WATER REUSE AND WASTE WATER MINIMISATION IN THE AUTOMOTIVE INDUSTRY: REVERSE OSMOSIS IN THE PHOSPHATING PROCESS

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ABSTRACT

One of the most important bottlenecks in surface treatment is undoubtedly the emission of heavy metals in the waste water flow. The industrial waste water is mostly treated in a physicochemical way by the precipitation of the heavy metals as the hydroxide through the addition of a base to a pH of minimum solubility. This is resulting in a high consumption of chemicals and an important quantity of waste sludge.

In the last few years, a lot of research was done to introduce new production techniques with less environmental impact. At Gent, Volvo Cars NV, in co-operation with the environmental engineering company Trevi NV, has developed a process to close the loop in the phosphate area of their pre-treatment line. After comprehensive research on pilot scale a reverse osmosis unit in two steps was implemented in the production line. The permeate is reused as rinsing water in the rinsing steps while the concentrate is (partly) recycled to the process bath.

The introduction of the reverse osmosis installation has resulted in a significant decrease of the water consumption, the related waste water production and the amount of waste sludge. As far as known, it is the first closed loop phosphate line world-wide using this technique with success.

MOTIVATION OF THE PROJECT

Description of the phosphating process

After the car body has been assembled in the welding shop, anti-corrosion operations prepare the body for the painting process. This is executed in the so-called pre-treatment line.

Initially the body is sprayed with and immersed in a cleaning agent, typically consisting of detergents, to remove residual oils and dirt. The body is then dipped into a phosphate bath, typically zinc phosphate, to prevent corrosion. The phosphate process also improves the adhesion of the primer to the metal. The body is finally rinsed with a passivation product (previously chromic acid, nowadays mostly chromium free products) further enhancing the anti-corrosion properties to the zinc phosphate coating.

In Europe, such a pre-treatment line is mostly build up as follows:

- degreasing baths;
- rinsing baths in cascade;
- activation bath;
- phosphate bath;
- rinsing baths in cascade;
- passivation bath;
- rinsing bath;
- drying.

Due to the carry-over of the process chemicals from the process baths to the rinsing steps, rinsing baths are contaminating a lot. A continuously water supply is necessary to keep the water quality in the rinsing baths acceptable, resulting in a continuous overflow to the waste water treatment plant. To reduce the amount of waste water to an absolute minimum, it is mostly useful to rinse in cascades.

The required water supply is depending on the number of cascades, the quantity of carry-over and the desired degree of dilution. For calculation of the required water supply next formula is used:

$$\boxed{Q = V \sqrt[n]{T}}$$

with Q : required water supply
V : carry-over losses
T : degree of dilution
N : number of cascades

Supposing a carry-over of 10 litres per car body and a desired degree of dilution of 1 to 150, the required water supply for rinsing in a two-steps cascade can be calculated on 122 litres per body. For a production rate of 45 bodies per hour, a continuously water supply of approximately 5,5 m³/h is needed.

Introduction of aluminium

Nowadays car bodies are mostly build up from different substrates which have to be treated simultaneously in the pre-treatment line. In the investigation for weight reduction, the last few years more and more new (light) materials were introduced to reduce the fuel consumption.

In literature, there is a lot published about magnesium and plastic materials, but at this moment a lot of attention is given to aluminium. This is resulting in a decreasing trend in the consumption of cold rolled steel and an increasing use of aluminium.

It should be noticed that especially for the zinc containing aluminium special attention is required because aluminium can poison the phosphate bath. This makes the addition of free fluoride in the phosphate bath necessary to bind the aluminium complex and to make it harmless.

Composition of the phosphate bath.

The new Volvo models S60 and V70 are containing aluminium parts, so also Volvo Cars Gent is dosing a fluoride containing product in the phosphate bath to keep the free fluoride content in the bath sufficient high.

The composition of the phosphate bath at Volvo Cars Gent is given in table 1.

