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# TREATMENT OF WASTE WATER FROM WET LIME(STONE) FLUE GAS DESULFURIZATION PLANTS WITH AID OF CROSSFLOW MICROFILTRATION

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## ABSTRACT

A treatment method has been developed to remove heavy metals such as As, Cd, Cr, Cu, Hg, Ni, Pb, Se and Zn very efficiently from waste water from wet lime(stone)-gypsum flue gas desulfurization plants (FGD).
This method has been based on coprecipitation of heavy metal hydroxides and sulfides followed by crossflow microfiltration as a post-treatment. The experiments were carried out on pilot plant scale with actual waste water from a FGD plant downstream of a coal fired boiler. The effect of membrane fouling as a function of several process parameters was investigated.
From SEM-EDS analysis it was found that the fouling layer on the membrane surface mainly consists of Mg-, Al-, Si-, Fe-compounds and gypsum. Membrane fouling could be decreased by periodical backwashing and by increasing the liquid velocity in the membranes. Moreover, a computer controlled start up procedure of the crossflow microfiltration unit was developed to minimize the effect of membrane fouling and to increase the operating time before chemical cleaning of the membranes is necessary. The developed chemical cleaning was found to be very successful, because it was possible to achieve the initial permeate flux after each experiment.

## INTRODUCTION

In Europe most of the flue gas desulfurization processes (FGD) installed downstream of coal fired boilers are wet lime(stone)-gypsum processes. These processes produce a gypsum of high quality which can be used for wall board production etc.
A waste water stream is coming from these wet FGD plants to remove impurities from the process such as dissolved salts (mainly chlorides of calcium, sodium and magnesium) and suspended solids (hydroxides of iron and aluminium, silica and fine gypsum).
Moreover, traces of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se and Zn) are present in the waste water. Most of these heavy metals are originally present in the lime or limestone used for desulfurization. Before discharging this waste water most of the heavy metals must be removed. The target values of heavy metals in the discharged waste water stated by the Dutch authorities are given in Table 1.

Table 1. Target values for emission of heavy metals and suspended solids in FGD waste water

| | $mg/m^3$ |
|---|---|
| As | 20 |
| Cd | 1 |
| Cr | 15 |
| Cu | 10 |
| Hg | 1 |
| Ni | 15 |
| Pb | 50 |
| Zn | 50 |
| | $g/m^3$ |
| suspended solids | 30 |

A few years ago N.V. KEMA developed a process to remove these heavy metals very efficiently. The process has been based on coprecipitation of hydroxides and sulfides of heavy metals followed by a coagulation/ flocculation technique. The flocs were separated from the waste water by gravity settling in a clarifier. The overflow of the clarifier was finally filtered in a sand filter to remove rests of suspended solids (1). In the present paper the application of crossflow microfiltration as a post-treatment to remove coprecipitated hydroxides and sulfides of heavy metals from FGD waste water was investigated. The experiments were carried out on pilot plant scale with actual waste water coming from a limestone-gypsum FGD plant installed downstream of a coal fired boiler.

## CROSSFLOW MICROFILTRATION

Crossflow microfiltration (CMF) is a modern pressure driven membrane process for the separation of suspended solids from liquids. A problem, however, with CMF is the phenomena of concentration polarization. Concentration polarization means that the concentration of retained particles or molecules is higher at the membrane surface than in the bulk of the feed stream.

According to a new model for CMF based on the filtration theory (2) an equation can be derived for the permeate flux as a function of several process parameters. Equation (A) predicts this permeate flux under turbulent flow conditions:

$$J = \frac{K \times \Delta P_{dr} \times (\rho_p - c_s) \times \rho_{fl}}{r_p \times c_s} \times \frac{v}{\eta_{fl}} \qquad (A)$$

From this equation it can be seen that an increase in fluid velocity in the tubular membrane gives an increase of the permeate flux. This is due to the fact that higher fluid velocities generate higher shear forces on the membrane surface. This results in thinner layers of deposits on the membrane surface. However, a higher fluid velocity implies a higher pressure drop over the membrane tube and therefore the energy consumption will increase. It is also clear from this equation that the transmembrane pressure difference (driving force) influences the permeate flux. Moreover, the thickness of a layer of deposits on the membrane surface will increase with increasing transmembrane pressure difference.

Summarizing, it can be concluded from the model that membrane fouling decreases by applying low transmembrane pressure differences and high fluid velocities. Another possibility to minimize the effect of membrane fouling on the permeate flux is periodical backwashing of the membranes, for example with permeate in the opposite direction to the permeate flux. In this way the layer of deposits on the membrane surface may be removed. The deposits can then be flushed away by the feed stream. However, despite all the measures mentioned above the permeate flux can decrease to unacceptable low values. In that case a chemical cleaning of the membranes should be applied, which depends on the kind of deposits on the membrane surface.

## DESCRIPTION OF PILOT PLANTS

The pilot plant for the coprecipitation/coagulation/flocculation is schematically presented in Figure 1 and has a capacity of 0.05 $m^3/h$.

