Reprinted from
PHARMACEUTICAL ENGINEERING
THE OFFICIAL TECHNICAL MAGAZINE OF ISPE
JULY/AUGUST 2014, VOL 34, NO 4

www.PharmaceuticalEngineering.org

Chemical and Media-Free Pretreatment for Biopharma RO – Electrolysis for Scale Precipitation and UV Dechlorination

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This article identifies the issues plaguing water systems with Reverse Osmosis (RO) and defines the proper criteria of operation.

Every system designer and end-user has to deal with many different criteria for the design and operation of biopharma pretreatment water systems. These criteria may include simplicity of operation, reliability, lower discharge of waste water or inexpensive lifetime costs.

As every system owner, operator, manager or design engineer has his own definition of what is an important criterion and what is not, it may be hard to identify accurately all priorities.

This article will focus the discussion on identifying the issues plaguing water systems with Reverse Osmosis (RO) and defining the proper criteria of operation. The RO membranes commonly have incorporated Polyamide (PA) as a main constituent which is sensitive to oxidation by free chlorine.[1] The reliable and efficient operation of the PA RO membrane is the main focus of this article.

A new system for pretreatment of pharmaceutical water systems will be presented that meets the prescribed design criteria with simplicity while providing effective results. This system operates without chemicals, media, or resins, and eliminates the need for regeneration, complicated instrumentation, and feedback loops. The system operates with no moving parts and without need of rinses or back washes.

Background

The traditional pretreatment of pharmaceutical water systems has installed modules to reduce contamination, reduce or eliminate chlorine/chloramine and remove double valent ion scalants, before feeding the water to the Reverse Osmosis (RO) system.[2] This modular approach has been successful in treating raw water for pharmaceutical usage, but the costs can be substantial for continued operations, salt purchase/usage, regeneration, water rinses, brine disposal, filtration, chemical additions of metabisulfite and microbial control. The Thin-film Composite (TFC) membranes used in RO systems are susceptible to microbial contamination and often require these modular components upstream to remove microbials and other contaminants from the water.[1]

Classical Designs

Common Solutions for Preventing Scale Precipitation in RO Systems: the Use of Softeners, Antiscalants (AS), and Acid Addition

Softeners use sodium ion exchange resin beads. Calcium and magnesium ions are removed from the water and exchanged with sodium ions. Depending on the system, the total hardness can be reliably reduced to below 10 ppm as $CaCO_3$. Resin bead based systems utilize sodium chloride to regenerate ion exchange resins that are saturated with calcium and magnesium. The total regeneration cycle has a series of rinses with varying concentrations of salts in the effluent. Once exchanged, the calcium and magnesium are sent to the drain by water rinse.

Often, the best operated softener system has wastage of fresh water needed for rinses. This intrinsic waste stream can vary from 5 to 25%[2,3] of total water volume depending on the incoming water hardness levels.

Local laws govern the disposal of salts and waste water disposal sent to the sewer; often a permit is needed for the disposal from the local Waste Water Treatment Plant (WWTP).

Runoff streams from the pretreatment and RO modules can be treated in the following ways:

- Collection and off-site disposal
- Treatment onsite to concentrate the solution for further disposal
- Drainage directly to municipality sewer with no further treatment
- Combinations of the above, dependent on conductivity

In addition to possible problems with effluent disposal, softeners filter out water borne contaminants. Organic resins can provide an environment for microbial growth due to the temperature and nutrient rich environment which often needs to be controlled. A sanitant, with a residual effect, is commonly added in the water. Oxidizers such as free chlorine or chloramine, are commonly administered for microbial destruction.

Chlorine/chloramines are not always an effective solution as the softener resin beds tend to channel. Channeling is a common phenomenon, in loose filtration media, as the water flow causes channels to develop which lessens the residence time in the media, causing diminished efficacy. When there is an appreciable build up of contaminants or thick biofilm, channeling can be affected. In this case, the sanitant will flow faster on the clean side of the resin leaving the clogged areas less exposed to the cleaning action.

All ion exchange resins are sensitive to free chlorine/chloramine oxidation. Resin beads break down and disintegrate over time as a result of either friction or chemical treatment. If the microbial Total Viable Count (TVC) starts to rise, the typical solution is to raise the oxidizer concentration, which causes more rapid softener resin disintegration[2] with an increased viable microbial environment. This, in turn, pushes the users to increase oxidizer concentration and so a vicious circle of cause and effect is formed. This cause and effect mechanism can be averted, as will be seen later in this article.

