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DOWEX

Ion Exchange Resins

Uniform Particle Size Ion Exchange Resins: Practical Application of Equilibrium Theory to Improve UPW Quality by Minimizing Ionic Leakage

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Abstract

Uniform particle size (UPS) ion exchange resins have been gaining a wider acceptance in the production of ultrapure water (UPW) for use by the semiconductor industry. Ionic leakage is measurably lower from UPS resins when compared to conventional resins with a typical Gaussian particle size distribution. These UPS resins also offer significant improvements in resistivity profiles as well as low levels of total organic carbon (TOC) contaminants. For example, in UPS mixed beds it has been shown that an effluent resistivity of 18.2 megohm-cm is attainable after only 2 bed volumes of rinse water, and Δ TOC concentrations as low as 2 ppb have been achieved after rinsing for less than one hour. These and other benefits associated with UPS resins in this application will be discussed. Complete separation of the anion and cation exchange resins in a mixed bed is necessary prior to regeneration to reduce or eliminate cross-contamination which will affect the amount of ionic leakage during the subsequent operating cycle. Calculations that predict sodium and chloride leakages based on the amount of resin remaining in the exhausted form after a regeneration (i.e., the degree of cross-contamination) will be presented. Ionic contamination and its relationship to the specifications for final ultrapure water quality will also be reviewed.

Introduction

Ultrapure water is absolutely essential to properly rinse silicon wafers and all semiconductor devices. It is the primary cleaning solvent used to rinse all chemicals and remnants of silicon and other impurities etched away during the many production process steps. The geometry of today's integrated circuits is so minute and complex that even the smallest contaminant can prevent a circuit from functioning properly. These contaminants decrease the production yield of saleable IC

product. As the degree of integration becomes increasingly more complex due to miniaturization and transistor density, the semiconductor industry requires higher levels of water purity. The amount of dissolved ionic solids, total organic carbon, live bacillus, suspended particulates and silica must approach zero or be non-detectable. In fact, the ultrapure water now required by the semiconductor industry typically must have a resistivity of at least 18.2 megohm-cm (0.055 microSiemens/cm) at 25°C, while other ionic and non-ionic contaminants must approach ppb or ppt levels as measured by on-line and off-line analytical instruments.

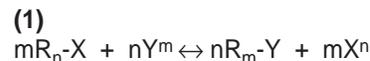
UPS ion exchange resins, when used in the primary (roughing) and secondary (polishing) loops in a regenerable and non-regenerable design, offer superior mass transfer properties. This performance can be optimally programmed to reduce waste water from regenerant chemicals while maximizing effluent UPW quality. Understanding the factors that can contribute to ionic contaminant release by ion exchange resins is critical to the development of superior products for the semiconductor industry that will provide the desired water purity. Dow has developed a line of ultrapure water grade resins which possess unsurpassed cleanliness and take advantage of Dow's patented process [1] for making resins with a uniform particle size distribution. The importance of a uniform particle size distribution for obtaining optimum water quality will be shown.

Equilibrium and the Selectivity Coefficient

By definition, ion exchange is a mass transfer process based on transport phenomena and, as such, ions must flow from a liquid phase to a solid phase. This flow of ions, or flux, depends on a balance between the driving force, which is controlled by the selectivity of the resin, and the resis-

tance to ion transport. Many conditions in both phases have an effect on the flux, such as temperature, ionic concentration, liquid viscosity, and resin particle size and water content. Selectivity is defined by chemical equilibria, whereas the transport resistance is related to rates of diffusion which are kinetically controlled.

Since ion exchange reactions are reversible, there is no net change in the ionic concentration at equilibrium when all forces are fully balanced and the ions are migrating into and out of the resin at a constant flux (i.e., dynamic state). The system at equilibrium can be defined by the following equation:



where m and $n = 1, 2$ or 3
and R = resin copolymer + functional group

The selectivity coefficient, K_X^Y , for this system at equilibrium is defined as

$$(2) \quad K_X^Y = \frac{[R_m-Y]^n [X^n]^m}{[R_n-X]^m [Y^m]^n}$$

where $[R_m-Y]$ = concentration of resin in the Y form
 $[X^n]$ = concentration of X in solution
 $[R_n-X]$ = concentration of resin in the X form
 $[Y^m]$ = concentration of Y in solution

K_X^Y describes the driving force for the removal of Y from solution. If $K_X^Y > 1$, the resin will have a greater affinity for Y over X; if $K_X^Y < 1$, the resin preferentially wants to remain in the X form. The selectivity coefficients are, therefore, relative values and are based on the ion selectivity ratios versus either H^+ or OH^- . They are determined by assigning a value of 1.0 for hydrogen on a strong acid cation exchange resin and a value of 1.0 for hydroxide on a strong base anion exchange resin [2].