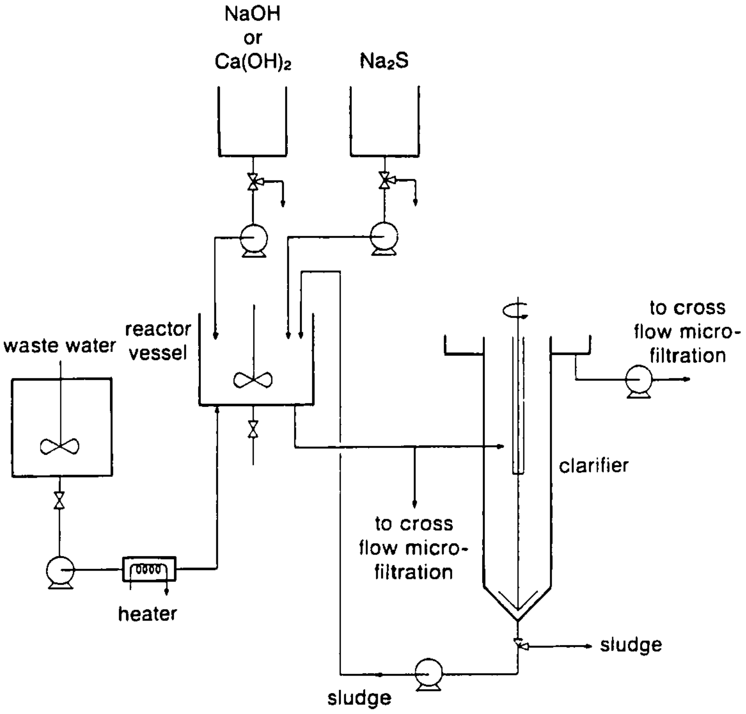

Figure 1. Pilot plant for pretreatment of waste water (capacity: 0.05 $m^3/h$)

Waste water entered the reactor with a temperature of about 50 °C and with a pH of 5 - 6. In the reactor, solutions of sodium hydroxide and sodium sulfide were added simultaneously to the waste water. The pH of the waste water was raised to about 9.5. At these pH values hydroxides and sulfides of heavy metals and hydroxides of iron and aluminium were precipitated. The residence time in the reactor amounted to 30 minutes. The waste water coming from the reactor entered the clarifier where the main part of the flocs were separated from the waste water by gravity settling. The upward linear velocity in the clarifier amounted to 0.7 m/h. Thickened sludge was collected in the bottom of the clarifier and was partially recycled (0.025 $m^3/h$) to the reactor to improve the settling characteristics of the flocs. The remaining part of the sludge was removed and can be dewatered with a filter press. During the experiments no flocculant aid (poly electrolyte) was added because it is known from earlier experiments that these substances gave a tremendous membrane fouling (3).

Lime can also be used as alkalizing agent instead of sodium hydroxide. If lime is used gypsum will be formed during the alkalizing step as the waste water has been saturated with gypsum. The production of gypsum results in more compact flocs with better settling characteristics and a higher solid content. More details of the coprecipitation/coagulation/flocculation pilot plant have been published elsewhere (1).

A part of the waste water coming from the overflow of the clarifier was sent to the supply vessel of the CMF pilot plant (see Figure 2).

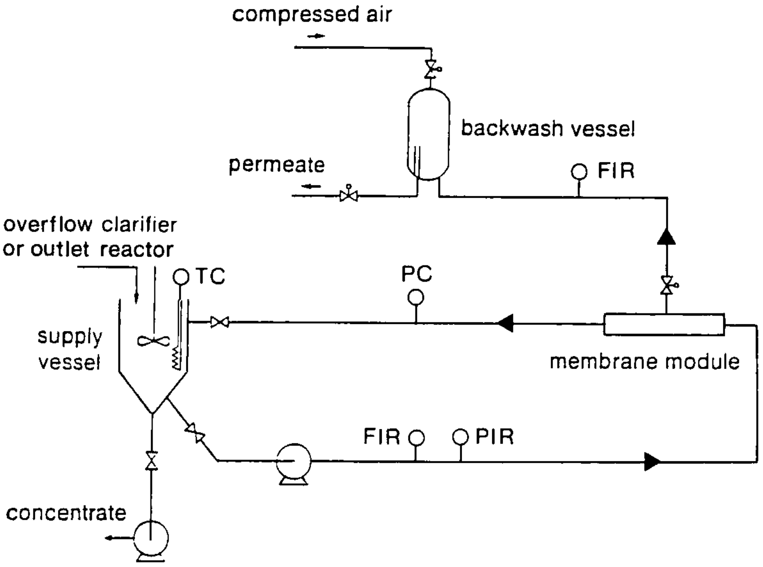

Figure 2. Pilot plant CMF

The liquid level in the supply vessel was kept constant by means of a level controller. The temperature of the waste water was controlled on 40 $^0C$ in all experiments. The waste water was led to a membrane module (ENKA-Microdyn filter module: MD 020 TP 2N). The specifications of the module are given in Table 2.

