite the ongoing very low separation efficiency, 2 ppm of Flopaam 3630 S were added to the feed in test E and the treatment performance was tested.

4.3.4.2 Testing Data

Testing Period: January 21 – 31, 2013 (CW 04 and 05)

Dosage of Chemical Set I: 52 ppm (Alustar 1010 L) and 0.35 ppm (Drewfloc 285)

Corresponding Volume Flow: 1.9 l/h (Alustar 1010 L) and 3.5 l/h (Drewfloc 285)

Dosing Points: DP 3.2 (Alustar 1010 L) and DP 3.3 (Drewfloc 285) (see **Figure 4-8**)

Hydraulic Residence Time: 9.7 min (Alustar 1010 L) and 7.8 min (Drewfloc 285)
(dosing → inlet flotation reactor)

Percentage of Reagent in Distilled Water in Prepared Solution: 10 % (Alustar 1010 L) and 0.05 % (Drewfloc 285)

Lot Number: 300412 (Alustar 1010 L), not known for Drewfloc 285 (it is continuously prepared in a mixing station at the site of the existing WTP)

Dosing Pump: Diaphragm pump (Alustar 1010 L) and helical rotor pump (Drewfloc 285)

Dosage of Flopaam 3630 S: 10, 5 and 2 ppm in the feed of the pilot plant

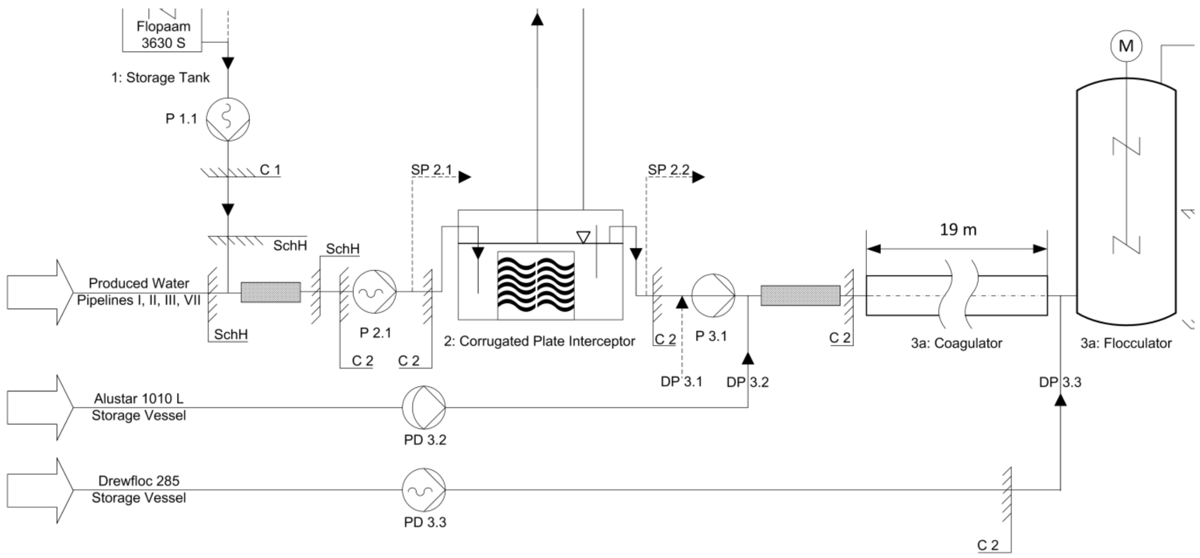


Figure 4-8: Detail of PFD in pilot plant experiment 3 with dosing location of Alustar 1010 L and Drewfloc 285

4.3.4.3 Hydrocarbon Separation Results of the Corrugated Plate Interceptor

The following description refers to the results of the hydrocarbon separation performance of the CPI shown in **Figure 4-9**, on page 81. The figure shows the hydrocarbon contents before and after the CPI in pilot plant experiment 3, as well as the correlating hydrocarbon separation efficiencies. Note: The dosing of chemical set 1 was after the CPI so the potentially influencing parameter was Flopaam 3630 S.

The inlet hydrocarbon contents in test A, B and C were within a range of 350 to 600 ppm with a tendency from lower to higher values. The median inlet hydrocarbon contents increased from 433 ppm in test A to 514 ppm in test C. The outlet hydrocarbon contents were relatively constant and below the limit value of 100 ppm in test A, B and C with a tendency from higher to lower values. The median outlet hydrocarbon contents decreased from 95 ppm to 84 ppm. As a result the median hydrocarbon separation efficiencies increased from 78 to 84 %.

In test D the inlet hydrocarbon contents jumped below 300 ppm. The median inlet hydrocarbon content was only 271 ppm. The outlet hydrocarbon contents went down too. The values were very constant. Their median value was 40 ppm. With sampling D30 the dosing of Flopaam 3630 S to the feed of the pilot plant was stopped due to problems with the water quality after flotation. The median values of test D were therefore calculated without the results from sampling D28 and D29 (bars of light contrast in **Figure 4-9**).

In test E the inlet hydrocarbon contents were very high in the beginning (up to 813 ppm) and then below 400 ppm. The median value was 401 ppm. The outlet hydrocarbon contents were assumingly higher, but still clearly below the limit value of 100 ppm. The median value was 67 ppm.

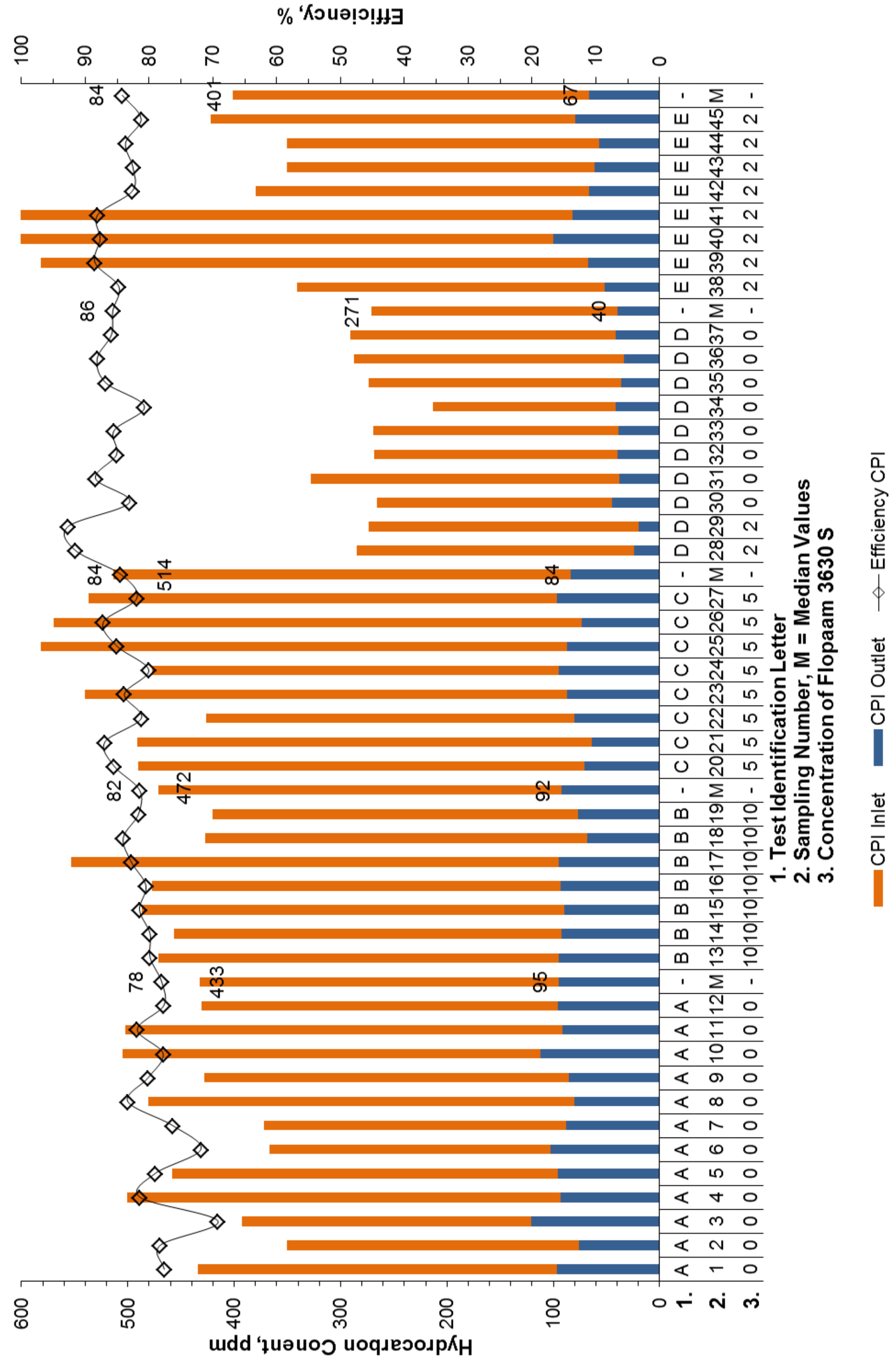


Figure 4-9: Pilot plant experiment 3 - Hydrocarbon separation results of the CPI at 0, 10, 5 and 2 ppm of Flopaam 3630 S in the feed of the pilot plant, as well as the resulting separation efficiencies (Inlet hydrocarbon values exceeding the y-axis: 813 ppm in E40 and 688 in E41; D28 and D29 were excluded from the calculation of the median values)

4.3.4.4 Hydrocarbon Separation Results of the Combined Flocculation and Flotation

The following description refers to the results of the hydrocarbon separation performance of the combined flocculation and flotation unit shown in **Figure 4-13**, on page 86. The figure shows the hydrocarbon contents before and after the combined flocculation and flotation unit in pilot plant experiment 3, as well as the correlating hydrocarbon separation efficiencies. The dosing of chemical set I was kept constant in all tests.

Test A - 0 ppm of Flopaam 3630 S

In test A only the chemical agents for flocculation were added. A stable water treatment process could very well establish. (The hydrocarbon content of the samples of flotation outlet in sampling number A1 and A2 are not included in the calculation of the median value; the process seemed not to be stationary at the time). The inlet hydrocarbon contents were mostly right below the limit value of 100 ppm with a median value of 95 ppm. The outlet hydrocarbon contents were relatively stable. Almost all values were below the limit value of 20 ppm. There were two augmented values (A7 and A12). The median value was 16 ppm. The separation efficiencies thereby were almost all close to the median value of 84 % (except A7 and A12). The performance of the flocculation and flotation process was good.

Test B - 10 ppm of Flopaam 3630 S

In test B the content of Flopaam 3630 S in the feed of the pilot plant was raised to 10 ppm. As it was expected the hydrocarbon separation performance was strongly affected. With a median inlet hydrocarbon content of 92 ppm the median outlet hydrocarbon content was augmented to 49 ppm. This results in a median hydrocarbon separation efficiency of only 46 %. An interesting fact is the high consistency of the efficiency values. In pilot plant experiment 2 it was presumed that the addition of Flopaam 3630 S causes the separation performance to become unstable. This is disproved by test B in this pilot plant experiment.

Test C - 5 ppm of Flopaam 3630 S

In test C the content of Flopaam 3630 S was reduced to 5 ppm. The inlet hydrocarbon contents were varying in the range of about 60 to 100 % of the limit value of 100 ppm. The median value was 84 ppm. With a median outlet hydrocarbon content of 30 ppm the median separation efficiency results in 62 %. The single separation efficiency values were quite erratic again in test C.

Test D – 2 and 0 ppm of Flopaam 3630 S

In test D the hydrocarbon separation performance with a content of 2 ppm of Flopaam 3630 S was supposed to be tested. Already in the first sampling of the test though (D28) flocs were observed in the outlet sample of the flotation (see **Figure 4-10** a). Most of the flocs showed settling behavior, some showed floating behavior as can be noticed in **Figure 4-10** b.

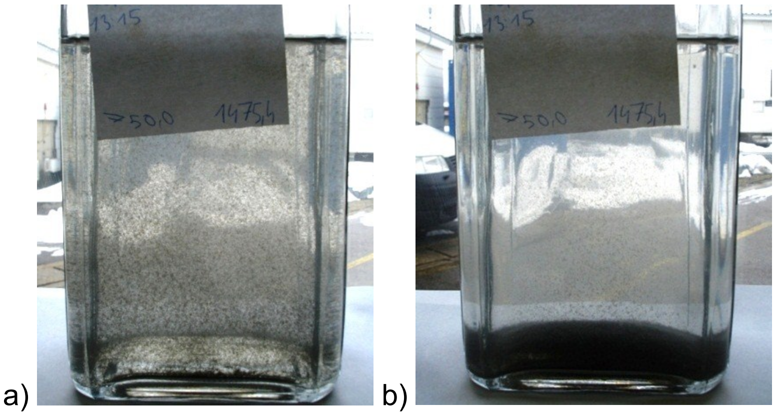


Figure 4-10: Flocs in the sample after flotation (Sampling D28 on January 28, 2013 at 13:15); a) right after sampling, b) 35 min later

In sampling D29 still were flocs in the sample after flotation. As a first reaction on the situation the dosing of Flopaam 3630 S was stopped. It was expected that the system would turn back to a similar performance than in test A without feed content of Flopaam 3630 S. But in sampling D30 (first sampling of the next day) the situation has not changed. As a second reaction fresh solution of Alustar 1010 L was prepared from an originally sealed storage container, but in sampling D31 the hydrocarbon separation efficiency of the combined flocculation and flotation process was even negative (minus 11 %). This was a strong sign for oil accumulating somehow in the flocculation unit. So it was decided to shut down the pilot plant in order to clean it.

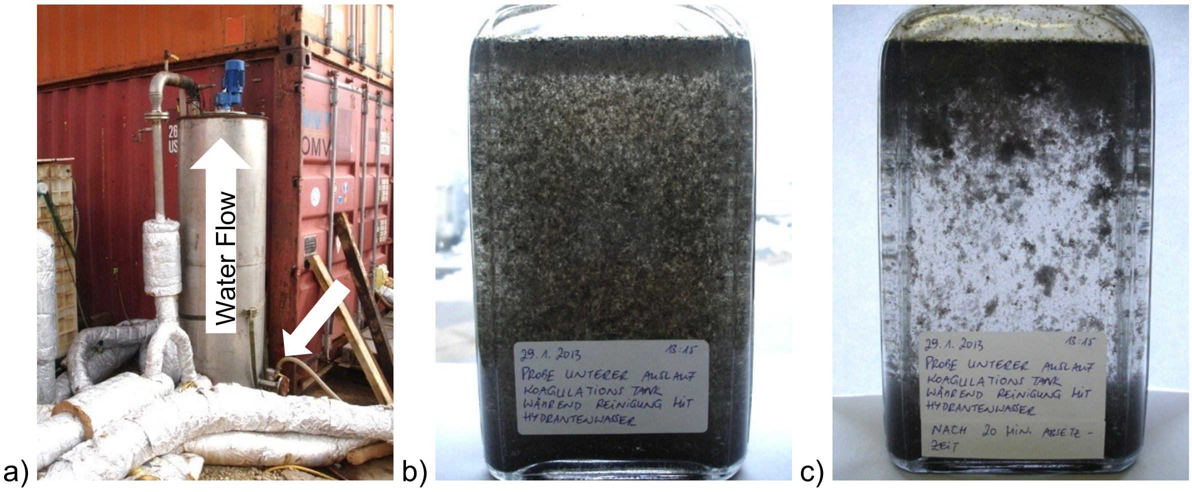


Figure 4-11: a) Hand valve for discharging the flocculator, b) sample of discharged water at the beginning of discharge, c) the same sample after 20 minutes of settling

The flotation reactor, the flocculator and the gas dissolving reactor were flushed (cleaning of the corrugated plates of the CPI was not necessary because its performance was not reduced). When the flocculator was emptied by the discharge valve indicated by the arrow in **Figure 4-11** a, big black flocs were in the discharge volume at the bottom of the reactor (see

Figure 4-11 b and c). There were rising, settling and floating flocs (see **Figure 4-11** c). Obviously, the flocs settled in the flocculator despite the up flowing water.

After the cleaning the pilot plant was started again with dosing of chemical set I, but still without Flopaam 3630 S in order to redetermine the performance of the pilot plant without Flopaam 3630 S in the feed (next sampling was D32). The inlet hydrocarbon contents were very low as they were in every sampling of test D. The median value was 40 ppm. (Mind that the resulting hydrocarbon contents of sampling number D28 to D31 were not included in the calculation of the median value due to the mentioned problems (see bars of light contrast in **Figure 4-13**)). The median outlet hydrocarbon content was 18 ppm. The resulting median separation efficiency was very low (52 % only). The separation performance was very poor, but there were no flocs any more after flotation.

Test E - 2 ppm of Flopaam 3630 S

In test E the dosing of Flopaam 3630 S was started again. The content of Flopaam 3630 S in the feed of the pilot plant set to 2 ppm. The inlet hydrocarbon contents were higher and quite erratic. Their median value was 67 ppm. Despite the higher inlet hydrocarbon contents and the dosing of Flopaam 3630 S the median outlet hydrocarbon content was the same than in test D (18 ppm). Starting with sampling D38 there were again flocs in the samples after flotation.

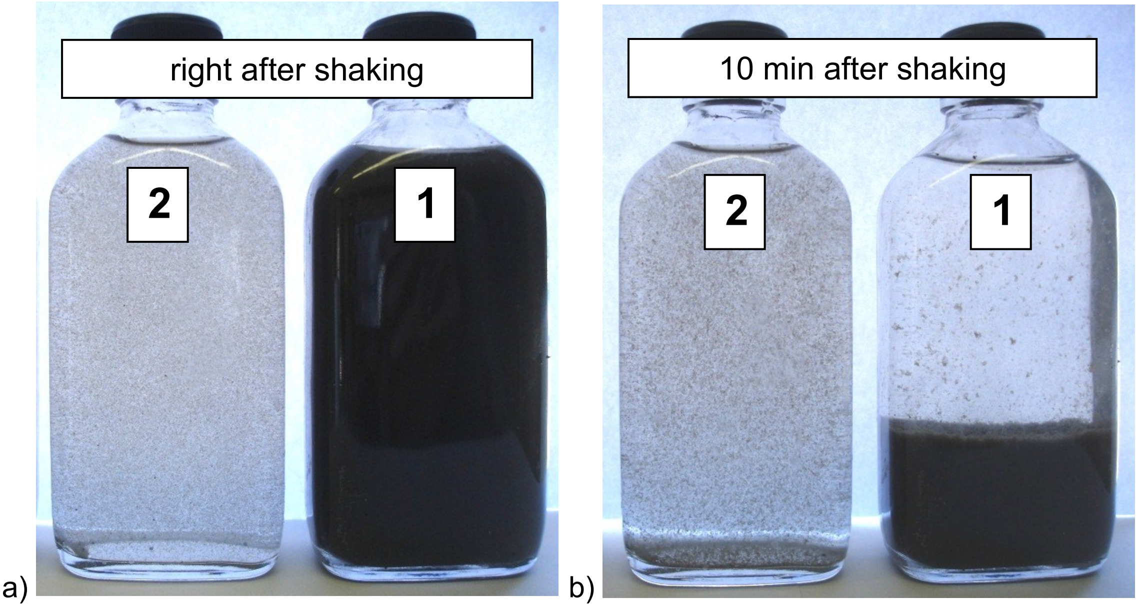


Figure 4-12: Samples of discharged water from the bottom of the flocculator (1) at the beginning of discharge and (2) a few seconds after beginning of discharge; a) right after shaking up the sample, b) 10 min later

With sampling D41 samples from the bottom of the flocculator were taken again in order to check for settling flocs. At a hydraulic upstream velocity of only 0.45 cm/s in the flocculator, settling of dense heavy flocs is very likely. As clearly can be seen in **Figure 4-12** there were plenty of settled flocs. They have quickly been discharged, because after a few seconds the floc content was sharply diminished (see sample number 2 in **Figure 4-12**). To check the settling/rising behavior of the flocs, the samples were shaken (see **Figure 4-12** a) and evaluated after 10 min (see **Figure 4-12** b). In sample number 1 the settling of almost all flocs can be observed. In sample number 2 the flocs do not settle, but floc growth can be observed. Compared to the flocs in the samples shown in **Figure 4-12** b and c the flocs were much smaller now which could be correlated to the lower content of Flopaam 3630 S.

