Use of High Purity Water to Eliminate Contamination And Achieve Cleanliness- A Discussion of Performance and Costs

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Abstract

PCB board manufacturers engage in a number of wet processes. Water is used ubiquitously in many of these processes for rinsing as well as bath make-up. The impacts of water quality on production processes and product quality are many times ignored. Cleaning surfaces to achieve defined levels of cleanliness in terms of particle and other contamination is now a topic of new ISO standards. Many PCB sites do not use high quality water due to the assumption of high costs. This paper discusses how high purity DI water can be produced at lower costs using a DI recycling approach using a technology called EDI (electrodeionization – which is an electro-membrane technology), in PCB production. A discussion of this new technology that allows lower costs of DI production and recycling will be presented. This paper will also present customer and various third party data on how high purity water reduces contamination build up on parts, during processing, improving product quality and reducing rejects.

Introduction

Continued miniaturization of high technology products in a wide range of industries has resulted in the increased need for cleaner parts. Contamination on the surfaces of electronic parts and mechanical assemblies can degrade performance, production yield and life expectancy of a product. Manufacturers have instituted cleaning procedures to ensure their precision component parts are clean and unlikely to adversely affect the completed product.

Also, as use of solvents in cleaning applications has been phased out with water, many users have moved to water-based cleaning and rinsing. Various wet processes use water to remove contaminants or chemistry after processing, such as coating and plating from the various chemistries used for PCB processing. Good water quality is fundamental to any aqueous process system. Excessive water hardness and total dissolved solids (TDS) limit the effectiveness of process effectiveness leading to surface contamination and built up impurities and residues on interconnection.

Softened water is not the answer. The softening process simply replaces heavier elements in the water with sodium. Sodium and other dissolved solids such as chlorides; sulfates and calcium salts remaining on the metal surface can initiate the corrosion process, causing delamination, even if the final rinse contains an acidified sealer.

Water is increasingly the most important raw material in the printed circuit board industry, in terms of quality and quantity, used in electroplating and other coating/finishing processes. However, most users in the PCB industry spent the least amount of resources on assuring high quality water for their processes. An average plating bath is made up of 80% water.

Most steps in plating and wet process operations are followed by one or more water rinses. Water can also be the cause of many problems in these operations. The source of raw water used in PCB shops for bath make-up and rinsing can be:

- City water from a municipal water supply,
- Raw surface water from a river, lake or reservoir,
- Raw ground water from a well or spring, or
- Overflow cooling water.

Water coming into a PCB shop contains impurities which may impair the processes and impact product quality. Table 1 below lists components of water and the problems encountered by their presence.

Table 1 - Impurities Present in Water Which may be Harmful to Plating and Coating Processes

Impurity Type	Problems Caused by Impurity
Dissolved mineral salts (ions)	
calcium and magnesium (hardness)	Relatively insoluble in water, solubility decreases on heating, and may concentrate with evaporation creating a film or scale on work pieces and sludge in the water
sodium and potassium	Substantial amounts may cause brittleness of nickel plate or lower the maximum allowable current density
heavy metals (present as salts)	May cause various problems such as diminishing the activity of ingredients in plating and coating baths; gives water a characteristic color
acids (present as salts)	Requires the use of corrosion-resistant lines and tanks, requires added alkali for neutralization
Dissolved organic salts such as bicarbonate	When heated, converts to carbonate which forms precipitates with calcium
Dissolved gases such as carbon dioxide, oxygen, and nitrogen	Carbon dioxide is corrosive in itself; in solution it forms carbonic acid which lowers the pH and accelerates corrosion; dissolved oxygen is highly corrosive to iron and steel
Un-dissolved matter such as turbidity (suspended matter) and sediment (suspended matter which settles rapidly)	Objectionable for most uses
Microorganisms	May cause staining, slimy deposits or clogging of pipes

Rinse and Make up Water Quality - Why is Water Quality Important?

The concentration of these impurities is measured in terms of parts per million (ppm). One ppm is equal to 0.001 gram (1 milligram) dissolved in a liter of water. Minute amounts of a single impurity can create major problems and result in lost time, materials, profits and possibly, customers. In the case of decorative plating, water spots and stains caused by impurities are objectionable and may require reworking, wiping or buffing. This adds to the cost of operation and, in the case of buffing, may reduce the corrosion resistance of the finish. The presence of 10 ppm of chromates in a nickel bath has the effect of decreasing the upper current density limit resulting in an unsatisfactory deposit.

Impurities in incoming water may be present in such low concentrations that they do not cause problems, but may become concentrated in heated plating baths or due to evaporation. Concentration of impurities can readily reach levels high enough to cause failure of the bath chemistry. An example of this is chlorides in an electroless nickel bath. Another important consideration is the effect of water quality on recovery of metals from process solutions. Impurities in the water may cause a recovery technique to fail or operate inefficiently. An effective use of ion exchange is the removal of hard water and other mineral salts prior to plating to render metals recovery more cost effective. The ion exchange resin for hard water ions is less costly than resin for heavy metals.

Techiques to Improve the Quality of Incoming Water

Many PCB shops employ some form of water pre-treatment. Municipal water supplies are generally clear and low in color, low in iron and manganese, safe for drinking purposes, but not sufficiently soft or low in total solids for all plating uses.

With current technology, it is possible to treat any raw water to be acceptable for plating and metal finishing. The costs associated with poor quality work outweigh the costs of water purification. Treatment of raw water to remove these impurities is accomplished mainly by ion exchange and reverse osmosis which are also used for wastewater treatment or metals recovery.

Ion Exchange

Ion exchange is used in about 95% of all water purification applications. Ion exchange purifies water by:

- Softening which uses a cation column to remove hardness (iron, calcium and magnesium), or
- Deionization (or demineralization), which uses both cation and anion columns to remove essentially all ionized substances (mineral salts) dissolved in water.

Reverse Osmosis

Reverse osmosis (RO) is a crossflow membrane filtration system used to purify raw water for use as rinsewater. RO produces water similar in quality to demineralized or distilled water by removing organic contaminants and inorgnic salts.

Advanced Electrodeionization (AEDI) for Process Rinse Water Recycling

The company has developed a product to recover and make high purity DI water in point of use, for wet process applications. This concept is to replace the conventional D.I./ion exchange pretreatment system with an Advanced Electrodeionization (AEDI) system and continually to recover and reuse the DI water that is much needed for most processes, but commonly is believed to be too expensive to produce.

