New Econometric Models for Ion Exchange Systems

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Introduction

Those of us who have been working in water plants for several decades have seen many changes in technology. The advent of UPS beads and packed beds in ion exchange, and the soaring development of membrane processes are good examples. The rapid deployment of computer-based control systems and massive central data warehouses are other good examples.

There have also been changes in management philosophy and business models. We have gone from "what's a water plant?" through the Quality Movement to current Best Practices. (RTI is currently working on identifying best practices for demineralizers and will announce in 2009 a new program based on that termed Five Star.)

In former times the operating costs of a water plant were considered a necessary overhead, a cost of running a paper mill or generating electricity. Now, like all departmental budgets, they are subject to heavy cost cutting efforts.

The purpose of this paper is simple: to provide a roadmap identifying ways to reduce costs in the operation of a water plant. We will focus specifically on resin-based demineralizers and we call this roadmap the Resin Management Program.

Ion Exchange 101

There are two major geometries of resin-based systems:

- Cation exchanger followed by anion exchanger
- Cation/Anion exchangers followed by mixed bed polishers

Within the cation and anion category, there are numerous variations with weak and strong resins, layered beds, packed beds, twin packed beds in a single vessel. All can be with or without decarbonator or degasifier.

Any of the above variations of cation/anion sets can be followed with a mixed bed polisher. When used in that geometry, the cation/anion part is called the "primary demineralizers," vs. the mixed bed, which acts as a "polisher," taking the water to ultimate purity.

The answer to the question "Why are there so many variations on demin design?" is that there are so many different inlet waters to treat and the degree of purity needed from the demin system varies with the application. This is very clear in the utility area where water chemistry limits vary strongly with boiler pressure and turbine design.

Virtually all ion exchange systems are batch processes. Water is purified in the service cycle, exhausting the chemical capacity of the resins. The exhausted resins are taken off line and prepared for the next service cycle by the process of regeneration with acid or caustic solutions. One can think of the resins as chemical machines. They do the chemical "work" of purifying water in the service cycle until they run out of energy. Then they need to be "wound up" again, like a clock, with acid and caustic. There are various ways to optimize the service cycle and there are many ways to optimize the regeneration phase of the operation.

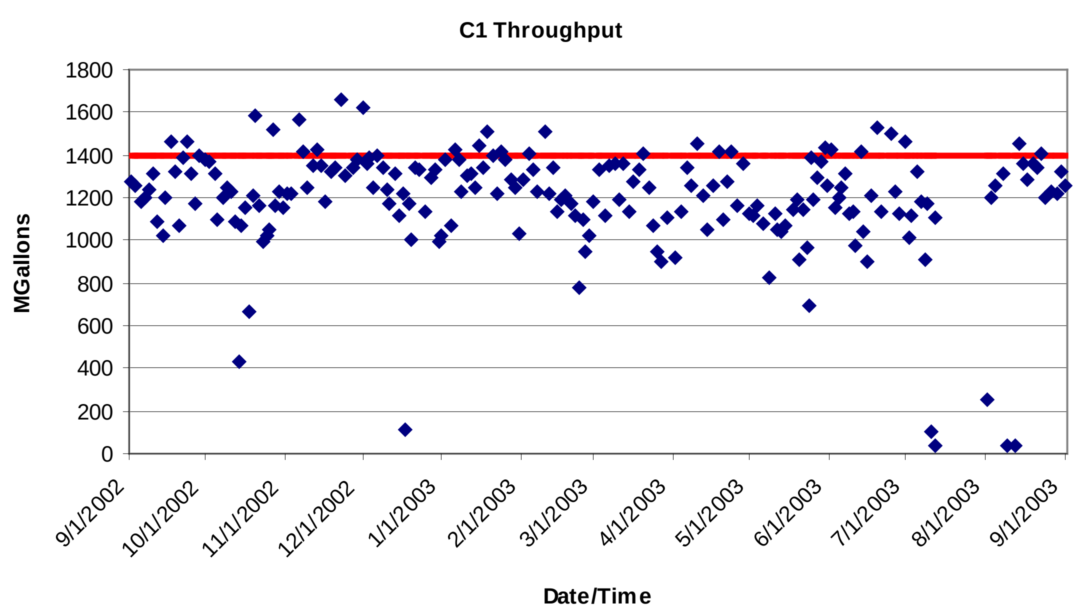
Service Cycle

The service cycle represents the hours on line purifying water or the total volume of purified water. There are two major ways to determine when to end the service run:

