

NO RESTRICTIONS

**Published in Environmental Protection
September 2002**

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HRMTM (Hydrocarbon Removal Matrix) technology protects ion exchange beds and other water polishing systems from oily organics and solvents without restricting flow

By Kirk Abbott

Historically, it has been difficult and expensive to remove or "polish out" the last small amount of water pollutants for industrial discharge and re-use applications. The old economic rule of thumb in water treatment is that "50 percent of the cost is for removing the first 99 percent of the pollutants; the other 50 percent of cost is for removing the last one percent."

Removing the last, elusive one percent of water pollutants is a job reserved for "polishing technologies." Polishing technologies are expensive to operate because removing that last little bit is very tough. In water treatment, "polishing" literally means to remove extremely dilute concentration levels that range from roughly one part per billion (1 ppb) to five hundred parts per million (500 ppm). Polishing technologies are used commercially for removing trace pollutants to meet U.S. Environmental Protection Agency (EPA) discharge limits and quality standards for industrial re-use and ultrapure water applications.

Conventional polishing systems, such as ion exchange (i.e., water softening), reverse osmosis (RO), activated carbon, biological digestion and chemical treatment are particularly compromised when oily petroleum-type substances are in the mix. Contaminating polishing technologies with compounds, such as oils, greases, fuels and solvents, causes serious inefficiencies. Petroleum hydrocarbons, like oils and solvents, plug, clog, corrode and greatly affect the ability of polishing technologies to function as designed.

Ahead of polishing systems are "gross removal technologies," which generally remove the first 95 percent to 99 percent of contaminants. Separation to this extent is relatively (and even naturally) achievable in most cases. Well-known processes, such as gravity separation, dissolved air flotation (DAF), coagulation, flocculation and clarification, as well as particle filtration down to 5 microns, can be used for gross removal. If maintained, gross removal technologies are capable of separating oily chemical contaminants down to 100 parts per million (ppm) or lower. An oil concentration of 100 ppm doesn't sound like much, but it adds up quickly. For example, 100 ppm oil in 1,000,000 gallons of water represents 100 gallons of oil; not an insignificant amount of pollution to feed into a downstream polishing system. In fact, one gallon of oil in 1,000,000 gallons of water (1 ppm) can cripple the efficiency of ion exchange, activated carbon, chemical treatment and RO systems.

Almost half of the cost of water filtration arises from clearing, cleaning and replacing clogged and fouled filtration systems.

Pre-filtering dilute oily hydrocarbons (<100 ppm) ahead of ion exchange beds and other polishing systems has been attempted in the past. It is a great concept and has been accomplished to a degree. Certainly, a lot of time and money has been invested in pre-filtering oils and solvents

from water to protect the capacity and efficiency of polishing systems for what they do best; namely, removing dissolved chemical compounds, metals, chlorine, odor and turbidity.

Historically, the end-result of pre-filtering oily water has been clogging, or "pressure drop". At the end of the day, protecting polishing systems from dilute oily compounds and solvents is a very expensive "Catch-22." Options have been: a.) Remove oily contaminants by clogging a filter/absorbent system, or b.) Live with the inefficiencies of polluting a downstream polishing system. Either way, you literally pay for the pressure drop.

Paying the Price for Plugging Up

P (Pressure Drop or Clogging) = E (Efficiency Loss or Energy Demand)

Presented by Black & Veatch* [Reference: "Condensate Polishing Cost Benefit Analysis," EPRI's 5 International Cycle Chemistry Conference, Electric Power Research Institute, Palo Alto, California (1997)], the top four benefits sought in water treatment are:

- 1.) Efficiency loss prevention for pumps;
- 2.) Reduced chemical additives and cleaning;
- 3.) Improved availability and cost of raw materials and equipment; and
- 4.) Quicker start-ups after material and equipment replacement

"Pressure Drop," or clogging, costs money. *Business Week* recently stated (February 26, 2001) that "almost half of the cost of water filtration" arises from clearing, cleaning and replacing clogged and fouled filtration systems. Clogging is the physical result of trapping small solid particles, microbes and oily compounds within a filter or absorbent matrix. As these pollutants are caught on a conventional filter or absorbent, water flow is restricted and pumps have to push harder, which consumes more energy (and money). To maintain capacity, you either pay the price of pumping harder, or clean and replace the clogged materials and equipment.

Energy consumed for pumping water can be over 50 percent of the treatment cost in many scenarios. This is based on reasonable and customary operating budgets for ion exchange, activated carbon and membrane systems such as RO and nanofiltration (NF). These technologies tend to clog rapidly, causing extreme pressure drops, efficiency loss for pumps and increased energy requirements. "Pressure Drop Penalties" (PDP) for pumps are included in annual operating costs and can range from \$0.03 to \$0.05 per kWh (kilowatt-hour).