In order to try to hinder the flocs from settling in the flocculator the rotation speed of the mechanical mixer was augmented to 30 rpm (20 rpm originally) after sampling D41. The purpose was to keep the flocs floating by increased turbulence. The desired goal could not be reached. Two more samples taken from the bottom discharge valve of the flocculator with sampling D42 and D45 contained settling flocs.

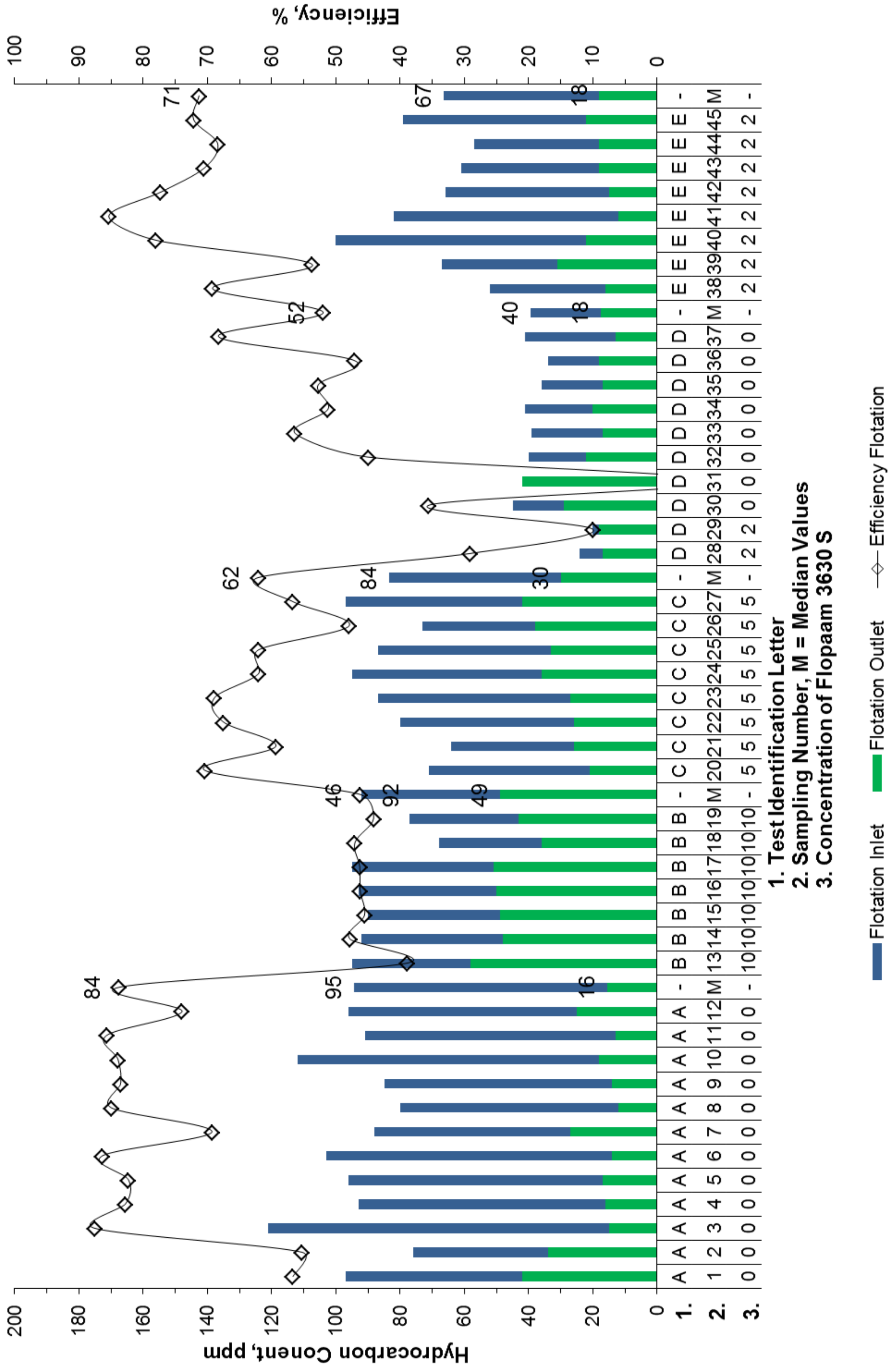


Figure 4-13: Pilot plant experiment 3 - Hydrocarbon separation results of the combined flocculation and flotation unit at 0, 10, 5 and 2 ppm of Flopaam 3630 S in the feed of the pilot plant but constant dosing of chemical set I, as well as the resulting separation efficiencies (A1, A2 and D28 – D31 are excluded from the calculation of the median values)

4.3.4.5 Results of Additional Testing after Flotation

In test E the median hydrocarbon contents after flotation were below the limit value of 20 ppm. To check if the quality of the treated water would be sufficient for a further treatment in the filtering unit (NSF) additional samples were taken after flotation to determine the WBF (8 µm), the WBF (3 µm), the content of suspended solids, the contents of solid and dissolved iron and the turbidity. In order to be able to compare the results with the quality of treated water without contained Flopaam 3630 S, the mentioned parameters were as well determined from samples after flotation in test A (0 ppm of Flopaam 3630 S). In **Table 4-5** the results of the additional tests are presented.

Table 4-5: Results of additional testing after flotation in pilot plant experiment 3

SAMPLES: Flotation Outlet						
Test ID			**A**	**A**	**A**	**E**
Sampling No.		#	**5**	**7 (*)**	**12 (*)**	**40**
Flopaam 3630 S		ppm	0	0	0	2
HC content		ppm	17	27	25	22
Turbidity		NTU	-	-	-	-
CASCADE FILTRATION	**WBF (8 µm → 3 µm)**	1/min	4.16 → 0.01	3.58 → 0.01	5.17 → -	6.10 → -
	SS, de-oiled (> 8 µm → 3 µm)	mg/l	5.1 → 0.1	4.6 → 0.4	10.1 → -	11.5 → -
	Total Iron	mg/l	2.15	2.55	2.57	2.04
	Iron (> 8 µm → 3 µm)	mg/l	1.63 → 1.61	2.37 → 2.29	2.05 → -	1.41 → -
	Dissolved Iron (< 0.45 µm)	mg/l	1.57	1.69	-	1.44
	Iron Conc. (> 0.45 µm)	mg/l	0.58	0.86	-	0.60

(*) Smell of ligroin

Looking at the suspended solids and the outlet hydrocarbon content of the flotation it gets clear that the WBF (8 µm) is mainly influenced by the amount of suspended solids in the water after flotation. The higher the amount of suspended solids the higher the WBF. With 2 ppm of Flopaam 3630 S in the feed of the pilot plant the WBF (8 µm) and the SS were the highest (6.10 s^{-1} and 11.5 mg/l in sampling E40). But it is important to note, that even in sampling A12 without Flopaam 3630 S in the feed of the pilot plant, the amount of suspended solids was very high and led to an augmented WBF (8 µm) of 5.17 min^{-1} .

The values for the WBF (8 µm) were generally rather high with Alustar 1010 L and Drewfloc 285 as flocculating agents. This has also been the case when the combination was tested in 2008 (compare Epp, 2010).

Due to the formation of a filtering cake on the 8 µm membrane filter in sampling A5 and A7 a lot of suspended solids < 8 µm were filtered at the same time. This led to a reduced amount of suspended solids on the 3 µm membrane filter and as well to very low values for the WBF (3 µm).

The hydrocarbon contents after flotation in sampling A7 and A12 were the only two values above 20 ppm. A strong smell of ligroin was detectable. The presence of ligroin would explain the augmented hydrocarbon contents in exactly those two samples.

4.3.4.6 Discussion and Conclusion

The median test results of pilot plant experiment 3 are summarized in **Figure 4-6**.

Table 4-6: Pilot plant experiment 3 - Summary of the median hydrocarbon (HC) contents and separation efficiencies of each test with correlating content of Flopaam 3630 S in the feed of the pilot plant (all hydrocarbon contents and separation efficiencies are median values)

		Corrugated Plate Interceptor		**Combined Flocculation & Flotation**		
Test ID	**Flopaam 3630 S**	**HC Contents Inlet → Outlet**	**Separation Efficiency**	**Chemical Set I**	**HC Contents Inlet → Outlet**	**Separation Efficiency**
-	**ppm**	**ppm**	**%**	**ppm**	**ppm**	**%**
A	0	433 → 95	78	52/0.35	95 → 16	84
D	0	271 → 40	86	52/0.35	40 → 18	52
E	2	401 → 67	84	52/0.35	67 → 18	67
C	5	514 → 84	84	52/0.35	84 → 30	62
B	10	472 → 92	82	52/0.35	92 → 49	46

Corrugated Plate Interceptor

The hydrocarbon separation performance of the CPI was again excellent throughout all tests. Despite the constantly rising inlet hydrocarbon contents in test A, B and C the separation efficiency increased from a median value of 78 up to 84 %. With the very low inlet hydrocarbon contents in test D the median separation efficiency even reaches 86 %. In test E the median separation efficiency was still high (84 %). This is a clear sign for a very stable separation process. The separation efficiency shows an independency of the inlet hydrocarbon content in this pilot plant experiment.

The CPI operates on the upper edge of the required inlet hydrocarbon content range of 300 to 500 ppm in test A, B and C. Despite this fact the median outlet hydrocarbon contents are below the limit value of 100 ppm. Even with the median inlet hydrocarbon content of 514 ppm in test C, the CPI performs very well and allows a median outlet hydrocarbon content of 84 ppm.

A correlation between the separation efficiency and the content of Flopaam 3630 S cannot be observed, as it could not in the pilot plant experiments 1 and 2. Even though in test B 10 ppm of Flopaam 3630 S were added to the feed the separation efficiency improved compared to the one in test A where no Flopaam 3630 S was added.

Combined Flocculation and Flotation

In pilot plant experiment 3 the hydrocarbon separation performance was decreasing with increasing content of Flopaam 3630 S as it is shown in **Table 4-6**. The best hydrocarbon separation performance could be reached in test E (2 ppm of Flopaam 3630 S in the feed of the pilot plant). The median outlet hydrocarbon content was 18 ppm. 3 values of 8 exceeded the limit value of 20 ppm. The hydrocarbon separation efficiencies were rather unstable, but a successful hydrocarbon separation in the combined flocculation and flotation unit seems to be possible. The median inlet hydrocarbon content in test E was relatively low (67 ppm). It cannot be assumed that the hydrocarbon separation performance would have been as good with higher inlet hydrocarbon contents.

The values for the WBF (8 µm) were rather high. This was not only the case with 2 ppm of Flopaam 3630 S (sampling E40, 6.1 min^{-1}), but also without Flopaam 3630 S (sampling A12, 5.17 min^{-1}) in the feed of the pilot plant. As a result the performance of the NSF in future tests could be negatively affected. Therefore no further tests with the NSF were performed.

With 2 ppm of Flopaam 3630 S in the feed there were flocs in the samples after flotation. With 10 and 5 ppm of Flopaam 3630 S in the feed no flocs could be observed in the samples after flotation. In all cases a big part of the flocs settled in the flocculator where the hydraulic rising velocity was relatively low (0.45 cm/s) and turbulence induced by the mechanical mixer was low either. It would be desirable to be able to watch the floc growth and settling/rising behavior through a vision panel in the flocculator. To get a better understanding of the floc formation and behavior at different contents of Flopaam 3630 S a laboratory test was performed (see section 4.3.4.7).

4.3.4.7 Laboratory jar tests

The formation of flocs with Alustar 1010 L and Drewfloc 285 under the influence of Flopaam 3630 S has been tested in jar tests in the laboratory. The evaluated parameters were: the specific weight of the flocs compared to the water resulting in rising, floating or settling, properties of the flocs like size, texture, adhesion behavior and mechanical stability.

In this experiment four water samples after gravity separation were prepared with different contents of Flopaam 3630 S (0, 2, 5 and 10 ppm). The samples were taken after the CPI from sampling point 2.2. Then the flocculation process with chemical set I was simultaneously performed with each sample using a laboratory device called “Lovibond”. With a Lovibond the simultaneous mixing of a maximum of six samples is possible. After an overall reaction time of 8 minutes (4 minutes for coagulation and another 4 minutes for flocculation) the mechanical mixers were stopped to observe the flocs. The flocs started settling. With increasing content of Flopaam 3630 S the flocs grew bigger and heavier resulting in quicker settling of the flocs. After 10 minutes almost all flocs had settled in each sample. The supernatant water of all samples appeared very clear.

It would be interesting to repeat the experiment with a bigger sample volume followed by sedimentation and the determination of the hydrocarbon content and the performance of a cascade filtration test with the supernatant water.

4.3.5 Pilot Plant Experiment 4 – Floquat FL 2949 (Chemical Set IV)

Floquat FL 2949 was recommended by the manufacterer for the flocculation of dissolved Flopaam 3630 S from produced water. The flocculation of Flopaam 3630 S with Floquat FL 2949 with subsequent separation has already been tested on a laboratory scale in April 2012 with a sample concentration of 10 ppm of Flopaam 3630 S imitating the process steps of the existing WTP. The test was performed by the Laboratory of E & P (Report CHE-2012-0096). Floquat FL 2949 was added to samples of water from the feed of the existing WTP (inlet basin 1). In addition a flocculation aid was used. The results were promising. Flopaam 3630 S was not detectable via gel permeation chromatography in the water sample after the treatment process. The filterability was very good. It was recommended in the report to test Floquat FL 2949 on the pilot plant utilizing the process steps of the new WTP. This was done in pilot plant experiment 4.

4.3.5.1 Goal and Approach

In pilot plant experiment 4 the hydrocarbon separation performance of the pilot plant was intended to be tested with a content of 10 ppm of Flopaam 3630 S in the feed of the pilot plant and with a content of 75 ppm of Floquat FL 2949 in the flocculation stage. This content was recommended by the manufacturer as well.

To investigate if an acceptable hydrocarbon separation performance is also possible with lower contents of Floquat FL 2949 two tests were performed with 57 and 38 ppm of Floquat FL 2949.

4.3.5.2 Testing Data

Testing Period: February 04 – 08, 2013 (CW 06)

Dosage of Chemical Set IV: 75 (test A and B), 38 ppm (test C) and 57 (test D)

Corresponding Volume Flow: 2.2 l/h (test A and B), 2.2 l/h (test C) and 3.3 l/h (test D)

Dosing Points: DP 3.1 (see **Figure 4-14**)

Hydraulic Residence Time: 9.7 min (dosing → inlet flotation reactor)

Percentage of Reagent in Distilled Water in Prepared Solution: 15 % (test A and B),
7.5 % (test C and D)

Lot Numbers: LCAV12/3695

Dosing Pump: Diaphragm pump (sampling A1 to B11), helical rotor pump (sampling B12 to D22)

Dosage of Flopaam 3630 S: 10 ppm in the feed of the pilot plant

Corresponding Volume Flow: 14.9 l/h

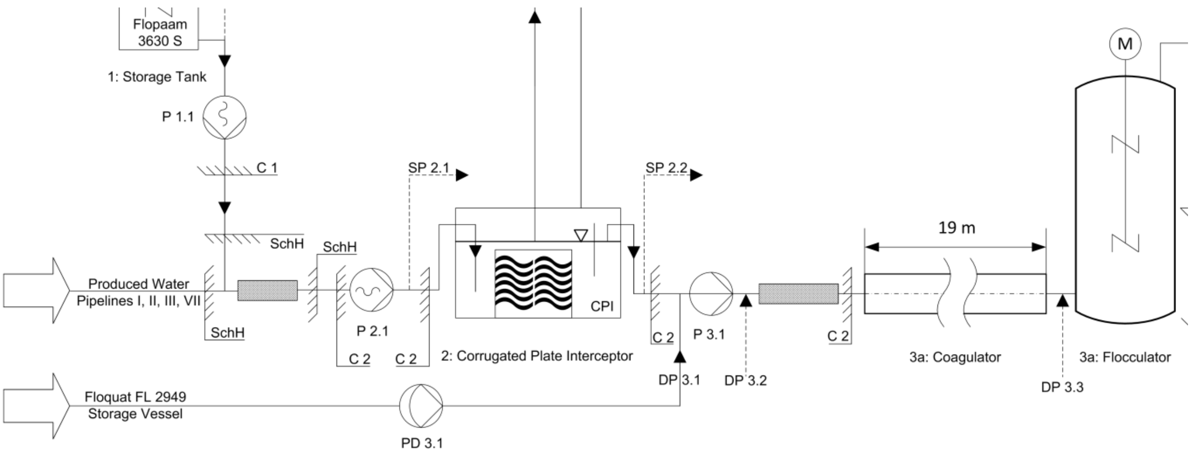


Figure 4-14: Detail of PFD in pilot plant experiment 4 with dosing location of Floquat FL 2949

4.3.5.3 Hydrocarbon Separation Results of the Corrugated Plate Interceptor

The following description refers to the results of the hydrocarbon separation performance of the CPI shown in **Figure 4-15**, on page 93. The figure shows the hydrocarbon contents before and after the CPI in pilot plant experiment 4, as well as the correlating hydrocarbon separation efficiencies. Note: The dosing of chemical set IV was after the CPI. So the potentially influencing parameter was Flopaam 3630 S.

The inlet hydrocarbon contents throughout the pilot plant experiment were within a range of about 200 to 550 ppm with a tendency from lower to higher values. The median hydrocarbon separation efficiencies range from a minimum of 75 % (test A) to a maximum of 87 % (test C). It is remarkable that the outlet hydrocarbon contents remained roughly the same in test B to D although the hydrocarbon contents in the feed constantly rise. A possible explanation could be that the oil droplets in the feed of the CPI adsorbed to the many flocs that were observed during the tests in the samples taken from the inlet of the CPI (sampling point SP 2.1). With its ability to act as flocculant Flopaam 3630 S could have flocked especially with solid contaminations during its passage through the inlet pipe of the pilot plant. It is possible that the flocs then partly settled in the CPI. Partly, because in the outlet samples of the CPI, flocs were observed as well throughout the hole pilot plant experiment, but not as many as in the inlet samples. This is a working hypothesis which has not been proven but it would explain why the hydrocarbon contents after the CPI stayed as low despite the incremental inlet hydrocarbon contents.