Advanced Electrodeionization (AEDI) removes Ionizable constituents from water using ion exchange membranes, ion exchange resins, and a DC electrical potential. AEDI provides two technologies in one module: electro dialysis and ion exchange. Ion exchange membranes separate an ion exchange mixed bed from electrodes. The ion exchange resins remove ionic matter from process water and the electrodes provide electro-regeneration of the resin when energized by a DC rectifier. AEDI systems provide a superior separation of ionic process solutions from wastewater and process water. AEDI applications include direct recovery of electrolytes from active rinses as well as recovery and recycling of process water and wastewater in industrial applications. Figure 1 shows a typical interior of a stack.

The AEDI requires water of certain quality or spec so it can operate most efficiently. This is why, the initial start-up of the system has to be with DI water quality. No hardness should be present or silica in the water when the system is started up. The system can then maintain the high grade of water and remove effectively all process impurities. The company also now offers besides the standard modules a high temperature module for medical applications.

The usual feed water source maybe RO water or process direct feed water if it has been previously DI or RO. The system can accept low pH to slightly higher pH and online pH adjustment is also available. The system must be receiving feed water with zero or no particulates or silica.

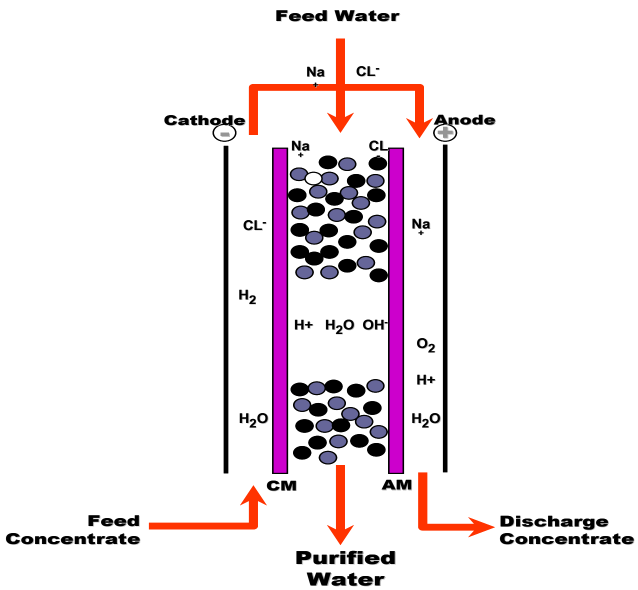

Figure 1 – AEDI Stack

AEDI systems can remove the impurities that can cause damage to parts during processing/production. For example, AEDI removes ion loads, and oxidizers from the incoming water used for rinsing. The continuous removal of impurities allows the process rinses to run contaminant free.

Table 2 shows a list of select industries and their application needs for particulate cleanliness, as well as the typical particle size of concern for the impurities that are allowed on the parts.

The complexity of rinse cleaning systems leads to a variety of potential problems including:

- Filter loading and failure
- Water supply issues
- Unusually dirty incoming parts or parts of different contamination levels

Deionized water can help manufacturers achieve particulate free processing and run processes contaminant free – and online water recovery and re-purification allows for unlimited high quality water for reuse.

Why a point of use recycling system?

A typical ultrapure water production system includes reverse osmosis, ion exchange, instruments and controls, degasification equipment, filtration equipment, pumps and valves, storage and piping, and disinfection – a lot of efforts and activities. It is vital that every component of the ultrapure water (UPW) system consistently maintain high purity. All in all, plenty of resources and costs are associated with the operation of such systems.

Ultrapure water specifications maybe varied by site or the type of manufacturing operations. For example, in semiconductor or disk drive processing, incoming rinse water has to meet Total Organic Compound (TOC) limit of 0.05 ppb as well as a consistent resistivity of 18 Megohm.cm. At 25°C, 18 Megohm.cm is the maximum resistivity that is practically achievable and measurable under industrial conditions. At such high resistivity (low conductivity) the accuracy of process instrumentation becomes critical and specialized materials are required where process equipment comes into contact with water to ensure no contaminants are released into the product water.

Table 2. Application requirements for parts cleaning within select industries		
INDUSTRY	APPLICATION	PARTICLE SIZE OF
Micro Electronics	Tool Components Wafer Handling and Storage MEMS Sensors	< 100 nm < 100 nm < 100 nm
Data Storage	Tool Components Drive Components	100 nm - 500 nm 100 nm - 500 nm
Aerospace	Sensors Fuel Components Specialty Parts	>2 microns >2 microns >2 microns
Automotive	Sensors Fuel Injectors	>2 microns >2 microns
Medical Devices	Implants Production Equipment	>10 microns >10 microns

It has been believed for many decades that fresh water must be used to make UPW for any wet process or tech. manufacturing operations. This paper discusses, how water already purified for production uses, (process water) can be recycled at "point of use" (POU) and returned back for reuse in to the same process; or to secondary polish before reuse.

Today many customers are facing the high costs of water resources purification and management, and so today more than ever the concept of POU recovery and reuse of UPW makes sense.

The AEDI product allows recovery and reuse of water at POU – either at the tool or a bay of tools, with a fully integrated system. This approach allows for re-purification and re-make of DI water to original specs by continuously removing impurities from the process.

In wet process application, the variety of chemistries (such as etch, cleaning, etc.) is normally followed by rinsing processes. Mixing of the various wastewater streams coming from each chemistry may not be compatible, and can cause issues for wastewater treatment as well as for effective water recovery systems that handle the mixed wastewaters. In cases, where the chemistries are compatible, as much as 90% of the rinses can be recovered for reuse. The recovered rinses may be sent back to the tool directly or re-polished to assure purity levels are consistent with the facility's in-house specs.

In the coming years, as chemistries evolve, and more complex processes are instituted, water recycling of mixed rinses results in lower recovery rates; and thus are less efficient. For example, new plating chemistries are being introduced to semiconductor processes. These chemistries require additional treatment if drained to central waste treatment systems – and the conventional acid waste neutralization processes will no longer suffice. So additional waste treatment has to be added which increase the cost of waste treatment. For example, facilities have to install precipitation, reduction/oxidation, or other treatments to deal with these complex chemistries.

POU allows for the removal and separation of these specific chemistries and allows for off-line recovery and recycling of these materials in particular if they have value. These chemistries, not only are expensive in many instances, but if they are metal-based (such as copper, cobalt, etc.) they will be more recovery worthy.