Table 2. Membrane specifications (ENKA-Microdyn filter module: MD 020 TP 2N)

| | |
|---|---|
| membrane material | polypropylene |
| length of module | 0.75 m |
| number of tubes per module | 3 |
| inner diameter of tube | $5.5\times10^{-3}$ m |
| membrane area | $3.6\times10^{-2}$ $m^2$ |
| normal pore size | $2\times10^{-7}$ m |
| maximum temperature | 60 °C |
| maximum driving force at 25 °C | $3.0\times10^5$ $N/m^2$ |
| maximum driving force at 60 °C | $2.0\times10^5$ $N/m^2$ |
| maximum backwash pressure at 25 °C | $2.0\times10^5$ $N/m^2$ |
| maximum backwash pressure at 60 °C | $1.0\times10^5$ $N/m^2$ |
| pH | 1 - 14 |

The permeate leaving the membrane was discharged via a backwash vessel. The concentrate leaving the membrane was recycled to the supply vessel. It was possible to backwash the membranes with permeate collected in the backwash vessel by compressed air. The adjustment and control of the transmembrane pressure difference, permeate flux, backwash interval and backwash time was done by a process computer.

The effect of process variables, such as fluid velocity, backwash interval, transmembrane pressure difference etc., on the permeate flux (membrane fouling) were studied in a mode where both the permeate flux and the concentrate flow were recycled to the supply vessel (closed loop). This means that there was no change in suspended solid concentration.

The long term experiment was carried out in a mode where the permeate flux was discharged via the backwash vessel. The liquid level in the supply vessel was kept constant by supplying water from the overflow from the clarifier. The suspended solid concentration in the supply vessel increased during the experiment because no concentrate was removed from this vessel.

## ANALYSIS OF HEAVY METALS

Samples were acidified to pH = 2 with nitric acid (supra pur) to dissolve colloidally dispersed sulfides and hydroxides of heavy metals. Concentrations of the heavy metals were determined with atomic absorption spectroscopy and inductively coupled plasma.

## RESULTS

All experiments were carried out with actual waste water from a limestone-gypsum FGD plant downstream of a coal fired boiler. The composition of the waste water is given in Table 3.

Table 3. Composition of waste water from a wet limestone-gypsum FGD plant

| component | composition of filtrate |
|---|---|
| pH | 6.0 |
| suspended solids | 154 $g/m^3$ |
| Cl | 2600 $g/m^3$ |
| $SO_4$ | 1250 $g/m^3$ |
| Ca | 1600 $g/m^3$ |
| Na | 150 $g/m^3$ |
| Mg | 160 $g/m^3$ |
| Al | 1 $g/m^3$ |
| F | 11 $g/m^3$ |
| As | 18 $mg/m^3$ |
| Cd | 6 $mg/m^3$ |
| Cr | 27 $mg/m^3$ |
| Cu | 36 $mg/m^3$ |
| Hg | 6 $mg/m^3$ |
| Ni | 84 $mg/m^3$ |
| Pb | 125 $mg/m^3$ |
| Se | 551 $mg/m^3$ |
| Zn | 316 $mg/m^3$ |

The waste water was first treated in the coprecipitation/coagulation/flocculation pilot plant. For the experiments where the influence of fluid velocity, backwashing, transmembrane pressure difference and suspended solids on the permeate flux were investigated, sodium hydroxide was used as alkalizing agent. The overflow of the clarifier was sent to the CMF. After each experiment the membranes were cleaned completely by a developed chemical cleaning method described later.

### Influence of fluid velocity on the permeate flux

The influence of the fluid velocity in the tubular membrane on the permeate flux was investigated at a transmembrane pressure difference of $1 \times 10^5$ $N/m^2$ and at a solid content in the supply vessel of 1.76 $kg/m^3$. The membranes were not backwashed during these experiments. The permeate flux as a function of the operating time for different fluid velocities is given in Figure 3.