- Operation to a preset volume of purified water
- Operation to chemical break

Operation to a preset volume has the advantage of simplicity and (usually) predictability, especially with constant flow. There can be unexpected problems during periods of really "bad" inlet water, where the system can be exhausted before the setpoint is reached. Some areas of the US are seeing unprecedented droughts and are faced with this exact problem.

Over the years we at RTI have seen that many systems alleged to be operating to setpoint are in fact being taken off early. Water plant operating engineers do and should have the authority to take a run off early. Their main objective is to deploy the various trains to space out the regenerations so the water plant will not get "backed up" with several vessels needing regeneration at the same time. But when the practice is carried to excess, we can get the following performance:



This data was from a very large water plant at a major Gulf Coast chemical company. Until our involvement, staff engineering as well as management was totally unaware of the large numbers of shortfalls or TOEs (Taken Off Early).

There is nothing inherently wrong with operation to setpoint, but there are some caveats:

- Make sure the majority of runs reach setpoint
- Identify the causes for those which do not
- Check the setpoint periodically to see if the value is correct for current conditions

In the above graph, notice the many runs which exceeded setpoint, some by a wide margin. This tells us the setpoint is likely too low. What does a setpoint 15% lower than theoretical do to your budget? You are spending 15% more each month for acid and caustic than necessary. If your monthly regenerant cost is $100,000, you are wasting $15,000 a month.

Chemical Break

Most demineralizer systems are operated to chemical break, not setpoint. Since anion resin costs more than cation resin, most systems are anion-limited. When the available capacity of an anion is used up in a service run, the first species to break through is silica. Since silica is of critical concern for boilers and turbines, we need to end the run when it shows up. This is operation to chemical break or breakthrough, and for the most part it represents the optimal way to run the service cycle. The service cycle can last from 12 hours to 24 hours or more.

Regeneration Cycle

Once the unit is offline, the resin bed must be regenerated; the clock must be wound up. Here are the main steps for the cation and anion regeneration:

- Backwashes (unless we are using counter-current regen or the vessel is a packed bed)
- Acid and caustic injection (maybe with an anion preheat)
- Displacement rinses
- Final rinses (maybe with a recycle step)

Depending on how the above steps are arranged, regeneration can take between 2.5 hours and 5 or 6 hours.

Resin Management Program

Ion exchange is a cost-benefit operation. The main costs are the amounts of acid and caustic needed for the regeneration cycle. The benefit is purified water from the service cycle. There are two key metrics used in ion exchange to quantify the cost-benefit: demineralizer efficiency and demineralizer cost to operate. They are defined as follows:

- Demin efficiency: thousands of gallons of DI per pound of acid or caustic
- Demin cost to operate: $ per thousand of gallons of DI water

Demin efficiency measures the chemical usage factors: how much DI water can we make with a unit amount of acid or caustic. Demin cost to operate is the reciprocal of efficiency, but using the actual costs of regenerant instead of amounts. We define the factors in this fashion in order for them to make sense. Everyone knows that efficiency should be as high as possible, so we aim for getting as much DI water production as we can for a given investment of acid and caustic. Likewise, the cost to operate should be as low as possible. These objectives can be achieved by the Resin Management Program.

In the earlier history of ion exchange, there was a version of efficiency termed "regeneration efficiency." It was an odd measurement in that strong acid resins were said to regenerate at 300% efficiency, whereas weak acid resins operated at 100% efficiency. Strong acid resins really regenerate at 33% efficiency and turning the number upside down does not magically take away the sting of waste acid. Likewise, strong base resins regenerate at 25% efficiency, not 400%. Regeneration efficiency was a triumph of marketing over common sense.