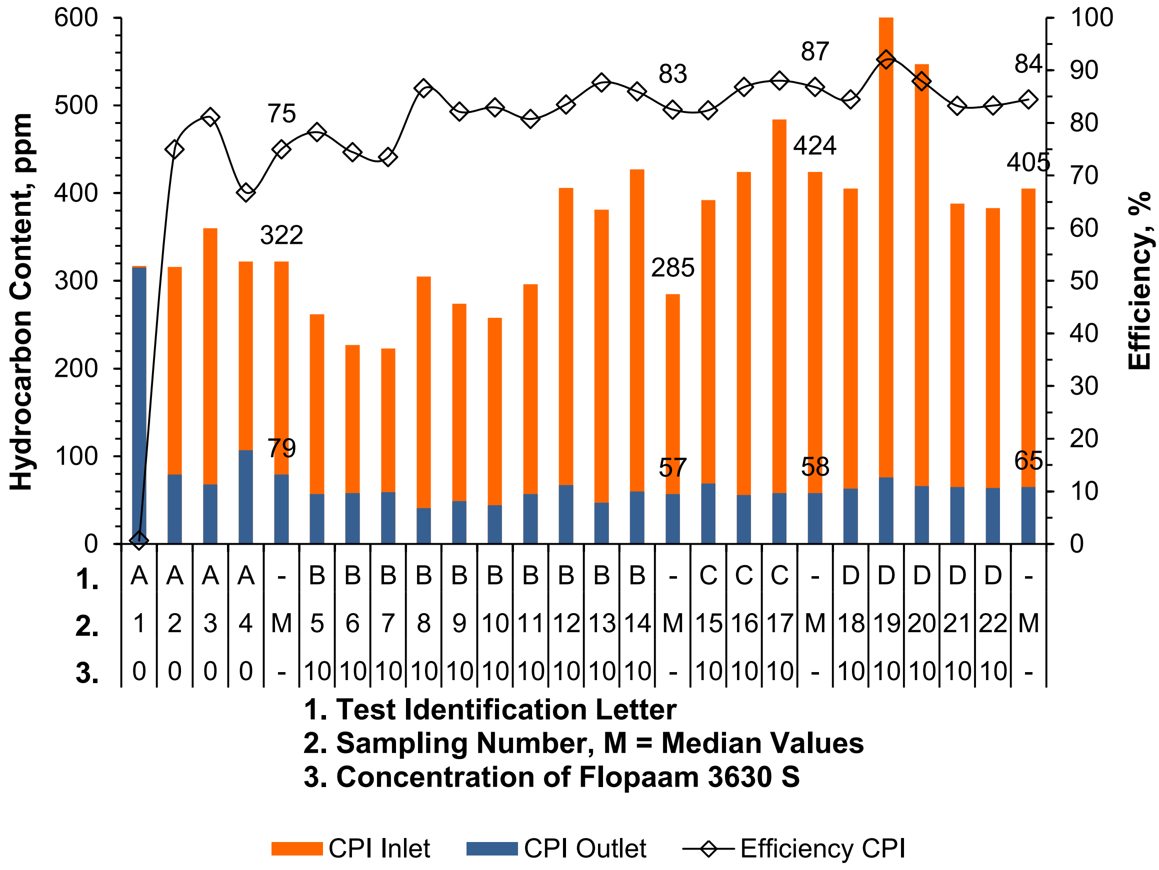


Figure 4-15: Pilot plant experiment 4 - Hydrocarbon separation results of the CPI at 10 ppm of Flopaam 3630 S in the feed of the pilot plant, as well as the resulting separation efficiencies (The inlet hydrocarbon content D19 with 954 ppm exceeds the y-axis)

4.3.5.4 Hydrocarbon Separation Results of the Combined Flocculation and Flotation

The following description refers to the results of the hydrocarbon separation performance of the combined flocculation and flotation unit shown in **Figure 4-16**, on page 94. The figure shows the hydrocarbon contents before and after the combined flocculation and flotation unit in pilot plant experiment 4 as well as the correlating hydrocarbon separation efficiencies.

Test A - 0 ppm of Flopaam 3630 S

In test A it was tested whether Floquat FL 2949 alone can successfully separate oil droplets by flocculation. The result of the test shows that this is not working. The median hydrocarbon separation efficiency is very poor (51 %) and the median outlet hydrocarbon content is far above the limit value 20 ppm (42 ppm).

Test B (10 ppm of Flopaam 3630 S)

Test B shows that the 75 ppm of Floquat FL 2949 react very well with 10 ppm of Flopaam 3630 S. The median hydrocarbon outlet content was 17 ppm which is clearly below the limit value of 20 ppm. With the very low median inlet hydrocarbon content of 57 ppm the median efficiency results in 66 %. With chemical set I and also with chemical set III the hydrocarbon separation efficiency at a feed content of 10 ppm of Flopaam 3630 S was about 20 % lower. With chemical set II the hydrocarbon separation efficiency was even 30 % lower under the same conditions.

Test C and - 10 ppm of Flopaam 3630 S

Test C and D show that lower concentrations of Floquat FL 2949 (38 and 57 ppm) did not lead to better hydrocarbon separation results. The median outlet hydrocarbon contents were 34 ppm and 37 ppm, far above the limit value of 20 ppm. The median hydrocarbon separation efficiency dropped down to 43 % in both tests.

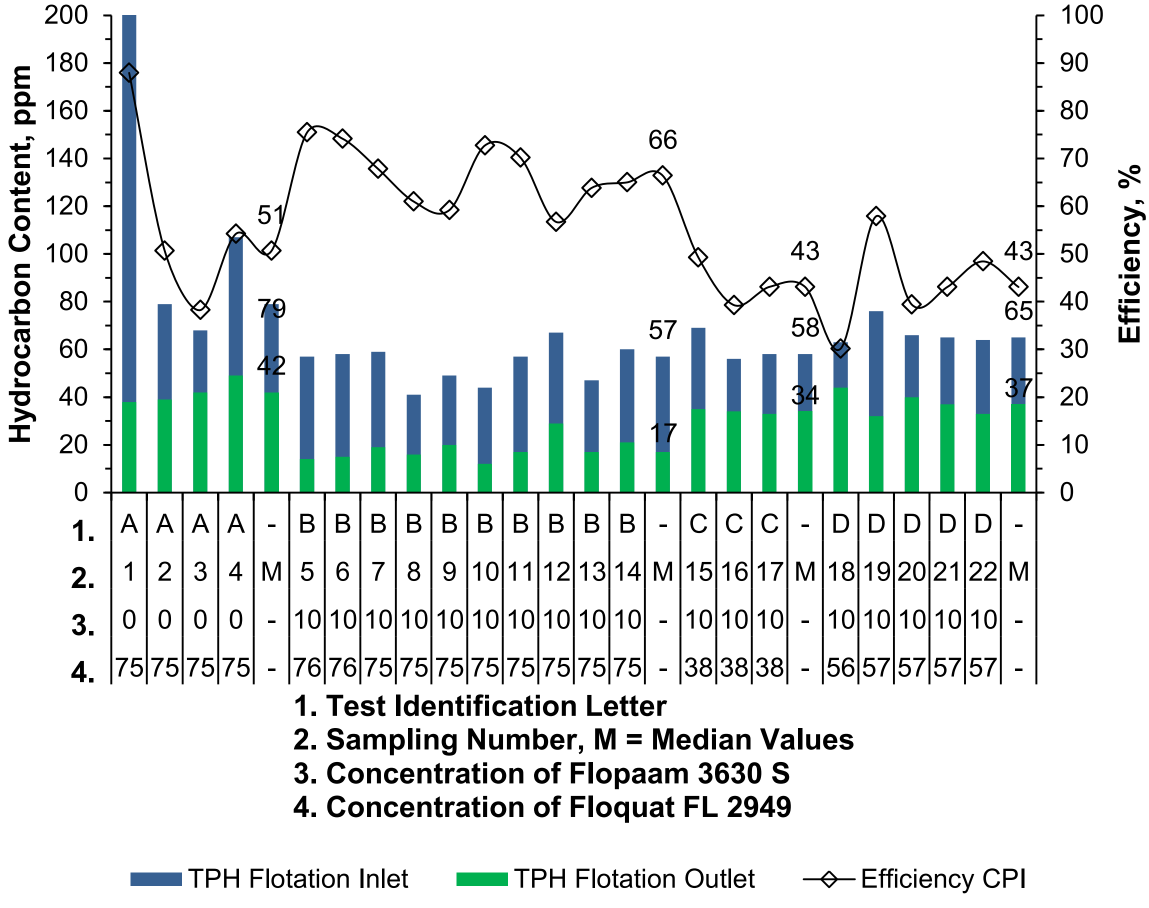


Figure 4-16: Pilot plant experiment 4 - Hydrocarbon separation results of the combined flocculation and flotation at 10 ppm of Flopaam 3630 S in the feed of the pilot plant but different dosing of chemical set IV, as well as the resulting separation efficiencies (The inlet hydrocarbon content A1 with 315 ppm exceeds the y-axis; the hydrocarbon contents of A1 are excluded from the calculation of the median values)

Especially in test B, but also in test C and D flocs have been observed in the outlet of the flotation unit. The flocs were very sticky and a lot of them adhered to the surface of the sampling bottles. The flocs prove of an insufficient separation within the flotation reactor or/and of a prolonged floc formation (4.3.3.5).

Samples that were taken from the bottom discharge valve of the flocculator, contained not only floating but also settled flocs (see **Figure 4-17** a). It is very likely that initially small flocs stick together to bigger ones. At a certain state of growth the flocs start showing settling behavior.

A visual inspection of the skimmer of the flotation reactor revealed that it was contaminated with patches of the sticky flocs (see **Figure 4-17** b).

a) b)

Figure 4-17: a) Sample with settled and floating flocs from the discharge water of the bottom side of the flocculator, b) contaminated skimmer of the flotation reactor

In the night before test D there was an automatic shutdown of the pilot plant because the static mixer after the centrifugal pump P 3.1 was clogged by agglomerates of flocs. Test D finally had to be stopped because even the circulating pump of the flotation water P 3.3 failed due to contamination and led to a shutdown of the pilot plant. The whole pilot plant was contaminated with flocs that adhered to the pipes and to the equipment. To be able to continue with the second stage of testing (additional testing of the NSF) the pilot plant had to be cleaned with hydrochloric acid (volumetric concentration of 8 %). The preparation work for the cleaning process (planning, modifying of the pilot plant and work release procedures) took a week. The cleaning process itself imposed HSSE (Health, Safety, Security and Environment) risks and was extensive not only in time but also in costs.

4.3.5.5 Results of Additional Testing after Flotation

Table 4-7 shows the results of the additional testing of the water quality for test B where the median hydrocarbon outlet content was below the limit value of 20 ppm.

The results show relatively low values for the WBF (8 µm) in the cascade filtration test. The values were about half the ones from the laboratory tests (see **Table 4-1** in section 4.2). The concentrations of suspended solids were very high, correlating quite well with the augmented values of the WBF (8 µm). However, the concentrations of suspended solids were higher than expected for a WBF (8 µm) in a range of 3 min^{-1}. In sampling A12 and E40 of pilot plant experiment 3 for instance, the values for the WBF (8 µm) at a similar concentration of suspended solids were 5.17 and 6.10 min^{-1}. It is very likely that most of the suspended solids separated on the membrane filters during the filtration tests are flocs of Flopaam 3630 S and Floquat FL 2949 that could not be separated in the flotation process or that formed in a prolonged process of floc formation in the outlet pipe of the flotation reactor.

Table 4-7: Results of additional testing after flotation in pilot plant experiment 4

SAMPLES: Flotation Outlet				
Test ID			**B**	**B**
Sampling No.		#	**7**	**14**
Flopaam 3630 S (PP Inlet)		ppm	10	10
hydrocarbon Content		ppm	19	21
Turbidity		NTU	-	-
CASCADE FILTRATION	**WBF (8 µm → 3 µm)**	1/min	3.08 → 0.01	3.29 → 0.01
	SS, de-oiled (> 8 µm → > 3 µm)	mg/l	10.0 → 0.4	11.3 → 0.6
	Total Iron	mg/l	2.15	2.14
	Iron (< 8 µm → < 3 µm)	mg/l	1.91 → 1.94 (*)	1.71 → 1.69
	Dissolved Iron (< 0.45 µm)	mg/l	1.79	1.49
	Iron (> 0.45 µm)	mg/l	0.36	0.65

(*) the second value cannot be higher than the first, so a determination error is very likely

Presuming the mentioned prolonged floc formation from observations in the laboratory tests, additional filtration curves were recorded consecutively with fresh 8 µm membrane filters in test B7. The phenomenon could be proved in the test as it is shown in **Figure 4-18**. The resulting filterability showed a clear dependency on time.

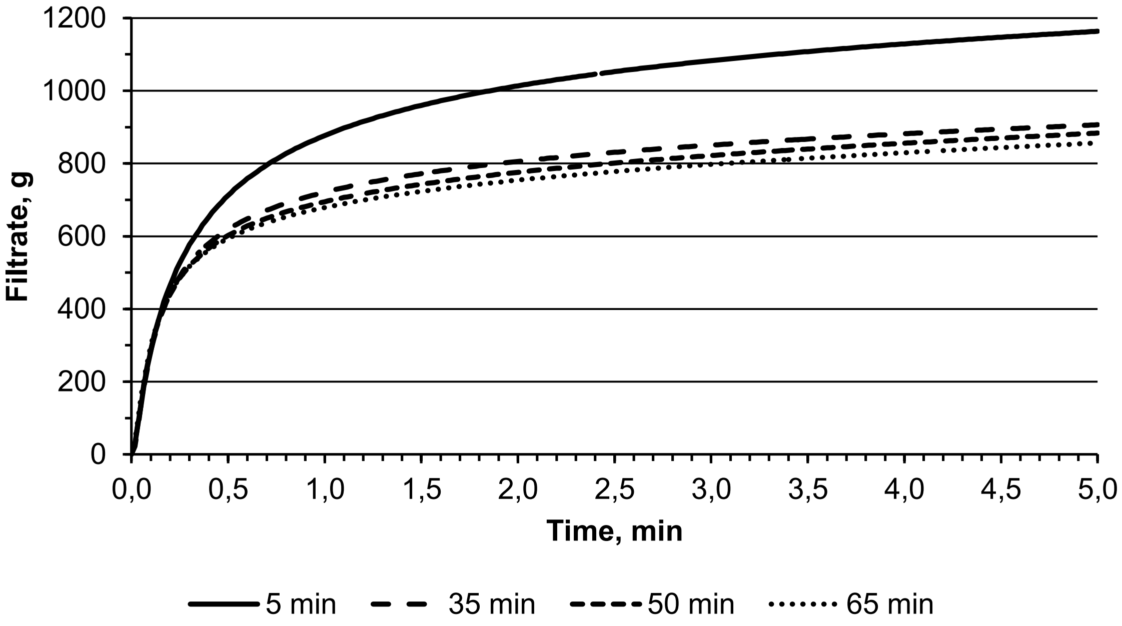


Figure 4-18: Filtration tests (8 µm) after flocculation of Flopaam 3630 S (10 ppm in the feed of the pilot plant) with 75 ppm of Floquat FL 2949; filtration tests were done consecutively with a sample after flotation from sampling B7 (testing pressure 1,4 bar)

Examining the dried filters in **Figure 4-19** the dark greyish color of the filters and the black spots can easily be noticed. They come from black colored precipitates of Flopaam 3630 S and Floquat FL 2949 separated on the filters. On the 8 µm membrane filter the density of precipitates is so high that the filter became water repellent. Trying to wash the filter with distilled water before de-oiling it, it was hardly possible to make the water pass the filter with the applied vacuum. This occurred in both tests from sampling B7 and B14. It can easily presumed that the precipitates would also stick to the granules of the nutshell filter leading to a reduction of their efficacy regarding the separation of residual oil.

Figure 4-19: 8 and 3 µm membrane filters after cascade filtration and drying (105°C)

4.3.5.6 Discussion and Conclusion

The median test results of pilot plant experiment 4 are summarized in **Table 4-8**.

Table 4-8: Pilot plant experiment 4 - hydrocarbon separation performance of the operated process units of the pilot plant with corresponding content of Flopaam 3630 S in the feed of the pilot plant (all hydrocarbon contents and separation efficiencies are median values)

		Corrugated Plate Interceptor		**Combined Flocculation & Flotation**		
Test ID	**Flopaam 3630 S**	**HC Contents Inlet → Outlet**	**Separation Efficiency**	**Chemical Set IV**	**HC Contents Inlet → Outlet**	**Separation Efficiency**
-	**ppm**	**ppm**	**%**	**ppm**	**ppm**	**%**
A	0	320 → 93	71	75	93 → 41	52
B	10	285 → 57	83	75	57 → 17	66
C	10	424 → 58	87	38	58 → 34	43
D	10	405 → 65	84	57	65 → 37	43

Corrugated Plate Interceptor

The CPI performed very well in the pilot plant experiment. The hydrocarbon contents after CPI showed an independency of the inlet hydrocarbon content in this pilot plant experiment. The content of 10 ppm of Flopaam 3630 S in the feed of the pilot plant in test B, C and D had no negative impact on the hydrocarbon separation performance of the CPI. The outlet hydrocarbon content in these tests was even better than without Flopaam 3630 S in the feed of the pilot plant. The hydrocarbon separation efficiency was approximately 80 % throughout the entire pilot plant experiment.

Combined Flocculation and Flotation

The results of the pilot plant experiment showed that the dosing of 75 ppm of Floquat FL 2949 leads to a good hydrocarbon separation performance of the combined flocculation and flotation process with 10 ppm of Flopaam 3630 S in the feed of the pilot plant (see test B). The median outlet hydrocarbon content in test B was 17 ppm. This is below the limit 20 ppm. The median inlet hydrocarbon content of 57 ppm though is rather low. It is not known whether the performance would be as well with a higher median inlet hydrocarbon content or not.

The afforded water quality after flotation regarding the content of hydrocarbons was achieved. With this result the testing of the NSF would be possible. But there are important reasons that exclude any further testing under the given circumstances:

1.) The stickiness of the flocs makes stable water treatment impossible; the enormous fouling can very quickly lead to plugging of the equipment;

2.) The generated flocs are initially small but stick together and form bigger specifically heavier flocs that show settling instead of the desired floating behavior;

3.) Sticky flocs in the water after flotation could lead to plugging of the NSF and could also lead to a reduction of the nutshell granules' efficacy regarding the separation of residual oil.

4.3.6 Result of the First Stage of Testing

The best performing set of chemical agents in the first testing stage was the combination of Chimec 5762 and Chimec 5498 (chemical set 2 in pilot plant experiment 2). At a content of 3 ppm of Flopaam 3630 S in the feed of the pilot plant the median hydrocarbon content after flotation was 16 ppm (2 of 6 were > 20 ppm). This was the lowest reached median hydrocarbon separation result with the highest content of Flopaam 3630 S in the feed of the pilot plant in all pilot plant experiments of the first testing stage. With a WBF (8 µm) of 2.36 min^{-1} the filterability was also sufficient for the testing of the NSF.

