INTELLIGENT DECISION-MAKING

What Recycling Methods Will Work Best?

When altering the recycling or waste treatment process within a cleaning system, savvy manufacturers will benefit from becoming their own "experts" in recycling technology.

by Rick Reynolds

In the parts cleaning industry, much of the data and information about products and services are supplied by vendors and individuals employed by vendors. This is not to say that such information is without merit; it simply means that favorable statistics are likely to be the focus of manufacturer-generated data regarding the relative performance of various products.

This can lead to difficulty and confusion in making decisions that are well informed and based on knowledge of the entire spectrum of available options. It is the intent of this article to offer a fairly broad and objective look at the good, the bad, and the sometimes ugly considerations that should be made when altering recycling and waste treatment processes within cleaning systems. The goal of this discussion is to promote creative and independent thinking, thus reducing reliance on singular and potentially biased sources of information. This discussion will not include an in-depth analysis of every available technology, nor will it promote specific products over others.



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Simple Distillation and Beyond

Presently, recycling of many solvents is common practice, just as it was before the Montreal Protocol (and subsequent boom of aqueous cleaning). Recycling offers an obvious cost benefit and eliminates disposal costs and concerns. The most popular method of accomplishing this task was by simple distillation, a process inherent in vapor degreasing systems.

Since each solvent, including water, has a given boiling point (T_b), contaminated solutions of solvent could be recycled by boiling them in an apparatus designed to capture and condense the vapors, similar to how a simple degreaser operates. Knowing the T_b of the pure solvent, the temperature of the vapor from distillation could be measured; when that temperature equaled the desired T_b, that vapor would be condensed and collected for reuse as pure solvent. What remains after distillation would represent the contamination and would be treated as waste.

This process could also be used to purify certain azeotropic solutions (solutions containing at least two components that cannot be separated by distillation). For a co-solvent system, the process is simply modified and termed "fractional distillation." This type of distillation takes place in the presence of two or more $T_{\rm b}$ s; as the vapor temperature shifts from one to another, the solvent condensate is collected in different containers to separate the solvents and later remix them at the appropriate ratio. These processes were, and still are, generally performed by the solvent manufacturers, solvent reclaim companies, and even at the cleaning operation if the required equipment is available.

There are methods available in which some solvents, especially chlorinated ones, can be recovered via adsorption onto activated carbon fibers. This method has been found especially useful in applications where solvents tend to be reactive and/or corrosive. Other simple methods—such as adding drying agents like zeolites and sodium sulfates to solvents—serve to remove water and some water-soluble contamination. There are still other methods of solvent reclaim available, but they will not be discussed here in the interest of space and relevance.

Methods of Recycling and Wastewater Treatment

It would be wise to start with a quick review of the major types of recycling processes that are available. It is important, before considering any action dealing with contaminant treatment, to first consider which of these processes best fits with the financial, ecologic, personnel, and time management goals of a given cleaning operation. There are three main categories into which an operation can fall:

- Closed-Loop Recycling—treating and recycling all wash and rinse baths for reuse in the cleaning system.
- Zero-Discharge—treating or recycling all, part, or none of the wash and rinse baths, with the remainder being collected and hauled to another location for treatment and/or disposal.
- End-of-Pipe Wastewater Treatment/Recycling—a system that treats all or part of the effluent from wash and rinse baths, such that the final product can be discharged directly to local sewer lines or streams. The remainder of solution is either reused or hauled away for treatment.

Weighing all the options is an important part of deciding the correct method of waste treatment. The time and effort to evaluate the short- and long-term costs of a waste treatment/recycling system versus dumping and hauling or dilution could lead to some surprising insights. Depending on the properties of the soils and cleaning agents, an effective treatment/recycling system may not be available, although some type of treatment system can generally be found. It merely becomes a question of whether that level of treatment is acceptable to the customer.

The cost of running a treatment system—in terms of manpower, fresh media and filters, and energy—may end up being higher than the cost of dumping spent solution and paying someone else to dispose of it properly. In some rare cases, depending on the soils in the washwater, the solution to pollution *might be* dilution. It is important however, to check with federal, state, and local regulations regarding what is acceptable in a waste stream in terms of identity and level of contaminant. Make a note of the liabilities for noncompliance because they can be severe. Again, this is rarely the case, so be sure before simply diluting and dumping.