The cost of regeneration includes the following factors:

- Cost of filtered water (if any)
- Total pounds of acid
- Current cost of acid
- Total pounds of caustic
- Current cost of caustic
- Cost of DI dilution water (if any)
- Cost of disposal of spent regenerant (if any)

The cost of purchasing acid and caustic are real costs, involving real money. The cost of filtered water, DI dilution water, and waste disposal are internal costs, "paper" money in the sense of budget entries. The latter costs might be allocated or pro-rated on volume, rather than driven by a purchase order to an outside vendor. In smaller operations, tracking purchases of acid and caustic might be the only cost factors in the water plant budget. In larger operations, which might have several users of filtered water and several sources of waste water, the budgeted entries also become important.

One of the tools available in the Resin Management Program to track demineralizer efficiency and cost to operate is EconoTrac. The latter was introduced at this conference two years ago and we will give an update after the following sections.

Resin Fouling

No machine operates at constant efficiency. A car might need an occasional tune up. The fireside of a boiler needs daily soot blowing, and the water side might have to be chemically cleaned every few years. Even a turbine needs an overhaul after five or ten years. Entropy always wins.

With ion exchange demineralizers, efficiency is slowly diminished by fouling, steadily increasing the cost to operate. Despite efforts to pre-treat the cation inlet (such as clarifiers, filters, activated carbon, etc.), there are still foulants which get through, as shown in the following table:

Foulant	Resin Affected	Problem
Silt (from clarifiers)	Cation (usually)	High pressure drop, channeling, short runs
Iron	Cation (usually)	Can coat the resins
Hardness (Ca, Ba)	Cation	Long rinses, shortened *anion* runs
Bacteria, fungi	Cation and Anion	Colonies can cause high pressure drop, channeling, short runs
"Natural organics"	Anion	Long rinses, shortened runs

Since most demineralizers are anion-limited, as mentioned above, the biggest and most common, long-term threat to demineralizer efficiency is organic fouling of the anion resin beads.

Organic Fouling

Natural organics occur in all surface waters and in shallow-well ground waters. They represent a huge family of compounds and there is a rich technical literature in their occurrence and chemistry. In sum, they are moderate to large molecules, anionic in charge, which get trapped within the anion exchange resin. Although their concentration in the water might be only a few ppm (measured as TOC, Total Organic Carbon), after millions of gallons have passed through an anion bed, this represents a large amount of material. This can be readily seen in practice: new, golden anion resin beads are quickly darkened as they accumulate organics, which themselves are colored molecules. Think of tea or coffee – that is precisely the same class of chemicals as natural organics in a river.

Some organics are removed during regeneration, but our work has shown that fraction to be quite small, <1%. This means the organics slowly accumulate within the anion resin bead, leading to fouling, intense darkening of the resins, and gradual operational problems.

There are two insidious results of this fouling:

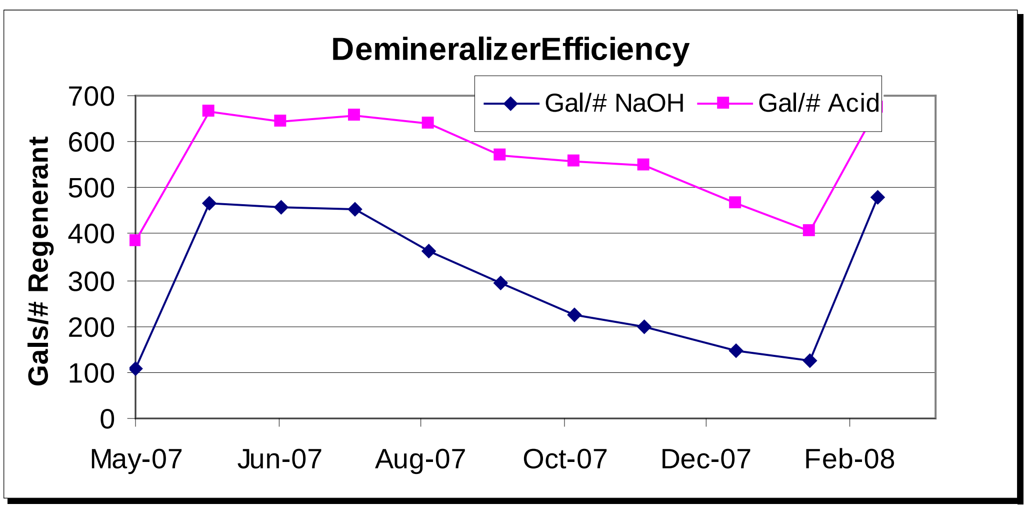
- Gradual reduction in throughput, and
- Gradual increase in the final rinse time

