



Application of nanofiltration in metal recovery

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Synopsis

Recently, a new kind of filtration has emerged, namely nanofiltration (NF). It is a membrane-based process which exhibits totally unique separation characteristics for dissolved salts as well as for many non-charged species. By exploiting the particular separation characteristics of this new membrane type, many unique and novel separations have been made possible.

The basis for separation by nanofiltration is the negative surface charge of the membrane. This results in rejection of multivalent anions, whilst associated cations are also rejected to maintain electro-neutrality. This peculiar property enables separation of dissolved ions such as sulphate and copper from acid, whilst the acid may be purified for reuse.

This paper aims at providing an overview of the principles of nanofiltration, illustrated by particular examples.

Introduction

Recently, a new kind of filtration, namely nanofiltration (NF) has emerged as a viable treatment option to separate valuable compounds from waste streams.

As a membrane-based process, NF falls in the region between reverse osmosis and ultrafiltration. It is sometimes referred to as 'loose reverse osmosis', although a better understanding of the performance characteristics of true nanofiltration membrane allows several novel separations to be performed, which previously was considered impractical.

Nature of nanofiltration

There are at least three distinctly different rejection phenomena which characterize a true nanofiltration membrane. These are:

Rejection of multivalent anions

Multivalent anions such as sulphate (SO_4^{2-}) are rejected by nanofiltration membranes to a high degree (95-99%). The strong negative charge of the molecule interacts with the negative membrane surface charge, resulting in an electric repulsion effect.

In contrast, rejection of monovalent anions is relatively low. Rejection of the chloride ion (Cl^-) is typically only 5-45%, depending on the ionic strength of the feed solution.

Rejection of cations

The nanofiltration membrane surface is negatively charged, therefore it could be argued that it will allow positively charged ions such as calcium (Ca^{2+}) aluminium (Al^{3+}) and sodium (Na^+) to pass through the permeate. However, it can be demonstrated that rejection of these species is high, when associated with multivalent anions to maintain electroneutrality.

For example, sodium, when associated with chloride, will pass readily through the membrane. However, when associated with sulphate, it will be rejected to roughly the same degree as the sulphate ion.

Rejection based on size

Uncharged dissolved materials, and some positively charged ions, will be rejected if they are of sufficient size.

Nanofiltration membranes have a molecular weight cut off of approximately 150-250 Dalton. Therefore, species such as glucose and fructose (MW 180 Daltons) are being rejected. Large, positively charged ions such as heavy metals are rejected, at least partly, based on molecular weight.

Table I compares typical rejection performance of nanofiltration with that of reverse osmosis and ultrafiltration.

Separation of acids and metals

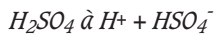
Table I shows rejection of sulphuric and hydrochloric acids to be close to 0%. The low rejection of sulphuric acid warrants further

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explanation, as rejection should be higher due to the presence of the multi valent low SO_4^{2-} anion:

The first dissociation of sulphuric acid is:



This dissociation step produces hydrogen and bisulphate ions. The bisulphate ion, with only one negative charge, will pass through the membrane with roughly the same ease as the chloride ion in hydrochloric acid. The next dissociation

step would produce a sulphate ion, but this requires very high concentrations of sulphuric acid which is rarely used in aqueous industrial applications. The sulphate ion will be rejected by the membrane. It follows, therefore, that metals associated with the sulphate ion when dissolved in aqueous sulphuric acid solutions, can be separated from sulphuric acid. This allows the concentration of metallic species and simultaneous recovery of the acid for re-use. The same applies for applications using phosphoric acid.

Metals dissolved in hydrochloric acid will be associated with the Cl^- anion and pass through the nanofiltration membrane with relative ease, hence recovery of metals from hydrochloric acid solutions is only feasible if

- (i) the metal ion is very large
- (ii) some sulphate ion can be introduced to the feed to improve rejection of the metal.

