



Nanofiltration Membranes and Nanofilters

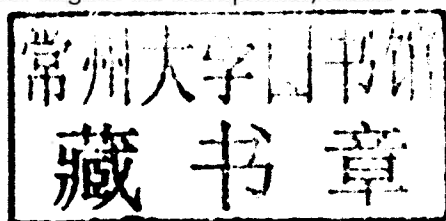
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Editor

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Nanofiltration Membranes and Nanofilters

Preface

Membrane separation is addressed as a pressure driven process. Pressure driven processes are commonly divided into four overlapping categories of increasing selectivity: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and hyperfiltration or reverse osmosis (RO). MF can be used to remove bacteria and suspended solids with pore sizes of 0.1 to micron. UF will remove colloids, viruses and certain proteins with pore size of 0.0003 to 0.1 microns. NF relies on physical rejection based on molecular size and charge. Pore sizes are in the range of 0.001 to 0.003 microns. RO has a pore size of about 0.0005 microns can be used for desalination. The nominal pore size of the membrane is typically about 1 nanometre. Nanofilter membranes are typically rated by molecular weight cut-off (MWCO) rather than nominal pore size. The MWCO is typically less than 1000 atomic mass units (daltons). The transmembrane pressure (pressure drop across the membrane) required is lower (up to 3 MPa) than the one used for RO, reducing the operating cost significantly. However, NF membranes are still subject to scaling and fouling and often modifiers such as anti-scalants are required for use.

Mechanical or chemical methods could be used for effective filtration techniques. One class of filtration techniques is based on the use of membranes with suitable hole sizes, whereby the liquid is pressed through the membrane. Nanoporous membranes are suitable for a mechanical filtration with extremely small pores smaller than 10 nm ("nanofiltration") and may be composed of nanotubes. Nanofiltration is mainly used for the removal of ions or the separation of different fluids. On a larger scale, the membrane filtration technique is named ultrafiltration, which works down to between 10 and 100 nm. One important field of application for ultrafiltration is medical purposes as can be found in renal dialysis. Magnetic nanoparticles may offer an effective and reliable method to remove heavy metal contaminants from waste water by making use of magnetic

separation techniques. Using nanoscale particles increases the efficiency to absorb the contaminants and is comparatively inexpensive compared to traditional precipitation and filtration methods. Some water-treatment devices incorporating nanotechnology are already on the market, with more in development. Low-cost nanostructured separation membranes methods have been shown to be effective in producing potable water in a recent study. In much of the developing world, clean drinking water is hard to come by, and nanotechnology provides one solution. While nanofiltration is used for the removal of contaminants from a water source, it is also commonly used for desalination. In a study in South Africa, tests were run using polymeric nanofiltration in conjunction with a reverse osmosis process to treat brackish groundwater. These tests produced potable water, but as the researchers expected, the reverse osmosis removed a large majority of solutes. This left the water void of any essential nutrients (calcium, magnesium ions, etc.), placing the nutrient levels below that of the required World Health Organization standards. This process was probably a little too much for the production of potable water, as researchers had to go back and add nutrients to bring solute levels to the standard levels for drinking water consumption. Providing nanofiltration methods to developing countries, to increase their supply of clean water, is a very inexpensive method compared to conventional treatment systems. However, there remain issues as to how these developing countries will be able to incorporate this new technology into their economy without creating a dependency on foreign assistance.

This book explores the latest advances in the field of this subject. The subject matter, both as regards the arrangement of chapters as well as contents is designed to meet the requirement of the students in several Universities.

—*Editor*

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Chapter 1

Nano Water Technology

Fouling

Fouling refers to the accumulation of unwanted material on solid surfaces, most often in an aquatic environment. The fouling material can consist of either living organisms (biofouling) or a non-living substance (inorganic or organic). Fouling is usually distinguished from other surface-growth phenomena in that it occurs on a surface of a component, system or plant performing a defined and useful function, and that the fouling process impedes or interferes with this function.