The point of use recovery results in avoidance of the disposal after one use, thus the continuous need to fresh water and waste treatment, on site or offsite. POU recycling and reuse allows manufacturing customers to reduce cost of production substantially. It eliminates the continuous consumption cycle and replaces it with complete re-utilization of material and resources.

Case Study: POU Rinse Water recycling

PCB Line Case Study

The Company has gathered cost of ownership data from prospective and actual customers. The following are two case studies where AEDI has been successfully demonstrated.

One of the first installed AEDI systems was in PCB, close-looping of a board cleaning line. Savings from installed systems have met or exceeded customers' expectations, by allowing the customer to eliminate the cost of systems. From this data, it is clear that the total cost of ownership of a company system is better than the cost of competing systems, driven by the effectiveness delivered by company product.

The purpose of the lines is to provide a clean inner layer core of the PCB and coat this core with a dry film resist. The facility was burdened with increased water and sewer costs due to the high usage of water and wastewater discharge. The plant was also subject to certain capacity limitations, which will limit future expansion and operating expenses.

AEDI provided high quality D.I. water for the lines since 2003, until the facility was shut down in 2014. The process lines demanded 16 gallons per minute (gpm) of continuous D.I. water supply. There were savings in city water and sewer charges, wastewater treatment and operating cost to the customer for the AEDI rinse water recycling system.

The water quality produced by the system was monitored for a period of 24 months by the customer to assure consistent and reliable quality.

The AEDI membrane modules are designed and built to ensure the purification of low TDS process water instead of using a mixed-bed ion ex-change system. A TDS reduction to more than 99% has been accomplished consistently and the product water is of D.I. water quality.

The diagram above shows the consistent high water quality produced by the AEDI which was installed over 40 months ago. Figure 2 shows a summary of this data for about 36 months of operation.

Disk Drive Cleaning System Case Study

Precision cleaning systems like the example shown in Figure 3 are used extensively in the tech production industries such as disk drive industry and PCB industry. In this particular cleaner, parts undergo a multi-step cleaning process. Parts are initially placed in a surfactant bath and subjected to ultrasonic waves, which form cavitation bubbles. The formation and collapse of the cavitation bubbles effectively scrub the many faceted surfaces of the mechanical parts. After the surfactant bath, the parts are sprayed with clean DI water and placed in progressively cleaner DI rinse baths. The DI rinse baths subject the parts to more ultrasonic waves and a continuous flow of clean DI water. After the last DI rinse bath, the parts are dried and taken to the production line.

Most precision cleaning systems rely on ultrasonics, but the individual baths are commonly aqueous based. The aqueous baths are either water plus surfactant based or simply (ultra-pure) DI water.

The following case study is based on data collected in 2014 and 2015 from wet processing involving the cleaning of disk drive in in-line cleaning operations. The point of use recovery system was tested and validated to meet the facility's ultrapure specs, thus allowing for the water to be re-used and recycled in-line. The pilot system was operated for several months, so the data presented below is only a brief snap shot of the test results.

The base platform used for the application utilized the AEDI technology, plus a pre-filtration unit for the removal of organics, and particle removal and disinfection elements to address particle and bacteria formation in a closed-loop set up.

A system was installed and started up in mid-2014. The data shown in Figure 4 was collected over a period of three months for Phase I of the project, which involved the removal of cleaner solutions from the rinse waters while recycling back the water to processes. The cleaners contained a number of organic acids. Figure 3 shows a summary of the test results for resistivity in and out of the system for a period over 3 months.

As can be noted, the system was able to produce UPW grade (18 megohms.cm) recovered water for reuse.

Conclusions

AEDI in process rinse water recycling offers online, real time impurity removal and consistent high purity water for rinsing applications in the PCB sector. The technology has been validated and approved by customers with much higher water quality specifications such as in the disk drive industry and several systems have been successfully installed in the PCB industry.

The AEDI point of use recovery approach allows customers to reduce water usage by process and reduces water related operational costs.