Antiscalant (AS)

These materials are dosed on the RO feed. The AS is a surface active material that interferes with precipitation reaction. The reaction can be retarded by dispersion, threshold inhibition or crystal modification.[2] AS addition is not dynamically controlled online; it is susceptible to fluctuations in ionic feed makeup. Typically, even with good AS performance, this system will need more acid cleaning of membranes than a softener-based pretreatment.

Acidification

Acidification has many of the characteristics of AS, as the acid is added to the RO feed. This acidification destroys carbonate ions, and stops calcium carbonate precipitation. This can be very effective in preventing the precipitation of calcium carbonate, but ineffective in preventing other types of scale, such as calcium sulfate.

In addition to nearly all the drawbacks of the AS addition, the acidification causes an excess of carbon dioxide (CO_2) in the RO permeate. Acids and all corrosive materials need controlled handling, storage and transport making the usage of these chemicals less desirable.

Common Solutions for Chlorine/Chloramine Removal in Pre RO Modules are Active Carbon Filtration (ACF) also known as Granulated Activated Charcoal (GAC) and Sodium Bisulfite (SBS)

Active Carbon Filtration (ACF)

Water is exposed to active carbon which removes the oxidizing chlorine/chloramine. The filters can be of the cartridge type, but more commonly are granules (GAC) packaged in a depth filter. GAC, although an excellent medium for chlorine/chloramine destruction, is also an excellent medium for microbial growth. The GAC bed must be backwashed and heat sanitized with a frequency of every few days to inhibit and control bacterial growth.[2,3]

Heat sanitization is a proven option for microbial control via clean steam or hot water above 85°C.[3] The heat sanitized ACF can be a complicated unit, with a plethora of pneumatic valves, temperature transmitters, pressure gauges and software needed for performance and documentation of the sanitization subroutine. In pharmaceutical pretreatment schemes, the ACF tank is usually manufactured from stainless steel. Typically, 316L stainless steel tanks are expensive to install.

Sodium bisulfite (SBS)

SBS is added to the feed water to remove free chlorine and chloramine. The reaction is fast, but an overdosing of two or three times above what is needed, is common. This safety factor is needed as the instrumentation has been known to drift, mixing may not be ideal, and other inaccuracies are possible due to fouling of the electrodes.

Without adequate chlorine/chloramine removal RO membranes are susceptible to damage. Inadequate or deficient sodium bisulfite administration can contribute significantly to membrane degradation.

Additionally, the constant overdosing of SBS can cause residue build-up on the membrane surface causing susceptibility to bacterial infestation of the membrane.

Common Solutions for Sanitization: Chemical Dosing

One of the most effective types of sanitization is the use of hot water. Some pretreatment systems are poorly suited for hot water sanitization as the piping and equipment is based on plastic polymers of PVC and other non-metallics.

Often, sanitization for city water and pretreatment is chemically based. Chemical sanitization can have many drawbacks. Some drawbacks can be the handling of dangerous chemicals, post sanitization validation, manpower involvement, and unconfirmed results. If the system is usually biofilm-free, chemical sanitization can be effective. If the system has a developed biofilm, chemical sanitization may or may not be effective. Dosing, time increment duration, design issues of dead legs and stagnant flow areas need to be thoroughly investigated after sanitization administration.

New Design

Solution for Preventing Scale Precipitation in RO: Electrolytic Scale Reduction (ESR)

ESR

This unit is composed of a metallic cylindrical reaction chamber with flow-through water from the top to the bottom of the cylinder. In the central axis of the cylinder, an electrode is installed and connected to a positive electrical pole, while the cylinder circumference body is connected to the opposite negative electrical pole. Thus, an electric field is generated between the central electrode and the cylinder. This field causes current to flow between the central electrode and the metallic cylinder body. The current dissociates the water to OH^- and H^+ ions.[7] As a result, a low pH is formed around the central anode/electrode and a high pH around the cathode/cylinder. The high pH near the inside surface of the cylinder will cause scale to precipitate from the water, collect on the cathode, and it settles to the bottom of the reaction chamber. The amount of scale is small and typically will be in the range of 2 to 6% of total $CaCO_3$.

