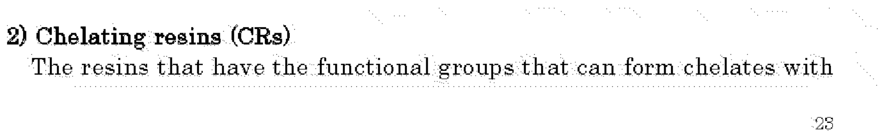
Chelating Resins Properties

(Extracted from the Diaion Manuals page 23 to 33)



2) Chelating resins (CRs)

The resins that have the functional groups that can form chelates with

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metal ions, instead of ion-exchangeable functional groups, capture metal ions in the raw solutions. Such resins are called chelating resins, and DIAION® CR11, CR20, CRB03 and CRB05 are in this category.

The typical chelating functional groups consist of more than two electron-donating elements such N, S, O and P, and chelating resins act as ordinary chelating agents. There are various kinds types of chelating resins, N-O type, S-N type, N-N type, O-O type and P-N type for examples, and the iminodiacetate type, $-N(CH_2COO)_2$, and polyamine type, $-NH(CH_2CH_2NH)_nH$, are well known. DIAION® CRB03 and CRB05 are specially developed ones to adsorb boric acid selectively.

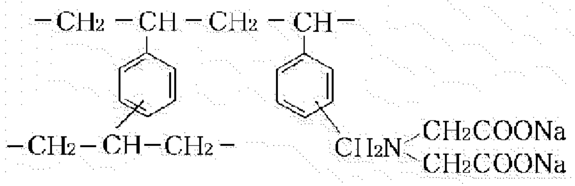
Chelating resins have much higher selectivity toward metal ions than normal IERs, so DIAION® CR11 can remove several mg/L of Ca^{2+}, Mg^{2+} or Sr^{2+} from saturated NaCl aqueous solutions, for an example. Although the conventional IERs also have high selectivity of such cations against Na^+, the differences are not so great as of the chelating resins. Thus, such conventional IERs cannot adsorb such metal ions when there are extremely large concentration differences; Na^+ concentration is 100,000 times as high as that of Ca^{2+}, Mg^{2+} or Sr^{2+}.

Mineral acids, such as hydrochloric acid or sulfuric acid, are used to detach the metal ions. This is because such metal chelates are unstable in low pH conditions. Some metal ions form complex salts in hydrochloric acid solution and it may cause the difficulty in the regeneration by HCl. Sulfuric acid is recommended in such cases.

(i) Iminodiacetate type chelating resins (DIAION® CR11 in Fig.I-2-21)

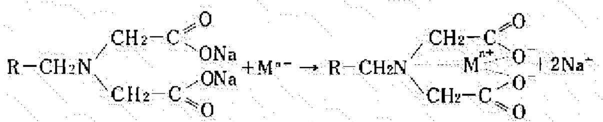
(CR10 is not available.)

It is very important to control pH of the influent to use DIAION® CR11 effectively, since the chelate-formation reaction, the adsorbing reaction of metal ions, depends on such pH as shown in Fig.I-2-22.

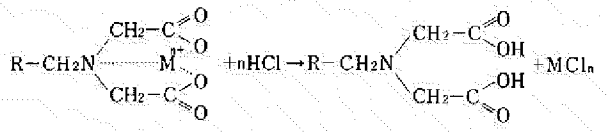


[Fig.I-2-21] Chemical Structure of DIAION® CR11

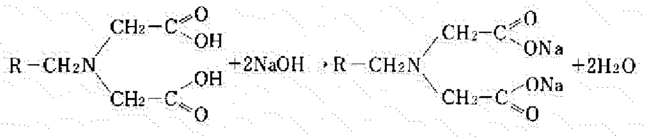
After desorbing metal ions by mineral acids and regenerating by NaOH to Na-form, DIAION® CR11 can be used again and again as in the following Eqs.I-2-13, I-2-14 and I-2-15.