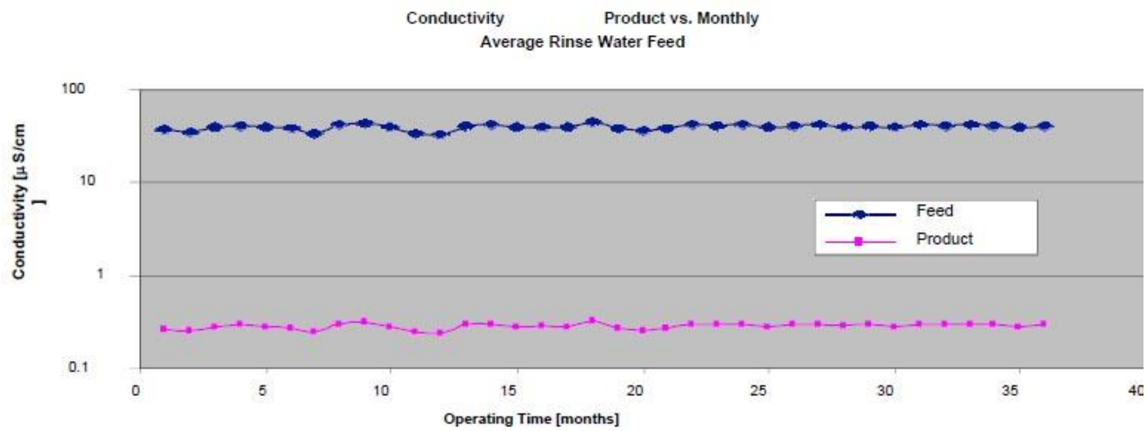

Figure 2 – Case Study – PCB Line

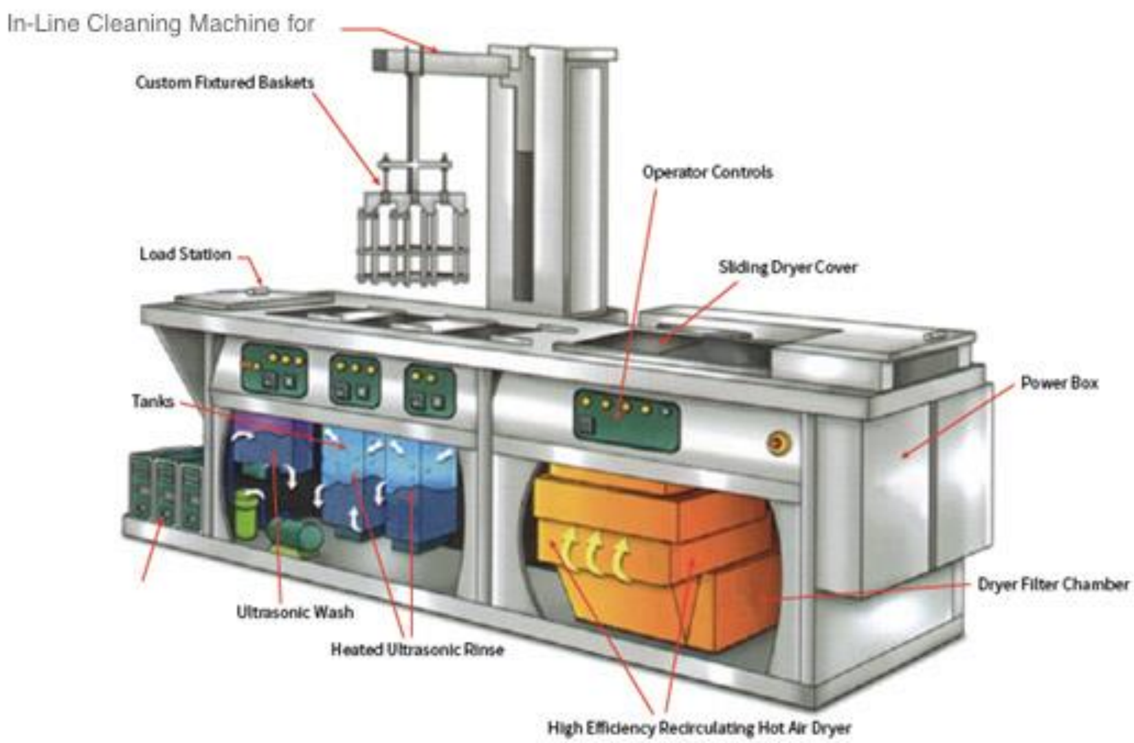

Figure 3 – Parts Cleaner System

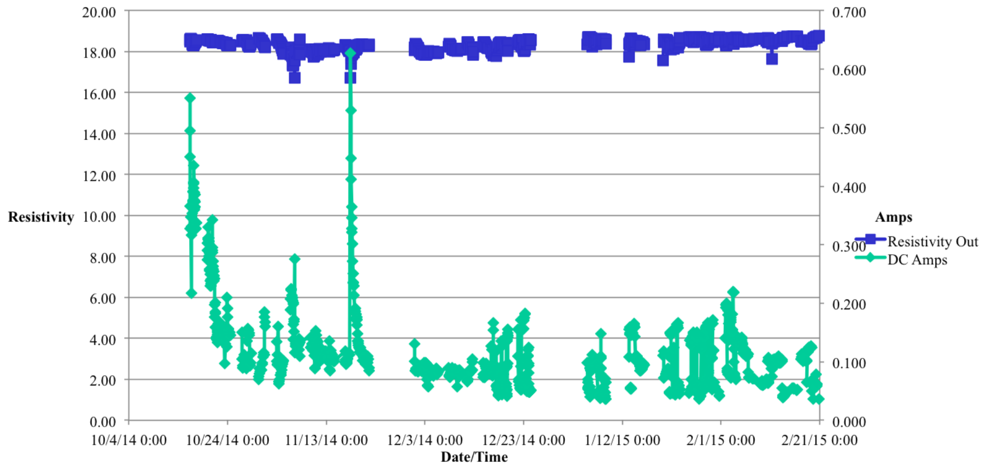

Figure 4 – Resistivity in and out during 3 months

USE OF HIGH PURITY WATER TO ELIMINATE CONTAMINATION AND ACHIEVE CLEANLINESS- A DISCUSSION OF PERFORMANCE AND COSTS

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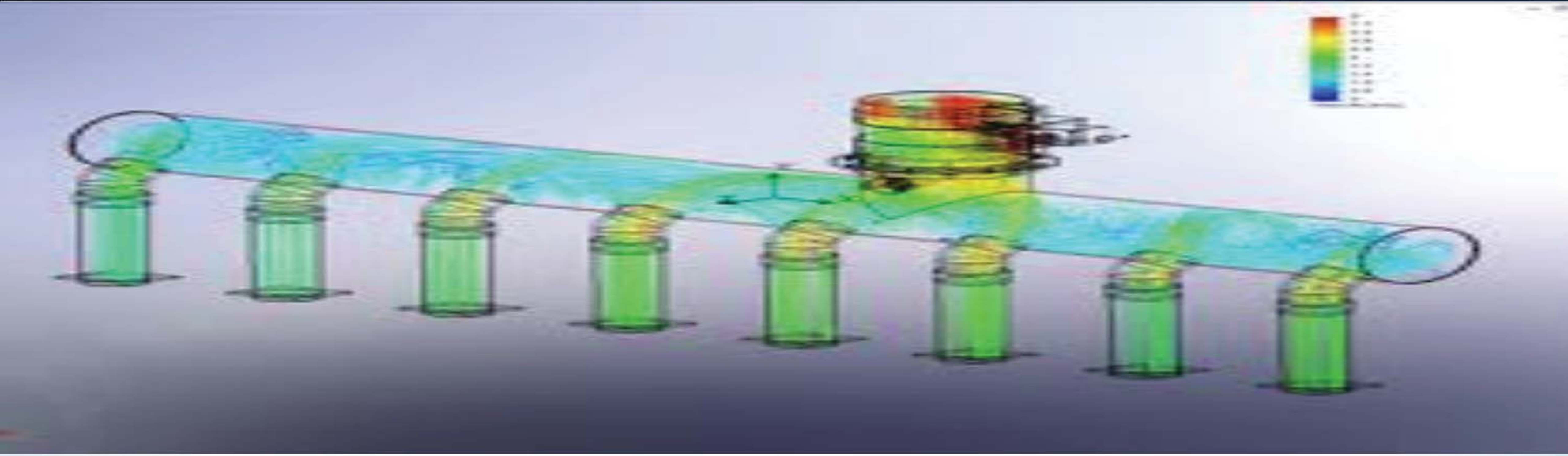
Background – Development Drivers

- Consumer electronics has become the driver of microelectronics resulting in smaller parts, tighter costs and schedule constraints
- Water the largest volume resource; is nearly the most important material used in its manufacturing processes
- Many facilities are utilizing low quality water for processing: water quality impacts product quality
- Issues with water availability and risings costs of water, sewer, and compliance demand that these manufacturers sites provide reliable, consistent water, in good quality and in ample volume to assure proper product processing

Water Recycling/Reuse = Water Abundance



Wasting to make High Tech

In today's large volume flow-thru manufacturing, all that does not make it onto the product is wasted – that is over 80% of raw material and resources

Why recycling and reuse and why High Purity and Ultrapure Water (UPW) ?