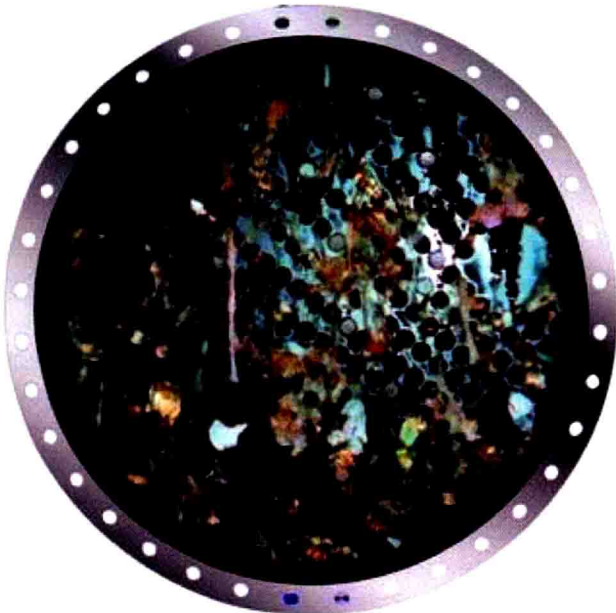


Figure: Heat exchanger in a steam power plant, fouled by macro fouling

Other terms used in the literature to describe fouling include: deposit formation, encrustation, crudding, deposition, scaling, scale formation, slagging, and sludge formation. The last six terms have a more narrow meaning than fouling within the scope of the fouling science and technology, and they also have meanings outside of this scope; therefore, they should be used with caution.

Fouling phenomena are common and diverse, ranging from fouling of ship hulls, natural surfaces in the marine environment (marine fouling), fouling of heat-transfer components through ingredients contained in the cooling water or gases, and even the development of plaque or calculus on teeth, or deposits on solar panels on Mars, among other examples.

This article is primarily devoted to the fouling of industrial heat exchangers, although the same theory is generally applicable to other varieties of fouling. In the cooling technology and other technical fields, a distinction is made between macro fouling and micro fouling. Of the two, micro fouling is the one which is usually more difficult to prevent and therefore more important.

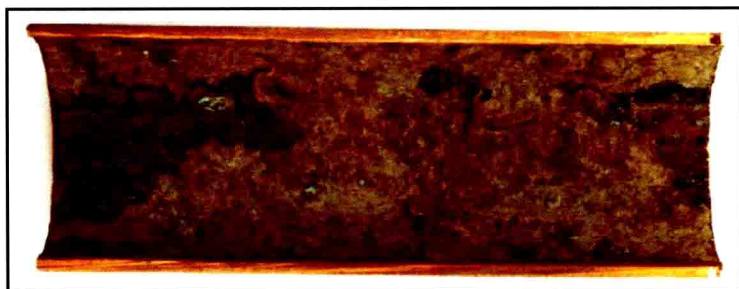


Figure: Condenser tube with residues of biofouling (cut open)

Components Subject to Fouling

Following are examples of components that may be subject to fouling and the corresponding effects of fouling:

- Heat exchanger surfaces - reduces thermal efficiency, decreases heat flux, increases temperature on the hot side, decreases temperature on the cold side, induces under-deposit corrosion, increases use of cooling water;
- Piping, flow channels - reduces flow, increases pressure drop, increases upstream pressure, increases energy expenditure, may cause flow oscillations, slugging in two-phase flow, cavitation; may increase flow velocity elsewhere, may induce vibrations, may cause flow blockage;

- Ship hulls - creates additional drag, increases fuel usage, reduces maximum speed;
- Turbines - reduces efficiency, increases probability of failure;
- Solar panels - decreases the electrical power generated;
- Reverse osmosis membranes - increases pressure drop, increases energy expenditure, reduces flux, membrane failure (in severe cases);
- Electrical heating elements - increases temperature of the element, increases corrosion, reduces lifespan;
- Nuclear fuel in pressurised water reactors - axial offset anomaly, may need to de-rate the power plant;
- Injection/spray nozzles (e.g., a nozzle spraying a fuel into a furnace) - incorrect amount injected, malformed jet, component inefficiency, component failure;
- Venturi tubes, orifice plates - inaccurate or incorrect measurement of flow rate;
- Pitot tubes in airplanes - inaccurate or incorrect indication of airplane speed;
- Spark plug electrodes in cars - engine misfiring;
- Production zone of petroleum reservoirs and oil wells - decreased petroleum production with time; plugging; in some cases complete stoppage of flow in a matter of days;
- Teeth - promotes tooth or gum disease, decreases aesthetics;
- Living organisms - deposition of excess minerals (e.g., calcium, iron, copper) in tissues is (sometimes controversially) linked to aging/senescence.