(I-2-13)



(I-2-14)

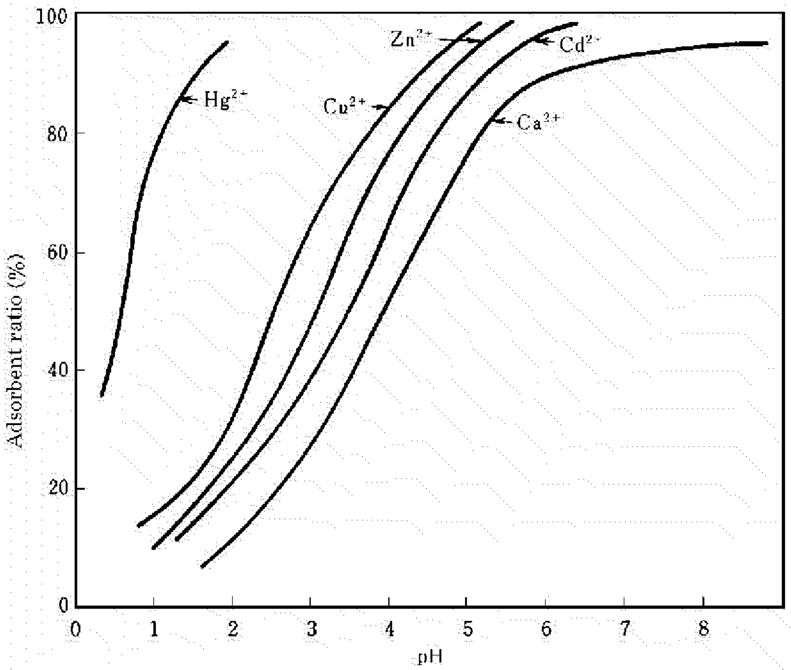


(I-2-15)

The selectivity of DIAION® CR11 toward metal ions is almost the same as the stability of the metal chelates of EDTA as written below and it has high selectivity toward trivalent metal ions:

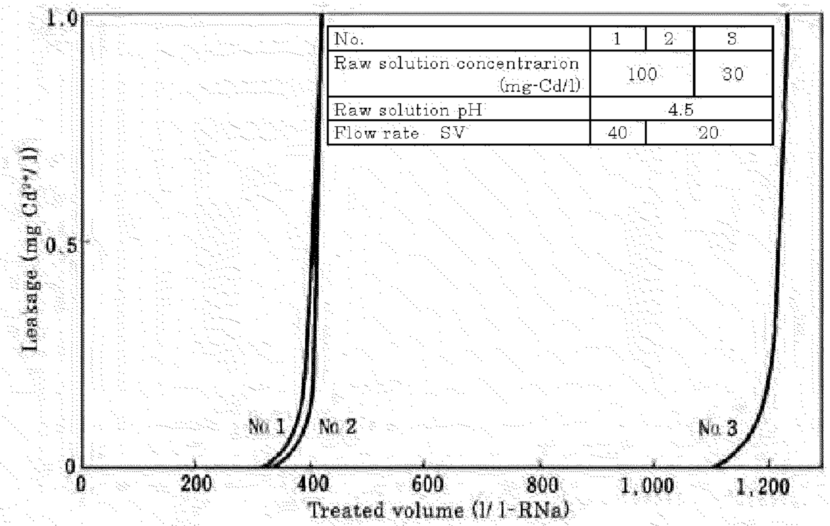
$$Cr^{3+} > In^{3+} > Fe^{3+} > Ce^{3+} > Al^{3+} > La^{3+} > Hg^{2+} > UO^{2+} > Cu^{2+} > VO^{2+} > Pb^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Mn^{2+} > Be^{2+} > Ca^{2+} > Mg^{2+} > Sr^{2+}$$

Regarding regenerations of metal ion chelates, those chelated with trivalent metal ions are most difficult, unable in some cases, to be regenerated and so need large amount of regenerants. Chelates with Hg^{2+} are also difficult to be regenerated, and the other method is more effective than ordinary regeneration by mineral acids; refer to Chapter IV Section 6: "Treatment of Mercury Waste Water". On the other hand, the chelates with other metals, the selectivity of which is lower than Hg^{2+}, can be easily regenerated.



