

Dow
Liquid Separations

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DOWEX

Ion Exchange Resins

Powerful Chemical Processing Tools

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Introduction

DOWEX Ion Exchange Resins - Powerful Chemical Processing Tools

Ion exchange resins have made important inroads in the field of chemical processing since the advent of the synthetic organic ion exchange resins in the 1940s. DOWEX[®] ion exchange resins have historically and consistently had the high physical and chemical stability necessary in this area of processing. The Dow Chemical Company has developed and introduced into the industry not only these more stable products, but products with functionalities that allowed the companion development of new processes utilizing these ion exchange related products. Processes such as Ion Retardation, Ion Exclusion, Acid Retardation, Desiccation, Radium Removal, Chelation, and Catalysis have been pioneered by The Dow Chemical Company, and Dow remains committed to the continuing support of this diverse industry.

Important Chemical and Physical Nature of Ion Exchange Resins

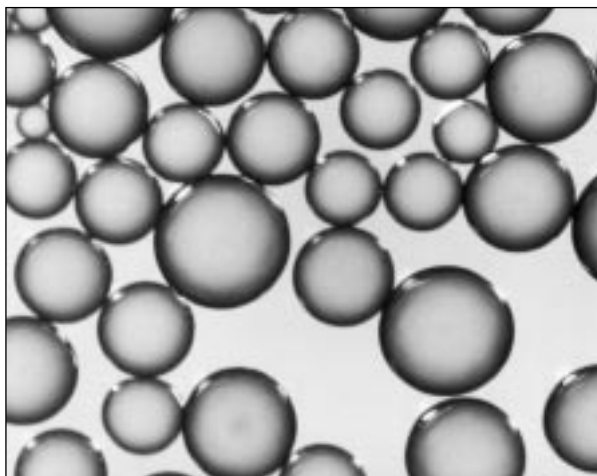
The Matrix. The majority of the ion exchange resins manufactured in the world today are based on the polymer chemistry of styrene, crosslinked with divinylbenzene. The variety of copolymers and their functionalized products, available both conceptually and commercially, are many. This polymer system has also stood the test of time as the most stable system, physically and chemically, of any commercially available to date.

Final resin properties may be significantly varied by changing the amount of divinylbenzene crosslinking agent, which alters the swollen gel porosity of the finished ion exchange resin. Reaction rates are thus variable and controllable, as are the size range of molecules that may diffuse into and out of the resin structure. True porosity can also be built into the matrix during the orig-

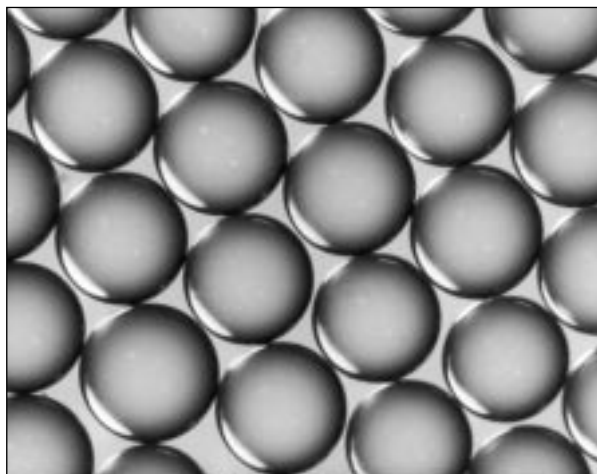
inal copolymerization, forming a macroporous structure, and increasing the flexibility of porosity control. Suspension polymerization results in spherical particles having a broader gaussian distribution. Dow's newer technology adds the ability to control the particle size distribution to within very narrow limits and is available commercially as the DOWEX MONOSPHERE[®] line of ion exchange resins. Improved kinetics, reduced pressure drop, and better resin transfer can often be achieved with these products.

The Functional Group. Following the formation of the styrene/divinylbenzene copolymer, functionalization of the polymer structure is done to convert the polymer into an ion exchange resin. Functionalities added to the copolymer include sulfonate, quaternary amine, and tertiary amine groups. The resulting resins will be discussed below. In addition, special functional groups are added for particular chemical processing applications, such as the picolylamine functionality which forms a chelating resin useful in copper recovery.