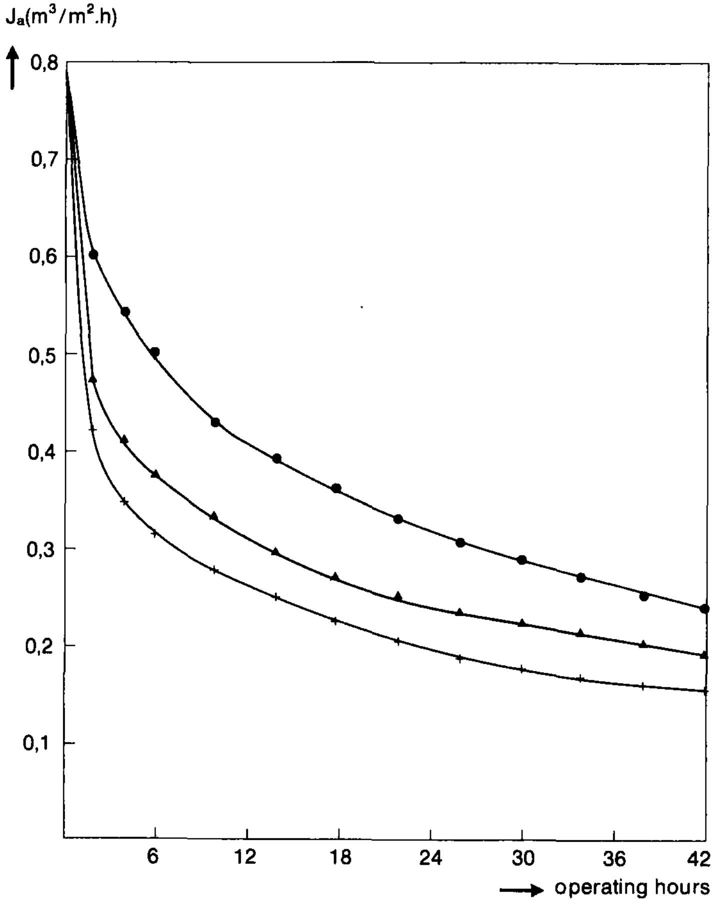

Figure 3. Influence of fluid velocity on the permeate flux (conditions: $\Delta P_{dr} = 1\times10^5$ N/m$^2$, temperature = 40 $^0$C, suspended solids = 1.76 kg/m$^3$, no backwashing)
+ v = 1 m/s
▲ v = 2 m/s
● v = 3 m/s

From this figure it can be concluded that a higher fluid velocity results in a higher permeate flux.

The permeate flux at an operating time of 42 hours is plotted as a function of the fluid velocity in the tubular membrane (see Figure 4). According to the model proposed by Schulz et al (2) there must be a linear relationship between the permeate flux and the fluid velocity in the turbulent flow regime which occurs at Re > 2320 (4). From Figure 4 it can be seen that our measurements can be explained by the proposed model.

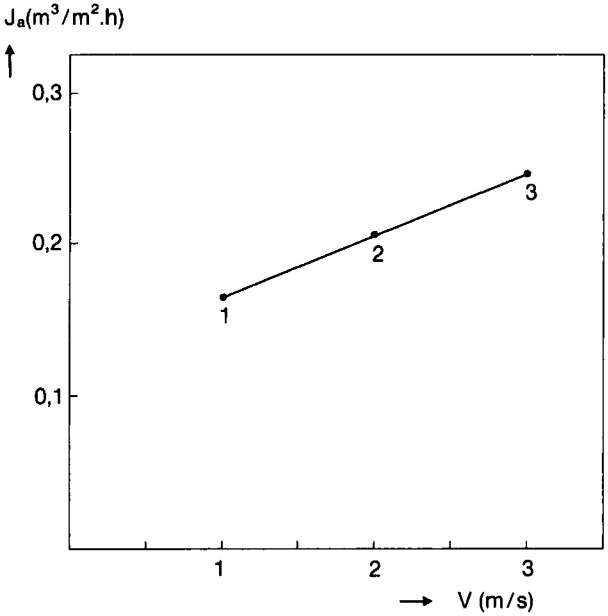

Figure 4. Relationship between the fluid velocity and the permeate flux (conditions: $\Delta P_{dr} = 1\times10^5$ N/m$^2$, temperature = 40 $^0$C, suspended solids = 1.76 kg/m$^3$, no backwashing)
1 Re = 7672
2 Re = 15344
3 Re = 23016

## Influence of backwashing on the permeate flux

The influence of backwashing on the permeate flux was investigated at a constant transmembrane pressure difference of $1\times10^5$ N/m$^2$ and at a fluid velocity in the membrane tube of 2 m/s (Re = 15344). The solid content in the supply vessel was 1.76 kg/m$^3$ during all experiments. The backwash time was adjusted on 3 seconds. The volume of permeate needed for backwashing during this time was 0.014 $m^3/m^2$ membrane surface. The influence of the backwash interval on the permeate flux is shown in Figure 5. From this figure it can be concluded that backwashing has a positive influence on the permeate flux.