Macro Fouling

Macro fouling is caused by coarse matter of either biological or inorganic origin, for example industrially produced refuse. Such matter enters into the cooling water circuit through the cooling water pumps from sources like the open sea, rivers or lakes. In closed circuits, like cooling towers, the ingress of macro fouling into the cooling tower basin is possible through open canals or by the wind. Sometimes, parts of the cooling tower internals detach themselves and are carried into the cooling water circuit. Such substances can foul the surfaces of heat exchangers and may cause deterioration of the relevant heat transfer coefficient. They may also create flow blockages, redistribute the flow inside the components, or cause fretting damage.

Examples:

- Manmade refuse;
- Detached internal parts of components;
- Tools and other “foreign objects” accidentally left after maintenance;
- Algae;
- Mussels;
- Leaves, parts of plants up to entire trunks.

Micro Fouling

As to micro fouling, distinctions are made between:

- Scaling or precipitation fouling, as crystallisation of solid salts, oxides and hydroxides from water solutions, for example, calcium carbonate or calcium sulphate;
- Particulate fouling, i.e., accumulation of particles, typically colloidal particles, on a surface;
- Corrosion fouling, i.e., in-situ growth of corrosion deposits, for example, magnetite on carbon steel surfaces;
- Chemical reaction fouling, for example, decomposition or polymerisation of organic matter on heating surfaces;
- Solidification fouling - when components of the flowing fluid with a high-melting point freeze onto a subcooled surface;
- Biofouling, like settlements of bacteria and algae;
- Composite fouling, whereby fouling involves more than one foulant or fouling mechanism.

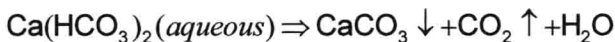
Precipitation Fouling

Temperature dependence of the solubility of calcium sulphate (3 phases) in pure water. The water is pressurised so that it can be maintained in the liquid state at the elevated temperatures.

Scaling or precipitation fouling involves crystallisation of solid salts, oxides and hydroxides from solutions. These are most often water solutions, but non-aqueous precipitation fouling is also known. Precipitation fouling is a very common problem in boilers and heat exchangers operating with hard water and often results in limescale.

Through changes in temperature, or solvent evaporation or degasification, the concentration of salts may exceed the saturation, leading to a precipitation of solids (usually crystals). As an example, the equilibrium between the readily soluble calcium bicarbonate -

always prevailing in natural water - and the poorly soluble calcium carbonate, the following chemical equation may be written:



The calcium carbonate that forms through this reaction precipitates. Due to the temperature dependence of the reaction, and increasing volatility of CO_2 with increasing temperature, the scaling is higher at the hotter outlet of the heat exchanger than at the cooler inlet.

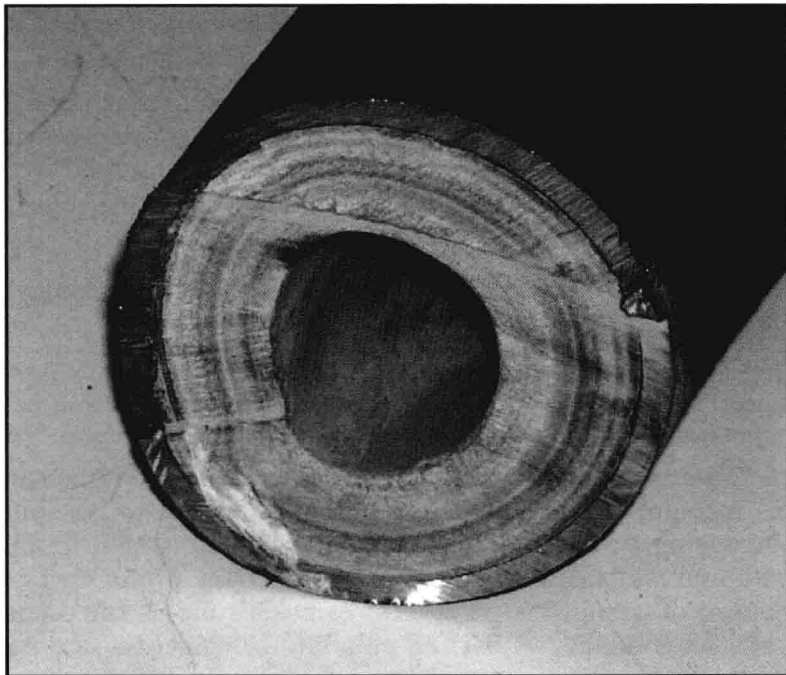


Figure: Limescale buildup inside a pipe both reduces liquid flow through the pipe, as well as reduces thermal conduction from the liquid to the outer pipe shell. Both effects will reduce the pipe's overall thermal efficiency when used as a heat exchanger.