Know Your Soil

It is important to note that there are different ways that soils can be presented to a treatment system. The nature of these soils will be instrumental in dictating how they can be removed:

- Tramp soils are soils that immediately float to the surface of the cleaning solution.
- Mechanically dispersed soils refer to oils/greases and other organic soils that have been dispersed though agitation; they will either eventually float to the top of the cleaning solution or fall to the bottom within a given period of time.
- Chemically dispersed soils are those that are naturally soluble in water or have been chemically dispersed by surfactants to form a *stable* emulsion.
- Particulate soils include carbon, rust, iron filings, etc.

Recycling and Treatment Technologies

There are a number of methods by which oils and other contaminants can be separated from and treated in wash- and rinsewater baths: (1) decanting; (2) skimming; (3) coalescing; (4) absorption/adsorption; (5) filtration (macro and membrane); (6) ion-exchange; and (7) UV radiation/oxidation. Each plays a unique role, and numerous combinations may be employed for optimum .efficiency; it all depends on the characteristics of the solution being treated.

All of the media and equipment in each category may be broadly represented as either disposable or reusable. Disposable media is simply discarded upon being saturated with contaminant, while reusable media either self-regenerates or is cleaned on- or off-site and reused. Again, it is up to the individual to decide which of these two categories offers more in terms of cost savings and performance for a given system.

Decanting. Decanting is generally only applicable when there are large amounts of tramp oils present in a solution. The oil is essentially overflowed from the surface of the solution into a holding tank. The limitations of this method are mainly that: (1) it does not account for any chemically dispersed soils; (2) it does not account for much of the mechanically dispersed soils (unless the solution is allowed to stand and break); and (3) it frequently allows the tramp oils to become contaminated with cleaning solution that also has overflowed.

A new design method somewhat related to decanting, termed thin-film fluid recovery,' shows a great deal of promise for removing tramp, mechanically dispersed, and chemically dispersed oils simultaneously from cleaning and rinse solutions. This method is based on an adaptation of the theory of the Bernoulli Effect, which simply means that the pressure of a stream of fluid along its streamline is reduced as its speed of flow is increased (see "Separation Anxiety." Parts Cleaning, October 1998).

Skimming. Skimming works on the premise that a lipophilic surface (wheel, rope, or belt) passes in and out of the cleaning solution. As oils adhere to the surface, they are removed from the solution and deposited elsewhere. Skimming has its benefits in that large levels of cleaning solution are typically not removed. However, it also has a strong potential to remove surfactants and some corrosion inhibitors in conjunction with the emulsified soils.

Coalescing. Coalescing works according to the notion that mechanically emulsified oil will move across plates or media that will selectively adsorb the oil. As more and more oil accumulates, it will coalesce and float to the surface, where it can be decanted or skimmed.

Absorption/Adsorption. Absorption technology involves passing a contaminated solution over a media (generally woven or granular), which is lipophilic and hydrophobic. In this manner only organic material is absorbed and all aqueous entities are retained in solution. Again, both of these methods suffer from the potential to remove surfactants and some corrosion inhibitors.

In many instances where organic contamination of baths is fairly low, activated carbon can be used to adsorb and remove organic materials and residual chlorine. Carbon is generally placed downstream from skimming and filtration processes to minimize its exposure to unnecessary contamination. It is generally used only for recycling rinsewater, due to the presence of organic surfactants removed from wash baths.

Activated carbon works by way of selectively adsorbing certain molecules (mostly organic ones) to the inner surface of the carbon structure. The ability of carbon to adsorb is dependent on the inner surface area, pore size, and the ability of molecules to wet and enter said pores. Naturally, there must also be an attraction between the contaminant and the carbon. It is important to work with the vendor to determine if carbon is appropriate for a given process and, if so, what grade to use.

Filtration. There are numerous types of filtration. They can be grossly classified into conventional and membrane technologies. Each technology works best within a given particulate size range (see Figure 1, page 22).²

Conventional filtration, or macro-filtration, covers a particle size range from about 1 micron and up. Common methods for this type of filtration involve bag filters and depth filters; however, sand filters and strainers are also used. These types of filters are generally used as a first step to remove any large particles or debris that could be harmful to the remainder of the system.