Table 1. *Composition of the phosphate bath at Volvo Cars Gent*

Parameter	Unit	Concentration
pH	-	3,6
Conductivity	µS/cm	19150
Zinc	mg Zn/l	1450
Nickel	mg Ni/l	640
Manganese	mg Mn/l	705
Total phosphate	mg P/l	5920
Nitrate	mg N/l	1510
Ammonium	mg N/l	218
Free fluoride	mg F/l	200
Total fluoride	mg F/l	1784
Sodium	mg Na/l	4750

Removal of fluoride in the waste water treatment plant

The introduction of aluminium has resulted in a higher concentration of fluoride in the industrial waste water. To keep the concentration below the discharge standard of 15 mg/l, a product based on poly-aluminium-chloride (PAC) is dosed in the physico-chemical waste water treatment plant.

Tests on laboratory scale have shown that the fluoride removal is much more efficient for influents with a relatively high concentration of fluoride. For lower concentrations of fluoride there has to be added a lot more product to remove the same load of fluoride.

The efficiency of the PAC dosage in function of the concentration of fluoride is shown in figure 1.

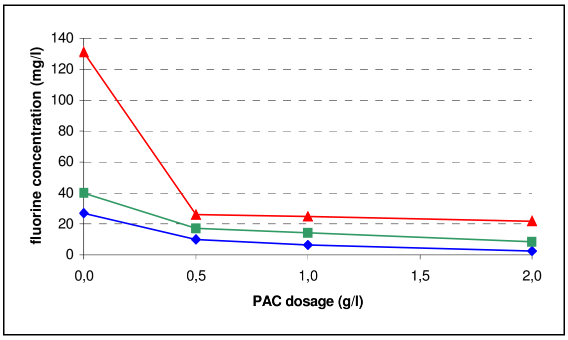

Figure 1. *Efficiency PAC dosage in function of initial fluoride concentration*

Closed loop phosphating with reverse osmosis

In order to reduce the consumption of PAC in the physico-chemical waste water treatment plant, a study was started to reduce the amount of industrial waste water and to increase the concentration of fluoride in the influent flow.

After some preliminary study at laboratory scale, pilot tests were started with reverse osmosis on the rinsing water of the phosphating process. In addition to the lower PAC dosage in the waste water treatment plant, permeate of the installation could probably be reused as rinsing water and concentrate could eventually be recycled to the phosphate bath.

A principle flow diagram of the closed loop system is given in figure 2.

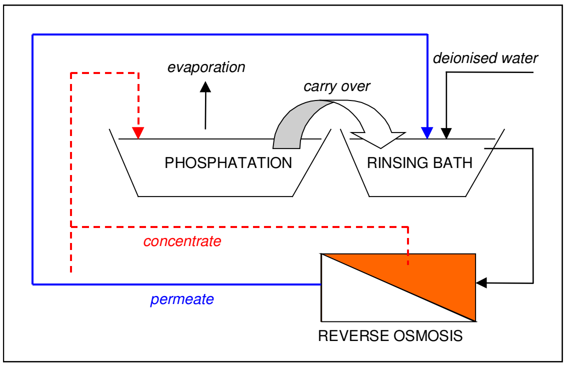

Figure 2. *Principle flow diagram closed loop phosphating with reverse osmosis*

The prospective advantages of a closed loop system with reverse osmosis can be summarised as follows :

- a higher concentration of fluoride in the concentrate, drained to the waste water treatment plant, will result in a higher efficiency of the PAC dosage and consequently a lower consumption;
- the reuse of permeate as rinsing water will result in a lower water consumption and a decrease of the amount of industrial waste water;

- the reuse of concentrate as compensation for the evaporation losses in the phosphate bath will reduce the discharged load of heavy metals (zinc, nickel, manganese,…), phosphate, nitrate and fluoride to the waste water treatment plant, resulting in a significant decrease of chemical consumption and waste sludge production;
- by recycling a part of the concentrate to the phosphate bath itself, the consumption of process chemicals will also decrease.