Ionic Leakage

The purity of an ion exchange resin at the bottom of the bed (assuming down-flow service) affects the quality of the effluent. Equilibrium leakage is the release of undesirable ions during the service cycle due to the fraction of ion exchange resin remaining in the exhausted state after the preceding regeneration. This type of leakage is "system" related and can be minimized by optimizing the regeneration procedure. In the example of a cocurrent, partially regenerated hydrogen form cation bed, the influent salt solution is converted to its corresponding dilute acid at the top of the column. When this acid solution contacts the resin containing sodium ions at the bottom of the bed, re-exchange of H^+ for Na^+ occurs, resulting in sodium leakage. Sodium leaks before, for example, calcium and magnesium due to the higher selectivity of the resin for the hardness ions.

On the other hand, kinetic leakage occurs when the concentration of the undesired ions in the effluent is higher than expected from the purity of the resin at the bottom of the bed. In this case, the exchange zone becomes elongated and the effluent water quality becomes worse than predicted by the selectivity characteristics of the resin. This kind of leakage is "resin" related and is usually attributable to some form of resin deterioration.

Resin Separation and Cross-Contamination

Prior to regeneration, the anion and cation exchange resins must be separated by backwashing the mixed bed. During backwash operation, the anion exchange resin rises to the top due to its smaller size and lighter density. Efficient separation of the resins is critical to avoid contamination of the anion exchange resin with cation resin, and contamination of the cation exchange resin with anion resin. Cation exchange resin in the anion resin will be converted to the sodium form during regeneration of the anion exchange resin with sodium hydroxide.

Likewise, anion exchange resin in the cation resin will be converted to the chloride or sulfate forms during regeneration of the cation exchange resin with hydrochloric or sulfuric acid. This cross-contamination can lead to a decrease in water quality as described in the following sections.

The optimal separation that can be obtained for resins during backwashing can be estimated from Stokes' law [3]:

$$(3) \quad V = \{2 g a^2 (d_1 - d_2)\} \div 9 \eta$$

where V = resin terminal settling velocity (cm/sec)

g = gravitational constant (981 cm/sec²)

a = radius of resin beads (cm)

d_1 = density of resin (1.06 g/cm³ for anion resin and 1.23 g/cm³ for cation resin)

d_2 = density of water (0.998 g/cm³ at 20°C)

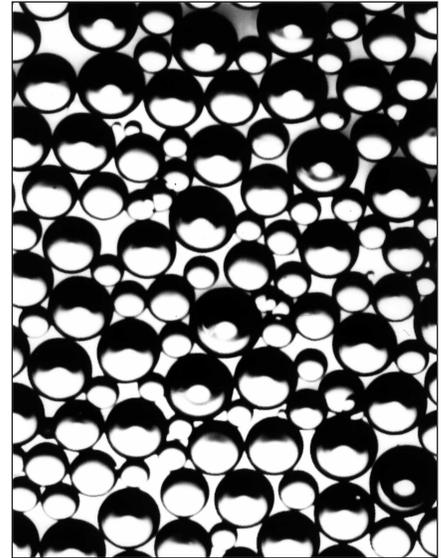
η = viscosity of water (0.01002 poise at 20°C)

Stokes' law defines the ultimate settling velocity for a sphere in a viscous solution. For ion exchange resins, this velocity is commonly referred to as the resin terminal settling velocity (TSV). Separation of resins during backwashing occurs due to the different settling velocities for the anion and cation exchange resins. The two resin properties that determine the efficiency of the resin separation are the size of the resin beads and the density of the resin. Since all gel type anion and cation exchange resins used in UPW purification systems have similar densities, particle size distribution is the only variable that can be altered to improve the separation characteristics of a resin to minimize the occurrence of resin cross-contamination.

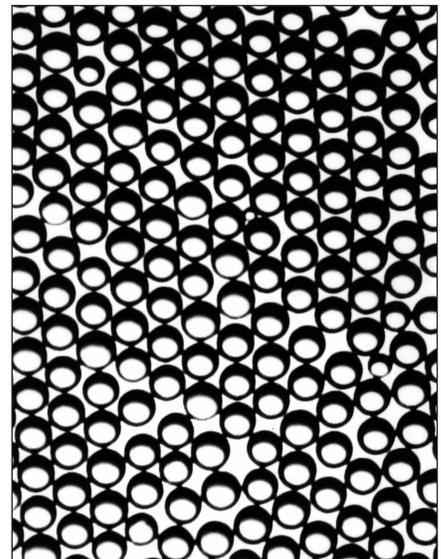
The particle size distribution of ion exchange resin beads with a conventional Gaussian distribution versus those with a uniform distribution are shown in the following photomicrographs:

Figure 1. Photomicrographs of Conventional and Uniform Particle Size Ion Exchange Resins

Conventional Ion Exchange Resin



Uniform Particle Size Ion Exchange Resin



The terminal settling velocities for three resin combinations are shown in Figures 2 - 4. Figure 2 shows the TSV for conventional anion and cation exchange resins that have a Gaussian particle size distribution. The settling velocities for both resins cover a wide range and more importantly show that

the TSV for both resins overlap between 3 - 5 cm/sec. These calculations show that even under ideal conditions there will be 1-2% cross-contamination of cation resin in the anion exchange resin, and vice-versa. In actual operations, the cross-contamination levels can be considerably higher due to interactions between the charges on the resin beads, physical interference from other resin beads, and limitations of the process equipment, design and operation. Thus, for resins with a Gaussian particle size distribution, complete separation is not possible and cross-contamination will occur.

