



ION EXCHANGE RESINS FOR WATER PURIFICATION :
PROPERTIES AND CHARACTERISATION

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PARTICLE SIZE

VOIDS

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1.0 Introduction

Ion exchange method for purification of water has become almost a universal method, as far as, important projects like nuclear power plants, heavy water plants and thermal power stations are concerned. This is mainly because of the simplicity of the method, the economy of the process and it's ability to produce water of desired purity. The ion exchange resins used in these applications are organic polymer products which are normally stable under normal operating conditions in which they are used. However, during their use, over a period of years, some deterioration is expected. This not only affects the quality of water produced but creates operational problems, which hamper the economy of the process. The deterioration is manifested in different ways such as (1) the loss of physical stability of the resins which leads to fragmentation of the resin beads to smaller particles, which may block the flow lines resulting in build-up of pressure inside the system, (2) the de-cross linking and resulting increased swelling of the resin beads, (3) the loss of chemical stability which results in loss of acidity or basicity of functional groups, which affects the total exchange capacity and (4) the breaking down of polymer skeleton which results in increased swelling of the resins resulting in increased water retention capacity and thereby reducing the total ion exchange capacity. When the resins are used in nuclear power plants the organic polymer material may decompose in the intense radiation fields inside the reactors and may lead to build-up of radioactivity.

The testing of ion exchange resins therefore becomes essential. The resins presently used in Indian nuclear power plants are products such as Dowex, Amberlite manufactured by Dow Chemical Company, USA and Roam and Hass of West Germany. These are nuclear grade products and are ensured for their performance over a period of years. These resins require no testing during their guarantee period. Of late, indigenously manufactured ion exchange resins are available and their use is increasing, particularly in applications, where very high purity is not called for. In thermal power stations where water is used for cooling purposes, in heavy water plants where water is used for the exchange processes, in municipal water supplying plants where water is partially purified, the indigenously manufactured resins are replacing the imported products. Indion, Tulsion, Doshion are some of the products manufactured indigenously by Ion Exchange India Ltd., Thermax Private Ltd.

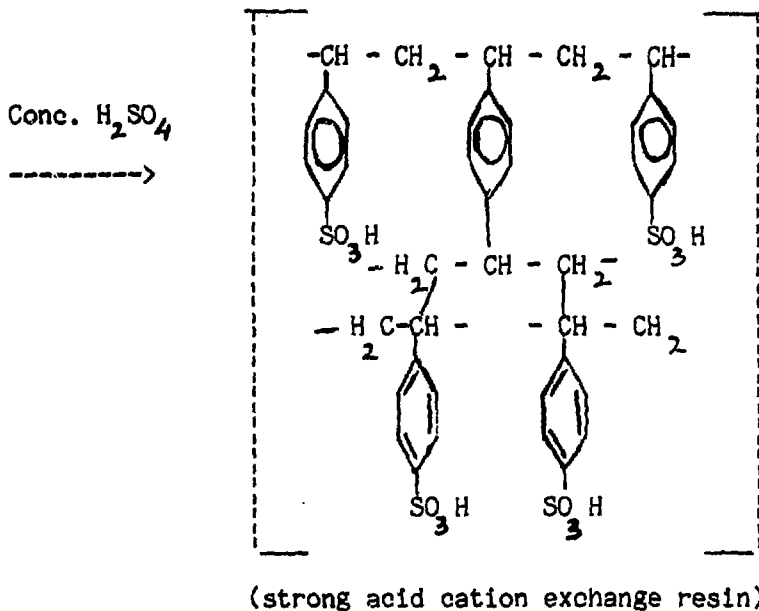
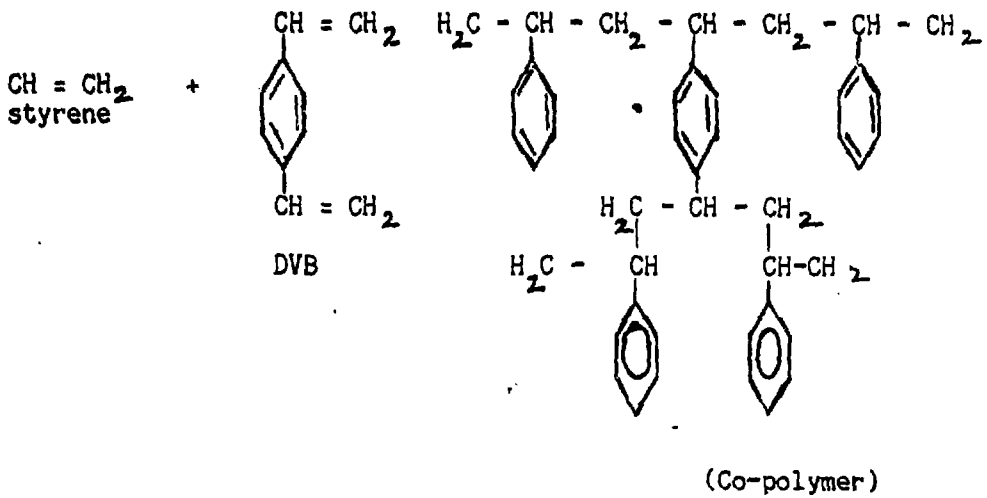
and Doshi Ion Exchange Industries Ltd., etc. It is desirable to test these resins during their use in the above mentioned important application.