- Water supply scarcity is growing in many areas across the globe
- Cost of UPW production is high; water and wastewater management costs have increased significantly
- Quality of UPW impacts product quality and reliability
- Resources such as water are no longer limitless

Why High Quality Water Matters?

Technical approach and Benefits

- "Point of Use" processing ensure:
  - *improved quality and process control*
  - *lower capital and operating costs*

- Electrochemical "One-Step" separation approach can offer improved thermodynamic efficiencies over conventional approaches resulting in :
  - *lower costs*

Advanced Electro-deionization combines these two approaches to meet the technical and commercial challenges facing the microelectronics industry process water requirements

UPW Product Quality Impacts

- Research shows that water processed by central plants commonly carries or picks up pollutants on its way to the processes

- This water impacts quality of parts processed due to various sources of contamination from central processing and delivery

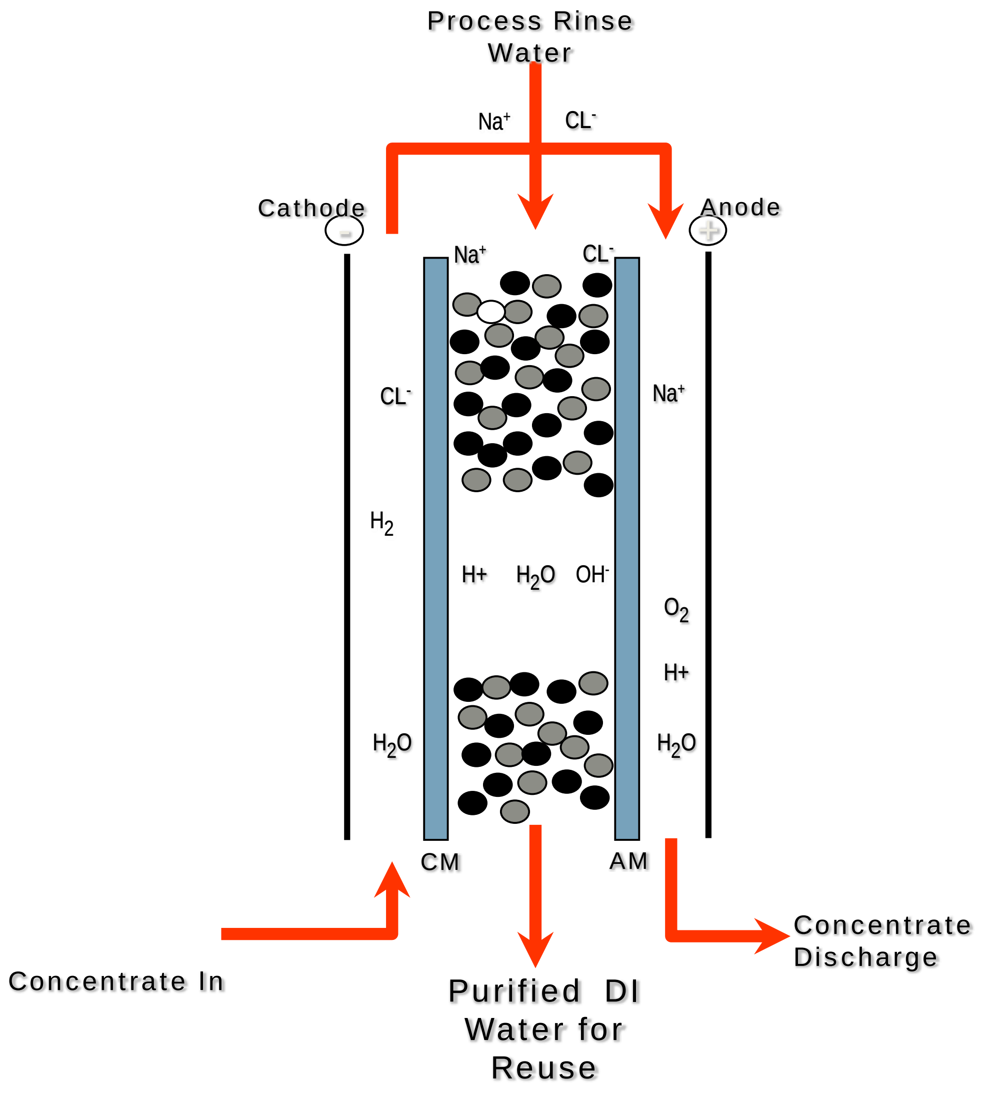
- Currently most facilities do not employ point of use monitoring for water quality by process or tool

Advanced Electrodeionization (AEDI) – What it is and how it works?

- A complete, fully automated water purification point of use process platform
- Designed to replace onsite DI generation using ion exchange (IX) bottle rental or conventional water pre-treatment systems
- Substantially reduces water and wastewater usage and treatment; eliminates the need for DI IX bottle service and regeneration

AEDI Cell - in Action

- Unit receives rinse water from rinse lines on a given tool
- The energized stack splits water and ionizes the various ions.
- Resins inside the stack is used as host site for the active ions, which are continually removed/separated by DC across IX membranes into concentrate
- Impurities are directed to the concentrate stream and is rejected continuously
- The system is engineered to remove up to 2,500 ppm of TDS in the feed streatm
- Achieves more than 99% TDS removal, 90% recovery rate and high purity grade ultrapure recovered water product
- Separated chemicals can also be recovered



The Cell Module

- Includes company developed AEDI stack and membranes

- Stack features:
  - Low energy consumption: 4 kW/1,000 gal
  - Low maintenance requirement
  - No Shut Down to replace resins, resin bottles or need for regeneration

AEDI: Water Impact on Impurities

- Oxidizers
  - *AEDI can remove oxidizers at certain concentrations; which can help prevent permanent PCB damage*
- Hardness
  - *Normally from City water, hardness can form scaling and deposits on the PCB; AEDI system is designed to remove water hardness (if city water is used)*
- Removal of Ion Load
  - *Fewer ions to remove means better contaminant free deposition onto PCBs*
  - *Ionic removal also lead to lower current demand thus, lower power/energy usage*