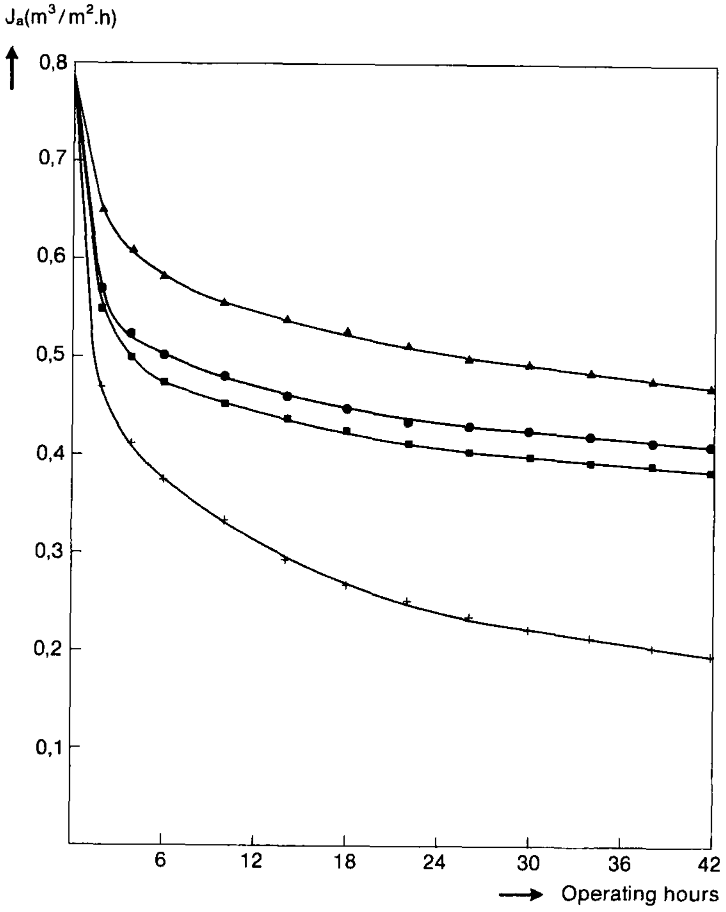

Figure 5. Influence of backwashing on the permeate flux (conditions: $\Delta P_{dr_0} = 1\times10^5$ $N/m^2$, v = 2 m/s, temperature = 40 °C, suspended solids = 1.76 $kg/m^3$, backwash time = 3 seconds, $\Delta P_{bw} = 1.5\times10^5$ $N/m^2$)
+ no backwashing
■ backwash interval of 9 minutes
● backwash interval of 3 minutes
▲ backwash interval of 1 minute

## Influence of the transmembrane pressure difference on the permeate flux

The influence of the transmembrane pressure difference on the permeate flux was investigated at a constant fluid velocity of 2 m/s (Re = 15344) and a solid content in the supply vessel of 1.76 kg/m$^3$. The backwash time and the backwash interval was during all experiments 3 seconds and 1 minute respectively. The permeate flux was determined after an operating time of 42 hours. The relative permeate flux, defined as the ratio between the actual permeate flux after 42 operating hours ($J_a$) and the initial permeate flux ($J_i$), is plotted as a function of the transmembrane pressure difference (see Figure 6).

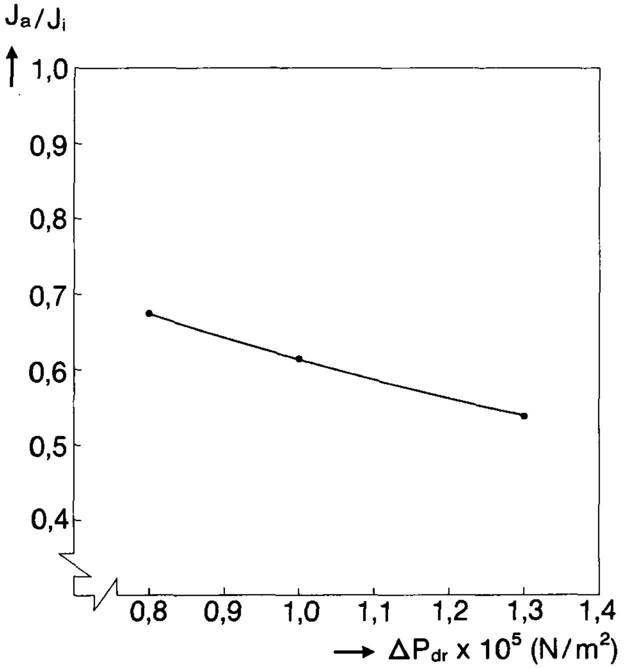

Figure 6. Influence of transmembrane pressure difference ($\Delta P_{dr}$) on the permeate flux (conditions: v = 2 m/s, temperature = 40 $^0$C, suspended solids = 1.76 kg/m$^3$, backwash interval = 1 minute, backwash time = 3 seconds, $\Delta P_{bw}$ = 1.5×10$^5$ N/m$^2$)

From this figure it can be concluded that the relative permeate flux decreases with increasing transmembrane pressure difference. This implies that crossflow microfiltration should be operated at the lowest possible transmembrane pressure difference to minimize the effect of membrane fouling.

### Effect of suspended solid content in the supply vessel on the permeate flux

The effect of the suspended solid content in the supply vessel on the permeate flux was investigated at a constant fluid velocity of 2 m/s and at a constant transmembrane pressure difference of $1\times10^5$ $N/m^2$. The backwash time and backwash interval were adjusted on 3 seconds and 1 minute respectively. The suspended solid content in the supply vessel was varied from 0.5 up to 25 $kg/m^3$. From the experiments it can be concluded that the suspended solid content in the supply vessel did not influence the permeate flux. This implies that waste water coming from the reactor where the coprecipitation takes place can be sent directly to the CMF plant. The clarifier can be omitted in this way. These results will be published in the near future (5).