Standard DOWEX Ion Exchange Beads



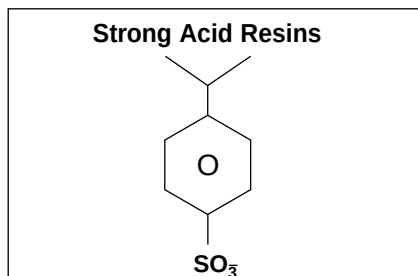
DOWEX MONOSPHERE Ion Exchange Beads



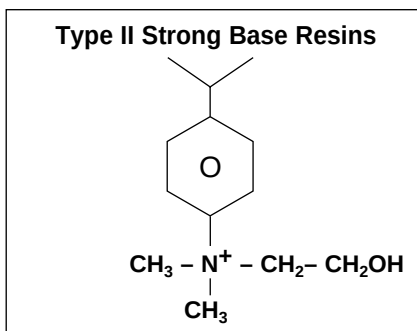
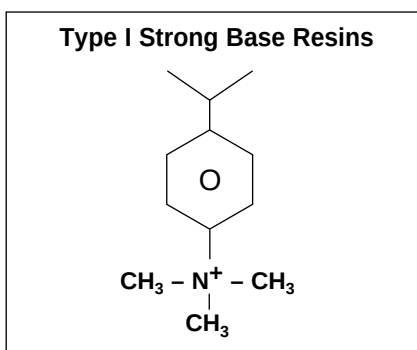
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DOWEX Resins Significant to Chemical Processing Applications

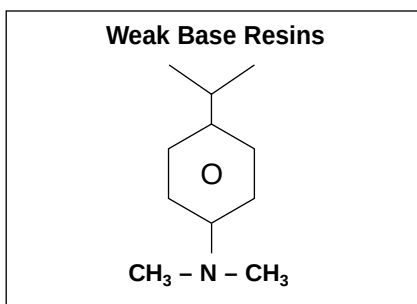
Strong Acid Resins. As produced, these resins contain exchangeable H^+ cations which give the resins the ability to behave as insoluble, but very reactive acids. Not only can these resins be used to exchange the H^+ ion for the cations of a salt in solution, effectively "salt splitting" and forming the acid of the salt involved in solution, but they can be used in place of soluble acid in many catalytic reactions. DOWEX cation resins include standard gel products such as DOWEX HCR-S, DOWEX HCR-W2, DOWEX HGR and DOWEX HGR-W2, macroporous products such as DOWEX M-31, uniform particle size products such as DOWEX G-26, and dried catalysts such as DOWEX DR 2030.



Strong Base Resins. These resins contain quaternary amine functionalities which have the ability to exchange anions. When in the OH^- ionic form, this class of resins is capable of acting like very strong insoluble bases in solution. Type I resins incorporate quaternary methylamines as the functionality and are the strongest bases of the anion resins, whereas a lower basicity (Type II) resin is formed when the amine used in the reaction is dimethylethanolamine, which results in improved regeneration efficiency. DOWEX anion resins include standard gel products such as DOWEX SBR, DOWEX SAR, and DOWEX SBR-P, macroporous products such as DOWEX MSA-1 and DOWEX MSA-2 and uniform particle size products such as DOWEX G-55.



Weak Base Resins. These resins contain tertiary amine functionalities which act as acid adsorbers. DOWEX weak base resins include macroporous products such as DOWEX M-43.



Weak Acid Resins. These resins contain carboxylic acid groups which act as base adsorbers. The family name for the macroporous, weak acid cation exchangers is DOWEX MAC-3.

Chelating Resins. Special functionalities can be incorporated in the copolymer to make chelating resins. Two resins that are highly selective for copper are DOWEX M4195 and developmental chelating resin XFS 43084. DOWEX M4195 is based on bispicolylamine chemistry, while XFS

43084 is based on hydroxypropyl picolylamine, which has somewhat different selectivity characteristics resulting in enhanced iron rejection properties.