4.4 Second Stage of Testing

4.4.1 Pilot plant experiment 5 – Flocculation and Flotation with Chimec 5762 and Chimec 5498 (Chemical Set II) and Filtration with the Nutshell Filter

4.4.1.1 Goals and Approach

The goals of pilot plant experiment 5 were:

- Validation of the testing results of pilot plant experiment 2 with incrementally *increased* content of Flopaam 3630 S (0, 2, 3 ppm) in the feed of the pilot plant;
- To find out if the content of Flopaam 3630 S can be raised to 4 ppm (3 ppm did work but 5 ppm did not work anymore in pilot plant experiment 2);
- Testing of the filtration unit (NSF) for its performance under the influence of Flopaam 3630 S

The dosing of chemical set II was kept constant throughout the entire pilot plant experiment. In this pilot plant experiment the dosing of Flopaam 3630 S was started with the lowest concentration and was raised in steps of 1 ppm. This is in contrast to the proceeding in the pilot plant experiments 1 – 4 where the dosing was started with 10 ppm and was subsequently reduced to 5 and 2 ppm.

Additional testing of the water quality was done at every level of content of Flopaam 3630 S to investigate the filterability, the concentration of suspended solids, the concentrations of dissolved and solid iron and the turbidity. The testing was conducted with water samples after the flotation reactor and after the NSF.

It was planned to operate the NSF 4 to 5 filtration cycles of 24 hours per week and to raise the content of Flopaam 3630 S in the feed of the pilot plant thereafter. After every cycle the filter bed was supposed to be regenerated by back-washing as it is described in the process description (see section 3.1.1).

The following was investigated regarding the performance of the NSF:

- Hydrocarbon separation performance;
- Achievable operating time of the NSF at a given content of Flopaam 3630 S in the feed of the pilot plant;
- Trend of the pressure drop over the NSF;
- Operational behavior of the nutshell filter during back-washing;
- Water consumption for the back-washing;

The operating parameters of the NSF and the criterions for the start of the back-washing are described in the operational description (see section 3.1.2).

4.4.1.2 Testing Data

Testing Period: February 19 – March 14, 2013 (CW 08 and 11)

Dosage of Chemical Set II: 20 ppm (Chimec 5762) and 0.15 ppm of (Chimec 5498)

Corresponding Volume Flow: 1.9 l/h (Chimec 5762) and 1.5 l/h (Chimec 5498)

Dosing Points: DP 3.2 (Chimec 5762) and DP 3.3 (Chimec 5498) (see **Figure 4-5**)

Hydrodynamic Detention Time: 9.7 min (Chimec 5762) and 7.8 min (Chimec 5498)
(dosing → inlet flotation reactor)

Percentage of Reagent in Distilled Water in Prepared Solution: 4.0 % (Chimec 5762) and 0.05 % (Chimec 5498)

Lot Number: 121366 (Chimec 5762) and 121367 (Chimec 5498)

Dosing Pump: Diaphragm pump (Chimec 5762) and helical rotor pump (Chimec 5498)

Dosage of Flopaam 3630 S: 2, 3 and 4 ppm in the feed of the pilot plant

4.4.1.3 Hydrocarbon Separation Results of the Pilot Plant

The following description refers to the results of the hydrocarbon separation performance of the pilot plant shown in **Figure 4-20** (page 104) for the CPI, in **Figure 4-21** (page 105) for the combined flocculation and flotation and in **Figure 4-22** (page 106) for the NSF.

Due to a falloff test concerning the polymer flooding pilot operation the polymer injection had to be stopped and the mixing plant was shut down. For this reason no fresh polymer solution was available for pilot plant experiment 5.

Test A - 0 ppm of Flopaam 3630 S

In test A the performance of the pilot plant was tested without Flopaam 3630 S in the feed. The NSF was provided with fresh nutshell granules of mesh 20/30 (0.59 – 0.84 mm). The median hydrocarbon content of 391 ppm in the feed of the pilot plant was in the required range of 300 to 500 ppm. The median hydrocarbon contents after all units were clearly below the specified limit values. The hydrocarbon content of 25 ppm after the NSF in sampling A5 was most probably a measuring error.

Test B and C - 2 ppm of Flopaam 3630 S

During these tests OMV landfill site was disposing of their waste water which was not known at the time. In this water residual polymer from oil sludge treatment was contained. The water entered the existing WTP in the feed and therefore was also contained in the feed of the pilot plant. As a consequence of the entering polymer the results of test B and C are falsified and could therefore not be taken into consideration. The testing with 2 ppm of Flopaam 3630 S in the feed of the pilot plant was repeated in test D.

The agreement upon a waste water discharge stop from Monday 7:00 until Friday 16:00 was reconfirmed with the responsible person of the OMV landfill site.

Test D - 2 ppm of Flopaam 3630 S

The NSF was provided with fresh nutshell granules (mesh 20/30). The testing was started again with 2 ppm of Flopaam 3630 S in the feed of the pilot plant. The median hydrocarbon content of 519 ppm in the feed of the pilot plant was slightly out of the required range of 300 to 500 ppm. Despite that fact the hydrocarbon separation performance of the CPI was good. Its median outlet hydrocarbon content of 108 ppm was only slightly above the limit value of 100 ppm. The median hydrocarbon contents after flotation (6.5 ppm) and after NSF (1.4 ppm) were clearly below the specified limit values of ≤ 20 ppm and ≤ 2 ppm.

Test E - 3 ppm of Flopaam 3630 S

The water treatment process was tested with 3 ppm of Flopaam 3630 S in the feed of the pilot plant. The median hydrocarbon content in the feed of the pilot plant (474 ppm) was within the required range of 300 to 500 ppm again, but the hydrocarbon separation performance of the CPI was decreased for some reason. The median outlet hydrocarbon content was raised to 149 ppm now. This is definitely above the limit value of 100 ppm. The median hydrocarbon contents after flotation (6.8 ppm) and after NSF (1.5 ppm) again were clearly below the specified limit values.

In the sample after flotation from sampling E70 flocs were observed. That was the reason for the augmented hydrocarbon content of 16 ppm in the outlet of the flotation.

Test F - 4 ppm of Flopaam 3630 S

The water treatment process was tested with 4 ppm of Flopaam 3630 S in the feed of the pilot plant. The median hydrocarbon content of 572 ppm in the feed of the pilot plant was clearly out of the specified range of 300 to 500 ppm. The inlet hydrocarbon contents of sampling F75, F78, F79, F80 were extraordinary high (905 – 2418 ppm). All of the following inlet hydrocarbon contents were lower again (around 550 ppm). The hydrocarbon separation performance of the CPI was significantly decreased. The median hydrocarbon content after CPI was 218 ppm, way above the limit value of 100 ppm. It is likely that the extraordinary high inlet hydrocarbon contents of the CPI in the beginning of test F lasted too long and led to overloading. In the following samplings F82 – F87 the hydrocarbon content in the feed was much lower than before, but the hydrocarbon separation performance stayed as bad as in the beginning of the test. This is a sign that the reason for the reduced performance was rather not overloading but contamination for instance.

Despite the very high inlet hydrocarbon values the median outlet hydrocarbon content of the flotation (7.9 ppm) was far below the limit value of 20 ppm again.

The median outlet hydrocarbon content of the nutshell filter was 1.4 ppm which is at about the same level as in all tests of pilot plant experiment 5.

In the sample from the inlet of the CPI in sampling F75 a lot of very oily flocs were observed; the same in sampling F78, F79 and F80. The hydrocarbon contents were very high in these samples. It is supposed that cleaning work had been done in the field somewhere.

In F80, F81 many fine flocs were observed after flotation. They led to the augmented hydrocarbon contents in the taken samples. In the samples after flotation in sampling F82 and F83 the hydrocarbon contents were also augmented which was most probably due to high inlet hydrocarbon contents.

The augmented hydrocarbon contents after NSF partly go along with the augmented hydrocarbon contents after flotation, for example in sampling F80, F81 and F83. The augmented hydrocarbon contents after NSF in sampling F76 and F77 cannot be explained.

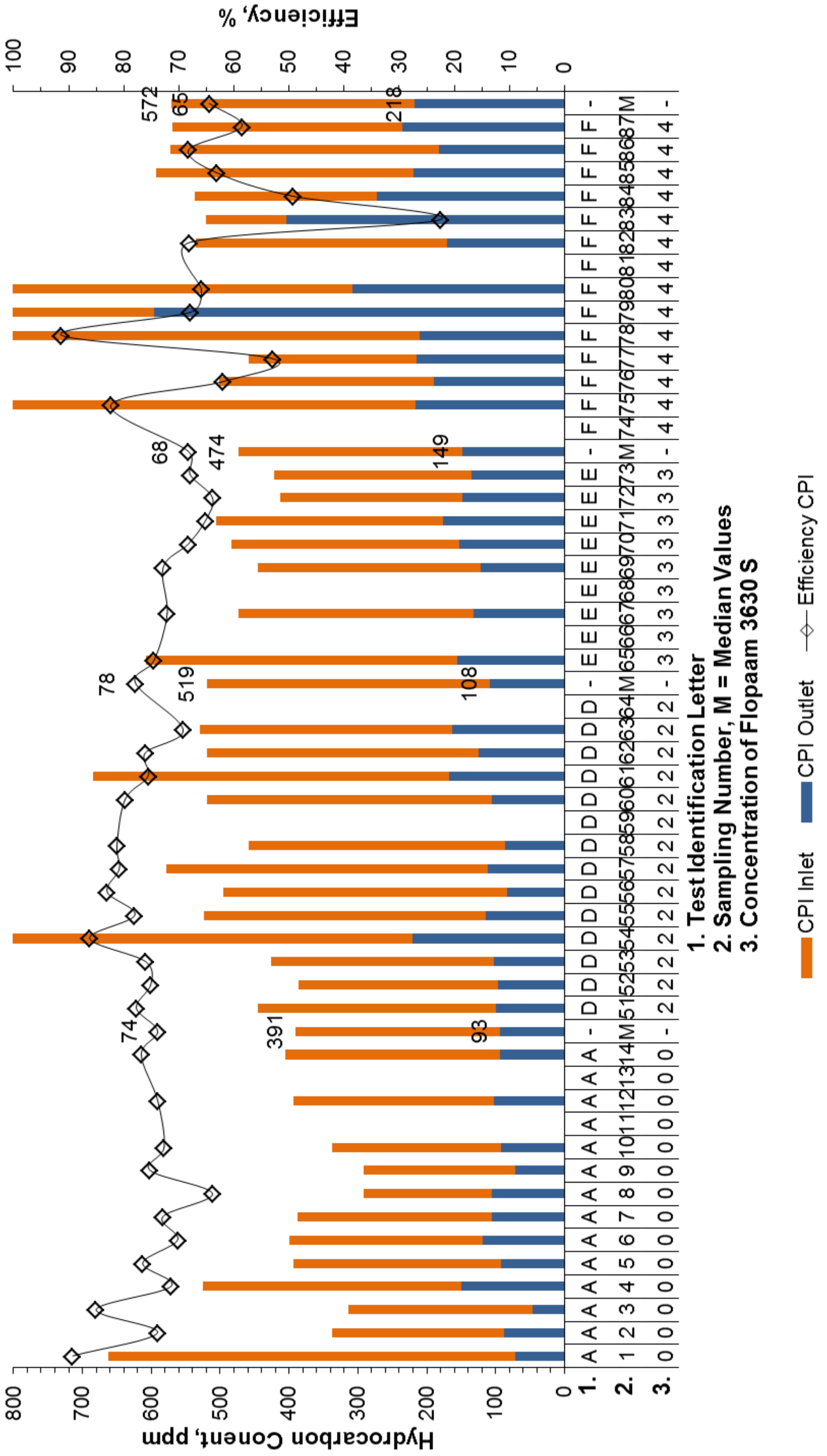


Figure 4-20: Pilot plant experiment 5 - Hydrocarbon separation results of the CPI at 0, 2, 3 and 4 ppm of Flopaam 3630 S in the feed of the pilot plant, as well as the resulting separation efficiencies (The following inlet hydrocarbon contents exceed the y-axis: D54 with 1595 ppm, F75 with 1224 ppm, F78 with 2418 ppm, F79 with 1854 ppm, F80 with 905 ppm)

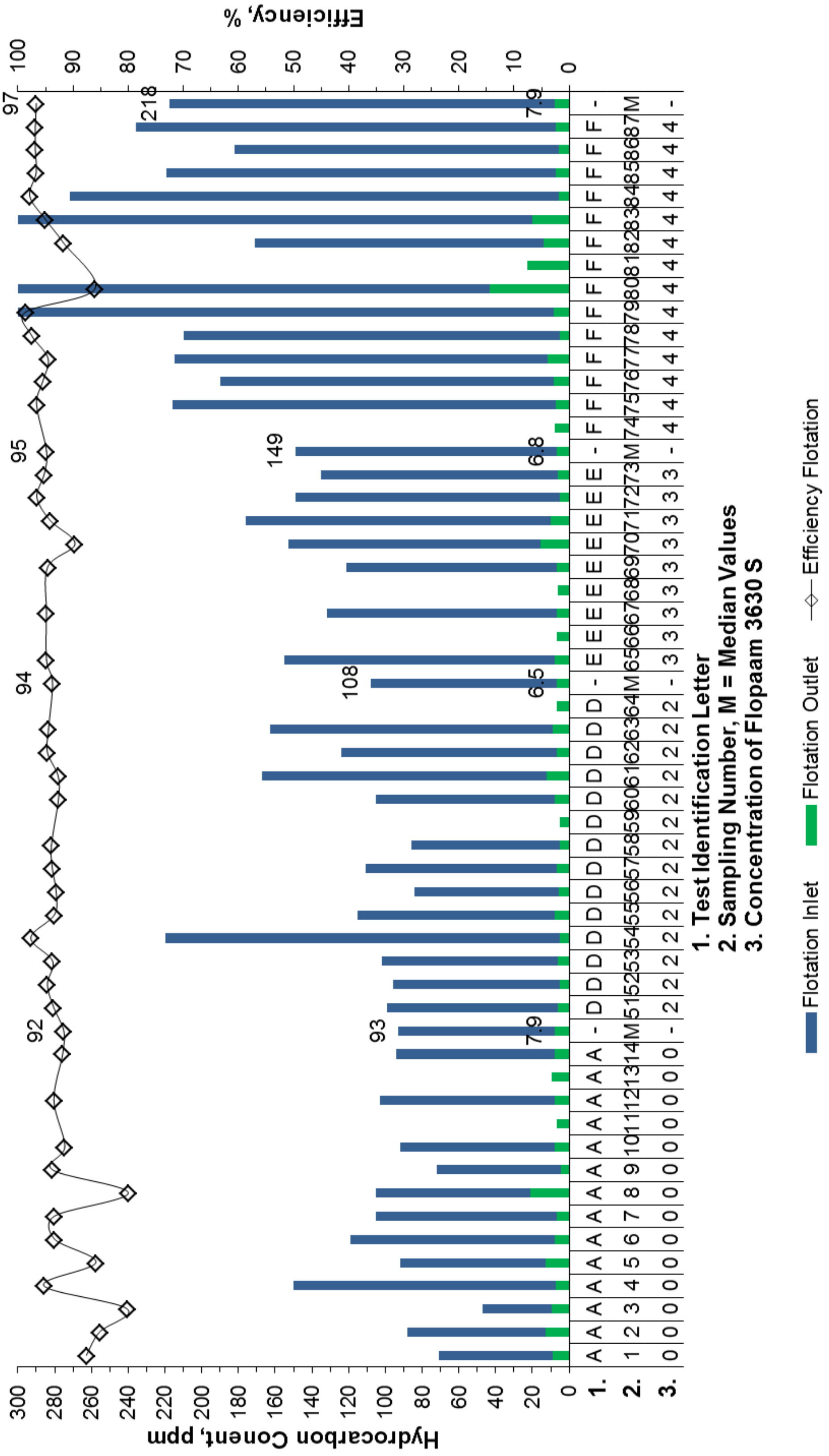


Figure 4-21: Pilot plant experiment 5 - Hydrocarbon separation results of the combined flocculation and flotation at 0, 2, 3 and 4 ppm of Flopaam 3630 S in the feed of the pilot plant, as well as the resulting separation efficiencies (The following inlet hydrocarbon contents exceed the y-axis: F79 with 596 ppm, F80 with 308 ppm, F83 with 404 ppm)

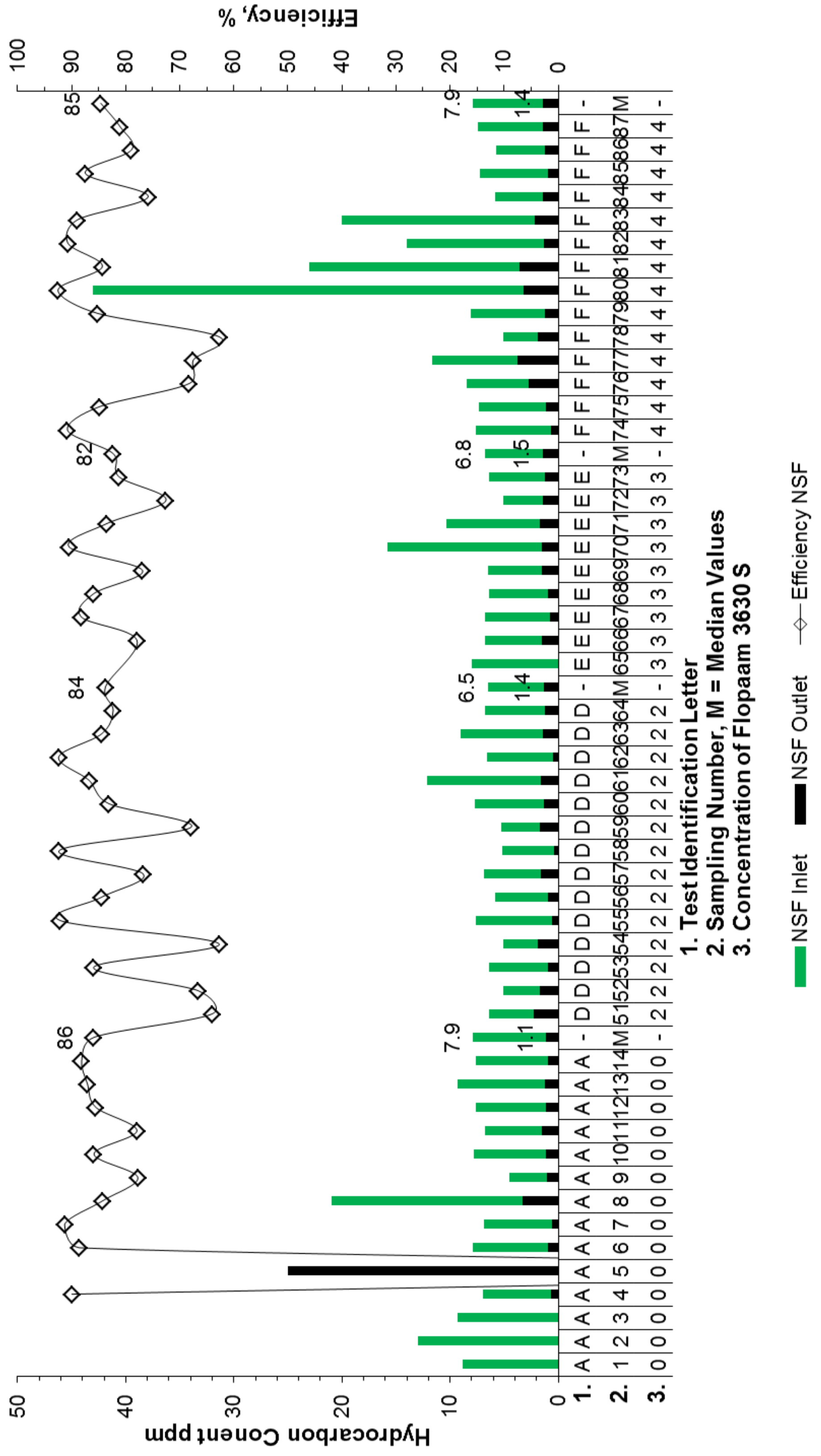


Figure 4-22: Pilot plant experiment 5 - Hydrocarbon separation results of the NSF at 0, 2, 3 and 4 ppm of Flopaam 3630 S in the feed of the pilot plant, as well as the resulting separation efficiencies (after the treatment of flotation water with chemical set II and subsequent flotation)

4.4.1.4 Results of Additional Testing of the Water Quality after Flotation and after the Nutshell Filter

In all tests of the pilot plant experiment the outlet hydrocarbon content of the combined flocculation and flotation was far below the specified limit value of 20 ppm. Therefore in each test additional testing of the water quality after flotation and after NSF was performed. The results of the additional testing after flotation is presented in **Table 4-9**. The results of the additional testing after NSF is presented in **Table 4-10**.