Figure 3 shows the TSV for anion (DOWEX* MONOSPHERE* 550A UPW (OH)) and cation (DOWEX MONOSPHERE 650C UPW (H)) exchange resins that have a uniform particle size distribution. The MONOSPHERE resins have a narrow range of settling velocities and the peaks are distinctly separate from one another. This makes separation of the resin easier and minimizes cross-contamination.

For the final polishing loops, non-regenerated ion exchange resins are used in many UPW systems. For non-regenerated resins, it is advantageous to use resins that do not separate during column loading or during process upsets. UPS resins can be tailored to provide a mixed bed that is non-separable. Figure 4 shows the TSV for a UPS anion exchange resin (DOWEX MONOSPHERE 550A UPW (OH)) with a small UPS cation exchange resin (DOWEX MONOSPHERE C350 UPW (H)). The TSV for these UPS anion and cation exchange resins are almost identical; thus, a completely non-separable homogeneous mixed bed (available as DOWEX MONOSPHERE MR-450 UPW) is obtained. This non-separable mixed bed is generally operated to a boron, silica or TOC breakthrough (ppb or ppt) representing a useful mixed bed resin life of 1 to 3 years depending on the influent ionic concentration.

Figure 2. Terminal Settling Velocity for Conventional Resins with a Gaussian Particle Size Distribution

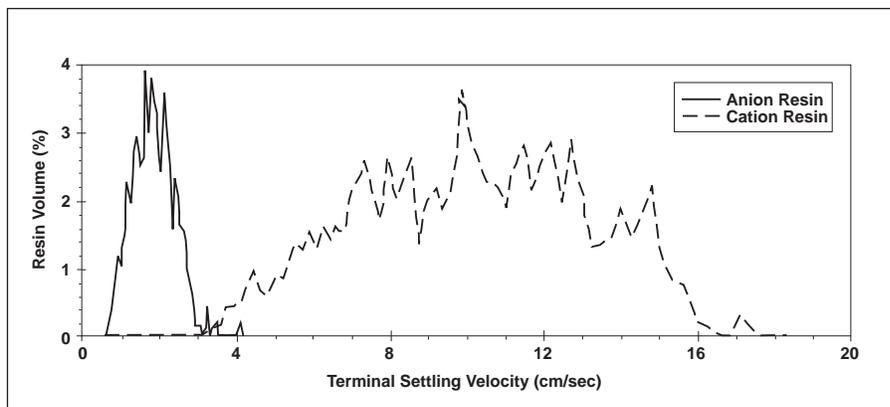


Figure 3. Terminal Settling Velocity for DOWEX MONOSPHERE 650C UPW (H) and DOWEX MONOSPHERE 550A UPW (OH) Resins (Regenerable Mixed Bed)

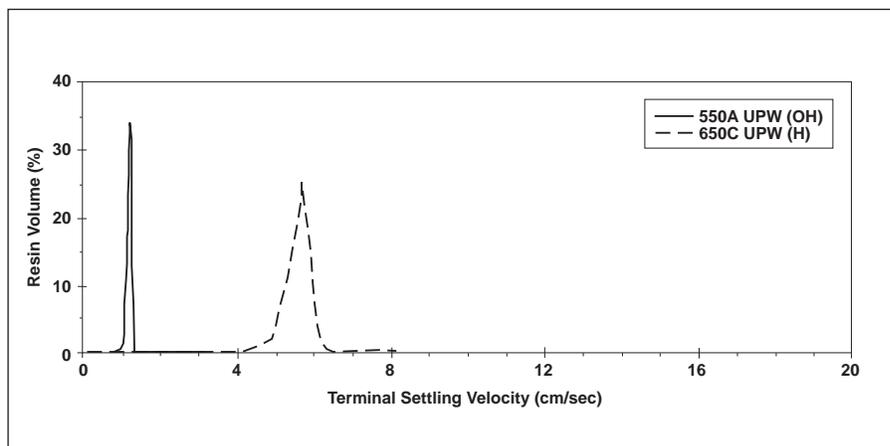
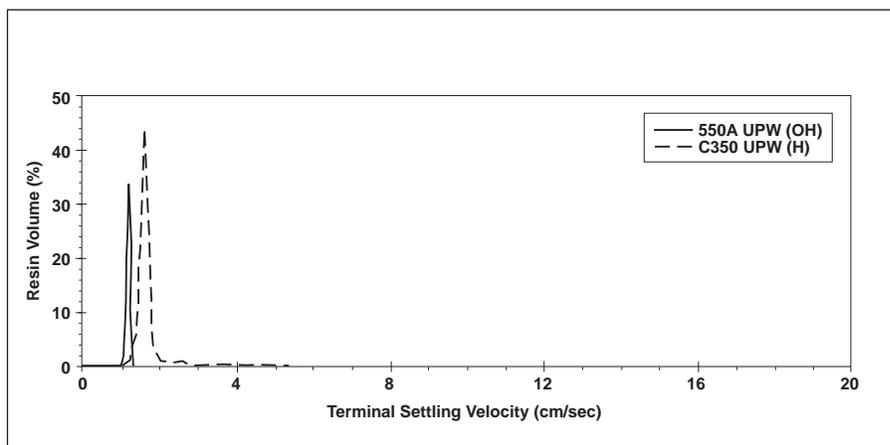