### Long term experiment

The long term experiment was carried out with the waste water of which the composition is given in Table 3. The waste water (flow: 0.050 $m^3/h$) entered the reactor of the coprecipitation/coagulation/flocculation plant. Samples were taken from the raw waste water, effluent from the clarifier and sludge from the clarifier after stationary state was obtained. If sodium hydroxide was used as alkalizing agent it appeared that the suspended solid content in the sludge from the clarifier was about 1.5% by weight. The volume of thickened sludge removed from the clarifier was 0.383 $m^3/m^3$ influent waste water. In practice this means that the filter press for dewatering of the thickened sludge may be too high loaded. Poly electrolyte can not be added to increase the solid content in the thickened sludge and to lower the volume of thickened sludge. It was found that the presence of poly electrolyte in the waste water gave a tremendous membrane fouling. A possibility to produce more compact flocs is the use of lime instead of sodium hydroxide as alkalizing agent. Therefore, some experiments were carried out with lime as alkalizing agent after the long term experiment. If lime is added to the waste water, gypsum will be formed as the waste water has been saturated with gypsum. The precipitation of gypsum produces more compact flocs resulting in a lower volume of thickened sludge (0.15 $m^3/m^3$ influent waste water) with a higher solid content (5% by weight). This thickened sludge can be dewatered in a filter press. In this case it can be concluded that the use of lime as alkalizing agent is more preferable than sodium hydroxide. The solid content in the overflow of the clarifier was in both cases about 10 - 40 g/m$^3$. A part of the overflow from the clarifier was sent to the CMF installation as a post-treatment step. The operating conditions for the CMF installation were adjusted to minimize the effect of membrane fouling on the permeate flux. These operating conditions which approach a practical situation are listed in Table 4 and are based on previous experiments.

Table 4. Operating conditions approaching a practical situation for the CMF installation during the long term experiment

| | |
|---|---|
| temperature | 40 $^0$C |
| fluid velocity | 2.5 m/s |
| backwash interval | 3 minutes |
| backwash time | 3 seconds |
| permeate flux | 0.15 m$^3$/m$^2$h |

A problem is that the permeate flux decreases with operating time due to membrane fouling. It was stated that a minimum permeate flux of 0.15 m$^3$/m$^2$h was required (see Table 4). A computer controlled start up procedure of the CMF pilot plant was developed to minimize membrane fouling. This procedure operates in the following way:

- the CMF pilot plant was started at the lowest possible transmembrane pressure difference to obtain a permeate flux of 0.15 m$^3$/m$^2$h
- if the permeate flux became less than the minimum permeate flux, the transmembrane pressure difference was stepped up with 0.1 - 0.2×10$^5$ N/m$^2$ by the process computer
- if the transmembrane pressure difference became higher than the maximum allowed transmembrane pressure difference the pilot plant was shut down and then the membranes should be chemically cleaned.

In Figure 7 the transmembrane pressure difference ($\Delta P_{dr}$) is plotted as a function of the operating time. This figure holds for sodium hydroxide as alkalizing agent. From this figure it can be seen that the experiment started at a $\Delta P_{dr}$ of 0.55×10$^5$ N/m$^2$ and was ended after 1008 operating hours at an $\Delta P_{dr}$ of $1.05\times10^5$ N/$m^2$. As the transmembrane pressure difference can have a maximum value of about $2.5\times10^5$ N/$m^2$ considerable operating times can be expected before chemical cleaning is necessary.

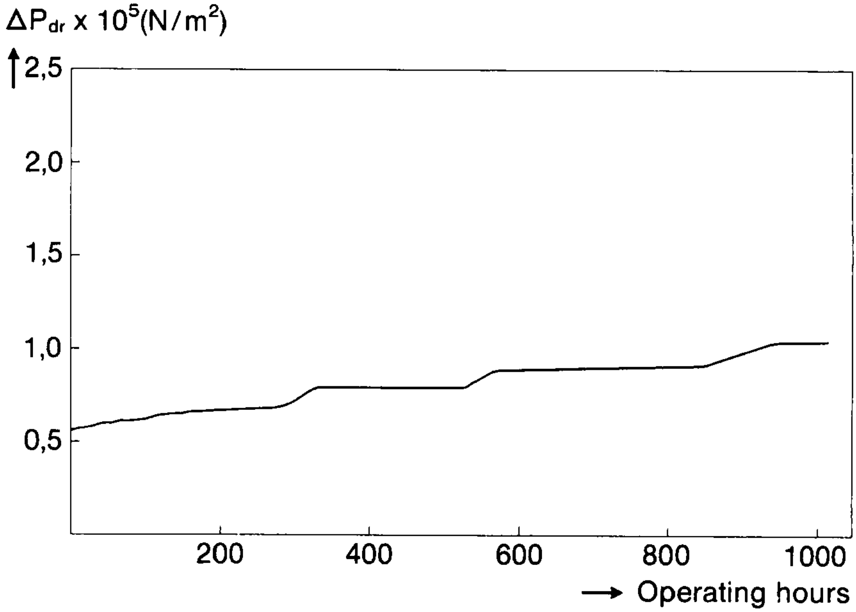

Figure 7. Long term experiment (conditions: suspended solids = 10 - 600 g/$m^3$, $\Delta P_{bw}$ = $1.5\times10^5$ N/$m^2$, further see Table 4)