Parcom recommendation

The convention for the protection of the marine environment of the north-east Atlantic (OSPAR Convention) was signed on 22 September 1992. The convention has been signed and ratified by all of the contracting parties to the Oslo and Paris conventions.

The Parcom Recommendation 92/4 on the reduction of emissions of the electroplating industry should apply primarily to plants in which surfaces are plated with metals chemically or electrolytically. This involves main operations as degreasing and phosphating.

Parcom is recommending the Best Available Technologies (BAT's), including the membrane techniques, to extend lifetime of process baths and to reuse rinsing water as much as possible. Besides, it is written that if possible, concentrate has to be recycled to obtain a complete closed loop.

PILOT TESTS WITH REVERSE OSMOSIS

Principle of reverse osmosis

Reverse osmosis can be explained by considering the normal osmosis process. Figure 3 shows a tank, divided in two compartments by a semipermeable membrane. When there is a salt solution on one side of the membrane and freshwater on the other side, the level in the compartment of the salt solution will rise. This phenomena is caused by the osmotic pressure created by the transport of water from the freshwater compartment through the membrane to the salt solution.

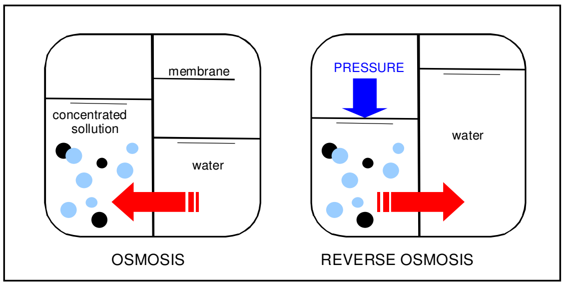

Figure 3. *Osmosis and reverse osmosis*

If a pressure in excess to the osmotic pressure is now applied to the salt solution chamber, water from the salt solution will diffuse through the membrane. The result of this "reverse osmosis" is a concentrated salt solution on one side of the membrane and a pure (desalt) water on the other side.

Membrane characteristics

The membrane used in the pilot tests, Filmtec TW30-4040, is a spiral wound thin-film composite polyamide membrane from the company Dow. The membrane can be used within a pH-range from 2 to 11. For chemical cleaning of the membranes, a pH-range from 1 to 12 can be allowed during a short time. The maximum operating temperature is 45 °C.

Pilot tests with one-step reverse osmosis

Description of the pilot plant

The pilot plant was build up by using two containers, respectively a phosphate bath filled with phosphate liquid from the process line and a rinsing bath filled with deionised water. Carry-over losses where simulated by means of a metering pump.

Water from the rinsing bath was pumped through two successive microfilters, respectively 10 µm and 1 µm, towards the reverse osmosis plant. The permeate was recycled to the rinsing bath; the concentrate was discharged to the waste water treatment plant. The pilot plant was equipped with a heating device and a pH electrode for the steering of the dosage of sodium hydroxide in order to check the influence of the temperature and the pH-value on the process.

By means of a regulation valve, steered in function of the level in the rinsing tank, deionised water was supplied to compensate the drain of concentrate to the waste water treatment plant and to guarantee a constant level in the rinsing bath. The recovery was adjusted to 75%. In other words, for a feed flow of 1000 l/h, 250 l/h concentrate was drained as waste water and 750 l/h permeate was recycled as rinsing water.

Results of the pilot tests.

In the first instance, some explanatory tests were executed to check the influence of the pH-value on the filtration process. As shown in figure 4, fluoride removal as well as membrane fouling were both strongly pH-dependent.

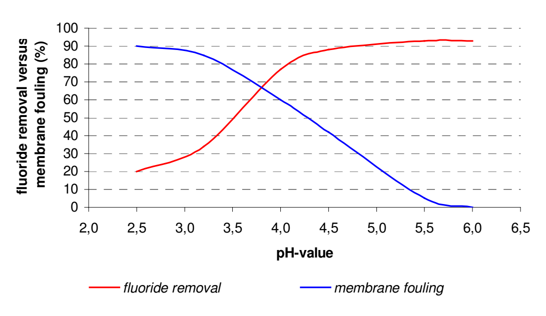

Figure 4. *Influence of pH-value on fluoride removal and membrane fouling*

At low pH-values, all heavy metals present in the waste water, are kept in solution and no metal hydroxides are formed. This is resulting in a long cycle time but in a low retention for fluoride.