Table 1
Comparative rejection values

Species	RO* (%)	NF† (%)	UF# (%)
NaCl	99	0-50	0
Na ₂ SO ₄	99	99	0
CaCl ₂	99	0-60	0
MgSO ₄	>99	>99	0
H ₂ SO ₄	98	0-10	0
HCl	90	0	0
Fructose	>99	>99	0
Sucrose	>99	>99	0
Humic acid	>99	>99	30
Virus	>99.99	>99.99	>99.99
Protein	>99.99	>99.99	>99.99
Bacteria	>99.99	>99.99	>99.99

* RO : Reverse Osmosis
 † NF : Nanofiltration
 # UF : Ultrafiltration

Typical applications

There are several documented applications for the use of nanofiltration to recover valuable compounds from waste water. These include:

- recovery of copper sulphate from acid rinse water
- purification of spent sulphuric acid
- recovery of boric acid from radio-active solutions
- reclamation of chromium from acidic wastes
- purification of nitric and phosphoric acids.

For the purposes of this paper, recovery of copper from acid rinse water will be used as a typical case study.

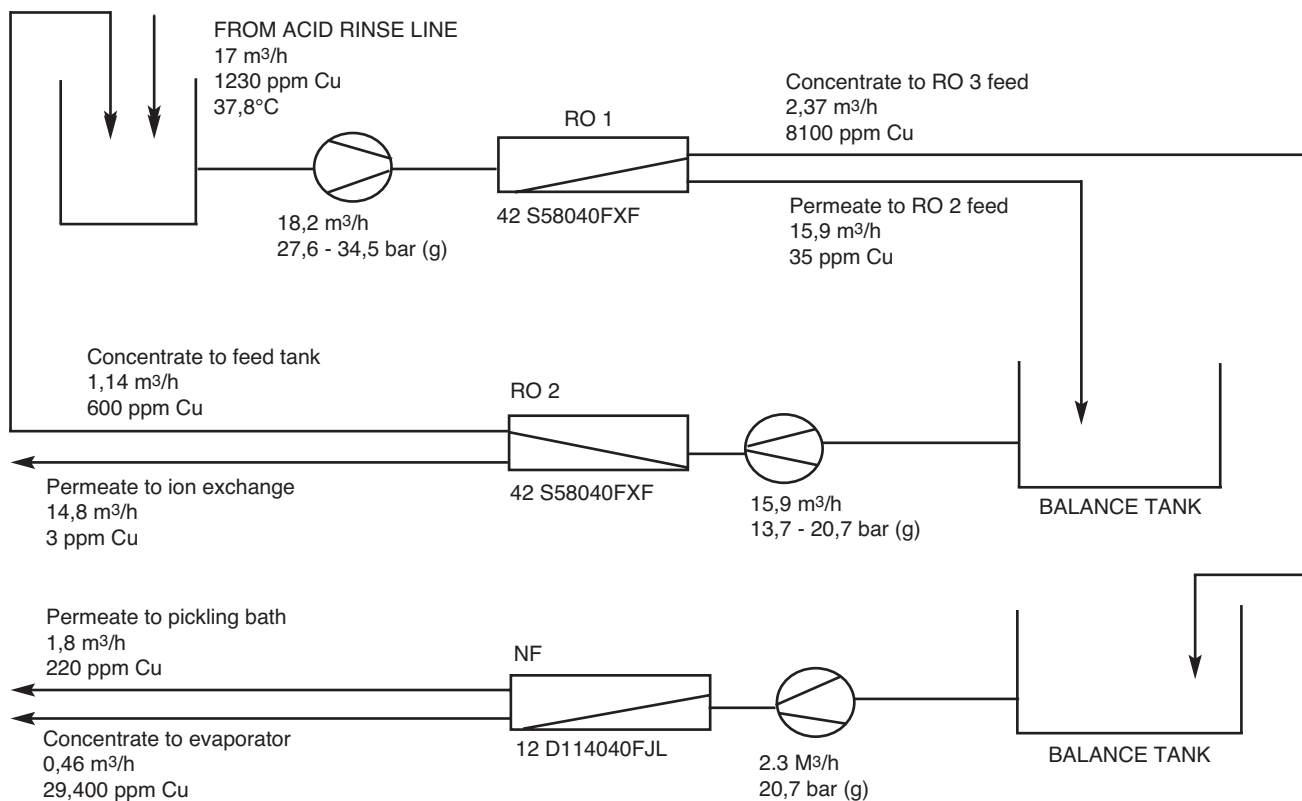


Figure 1—Application of membrane technology for copper sulphate recovery

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Table II

Typical operating conditions

Stage	pH Feed	pH Permeate	pH Concentrate	CH Rejection (%)	H ₂ SO ₄ Rejection (%)
Primary RO step	1.2	2.1	0.9	>97	97%
Secondary RO step	2.1	2.9	1.6	>95	98,9%
NF step	0.9	0.9	0.9	>97	<5%