In an electrolytic cell, such as the above, low voltage direct current creates a positive electrical pole (anode) and a negative pole (cathode). In the presence of electrically conductive water, hydrogen ion and oxygen are formed at the anode and hydroxyl ion and hydrogen are generated at the cathode. A cathodically formed hydroxyl ion has the ability to greatly accelerate formation of calcium carbonate. Formulation of calcium carbonate ion clusters and nano-crystals are selectively diverted to the cathode. This formulation subverts bulk phase nucleation and limits both nano-crystal size and age.

The following equilibrium denotes the chemical reaction:

$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-$

$HCO_3^{-1} + OH^{-1}$ (hydroxide ion from strong caustic or electrolytically formed) $\leftrightarrow CO_3^{-2}$

$Ca^{+2} + CO_3^{-2} \leftrightarrow CaCO_3$

As shown above, the hydroxyl ion reacts with the bicarbonate ion to form carbonate ion.

The extreme insolubility created at the cathode and the power employed to drive the electrochemistry focused at the cathode produces rapid formation of very small crystals of calcium carbonate. Under such conditions, a tightly packed array of closely bound crystals cannot form. Deposition in an electrochemical precipitation cell tends to be soft, porous, and voluminous. The porous nature of deposition on the cathode does not retard electrolysis or migration of hardness ions. This allows the electrochemistry of precipitation to proceed unhindered even when sizable amounts of scale are deposited.

The water produced, after the selective precipitation of scale, is not defined as "soft" water as the output usually contains more than 100 ppm hardness.

So, What Have We Achieved?

We have achieved *kinetics modification* to slow precipitation to the point where deposits appear not to form. Because some of the scale has been removed from recirculating water, the *kinetics* of scale formation has changed even though scale could still form under certain conditions. The water is not soft at the outlet of the ESR; however, the scale forming ion content has been reduced to a level that has changed the period of time needed for hardness precipitation. If the system has been designed for the water to exit the RO membranes before the hardness has had time to precipitate – no scale will form in the RO membranes.

The ESR will precipitate *all* scale forming ions, not just magnesium and calcium, but any other trace ions that are susceptible to precipitation from the liquid at high pH, for example: silica, barium, manganese, iron, etc. Removal of only a small amount of the most problematic scaling ions will inhibit hardness crystal formation in the RO. This strategy works well for systems where water retention time, or flow-through, is relatively short. If water is retained too long in the RO, precipitate of scale will occur. If the ESR is improperly sized, scaling will form on the membrane reject surfaces and buildup on associated piping may become significant. This technology is well entrenched and proven in the cooling tower ion removal.

The electrolytic method for industrial RO treatment is well established with more than 100 worldwide installations. In addition, free chlorine is generated in the ESR as a byproduct.

The following equilibrium denotes this reaction:

$Cl^- + H^+ \rightarrow HCL$

$HCl + HCl \rightarrow Cl_2 + H_2$

This free chlorine by-product is a natural occurring factor keeping the ESR clean of biofilm.

Removal of Oxidants in RO Feed Water by Way of UV Irradiation – Hydraulic Oxidant Deactivation (HOD)

It is common knowledge that UV radiation will reduce concentration of free chlorine and chloramines.[5,6] UV breaks the chemical bonds of free chlorine or chloramine to form hydrochloric acid and other byproducts. When irradiated with a sufficient dose of UV, the reaction for free chlorine, as hypochlorous acid, is as follows:

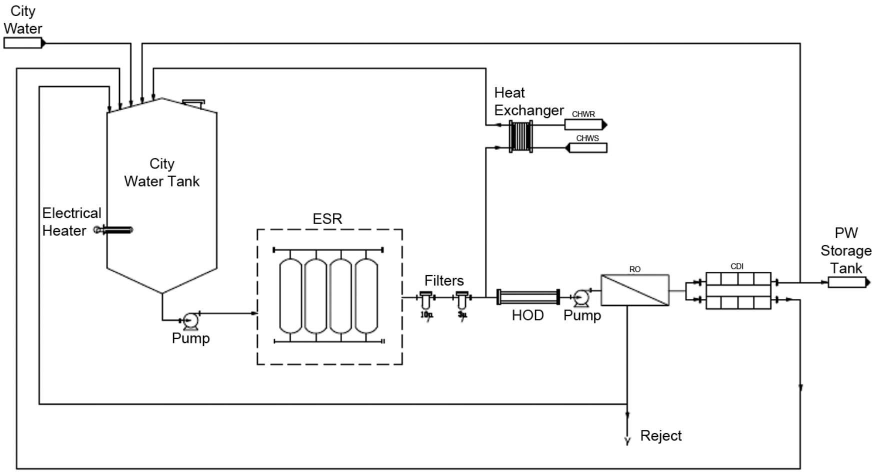

Figure 1. ESR and HOD configured in system.