Additional Testing of the Water Quality after Flotation

All values of the WBF (8 µm) were sufficient for further filtration of the treated water with the NSF. The concentrations of suspended solids (> 8 µm) were normal operating with chemical set II in the flocculation unit. The values for the WBF (8 µm) in sampling F78 and F84 were surprisingly low considering the content of 4 ppm of Flopaam 3630 S in the feed of the pilot plant.

Table 4-9: Results of additional testing after flotation in pilot plant experiment 5

SAMPLES: Flotation Outlet							
Test ID			**A**	**D**	**E**	**F**	**F**
Sampling No.		**#**	**9**	**56**	**71**	**78**	**84**
Flopaam 3630 S (feed of pilot plant)		ppm	0	2	3	4	4
hydrocarbon Content		ppm	4.5	5.8	10.3	5.1	5.8
Turbidity		NTU	14	12	12	11	8
SINGLE FILTRATION	**WBF (8 µm)**	1/min	1.23	2.03	2.67	1.98	1.95
	SS, de-oiled (> 8 µm)	mg/l	2.7	3.4	3.4	2.6	2.5
	Total Iron	mg/l	1.20	1.31	1.04	1.26	1.55
	Iron (< 8 µm)	mg/l	1.08	0.86	0.84	1.00	1.41
	Dissolved Iron (< 0.45 µm)	mg/l	1.04	0.96 (*)	0.84	1.06 (*)	1.38
	Calculated Iron (> 0.45 µm)	mg/l	0.16	0.35	0.20	0.20	0.17

(*) a determination error is very likely

The total iron concentration as well as the concentration of solid iron (> 0.45 µm) were significantly lower than in the additional tests from pilot plant experiment 2, 3 and 4. The total iron concentration was about 1 mg/l lower and the solid iron concentration was about 0.20 to 0.40 mg/l lower. This probably was due to the cleaning of the pilot plant with hydrochloric acid after pilot plant experiment 4. Another reason could be, that the iron concentrations in the feed of the pilot plant were also lower.

The dissolved iron concentration of 0.96 mg/l in sampling D56 is most probably a determination error, because the value of the iron concentration that passed the 8 µm membrane filter is lower (0.86 mg/l).

Additional Testing of the Water Quality after the Nutshell Filter

All values of the WBF (3 µm) were below the required limit value of 0.7 min^{-1} after the NSF. Also the suspended solids (> 3 µm) were clearly below the required limit value of 1 mg/l after the NSF. Hence, the water quality fulfills the specification for re-injection.

Table 4-10: Results of additional testing after NSF in pilot plant experiment 5

SAMPLES: NSF Outlet						
Test ID			**A**	**D**	**E**	**F**
Sampling No.		**#**	**9**	**56**	**71**	**84**
Flopaam 3630 S		ppm	0	2	3	4
HC Content		ppm	1.0	0.9	1.7	1.4
Turbidity		NTU	5	3	1	1
CASCADE FILTRATION	**WBF (3 → 0.45 µm)**	1/min	0.01 → 0.15	0.01 → 0.27	0.01 → 0.20	0.01 → 0.07
	SS, de-oiled (> 3 µm → > 0.45 µm)	mg/l	0.0 → 0.04	0.6 → 0.4	0.1 → 0.4	0.1 → 0.2
	Total Iron	mg/l	1.23	1.17	1.00	1.45
	Iron (< 3 µm → < 0.45 µm)	mg/l	1.21 → 1.20	1.06 → 1.14	0.99 → 0.99	1.41 → 1.39
	Calculated Iron (> 0.45 µm)	mg/l	0.03	0.03	0.01	0.06

4.4.1.5 Operational Performance of the Nutshell Filter

Each filtration cycle is identified by a capital letter referring to the test within the pilot plant experiment during which it was performed. The number which is shown together with the identifying letter describes the chronological order in which the cycles were operated. Filtration cycle 1A, for instance, was the first filtration cycle which was performed during test A.

Filtration Cycles 1A and 2A

The NSF could be operated for 24 hours before back-washing in both cycles. The pressure drop over the filter bed rose continuously due to separated oil that is accumulated in the filter. There was no sign for a hydrocarbon breakthrough. The pressure drop after 24 hours was below 0.6 bars in both cycles. The ratio of back-washing water to filtered water was 1.9 % in 1A and 1.7 % in 2A. The pressure drop curve of 1A is shown as example in **Figure 4-23**. Back-washing worked normally.

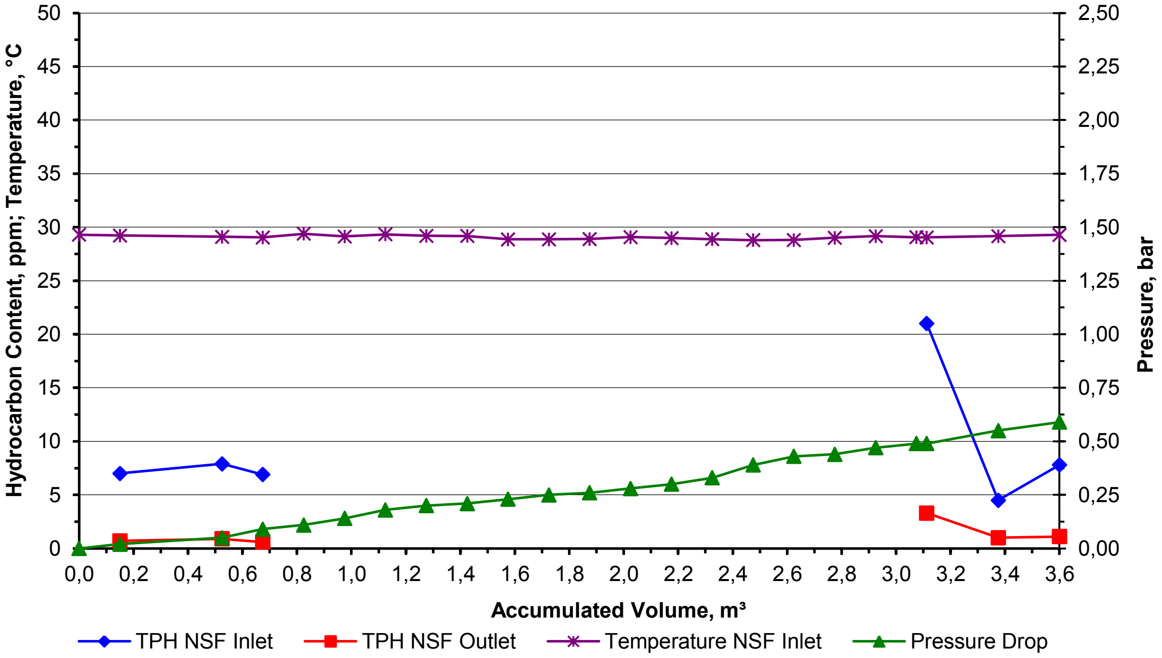


Figure 4-23: Filtration cycle 1A of test A with a 24 hours operating time before back-washing

Filtration Cycles 1B - 3B and 1C - 2C

The filtration cycles were not evaluated (see section 4.4.1.3, test B and C).

Filtration Cycles 1D and 2D

The NSF was provided with fresh nutshell granules for reasons mentioned in 4.4.1.3 It could be operated for 24 hours before back-washing in both cycles. The pressure drop over the filter bed raised continuously due to separated oil that is accumulated in the filter. There was no sign for a hydrocarbon breakthrough. The pressure drop after 24 hours was 0.7 bars in 1D and 0.8 bars in 2D. The ratio of back-washing water to filtered water was 1.9 % in 1D and 2.2 % in 2D.

During back-washing the direction of water flow is changed to an upwards flow through the filter bed. In the beginning of the back-washing after filtration cycle 1D an agglomeration of about 9 cm of the filter bed was lifted with the water flow as it is shown in **Figure 4-24** a. Some nutshells detached again from the agglomeration. The final thickness of the agglomeration of nutshells was about 3 to 4 cm as it is shown in **Figure 4-24** b. Starting pump P 4.2 in order to wash the nutshells as described in the process description the agglomeration was destroyed again and the NSF could be regenerated for the next filtration cycle.

The same observations were done in cycle 2D.

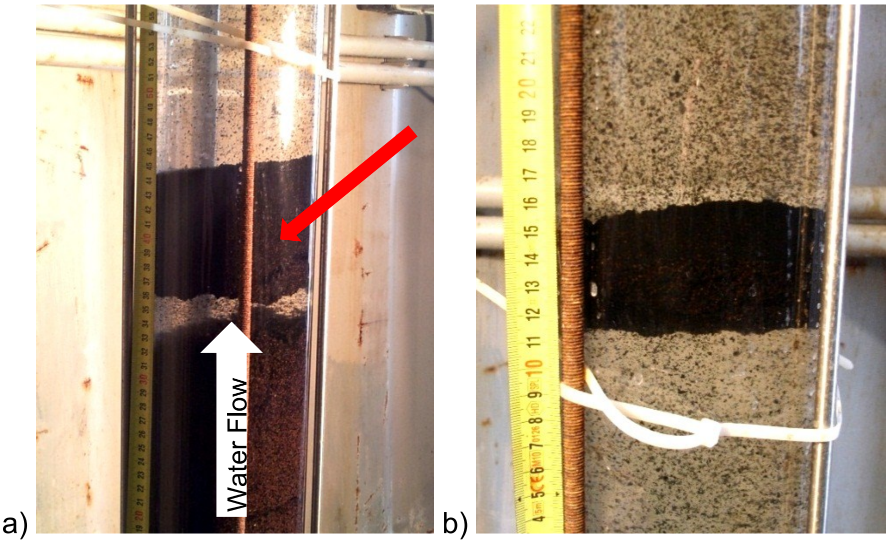


Figure 4-24: Agglomeration of nutshells (red arrow) when back-washing was started a) lifted by the upwards water flow b) diminished in thickness after 1 minute.

Filtration Cycle 1E

The NSF could be operated for 24 hours before back-washing. The pressure drop over the filter bed rose continuously due to separated oil that is accumulated in the filter. There was no sign for a hydrocarbon breakthrough. The pressure drop after 24 hours was below 0.7 bars. The ratio of back-washing water to filtered water was 2.2 %.

The back-washing behavior was the same as already observed in test D.

Filtration Cycle 1F and 2F

The NSF could be operated for 24 hours before back-washing in both cycles. The pressure drop over the filter bed raised continuously due to separated oil that is accumulated in the filter. There was no sign for a hydrocarbon breakthrough. The pressure drop after 24 hours was slightly above 0.7 bars in 1F and 0.7 bars in 2F. The ratio of back-washing water to filtered water was 2.5 % in both cycles.

The back-washing behavior was the same as already observed in test D and test E.

4.4.1.6 Discussion and Conclusion

The median test results of pilot plant experiment 5 are summarized in **Table 4-11**.

Table 4-11: Pilot plant experiment 5 - Hydrocarbon (HC) separation performance of the operated process units of the pilot plant with correlating content of Flopaam 3630 S in the feed of the pilot plant (all hydrocarbon contents and separation efficiencies are median values)

PROCESS UNITS	**Test ID**	-	**A**	**D**	**E**	**F**
	Flopaam 3630 S	ppm	0	2	3	4
Corrugated Plate Interceptor	**HC Contents Inlet → Outlet**	ppm	391 → 93	519 → 108	474 → 149	572 → 218
	Separation Efficiency	%	74	78	68	65
Combined Flocculation & Flotation	**Chemical Set II**	ppm	20/0.15	20/0.15	20/0.15	20/0.15
	HC Contents Inlet → Outlet	ppm	93 → 7.9	108 → 6.5	149 → 6.8	218 → 7.9
	Separation Efficiency	%	92	94	95	97
Nutschell Filter	**HC Contents Inlet → Outlet**	ppm	7.9 → 1.1	6.5 → 1.4	6.8 → 1.5	7.9 → 1.4
	Separation Efficiency	%	86	84	82	85

Corrugated Plate Interceptor

Considering the hydrocarbon separation efficiencies of the CPI during the whole pilot plant experiment, a general decline can be noticed. The maximum and minimum values were 78 % (test D) and 65 % (test F). The hydrocarbon separation performance of the CPI is rather poor compared to the performances in pilot plant experiment 2, 3 and 4.

The decreasing separation efficiency could be caused by the increased inlet hydrocarbon contents exceeding 500 ppm (like in test D and F) but contamination of the corrugated plates of the CPI may also have been a reason for the decline.

Combined Flocculation and Flotation

Hydrocarbon Separation Performance

The processes of flocculation and flotation worked perfectly well. The median outlet hydrocarbon contents after flotation stayed very low irrespective of the content of Flopaam 3630 S in the feed of the pilot plant or the constantly rising inlet hydrocarbon contents. This is very surprising comparing the results to the ones of pilot plant experiment 2 (see **Table 4-12**). In the tests D and E of pilot plant experiment 2 with 2 and 3 ppm of Flopaam 3630 S in the feed of the pilot plant the median outlet hydrocarbon contents were already close to the specified limit value of 20 ppm (14 and 16 ppm). In pilot plant experiment 5 however the median outlet hydrocarbon content at 2 ppm of Flopaam 3630 S was only 6.5 ppm (test D) and the median outlet hydrocarbon content at 3 ppm of Flopaam 3630 S only 6.8 ppm (test E). Furthermore it surprises that the hydrocarbon separation performance in pilot plant experiment 5 even increased with Flopaam 3630 S in the feed of the pilot plant.

Table 4-12: Comparison of hydrocarbon separation results of the combined flocculation and flotation in pilot plant experiment 2 and 5 at different contents of Flopaam 3630 S in the feed of the pilot plant

	Flocculation Unit	**Pilot Plant Experiment 2**		**Pilot Plant Experiment 5**	
Flopaam 3630 S	**Chemical Set II**	**HC Contents Inlet → Outlet**	**Separation Efficiency**	**HC Contents Inlet → Outlet**	**Separation Efficiency**
ppm	ppm	ppm	%	ppm	%
0	20/0.15	58 → 7.4	87	93 → 7.9	92
2	20/0.15	58 → 14	77	108 → 6.5	94
3	20/0.15	55 → 16	70	149 → 6.8	95
4	20/0.15	-	-	218 → 7.9	97

The much better hydrocarbon separation performance in the combined flocculation and flotation units is not easy to explain. Four possible reasons can be listed:

- The dosing of aged polymer solution (Flopaam 3630 S) in the tests D, E and F
- The inversed order of contents of Flopaam 3630 S form low to higher contents (2, 3 and then 4 ppm) in this pilot plant experiment
- Too little dosing of Flopaam 3630 S to the feed of the pilot plant

- Comparably clean system after the cleaning with hydrochloric acid – resulting in higher efficacy of the added flocculants

The first reason probably has only a very low impact. It is assumed that the polymer solution did not degrade to a significant extend.

The second reason is more probable being responsible for the better hydrocarbon separation performance in pilot plant experiment 5. In pilot plant experiment 2 the order of Flopaam 3630 S contents in the feed of the pilot plant was from higher to lower values (10, 5 and then 2 ppm). It is possible that the added Flopaam 3630 S in pilot plant experiment 2 accumulated in zones of poor flow and was slowly swept out by the water stream during tests with lower contents of Flopaam 3630 S. Thus a higher actual concentration of Flopaam 3630 S could have been the result. The assumption could only be proved by analysis of the real residence time distribution of the pilot plant with a tracer.

Too little dosing of Flopaam 3630 S is very unlikely, but has to be considered as well.

Chemical set I (Flopam SFC 60) was tested over a very long period of time before the pilot plant experiments presented in this thesis (August until November). Flopam SFC 60 contains a polyelectrolyte and also forms sticky jellylike flocs. It seems possible that the cleaning with normal cold water may not have been sufficient to remove all leftovers from the system. (Note: Hot water was not available for the cleaning of the pilot plant.)

However, it is recommended to repeat pilot plant experiment 5 in order to evaluate the reproducibility of the results. The same can basically be said for pilot plant experiment 2, which is of minor importance though. A repetition of pilot plant experiment 2 could be of interest because if the results were correct, they show that a reduction of Flopaam 3630 S in the feed of the WTP only very slowly leads to an improvement of the hydrocarbon separation performance.

Filterability

All values of the WBF (8 µm) were low enough for further filtration of the treated water with the NSF.

Nutshell Filter

Hydrocarbon Separation Performance

The hydrocarbon separation performance of the NSF in pilot plant experiment 5 basically is satisfying. All median outlet hydrocarbon contents are below the desired limit value of 2 ppm after the NSF. The water is therefore suitable for re-injection. However it has to be noticed that the inlet hydrocarbon contents were all very low. They hardly ever reached/exceeded 20 ppm; only once in test A and three times in test F. Considering the very low inlet hydrocarbon contents (6.5 to 7.9 ppm) the hydrocarbon separation efficiencies are rather poor. Their median values were all around 84 %. The single hydrocarbon separation efficiencies were not very stable, they popped up and down between 60 and 95 %. It would be important to test the hydrocarbon separation performance of the NSF also with higher inlet hydrocarbon contents around 20 ppm.

Filterability

All values of the WBF (3 µm) were below the desired limit value of 0.7 min^{-1} after NSF. Also the SS (de-oiled, > 3 µm) are clearly below the desired limit value of 1 mg/l after NSF. The water quality is therefore perfectly good for re-injection.

Operational Performance

The desired operating period of 24 hours was reached in all evaluated filtration cycles. The pressure drop over the NSF always stayed below 1 bar and there was no hydrocarbon breakthrough in any of the filtration cycles. Considering the very low inlet hydrocarbon contents of the NSF the good operating performance is not surprise. Further tests are recommended to proof that the NSF can also be operated for 24 hours with higher inlet hydrocarbon contents.

The part of the filter bed that was agglomerated by Flopaam 3630 S facing the inlet water stream could be destroyed in each back-washing. The nutshells could be used again for filtration without noticeable reduction of its efficacy. The accumulated Flopaam 3630 S probably leaves the NSF during back-washing with the discharged water. The thickness of the agglomerated filter bed stayed roughly the same in all concerned tests. It seems that it only depends on the operating time of one filtration cycle. The longer the operating period the thicker probably the agglomerated filter bed. To investigate if the filter bed fully regenerates also during long-term operation, further tests are recommended.