Figure 4. Terminal Settling Velocity for DOWEX MONOSPHERE C350 UPW (H) and DOWEX MONOSPHERE 550A UPW (OH) Resins (Non-regenerable Mixed Bed)



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Effect of Cross-Contamination and pH on Leakage

I. Sodium Leakage from a Cation Resin

The separation efficiency can be determined from the amount of cross-contamination in a mixed bed which can be estimated if the effluent leakage and pH values are known. For example, the amount of the cation resin converted to the sodium form from NaOH used to regenerate the anion resin can be calculated and the impact on the sodium leakage can be determined. As an example, it is assumed that the sodium leakage is 1.4 ppt Na⁺, effluent pH = 7, sodium selectivity coefficient, $K_{H}^{Na} = 1.6$ @ 25°C for a 10% crosslinked strong acid cation (SAC) resin like DOWEX MONOSPHERE 650C UPW (H), and any sodium in the effluent is due primarily to equilibrium leakage. Recall that equilibrium leakage is defined as the release of undesirable ions during the service cycle due to the fraction of the resin remaining in the exhausted form after the preceding regeneration. In this example, using equation (1) where R = resin copolymer + SO₃⁻

$$m = n = 1$$

$$X = H$$

$$Y = Na$$


(5) and $K_{H}^{Na} = \frac{[R-Na][H^+]}{[R-H][Na^+]}$

(6) $\therefore [R-Na] \div [R-H] = K_{H}^{Na} \left(\frac{[Na^+]}{[H^+]} \right)$

(7) Since $K_{H}^{Na} = 1.6$

(8) and $[Na^+] = \left\{ \frac{(1.4 \times 10^{-12}) \div 23}{1000} \right\}$
 $= 6.1 \times 10^{-11}$ eq/l

where 23 = Equivalent Weight (EW_{Na}) of sodium

(9) and $[H^+] = 10^{-7}$ eq/l at pH = -log₁₀[H⁺] = 7

Substituting (7), (8) and (9) into (6) gives

(10) $[R-Na] \div [R-H] = 1.6 \left\{ \frac{(6.1 \times 10^{-11}) \div 10^{-7}}{1000} \right\}$
 $= 9.8 \times 10^{-4}$

(11) \therefore % in sodium form
 $= 100 \left\{ \frac{[R-Na] \div [R-H]}{1 + ([R-Na] \div [R-H])} \right\}$
 $= 100(0.00098 \div 1.00098)$
 $= 0.1$

Therefore, if the sodium leakage exceeds 1.4 ppt at pH 7, $\geq 0.1\%$ of the cation resin is in the sodium form. Similar calculations can be done for additional sodium and other cation leakages.

II. Chloride Leakage from an Anion Resin

Alternatively, the amount of the anion resin in the chloride form can be calculated and the impact on the chloride leakage can be determined. In this example, it is assumed that hydrochloric acid is used to regenerate the cation resin, the chloride leakage from the anion resin is 0.16 ppt Cl⁻, effluent pH = 7, chloride selectivity coefficient, $K_{OH}^{Cl} = 22$ @ 25°C for a Type I strong base anion (SBA) resin like DOWEX MONOSPHERE 550A UPW (OH), and any chloride in the effluent is due primarily to equilibrium leakage.

Therefore, in this case, using equation (1) where R' = resin copolymer +

$$CH_2N^+(CH_3)_3$$

$$m = n = 1$$

$$X = OH$$

$$Y = Cl$$


(13) and $K_{OH}^{Cl} = \frac{[R'-Cl][OH^-]}{[R'-OH][Cl^-]}$

(14) $\therefore [R'-Cl] \div [R'-OH] = K_{OH}^{Cl} \left(\frac{[Cl^-]}{[OH^-]} \right)$

(15) Since $K_{OH}^{Cl} = 22$

(16) and $[Cl^-] = \left\{ \frac{(0.16 \times 10^{-12}) \div 35.5}{1000} \right\}$
 $= 4.5 \times 10^{-12}$ eq/l

where 35.5 = Equivalent Weight (EW_{Cl}) of chlorine

(17) and $[OH^-] = 10^{-7}$ eq/l at pH = 7

Substituting (15), (16) and (17) into (14) gives

(18) $[R'-Cl] \div [R'-OH] = 22 \left\{ \frac{(4.5 \times 10^{-12}) \div 10^{-7}}{1000} \right\}$
 $= 9.9 \times 10^{-4}$