In general, the dependence of the salt solubility on temperature or presence of evaporation will often be the driving force for precipitation fouling. The important distinction is between salts with “normal” or “retrograde” dependence of solubility on temperature. The salts with the “normal” solubility increase their solubility with increasing temperature and thus will foul the cooling surfaces. The salts with “inverse” or “retrograde” solubility will foul the heating surfaces. An example of the temperature dependence of solubility. Calcium sulphate is a common precipitation foulant of heating surfaces due to its retrograde solubility.

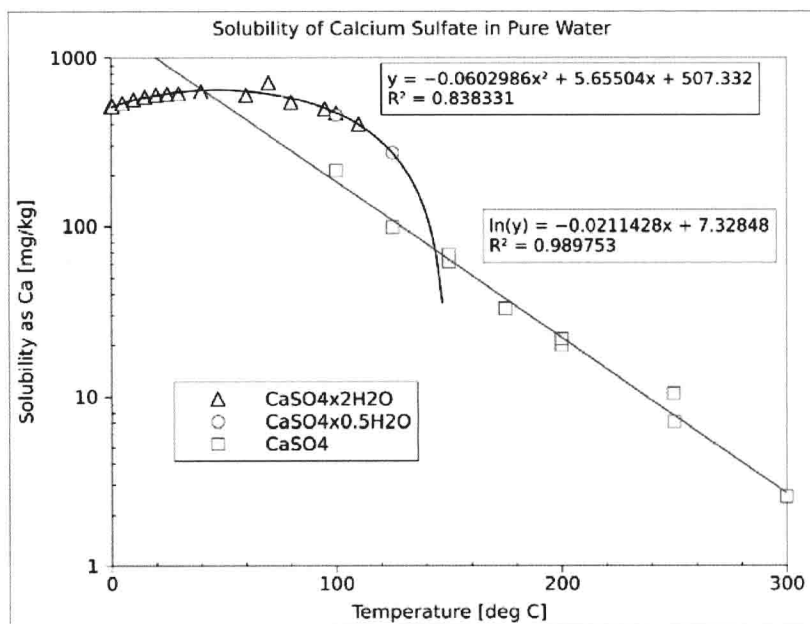


Figure: Temperature dependence of the solubility of calcium sulfate (3 phases) in pure water. The water is pressurized so that it can be maintained in the liquid state at the elevated temperatures.

Precipitation fouling can also occur in the absence of heating or vaporisation. For example, calcium sulphate decreases its solubility with decreasing pressure. This can lead to precipitation fouling of reservoirs and wells in oil fields, decreasing their productivity with time. Fouling of membranes in reverse osmosis systems can occur due to differential solubility of barium sulphate in solutions of different ionic strength. Similarly, precipitation fouling can occur because of solubility changes induced by other factors, e.g., liquid flashing, liquid degassing, redox potential changes, or mixing of incompatible fluid streams.

The following lists some of the industrially common phases of precipitation fouling deposits observed in practice to form from aqueous solutions:

- Calcium carbonate (calcite, aragonite usually at $t > \sim 50^\circ\text{C}$, or rarely vaterite);
- Calcium sulphate (anhydrite, hemihydrate, gypsum);
- Calcium oxalate (e.g., beerstone);
- Barium sulphate (barite);
- Magnesium hydroxide (brucite); magnesium oxide (periclase);

- Silicates (serpentine, acmite, gyrolite, gehlenite, amorphous silica, quartz, cristobalite, pectolite, xonotlite);
- Aluminium oxide hydroxides (boehmite, gibbsite, diaspore, corundum);
- Aluminosilicates (analcite, cancrinite, noselite);
- Copper (metallic copper, cuprite, tenorite);
- Phosphates (hydroxyapatite);
- Magnetite or nickel ferrite (NiFe_2O_4) from extremely pure, low-iron water.