If lime is used as alkalizing agent similar operating times can be expected because the same compounds are found in the overflow from the clarifier. After about 300 operating hours samples were taken to analyse the concentrations of the heavy metals in the effluent of the clarifier and the permeate. The results of these analysis and the dosages of chemicals are listed in Table 5. It can be concluded from this table that the concentrations of heavy metals in the permeate are lower than the concentrations in the overflow of the clarifier. This can be explained by the fact that the concentration of suspended solids, which contain heavy metals, is lower in the permeate than in the overflow of the clarifier. An experiment with lime as alkalizing agent gave the same concentrations of heavy metals in the permeate as is listed in Table 5. It can be concluded from this table that the permeate meets the target values with respect to the heavy metals and the suspended solids stated by the Dutch authorities.

Table 5. Analysis results of heavy metals and suspended solids in different water streams
Dosages: NaOH 1800 g/m$^3$ waste water
or
$Ca(OH)_2$ 2500 g/m$^3$ waste water
$Na_2S.9H_2O$ 8 g/m$^3$ waste water

| | raw waste water | effluent of clarifier | permeate |
|---|---|---|---|
| pH | 6.0 | 9.6 | 9.6 |
| | mg/m$^3$ | mg/m$^3$ | mg/m$^3$ |
| As | 18 | 5 | 4 |
| Cd | 6 | 0.5 | 0.5 |
| Cr | 27 | 7 | < 0.3 |
| Cu | 36 | 19 | 2 |
| Hg | 6 | < 1 | < 1 |
| Ni | 84 | 19 | 3 |
| Pb | 125 | 15 | < 3 |
| Se | 551 | 123 | 80 |
| Zn | 316 | 46 | <20 |
| | g/m$^3$ | g/m$^3$ | g/m$^3$ |
| suspended solids | 154 | 38 | < 1 |

After this long term experiment the membrane module was disassembled to look at the membrane fouling with Scanning Electron Microscopy (SEM) - Energy Dispersive Spectroscopy (EDS). In figure 8 this fouling layer can be seen. The fouling layer has a thickness of about $3\times10^{-4}$ m.

In Figure 9 an EDS spectrum of this fouling layer is presented. It can be concluded that the most occuring elements in the fouling layer were compounds containing Mg-Al-Si-Fe and gypsum. With lime as alkalizing agent the same compounds were found in the fouling layer.

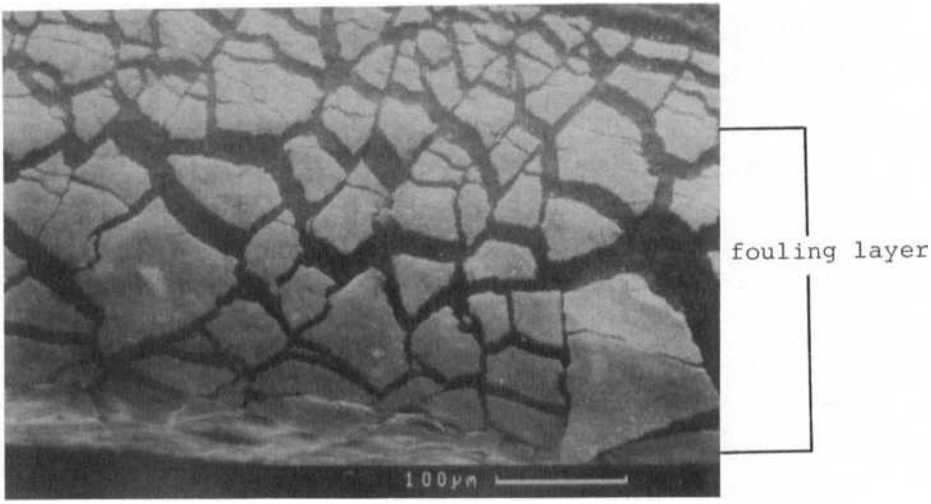

Figure 8. SEM picture of fouling layer at the membrane surface (cross section)

## CHEMICAL CLEANING

The developed chemical cleaning was found to be very successful because it was possible to achieve the initial permeate flux after each experiment. This chemical cleaning was always carried out from two sides. First, the cleaning solution was pumped through the tubular membranes to dissolve the fouling layer on the membrane surface. After this, the membranes were cleaned from the permeate side by filling the backwash vessel with the chemical cleaning solution. In this way the chemical cleaning solution slowly penetrates into the pores of the membranes. The whole operation of chemical cleaning takes about 20 hours in time. It was found that a 5% by weight HCl solution cleaned the membranes totally and the initial permeate flux was obtained after each experiment. This means that the developed chemical cleaning was a reproducible process.