Polymeric Adsorbents. Polymeric adsorbents are alternatives to activated carbons that have high surface areas, low levels of extractable materials and excellent physical stability. These materials are useful for decolorizing products, product recovery from waste streams and organics purification. They have been designed for ease of regeneration on site. The product family name is DOWEX OPTIPORE*.

Ion Retardation Resins. Made by reacting polyacrylic acid into the polymer structure of a Type I strong base resin, the Ion Retardation resin, DOWEX Retardion 11A8, has the unique ability to absorb ion pairs (of salts) from solution, retarding their progress through a column, while not affecting organic molecules, thus setting up a partition which facilitates chromatographic separation. Another application of this unique resin is to remove salt contamination from caustic solution.

Styrene-DVB Copolymers. Dow Styrene-DVB copolymers are free flowing, spherical beads made from styrenic polymers that have been cross linked with divinylbenzene. They are clear to colorless opaque spheres. They are hard, spherical beads that are often used as plastic ball bearings. Applications include; lubrication, void space maintainers, grinding media, absorption and decolorization and precision fillers.

Applications - Ion Exchange Resins In Chemical Processing

General Considerations for Use of Ion Exchange Resins

Aqueous Solutions. Ion Exchange resins are considered economically useful in treatment of aqueous solutions when the ion to be modified is at concentrations low enough to allow a reasonable throughput before capacity exhaustion. Since the total capacity of ion exchange resins ranges to up to 2 chemical equivalents per liter of resin, if the acceptable throughput is 1,000 liters per liter of resin, the desired maximum total concentration in the feed solution is 0.002 equivalents per liter. When higher concentrations are encountered, a membrane separation is often used as a primary treatment step.

There is the additional limitation that high concentrations of salts or ions in the solution, other than the one which requires modification, will compete with the desired reaction. This competition is part of the reason for the development of special resins having enhanced selectivity characteristics.

Organic Solutions. In general, ion exchange reactions can be carried out in any solvent system that supports ionization of the species to be modified. From a practical standpoint, the more polar the solvent, the better the ionization, and thus, the better the chance for ion exchange reactions to occur. Ethanol and methanol support ionization reasonably well.

Solvents, which tend to be strong oxidizing agents, should be avoided. These materials can attack the resin and perhaps even cause a hazardous condition.

Stability Considerations.

DOWEX ion exchange resins may be used as acid catalysts at temperatures as high as 120°C, beyond which resin degradation occurs. The strong base resin in hydroxide form may be used as base catalysts at temperatures as high as 50°C.

The stability of the resin improves if used in a salt form rather than the hydroxide form. Resin life is also adversely affected by strong oxidizing agents.

Resins as Solid Acid/Base Catalysts

Strong Acid Resins are used in a number of instances as strong acid catalysts in place of soluble acids. Resins show similar catalytic activity to sulfuric acid in esterifications, epoxidations, hydrolyses, phenol alkylations and other acid catalyzed reactions. For example, the gasoline additive MTBE (methyl tertiary-butyl ether) is formed by the catalytic reaction of methanol with isobutylene when passed through a bed of DOWEX M-31 catalyst. (See Figure 1)

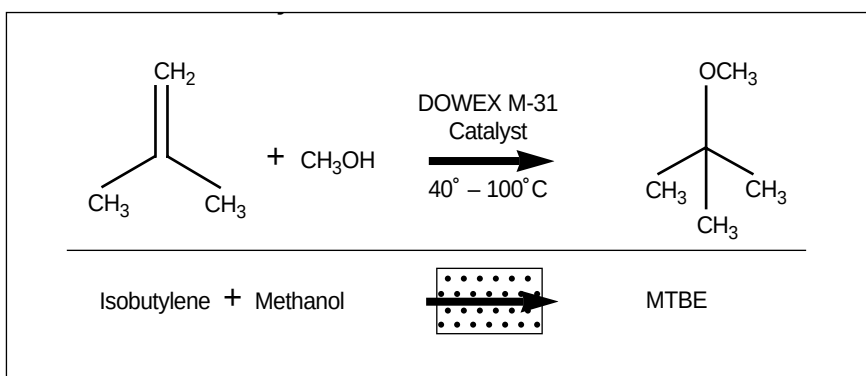
Occasionally, dried catalysts are necessary for enhanced reactivity and conversion rates or where addition of water is a problem. DOWEX DR-2030 catalyst is being effectively used in phenol alkylation.