The deposition rate by precipitation is often described by the following equations:

$$\text{Transport: } \frac{dm}{dt} = k_t(C_b - C_i)$$

$$\text{Surface crystallisation: } \frac{dm}{dt} = k_r(C_i - C_e)^{n1}$$

$$\text{Overall: } \frac{dm}{dt} = k_d(C_b - C_e)^{n2}$$

where:

m - mass of the material (per unit surface area), kg/m^2

t - time, s

C_b - concentration of the substance in the bulk of the fluid, kg/m^3

C_i - concentration of the substance at the interface, kg/m^3

C_e - equilibrium concentration of the substance at the conditions of the interface, kg/m^3

$n1, n2$ - order of reaction for the crystallisation reaction and the overall deposition process, respectively, dimensionless

k_t, k_r, k_d - kinetic rate constants for the transport, the surface reaction, and the overall deposition reaction, respectively; with the dimension of m/s (when $n1$ and $n2 = 1$)

Particulate Fouling

Fouling by particles suspended in water ("crud") or in gas progresses by a mechanism different than precipitation fouling. This process is usually most important for colloidal particles, i.e., particles

smaller than about 1 μm in at least one dimension (but which are much larger than atomic dimensions). Particles are transported to the surface by a number of mechanisms and there they can attach themselves, e.g., by flocculation or coagulation.

Note that the attachment of colloidal particles typically involves electrical forces and thus the particle behaviour defies the experience from the macroscopic world. The probability of attachment is sometimes referred to as “sticking probability”, P :

$$k_d = Pk_t$$

where k_d and k_t are the kinetic rate constants for deposition and transport, respectively. The value of P for colloidal particles is a function of both the surface chemistry, geometry, and the local thermohydraulic conditions.

An alternative to using the sticking probability is to use a kinetic attachment rate constant, assuming the first order reaction:

$$\frac{dm}{dt} = k_a C_i$$

and then the transport and attachment kinetic coefficients are combined as two processes occurring in series:

$$k_d = \left(\frac{1}{k_a} + \frac{1}{k_t} \right)^{-1}$$

$$\frac{dm}{dt} = k_d C_b$$

where:

- dm/dt is the rate of the deposition by particles, $\text{kg m}^{-2} \text{s}^{-1}$,
- k_a , k_t and k_d are the kinetic rate constants for deposition, m/s ,
- C_i and C_b are the concentration of the particle foulant at the interface and in the bulk fluid, respectively; kg m^{-3} .

Being essentially a surface chemistry phenomenon, this fouling mechanism can be very sensitive to factors that affect colloidal stability, e.g., zeta potential. A maximum fouling rate is usually observed when the fouling particles and the substrate exhibit opposite electrical charge, or near the point of zero charge of either of them.

Particles larger than those of colloidal dimensions may also foul e.g., by sedimentation (“sedimentation fouling”) or straining in small-size openings.

With time, the resulting surface deposit may harden through processes collectively known as “deposit consolidation” or, colloquially, “aging”.

The common particulate fouling deposits formed from aqueous suspensions include:

- iron oxides and iron oxyhydroxides (magnetite, hematite, lepidocrocite, maghemite, goethite);
- Sedimentation fouling by silt and other relatively coarse suspended matter.

Fouling by particles from gas aerosols is also of industrial significance. The particles can be either solid or liquid. The common examples can be fouling by flue gases, or fouling of air-cooled components by dust in air. The mechanisms are discussed in article on aerosol deposition.

Corrosion Fouling

Corrosion deposits are created in-situ by the corrosion of the substrate. They are distinguished from fouling deposits, which form from material originating ex-situ. Corrosion deposits should not be confused with fouling deposits formed by ex-situ generated corrosion products. Corrosion deposits will normally have composition related to the composition of the substrate.

Also, the geometry of the metal-oxide and oxide-fluid interfaces may allow practical distinction between the corrosion and fouling deposits. An example of corrosion fouling can be formation of an iron oxide or oxyhydroxide deposit from corrosion of the carbon steel underneath. Corrosion fouling should not be confused with fouling corrosion, i.e., any of the types of corrosion that may be induced by fouling.

Chemical Reaction Fouling

Chemical reactions may occur on contact of the chemical species in the process fluid with heat transfer surfaces. In such cases, the metallic surface sometimes acts as a catalyst. For example, corrosion and polymerisation occurs in cooling water for the chemical industry which has a minor content of hydrocarbons. Systems in petroleum processing are prone to polymerisation of olefins or deposition of heavy fractions (asphaltenes, waxes, etc.). High tube wall temperatures may lead to carbonising of organic matter. Food industry, for example milk processing, also experiences fouling problems by chemical reactions.