Bag filters are most commonly constructed from woven cloth or plastic fibers, such as nylon, polypropylene, and polyethylene. These filters simply fit inside a sealed housing. Fluid flows into the top of the housing and hag, it is then strained through the entire bag, and the filtered fluid exits through the bottom of the housing. Depth filters typically are quite coarse at the entrance face of the filter and then taper down to a finer porosity at the exit face. In this manner, larger particles are screened out first, thereby improving the speed and efficiency of the filter.

Some new and emerging macro-filtration media technologies have been recently discussed in the literature' and include:

- Cold fiber technology. This works on the principle of incorporating large-diameter polypropylene fibers within a filter matrix to provide extended filter life and more efficient filtration of viscous fluids.
- Triboelectric media. This works on the principle of an inherent magnetic attraction between the filter media and the soils being removed.
- Fluoropolymer media. This technology offers superior chemical resistance in many aggressive chemical environments.
- Gradient-density melt-blown fabric. Gradient density has the potential to increase liquid flow and soil retention over traditional fabrics.
- Multi-round plastic housings. These have the potential to offer increased chemical resistance where needed, as well as a smoother surface.

Membrane technologies, like macro filtration, serve the purpose of separating contamination from the water. Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are all membrane technologies with relatively descending pore sizes (see Figure 1). They are tailored to be most effective within certain contaminant size ranges. This is done via engineering specific pore sizes in the membrane material.

All of these technologies work on the principle of passing a stream of contaminated water over the membrane. As this is done, there will be two streams that are ejected. One stream is termed the "permeate" stream and represents that which was small enough to pass through the membrane. The other stream is termed the "concentrate," or "retentate," stream and represents the initial stream that contains all of the particles that did not make it through the membrane. This retentate stream can be either rejected or passed across the membrane again for further purification.

Figure 2 provides a rough indication of the types of filtration imparted by various forms of membrane technologies.' Most membrane technologies are limited by the tendency to remove emulsified soils along with the surfactants that encapsulate them. It is therefore important to understand that, depending on the type of cleaning agent being used, the agent may need to he continuously replaced in the bath. These systems are exceptionally well suited for rinsewater recycling, assuming that contamination is minimized in the rinsewater.





Membranes also have the inherent potential for clogging. Again, depending on the solution being treated and how that solution is prepped before entering the membrane zone, membranes may need to be cleaned and/or replaced periodically.

Technologies have been developed' in the micro- and ultrafiltration range that help to continuously clean and refresh the surface of the mernbrane, thereby preventing or eliminating clogging and extending their operational lifetime.

In any situation where membrane filtration technology is considered, it is important to be certain not only that it is indeed the most appropriate method, but that it is not overagressive for the job at hand. This filtration does have the potential to strip valuable constituents from the cleaning agent. Again, proper synergy between the cleaning agent and recycling system is important.

Ion Exchange. Ion exchange is primarily used for the treatment and recycling of rinsewater. This is due to the fact that rinsewater should have a very low level of ionic contamination such that the lifetime of the ion exchange media will not be unnecessarily short. Ion exchange media is generally supplied in the form of resins contained in enclosed "resin beds." The resin material generally consists of functional groups attached to naturally occurring or synthetic polymer backbones. These functional groups carry either a positive or a negative ionic charge and serve to retain anions and cations, respectively. An example of this is a cationic resin containing sulfonic acid. This mechanism will retain cations, such as magnesium and calcium, by "exchanging" the Mg^{2+} or Ca^{2+} ion for the hydrogen (H⁺) ion on the sulfonic acid. In this manner, calcium carbonate (CaCO₃) will enter the resin and leave as carbonic acid (H₂CO₃), which will auto-degrade in neutral-alkaline conditions to water (H₂O) and carbon dioxide (CO₂), thus removing the contamination.

Ion exchange media can be purchased in a variety of types, depending on the application. Naturally, this type of system has the potential to remove any ionic constituents from aqueous cleaners: saponifiers, builders, corrosion inhibitors, etc. It is important to be sure of its necessity and its effects on the system before installing.

UV Radiation. In lieu of using carbon to remove organic residues, there is also a technology known as UV radiation or catalytic oxidation." This technique is widely used in the water purifying arena for its biological sterilization abilities.