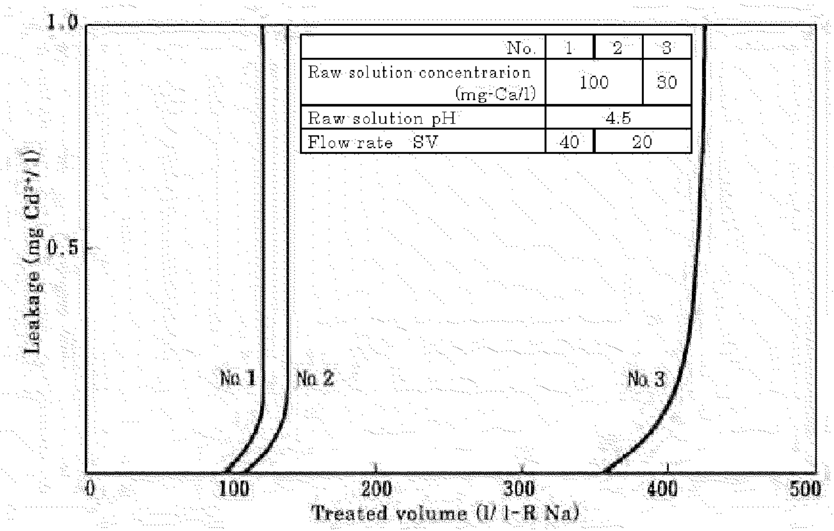
[Fig.I-2-22] pH dependence of adsorbent ratio of metal ions by DIAION® CR10

When one treats water that contains metals by DIAION® CR11, metal hydroxides are sometimes generated and deposited at last within the resin layer by the reaction of metal ions with NaOH, Na^+ of which is eluted from resins in accordance with the chelate formation. In order to prevent such deposit, one had better keep the regeneration ratio by NaOH, in Eq.I-2-15, at a low level; 75% of the theoretical exchange capacity for example. Mixing of such resins before use is recommended to distribute Na-form and H-form resins uniformly.



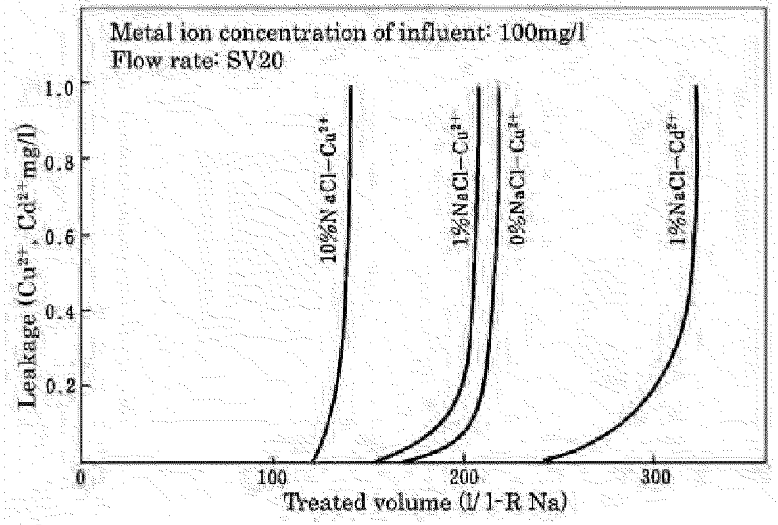
No.	1	2	3
Raw solution concentrarion (mg-Cd/l)	100		30
Raw solution pH	4.5		
Flow rate SV	40	20	