Low concentrations (1 ppb to 100 ppm) of crude oil components mix or emulsify very well with water.

Although it can be expensive and labor intensive, pre-filtering solids down to a reasonable size (e.g., 1 to 5 microns) is relatively straightforward. As a reference, a human hair has a diameter of

roughly 100 microns. Removing dilute chemical compounds however, traditionally requires a sophisticated system with a large footprint that is sensitive to oily compounds and solvents.

Effects of Dilute Oily Compounds and Solvents

Why is the last little bit of water pollution so tough and expensive to remove? Fundamentally, water is a great solvent. Contrary to popular belief, oil and water do mix. Low concentrations (1 ppb to 100 ppm) of crude oil components mix or emulsify very well with water. In fact, Benzene, Toluene, Ethylbenzene and Xylene(s) -- the toxic aromatic "BTEX" components of crude oil -- dissolve in water at dilute concentrations. Dilute BTEX components are therefore very difficult to remove from water, and in the laboratory show up in the last 100 ppm as components of COD (Chemical Oxygen Demand), BOD (Biological Oxygen Demand) and TOC (Total Organic Carbon). Furthermore, these and other petroleum-based compounds are the chemical components notorious for contaminating, choking and clogging conventional filtration systems and polishing technologies.

BTEX compounds are not only toxic to humans and the environment, but also particularly harmful to ion exchange and membrane filtration systems using organic polymers. Oils and solvents are similar in nature and chemically attack organic polymers. Oils coat and plug the inner pores of polymers; organic solvents dissolve, swell and denature the polymers.

As an example, ion exchange resins are made of organic polymer beads or "resins". They are designed to swap dissolved species of positive charge (cations) and negative charge (anions). Resins are chosen based on their ability to generate a less hazardous salt from a more hazardous one. Ion exchange resins work until the ability for further exchange is used up. All ion exchange resins have a fixed capacity and are permeable at molecular dimensions. In theory, the exchange capacity remains constant. In reality, exceptions arise when oily hydrocarbons and solvents are present in the liquid to be purified.

Ion exchange resins naturally attract petroleum-based compounds that coat, dissolve, denature and inactivate the resin. Contamination of this nature causes the real capacity of the resin to be significantly less than the predicted value. Reduction of exchange capacity results, as well as clogging, swelling and choking across the resin bed (i.e., pressure drop). This leads to costly inefficiencies and additional energy requirements to pump over clogged resin beds. Because of this, industrial clients have been historically frustrated over the big difference between design efficiencies and actual results for full-scale polishing systems.

RO and NF membranes basically work as molecular sieves and are typically made from polymers that attract and attach oily petroleum-type compounds. The result again is clogging and extreme efficiency loss. (Ref. "Protection from Organic Fouling," *Environmental Protection*, June 2001).

Clay, carbon and other traditional absorbents are susceptible to clogging, channeling and desorption when exposed to oily compounds and solvents. Channeling causes pre-mature breakthrough and cripples efficiency because only a fraction of the absorbent capacity is exposed to the contaminants. Other polishing systems such as air strippers, bioreactors, ultraviolet and chemical destruction, are also compromised by dilute oils and solvents.

Removing oils and solvents is critical for proper performance of polishing technologies. Traditionally, it has been accomplished at the expense of clogging pre-filtration systems.

Removing Dilute Oily Compounds with HRM Technology

HRM substrates are natural (e.g., cotton) and synthetic materials (e.g., polypropylene) infused with the reaction product of drying oils and acrylic polymers consistent with the Oil Coagulant Composition of Matter Patents 5,437,793 and 5,746,925. HRM substrates are designed to permanently attract, bond and remove oily hydrocarbons and solvents from water without desorption or flow restriction.

HRM technology is operationally "anti-stenotic," which means the flow spaces and pores do not narrow or swell as chemical compounds are absorbed. Although HRM substrates are chemically passive, they bind organic components of various phases (liquids and vapors) into a viscous semi-solid state. The contaminants "densify" on the media and consequently take up less space versus their normal liquid or vapor form. In essence, the opposite of swelling takes place. As water flows through HRM substrates, the coagulate contracts and allows for instantaneous removal of hydrocarbons without clogging, swelling or restricting flow. This novel feature results in less than 1 psi pressure drop across a saturated HRM cartridge.