(19) \therefore % in chloride form
 $= 100 \left\{ \frac{[R'-Cl] \div [R'-OH]}{1 + ([R'-Cl] \div [R'-OH])} \right\}$
 $= 100(0.00099 \div 1.00099)$
 $= 0.1$

Hence, if the chloride leakage exceeds 0.16 ppt at pH 7, $\geq 0.1\%$ of the anion resin is in the chloride form. Similar calculations can be done for additional chloride and other anion leakages.

III. pH Dependency

In both preceding examples, it was assumed that the effluent pH was 7; however, a variation in the pH can produce the same amount of leakage from a resin that has a significant difference in the amount of cross-contamination. For example, consider the case where the sodium leakage is 400 ppt Na⁺, effluent pH = 7, sodium selectivity coefficient, $K_{H}^{Na} = 1.6$ @ 25°C for a 10% crosslinked cation resin like DOWEX MONOSPHERE 650C UPW (H), and any sodium in the effluent is due primarily to equilibrium leakage:

(20) $[Na^+] = \left\{ \frac{(400 \times 10^{-12}) \div 23}{1000} \right\}$
 $= 1.74 \times 10^{-8}$ eq/l

Substituting (7), (9) and (20) into (6) gives

$$(21) \quad [R-Na] \div [R-H] = 1.6 \{ (1.74 \times 10^{-8}) \div 10^{-7} \} = 2.78 \times 10^{-1}$$

or $(0.278 \div 1.278)100 = 21.8\%$ of the cation resin is in the sodium form.

Therefore, if the sodium leakage is 400 ppt at pH 7, **21.8%** of the cation resin is in the sodium form. But, this is very pH dependent. For example:

$$(22) \quad \text{If } [H^+] = 10^{-6} \text{ eq/l at pH} = 6$$

Substituting (7), (20) and (22) into (6) gives

$$(23) \quad [R-Na] \div [R-H] = 1.6 \{ (1.74 \times 10^{-8}) \div 10^{-6} \} = 2.78 \times 10^{-2}$$

or $(0.0278 \div 1.0278)100 = \text{only } 2.7\%$ of the cation resin is in the sodium form.

Furthermore, the amount of cation resin in the sodium form for any pH and leakage (which are measurable values) can be calculated from equation (11).

Rearranging (11) gives

$$(24) \quad \% \div (100 - \%) = [R-Na] \div [R-H]$$

Substituting (24) into (6) gives

$$(25) \quad \% \div (100 - \%) = K_H^{Na} \{ [Na^+] \div [H^+] \} = 1000 \{ (K_H^{Na} \times L_{Na}) \div (EW_{Na} \times [H^+]) \}$$

where L_{Na} = sodium leakage (g_{Na} / g_{soln})

Rearranging (25) gives

$$(26) \quad \% = 100 \div \{ \{ (EW_{Na} \times [H^+]) \div (1000 \times K_H^{Na} \times L_{Na}) \} + 1 \}$$

Table 1. Relationship Between pH and Sodium Leakage on Cation Resin Cross-Contamination

pH	$[H^+]$	Sodium Leakage (ppt)				
		1.0	10	100	1000	10000
6.0	10^{-6}	0.007	0.07	0.7	6.5	41.0
6.5	3.162×10^{-7}	0.02	0.2	2.2	18.1	68.8
7.0	10^{-7}	0.07	0.7	6.5	41.0	87.4
7.5	3.162×10^{-8}	0.2	2.2	18.1	68.8	95.7
8.0	10^{-8}	0.7	6.5	41.0	87.4	98.6
<i>Percent of Cation Resin in Sodium Form</i>						