The testing of ion exchange resins involves, (1) criteria which are important through thermodynamic and kinetic points of view such as porosity, percent cross linking, total ion exchange capacity, thermal stability and (2) criteria such as volume capacity, bulk density, physical and chemical stability, which are important through operational point of view. The aim of this report is to help a plant chemist to carry out the testing of ion exchange resins used in the plant on a routine basis. The methods selected are simple, sufficiently precise, and neither require any sophisticated instruments nor any specialised techniques. These methods are widely used and are standardised in our laboratory.

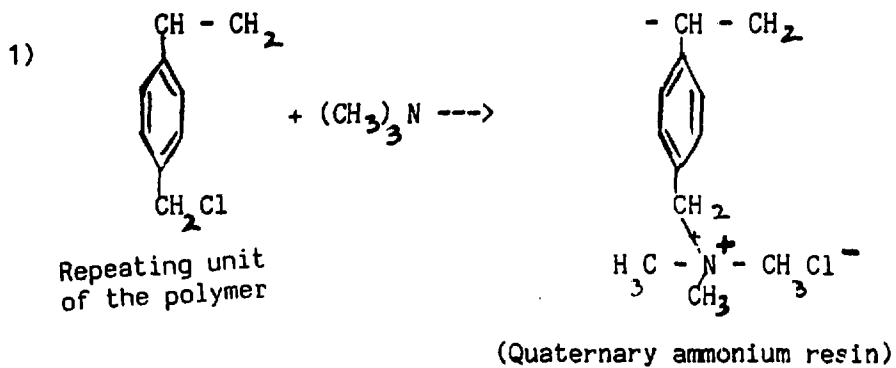
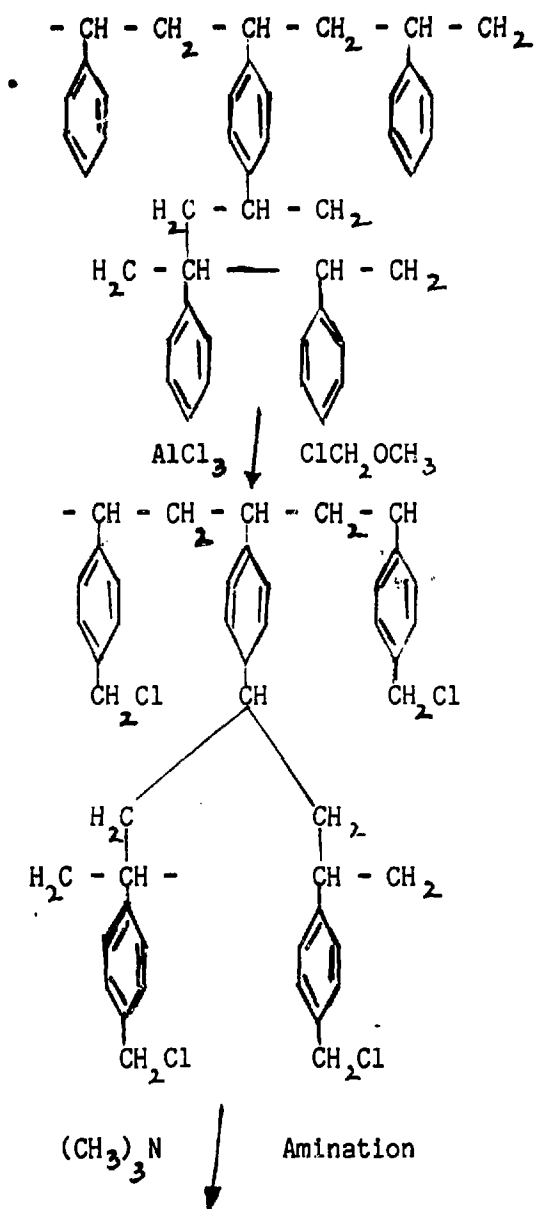
The report is divided into three sections. The first section contains a general introduction to ion exchange resins used in various processes, the second section describes characteristic properties of the polymer materials and the inter relation between them. This will, in turn, be useful to interpret the data obtained from the various tests carried out on the resins in the laboratory. In the third section of the report, are given the details of each method used for a particular test to be carried out on a routine basis. Each method describes the principle involved, the reagents and apparatus used in the experiment, the actual procedure and calculations and recording of the data.