Effects of Contaminants on the EDI Stack (1 of 2)

- Hardness: Ca^{+2}, Mg^{+2}
  - *can cause scale in the concentrate spacer, depends on voltage (level of water splitting), concentration, CO_2, pH, and concentrate ratio.*
- Organics
  - *TOC from the feed water can coat the membranes and resins and prevent ion transfer.*
- Cation Softening Resin:
  - *colored anionic organic from softening resin fouls anion resin and membrane, makes the membrane amber-orange.*
- Particulates and Suspended Solids (SDI):
  - *can enter and clog the resin bed, can increase pressure drop, can foul the resins.*

Effects of Contaminants on EDI stack (2 of 2)

- Active Metals, such as iron (Fe):
  - *catalyze oxidation and strongly adhere to resins and membranes. Fe makes the membranes turn red-orange.*
- Oxidizers: Cl_2 and O_3
  - *oxidize the resins and membranes, the quality decreases and the pressure drop increases as the resins turn from solid to mush.*
- CO_2 and HCO_3^-
  - *are weakly adsorbed and pass through the EDI, they lower the quality and by competing with silica (SiO_2) they prevent the EDI from effectively removing it.*

Feed water Specifications (1 of 2)

Specification	Notes	Working Range	Optimum Performance
Feed water Source	RO water, direct feed, or with intermediate break tank plus filter		
EDI Feed Conductivity	Ionic load determines size of the working bed and polishing bed within the EDI	1-20 µS/cm	1-6 µS/cm
pH	Low pH feed water typically indicates the presence of CO_2 which will decrease quality.	5.0-9.5	7.0-7.5
Total CO_2	Combined CO_2 and HCO_3-	< 5 ppm	< 2 ppm
Temperature		5° C to 35° C (High Temp Stacks to 80° C)	N/A

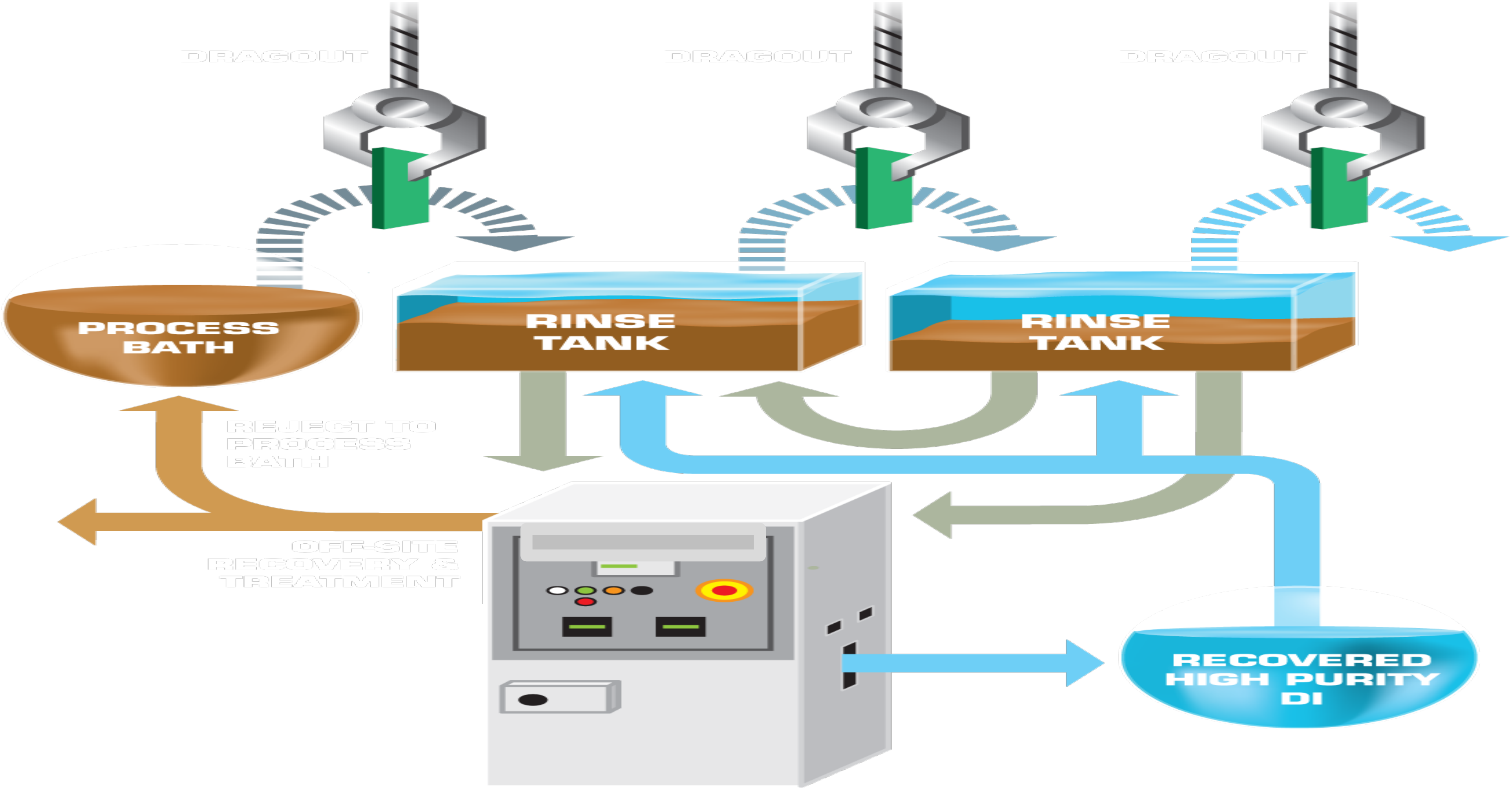
Feed water Specifications (2 of 2)

Specification	Notes	Working Range	Optimum Performance
Hardness	Ca^{+2} and Mg^{+2} as $CaCO_3$	<1.0 ppm at 90% recovery	
Silica	Typically dissolved, reactive	< 0.5 ppm	< 0.2 ppm
Particles	Recommended direct feed particle-free RO permeate, or 1 µm pre-filtration of feed from intermediate tank		
Inlet Pressure	Depends on flow and temperature	5 bar (75 psi) max	2-3 bar typical
Outlet Pressure	Concentrate and Electrolyte outlet pressures to be lower than the Product outlet pressure		

