

**DOWEX™ M4195**

Chelating resin for copper, nickel, and cobalt processing

Product	Type	Matrix	Functional Group
DOWEX™ M4195	Chelating resin	Styrene-DVB, macroporous	Bis-Picolylamine

Specification and typical properties

Item	Specification Limit	Typical Property Range
Copper loading (pH 2, 6 gram/L feed)	Min. 35 grams per liter	35-42 grams/L
Functionality		Multi-dentate amine ligand
Particle size		20/50 US Mesh
Form		Weak base/partial H ₂ SO ₄ salt
Physical appearance		Opaque bead
Color		Tan to dark brown to dark green
Bulk density (as shipped)		42 lbs/ft ³
Moisture		40-60%
Shelf life		8-10 years

General

DOWEX™ M4195 chelating resin is unique in the chemical processing world. No other commercially available resin product is capable of selectively capturing transition metal ions from solutions with pH less than 2, or in the presence of homogeneous chelating agents such as EDTA. The chemistry of DOWEX M4195 is based upon a special chelating amine ligand which is partially quaternized by sulfuric acid as received. When in this conjugate sulfuric acid salt form, the resin is fully swollen and hydrated, and ready for scavenging metals from acidic media.

Most metal scavenging jobs can be handled easily with standard iminodiacetic acid or aminophosphonic type chelating resins; however, the tough jobs require the extra chelating power of DOWEX M4195 chelating resin:

- If you need to remove copper or nickel from very strong acid (pH <2) solutions, such as those common in plating electrolyte or in microelectronic etching solutions.
- If you need to remove chelated copper or nickel from solution.
- If you need to strip copper or nickel from strong brine solutions DOWEX M4195 chelating resin may be your answer.

Two commercial applications which have found the unique properties of DOWEX™ M4195 chelating resin to be indispensable for their low cost metal processing needs:

1. Cobalt Electrolyte Purification (Cobalt/Nickel Separation)¹⁻⁶

Two of the world's major cobalt producers are operating world-class low cost cobalt electrolyte purification processes employing DOWEX M4195 chelating resin to scavenge nickel from cobalt electrolyte.

Table 1 shows the relative loading values of various metals for DOWEX M4195 chelating resin. The resin exhibits an extremely strong affinity for copper, even at low pH, whereas other metals have higher loading values at higher pH. Complexed metals can be removed with strong acid (10N H₂SO₄) or ammonium hydroxide. Sometimes selective elution can be accomplished using varying strengths of acid.

Table 1. Conditional absorption constants (K) for the DOWEX M4195 chelating resin

Metal	pH	K (l/mol)
Cu(II)	2.0	1280
Ni	2.0	375
U(VI)	2.0	190
Fe(III)	2.0	181
Zn	2.0	82
	2.7	184
Co(II)	2.0	51
	3.2	280
Cd	2.0	43
	2.8	196
Fe(II)	2.3	23

Rosato et. al.⁴ describe a process for the selective removal of nickel from acidic cobalt sulphate using the DOWEX M4195 (XFS-4195.02) chelating resin. A variety of conditions were examined such as temperature, flow rate, feed concentration and acid strength for elution. Feeds of 15-30 g/L cobalt and 0.3-0.7 g/L nickel at pH 2.5 were treated. At pH 2.5 the resin has a high affinity for cobalt and nickel. The cobalt was rapidly absorbed, but with continued flow the nickel displaced the cobalt since nickel is more strongly held than cobalt. Flow rate was found to be important since the nickel/cobalt exchange was slow. A cobalt-rich effluent was obtained with a gradual increase in nickel concentration. Elution of loaded resin was accomplished with sulfuric acid at several strengths, taking advantage of the difference in nickel cobalt binding. Using a split elution technique, the cobalt-rich fractions were isolated to obtain a low nickel-content product. In a mini-plant operation with multiple columns and split elution, solutions containing cobalt-to-nickel ratios >500:1 were repeatedly obtained.

Jeffers² describes a process for recovering cobalt from copper-recycling leach solutions using the DOWEX M4195 chelating resin. At pH 3.0 the resin is loaded with several metals: cobalt, copper, nickel, iron and zinc. However, using 50 g/L sulfuric acid, all but copper is eluted from the resin, which can then be removed with 2N ammonium hydroxide.

2. Trivalent Chromium Plating Bath Purification¹¹

Dozens of the world's trivalent chromium platers are pocketing the benefits of using DOWEX™ M4195 chelating resin. Strap-on type systems utilize DOWEX M4195 chelating resin to capture copper and nickel from the trivalent chromium plating bath solution, eliminating the need for costly periodic shutdown and flushing.