Figure 5. Effect of Cation Resin Cross-Contamination on Sodium Leakage

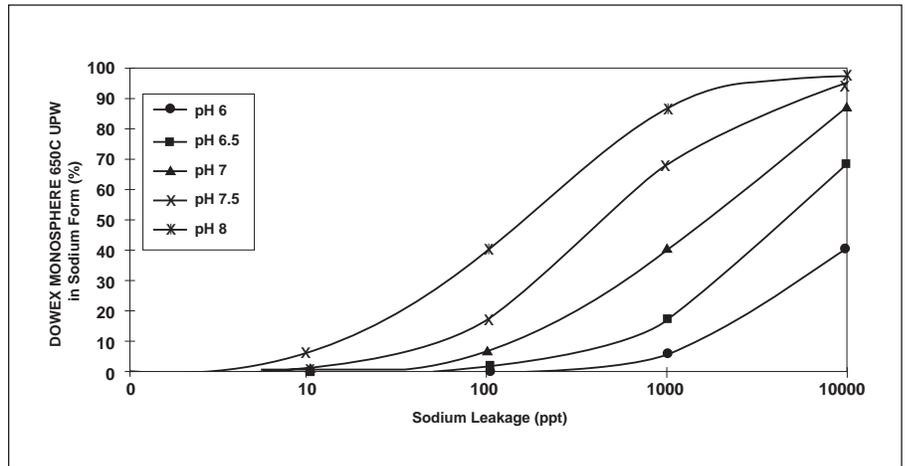
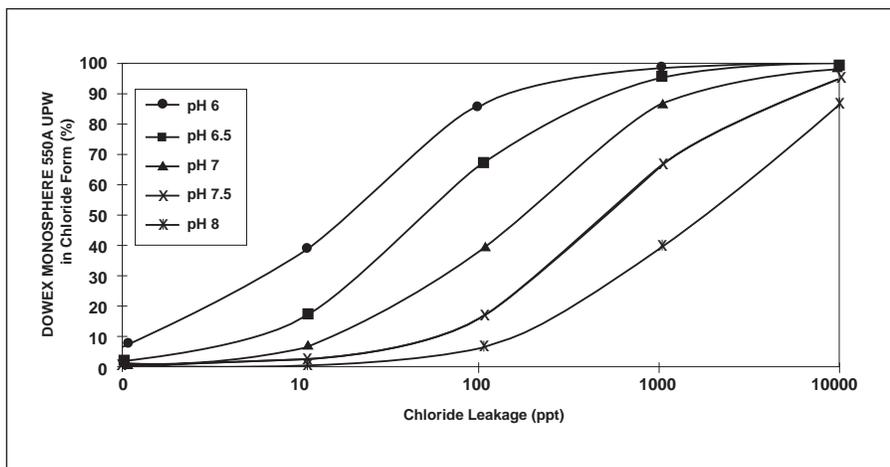


Table 2. Relationship Between pH and Chloride Leakage on Anion Resin Cross-Contamination

pH	$[OH^-]$	Chloride Leakage (ppt)				
		1.0	10	100	1000	10000
6.0	10^{-8}	5.8	38.3	86.1	98.4	99.8
6.5	3.162×10^{-8}	1.9	16.4	66.2	95.1	99.5
7.0	10^{-7}	0.6	5.8	38.3	86.1	98.4
7.5	3.162×10^{-7}	0.2	1.9	16.4	66.2	95.1
8.0	10^{-6}	0.06	0.6	5.8	38.3	86.1
<i>Percent of Anion Resin in Chloride Form</i>						

Figure 6. Effect of Anion Resin Cross-Contamination on Chloride Leakage



The percentage of DOWEX MONOSPHERE 650C UPW (H) cation resin in the sodium form is shown in Table 1 and Figure 5 at various pH values and leakages:

An equation similar to (26) can be derived to calculate the amount of anion resin in the chloride form for any pH and leakage (which are measurable values):

$$(27) \quad \% = 100 \div \{ \{ (EW_{Cl} \times [OH^-]) \div (1000 \times K_{OH}^{Cl} \times L_{Cl}) \} + 1 \}$$

where L_{Cl} = chloride leakage (g_{Cl}/g_{soln})

The percentage of DOWEX MONOSPHERE 550A UPW (OH) anion resin in the chloride form is shown in Table 2 and Figure 6 at various pH values and leakages:

Consequently, it is shown that the amount of leakage increases with the amount of cross-contamination, and an increase in pH results in a decrease in sodium leakage from a cation resin and an increase in chloride leakage from an anion resin at a constant amount of cross-contamination. From a practical perspective, these calculations are most useful when the total ionic load in the resin is below 25%. At higher levels of resin exhaustion our experience has shown that other fac-

tors such as resin kinetics begin to play a more important role on the level of ionic leakage.

IV. Predicting Effluent pH and Leakage

From a laboratory analysis, the amount of resin in the exhausted form can be measured. In the previous example, it was determined that 4.8% of the functional sites on the cation resin were in the sodium form after the anion resin was regenerated with NaOH.

$$(28) \quad \therefore [R-Na] \div [R-H] = 0.048 \div 0.952 = 5.04 \times 10^{-2}$$

Substituting (28) into (23) gives

$$(29) \quad 5.04 \times 10^{-2} = 1.6 \{ (1.74 \times 10^{-8}) \times [H^+] \}$$

$$(30) \quad \text{or } [H^+] = 1.6 \{ (1.74 \times 10^{-8}) \div 5.04 \times 10^{-2} \} = 5.52 \times 10^{-7} \text{ eq/l}$$

$$(31) \quad \therefore \text{pH} = -\log_{10}[H^+] = -\log_{10}[5.52 \times 10^{-7}] = 6.26$$