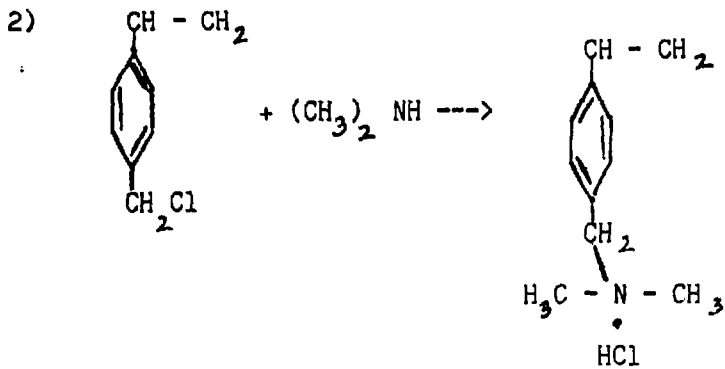
1.1 General Considerations:

Ion exchange resins are solid, water insoluble high molecular weight organic polymers which exchange their mobile ions (counter ions) for ions of like charge from surrounding liquid medium. They can be thought as high molecular weight acids or bases which exchange their H^+ or OH^- ions and get converted into respective salts. Many organic polymers can be imparted with ion exchange properties, however, their solubilities and stabilities towards physical and chemical attritions impose certain limitations. The styrene cross linked with divinyl benzene based strong acid cation exchange resins, the strong and weak base anion exchange resins, and the acrylic acid based weak acid cation exchange resins, therefore, represent the most stable ion exchange resins that are available to day. Vinyl polymerisation and polycondensation are the two most popular techniques to produce the skeleton structures of these polymers. The strong acid cation exchangers are produced by sulfonation of the skeleton structure with concentrated sulfuric acid whereby the ions are fixed on the skeleton structure as co-ions and H^+ ions remain as mobile ions called counter ions. The path of synthesis and the structure of these resins is shown below.