## CONCLUSIONS

The removal of heavy metals and suspended solids from waste water of wet lime(stone)-gypsum FGD processes was investigated on pilot plant scale. The method is based on a coprecipitation/coagulation/flocculation technique followed by gravity settling of the flocs and crossflow microfiltration as post-treatment.

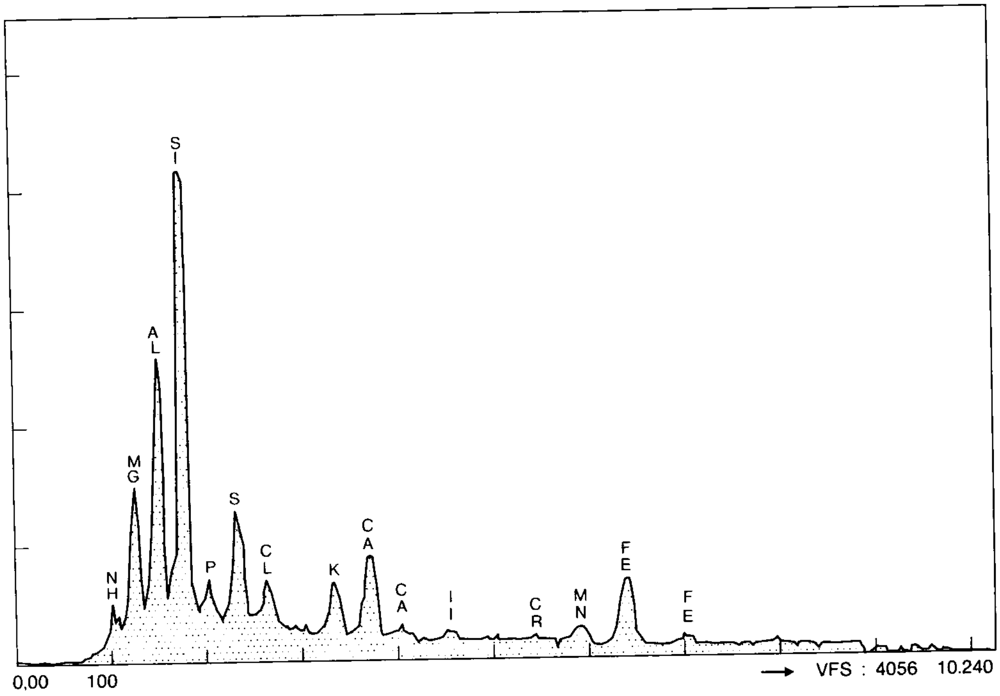

Figure 9. EDS spectrum of fouling layer (cross section)

It can be concluded that the use of sodium hydroxide as alkalizing agent will give large volumes of settled flocs with a low solid content. The volume of settled flocs can be strongly reduced by applying lime as alkalizing agent. From the experimental results it can be concluded that heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se and Zn) can be removed very efficiently. The effect of membrane fouling, which is a serious problem, could be decreased by:

- a higher fluid velocity in the tubular membrane
- a lower transmembrane pressure difference
- frequent backwashing of the membranes.

Based on these findings a computer controlled start up procedure was developed to minimize the effect of membrane fouling and to increase the operating time before chemical cleaning of the membranes is necessary. From a long term experiment it can be concluded that in this way operating hours are possible which exceed 1000 hours.

The composition of the fouling layer was investigated by means of SEM-EDS and it was found that the fouling layer contained compounds of Mg, Al, Si, Fe and gypsum.

With the proposed chemical cleaning method for the membranes it was possible to achieve the initial permeate flux after each experiment.

## LIST OF SYMBOLS

| | | |
|---|---|---|
| $c_s$ | concentration of material in the bulk stream | $kg/m^3$ |
| $J$ | permeate flux | $m/s$ |
| $J_a$ | actual permeate flux | $m^3/m^2h$ |
| $J_i$ | initial permeate flux | $m^3/m^2h$ |
| $K$ | dimensionless constant | - |
| $\Delta P_{bw}$ | backwash pressure | $N/m^2$ |
| $\Delta P_{dr}$ | transmembrane pressure difference (driving force) | $N/m^2$ |
| Re | Reynolds number | - |
| $r_p$ | specific hydraulic resistance of the fouling layer | $m^{-2}$ |
| $v$ | fluid velocity | $m/s$ |
| $\rho_{fl}$ | density of fluid | $kg/m^3$ |
| $\rho_p$ | density of the retained material | $kg/m^3$ |
| $\eta_{fl}$ | dynamic viscosity of fluid | $Ns/m^2$ |

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