The consumption of back-washing water rose slightly over the course of filtration cycles operated with the same nutshell granulate in test D, E and F (see **Table 4-13**). 2.5 % is still an acceptable value, but it is very likely that the consumption would constantly rise over the course of ongoing filtration cycles. The water consumption of the filtration cycles performed in test A, B and C could not be evaluated. The reason is the influence of the discharged waste water of the OMV landfill site during test B and C.

Table 4-13: Water consumption for back-washing in filtration cycles that were operated with the same nutshell granules in pilot plant experiment 5

Filtration Cycle	Flopaam 3630S	Quantity of Back-Flushing Cycles	Volume of Back-washing Water	Ratio of Back-washing/ Filtered Water
#	ppm	#	l	%
1D	2	7	70	1.9
2D	2	8	80	2.2
1E	3	8	80	2.2
1F	4	9	90	2.5
2F	4	9	90	2.5

5 Summary of Results and General Discussion

5.1 Corrugated Plate Interceptor

At higher concentrations Flopaam 3630 S leads to a significant rise in viscosity which influences the hydrocarbon separation performance of the CPI. According to Stokes' Law the rising velocity of the oil droplets is reduced and the residence time becomes too short for the desired separation of oil and water. With higher viscosity also the coalescence of oil droplets is reduced. The film of water the oil droplets have to penetrated in order to coalesce is harder to pass than at lower viscosity. As a result the oil droplets are smaller and rise slower according to Stokes' Law. (Compare (Deng, et al., 2002 p. 211))

The concentration of Flopaam 3630 S in the water for the treatment to test in the pilot plant experiments was certainly too little to have caused a significant raise in viscosity. In the pilot plant experiments 2, 3 and 4 the hydrocarbon separation efficiency of the CPI was very good (around 80 %). Hence, a correlation of the content of Flopaam 3630 S in the feed of the pilot plant and the hydrocarbon separation performance of the CPI in these cases could not be observed.

In the pilot plant experiments 1 and 5 however, the hydrocarbon separation performance was worse than usual. Overloading with oil from produced water with hydrocarbon contents of > 500 ppm could only have caused a short-term reduction of the efficiency. So overloading could not have been the reason for the decreasing hydrocarbon separation efficiency during both pilot plant experiments. Moreover, the hydrocarbon separation efficiency in some cases was excellent despite very high hydrocarbon contents at the inlet (see pilot plant experiment 3: test B and C; pilot plant experiment 5: test D).

A reason for the decrease in hydrocarbon separation efficiency could be plugging of parts of the channels between the corrugated plates by contaminants, for instance, in pilot plant experiment 1: test F and G and in pilot plant experiment 5: test E and F. The origin and the kind of the contaminants are not clear, but they could come from flocculation of Flopaam 3630 S with suspended solids or from cross-linking of the polymer due to the presence of bivalent ions like Ca^{+2}.

Another possible reason could be chemicals (e.g. corrosion inhibitors) that are used in production facilities ahead of the water treatment plant, stabilizing oil droplets and thus reduce the hydrocarbon separation in the CPI.

During pilot plant experiment 1 the piping connections between the production facilities and the existing WTP partly have been changed. That also could have affected the hydrocarbon separation performance of the CPI by a change in quality of the entering oil, by the use of chemicals, by discharge of settled material from tanks which had to be emptied.

With higher contents of Flopaam 3630 S in the water to be treated a decrease in hydrocarbon separation performance by gravity can certainly be expected. To find out at which contents of Flopaam 3630 S in produced water the viscosity significantly rises, laboratory measurements could be performed.

5.2 Combined Flocculation and Flotation

5.2.1 Summary of Results

Table 5-1 shows a summary of the best testing results of each chemical set. For chemical set II the best testing results from pilot plant experiment 2 (PPE 2) and 5 (PPE 5) are presented. The testing results concern the hydrocarbon separation performance and the resulting water quality regarding the filterability. The influence of a changing concentration of the chemical sets was only tested with chemical set III and IV.

Table 5-1: Summary of best testing results of each chemical set with corresponding content of Flopaam 3630 S in the feed of the pilot plant (PPE = pilot plant experiment)

Chemical Set	**Flopaam 3630 S**	**Dosing**	**HC Inlet → Outlet**	**HC: Single Values**	**η**	**Sampl. No.**	**WBF (8 µm)**	**SS, de-oiled (> 8 µm)**
#	ppm	ppm	ppm	>20 ppm	%	#	1/min	mg/l
I	0	52/0.35	95 → 16	2 of 10	84	A5	4.16	5.1
	2	52/0.35	67 → 18	3 of 8	67	E40	6.10	11.5
II/PPE 2	0	20/0.15	58 → 7.4	0 of 11	87	A5	1.76	3.7
	3	20/0.15	55 → 16	2 of 6	70	E35	2.36	4.7
II/PPE 5	0	20/0.15	93 → 7.9	1 of 14	92	A9	1.23	2.7
	4	20/0.15	218 → 7.9	3 of 14	97	F84	1.95	2.5
III	0	3.5	73 → 24	15 of 18	69	-	-	-
	10	6.0	109 → 47	4 of 4	53	-	-	-
IV	10	75	57 → 17	2 of 10	66	B14	3.29	11.3

Chemical Set I

Chemical set I is the combination of PAC (Alustar 1010 L) and an anionic polyelectrolyte (Drewfloc 285) with medium molecular mass and high charge density. Alustar 1010 L was used as coagulant and Drewfloc 285 as flocculation aid.

The hydrocarbon separation performance of chemical set I with 2 ppm of Flopaam 3630 S in the feed of the pilot plant was successful. But there are two facts that are against the application of Alustar 1010 L and Drewfloc 285 in the combined flocculation and flotation process of the new WTP:

1. The high WBF (8 µm) after flotation which was 6.10 min^{-1} (Sampling E40);
2. The fact that the flocs show a settling behavior especially at higher contents of Flopaam 3630 S;
3. The generated flocs are fragile.

Chemical set I is therefore not suitable for the treatment of produced water containing Flopaam 3630 S with the new WTP. However, (e.g. settling tank) chemical set I can be reconsidered with a modified process.

At the moment no further experiments are planned, but the use of Alustar 1010 L as single chemical in the flocculation process or in combination with a cationic flocculation aid could possibly lead to better separation results.

Chemical Set II

Chemical set II is the combination of PAC (Chimec 5762) and a cationic polyelectrolyte (Chimec 5498) with high molecular mass (charge density is not known). Chimec 5762 was used as coagulant and Chimec 5498 as flocculation aid.

Chemical set II was tested in pilot plant experiment 2 (first) and 5 (second testing stage).

In pilot plant experiment 2 the hydrocarbon separation performance with 3 ppm of Flopaam 3630 S in the feed of the pilot plant was satisfactory. The filterability was also sufficient for future tests with the NSF.

In pilot plant experiment 5 the hydrocarbon separation performance with 4 ppm of Flopaam 3630 S in the feed of the pilot plant surprisingly was still excellent and so was the filterability.

Possible reasons for the much better performance in pilot plant experiment 5 were largely discussed in section 4.4.1.6. It is recommended to repeat pilot plant experiment 5 to verify the results.

Generally chemical set II is very promising for a successful use in the treatment of produced water containing Flopaam 3630 S with the new WTP.

Chemical Set III

Chemical set III (Flopam SFC 60) is a cationic polyelectrolyte of medium molecular mass and very high charge density. Flopam SFC 60 was used as a single flocculant.

Chemical set III did not successfully perform in any of the tests. Chemical set III is therefore not suitable for the treatment of produced water containing Flopaam 3630 S with the new WTP.

Chemical Set IV

Chemical set IV (Floquat FL 2949) is a cationic polyelectrolyte of very high charge density (molecular mass is not known). Floquat FL 2949 was used as a single flocculant.

Chemical set IV was recommended by the manufacturer for the separation of Flopaam 3630 S at a content ratio of 75 to 10 ppm. The hydrocarbon separation performance of chemical set IV was satisfactory. Moreover, the filterability after flotation was acceptable for a filtration with the NSF (WBF: about 3.2 min^{-1}). However, there are important reasons that exclude the application of chemical set IV in the combined flocculation and flotation process of the new WTP

1. The stickiness of the flocs makes stable water treatment impossible; the enormous fouling very quickly leads to plugging of the equipment;
2. The generated flocs are initially small but stick together and form bigger specifically heavier flocs that show settling behavior;
3. Sticky flocs in the outlet stream of the flotation unit would have a negative effect on the NSF.

A qualitative evaluation of the results of the first stage of testing is presented in **Table 5-2**.

Table 5-2: Qualitative evaluation of the results of the first stage of testing

FIRST STAGE OF TESTING (Pilot Batches 1 - 4)				
Chemical Set	I	II	III	IV
Flopaam 3630 S, ppm	≤ 2	≤ 3	2, 5, 10	10
Median HC Content after Flotation < 20 ppm	yes	yes	no	yes
WBF (8 µm)	- -	++	not tested	+
Solid Flocs	yes	yes	no	no
Type of Floc	settling	floating	sticky gel	very sticky gel
SS de-oiled (> 8 µm)	augmented	o.K.	not tested	augmented
Residence Time before Flotation	o.K.	o.K.	o.K.	too short
O.k. for New WTP	no	**yes**	no	no

5.2.2 General Discussion

The chemical reagents for the flocculation of oil and suspended solids have to fulfill the following requirements (compare (Owen, 2013)):

- Quick floc formation (short residence time in flocculation unit)
- Formation of mechanically stable and shear resistant flocs
- Complete flocculation of the chemicals, especially of the flocculation aids in order to avoid clogging of the NSF
- Lowest possible dosage, in order to favor a complete separation before the NSF

The flocs have to

- efficiently bind oil and suspended solids
- be easily wettable by air for a quick separation by flotation (short residence time)

Oil and oil-wetted suspended solids are finely dispersed in the water after gravity separation of oil and suspended solids as it is shown in **Figure 5-1**. The content of emulsified oil after gravity separation is assumed to be rather constant. To a big part remaining free oil (for definition see 4.1.5) is assumed to be able to rise on its own in the flotation process.

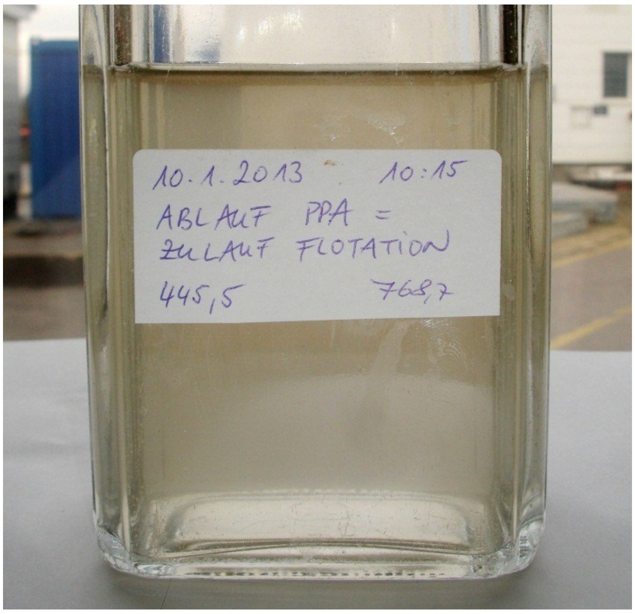


Figure 5-1: A sample of treated water after CPI as it enters the combined flocculation and flotation unit

Possible Mechanisms of Efficacy of the Used Flocculants

Polyaluminum - Alustar 1010 L and Chimec 5762

There are two possibilities of interaction between polyaluminum and oil or suspended solids at the present pH of around 7:

- Polyaluminum destabilizes the suspended particles by chemical adsorption and resulting neutralization of the particles surface charge, inducing coalescence of the particles

- Polyaluminum precipitates after dosing to the water, forming many little flocs including and adsorbing the oil and the suspended solids (big surface area)

Which of the two mechanisms prevails is a matter of molar concentration of polyaluminum. Above a concentration of 10^{-1} mol/l of $Al(OH)_n^{+(3-n)}$ precipitation of polyaluminum is prevailing (see **Figure 2-2**). The molar concentration of the dosing of polyaluminum in the pilot plant experiments can unfortunately not be calculated, because the molar masses are not known.

The separation of dispersed oil and suspended solids by adsorption to precipitated polyaluminum is more probable. The following example concerning the application of polyaluminum from Chimec 5762 confirms the assumption:

With a higher median inlet hydrocarbon content as in test A of pilot plant experiment 5 (93 → 7.9 ppm) almost the same median outlet hydrocarbon content can be achieved as in test A of pilot plant experiment 2 (58 → 7.4 ppm). With the mechanism of coagulation by neutralization of the particles surface charge recurring stabilization of the particles would occur at lower inlet hydrocarbon contents and the resulting outlet hydrocarbon results should be augmented. This was not the case. Overdosing of polyaluminum thereafter is not a problem. The generated solid flocs are easily separated in the following flotation process even without adsorbed oil/suspended solids.

Polyelectrolytes - Drewfloc 285, Chimec 5498, Flopam SFC 60 and Floquat FL 2949

Generally polyelectrolytes act by polymer bridging (high molecular mass) or by charge patching (low molecular mass, high (cationic) charge density). The disadvantage of polyelectrolytes as single flocculants is, that they do not form solid flocs. Hence, solid surface for adsorption is not produced. They rather form a gel interacting with ions of contrary charge (like chemical set IV and Flopaam 3630 S). As a result polyelectrolytes are not as applicable for the separation of oil and suspended solids as polyaluminum, nor are the generated flocs as resistant to shear forces as the flocs generated with polyaluminum. Without Flopaam 3630 S in the feed their efficacy is still sufficient for a successful separation of hydrocarbons as it was proved with Flopam SFC 60 in the testing period from August to November 2012.

Polyelectrolytes are very important as flocculation aid in combination with a coagulant. They can lead to the formation of bigger and more shear resistant flocs. They can also help to reduce the dosage of coagulant.

Possible Influence of Flopaam 3630 S on the used Flocculants

Flopaam 3630 S worsens the separation of oil and suspended solids from water. The worsening first of all concerns the flocculation process. The flotation process itself could also be concerned. A sign for that was found in laboratory flotation experiments (see section 4.2.3).

The added chemicals in the flocculation unit seem to first react with Flopaam 3630 S instead of with the oil and suspended solids in the matrix. So the efficacy of the chemicals for their original purpose is reduced.

Influence on Polyaluminum

Regular produced water from water flooding operations only could be treated with polyaluminum chloride as coagulant and Flopaam 3630 S as flocculation aid. In such a case the latter would be added in a very small dose (approx. 0.01 ppm) due to its very high molecular weight. In the described experiments Flopaam 3630 S was already contained in the water when it entered the coagulator. Moreover, the concentrations of the polymer were very high (approx. 2 - 10 ppm) compared to the concentration that would be used as flocculation aid. As a result dispersed oil and suspended solids are rather stabilized. With an appropriate augmented dosage of polyaluminum chloride it seems to be possible that enough flocs would form to lead to polymer bridging of all Flopaam 3630 S molecules.

In the usual process of combined coagulation and flocculation first a coagulant like polyaluminum chloride is added to the water and then a flocculation aid. In a *reversed process* of combined coagulation and flocculation like described above the flocculation aid is already present and an appropriate amount of coagulant like polyaluminum chloride has to be added in order to react with all polymer molecules.

Comparing Alustar 1010 L (coagulant in chemical set I) and Chimec 5762 (coagulant in chemical set II) the only difference that is obvious is the higher content of polyaluminum chloride in Alustar 1010 L. An open question is, why chemical set II worked so much better than chemical set I. A reason could be that the cationic character of Chimec 5498 act neutralizing on Flopaam 3630 S and at the same time efficiently acts as flocculation aid due to its high molecular mass. Drewfloc on the other hand is very similar to Flopaam 3630 S. It is anionic and has the same chemistry. Only its molecular mass is much lower than the one of Flopaam 3630 S. In laboratory tests it was found that flocs from chemical set I become comparably big and settle even without the presence of Flopaam 3630 S in the water. With increasing content of Flopaam 3630 S the flocs tend to grow even bigger and settle quicker (see section 4.3.4.7). Using chemical set II this obviously is not the case. The flocs are specifically lighter than water and rise.

Influence on Cationic Polyelectrolytes

Highly charged cationic polyelectrolytes react with the anionic Flopaam 3630 S. Electrostatic forces lead to attraction and jellylike precipitates (coacervates) can form. This happened using chemical set IV in pilot plant experiment 4. Chemical set III could probably interact the same way with Flopaam 3630 S, but its content in pilot plant experiment 1 (maximum 9.9 ppm) was much lower than the content of chemical set IV in pilot plant experiment 4 (75 ppm).

Flopam SFC 60 is a cationic organic polyelectrolyte of medium molecular mass and high charge density. Due to its medium molecular mass the prevailing mechanism of destabilization of oil and suspended solids might be polymer bridging. Electrostatic forces between the negatively charged suspended particles and the cationic polyelectrolyte probably lead to attraction and adsorption onto it.

When Flopaam 3630 S is present in the water Flopam SFC 60 obviously rather interacts with the big anionic molecules of Flopaam 3630 S and loses its efficacy on the suspended particles. The generally augmented hydrocarbon contents after flotation in all tests of pilot plant experiment 1 is a proof for that.

5.3 Nutshell filter

Hydrocarbon Separation and Water Quality after Filtration

The hydrocarbon separation performance of the NSF in pilot plant experiment 5 was satisfactory (< 2 ppm) in all tests irrespective of the content of Flopaam 3630 S in the feed of the pilot plant. At the same time the inlet hydrocarbon content of the NSF was very low throughout all tests (6.5 to 7.9 ppm). However, even with 20 ppm of hydrocarbons in the feed of the NSF the outlet hydrocarbon content should be < 2 ppm. Therefore, further testing with the 20 ppm of hydrocarbons at the inlet of the NSF is recommended.

The rising of the agglomerated filter bed as described in section 4.4.1.5 indicates that it was only partly permeable for the water. It is very likely that most of the water passed this section between filter bed and wall. Despite this fact, the hydrocarbon separation efficiency of the NSF was still as afforded.

The water quality after filtration fulfilled the criterions of injection water as it was specified in 3.3.

Operational Performance

The desired operating period of 24 hours could be reached in all evaluated filtration cycles.

In the tests with Flopaam 3630 S in the feed of the pilot plant (tests D, E and F of pilot plant experiment 5) the first centimeters of the filter bed facing the inlet stream became agglomerated by Flopaam 3630 S during filtration. The agglomerated part could easily be destroyed in each back-washing. It is very likely that the agglomerated nutshells are not sustainably deactivated by Flopaam 3630 S. Flopaam 3630 S is a hydrophilic substance and most probably did not adsorb to the nutshells, but deposited in between the nutshells due to its sheer size. If this is the case the nutshells may stay able to adsorb oil in the long run. The agglomeration caused by Flopaam 3630 S could possibly be minimized by intermediate washing as it was discussed anyway for the operation of the NSF in a large scale (compare (Steinbrugger, 2009 pp. 57-58)). It is most possible that the accumulated Flopaam 3630 S was discharged to the slop system during back-washing. The water consumption for back-washing increased slightly but not significantly during the tests of pilot plant experiment 5.