Consequently, it is possible that at pH 6.26 and 4.8% of the cation resin in the sodium form, the sodium leakage can be as much as 400 ppt Na^+ . Alternatively, the effluent pH can be calculated by rearranging (25) to give

$$(32) \quad [H^+] = \{ 1000 \times K_H^{Na} \times L_{Na} (100 - \%) \} \div (EW_{Na} \times \%)$$

$$(33) \quad \therefore \text{pH} = -\log_{10} \{ \{ 1000 \times K_H^{Na} \times L_{Na} (100 - \%) \} \div (EW_{Na} \times \%) \}$$

Similarly, the leakage can be calculated by rearranging (25) to give

$$(34) \quad L_{Na} = (EW_{Na} \times [H^+] \times \%) \div \{ 1000 \times K_H^{Na} (100 - \%) \}$$

Relationship of Ionic Contamination to Water Quality Specifications

In addition to cross-contamination arising from chemical regeneration, the level of ionic contaminants present in ion exchange resins may affect the ionic leakage from the resin bed. For UPW grade resins, special processing conditions should be used to minimize the residual levels of ionic contaminants. In 1993, Balazs Analytical Laboratory issued a document [4] that included a table outlining the specifications for final water quality from a UPW system. The **attainable** cation and anion concentrations listed in this table can be assumed to be the **acceptable** leakages for UPW used to rinse today's generation of silicon wafers, memory, and computational and other ASIC devices. The level of ionic contamination in cation and anion exchange resins that will lead to equilibrium leakage can be calculated from equation (2) using equations (35) and (36), respectively:

$$(35) \quad [R_m^- Y] = K_H^Y [R-H]^m [Y^m] \div [H^+]^m$$

for cation exchange resins where $n = 1$ and $X = H$, and

$$(36) \quad [R_m^- Y] = K_{OH}^Y [R-OH]^m [Y^m] \div [OH^-]^m$$

for anion exchange resins where $n = 1$ and $X = OH$.

Table 3. Relationship Between Ionic Leakage and Contaminant Level in Resins at pH 7

Cation Exchange Resins

Ion (Y ^m)	K _H ^Y [2]	Ionic Leakage Target [4] (ppt)	Resin Contaminant Level R _m -Y (% resin sites)	Y ^m (ppm)**	650C UPW (H) Specification ppm, max.**
Li ⁺	0.85	4	0.49	176	—
Na ⁺	1.5	10	0.65	780	25
K ⁺	2.5	20	1.27	2,600	—
NH ₄ ⁺	1.95	60	6.10	5,700	—
Mg ²⁺	2.5	20	99.7	63,000	—
Ca ²⁺	3.9	20	99.9	104,000	—
Sr ²⁺	5.0	2	99.5	227,000	—
Ba ²⁺	8.7	2	99.6	356,000	—
Mn ²⁺	2.35	4	99.6	143,000	—
Fe ²⁺	2.55	10	99.8	145,000	25
Ni ²⁺	3.0	5	99.7	152,000	—
Cu ²⁺	2.9	5	99.7	165,000	15
Zn ²⁺	2.7	8	99.7	170,000	—

Anion Exchange Resins

Ion (Y ^m)	K _{OH} ^Y [2]	Ionic Leakage Target [4] (ppt)	Resin Contaminant Level R _m -Y (% resin sites)	Y ^m (ppm)**	550A UPW (OH) Specification % resin sites, max.
F ⁻	1.6	100	7.75	4,200	—
Cl ⁻	22	20	11.0	11,300	0.1
Br ⁻	50	20	11.1	25,000	—
NO ₂ ⁻	24	20	9.45	12,500	—
NO ₃ ⁻	65	20	17.4	31,000	—
HCO ₃ ⁻	6	n/a			
Silica	see discussion	200			
Boron	see discussion	300			

** Dry Resin Basis

In a mixed bed with an effluent pH = 7, [H⁺] = [OH⁻] = 10⁻⁷ eq/l. The ionic contamination that can build up in the resin before the specified leakage level is exceeded at pH 7 is given in Table 3. Experience has shown that equilibrium leakage should only be considered the dominant factor if the ionic leakage level is reached before 25% of the resin exchange sites become loaded

with the ion. When more than 25% of the resin exchange sites are exhausted, kinetic factors tend to dominate the amount of resin leakage. From Table 3 it can be seen that at pH 7 only the monovalent anions and cations will leak through a resin bed due to equilibrium leakage. For example, if 0.65% of the sites in a cation exchange resin at the

bottom of a mixed bed are in the sodium form, then the sodium level in the effluent will be 10 ppt since the equilibrium point for sodium with the resin has been reached. Even if the influent sodium level to the mixed bed is less than 10 ppt, the effluent level will be 10 ppt once 0.65% of the resin sites are in the sodium form.