The reduction in throughput occurs because the organic molecules, as anions, take up active sites in the resin beads, lowering the number of sites available to treat the other anions in the water. Because they are literally trapped within the resin, they can also mask active groups even during resin testing.

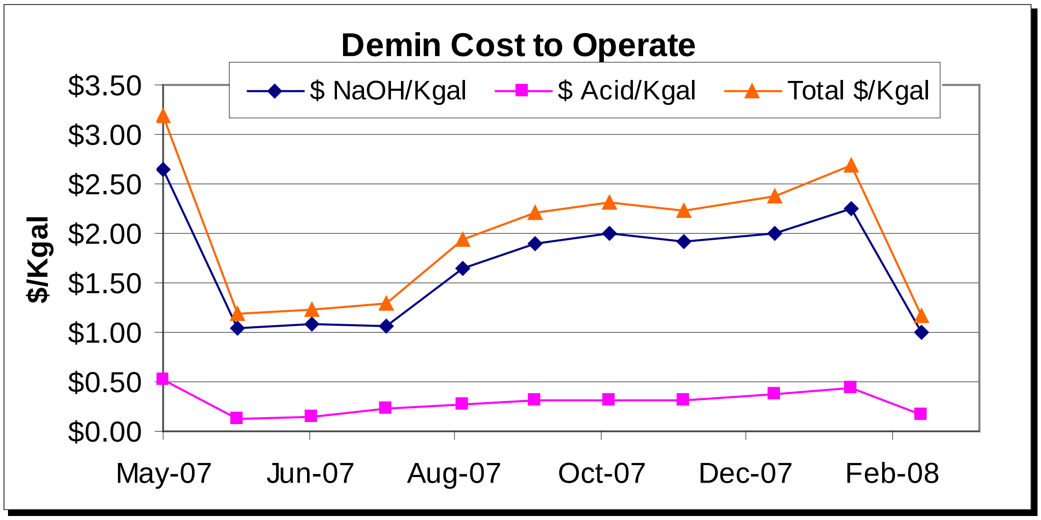
Organic fouling can also prolong the anion final rinse by "bleeding out" sodium ions. This raises the conductivity and a longer (sometimes a much longer) rinse time is needed to reach the return-to-service conductivity target. This longer rinse also subtracts from the run time available in the next service cycle.

EconoTrac

To accurately measure the fall-off in performance, i.e., the drop in demineralizer efficiency, we use EconoTrac. There are three plots below. One is demin efficiency, expressed as 1000 gallons per pound of acid and caustic. The second is demin cost of operation, expressed as $ per 1000 gallons DI water on a monthly basis. The third is EconoTrac, the main economic metric. All the plots are real plant data.



The system was cleaned in June of 2007 and in March of this year. Demin efficiency increased after each cleaning, as we expect. This was followed by organic re-fouling.



Note the gradual rise in the cost to purify 1000 gallons of water, after an initial delay. This is the direct effect of organic fouling.

There are several complications associated with tracking demineralizer efficiency and cost to operate. There are factors other than resin fouling which have to be considered – and factored out.

With a surface water, the total mineral contamination level (dissolved salts) can vary monthly, seasonally, even over longer time frames. Heavy runoff can lower inlet conductivity (but raise organic fouling levels). Lower inlet conductivity means the demineralizers can treat more water, since the ionic loading is lower. On the other hand, drought can raise inlet conductivity and this will directly result in less treated water. Here's a simple table showing this effect:

Inlet Conductivity	**Throughput, gallons**
300 µS	500,000
600 µS	250,000

The reduction in throughput is not a demineralizer mal-performance. It is a fact of chemistry. Therefore, we do a normalization step to subtract out these inlet chemistry changes, so they do not obscure the fouling effect. With a well water showing fairly level conductivity, the normalization step is not needed. We also need to adjust for the variable days in a month, but that is simple to do.