Strong Base Resins can replace strong caustic in some base catalyzed reactions. Reactions such as ester hydrolysis and condensations have been reported.

Advantages. DOWEX ion exchange resins have the following advantages when used as acid/base catalysts:

1. Separation of the catalyst from the reaction mass is greatly simplified. Filtration removes the spherical resin while extraction or neutralization with filtration are necessary to remove a soluble sulfuric acid catalyst. Indeed, resin catalysts can be used in column operation, facilitating the use of a more continuous process.
2. The resin catalyst may be reused repeatedly. The recovered resin can be used as the catalyst in additional batch reactions, thus the cost of resin use per batch is significantly reduced. Catalyst cost can be equal to or below the cost of sulfuric acid per unit of productivity.
3. Greater selectivity of reaction direction is often possible using ion exchange resins as catalysts. Side reactions are sometimes reduced or eliminated. In some cases, it is possible to isolate reaction intermediates not obtainable with soluble catalysts.
4. Ion exchange resins are easier to handle than their soluble counterpart. They do not present the hazard to personnel nor do they cause severe equipment corrosion. Resin is easily transferred from one tank to another in slurry form, using air pressure or pumps designed to handle slurries.

Figure 1. Catalytic Reaction - MTBE Production



Metal Recovery and/or Concentration

Ion exchange resins may be used to selectively isolate and concentrate the desired metal where it is a minor component in a large stream or complicated mixture. Listed below are several examples of this chemical processing capability.

Uranium Recovery. Of the many processes using this concept, perhaps the best known is the recovery of uranium from sulfuric acid leach solution. DOWEX strong base resins are used in this complex ion separation process. The DOWEX 21K family of resins (16-20 mesh, 16-30 mesh, 20-40 mesh) are used extensively in this application. While the uranyl cation predominates in acid solution, in sulfuric acid there is a minor amount of quadrivalent uranyl sulfate anion in equilibrium with the uranyl cation. Successful use of a strong base resin for uranium recovery is based on the fact that the affinity of the resin for the quadrivalent uranyl sulfate anion in acid solution is very high. When removed by the resin, the complex ion is replenished by reestablishment of the equilibrium with the uranyl ion. Uranium may be removed from these leach solutions to nearly undetectable levels. Resin regeneration is readily accomplished by elution of the complex ion from the resin using a salt (other than a sulfate) solution. Not only is the uranium recovered from the leach solution, it is also purified and concentrated.

Dow has applied its resin technology for making uniform particle size to this application in the form of DOWEX 21K XLT resins. Here, all the beads are the same size resulting in faster kinetics, higher operating capacities and lower chemical usage and cost.

Precious Metal Recovery. In the recovery of precious metals, many of the processes involve the formation of complexes with cyanides or chlorides. These complexes are very often recoverable by uptake on, and elution

from, a strong base anion exchange resin. Platinum is often present as complex chloroplatinate anions in HCl solution. This complex anion has an extremely high affinity for the strong base resin, and is easily removed from the solution. The affinity is so high, that recovery of the platinum from the resin is done by burning of the resin, a practice that is economical due to the high loading of platinum on the resin and the high value of platinum. Gold recovery from cyanide plating rinse waters and mining operations is accomplished using this same general approach.

Chromate Recovery. Chromic acid removed by rinse waters from plating operations may be recovered for reuse by ion exchange demineralization using a strong acid resin followed by a weak base resin such as DOWEX M-43. The chromic acid is taken up on the weak base resin and recovered at a higher concentration in the salt form by regeneration of the weak base resin with a base. This more concentrated chromate salt is then converted to recyclable chromic acid by column contact with the hydrogen form of a strong acid resin such as DOWEX MSC-1 H⁺ resin. The demineralized rinse water is suitable for recycle in the process.