Silica and boron are two important ions that can also break through a mixed resin bed due to equilibrium leakage. It is common for silica or boron to break through a mixed bed before other ions and to use the silica or boron breakthrough point to determine when a mixed bed needs to be replaced or regenerated [5]. Unfortunately, silica and boron do not exist as a single chemical species under mixed bed operating conditions. Boron, as boric acid, with a $pK_a(1) = 9.14$ is only very slightly ionized at pH 7 and, therefore, its removal by strong base anion exchange resins is difficult. Both of these compounds can also exist as polymeric species that may lead to kinetic leakage as well as equilibrium leakage. As a result, it is difficult to obtain a realistic selectivity coefficient for these ions and compare the results with the other anions in Table 3. The relative selectivity coefficients for silica and boron can be inferred from the relative order that they break through a mixed bed: $HCO_3^- > \text{silica} > \text{boron}$.

Table 3 shows that leakage of polyvalent ions due to equilibrium does not occur until very high loading of the ion into the resin occurs. As a result, the leakage of polyvalent ions from mixed beds over a pH range of 5 - 9 and at low (<0.1 ppm) influent concentrations does not usually occur due to equilibrium leakage. The uptake and leakage of polyvalent ions is dominated by kinetic rather than equilibrium factors. A detailed discussion of the kinetic factors that affect ion exchange resin performance is beyond the scope of this paper, but one critical factor is the particle size distribution of the resins [6,7]. The diffusion rate of ions into a resin is inversely proportional to r^2 where r is the radius of the resin bead; thus, ions diffuse faster into smaller resin beads. UPS resins offer an advantage in kinetic performance compared to resins with a conventional Gaussian size distribution due to their smaller and narrower particle sizes (see Figure 1). For example, the average particle diameter for conventional anion exchange resins is about

700 μm , whereas the average diameter for DOWEX MONOSPHERE 550A UPW (OH) is 580 μm and less than 1% of the resin beads are $\geq 700 \mu\text{m}$. Similarly, the average particle diameter for conventional cation exchange resins is about 850 μm , whereas the average diameters for DOWEX MONOSPHERE 650C UPW (H) and C350 UPW (H) are 650 μm and 350 μm , respectively. The small and uniform size of the UPS resins enhances the kinetic performance for removing polyvalent ions from solution.

Equilibrium leakage of polyvalent ions from resins can occur if the pH in the resin bed deviates significantly from 7, especially if the pH is less than 4 or greater than 10. These conditions are not typically encountered in UPW polishing systems, but may arise in single bed systems or in primary mixed beds where there is a high influent ionic concentration and the mixed bed is not well mixed or there is an imbalance in the anion to cation exchange resin ratio. The ionic contamination that can build up in the resin before the specified leakage level is exceeded under these unusual operating conditions is given in Table 4. From Table 4 it can be seen that under low pH conditions, the leakage of metal ions exceeds the targeted water quality levels even though the level of the ions in the resin are at very low levels (<0.1% of resin sites). A similar phenomenon occurs for polyvalent anions with anion exchange resins at high pH levels. Insuring that mixed beds are completely mixed would prevent this problem from occurring. UPS resins are easier to keep mixed together because there are no large cation resin beads or very small anion resin beads which quickly separate from one another.

Table 4. Polyvalent Cation Leakage from Cation Exchange Resins Under Low pH Conditions

Ion (Y^m)	K_{YH}^Y [2]	Ionic Leakage Target [4] (ppt)	Effluent pH	Resin Contaminant Level $R_m \cdot Y$ (% resin sites)	Y^m (ppm)**
Mg ²⁺	2.5	20	2.9	0.059	37
Ca ²⁺	3.9	20	2.6	0.125	130
Sr ²⁺	5.0	2	3.0	0.049	110
Ba ²⁺	8.7	2	3.0	0.050	180
Mn ²⁺	2.35	4	3.0	0.056	80
Fe ²⁺	2.55	10	2.8	0.077	110
Ni ²⁺	3.0	5	2.9	0.064	100
Cu ²⁺	2.9	5	2.9	0.061	100
Zn ²⁺	2.7	8	2.9	0.069	120

** Dry Resin Basis

Summary

It has been shown that the amount of cross-contamination and ionic contamination, which both affect the quality of the ion exchange effluent, can be calculated from equilibrium theory. Equations have been derived to predict the amount of resin in the exhausted form as well as the pH of the effluent and the leakage from a resin bed. The residual levels of ionic contaminants in ion exchange resins have been correlated to the industry standards for final water quality from a UPW system.

It has also been shown that uniform particle size ion exchange resins have the properties to meet the ever stringent ultrapure water quality needs of the semiconductor industry. When selecting a certain type of UPS ion exchange resin, the best product choice will depend on the type and location of the ion exchange resin bed in the UPW system. The following criteria should be considered:

Individual and Mixed Resin Beds

- lowest ionic leakage
- highest operating capacity
- optimal surface area to volume ratio
- rapid ion diffusional kinetics

Regenerable Mixed Beds

- complete separation due to uniform particle size distribution
- distinct color differentiation

Non-regenerable Mixed Beds

- initial purity of cation and anion exchange resins
- no separation during vessel loading or operation

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Warning: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions. This could lead to anything from slight resin degradation to a violent exothermic reaction (explosion). Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

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