Operators in some plants will change the regeneration protocol to adjust for problems. For example, many operators have found that extending the caustic injection step can often compensate for organic fouling. While it is true that using more caustic can, in certain circumstances, result in a longer run, this practice has a very damaging impact on demineralizer efficiency by directly raising the operating costs with only a marginal increase (if any) in the volume of purified water.

The large steps in the preceding diagram were produced by just such a change in caustic injection times. Since the system was being operated to a preset value, there was actually *no gain* in throughput. The extra caustic simply gave an acceptable rinse down, but the operators had no way of knowing the full economic impact of their decisions until we started EconoTrac.

Resin Cleaning

Organic fouling has been recognized as a demin problem for decades. Many plants have tried brine/caustic cleaning, a venerable but rather ineffective option. In the absence of effective cleaning procedures, it was common practice to replace expensive anion resin simply because it was fouled both in lab testing and in field use. That is no longer the case.

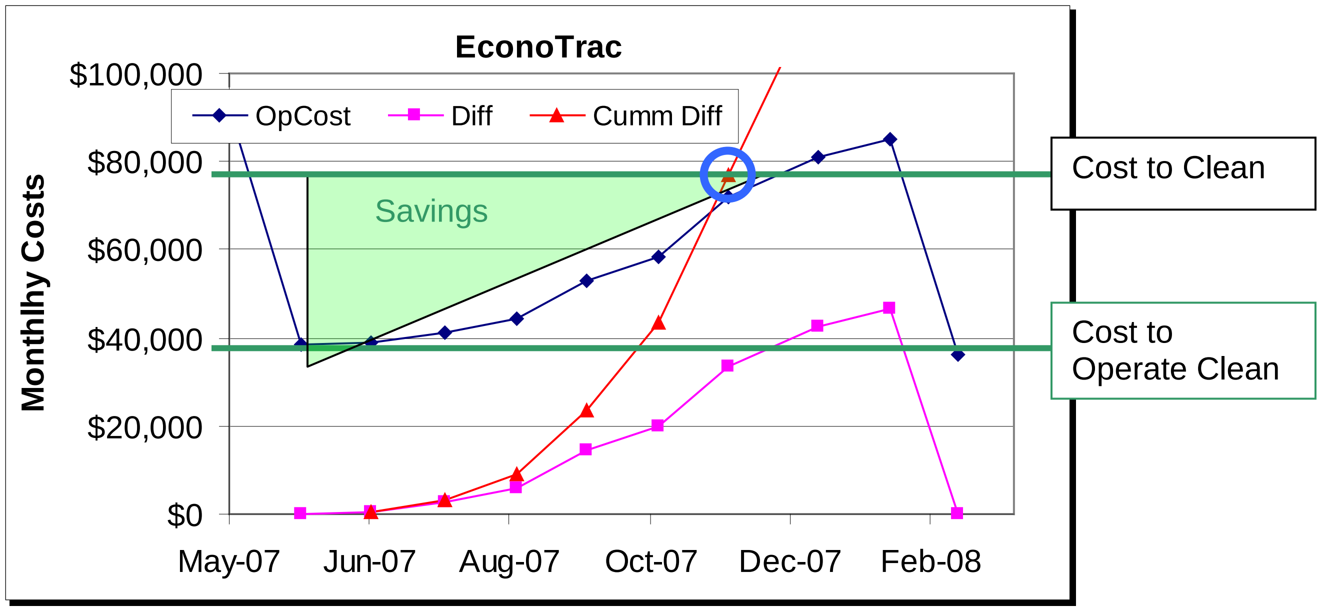
RTI has published numerous papers, including two at this conference, detailing the advent of ReStore +, a truly revolutionary cleaning option which very effectively destroys organic fouling within the resin beads, unmasking capacity and restoring the resin to an almost new condition. Cleaning anion resin is far more cost-effective than replacement.