$$2HOCl \rightarrow 2HCl + O_2$$

When irradiated with a sufficient dose of UV, the reaction for water containing chloramine and free chlorine, as hypochlorous acid, is as follows:

$$2NH_2Cl + HOCl \rightarrow N_2 + 3HCl + H_2O$$

The reaction for reduction of free chlorine in the hypochlorous acid form:

$$2HOCl \rightarrow 2HCl + O_2$$

The reaction for reduction of free chlorine in the hypochlorous acid form:

$$2NH_2Cl + HOCl \rightarrow N_2 + 3HCl + H_2O$$

The by-products of the reactions are easily rejected by the RO membrane.[5]

In effect, the HOD has removed the oxidizing substances in the water which could damage polyamide membranes, allows ion passage through membranes, and/or prevents damage to the downstream Continuous Electrical Deionization (CEDI) unit.

ESR and HOD in a System
Configuration

How are these complementary technologies integrated?

As we can see in Figure 1, the ESR is mounted as the pre-RO treatment stage ensuring the RO will not suffer scale while the HOD removes the chlorine/chloramines from the RO feed water. This dual approach system, comprising the ESR and the HOD, can ensure the city water will not cause RO blockage or decomposition of the membranes, and will provide chlorine/chloramine removal without traditional chemicals or organic media (GAC).

Some advantages are immediately gained, as both the ESR and HOD modules are fabricated out of heat resistant materials (SS and Quartz). Hot water sanitization for both modules can be employed reducing any possible microbial biofilm development.

The ESR and HOD modules prevent entrapment of free-floating bacteria and biofilm development, as no extraneous organic media (GAC), no resin beads, and no chemical additions are entrained in the pretreatment system.

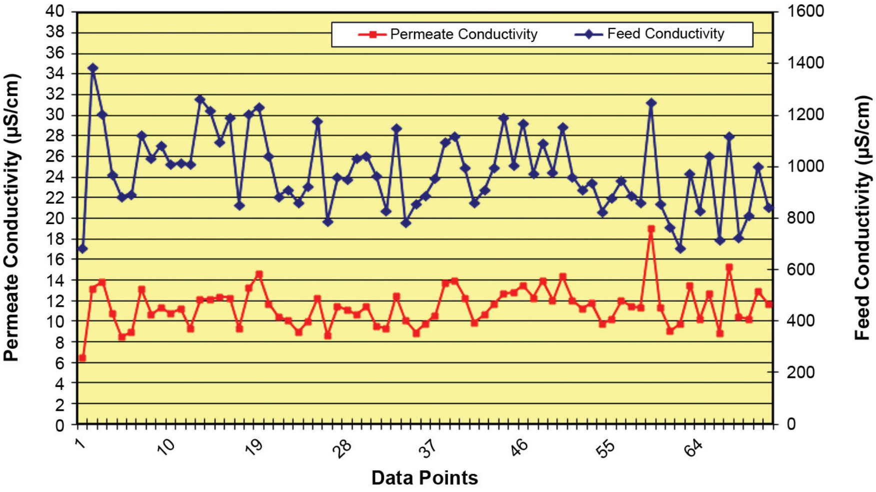

Figure 2. Conductivity over time.

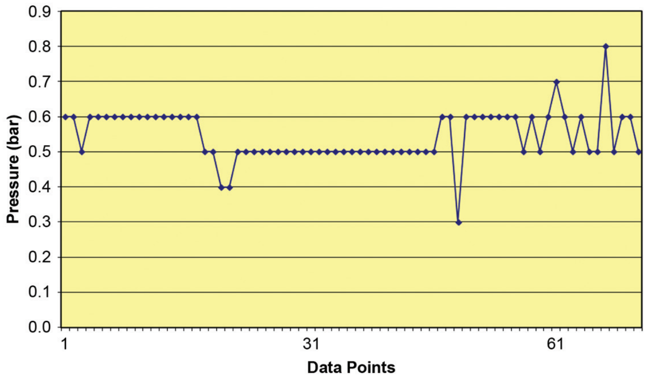

Figure 3. Pressure drop on the membranes.

