Crossflow Microfiltration For Extending the Service Life Of Aqueous Alkali Decreasing Solutions

By Dr. Hans Schwering, Peter Golisch and Alan Kemp

Aqueous cleaners are being substituted for chlorofluorocarbon solvents in both the metal and electronics industries. Alkaline cleaners are often used at elevated temperatures and at high alkalinity, but require replacement when the levels of oil and other contaminants become too high. Microfiltration, using a ceramic membrane, has proven to be a successful method of extending the service life of alkaline cleaners, by maintaining a low contaminant level of the bath. This article presents a case history and other applications data gained over the past four years.

During the operation of a decreasing bath there is a gradual build-up of oil, grease and soils. Once the oil content reaches a certain concentration, the cleaning efficiency of the bath is adversely affected. The solution must then be discarded, despite the fact that much of the inorganic bath constituents and the majority of wetting agents and surfactants are still usable.

Process Background

If one can remove the oil and soil contaminants that are introduced into the bath, and if the spent wetting agents and surfactants can be replenished, it is basically possible to extend the service life of the solution indefinitely.

The oil in aqueous cleaning systems occurs in two forms: Free oil and emulsified oil. Which one of these two forms predominates depends on the type of cleaner employed. Free oil is readily removed with an oil separator. Cleaners that emulsify at high temperatures—around 80 °C (175 °F)—but lose this property when cooling to around 40 °C (105 °F), are particularly well suited for recycling, because the floating oil layer is easily skimmed off. The emulsified oil fraction can be efficiently separated, using crossflow membrane filtration. This technology has been employed in industry for more than 15 years, for treating waste coolant emulsions and on other applications of effluent contaminated with oil.

Early attempts to use this technology for the recycling of aqueous decreasing solutions met with limited success, because of problems that could not be overcome at the time.

Membrane Selection

The first available polymer-based membranes had limited resistance to alkalinity and temperature. In addition, they were also mechanically sensitive to operating pressure.

Just in this area alone-namely, the processing of a heavy-duty degreaser, loaded with a high input of oil, and operating at high temperature and high alkalinity-where recycling brings the biggest economic and ecological advantages, polymeric membranes cannot be employed.

New Membranes

The earlier available membranes were developed for their ability to retain a maximum amount of organic substances, so that statutory disposal limits (typically 10 mg/L oil and grease) could be met. In addition to removing oil, the free surfactants were also removed, so the bath quickly lost its decreasing efficiency. As a result of the energy crisis, decreasing compounds were developed with good cleaning properties at lower temperatures—around 60 °C (140 °F)—and lower alkalinity. This was achieved by blending a complex formulation of various surfactants.

At the same time, membranes having a larger pore size (microfiltration) became available, permitting a larger percentage of the surfactants to pass through the ultrafiltration membrane. The individual components of the surfactant formulation, however, were depleted at different rates. Although this imbalance can be corrected by replenishing the individual components proportionately, the analytical determination for surfactants is incredibly complex and difficult to carry out accurately. The manufacturers and suppliers of the cleaners showed a complete lack of enthusiasm for developing recyclable products, for fear of losing revenue. These factors were partially responsible for restricting the recycling of aqueous alkali cleaners on a broad scale, and confining them to a few, single applications.

New Technology

During the middle of the 1980s, a new tendency emerged. Haunted by the problems caused through groundwater contamination and air pollution, cleaning processes, which were based on chlorofluorocarbons, started to be converted to aqueous alkali decreasing systems. Suddenly, the operators of these processes were faced with the problem of wastewater disposal, because, apart from their high alkali content, these spent process solutions still contained a high percentage of surfactants. At the same time, the recycling idea became a political issue that induced manufacturers to rethink their strategy.

Two other technical developments occurred in parallel: First, it was realized that higher operating temperatures around 70-80 ‘C (160-175 “F) coupled with forced and induced air extraction changed the decreasing bath into an evaporator. Consequently, when combined with innovative rinsing techniques, it was feasible to evaporate the water required for rinsing, thus achieving a zero-discharge decreasing and rinsing loop.

Secondly, new ceramic membranes became commercially available. These membranes were originally used in the food and beverage industry, where the requirement was for membranes that could resist steam sterilization at 130 ‘C (265 “F).