[Fig.I-2-23] Adsorption of Cd^{2+} by DIAION® CR10

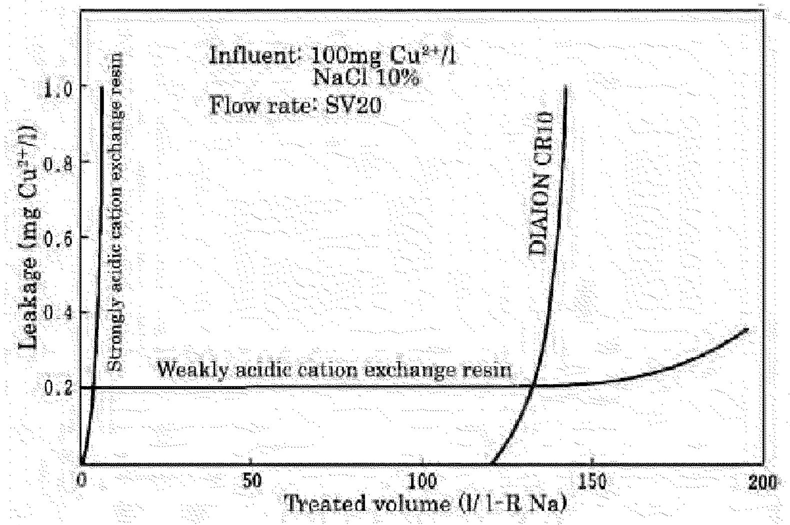


No.	1	2	3
Raw solution concentrarion (mg-Ca/l)	100		30
Raw solution pH	4.5		
Flow rate SV	40	20	

[Fig.I-2-24] Adsorption of Ca^{2+} by DIAION® CR10



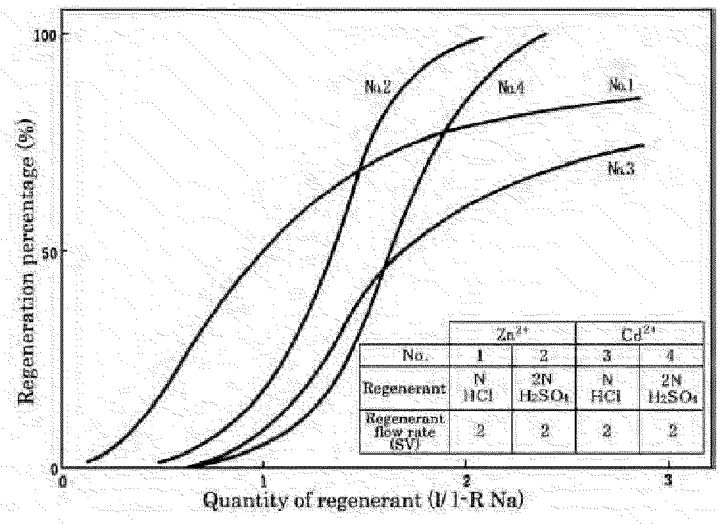
[Fig.I-2-25] Effect by NaCl in the influent on the adsorption of Cu^{2+} and Cd^{2+} by DIAION® CR10



[Fig.I-2-26] Adsorption of Cu^{2+} of influent with NaCl by DIAION® CR10

Figs.I-2-23 through I-2-27 show the typical examples of the removal of metal ions by CR10; CR10 itself is not available and CR11 is the alternative product. Fig.I-2-24, in particular, shows the effect of NaCl concentration of the influents, and you may understand that the metal ions in 10% NaCl aqueous solution can be removed. Though the amount of treated water decreases as the NaCl concentration becomes high, it is clear that the chelating resins are superior to SACERs or WACERs (Fig.I-2-26). That WACERs have some potential to eliminate metal ions can be explained by the chelating function of the carboxylic acid groups, -COO$^-$, within WACERs. Fig.I-2-27 is the result of the regeneration of the resins chelated with Zn^{2+} or Cd^{2+} by 1N-HCl or 2N-H$_2$SO$_4$ aqueous solution.

Care must be taken when one regenerates CR11 from H-form into Na-form, since its volume becomes large as is the case in WACERs. One of the recommendations is the upflow injection of NaOH, the regenerant, in the fluidized bed columns.