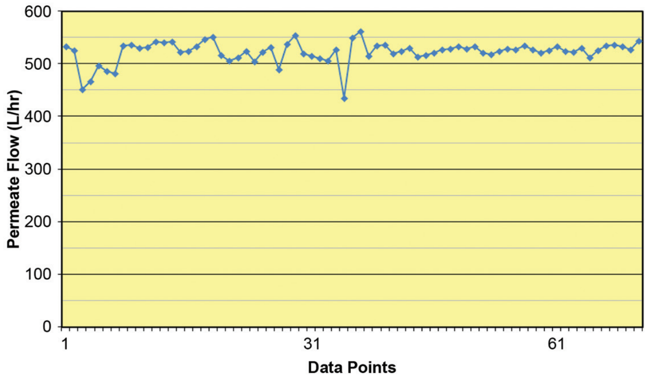

Figure 4. Permeate flow.

Continuous Bioburden Reduction

The supplied ESR and HOD pretreatment modules are not susceptible to bioburden, as previously stated, as all the surfaces are manufactured of SS or quartz and are easily hot-water sanitizable. The addition of a hot water retention tank, heater, and heat exchanger with the proper sanitizing time duration protocols will enable a bacteria-free or bacteria-reduced environment, thus, placing less stress on downstream water treatment modules.

The ESR and HOD will reliably reduce incoming bacteria counts because of the free chlorine by product in the ESR and the high levels of UV radiation in the HOD.

Case Study

The ESR-HOD pretreatment combination was studied over an eight month period.

Figure 2 shows the conductivity over time. The X axis data points are the consecutive numbered dates that the readings of conductivity were recorded. The top graph scale is read off the right axis, the range of incoming conductivity is from a minimum of 700 µS/cm to a maximum of 1400 µS/cm. Note: the permeate output conductivity closely follows the inlet conductivity. No clogging or perforation of the membrane is apparent after eight months of operation.

Figure 3 shows the pressure drop on the membranes. The X axis **data points** are the consecutive numbered dates that the readings of differential pressure were recorded. Note: there is little change in differential pressure over time. No clogging or perforation of the membrane is apparent after eight months of operation.

Figure 4 shows the permeate flow. The X axis **data points** are the consecutive numbered dates that the readings of permeate flow were recorded. Note: there is little change in permeate flow over time. No deterioration of the membrane is apparent after eight months of operation.

Site data for bioburden reduction is seen in Table A. Note: the logarithmic reduction in all micro counts as soon as the water enters the system.

Note: the E. Coli and Pseudomonas were both measured per 100 ml and **not** per the usual 1 ml. If the system was evaluated per the usual 1 ml – no detections of Pseudomonas or any other specific species would have been made.

Cost Comparisons between ESR-HOD modules and Activated Carbon Filtration, Softener, Bisulfite

Table B and C are based on a system providing 7 M^3/hr (30.82 gpm) of RO permeate.

	Micro Total count CFU/ml		E. COLI CFU/100 ml		Pseudomonas CFU/100 ml		Coliforms CFU/100 ml		Fungus CFU/100 ml	
Position in System	Average	Range	Average	Range	Average	Range	Average	Range	Average	Range
City Water Inlet	158	0 - 780	47	1 - 227	24	0 - 82	201	28 - 910	13	0 - 48
Exit City Water Storage Tank	1.27	0 - 10	0	0	0.167	0 - 1	1.375	0 - 11	0	0
Inlet to HOD	0.5	0 - 3	0	0	0.167	0 - 1	0.25	0 - 4	0	0
After HOD	0.05	0 - 1	0	0	0.167	0 - 1	0	0	0.167	0 - 1
After RO	0.05	0 - 1	0	0	0	0	0	0	0	0

Table A. Site microresults from a two month period of PQ.