Ceramic membranes are available in nearly all of the required pore sizes and

Table 1
Annual Wastewater Balance

Before System Redesign		After System Redesign	
Waste cleaning solution	50 m^3		
		1.2 m^3	Oily waste concentrate
Cleaning water	5 m’	5 m^3	Cleaning water
Rinse water	**2000** m’		
Total	**2055** m^3	**6.2** m^3	

in porosities ranging from ultrafiltration to microfiltration and into the range of conventional particle filtration. There are practically no limitations with respect to temperature, pH (alkalinity), and mechanical stability.

Some difficulties are encountered when dealing with cleaning formulations with a high silicate content, because cleaners with silicates contain a certain amount of colloidal silicic acid, which has a tendency to plug the pores of the ceramic membrane.

in any event, silicate cleaners are easily replaced with non-silicated equivalents and, thanks to recycling, the higher price of non-silicated products is no longer a significant issue.

Keeping all of these factors in mind, the zero-discharge, low-waste-generating decreasing system of the 1990s can be presented as follows:

- A simply structured non-silicate degreasing bath that operates in the higher temperature range around 70-80 ‘C (160-175 ‘F) and that can be easily replenished with additives.
- Particularly well suited for recycling are cleaners that emulsify oils in the high temperature range (effective decreasing action) and then have the ability to release these emulsified oils at lower temperatures and during plant shutdown.
- Coupled with an efficient extraction system, it is possible to evaporate the required amount of system rinse water, thus achieving a zero-discharge rinsewater circuit.
- The ability to continuously remove oil and contaminants by pumping the solution through a ceramic membrane.

The pore size of this membrane lies in the range between microfiltration and conventional particle filtration. This permits nearly all of the surfactants and wetting agents to pass through the membrane while retaining the oil (residual about 100 ppm). The permeate flux rate of these membranes is greatly enhanced by running at a high operating temperature; high pH presents no limitations.

The excellent mechanical stability of these membranes permits the system to be operated at a transmembrane pressure of 3-4 bar (45 to 60 psig), resulting in an increased permeate flux rate.

The membrane surface is kept open by utilizing a periodic back-pulsing cycle. This back-pulsing technique is set out in greater detail in the following description of the system.

System Configuration

A recycling system to satisfy the above-mentioned requirements must meet the following equipment criteria:

- Simple mechanical configuration—robust and compact—low maintenance requirement.
- Minimum floor space.
- All of the construction materials, including gaskets and seals, must be resistant to high alkalinity, high temperature and sharp temperature fluctuations.
- Soils and fine metal shavings must not impede the proper functioning of the system.
- Low capital cost of the initial investment and low operating expense (energy use and frequency of membrane replacement).

Among the systems that are available in the USA and in Europe, the authors selected one cleaner recycling unit for this study, This was a compact system that could be connected to existing decreasing tanks having their own recirculation and surface oil skimming facilities.

The cleaning unit has two sections, one being an oil separator for removing tramp oil and the other forming the working tank. Aside stream from the cleaning bath loop is passed through the unit with clean permeate being recycled into the main decreasing tank.

A ceramic filter element is built directly into the working tank adjacent to a vertical immersion pump. An automatic three-way pulsing valve is fitted into the permeate line. Compressed air is periodically cycled into the permeate discharge line to generate a series of back pulses, creating a momentary reversal in the direction of the permeate flow. Any film or coating of the membrane is either prevented or dislodged, resulting in a stable permeate flux rate over prolonged periods of operation. There is no need for additional rinsing procedures.

Case History

Prompted by waste minimization requirements, an existing metal cleaning line was converted to a zero-discharge rinsewater configuration.

Before Conversion

The cleaning line comprised:

- Soak decreasing tank, 2 stations, tank volume 1000 L (250 gal), temp. 75 °C (167 °F), hourly evaporation loss = 10 L (2.5 gal), cleaner make up @ 40 g/L (5.5 oz/gal).
- Dragout rinse, volume = 500 L (128 gal). This tank is used to replenish cleaner evaporation loss.
- Running rinse, volume = 500 L (125 gal), one volume change per hour.
- Hot rinse, tank volume 500 L (125 gal), temp. 75°C(176 °F). This rinse is used to replenish dragout tank #2.

Process Data Before Conversion

This plant processes 10 barrels per hour, producing a dragout loss of 20 L/hr (about 5 g/hr). Oil is dragged in at the rate of 100 g/hr (3.5 oz), resulting in an oil content of about 8 g/L (1.1 oz/gal) at the end of an 80-hour working week. The bath is then dumped and made up fresh using the dragout, which is replenished in turn with water from the hot rinse.