Elution is accomplished with 2N ammonium hydroxide. Recycle of the eluant can minimize waste generation and can result in ammonia/copper waste streams having very high copper content (in excess of 100 g/L). Recycle eluant is employed for the initial elution (1-3 bed volumes) followed by fresh 2N ammonium hydroxide solution (1/2 to 1 bed volumes). The resin is then rinsed briefly with water and regenerated to the sulfate form with dilute H₂SO₄ before placing back into service. Please be aware that the resin swells up to 20% when re-acidified.

Literature Survey. DOWEX M4195 (XFS-4195.02, DOW N3) Chelating Resin

Cobalt/Nickel Separation

- 1 Kennedy, D. C.; Becker, A.; Worcester III, A. A. "Development of an ion exchange process to recover cobalt and nickel from primary lead smelter residues." Conference, Metals Specification, Separation, and Recovery, Chicago, Illinois, USA, 27 July - 1 August, 1986. *Lewis Publishers, Inc.*, 121 South Main St., PO Drawer 519, Chelsea, Michigan, 48118, USA, 1987. English.
- 2 Jeffers, T. H.; Harvey, M. R. "Cobalt recovery from copper leach solutions." *US, Bur. Mines* (1985), RI 8927, 16 pp. Report Invest. English.
- 3 Jeffers, T. H. "Separation and recovery of cobalt from copper leach solutions." 37(1), 47-50. *Journal Met.* (1985). English.
- 4 Rosato, L.; Harris, G. B.; Stanley, R. W. "Separation of nickel from cobalt in sulfate medium by ion exchange." *Hydrometallurgy* (1984), 13(1), 33-44. Journal. English.
- 5 Grinstead, Robert R. "Selective absorption of copper, nickel, cobalt and other transition metal ions from sulfuric acid solutions with the chelating ion exchange resin XFS 4195." *The Dow Chemical Company, USA*, 3 pp. Patent US 4451375 A 840529, US 83-526303 830825. English.
- 6 Byleveld, Eduard. "Ammoniacal elution of copper from ion exchange resins." *Himsley Engineering Ltd.*, Can. US, 8 pp. Patent US 4371506 A 830201, US 81-274865 810618. English.

Chemical Processing

- 7 Sherrington, D. C.; Simpson, S. "Polymer-supported molybdenum alkene epoxidation catalysts." *Dep. Pure Appl. Chem., Univ. Strathclyde*, Glasgow, GL 1XL, UK. Journal. English.
- 8 Meadow, Morton; Lymburner, Charles J.; Thompson, Clarence Andrew. "Purification of aqueous peroxy acids and peroxy salt solutions." *FMC Corp.*, USA; 11 pp. Patent EP 527537 A1 930217. English.
- 9 Gelbard, Georges; Breton, Francois; Charreyre, Marie Therese; Dong, Doan. "Polypyridine-based catalysts: epoxidation of olefins with supported peroxotungstic complexes." *Makromol. Chem., Macromol. Symp.* (192), 59(Int. Symp. Macromol - Met. Complexes, 4th, 1991), 353-61. Journal. English.
- 10 Elden, R. E.; Baker, P. C.; Andersen, R. L. "Metals removal from aqueous peroxy acids or peroxy salts." *FMC Corporation*, Philadelphia, PA, US. Patent US 5262018 931116, US 91-743953 910812 (7). English.

Trivalent Chromium Electroplating Bath Purification

- 11 Darnall, Dennis W.; McPherson, Robert A.; Gardea-Torresdey, Jorge L. "Method for purification of trivalent chromium electroplating baths contaminated with cationic metal ions." *Bio-Recovery Systems, Inc. USA.*; 8 pp. Patent US 5178746 A 930112, US 90-609350 901105. English.

General Metal Removal

- 12 Zzhu, Yuewei; Sengupta, Arup K. "Sorption enhancement of some hydrophilic organic solutes through polymeric ligand exchange." *Environ. Sci. Technol.* (1992), 26(10), 1990-8. Journal. English.
- 13 Sengupta, Arup K.; Zhu, Yuewei. "Chelating polymers with nitrogen donor atoms: some unique properties and related application potentials." *New De. Ion Exch. Proc. Int. Conf. Ion Exch.* (1991), 561-6. Conference. English.
- 14 Hossea, J. Michael; Michael D.; Darnall Dennis W. "Recovery of metal ions from electroless plating solutions." *Bio-Recovery Systems, Inc. USA*; 8 pp. Patent US 5108615 A 920428, US 98-442744 891128. English.
- 15 Mijangos Anton, Federico; Galarza Ibarrondo, Inigo; Apezteguia Salvador, Pilar; Diaz Fernandez, Mario. "Heavy metal recovery with selective resins. II. Selective recovery of low-affinity ions." *Fac. Cienc., Univ. Pais Vasco*, Bilbao, 48080, Spain. *Afinidad* (1991), 48(436), 367-70. Journal. Spanish.
- 16 Sengupta, Arup I.; Zhu, Yuewei. "Metals sorption by chelating polymers: a unique role of ionic strength." *AIChE J.* (1992), 38(1), 153-7. Journal. English.
- 17 Mijangos Anton, Federico; Galarza Ibarrondo, Inigo; Apezteguia Salvador, Pilar; Diaz Fernandez, Mario. "Heavy metal recovery with selective resins. I. Experiments in fixed bed with complex dissolutions." *Fac. Cienc., Univ. Pais Vasco*, Bilbao, 48080, Spain *Afinidad* (1991), 48(434), 227-31. Journal. Spanish.
- 18 Dias, Shelton A.; Nott, Babu R. "Selective sorbents for water purification in nuclear systems." *Ontario Hydro Res. Div.*, Toronto, ON, Can. Journal. English.