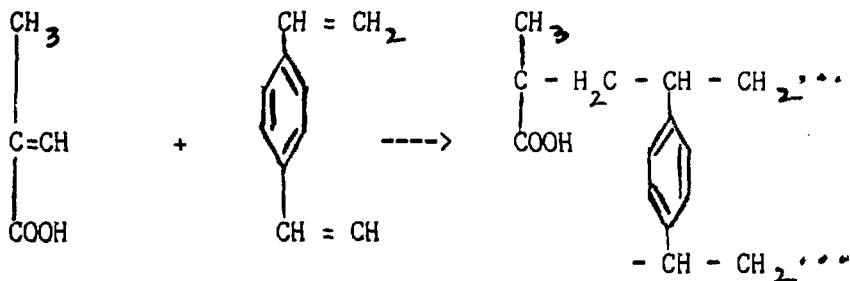
The anion exchange resins are produced by chloromethylation of the styrene divinyl benzene co-polymer shown above. This chloromethylated polymer can then be used to produce a series of strongly basic and weakly basic anion exchange resins by amination with various amines, as shown below:





(tertiary ammonium resin)

Similarly, secondary and primary ammonium resins are produced. The weak acid cation exchange resins are produced by co polymerisation of acrylic acid or methacrylic acid and divinyl benzene as shown below:



Two types of commercial ion exchange resins are in common use. The microporous or the gel type and the macroporous or the macroreticular type. The macroreticular resins contain macroporous matrix structures which have large internal surfaces. They can be viewed as truly porous materials. They are extremely uniform in shape and are opaque in appearance. They have large pore sizes (of the order of several thousand angstroms diameters and surfaces upto $100 \text{ m}^2/\text{g}$) They exhibit small difference in swelling in polar and non polar solvents, small loss of volume on drying and higher resistance to oxidation and osmotic shocks. Large ions can easily penetrate through the structure because of their large pore sizes, and the resins exhibit maximum exchange capacities. The gel type resins, on the other hand, are clear, transparent, glazy in appearance. They can be viewed as apparently porous. The swelling behaviour, resistance to oxidation and osmotic shocks and exchange capacities depend upon the percent cross linking present in these resins. However, they are of still great practical importance because of their use in industry. The polycondensation resins are supplied as milled granules while the polymerisation resins are supplied as spherical beads. Their colours range from white through yellow, brown, dark brown, to black. The diameters of the spherical beads range from 0.1 mm to 1.0 mm. The resins are also available as fine powders or as sheets.

The qualities expected from the ion exchange resins include their physical and chemical resistance and the characteristics to release none of their own components to the surrounding medium. In short, the hydrolytic, thermal and radioactive influences should not produce or accelerate such a release to the surrounding medium in which these resins are used. Most of the resins manufactured today fulfill these conditions. Still the life of the resin should be monitored. This is done by measuring the volume of solution passed through them or volume of resin required or the number of loading and regeneration cycles required under the operational conditions, in which they are used in a particular process. The flow rate, the pressure drop and the break-through capacity are the three parameters which help to describe the fluid dynamics and chemical processes taking part in the columns in a particular application. The flow rate is given in terms of ml/cm²/min or lit/m²/hr and should be specified with the diameter to height ratio of the column. The pressure drop is a function of the apparent density and particle size and shape of the ion exchange resin beads. The break-through capacity curves present an overall picture of the processes taking place in the column operation under the given conditions. A typical set of specifications for a strong acid cation exchange resin is given below to further explain the above.

<u>PROPERTY</u>	<u>SPECIFICATION</u>
1. Wet capacity	4.50 meq/gram (min)
2. Volume capacity	1.90 meq/ml (min)
3. Moisture	44-48% (w/v)
4. Density	48-54 lb/cu ft.
5. Effective size (av.dia)	0.4 to 0.6 mm
6. Uniformity coefficient	1.7 (max)
7. Whole beads	70% (min)
8. pH	6.0 to 7.0
9. Colour throw	25 APHA (max)
10. Odour and taste	Nil

These specifications must be adhered to ensure the optimum and uniform performance of the resins in all commercial applications. The effective size and uniformity coefficient ensure proper hydraulic performance with respect to pressure drop and bed expansion. The particle size limitations control the rate of exchange. Moisture specification is essentially a measure of degree of cross linking which in turn controls the factors such as the rate of exchange, the selectivity towards particular ions and swelling behaviour.