Table B. Pretreatment Options

Description	CAPEX $ (Estimate)	Yearly OPEX (Calculated)
ESR and HOD	$300,000	$9,443
Softener – Active Carbon Filter	$100,000	$77,974
Active Carbon Filter – 2 units AS RO	$136,000	$164,910

Table C. Input Data for Costing

Sample costs for:		
Water Prices	7.00	$/m3
Sewer Use Fee	0.00	$/m3
Cost of Labor	25.00	$/hr
Price for Spent Brine Disposal	0.00	$/m3
Price for Fresh Salt	0.23	$/kg
Ion Exchange Resin	5.71	$/liter
AC Replacement Cost	11.43	$/liter
Electrical Price	0.50	$kW/hr
Industrial Steam (NG/LPG Burner)	93.14	$/ton
Price per Filter	28.57	$/Unit
Price per UV Lamp	607.14	$/Unit
Price per Industrial 8" Membrane	850.00	$/Unit

Tables B and C. Cost comparisons between ESR-HOD modules and activated carbon filtration, softener, bisulfite.

Comparison of total costs (CAPEX + OPEX) as a function of years of operation as seen in Figure 5. The horizontal axis in Figure 5 refers to time in years. The perpendicular axis is in US Dollars ($). The red line is the operating expenses over time including the initial capital expenditure of the ESR-HOD modules. The operating expenses over a seven year period are approximately $66,000. The Softener and GAC option in the green line shows a lower capital expenditure, but a much larger operating cost of $550,000 over the next seven years. The GAC + AS RO of the purple line shows a slightly lower capital expenditure, but very high operating costs of $1,150,000 over the seven year time period. The differential in operating expenses between ESR-HOD and traditional pretreatment systems can range from $500,000 to $1,000,000 over a seven year period using the above calculations of water pricing. Any increases in costs will develop larger differentials as the ESR-HOD costs do not change overtime.

Conclusion

Installation of an ESR and HOD combination is a superior system with significant advantages when compared to traditional ACF, softener, and bisulfite installations. The advantages are: no chemicals, no media, no back wash, no regeneration and no waste stream.

The maintenance is minimal as the units have no moving parts. Operating expenses are immensely reduced compared with traditional pretreatment modules, showing savings of almost $500,000 to approximately $1,200,000 over a seven year period. The implementation of the ESR and HOD modules alleviates many of the limitations and operational problems of traditional pretreatment modules described in the first sections of this article. Performance of the ROs is enhanced by not using antiscalants and bisulfite chemicals as pretreatment modules to the membranes. Continuous bioburden reduction by and throughout the system is exceptional and robust with the added feature of hot water sanitization when needed. The future for our industry lies with simple, reliable and "green" technologies. The ESR and HOD modules are "green" with no wastage, no disposal, no chemicals, no organics, no waste stream, with markedly reduced operating costs for the life of the installation.

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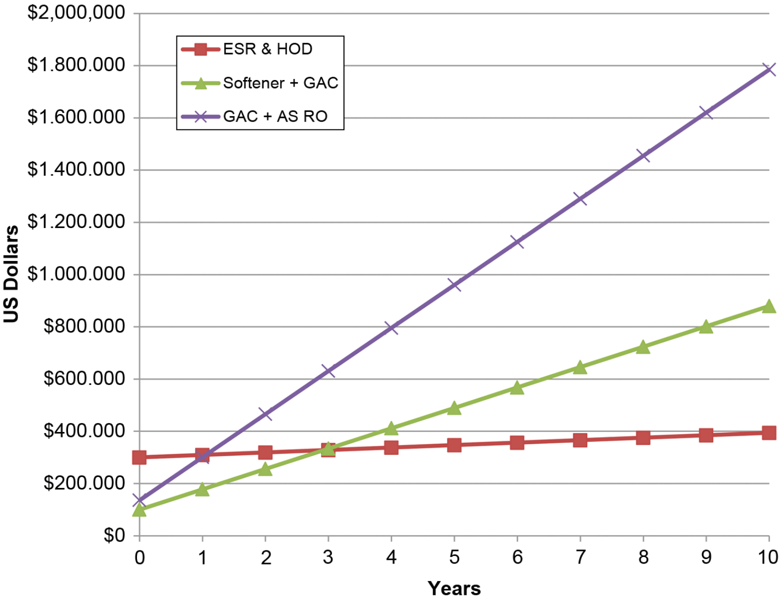

Figure 5. Comparison of total costs (CAPEX + OPEX) as a function of years of operation.

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