Five-micron HRM cartridges, in particular, bring the perfect balance of efficiency (99+ percent), flow and pressure drop. The result is a high capacity, single pass separation technology that will not clog, restrict flow or re-release pollutants. HRM technology has affinity for all aqueous insoluble, semi-soluble and mechanically emulsified chemical compounds. Organic pollutants separated with single-pass efficiencies of 99+ percent include the following hydrocarbons:

- Fats, oils and grease (FOG); Petroleum Hydrocarbons (TPH)
- Aromatics (Benzene, Toluene, Ethylbenzene and Xylene(s) - BTEX);
- Polyaromatics (PAH); Naphthalene;
- Aliphatic fuels and solvents; cycloalkanes;
- Chlorinated compounds and solvents;
- Organic polymers; Vinyl compounds; and

HRM substrates are designed to permanently attract, bond and remove dilute oily hydrocarbons and solvents from water without desorption or flow restriction.

- Pesticides, Persistent Organic Pollutants (POPs), PCBs, Dioxins and surrogates of ACE inhibitors, such as insecticides, LSD and nerve agents

Benefits of HRM High Capacity Low Pressure Drop Systems

Because HRM cartridges operate with insignificant differential pressure ($P < 1.0$ psi), and permanently capture the organic compounds that clog and/or foul existing technologies, HRM systems save money by reducing pressure drop. Field data and energy (E) calculations on ultra-low pressure drop HRM systems suggest a 15 to 25 percent efficiency increase for pumps in applications involving mixed hydrocarbons.

For ion exchange, membrane systems, activated carbon and other polishing technologies, additional savings are realized from the following:

- HRM systems preserve capacity, flux and percent recovery while extending service life typically 5 to 10 fold.
- HRM systems reduce the need for chemical additives, cleaning, regeneration and replacement of raw materials and membranes.
- Contaminants are immobilized and will not desorb, re-release and pollute downstream systems.
- High flow and small footprint (60 gallons per minute with 10-inch diameter vessel; 780 gallons per minute with 57-inch diameter vessel) employing standard 30-inch high HRM cartridges.
- Hazardous waste reduction: One pound of HRM polypropylene media captures between one and two pounds of hydrocarbons before saturation.
- Easily and inexpensively disposed (no residual water, high BTU valve).
- HRM units run in parallel for continuous operations, eliminating shutdowns; HRM cartridges are quickly changed, saving downtime due to maintenance and start-up.

Discharging and Closing the Loop with HRM Technology

HRM technology, first made commercially available in 1998, is proven industry-wide for the removal of petroleum-type hydrocarbons from industrial wastewater, process water, storm water and bilge water. HRM systems are best used after gross removal and before conventional polishing technologies, and are most economical treating water with less than 100 ppm hydrocarbon contamination. Particle filtration to 5 microns may be required to protect the HRM from loading with suspended solids.

HRM treated water can be discharged in most cases, and it is only a polishing step away from being re-used.

Case Study: Machining Plant with Lube Oil in Wastewater

Four (30 inch tall) HRM 5 micron cartridges were installed prior to Nanofiltration (NF) membranes to protect them from loading and fouling with emulsified lube oil. The configuration of the system is as follows:

UF → HRM Cartridge Unit (10" x 40" Vessel) → Hold Tank → NF → RO

- An ultrafiltration (UF) system, consisting of "sintered stainless steel" (0.1 micron) membranes, removes gross lube oil and metal particles; the UF system intermittently discharges between 20 to 80 ppm emulsified oil in water at 40 gallons per minute (gpm).
- The NF system consists of spiral-wound polymer membranes (40 gpm). The NF system feeds two 20 gpm RO systems for a final polish.
- The HRM unit, containing 4 pounds of cartridge media, captures on average 2.7 kilograms or 5.9 pounds of lube oil and treats between 85,000-100,000 gallons of water (this works out to roughly 0.36 cents per gallon over 100,000 gallons, and depends on the total inlet concentration of oil).
- Typical operating pressure drops across the HRM vessel are between 2.5 psi (initial) and 3.0 psi (final).

The HRM unit significantly reduces the rate of NF membrane fouling and preserves the NF system's efficiency and percent recovery. Data indicates that the HRM unit will extend NF membrane service-life five to seven times, as well as reduce annual energy, maintenance and downtime requirements.

Conclusion

Treating and filtering feed water prior to conventional polishing systems is critical to maintain performance and limit operational costs. Separating dilute oily hydrocarbons and solvents in a single-pass without restricting flow is novel and creates newfound economics for oily water applications. Treatment systems employing HRM technology are more robust and generate savings by reducing energy, raw material, chemical, maintenance and downtime requirements.

HRM technology is allowing industrial facilities to more effectively address wastewater discharge, process water recovery, water re-use and zero liquid discharge (ZLD). HRM applications also include boilers, cooling towers, chillers, swimming pools and other close-loop water systems.

This article originally appeared in the September 2002 issue of *Environmental Protection*, Vol. 13, No. 8, p. 41.

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