Copper Recovery Using Chelating Resins. Chelating resins are available which have functionality based on picolylamine derivatives (DOWEX M4195 and developmental chelating resin XFS 43084). These functionalities form very strong complexes with various transition metals, and particularly so with copper, even at low pH. This property allows recovery of copper from acid leach solutions. The removal of copper from this strong complex with the resin can be done using strong acid solutions or ammonium hydroxide solutions. Since the resin can also pick up other transition metals, recovery and subsequent separation can be accomplished using selective

elution with different strength acid solutions.

Cobalt/Nickel Recovery and Separation. For more than a decade, Dow has provided the cobalt refining industry with the unique chelating resin, DOWEX M4195. Among other valuable capabilities, this truly unconventional resin product selectively removes nickel from very strong cobalt electrolytes, even at very low pH (<1). In addition, it can be economically regenerated for years of tough service. With a long history of excellent performance and reliability, several of the industries new cobalt processing facilities are turning to DOWEX M4194 as a low cost hydrometallurgical processing option.

Solution Purification

Complex mixtures of acids, alkalis or salts can be purified using ion exchange resins as the following examples illustrate.

Iron Removal from Hydrochloric (Muriatic) Acid. Hydrochloric acid used in steel pickling baths becomes contaminated with iron. To maintain the effectiveness of the bath, iron contamination must be maintained at a low level. The strong base resin, DOWEX MSA-1, has a high affinity for iron in high concentrations of HCl and has been used to remove the contaminating iron. The affinity which the resin has for the anionic iron complex decreases, as the HCl concentration decreases, facilitating the stripping of iron from the resin with a water wash. The wash water is pH adjusted to keep trivalent iron in solution in the effluent strip solution. Figure 2 shows this operation schematically.

Nitrate Removal from Water.

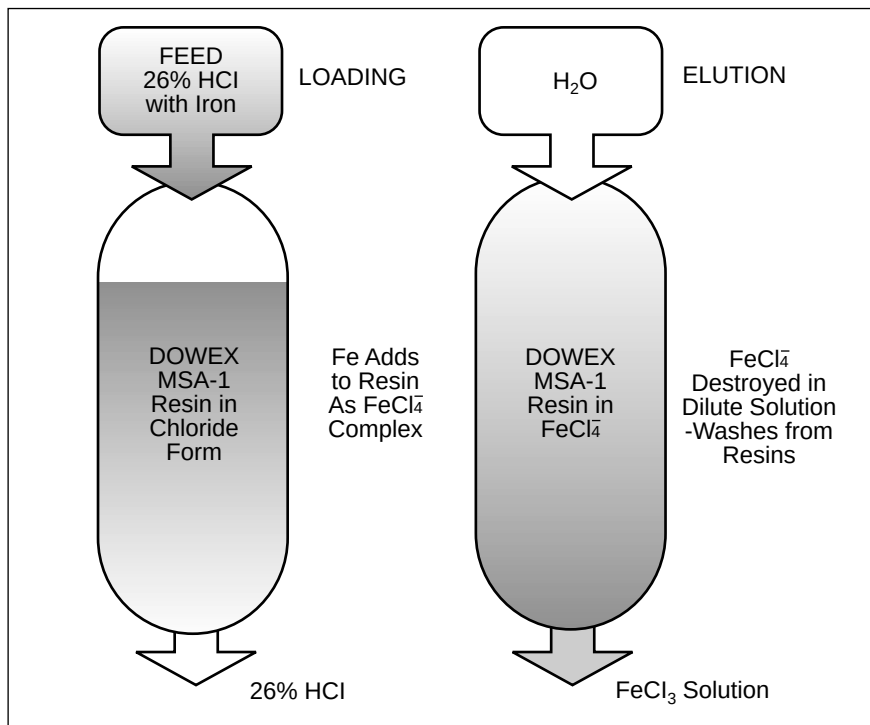
Nitrate levels in water must be kept low to meet public health standards. DOWEX SBR or SAR anion resins are used in their chloride salt form to reduce the nitrate to acceptable levels. Regeneration is readily carried out using sodium chloride solutions. Sulfate ions in the water are also exchanged for the chloride ion.