In this process, water is treated with hydrogen peroxide and/or ozone gas. The solution is then pumped through a UV light tube that converts the dissolved oxygen into hydroxyl radicals. Hydroxyl radicals are exceptionally strong oxidizers and serve to react with and break down organic molecules. The addition of titanium dioxide has been shown to catalyze the reaction; however, the titanium ion does not disappear. Being a heavy metal cation, the presence of this ion could negatively impact the performance of the cleaning system if recycled. The true performance of such a system should be tested for efficacy with each individual application, since organic type and loading will vary from application to application.

Factors That Influence Recycling

In choosing any recycling system, it is helpful to remember that the following factors will play a role in the efficiency of the system: pH, foam, surfactant type, suspended soils, temperature, oil/grease/soil type, and pressure. Make sure that the manufacturer explains the effects of each of these parameters on the system that is chosen. What you expect from a recycling system and the nature of the chemistry involved will dictate which method you choose.

Drag-out is another issue that must be considered in many aqueous systems. Drag-out is liquid (primarily contaminated cleaning agents) that is carried from one cleaning process (ie, washing) to another (ie, rinsing). It comes generally in the form of liquid spray from adjacent zones in in-line machines, cycle-to-cycle overflow from partially draining reservoirs in batch machines, and liquid clinging to parts that are moving from one stage to the next during the cleaning process.

Minimizing drag-out in cleaning systems serves two major functions: (1) it preserves the cleanliness and quality of successive wash/rinse baths; and (2) it minimizes strain on recycling operations for these baths. Methods of accomplishing this should be discussed with the equipment manufacturer.

The quality of the incoming water is another important factor to consider when selecting a recycling method. Incoming water has the potential to bring along a host of contaminants that can hinder the performance of aqueous cleaning agents and the treatment and recycling systems with which they are coupled. Often, cleaners that contain carbonates, silicates, borates, and other anions will come in contact with magnesium, calcium, and trace amounts of other metals (common to tap water). The result will be the formation of insoluble and sometimes tenacious precipitates. Also, tap water generally contains low levels of silica, which can leave residues on parts and equipment. All of these water-based contaminants are capable of adhering to surfaces being cleaned, adding to filtration and recycling difficulties and leading to residue problems on parts down the line.

On the other hand, ultra-high purity water, with resistivities in the 10 Ω -18 Ω range, is rarely necessary at all points in the system. Even in the final rinse, this type of purity is rarely seen anywhere outside the enclosed purifier unit. As soon as the water leaves the system and comes into contact with air and carbon dioxide, this CO₂ is quickly absorbed, bringing a significant drop in the resistivity. This dissolved CO₂ very rarely has any impact on the performance of a cleaner or the tendency of a rinse to leave a residue.

The key is to pay for a system that adequately removes the contaminants that are of real concern. For wash baths, a purity range of 0.5 Ω -1.0 Ω is generally adequate. For rinsing operations, these standards might be raised depending on the cleanliness specs that have been set. Why pay to ultrapurify all the water when only a small part of the process may need such treatment as a final rinse?

Of course, there are always some things that just cannot be recycled efficiently due to their nature (eg, contaminants cannot be separated and/or the active cleaner cannot be effectively preserved). In such cases, the spent bath solution must be either incinerated, evaporated, or chemically treated, filtered, and disposed once the content has been brought to environmentally acceptable levels.

Getting What You Need From the Vendor

The subject of formulating cleaning agents is a multifaceted challenge for chemical vendors. They are faced with developing cleaning solutions that will:

- clean efficiently;
- prevent corrosion in the cleaning process;
- prevent soil redeposition;
- potentially prevent corrosion and resoiling *after* the cleaning process;
- be environmentally and worker safe;
- be compatible with current and upcoming types of recycling and waste treatment equipment; and
- be cost-effective.

On the issue of making surfactants and emulsions compatible with many types of filtration equipment, a study has been published' that describes a family(ies) of surfactants that is (are) being engineered to be "membrane friendly." Naturally, the key to the entire equation lies in maintaining a high level of cleaning capability all through the development. Finding the environments in which these surfactants perform best will also be important. These challenges rest with the cleaning agent vendors and their fieldtesting staffs, should they decide to pursue them.