Chelated Copper

Dow Published

- 19 Vater, Christian; Enders, Reiner; Feufel, Manfred; Bolz, Rainer; Jekel, Martin. "Purification of wastewater from municipal waste incinerators by chelating ion exchange resins." *Inst. Tech. Umweltschutz, Tech. Univ. Berlin*, Berlin, D-1000/12. Vom Wasser (1990), 75, 47-58. Journal. German.
- 20 Sengupta, Arup K.; Zhu, Yuewei; Hauze, Diane. "Metal (II) in binding onto chelating exchangers with nitrogen donor atoms: some new observations and related implications." *Environ. Sci. Technol.* (1991), 25(3), 481-8. Journal. English.
- 21 Zhu, Yuewei; Millan, Esmeralda; Sengupta, Arup K. "Toward separation of toxic metal (II) cations by chelating polymers: some noteworthy observations." *React. Polym.* (1990), 13(3), 241-53. Journal. English.
- 22 Chanda, M.; O'Driscoll, K. F.; Rempel, G. L. "Removal and recovery of thiocyanate by ligand sorption on polymer-bound ferric ion." *React. Polym., Ion Exch., Sorbents* (1984), 2(3), 175-87. Journal. English.
- 23 Chanda, M.; O'Driscoll, K. F.; Rempel, G. L. "Ligand exchange sorption of arsenate and arsenite anions by chelating resins in ferric ion form. I. Weak-base chelating resin Dow XFS-4195." *React. Polym., Ion Exch., Sorbents* (1988), 7(2-3), 251-61. Journal. English.
- 24 Davis, James C. "Process for selective dialysis using polymeric affinity adsorbents and size selective membranes." *Eur. Pat. Appl.*, 30 pp. Patent EP 86-305-93 860701. English.
- 25 Adams, M. D.; McDougall, G. J.; Hancock, R. D. "Models for the absorption of aurocyanide onto activated carbon. Part II: Extraction of aurocyanide ion pairs by polymeric adsorbents." *Hydrometallurgy* (1987), 18(2), 139-54. Journal. English.
- 26 Byleveld, Eduard. "Elution of copper from ion exchange resins." *Himsley Engineering Ltd., Can.*, 21 pp. Patent CA 1193445 A1 950917, CA 82-411485 820915. English.
- 27 Riveros, P.A.; Coopers, W. Charles. "The extraction of silver from cyanide solutions with ion exchange resins." *Solvent Extr. Ion Exch.* (1985), 3(3), 357-75. Journal. English.
- 28 Brown, Craig J.; Dejak, Michael J. "Process for removal of copper from solutions of chelating agent and copper." *Eco-Tec Ltd., Can.* Patent US 4666683 A 8705519, US 85-800247 851121. English.
- 29 Grinstead, Robert R. "New developments in the chemistry of XFS 4195 and XFS 43084 chelating ion exchange resins." *Ion Exch. Technol.* (1984), 509-18, Editor(s): Naden, Davis; Streat, Michael. Publisher: *Horwood*, Chichester, UK. Conference. English.
- 30 Grinstead, Robert R. "Iodine adsorption via picolylamine ion exchange resins." *The Dow Chemical Company*, Midland, MI, US. Patent US 4451375 840529, US 83-526303 830825 (6). English.



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.

Notice: No freedom from any patent owned by Seller or others is to be inferred. Because use conditions and applicable laws may differ from one location to another and may change with time, Customer is responsible for determining whether products and the information in this document are appropriate for Customer's use and for ensuring that Customer's workplace and disposal practices are in compliance with applicable laws and other governmental enactments. Seller assumes no obligation or liability for the information in this document. NO WARRANTIES ARE GIVEN; ALL IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE ARE EXPRESSLY EXCLUDED.

LENNTECH WATER TREATMENT AND Air purification