To evaluate the long-term performance of the NSF with treated water that originally contained Flopaam 3630 S the NSF has to be tested in the long run.

In **Table 5-3** a qualitative evaluation of the results of the second stage of testing is presented.

Table 5-3: Qualitative summary of results from the second stage of testing with the water treatment pilot plant

<table>
<tr><td colspan="5">**SECOND TESTING STAGE (Pilot Plant Experiment 5)**</td></tr>
<tr><td colspan="5">Chemical Set II for Flocculation prior Flotation</td></tr>
<tr><td colspan="5">**4 ppm** of Flopaam 3630 S in the Feed of the Pilot Plant</td></tr>
<tr><td colspan="2">**Combined Flocculation & Flotation**</td><td colspan="3">**Nutshell Filter**</td></tr>
<tr><td>**Median Outlet HC Content < 20 ppm**</td><td>yes</td><td colspan="2">**Median Outlet HC Content ≤ 2 ppm**</td><td>yes</td></tr>
<tr><td>**WBF (8 µm)**</td><td>+++</td><td colspan="2">**WBF (3 µm)**</td><td>+++</td></tr>
<tr><td>**Solid Flocs**</td><td>yes</td><td colspan="2">**SS de-oiled (> 3 µm) ≤ 1 µm**</td><td>yes</td></tr>
<tr><td>**Type of Floc**</td><td>floating</td><td colspan="2">**Agglomeration of Nutshells**</td><td>partly</td></tr>
<tr><td>**SS de-oiled (> 8 µm)**</td><td>o.K.</td><td rowspan="2">**Regeneration by Back-washing**</td><td>**short-term**</td><td>yes</td></tr>
<tr><td colspan="2" rowspan="2"></td><td>**long-term**</td><td>?</td></tr>
<tr><td colspan="2">**24 h Operating Time**</td><td>yes</td></tr>
</table>

5.4 List of Future Work

- Repetition of pilot plant experiment 5 with chemical set II to verify the HC separation performance of the combined flocculation and flotation with gradual augmentation of the polymer concentration (e.g. 0, 3, 6, 9, 12 ppm);
- Investigation of correlating concentrations of Flopaam 3630 S and chemical set II regarding the achievement of the required water quality after flotation;
- Testing of alternative chemicals or alternative combinations of chemicals as discussed in the workshop with David Owen (Co.Treatchem Ltd) on March 21, 2013;
- Provision of more constant hydrocarbon contents in the feed of the water treatment pilot plant by installing a buffer tank before the inlet;
- Analysis of the jellylike agglomerates from the CPI to investigate if it possibly originates from flocculated or cross-linked polymer;
- Finding methods to artificially degrade Flopaam 3630 S to imitate back-produced polymer for experiments with the water treatment pilot plant;
- Investigation of the rate and degree of degradation of produced polymer stock solution during storage in the dosing station of the water treatment pilot plant and in the maturation tanks of the polymer mixing plant during falloff tests. The last is of interest because during pilot plant experiment 5 the polymer mixing plant could not produce fresh polymer stock solution due to a falloff test of the injection well. Therefore, the polymer stock solution delivered for the purpose of dosing in the experiment was older than the ones used in the other experiments. It appeared more turbid than usually and was of a greyish color.

6 Executive Summary

Oilfield water that is co-produced with the production of petroleum needs to be collected and treated prior to re-injection into the reservoirs. The treatment of the produced water is important, amongst other reasons, to keep the injection pressure as low as possible. Moreover, remaining oil is recovered and conveyed to production. At the moment, a new water treatment plant is under construction and will start operating by 2014. Oil and suspended solids will be removed in three process steps:

- by gravity separation in corrugated plate separators
- by dissolved gas flotation after flocculation
- by filtration with nutshell filters.

Since 2012 OMV Austria Exploration & Production GmbH operates a polymer flooding pilot in order to increase the hydrocarbon recovery of their mature oil fields. As a consequence polymer will also be back-produced and could therefore enter the new water treatment plant within the feed. The polymer used in the polymer flooding pilot operation is a high molecular organic compound (trade name “Flopaam 3630 S”). This would result in a decreased separation efficiency of the dissolved gas flotation due to a disturbance of the preceding flocculation process and a reduction of the separation efficiency and of the operational availability of the nutshell filters, reducing injection water quality.

For development purposes, the water treatment process under the influence of the polymer was simulated with a water treatment pilot plant, utilizing the same process steps than the future water treatment plant. This pilot plant was built after the process of the new WTP was designed. At this stage the application of chemical flocculation agents prior to flotation was tested. Selected chemicals which had performed successfully were tested again under the influence of the polymer in the feed.

In a first stage of testing four preselected sets of chemicals (I – IV) were tested for flocculation efficiency regarding the achievable separation of hydrocarbons and the filterability of the water after the dissolved gas flotation. The feed concentration of the polymer was varied during the testing of each chemical set between 0 and 10 ppm, according to an estimation of the possible future amount of back-produced polymer based on current operating conditions of the polymer flooding pilot and dilution by all produced water that enters the existing water treatment plant. The chemical sets III and IV were also tested regarding the variation of their concentration prior to flotation.

Chemical set I and II, each are a combination of polyaluminum chloride (PAC), an inorganic flocculant, and an organic flocculation aid. The flocculant induces floc formation and the flocculation aid induces floc growth. Chemical set III is an organic flocculant designed for the flocculation of oil and suspended solids. Chemical set IV is also an organic flocculant used on recommendation of the polymer manufacturer for the flocculation of the polymer from the polymer flooding pilot operation.

The application of chemical set II for flocculation and subsequent flotation has proven to be promising at polymer concentrations ≤ 3 ppm in the feed of the pilot plant. After flotation a median hydrocarbon content of < 20 ppm could be achieved, as is required for the future new water treatment plant. The filterability which is assessed as water blocking factor (WBF) was sufficient for a further treatment with the nutshell filter. For differing reasons, all other chemical sets are not suitable for application in the treatment process of the new water treatment plant. A qualitative evaluation of the results of the first stage of testing is presented in **Table 6-1**.

Table 6-1: Qualitative summary of results from the first stage of testing of selected chemical sets with the water treatment pilot plant

FIRST STAGE OF TESTING (Pilot Batches 1 - 4)				
Chemical Set	I	II	III	IV
Flopaam 3630 S, ppm	≤ 2	≤ 3	2, 5, 10	10
Median HC Content after Flotation < 20 ppm	yes	yes	no	yes
WBF (8 µm)	- -	++	not tested	+
Solid Flocs	yes	yes	no	no
Type of Floc	settling	floating	sticky gel	very sticky gel
SS de-oiled (> 8 µm)	augmented	o.K.	not tested	augmented
Residence Time before Flotation	o.K.	o.K.	o.K.	too short
O.k. for New WTP	no	**yes**	no	no

In a second stage of testing the separation efficiency and the operational behavior of the final filtration process with the nutshell filter were tested. Produced polymer containing water was pretreated by gravity separation and flotation following flocculation with chemical set II and then fed to the nutshell filter.

The required water quality for re-injection could be achieved, but the hydrocarbon content within the inlet of the nutshell filter was only half of the desired target value that is specified for the new water treatment plant. After the nutshell filter a median hydrocarbon content of < 2 ppm, as required for injection water, could be achieved. The filterability also met the required criterion of a WBF < 0.7 min^{-1}. However, the operational behavior of the nutshell filter was influenced by residual polymer. Part of the filter bed facing the inlet water stream agglomerated with remaining polymer. The agglomeration caused no additional increase of the pressure drop over the filter bed, allowing a regular operating period of 24 hours before back-washing. The regenerative back-washing was also not affected by the agglomeration so far. However, the long-term impact of Flopaam 3630 S on the nutshell granules' capacity for hydrocarbon separation and on the operational behavior of the nutshell filter has to be investigated in further tests. In **Table 6-2** a qualitative evaluation of the results of the second stage of testing is presented.

Table 6-2: Qualitative summary of results from the second stage of testing with the water treatment pilot plant

<table>
<tr><th colspan="5">SECOND TESTING STAGE (Pilot Plant Experiment 5)</th></tr>
<tr><td colspan="5">Chemical Set II for Flocculation prior Flotation</td></tr>
<tr><td colspan="5">4 ppm of Flopaam 3630 S in the Feed of the Pilot Plant</td></tr>
<tr><th colspan="2">Combined Flocculation & Flotation</th><th colspan="3">Nutshell Filter</th></tr>
<tr><td>Median Outlet HC Content < 20 ppm</td><td>yes</td><td colspan="2">Median Outlet HC Content ≤ 2 ppm</td><td>yes</td></tr>
<tr><td>WBF (8 µm)</td><td>+++</td><td colspan="2">WBF (3 µm)</td><td>+++</td></tr>
<tr><td>Solid Flocs</td><td>yes</td><td colspan="2">SS de-oiled (> 3 µm) ≤ 1 µm</td><td>yes</td></tr>
<tr><td>Type of Floc</td><td>floating</td><td colspan="2">Agglomeration of Nutshells</td><td>partly</td></tr>
<tr><td>SS de-oiled (> 8 µm)</td><td>o.K.</td><td rowspan="2">Regeneration by Back-washing</td><td>short-term</td><td>yes</td></tr>
<tr><td colspan="2" rowspan="2"></td><td>long-term</td><td>?</td></tr>
<tr><td colspan="2">24 h Operating Time</td><td>yes</td></tr>
</table>

The corrugated plate interceptor showed no signs of being influenced by the presence of Flopaam 3630 S in the feed water. However, at higher concentrations of the polymer a decrease in hydrocarbon separation efficiency cannot be excluded. With inlet hydrocarbon concentrations of > 500 ppm the outlet hydrocarbon concentrations exceed 100 ppm in most cases. That leads to overloading of the combined flocculation and flotation which decreases the significance of the testing results.

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7.2 Abbreviations

Al	aluminum
approx.	approximately
IBC	intermediate bulk container, volume = 1 m^3
C	carbon
CD	charge density
Cl	chloride
conc.	concentration
CPI	corrugated plate interceptor
dist.	distilled
DGF	dissolved gas flotation
E&P	Exploration and Production
Fe	Iron
Flot.	flotation
GDR	Gas Dissolving Reactor
H	hydrogen
HC	hydrocarbon(s); equals TPH
HPAM	hydrolized polyacrylamide
ID	Identity
MDa	million Dalton
MM	molecular mass
N	nitrogen
NTU	nephelometer turbidity units
Na	sodium
No.	number
NSF	nutshell filter
O	oxygen
OH	hydroxide
OMV LEP	OMV Laboratory for Exploration and Production
PAC	polyaluminum chloride
PPE	pilot plant experiment
PFD	process flow diagram
PP	pilot plant
WBF	water blocking factor
WTP	water treatment plant
Sampl.	sampling
SS	suspended solids
TH	Tortonian horizon
TPH	total petroleum hydrocarbons = hydrocarbon content
°C	degree Celsius
%	percent

cm	centimeter
dm^3	cubic decimeter
g	gram
h	hour
kg	kilogram
l	liter
m	meter
mm	millimeter
ml	milliliter
m^2	square Meter
m^3	cubic Meter
min	minute
n.s.	not specified
ppm	parts per million
s	second
η	hydrocarbon separation efficiency
λ	lambda (equals WBF)
µm	micrometer

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Appendix

Experimental data of the reference period for pilot plant experiment 1

Date	Time	Sampl. No.	Flopaam 3630 S	TPH CPI Inlet	TPH CPI Outlet	η CPI	Flopam SFC 60	TPH Flot. Inlet	TPH Flot. Outlet	η Flot.
		#	ppm	ppm	ppm	%	ppm	ppm	ppm	%
29-Nov-12	12:00	282	0	345	72	79	3.48	72	22	69
29-Nov-12	13:30	283	0	334	61	82	3.48	61	21	66
30-Nov-12										
3-Dec-12	10:00	284	0	238	75	68	3.49	75	24	68
3-Dec-12	11:30	285	0				3.50		28	
3-Dec-12	14:00	286	0	291	108	63	3.51	108	32	70
4-Dec-12	7:15	287	0	343	173	50	3.92	173	50	71
4-Dec-12	9:30	288	0				3.97		42	
4-Dec-12	11:30	289	0	212	55	74	3.96	55	20	64
4-Dec-12	13:30	290	0				3.95		23	
5-Dec-12	9:00	291	0				3.95		14	
5-Dec-12										
6-Dec-12	13:00	292	0	251	50	80	3.01	50	15	70
6-Dec-12	14:00	293	0				3.01		18	
6-Dec-12	15:00	294	0	384	88	77	3.00	88	23	74
7-Dec-12	7:15	295	0	253	73	71	3.01	73	37	49
7-Dec-12	9:00	296	0				3.01		26	
7-Dec-12	10:15	297	0				2.99		29	
7-Dec-12	11:15	298	0				2.99		21	
7-Dec-12	12:15	299	0				2.99		25	
Medians				**291**	**73**	**74**	**3.5**	**73**	**24**	**69**

Experimental data of pilot plant experiment 1

Date	Time	Test ID	Sampl. No.	Flopaam 3630 S	TPH CPI Inlet	TPH CPI Outlet	η CPI	Flopam SFC 60	TPH Flot. Inlet	TPH Flot. Outlet	η Flot.
			#	ppm	ppm	ppm	%	ppm	ppm	ppm	%
10-Dec-12	13:30	A	1	10.0	565	76	87	3.5	76	41	46
10-Dec-12	14:45	A	2	10.0	437	109	75	3.5	109	62	43
11-Dec-12	7:15	A	3	10.1	355	110	69	3.5	110	87	21
11-Dec-12	8:30	A	4	10.0	393	111	72	3.5	111	53	52
Medians					**415**	**110**	**73**		**110**	**58**	**45**
11-Dec-12	10:00	B	5	10.0	279	83	70	6.0	83	38	54
11-Dec-12	11:00	B	6	10.1		114		6.0	114	41	64
11-Dec-12	12:30	B	7	10.0		103		6.0	103	52	50
11-Dec-12	14:00	B	8	10.0	358	120	66	6.0	120	59	51
Medians					**319**	**109**	**68**		**109**	**47**	**53**
12-Dec-12	7:15	C	9	10.0	461	86	81	3.5	86	*42*	51
12-Dec-12	10:45	C	10	10.0	516	147	72	9.9	147	84	43
12-Dec-12	12:00	C	11	10.0	446	173	61	9.9	173	86	50
12-Dec-12	13:15	C	12	10.0	443	120	73	9.9	120	65	46
12-Dec-12	14:30	C	13	10.0	369	109	70	9.9	109	59	46
Medians					**446**	**120**	**72**		**120**	**75**	**46**
13-Dec-12	7:45	D	14	10.0	343	170	50	0.0	170	73	57
13-Dec-12	9:00	D	15	10.0	536	131	76	0.0	131	75	43
13-Dec-12	10:30	D	16	10.0	426	129	70	0.0	129	82	36
13-Dec-12	11:30	D	17	10.0	377	108	71	0.0	108	65	40
13-Dec-12	13:00	D	18	10.0	355	123	65	0.0	123	67	46
13-Dec-12	14:30	D	19	10.1	411	149	64	0.0	149	62	58
Medians					**394**	**130**	**68**		**130**	**70**	**44**
14-Dec-12	7:15	E	20	4.9	455	134	71	0.0	134	72	46
14-Dec-12	8:30	E	21	4.9	377	104	72	0.0	104	55	47
14-Dec-12	9:30	E	22	4.9	338	134	60	0.0	134	81	40
14-Dec-12	10:30	E	23	4.9	328	165	50	0.0	165	85	48
14-Dec-12	11:30	E	24	4.9	367	124	66	0.0	124	68	45
Medians					**367**	**134**	**66**		**134**	**72**	**46**
17-Dec-12	13:30	F	25	5.0	284	89	69	3.4	89	45	49
17-Dec-12	15:00	F	26	5.0	387	90	77	3.5	90	46	49
18-Dec-12											
19-Dec-12	7:30	F	27	5.1	483	356	26	3.5	356	124	65
19-Dec-12	9:00	F	28	5.0	477	226	53	3.5	226	93	59
19-Dec-12	10:00	F	29	5.0	974	211	78	3.5	211	69	67
19-Dec-12	11:30	G	30	2.0	367	182	50	3.5	182	83	54
19-Dec-12	12:30	G	31	2.0	408	161	61	3.5	161	82	49
19-Dec-12	13:30	G	32	2.0	493	151	69	3.5	151	62	59
19-Dec-12	14:30	G	33	2.0	551	208	62	3.5	208	75	64
20-Dec-12	7:15	G	34	2.0	2021	207	90	3.5	207	100	52
Medians					**493**	**182**	**62**		**182**	**82**	**54**

Experimental data of pilot plant experiment 2

Date	**Time**	**Test ID**	**Sampl. No.**	**Flopaam 3630 S**	**TPH CPI Inlet**	**TPH CPI Outlet**	**η CPI**	**Chimec 5762**	**Chimec 5498**	**TPH Flot. Inlet**	**TPH Flot. Outlet**	**η Flot.**
				ppm	**ppm**	**ppm**	**%**	**ppm**	**ppm**	**ppm**	**ppm**	**%**
9-Jan-13	7:15	A	1	0.0	327	66	80	19	0.15	66	8.9	87
9-Jan-13	8:45	A	2	0.0	547	58	89	20	0.15	58	6.0	90
9-Jan-13	10:15	A	3	0.0	391	85	78	20	0.15	85	9.0	89
9-Jan-13	11:45	A	4	0.0	361	68	81	20	0.15	68	8.7	87
9-Jan-13	13:45	A	5	0.0	273	54	80	20	0.15	54	4.3	92
9-Jan-13	15:00	A	6	0.0	276	46	83	20	0.15	46	7.4	84
10-Jan-13	7:15	A	7	0.0	301	76	75	20	0.15	76	12	85
10-Jan-13	8:45	A	8	0.0	337	42	88	20	0.15	42	3.1	93
10-Jan-13	10:15	A	9	0.0	295	56	81	20	0.15	56	5.6	90
10-Jan-13	11:45	A	10	0.0	376	57	85	20	0.15	57	7.2	87
10-Jan-13	13:15	A	11	0.0	332	60	82	20	0.15	60	8.1	87
Medians					**332**	**58**	**81**			**58**	**7.4**	**87**
10-Jan-13	15:30	B	12	10.0	269	56	79	20	0.15	56	38	32
11-Jan-13	7:15	B	13	10.0	326	68	79	20	0.15	68	44	35
11-Jan-13	8:15	B	14	10.1	351	89	75	20	0.15	**89**	32	64
11-Jan-13	9:00	B	15	10.1	392	51	87	20	0.15	51	32	37
11-Jan-13	10:00	B	16	10.0	319	44	86	20	0.15	44	37	16
11-Jan-13	11:00	B	17	10.0	352	59	83	20	0.15	59	30	49
Medians					**339**	**58**	**81**			**58**	**35**	**36**
14-Jan-13	13:30	C	18	4.9	403	92	77	20	0.15	92	40	57
14-Jan-13	15:00	C	19	5.0	327	89	73	20	0.15	89	36	60
15-Jan-13	7:15	C	20	5.0	283	105	63	20	0.15	105	50	52
15-Jan-13	8:45	C	21	5.0	646	109	83	20	0.15	109	29	73
15-Jan-13	10:00	C	22	5.0	477	92	81	20	0.15	92	57	38
15-Jan-13	11:30	C	23	5.0	410	95	77	20	0.15	95	50	47
Medians					**407**	**94**	**77**			**94**	**45**	**54**
15-Jan-13	14:00	D	24	2.0	383	87	77	20	0.15	87	19	78
15-Jan-13	15:00	D	25	2.0	390	72	82	20	0.15	72	15	79
16-Jan-13	7:15	D	26	2.0	394	91	77	20	0.15	91	21	77
16-Jan-13	8:30	D	27	2.0	382	61	84	20	0.15	61	17	72
16-Jan-13	10:00	D	28	2.0	373	56	85	20	0.15	56	13	77
16-Jan-13	11:00	D	29	2.0	358	58	84	20	0.15	58	14	76
16-Jan-13	12:00	D	30	2.0	326	54	83	20	0.15	54	11	80
16-Jan-13	13:15	D	31	2.0	316	52	84	20	0.15	52	8	84
16-Jan-13	14:15	D	32	2.0	464	45	90	20	0.15	45	10	77
Medians					**382**	**58**	**84**			**58**	**14**	**77**
17-Jan-13	7:30	E	33	3.0	406	54	87	20	0.15	54	14	74
17-Jan-13	8:45	E	34	3.0	361	55	85	20	0.15	55	10	82
17-Jan-13	10:00	E	35	3.0	317	53	83	20	0.15	53	18	66
17-Jan-13	11:00	E	36	3.0	355	52	85	20	0.15	52	14	73
17-Jan-13	12:00	E	37	3.0	336	60	82	20	0.15	60	28	53
17-Jan-13	13:00	E	38	3.0	336	66	80	20	0.15	66	23	65
Medians					**346**	**55**	**84**			**55**	**16**	**70**