At high pH-values, the retention of fluoride is much better but, due to the formation of metal hydroxides, a very short cycle time is obtained. Membranes should be cleaned very often, resulting in a short lifetime and a high running cost for cleaning and replacement of the membranes.

Best results were achieved at pH 4,0. At this pH-value the retention for fluoride was about 80% and the average cycle time about two days. As shown in figure 5, there is a fast decrease in flux.

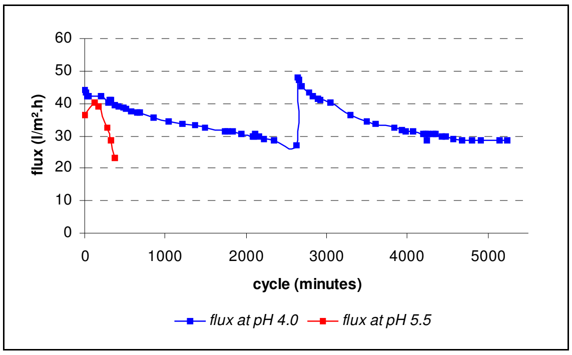

Figure 5. *Evolution of the flux at pH 4,0 and pH 5,5 for the one-step reverse osmosis*

However, a remarkable conclusion is that at low pH value only the retention of fluoride is not acceptable. On the other hand, the retention for the other parameters, such as zinc, nickel, manganese, phosphate, etc… is mostly sufficient high.

The long and the short of it is that the installation eventually can be divided into two steps. A first step can be operated at low pH-value to remove the different heavy metals while after neutralisation fluoride can be removed in a second step. There is no risk of membrane fouling at this high pH-value since all heavy metals already are removed in the fist step. This will probably allow a longer cycle time.

Pilot tests with two-steps reverse osmosis

Description of the pilot plant

For this reason, the pilot plant was extended with a second step. The first step was completed with a dosage of phosphoric acid (H_3PO_4); the second step was equipped with a neutralisation with sodium hydroxide (NaOH).

The recovery of the first step was kept on 75% while the recovery for the second step was adjusted to 95%. The pH-value in the first step was about 2,5 to 3,5. In the second step neutralisation was executed until pH 6,0 to 7,0.

Results of the pilot plant

Figure 6 shows that by adapting the installation to the new situation a more stabile flux could be obtained (27 l/m^2.h), resulting in a much longer cycle time (approximately 7 working days).

A summary of the retention for the most relevant parameters is shown in table 2.

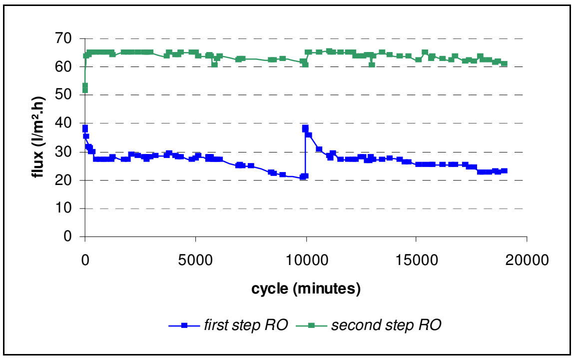

Figure 6. *Evolution of the flux at pH 3,0 in the first step and pH 6,0 in the second step of the two-steps reverse osmosis plant*

Table 2. *Retention of the most relevant parameters of the two-steps reverse osmosis plant*