Formic Acid Removal from Formaldehyde Solution. Formic acid develops as a contaminant of formaldehyde solutions during manufacturing. Weak base resins, such as DOWEX M-43 are used to remove the formic acid from formaldehyde solutions. Formaldehyde solutions as concentrated as 55%, and at temperatures of 65°C, can be treated. Regeneration to the free base form is done with a suitable base.

Radium Removal from Water.

Radium is often present in mine water and in ground water supplies around uranium mining operations. This radium can be removed using DOWEX HCR-W2 or DOWEX MAC-3 resin in a water softening operation. Since the resins load the hardness ions normally

Figure 2. Iron Removal from Concentrated HCl



found in ground water supplies as well, the resin loading for radium is relatively small. Dow has developed a radium selective complexer, designated DOWEX RSC, which removes radium and barium from water. Since the resin accumulates radium selectively, long runs are obtained. However, proper disposal of the used complexer is mandatory. Appropriate licenses are required for use and disposal of the spent DOWEX RSC.

Aluminum Removal from Phosphoric Acid Bright Dip Bath. With use, aluminum bright dip baths containing 75-80% phosphoric acid become contaminated with aluminum. Disposal of the spent bath presents a considerable problem. DOWEX HGR-W2 resin is used to remove the aluminum from the bath solution, substituting the H⁺ ion in its place. The bright dip phosphoric acid bath is thereby reconstituted. The much cheaper sulfuric acid regenerant yields an aluminum sulfate solution, a more easily disposable waste.

Iron Removal from Phosphoric Acid Pickling Solution. Steel pick-

ling baths containing 15-20% phosphoric acid must have low iron levels to function effectively. Since the pickling operation increases the iron content in the bath, DOWEX HGR-W2 resin is used to remove the iron, reconstituting the pickling bath. Sulfuric acid solution is the regenerant chemical.

Phenol Removal from Aqueous Solution. Phenol contamination of aqueous solutions can be removed using the strong base resin, DOWEX MSA-1. The affinity which the resin exhibits for the phenol moiety is so great that regeneration with aqueous caustic is not adequate. Regeneration is effective however, when methanol and caustic are used in the regeneration mode. Another option for phenol in water is DOWEX OPTIPORE polymeric adsorbents. Here the phenol is adsorbed with other organic materials and can be regenerated with steam or alcohol.

Chemical Conversions

Applications of ion exchange can

involve a chemical conversion of a material from one salt form to another. For example:

Silica Sol Production from Sodium Silicate. In the production of silica sol, a near colloidal form of silica acid, DOWEX HGR-W2 H^+ resin is used to replace the sodium ion of the sodium silicate with the hydrogen ion. The reaction conditions are critical, since the silicic acid formed becomes insoluble and precipitates out of the solution. Care must be taken to cause this solidification to take place outside of the reaction column.

Fractionations/Separations

A number of ion exchange processes are chromatographic in nature. Several examples follow:

Acid Retardation Separation of Sulfuric Acid from Salts. Mixtures of sulfuric acid and its salts are separated by passage through a bed of DOWEX MSA-1 resin, which selectively imbibes the acid moiety relative to the salt. The partition set up is enhanced by chromatographic operating techniques when the elution with water is applied. Since the acid is the imbibed species, separation from large organic salts is also feasible.

Ion Exclusion Separation of Glycerin from Salts. Using similar chromatographic operating techniques, glycerin has been separated from salts by passing the solution through DOWEX HCR-W2 resin in the compatible form. A partition between the two is set up when glycerin is imbibed by the resin while the salt is excluded by Donnan membrane exclusion effects.

Ion Retardation Separation of Salts from Caustic. Caustic solutions (NaOH, KOH, etc.) are contaminated with various levels of chloride salts in some production processes and in some uses. These materials can be substantially freed of the salt contamination by treating a caustic solution through a specific DOWEX

ion retardation resin. The salts are taken up on the resin as an ion pair leaving the processed caustic relatively salt free. The salt is stripped from the resin with a water rinse. See Figure 3.