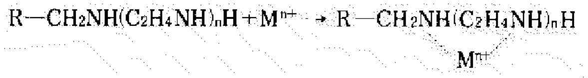


	Zn^{2+}		Cd^{2+}	
No.	1	2	3	4
Regenerant	N HCl	2N H$_2$SO$_4$	N HCl	2N H$_2$SO$_4$
Regenerant flow rate (SV)	2	2	2	2

[Fig.I-2-27] Regeneration of DIAION® CR10

(ii) Polyamine type chelating resins (CR20)

DIAION® CR20 is one of the chelating resins with the polystyrene matrix and polyamine functional groups and it captures metal ions as in Eq.I-2-16.



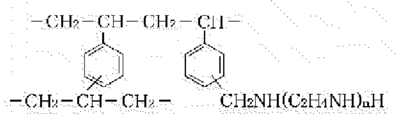
$$R{-}CH_2NH(C_2H_4NH)_nH + M^{n+} \rightarrow \underset{M^{n+}}{R{-}CH_2NH(C_2H_4NH)_nH}$$ (I-2-16)

Fig. I-2-29 shows the pH dependency of metal chelating by DIAION® CR20, and its selectivity toward metal ions is as follows:

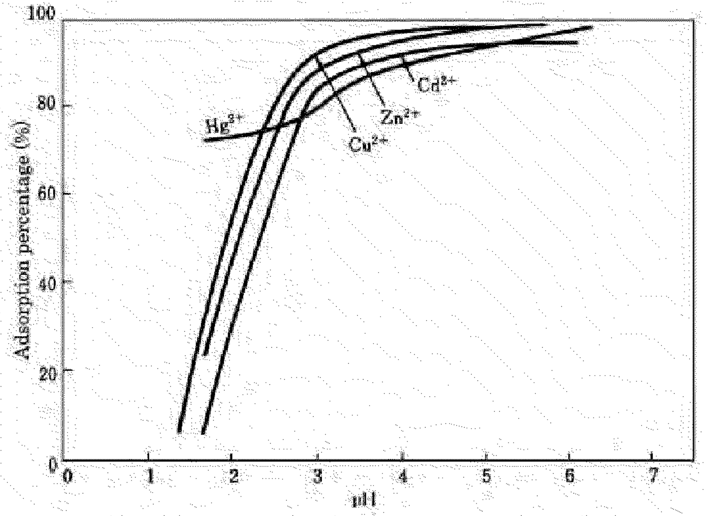
$Hg^{2+} > Fe^{3+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Ag^{+} > Mn^{2+}$

Hg^{2+}, the highest one, is difficult to be regenerated, so regeneration should be done by the specialized method as in DIAION® CR11.

DIAION® CR20 is unable to capture metal ions of K, Na, Li, Rb, Cs, Ca, Mg, Sr, Sn, Zr, Th, Al, and Fe(II). The big difference from CR11 is that CR20 can capture neither Ca ion nor Mg ion, and it is reasonable to use CR20 to treat the influents with much Ca and/or Mg.



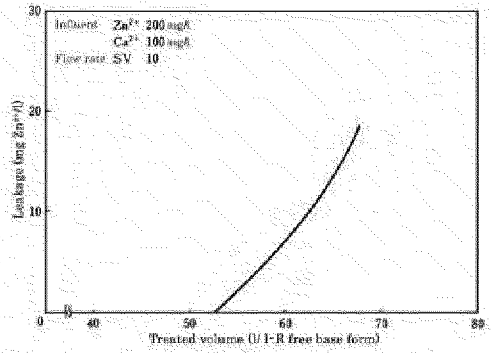
[Fig.I-2-28] Chemical structure of DIAION® CRB03 and CRB05



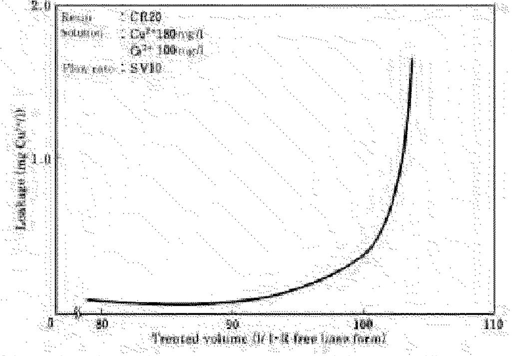
[Fig.I-2-29] pH dependency of metal adsorption by DIAION® CR20