We have detailed the gain in operating capacity, never seen before, after deep cleaning organic fouling off the beads, and we have many documented case histories of genuine gains in throughput.

When to Clean?

One of the vexing questions which quickly arose after the advent of ReStore + was "When is the optimal time to clean for fouling?" Many customers send us resins samples which are very highly fouled and the clear answer here is "You should have cleaned six months ago!" We continue to support resin analysis (see below), but we wanted a quantitative tool to track and **predict** when the optimal time to clean would be.

We showed earlier how the monthly demineralizer efficiency can drop with fouling. The new wrinkle here is to plot monthly operating costs and compare them against the cost of cleaning. To do that we use the monthly operating costs for the cleaned resin vs. the fouled resin as the base case. Once the resin is cleaned, the efficiency improves dramatically and the customer will now start to save operating expenses.



Organic re-fouling starts right after the cleaning, of course, but in most cases it takes a few months for the fouling to build up to the level where it impacts on the operation. When that occurs, the monthly costs will start to rise, eating into the savings. The key metric we use now is the cumulative increase in operating costs, representing the total increase in costs month by month over the base case. This is the red line, and it rises at an accelerating pace.

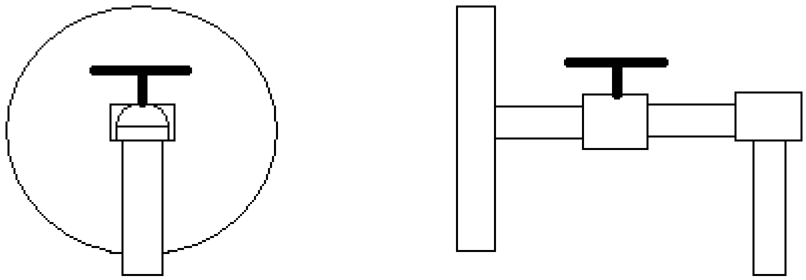
The optimal time to clean is when the cumulative increase in operating cost equals the cost to clean, as shown by the blue circle in the above graph. Cleaning before that time ignores savings from the first cleaning which can still be accrued. Cleaning after that time greatly increases the operating cost needlessly. That is, cleaning the resin at that point makes more sense economically than continuing to operate a further fouling system.

Resin Analysis

We ask customers on EconoTrac to submit yearly cation samples and quarterly anion samples. Cation re-fouling does not occur at the same rate as anion re-fouling, thus the spacing out of the sampling frequency. We track the re-accumulation of organics after the cleaning, as well as the drop off in available capacity which the organics cause.

Many customers find it extremely difficult to get resin samples. We have simplified the process by furnishing resin samplers installed on the vessel resin removal ports. Once the samplers are installed, it is very easy to get a resin sample in minutes. In addition, the manway of the vessel need not be opened. This eliminates the need for vessel lock out/tag out and other elaborate safety precautions, including the erection of scaffolding, again greatly speeding up the sampling.

A diagram of the sampling device is shown below:



The sampler replaces the blind flange normally sealing the resin removal port. The valve depicted above is a lockable ball valve. The lock is needed to prevent accidental opening of the valve while the unit is on-line; this would allow resin to quickly flood from the vessel onto the ground. The samplers should be made out of stainless steel.

A question naturally arises about the validity of sampling resin only from the bottom of the bed. For some resin tests, such as percent fines or bead size distribution, a core sample is required. For fouling levels and resin capacity tests, however, a sample from any part of the bed will provide accurate test results since the fouling chemistry and capacity values are uniform throughout the bed.

Conclusion

Like all other departments, the water plant has to trim operating costs. This can best be done by optimizing the efficiency of the operation and minimizing the costs, two sides of the same coin. Under a Resin Management Program, we can assist in tracking these costs, identifying negative trends, and suggesting various interventions, including cleaning the resins. With EconoTrac software, the main costs associated with demineralization are clearly displayed, providing objective criteria to finally answer the questions: "When is the best time to clean the resin? When does the resin need replacement?"