After Conversion

Changes made to meet the waste minimization objectives substantially amounted to

- The decreasing tank was split into two sections of 500 L (125 gal) each, comprising primary and secondary decreasing stages and maintaining the overall tank size.
- The temperature was raised to 85 °C (185 °F) and the cleaner concentration increased to 50 g/L (7 oz/gal) in the first

Table 2
Schedule of Operating Costs

Costs Before Redesign		Costs After Redesign	
Offsite disposal of degreasing bath and cleaning water. 15,000 gal @ $1.50/gal	$22,500	$2,400	Offsite disposal of degreasing bath and cleaning water. 1600 gal @ $1.50/gal
Water, effluent and utilities tariff. 51,500 gal @ $5/1000 gal	$258	$75	Demineralized water. 50,000 gal @ $1.50/1,000 gal
Degreasing bath make-up 10,000 gal @ $0.75 gal	$7,500	$1,000	Replenishment of additives
Total	**$30,258**	**$3,475**	
Annual Savings		**$26,783**	

and reduced to 20 g/L (2.75 oz/gal) in the second compartment.

- A microfiltration recycling unit with a built-in oil separator was installed on the pre-decreasing stage.
- The three rinse tanks were changed into a three-stage counterflow cascade rinse with a feed rate of 50 L/hr (3.2 gpm). (20 L/hr dragout and 30 L/hr evaporation loss)
- A storage tank was provided to hold the decreasing solution during cleaning and maintenance work.

Process Data After Conversion

With the installation of the microfiltration recycling unit, a constant oil content of 1 g/L (0. 13 oz/gal) was maintained in the first stage. The solution in the second stage leveled out at about 0.2 g/L (0.02 oz/gal) of oil.

The oil and contaminants that were removed by the recycling unit were disposed of off-site, and amounted to approximately 600 L (154 gal) of 30 percent emulsion every six months. This volumetric loss was replenished with fresh degreaser makeup as needed.

With the conversion to a three-tank cascade rinse, the continuous processing of the hot barrel-plating components heated up the rinse tanks, further improving the rinsing efficiency. Dispensing with the running rinse more than compensated for the extra energy required to operate the cleaner at the higher temperature. Oil content in the last hot rinse leveled out at a constant 10 mg/L. Compared with the residual oil concentration of 50 mg/L in the previous configuration, this represented a considerable improvement in component surface quality.

The DI water supply to the last rinsing stage was supplied from a cartridge DI system that was regenerated off-site. This feed water quality could have equally been provided from a low pressure RO system. The use of DI water has several advantages:

- Improved quality, no staining of parts;
- No encrustation of heating coils, resulting in lower maintenance, improved heat transfer and energy savings;
- Completing agents for dealing with water hardness are no longer needed, resulting in simplified effluent treatment;
- Lower TDS content in the wastewater was achieved despite the higher evaporation loss.

Economical Viability

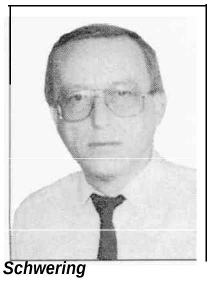
As can be imagined, economic viability and payback period will vary greatly, depending on various factors, such as the price paid for the make up of cleaner, water and energy, as well as disposal costs that can vary substantially from place to place. It is therefore necessary to evaluate individual circumstances carefully, taking all of these peripheral factors into account.

Tables 1 and 2 show a typical economic evaluation, which is based on the application discussed in this paper, adapted to average prevailing costs in the U.S. at the time of publication.

Last, but not least, whatever the payback period appears to be at the time of preparing this evaluation, the escalating cost of disposal will quickly improve the payback equation.

Water-based alkali cleaners will see a dramatic increase in use because of the phasing out of solvent degreasers. Recycling of these aqueous cleaners can be achieved quite simply with equipment that employs membranes mat can withstand the harsh chemical process conditions of high pH and elevated temperature.

This process is a valid and recognized waste minimization method that can be retrofitted without much difficulty and at a realistic cost. In addition to being a significant contribution to environmental conservation measures, it is equally important in improving quality standards by maintaining a consistent level of cleaning efficiency.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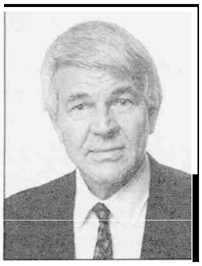
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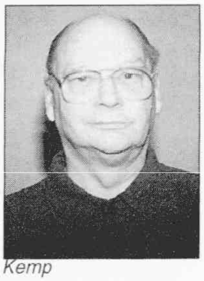
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