Resins as Desiccants

DOWEX HCR-W2 cation resin in the sodium or potassium form can be dried and used as a desiccant. Column operation is generally used.

Ideal for Non-polar Solvents.

Solvents such as the chlorinated hydrocarbons are dried at shipping terminals around the country by passing through beds of DOWEX

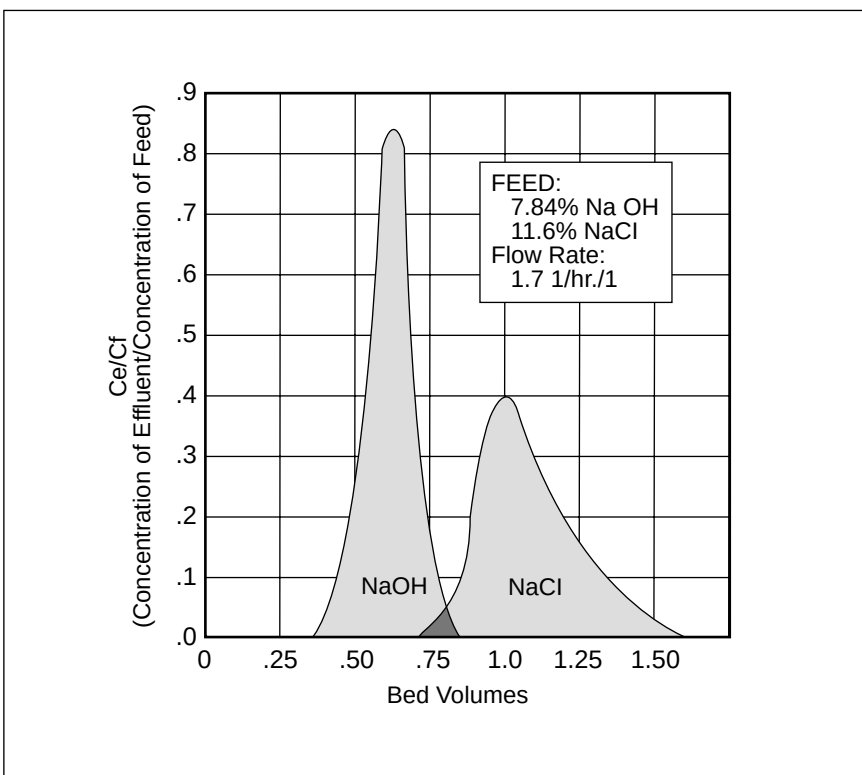
resin desiccants. The resin has a much stronger affinity for water than for the non-polar solvent and therefore very dry solvents result.

Reactivation Considerations.

DOWEX resin desiccants are reactivated by drying at relatively low temperatures ($150^{\circ}C$; $300^{\circ}F$). As such, they exhibit a significant advantage over other desiccant materials, such as silica gel and molecular sieves.

For more information see "DOWEX Resins as Organic Solvent Desiccants".

Figure 3. Ion Retardation Separation of NaOH & NaCl



Laboratory - Evaluation Considerations

Batch Operation. Occasionally, the reactions being performed by the resin are so complete in a single stage that agitated batch reactors may effectively be used. An example is a simple neutralization reaction. In this case, the reactors need only to be fitted with some filtration ability to facilitate the separation of the resin from the reaction mass.

Batch testing is a useful way to determine the chemical feasibility of a desired separation. In this approach, equilibrium adsorption isotherms are generated using shake flask tests that allow the calculation of the capacity of a separation media and an initial cost of a given separation. A method for determining equilibrium adsorption isotherms is described in the brochure "Equilibrium Isotherm Testing for Liquid Phase Applications" (Form No. 177-01721/CH 171-424-E).