As already mentioned, the strong acid cation exchange resins and strong base anion exchange resins exchange ions over the entire pH range of the medium while the weak acid cation exchange resins and weak base anion exchange resins show their maximum capacities in basic and acidic pH regions, respectively. Therefore, the weak acid resins are used for the cleanage of weakly alkaline salts of polyvalent cations like iron, aluminium, calcium, magnesium etc., while the strong acid cation exchangers

can purify the neutral sodium and potassium salt solutions. The weak base anion exchangers have low basicities, and therefore, can exchange anions of strong acids like HCl, H_2SO_4 etc., almost completely but anions of weak acids such SiO_3^{2-} or HCO_3^- are not exchanged extensively. The strong base resins, on the other hand, act as strong bases and are capable of exchanging the silicate and carbonate ions along with the chloride and sulphate ions. The same theory is equally applicable for the regeneration of the resins, that is bringing them again in the usable form. Thus the strong acid cation exchangers can be regenerated with strong acids such as HCl, H_2SO_4 , HNO_3 to bring them in the H^+ form or with neutral salt solutions like NaCl, KCl or KNO_3 to bring them in the Na^+ or K^+ form. The weak acid resins can be brought in H^+ form by means of strong acids but not with neutral salt solutions. Also these resins have high selectivity for calcium and magnesium ions and therefore regeneration with NaCl or KCl solution is practically impossible. The strong base anion exchange resins can be easily brought into OH^- form from Cl^- form by treatment with strong alkalies like NaOH but regeneration with weakly alkaline solutions of Na_2CO_3 is difficult and with NH_4OH it is almost impossible. The weak base resins can be brought in OH^- form by weak bases such as Na_2CO_3 or NH_4OH as well as with strongly basic NaOH.

In addition to above described cation and anion exchange resins, amphoteric resins are also available which contain both acidic and basic groups. Poly functional resins containing both strong and weak acid groups on the same skeleton are also available.

In addition to their applications in industry, these resins are also used extensively in various fields such as analytical chemistry, pharmacy, medicine, food processing, etc. These resins are equally useful in the aqueous and non aqueous media.

2.0 Important Properties of Ion Exchange Resins

As already mentioned the total ion exchange capacity, the degree of cross linking, selectivity and thermal stability are some of the properties which are important through thermodynamic and kinetic points of view. These criteria are rarely examined for testing the performance of the resins for their commercial application. However, knowledge of these values may become helpful in interpreting the data obtained in a practical application. A brief information of these criteria is therefore given in this section.

2.1 Total Ion Exchange Capacity:

This important property of the resins indicates the total number of exchangable sites present in one mole of the resin. The theoretically calculated value is 5.0 meq/gram for a dry resin. It is usually determined by sulphur estimation in case of cation exchange resins, and by ammonia estimation for anion

exchange resins and usually matches with the above theoretically calculated value. In actual use, however, this theoretical capacity is never achieved because of several reasons, such as the ions may not be able to penetrate through the pores of the matrix structure upto the exchange sites, the ion exchange resin may "adsorb" neutral salts thereby blocking the exchange sites, etc.

2.2 Selectivity:

This is a property by which an ion exchange resin exhibits preferential activity towards certain ions. This is mainly because ion exchange is a stoichiometric and reversible process and obeys the law of mass action. The distribution coefficient in equilibrium depends upon several factors such as the percent cross linking agent present in the resin, the size of the ions present in solution, etc. which determine the selectivity of the resins towards particular ions in surrounding medium.