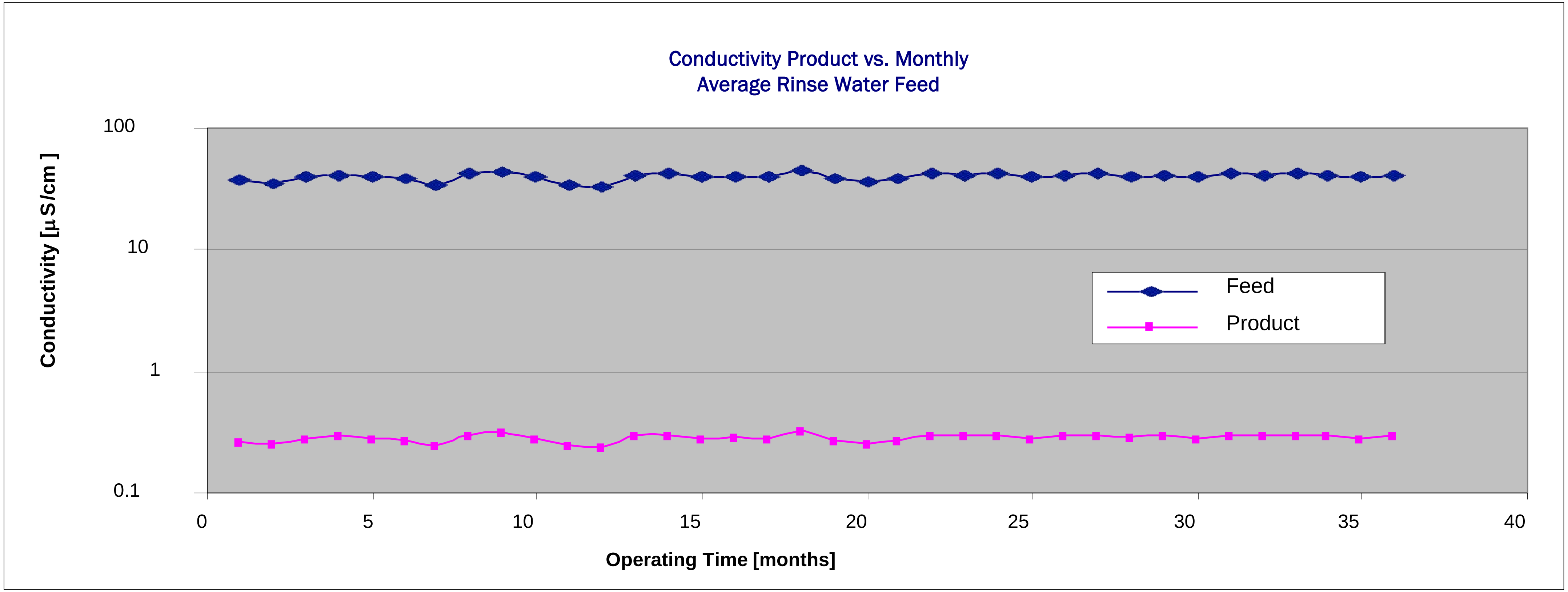
Normal Operating Conditions

- Steady State: ions in = ions out in Concentrate; DI in various grades is recovered and recycled back to line
- Concentrate at 10% of Feed; concentrate concentration will be 11x the Feed concentration (e.g., 3 microSiemens from RO, 33 microSiemens in Conc. Out).
- Concentrate will be acidic (scale prevention feature)
- Good water splitting at normal voltage
- Current will be proportional to ion concentration in Concentrate outlet
- Gas bubbles will be in Electrolyte outlet