Column Operation. Ion exchange processes are, for the most part, carried out in flow-through column operations. Typical laboratory test beds consist of glass or plastic tubing approximately 1 inch in diameter by 5 feet deep. Resin bed depth is generally fixed at about 3 feet. The additional column depth is to allow the resin to be backwashed periodically to reestablish a uniformly packed bed and to clean any particulate material from the bed which may have been filtered from the solutions being processed. Also, in some applications resins may swell significantly and care must be taken to avoid column breakage. (NOTE: Resin expansion requires that column configuration be such that the volume change can occur vertically. Tall, narrow columns might restrain this expansion and cause strong lateral pressures to develop in the column, resulting in resin being crushed, or in a column being ruptured).

Flow is controlled by pumping or constant head pressure devices. Analysis of the effluent can be by sample collection and testing, or by on-line instrumentation. Care must be taken to maintain the resin in liquid at all times. If air enters the column causing channeling of flow, the bed needs to be backwashed to release trapped air from between the beads. For more information see "Equilibrium Isotherm Testing".

Consider DOWEX Ion Exchange Resins for your Application

As is obvious from the above discussion, DOWEX ion exchange resins are used in many ways and in many areas of application in the chemical processing field. The above listings are far from exhaustive. In addition, Dow's experienced chemical processing specialists are willing to work with potential users to define the resins to be used in their areas of need, including development of special resins if the potential warrants.

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For mining and metal separation applications contact:
cmarston@dow.com

Visit our website at
<http://www.dow.com/liquidseps>
for additional information.

Applications and Recommended DOWEX Resins

Catalysis

Methyl tertiary-Butyl Ether	DOWEX M-31
Phenol Alkylation	DOWEX DR-2030
Ester Hydrolysis	DOWEX HCR-W2
Esterification	DR-2030

Desiccation

Desiccation of Organic Liquids	DOWEX HCR-W2, Na ⁺ form
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Solution Purification

Acid Removal from Process Stream	DOWEX M-43
Formic Acid Removal from	
Formaldehyde	DOWEX M-43
Amine Removal from Process Stream	DOWEX MSC-1; DOWEX HCR-W2
Iron Removal from Hydrochloric Acid	DOWEX MSA-1
Iron Removal from Phosphoric Acid	DOWEX HGR-W2
Aluminum Removal from	
Phosphoric Acid	DOWEX HGR-W2
Chromate Removal	DOWEX M-43
Trivalent Chromium Removal from	
Chromate Solutions	DOWEX MSC-1
Trichrome plating bath purification	DOWEX M4195
Copper and Vanadium Recovery from	
Adipic Acid Manufacture	DOWEX HGR-W2

Metal Recovery And/Or Concentration

Uranium Recovery	DOWEX 21K; DOWEX 21K XLT
Copper Recovery	DOWEX M4195; XFS 43084
Radium Removal	DOWEX RSC
Cobalt/Nickel Separations	DOWEX M4195
Gold Cyanide Recovery	DOWEX SBR; DOWEX G-55
Platinum Metal Recovery	DOWEX SBR
Cyanide Recovery	DOWEX SBR; DOWEX G-55
Phenol Recovery	DOWEX SBP-P; DOWEX M 41;
	DOWEX OPTIPORE L285 OR L493

Fractionation/Separation

Salt removal from base	DOWEX Retardion 11A8
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Styrene-DVB Copolymers

For lubrication, void space maintainers, grinding media,	STYRENE-DVB Copolymer 18-50P
absorption and decolorization and precision fillers.	STYRENE-DVB Copolymer 14-40
Other grades and sizes can be manufactured upon request	

Polymeric Adsorbents

For Liquid Applications

HFCS Decolorization	DOWEX OPTIPORE 44
Sucrose Decolorization	DOWEX OPTIPORE SD2
Apple, Pear, Citrus Juice	DOWEX OPTIPORE L285
Pharmaceutical, Environmental	DOWEX OPTIPORE L323
Chem Process, Environmental	DOWEX OPTIPORE L493

For Vapor Applications

Higher BP VOCs	DOWEX OPTIPORE V323
Medium BP VOCs	DOWEX OPTIPORE V493
Larger Particle Size	DOWEX OPTIPORE V502
Hydrophobic Adsorbent	XUS 43565.01

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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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