Background

An existing mining operation, using an acid leaching process for copper recovery, was confronted with two problems which prevented further expansion, namely.

- (i) water in the mine's area was scarce, and new wells expensive to drill
- (ii) neutralization of spent sulphuric acid resulted in large sludge volumes with 2–3 mg/l residual copper.

To overcome these limitations, a three-step membrane process was installed as depicted in Figure 1.

Feed from the acid rinse line was introduced to the feed tank at a pH of 1.2 and copper content of 1230 ppm. This was pumped to a reverse osmosis system under high pressure (27–35 bar (g)) to concentrate the copper to 8100 ppm whilst the diluted permeate contained only 35 ppm copper.

The diluted permeate was routed to a second reverse osmosis system to recover the remainder of the copper, whilst the brine stream from this step was routed to the primary feed tank. The operating pressure in the second reverse osmosis system was significantly lower than stage 1 (13–20 bar (g)).

The concentrate from the first reverse osmosis step had 8100 ppm copper at a pH of 0.9. It is not possible to concentrate this further using reverse osmosis, due to osmotic pressures exerted by the sulphuric acid. Nanofiltration was therefore used to concentrate the copper further, as the acid will pass through the membrane without adding significantly to the osmotic pressure. The concentrate from the nanofiltration step contained 29 400 ppm copper, whilst only 220 ppm copper was found in the permeate. The permeate could therefore be re-used in the pickling bath whilst copper was further concentrated in an existing evaporator.

Performance

Table II summarizes the operating conditions of the system. Note the high removal efficiency of copper by nanofiltration, although virtually no acid is retained by the membrane.

Economics

As could be expected, economics are totally dependant on actual site conditions, such as:

- Existing infrastructure
- Effluent disposal cost
- Cost of chemicals
- Cost of valuable product
- Operating requirements, etc.

The numbers given here should, therefore, only be used as indicative values and are specific for this particular application.

- Capital cost of membrane units: R3 million (1998).
- Operating cost: R4.20 per m³ feed (1998).

It should be noted that the operating cost includes:

- General equipment maintenance
- Electricity
- Labour
- Membrane replacement.

The cost of capital is not included

Membrane life

The membranes used in the process are manufactured from poly-amide and rated for continuous long-term operation in pH conditions from pH 4–11. Under these conditions, membrane life of 3–5 years is not uncommon. The very low pH conditions in this application will, therefore, have a detrimental effect on membrane life. Experience has shown that membranes have to be replaced every 9–15 months.

The high replacement frequency has a marked effect on operating cost. However, considering the alternatives, it was seen as a viable option to dispose of a hazardous waste, whilst recovering a valuable product.

State of technology

Membrane technology is very well established in a wide range of applications. In South Africa, a number of membrane plants are operating successfully.

Nanofiltration in particular is well proven in the municipal field for softening of hard water and in the dairy industry to remove salts from cheese whey.

Operation at extreme pH conditions is a relatively new concept but new membranes are becoming available for continuous operation in pH 0–14. This will undoubtedly improve operating costs and the range of applications.

Currently, recovery of metals from acidic waste streams require pilot testing to establish actual operating costs and to verify economic viability. The existence of a number of installations world-wide, however, suggests that the technology offers distinct advantages.

Research and development in this field is growing and new applications are identified on a regular basis.

Reference

1. NICOLLAISEN, B. 'Nanofiltration overview' Proceedings Membrane Technology Workshop, Johannesburg, May 1995. ◆

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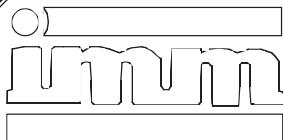
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