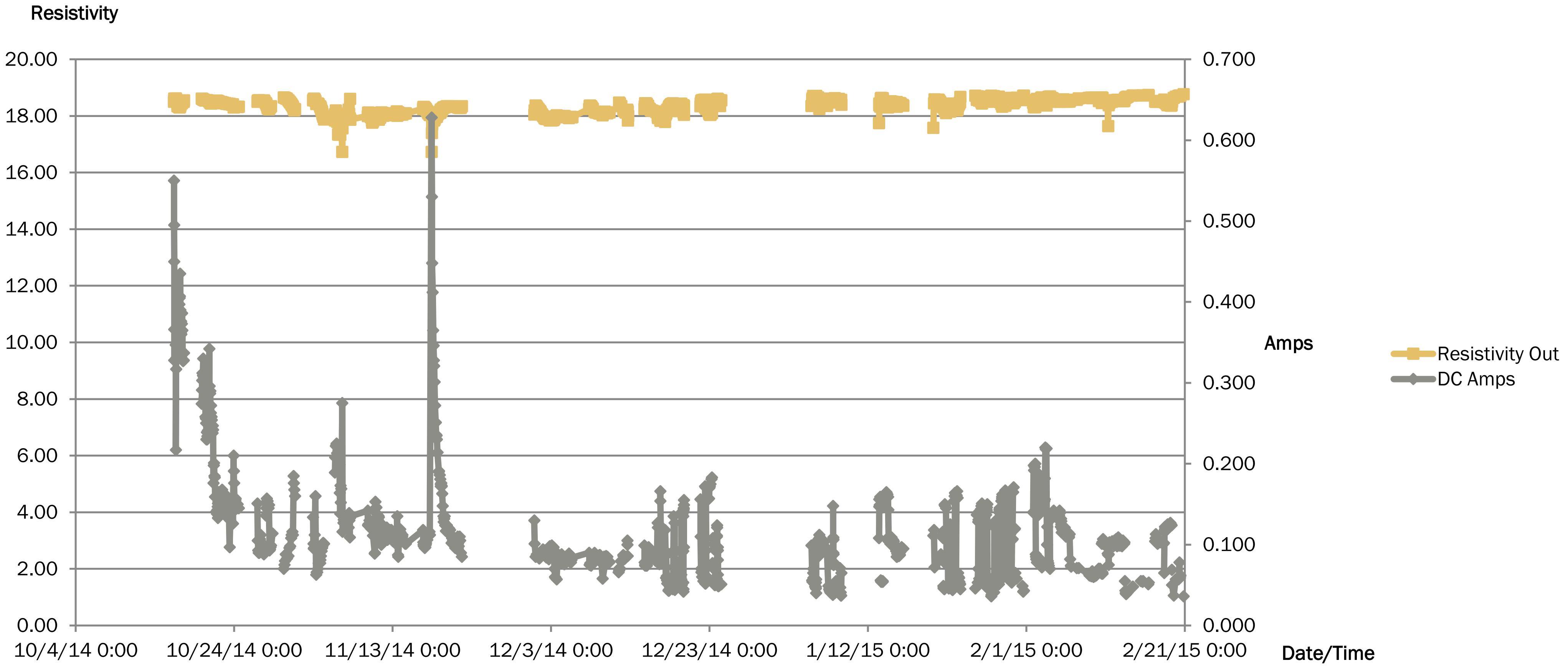
Integration Concept



Case Study: PCB Line



Case Study: Disk Drive Clean Line

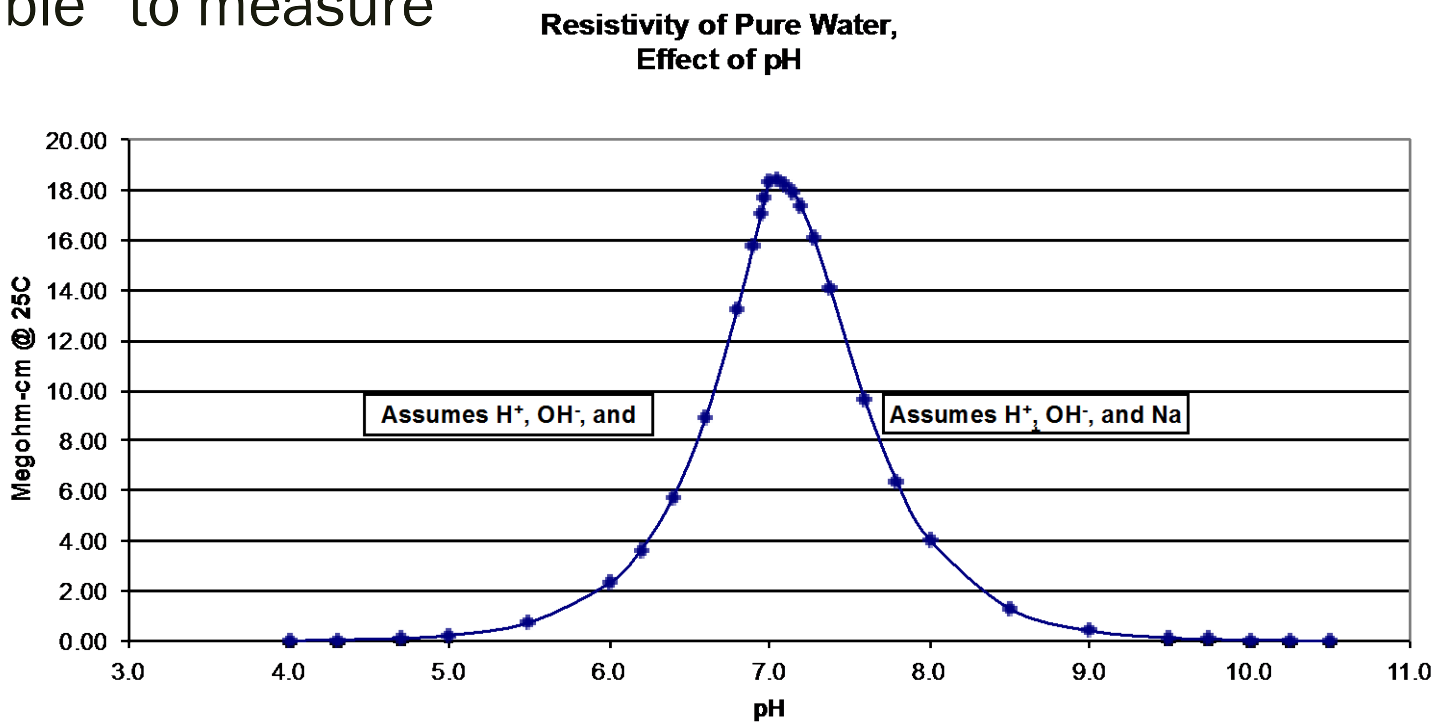


Benefits of AEDI Systems Design and Membrane Modules

- Cell technology has been improved since 1977: Simple System Concept
- Thin-cell Technology and thin-concentrate Technology
- Unique non-scaling electrode system
- Unique concentrate reject stream
- Compact, light, easy to ship and install and allows for smaller footprints
- Lower voltage, less expensive power supply
- Up-flow, no air traps

pH and Ultrapure Water

- pH of RO is 6.95-7.05
- pH of DI is "difficult" to measure
- pH of Ultrapure water is "impossible" to measure



Water Impacts on Parts: Pretreatment, Pretreatment, Pretreatment

- Pretreatment is critical to performance & lifetime of parts made; AEDI systems can remove:
  - *Chlorine*
  - *Adjustment of pH*
  - *Feed pH adjustment for CO_2 and SiO_2*
  - *UV (watch out for O_3 generation)*
  - *CO_2 removal*

Other Contaminants

- Iron
  - *Frequent fouling on parts*
- Chlorine
  - *Could impact innerconnect and various coating*

Technology Comparisons

- AEDI
  - *AEDI with pretreatment, 10-15% reject, 85-90% recovery*
- D.I. Water Service, no recovery
  - *Bottle Service, no recovery*
- Conventional RO/IX, no recovery
  - *RO + IX (Ion Exchange) Bottle Service, 25% reject, no recovery*
- Conventional RO/IX with recovery*
  - *RO + IX Bottle Service, 30% reject and IX Regeneration costs, 70% recovery*

*System Size for Comparison: 40 GPM

Value Proposition

- AEDI offers the following benefits:
  - ✓ Reduction in water and wastewater related costs
  - ✓ Reduction in water usage and wastewater generation by as much as 90%

Business Use Case

- Legacy/Existing Site
  - *Addition of AEDI systems in process lines reduce operating costs by reducing pre and post treatment water requirements*

- New manufacturing site
  - *Additional benefit at the site by reducing capital costs associated with pre and post treatment*

Summary

- Water is a main and critical component of electronics processing
- Automatic advanced electrodeionization is a proven method to improve quality and decrease costs versus conventional approaches
- AEDI offers cost savings; low water usage and low water use and wastewater generation reduction; COO less than other technologies
- AEDI enables growing number of recycling mandates and process control
- Since availability and quality of water is a major issue in most Asian Regions, recycling is a desired approach
- Additional savings from recycling and reclaim of chemicals

Thank you for your attention !

Any Questions?

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