Parameter	Unit	Rinsing bath	Permeate RO step 1	Permeate RO step 2	retention
pH	-	3,6	3,3	6,6	-
Conductivity	µS/cm	402	192	25	94%
Zinc	mg Zn/l	17	0,21	< 0,2	> 99%
Nickel	mg Ni/l	7,5	< 0,1	< 0,1	> 99%
Manganese	mg Mn/l	7,4	< 0,2	< 0,2	> 97%
Total phosphate	mg P/l	63	0,13	< 0,05	> 99%
Nitrate	mg N/l	18	3,7	0,90	95%
Ammonium	mg N/l	2,6	0,44	< 0,015	> 99%
Total fluoride	mg F/l	21	9,5	2,9	86%
Sodium	mg Na/l	59	0,6	4,9	92%

Chemical cleaning of the membranes

The membranes were cleaned after each test. The chemical cleaning includes successively an acid rinsing, a deionised water rinsing, an alkaline rinsing and finally again a deionised water rinsing.

The acid rinsing was executed with a product based on nitric acid (HNO_3) and took about 30 minutes. After 10 minutes rinsing with deionised water, the next rinsing with a product based on sodium hydroxide was started for about 30 minutes. Finally the membrane was rinsed during 60 minutes with deionised water.

The efficiency of the chemical cleaning (evaluated by flux restoration) was significant better at higher temperatures. During the pilot tests there has been cleaned at 5 °C above the operating temperature.

INSTALLATION OF A TWO-STEPS REVERSE OSMOSIS PLANT AT VOLVO CARS GENT

Principle flow diagram

The two-steps reverse osmosis plant erected at Volvo Cars Gent is dimensioned for a capacity of 5,0 m³/h. By adjusting the recovery of the first step at 80 % a permeate flow of 4,0 m³/h is obtained. The permeate flow of the second step is about 3,2 m³/h since the second step is also operated at a recovery of 80 %. This quantity is completely recycled to the rinsing step after the phosphate bath. The water consumption, as well as the amount of industrial waste water in this area, originally 6,0 m³/h is consequently decreasing with 4,2 m³/h.

Both concentrate flows (1,0 m³/h for the first step and 0,8 m³/h for the second one) are collected in a buffer tank from where a part of it (approximately 0,3 m³/h) is reused to compensate the evaporation losses in the phosphate bath. The excess of concentrate is discharged to the physicochemical waste water treatment plant.

A principle flow diagram of the installation is shown in figure 7.

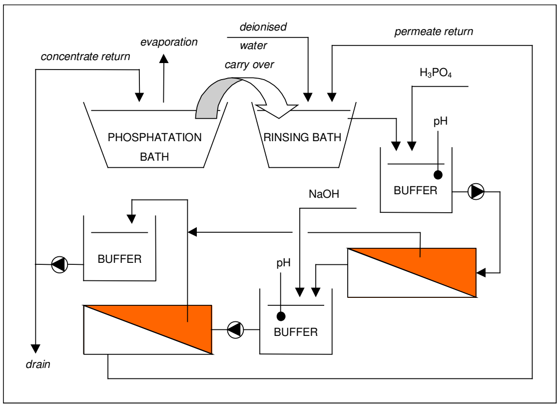

Figure 7. *Principle flow diagram of the two-steps reverse osmosis plant at VCG*

OPTIMISATION OF THE REVERSE OSMOSIS PLANT AT VOLVO CARS GENT

Formulation of the problem

During the final start-up of the installation, permeate quality was as expected but only a very short cycle time was obtained. The membranes of the first stage were already blocked within a few hours.

After inspection of the membranes and after analysis of the rinsing water quality, the problem could be attributed to the presence of mineral oil and oils and fat in the feed water, caused by the lubrication of the conveyer. The problem was not detected during the pilot test due to the fact that the pilot test was executed off-line so no conveyer was entering the rinsing bath.

Optimisation of the pre-filtration

After some new tests, the pre-filtration was extended with a centrifugal machine, a sand filter and two activated carbon filters in series.

A principle flow diagram of the optimised installation is given in figure 8.