The examples to eliminate Zn^{2+}, Cu^{2+} ions from the influent that contains Ca^{2+} by DIAION® CR20 are shown in Fig.I-2-30 and Fig.I-2-31. It is noteworthy that CR20 can remove heavy metal ions effectively from the influents that contain not only Na^{+} but Ca^{2+}. Fig.I-2-32 is an example of the regeneration of CR20 by mineral acids; HCl and H_2SO_4.

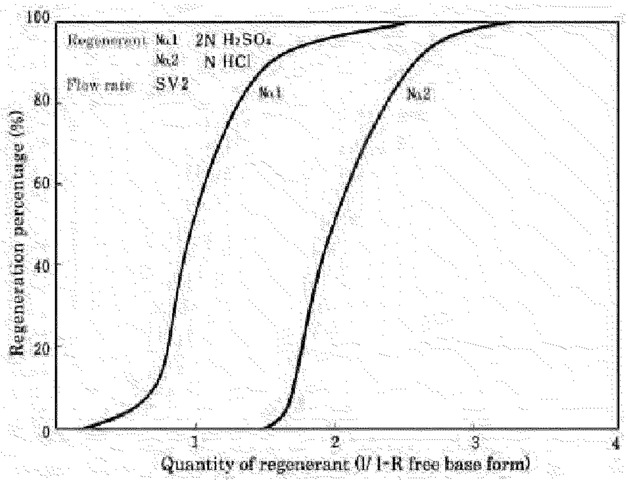
As in the case of DIAION® CR11, metal hydroxides are sometimes generated and deposited within the resin layer at the early stage, in particular, of treatment of the water that contains metals, by the reaction of metal ions with NaOH, Na^{+} of which is eluted from resins in accordance with the chelate formation. In order to prevent such deposit, the regeneration ratio by NaOH should be kept at a low level; 75% of the theoretical exchange capacity for example. Mixing of such resins before use is recommended to distribute Na-form and H-form resins uniformly.



[Fig.I-2-30] Zn^{2+} adsorption by DIAION® CR20 from the influent with Ca^{2+}



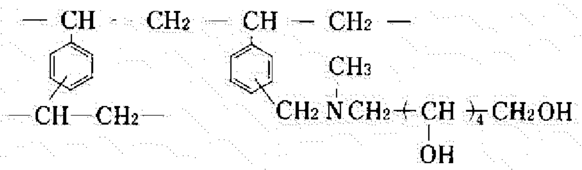
[Fig.I-2-31] Cu^{2+} adsorption by DIAION® CR20 from the influent with Ca^{2+}



[Fig.I-2-32] Regeneration of DIAION® CR20 that adsorbs Cu^{2+}

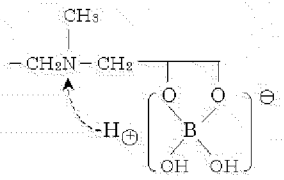
(iii) Boric acid selective adsorption resin (CRB03, CRB05):

DIAION® CRB03 and CRB05, polystyrene as polymer matrix with N-methylglucamine groups as functional groups, have a strong affinity with boric acid anions and they can adsorb them selectively among other kinds of anions.



[Fig.I-2-33] Chemical structure of DIAION® CRB03 and CRB05

The mechanism for CRB03 and CRB05 to capture boric acid anions is interpreted as the formation of the inner salt between the cationic amine group and the borate anion that is derived from esterification of boric acid and hydroxyl group in the sugar-chain. The adsorption capacity decreases drastically when CRB03 and CRB05 are used as 100% H_2SO_4-form. This is because the cationic amine group, weak electrolyte and on the acidic side, has no potential to adsorb, neutralize with, the borate anion and to keep it on the inside of the resin matrix.



[Fig.I-2-34] Mechanism for CRBs to capture boric acid anion