Experimental data of pilot plant experiment 3

Date	Time	Test ID	Sampl. No.	Flopaam 3630 S	TPH CPI Inlet	TPH CPI Outlet	η CPI	Alustar 1010 L	Drewfloc 285	TPH Flot. Inlet	TPH Flot. Outlet	η Flot.
			#	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	%
21-Jan-13	14:15	A	1	0	434	97	78	52	0.35	97	42	57
21-Jan-13	15:15	A	2	0	350	76	78	52	0.35	76	34	55
22-Jan-13	7:15	A	3	0	393	121	69	51	0.35	121	15	88
22-Jan-13	8:45	A	4	0	501	93	81	52	0.35	93	16	83
22-Jan-13	9:45	A	5	0	458	96	79	52	0.35	96	17	82
22-Jan-13	11:15	A	6	0	367	103	72	52	0.35	103	14	86
22-Jan-13	13:00	A	7	0	372	88	76	52	0.35	88	27	69
22-Jan-13	14:00	A	8	0	481	80	83	52	0.35	80	12	85
22-Jan-13	15:00	A	9	0	428	85	80	52	0.35	85	14	84
23-Jan-13	7:15	A	10	0	505	112	78	52	0.35	112	18	84
23-Jan-13	8:15	A	11	0	502	91	82	52	0.35	91	13	86
23-Jan-13	9:15	A	12	0	431	96	78	52	0.35	96	25	74
Medians					**433**	**95**	**78**			**95**	**16**	**84**
23-Jan-13	11:30	B	13	10	472	95	80	52	0.35	95	58	39
23-Jan-13	12:30	B	14	10	457	92	80	52	0.35	92	48	48
23-Jan-13	13:30	B	15	10	487	90	82	52	0.35	90	49	46
23-Jan-13	15:00	B	16	10	477	93	81	52	0.35	93	50	46
24-Jan-13	7:30	B	17	10	553	95	83	52	0.35	95	51	46
24-Jan-13	8:30	B	18	10	427	68	84	52	0.35	68	36	47
24-Jan-13	9:30	B	19	10	420	77	82	52	0.35	77	43	44
Medians					**472**	**92**	**82**			**92**	**49**	**46**
24-Jan-13	11:00	C	20	5	490	71	86	52	0.35	71	21	70
24-Jan-13	12:00	C	21	5	491	64	87	52	0.35	64	26	59
24-Jan-13	13:30	C	22	5	426	80	81	52	0.35	80	26	68
24-Jan-13	14:30	C	23	5	540	87	84	52	0.35	87	27	69
25-Jan-13	7:15	C	24	5	477	95	80	52	0.35	95	36	62
25-Jan-13	8:30	C	25	5	582	87	85	52	0.35	87	33	62
25-Jan-13	9:30	C	26	5	570	73	87	52	0.35	73	38	48
25-Jan-13	10:30	C	27	5	537	97	82	52	0.35	97	42	57

Date	Time	Test ID	Sampl. No.	Flopaam 3630 S	TPH CPI Inlet	TPH CPI Outlet	η CPI	Alustar 1010 L	Drewfloc 285	TPH Flot. Inlet	TPH Flot. Outlet	η Flot.
			#	**ppm**	**ppm**	**ppm**	**%**	**ppm**	**ppm**	**ppm**	**ppm**	**%**
Medians					**514**	**84**	**84**			**84**	**30**	**62**
28-Jan-13	13:15	D	28	2	285	24	92	53	0.35	24	17	29
28-Jan-13	15:00	D	29	2	274	20	93	52	0.35	20	18	10
29-Jan-13	7:15	D	30	0	266	45	83	53	0.35	45	29	36
29-Jan-13	9:00	D	31	0	328	38	88	52	0.35	38	42	-11
30-Jan-12	10:00	D	32	0	269	40	85	52	0.35	40	22	45
30-Jan-12	11:00	D	33	0	269	39	86	52	0.35	39	17	56
30-Jan-12	12:00	D	34	0	213	41	81	52	0.35	41	20	51
30-Jan-12	13:00	D	35	0	274	36	87	52	0.35	36	17	53
30-Jan-12	14:00	D	36	0	287	34	88	52	0.35	34	18	47
30-Jan-12	15:00	D	37	0	291	41	86	52	0.35	41	13	68
Medians					**274**	**39**	**86**			**39**	**18**	**52**
31-Jan-12	7:30	E	38	2	341	52	85	53	0.36	52	16	69
31-Jan-12	8:30	E	39	2	582	67	88	52	0.35	67	31	54
31-Jan-12	9:30	E	40	2	813	100	88	52	0.35	100	22	78
31-Jan-12	10:15	E	41	2	688	82	88	52	0.35	82	12	85
31-Jan-12	11:45	E	42	2	380	66	83	52	0.35	66	15	77
31-Jan-12	13:15	E	43	2	350	61	83	52	0.35	61	18	70
31-Jan-12	14:15	E	44	2	350	57	84	52	0.35	57	18	68
31-Jan-12	15:00	E	45	2	422	79	81	52	0.35	79	22	72
Medians					**401**	**67**	**84**			**67**	**18**	**71**

Experimental data of pilot plant experiment 4

Date	Time	Test ID	Sampl. No.	Flopaam 3630 S	TPH CPI Inlet	TPH CPI Outlet	η CPI	Floquat FL 2949	TPH Flot. Inlet	TPH Flot. Outlet	η Flot.
			#	ppm	ppm	ppm	%	ppm	ppm	ppm	%
4-Feb-13	13:30	A	1	0	317	315	1	75	315	38	88
4-Feb-13	14:00	A	2	0	316	79	75	75	79	39	51
4-Feb-13	14:30	A	3	0	360	68	81	75	68	42	38
4-Feb-13	15:15	A	4	0	322	107	67	75	107	49	54
Medians					**320**	**93**	**71**		**93**	**41**	**52**
5-Feb-13	7:15	B	5	10	262	57	78	76	57	14	75
5-Feb-13	8:15	B	6	10	227	58	74	76	58	15	74
5-Feb-13	10:30	B	7	10	223	59	74	75	59	19	68
5-Feb-13	11:30	B	8	10	305	41	87	75	41	16	61
5-Feb-13	13:00	B	9	10	274	49	82	75	49	20	59
5-Feb-13	14:00	B	10	10	258	44	83	75	44	12	73
5-Feb-13	15:00	B	11	10	296	57	81	75	57	17	70
6-Feb-13	7:30	B	12	10	406	67	83	75	67	29	57
6-Feb-13	9:00	B	13	10	381	47	88	75	47	17	64
6-Feb-13	10:00	B	14	10	427	60	86	75	60	21	65
Medians					**285**	**57**	**83**		**57**	**17**	**66**
6-Feb-13	13:15	C	15	10	392	69	82	38	69	35	49
6-Feb-13	14:00	C	16	10	424	56	87	38	56	34	39
6-Feb-13	15:00	C	17	10	484	58	88	38	58	33	43
Medians					**424**	**58**	**87**		**58**	**34**	**43**
7-Feb-13	13:00	D	18	10	405	63	84	56	63	44	30
7-Feb-13	14:00	D	19	10	954	76	92	57	76	32	58
7-Feb-13	15:00	D	20	10	547	66	88	57	66	40	39
8-Feb-13	8:00	D	21	10	388	65	83	57	65	37	43
8-Feb-13	9:00	D	22	10	383	64	83	57	64	33	48
Medians					**405**	**65**	**84**		**65**	**37**	**43**

Experimental data of pilot plant experiment 5

(Chimec 5762: 20 ppm, Chimec 5498: 0.15 ppm after CPI)

Date	Time	Test ID	Sampl. No.	Flopaam 3630 S	TPH CPI Inlet	TPH CPI Outlet	η CPI	TPH Flot. Inlet	TPH Flot. Outlet	η Flot.	TPH NSF Inlet	TPH NSF Outlet	η NSF
			#	**ppm**	**ppm**	**ppm**	**%**	**ppm**	**ppm**	**%**	**ppm**	**ppm**	**%**
19-Feb-13	13:00	A	1	0	663	71	89	71	8.8	88	8.8		
19-Feb-13	14:00	A	2	0	337	88	74	88	13	85	13		
19-Feb-13	15:00	A	3	0	314	47	85	47	9.3	80	9.3		
20-Feb-13	11:30	A	4	0	525	150	71	150	7.0	95	7.0	0.7	90
20-Feb-13	13:00	A	5	0	393	92	77	92	13	86	13	**25**	**-92**
20-Feb-13	14:00	A	6	0	400	119	70	119	7.9	93	7.9	0.9	89
20-Feb-13	15:00	A	7	0	388	105	73	105	6.9	93	6.9	0.6	91
21-Feb-13	7:15	A	8	0	291	105	64	105	21	80	21	3.3	84
21-Feb-13	9:00	A	9	0	291	72	75	72	4.5	94	4.5	1.0	78
21-Feb-13	10:30	A	10	0	337	92	73	92	7.8	92	7.8	1.1	86
21-Feb-13	11:45	A	11	0					6.8		6.8	1.5	78
21-Feb-13	13:00	A	12	0	394	103	74	103	7.6	93	7.6	1.1	86
21-Feb-13	14:00	A	13	0					9.3		9.3	1.2	87
21-Feb-13	15:00	A	14	0	406	94	77	94	7.6	92	7.6	0.9	88
Medians					**391**	**93**	**74**	**93**	**7.9**	**92**	**7.9**	**1.1**	**86**
22-Feb-13	7:00	A	15	0	805	247	69	247	14	94	14	1.1	92
22-Feb-13	9:15	A	16	0	556	334	40	334	39	88	39	2.5	94
22-Feb-13	10:30	A	17	0	542	199	63	199	10	95	10	1.2	88
22-Feb-13	11:30	A	18	0	531	174	67	174	12	93	12	2.6	78
25-Feb-13	11:00	B	19	2	423	118	72	118	17	86	17		
25-Feb-13	12:00	B	20	2	396	95	76	95	9.1	90	9.1		
25-Feb-13	14:15	B	21	2	678	117	83	117	9.1	92	9.1	1.4	85
25-Feb-13	15:00	B	22	2	1096	157	86	157	9.2	94	9.2	1.5	84
26-Feb-13	7:00	B	23	2	414	295	29	295	10	97	10	0.9	91
26-Feb-13	8:30	B	24	2	500	169	66	169	9.1	95	9.1	1.6	82
26-Feb-13	10:30	B	25	2	464	172	63	172	7.7	96	7.7	1.0	87
26-Feb-13	12:00	B	26	2	443	150	66	150	13	92	13	1.1	91
26-Feb-13	13:30	B	27	2	480	243	49	243	16	93	16	2.2	86
26-Feb-13	14:45	B	28	2					5.1		5.1	2.6	49
27-Feb-13	7:00	B	29	2	408	213	48	213	12	94	12	2.9	76
27-Feb-13	8:00	B	30	2	466	168	64	168	10	94	10	1.2	88
27-Feb-13	9:30	B	31	2	592	134	77	134	7.7	94	7.7	1.2	84
27-Feb-13	11:00	B	32	2	436	196	55	196	6.9	96	6.9	0.8	88
27-Feb-13	12:00	B	33	2	456	172	62	172	7.8	95	7.8	0.9	88
27-Feb-13	13:45	B	34	2	899	330	63	330	11	97	11	0.8	93
27-Feb-13	15:15	B	35	2					16		16	1.9	88
28-Feb-13	7:00	B	36	2					15		15	0.8	95
28-Feb-13	8:30	B	37	2	501	369	26	369	4.9	99	4.9	0.9	82
28-Feb-13	10:00	B	38	2	473	222	53	222	7.6	97	7.6	0.9	88
28-Feb-13	11:30	B	39	2	494	192	61	192	11	94	11	0.8	93
Medians					**470**	**172**	**63**	**172**	**9.2**	**94**	**9.2**	**1.1**	**88**

Date	Time	Test ID	Sampl. No.	Flopaam 3630 S	TPH CPI Inlet	TPH CPI Outlet	η CPI	TPH Flot. Inlet	TPH Flot. Outlet	η Flot.	TPH NSF Inlet	TPH NSF Outlet	η NSF
			#	ppm	ppm	ppm	%	ppm	ppm	%	ppm	ppm	%
4-Mar-13	14:30	C	40	2	485	338	30	338	7.6	98	7.6	3.5	54
4-Mar-13	15:00	C	41	2					4.2		4.2	1.5	64
5-Mar-13	7:00	C	42	2	534	154	71	154	7.9	95	7.9	0.9	89
5-Mar-13	9:00	C	43	2	579	249	57	249	9.4	96	9.4	2.4	74
5-Mar-13	10:30	C	44	2	481	118	75	118	6.4	95	6.4	1.3	80
5-Mar-13	12:00	C	45	2	541	109	80	109	5.9	95	5.9	0.6	90
5-Mar-13	13:15	C	46	2	567	128	77	128	7.3	94	7.3	0.9	88
5-Mar-13	14:15	C	47	2					6.4		6.4	0.6	91
5-Mar-13	15:15	C	48	2	447	109	76	109	11	89	11	2.7	75
6-Mar-13	7:15	C	49	2	440	218	50	218	12	94	12	2.1	83
6-Mar-13	9:00	C	50	2	802	210	74	210	11	95	11	1.9	82
Medians					**534**	**154**	**74**	**154**	**7.6**	**95**	**7.6**	**1.5**	**82**
6-Mar-13	12:15	D	51	2	445	99	78	99	6.4	94	6.4	2.3	64
6-Mar-13	13:00	D	52	2	386	96	75	96	5.1	95	5.1	1.7	67
6-Mar-13	14:00	D	53	2	426	102	76	102	6.4	94	6.4	0.9	86
6-Mar-13	15:00	D	54	2	1595	220	86	220	5.1	98	5.1	1.9	63
7-Mar-13	7:00	D	55	2	523	115	78	115	7.6	93	7.6	0.6	92
7-Mar-13	9:00	D	56	2	495	84	83	84	5.8	93	5.8	0.9	84
7-Mar-13	11:00	D	57	2	579	111	81	111	6.9	94	6.9	1.6	77
7-Mar-13	12:00	D	58	2	459	86	81	86	5.2	94	5.2	0.4	92
7-Mar-13	13:15	D	59	2					5.3		5.3	1.7	68
7-Mar-13	14:45	D	60	2	519	105	80	105	7.7	93	7.7	1.3	83
8-Mar-13	7:15	D	61	2	684	167	76	167	12	93	12	1.6	87
8-Mar-13	9:30	D	62	2	519	124	76	124	6.6	95	6.6	0.5	92
8-Mar-13	11:30	D	63	2	530	163	69	163	9.0	94	9.0	1.4	84
8-Mar-13	12:45	D	64	2					6.8		6.8	1.2	82
Medians					**519**	**108**	**78**	**108**	**6.5**	**94**	**6.5**	**1.4**	**84**
11-Mar-13	10:00	E	65	3	608	155	75	155	8.0	95	8.0		
11-Mar-13	11:30	E	66	3					6.8		6.8	1.5	78
11-Mar-13	12:30	E	67	3	474	132	72	132	6.8	95	6.8	0.8	88
11-Mar-13	13:30	E	68	3					6.4		6.4	0.9	86
11-Mar-13	14:30	E	69	3	446	121	73	121	6.5	95	6.5	1.5	77
12-Mar-13	7:00	E	70	3	483	153	68	153	16	90	16	1.5	91
12-Mar-13	8:30	E	71	3	506	176	65	176	10	94	10	1.7	83
12-Mar-13	10:00	E	72	3	413	149	64	149	5.1	97	5.1	1.4	73
12-Mar-13	11:15	E	73	3	422	135	68	135	6.4	95	6.4	1.2	81

Date	Time	Test ID	Sampl. No.	Flopaam 3630 S	TPH CPI Inlet	TPH CPI Outlet	η CPI	TPH Flot. Inlet	TPH Flot. Outlet	η Flot.	TPH NSF Inlet	TPH NSF Outlet	η NSF
			#	ppm	ppm	ppm	%	ppm	ppm	%	ppm	ppm	%
Medians					**474**	**149**	**68**	**149**	**6.8**	**95**	**6.8**	**1.5**	**82**
12-Mar-13	12:30	F	74	4					7.6		7.6	0.7	91
12-Mar-13	14:00	F	75	4	1224	216	82	216	7.3	97	7.3	1.1	85
12-Mar-13	15:00	F	76	4	501	190	62	190	8.5	96	8.5	2.7	68
13-Mar-13	7:00	F	77	4	458	215	53	215	12	95	12	3.8	68
13-Mar-13	9:00	F	78	4	2418	210	91	210	5.1	98	5.1	1.9	63
13-Mar-13	10:45	F	79	4	1854	596	68	596	8.1	99	8.1	1.2	85
13-Mar-13	12:15	F	80	4	905	308	66	308	43	86	43	3.2	93
13-Mar-13	13:30	F	81	4					23		23	3.6	84
13-Mar-13	14:45	F	82	4	536	171	68	171	14	92	14	1.3	91
14-Mar-13	7:15	F	83	4	521	404	22	404	20	95	20	2.2	89
14-Mar-13	9:00	F	84	4	537	272	49	272	5.8	98	5.8	1.4	76
14-Mar-13	10:30	F	85	4	593	219	63	219	7.2	97	7.2	0.9	88
14-Mar-13	11:45	F	86	4	573	182	68	182	5.7	97	5.7	1.2	79
14-Mar-13	13:15	F	87	4	570	236	59	236	7.4	97	7.4	1.4	81
Medians					**572**	**218**	**65**	**218**	**7.9**	**97**	**7.9**	**1.4**	**85**