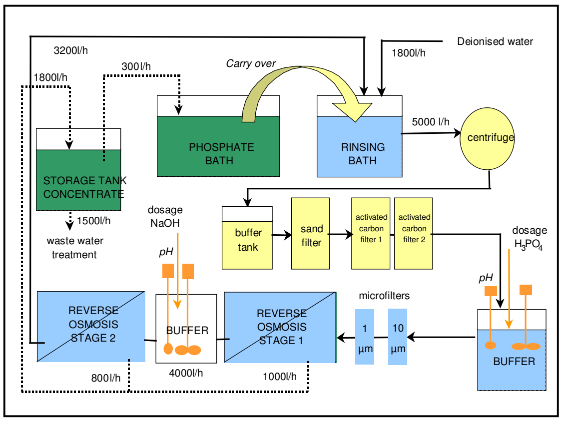

Figure 8. *Principle flow diagram of the two-steps reverse osmosis plant at VCG after optimisation of the pre-filtration*

Results

The installation of the centrifuge, the sand- en the activated carbon filters has resulted in a significant increase of the cycle time, even much better than the cycle time obtained during the first series of pilot tests. The frequency of cleaning of the membranes is about 4 to 6 weeks.

After fine-tuning of the installation, the amount of waste water is decreased from 6 m³/h to 1,5 m³/h or a saving of more than 100 m³/day.

Costs / profits analysis

An estimation of the realised savings and the operating costs is summarised in table 3.

Table 3. *Estimation savings versus operating costs for the two-steps reverse osmosis plant at VCG*

estimation yearly savings:	
- decreased consumption of deionised water	40 000 EUR
- reduction waste water production	125 000 EUR
- recuperation of process chemicals (phosphate bath liquid)	5 000 EUR
- lower cleaning frequency rinsing baths	10 000 EUR
- TOTAL	180 000 EUR
estimation yearly operating costs:	
- consumption of electricity	7 500 EUR
- cleaning membranes and chemical consumption	5 000 EUR
- replacement of reverse osmosis membranes	15 000 EUR
- operator cost for follow-up	6 000 EUR
- TOTAL	33 500 EUR
reduction in water consumption and amount of industrial waste water	24 192 m³/year

Estimated savings versus operating costs for the two-steps reverse osmosis plant at VCG

As shown in table 3, the total saving thanks to the reverse osmosis plant can be estimated on approximately 180 000 EUR gross per year. Taken into account a total operating cost of approximately 33 500 EUR per year, the total saving on yearly base can be estimated on 146 500 EUR net.

The pay-back period of the total investment of about 600 000 EUR can consequently be estimated on four years.

CONCLUSIONS

The introduction of aluminium parts on the new Volvo models has resulted in an increasing concentration of fluoride in the waste water. The most important source of fluoride is the overflow of the rinsing stages after the phosphate bath.

In order to obtain a maximum efficiency of the PAC dosage for the fluoride removal in the physico-chemical waste water treatment plant, investigation was started to look for a suitable technique to have a more concentrated waste water flow. For that, different pilot tests with reverse osmosis were executed.

To avoid membrane fouling and also to keep the retention for fluoride to an acceptable level, a reverse osmosis plant in two steps, operated at different pH-value, proved to be the best solution. The first step is operated at a low pH-value to avoid the formation of metal hydroxides. Nearly all heavy metals, but also phosphate, is eliminated in the first stage of the RO plant. However, due to the low pH-value, the fluoride removal in the first step remains very low. For this reason permeate of stage 1 is next neutralised and treated by a second stage to eliminate the remaining amount of fluoride.

Finally, a permeate is obtained with a quality, suitable for reuse in the rinsing baths. The drained concentrate can partly be recycled to the phosphate bath to compensate the evaporation losses. The excess of concentrate has to be discharged to the waste water treatment plant.

The installation of the two-steps reverse osmosis plant at Volvo Cars Gent has resulted in a saving of approximately 146 500 EUR net. The pay-back period of the total investment of 600 000 EUR is consequently about 4 years.

Besides, water consumption and waste water production has been decreased with 24 192 m³/year or 160 litres per produced car. This is a reduction of more than 25% of the total amount of industrial waste water of the Volvo Cars production plant at Gent.

SOURCES

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