But don't let all of the sympathy fall on the chemical vendors. Equipment and recycling/treatment system manufacturers face a lot of the same issues, having to develop products that will be compatible with each other and the cleaning agents. This further illustrates the need for each of these industries to explore the potential benefits of working together in some fashion to develop an optimum cleaning process. In the end it is the customers who must recommend that these vendors work together to produce the best possible system for their cleaning needs; after all, they're the ones paying the bills!

Regardless of size, what separates a valuable supplier in this industry from the rest are the following characteristics:

- A strong base of knowledge about aqueous cleaning chemistry and how it functions.
- A willingness to explore new options and ideas.
- The ability to work directly with customers and their unique applications, given that very few are doing the exact same thing. Another valuable aspect of developing a winning system—although not absolutely necessary -is a good working relationship between recycling/treatment, cleaning agent, and equipment suppliers. This can greatly improve the ease of implementation of the entire process due to the simple fact that total cleaning system performance is never directly related to just one factor. It takes everything working in harmony-chemistry, time, temperature, agitation, and treatment -to make a cleaning process truly successful.

It is a good idea to ask vendors for references of other customers with similar applications. If a vendor is "on the level" and truly has a quality system, this should not be a problem. Ask these customers about the systems they purchased; naturally, they cannot be expected to divulge proprietary information, but a general feeling about the efficiency and the capabilities of the system are easily answered questions.

The industry is definitely moving in the right direction. Suppliers of every aspect of the cleaning process are looking for value-added methods of improving the recycling/treatment capabilities of cleaning systems. Just like the race to develop replacements for CFCs, the focus is on who can do it first, best, and in a manner that will be most cost-efficient in the long run.

Although it is not always an option, don't forget that changing the soil (oil, grease, flux, etc.) to one that is more easily cleaned and treated can be a simple and viable solution to wastewater treatment problems. Sometimes, merely switching to water-soluble oil can be an option. Manufacturers need to understand that no matter what new process they are adding to or removing from their system, the effects of that change must be compatible with the rest of the system or it simply will not work.

Simply blaming the lack of efficiency on one or more of the components in the system is fruitless. Each of these components is a valuable and effective entity when used in an appropriate situation. The key is simply to choose components that work well together. For example, when someone wishes to change from a vapor degreaser to an aqueous chemistry, it is widely understood that the equipment must change, too. To a lesser extent, the same scenario is true when adding or replacing waste treatment/recycling options.

Just because a wash bath recycling system needs to be added to the cleaning system, that does not necessarily mean that the chemistry is compatible. There are many cases where a drop-in solution works well, but there are many cases where it does not. Sometimes the recycling system is not the ideal for the chemistry being used; sometimes a new chemistry must be found that will offer cleaning performance and be compatible with the chosen waste treatment system. Before any decision is made about changing an integral part of the cleaning system, system priorities should be established.

Conclusion

With all of the available options for recycling and treating wastewater, choosing the one that is right can seem like an impossible task. The key to making intelligent and economically successful decisions is to first gain a complete knowledge of the system to be treated. Then, make a checklist of all the possible links in the system that will be affected by a change. Remember that a change in one could bring a change in the rest. Determine which elements within the system have the most rigid limitations, both from performance and financial standpoints. Those are the elements that must be placed first when considering compatibility issues. Wherever else change may come to the process, leave the option available for making that change one that will be compatible with the new and/or improved systems.

Try to make a primary assessment of what type of system will

work best for your process. Then work closely with reputable vendors who deal with those systems to find the best solution. Sometimes it can involve a lot of tedious work, but in the end the result will be an efficient, worry-free system.

References

1. Scambos, JP. A mechanical innovation for oil separation. Precision Cleaning. August 1997:9–11.

2. Peterson DS. Practical Guide to Industrial Metal Cleaning. Cincinnati, Ohio: Hanser Gardner Publications. 1997: 116–133.

3. Gregor EC. New and emerging filtration media come through. Precision Cleaning. September 1997:29–34.

4. Cartwright PS. Useful applications of membrane technologies in precision cleaning processes. Precision Cleaning. September 1995:23–38.

5. Savage GS. Optimizing aqueous cleaning wing vortex flow filtration. Precision Cleaning. March 1998:18–21.

6. Fink RG. Wash water recycling in the metals industry using the catalytic oxidation process. Parts Cleaning. April 1997:31-33.

7. Ventura M and Dahanayake M. Surfactant class resolves separation anxiety. Precision Cleaning. July 1998: 14–18.

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