2.3 Degree of Cross Linking:

This property indicates the concentration of "bridges" present in the polymer material. In case of cation exchange resins the sulfonation step introduces only a small percentage of additional cross linking and therefore the degree of cross linking is almost equivalent to the concentration of cross linking agent present in the polymer. In case of anion exchange resins, however, the chloromethylation step in their production introduces a large number of cross linkages and therefore the percentage of cross linking agent present in the polymer is only an approximate representation of degree of cross linking. Commercial resins usually contain 2 to 12% divinyl benzene as the cross linking agent. The degree of cross linking influences not only the solubility but almost every characteristic of the resins. Thus the stability, exchange capacity, water uptake, swelling behaviour, volume changes in different ionic forms, selectivity and resistance to chemical and oxidising agents depend upon the degree of cross linking agent present in the resins.

The poorly cross linked resins are soft and unstable. They have high moisture content, they swell more and exhibit low volume capacity. They show greater volume changes in different ionic forms. However, they exhibit higher exchange rates. The highly crosslinked resins on the other hand are hard and brittle and less resistant to osmotic shocks. However they exhibit less swelling, low volume changes and therefore higher capacity and selectivity. They are more resistant to chemical and oxidative species. Thus by adjusting the degree of cross linking the resins can be "tailor made" for a specific purpose.

2.4 Porosity:

The porosity value indicates the size of the pores of the capillary channels. The size of the channels is usually not

uniform. The net work present in the resins always contains some "voids" which have different water retention capacities depending upon the degree of cross linking. The degree of cross linking thus mainly determines the size of the channels. Two types of ion exchange resins are commercially produced now a days. The macroreticular or macroporous resins which have large pore sizes and the "gel type" or microporous resins having small pore dimensions.

2.5 Thermal Stability:

This property indicates the stability of an ion exchange resin in a particular temperature range. These temperature limits are never reached in a normal operation. Thus the cation exchange resins are stable in all ionic forms in pure water upto 120°C. The Na⁺, K⁺, Li⁺ forms are stable even upto 200°C. The strong base anion exchange resins in the OH⁻ forms become unstable at 150°C but the salt forms are stable at this temperature. Sulfite and sulphate ions are produced on degradation of cation exchangers while the anion exchange resins produce trimethyl amine and methanol. These degradation products can be estimated to establish the thermal stability.

2.6 Radiation Stability:

Ion exchange beds in nuclear plants are subject to two possible sources of radiation exposure. These are shortlived N-16 radiations and the longer lived induced or fission product nuclides in the water which are removed by the ion exchanger. Dosage from the N-16 activity can be controlled by building in adequate delay time in the ion exchange circuit. However, exposure to the longer lived activities is an intrinsic part of the ion exchanger function. On the basis of the laboratory and plant radiation damage studies on strong acid/strong base resins, the threshold dose for radiation damage is about 1×10^7 rads. Loss of useful exchange capacity in mixed bed resins results from loss of functional groups by radiation damage and exhaustion of the capacity by degradation products. In a mixed bed there is little leakage of degradation products because of absorption of the degradation products. Satisfactory service life of plant mixed beds has been observed even after a 30% loss of capacity due to radiation damage corresponding to the dosages of the order of 5×10^7 rads.

3.0 Laboratory Testing of Ion Exchange Resins

3.1 Pretreatment:

a) Preliminary:

Before any examination or characterisation of an ion exchange resin sample is performed the resin must be pretreated to bring it in the proper ionic form. Normally the standard ionic forms selected are H⁺ for cation exchangers and Cl⁻ for anion exchangers. This is an essential step, otherwise the results

obtained may be totally misinterpreted. This is because the equivalent weights of different ions are different and characteristics like swelling behaviour, moisture content etc, are different for different ionic forms of the same resin. This is particularly important when the resin samples to be tested have been used in a particular process for quite sometime.

b) Reagents and Apparatus:

- i) NaCl 10% solution
- ii) NaOH 1 M solution
- iii) HCl 1M solution
- iv) Glass column: 4 cms diameter x 50 cms length with glass wool plug and arrangement to fix rubber tubing. [Fig. 1 (a)] 4 (b)

c) Procedure:

Transfer about 500 ml of the sample into the column and back wash with tap water at 100% bed expansion until a clear back wash effluent is obtained. (Test turbidity of influent and effluent water if required). Allow the bed to settle. Pass atleast 10 bed volumes of 10% NaCl solution if the sample is strong acid cation exchanger or strong base anion exchanger. Pass atleast 5 bed volumes of 1 M HCl and 1 M NaOH in case the sample is a weak acid or weak base exchanger. Wash the cation exchange resins with the DM water and anion exchange resins with little water and then with alcohol till free from the reagents, used for the regeneration. Transfer the sample to a buchner funnel and apply suction till the excess water or alcohol is removed. Store the resin sample in a stoppered bottle taking care that not much air gap remains over the resin. Use this sample in all further work.

3.2 Appearance:

a) Preliminary:

The colour and the shape of fully swollen resin beads may be observed under a microscope. Surface cracks, broken beads, and deshaped beads can be very clearly observed and counted.

b) Reagents and Apparatus:

- 1) Microscope with 100 times magnification

c) Procedure:

Swell a small amount of resin sample in DM water for half an hour. Take a few beads at random and observe under the microscope with 100 magnification and using a powerful beam of light. Count the number of cracked beads, deshaped beads, and broken pieces.

d) Observation:

Gel type resins: Clear, transparent, glazy and soft beads of various colours.

Macroporous resins: Opaque, nonglazy beads of various colours.

e) Calculations:

Calculate the percent broken beads, percent cracked beads by actually counting the broken and the cracked pieces. A good sample normally contains a minimum of 70% crack free spherical beads.

3.3 Particle size (Screen grading):a) Preliminary:

Normally the resin is supplied as spherical beads of diameters varying from 0.04 mm to 1.00 mm depending upon the application. It is represented as "mm dia" or "US mesh" or "BSS mesh" and can be converted into "mm dia" by the formula $16/\text{US mesh}$ or 12.2 to 15.5 (depending upon the ionic form)/BSS mesh. The bead sizes differ in dry and wet forms of the sample because of its moisture holding capacity which depends upon the nature of the functional groups and the degree of cross linking. A suitable method for comparison of particle size is to express it in terms of effective particle size and similarity coefficient. The effective size is the screen size which passes 10% of the total quantity and retains 90% of it. The similarity coefficient is the ratio of the mesh size in mm of the screen which passes 60% of the quantity of the resin to that which passes 10% of the quantity. These values offer information on the sharpness of the particle size distribution. Smaller the coefficient, sharper is the distribution. The optimum values are 0.36 mm for effective size and 1.92 for the similarity coefficient. The rate of exchange, pressure drop and the backwash expansion characteristics depend upon the particle size of the beads. The exchange rate and the volume loss or gain of the bed during the descending and ascending liquid fronts are greater for smaller particle size. The pressure drop is also more for smaller particles.

b) Reagents and Apparatus:

A set of sieves of US mesh Nos 22 to 100.

c) Procedure:

Place the sieves one above the other, the coarse being on the top and the finest at the bottom. Place about 100 ml of the fully hydrated resin sample over the first screen. With the help of rubber tubing, flush tap water over the screens one by one so that all the particles of smaller size will pass through the screen. Collect the fractions in measuring cylinders of appropriate size with the help of tap water. Allow the resin

fractions to settle in water. Leave one bed volume of water over the fractions. Read the volume accurately upto 0.1 ml. Or dry the fractions at 110°C in air oven for 1 hour, cool to room temperature and record the constant weights. Plot the results on semilog paper as % cumulative retained v/s screen openings in mm. Calculate the effective size and uniformity coefficient from the graph.

d) Remarks:

If a very sharp distribution is required, the method of Hamilton can be used. It gives distribution of ± 3 microns with 2 lit separatory funnel and using about 40 liters of DM water.

3.4 Absolute Density:

a) Preliminary:

The volume occupied by an ion exchange resin in a column is of considerable importance. The bed volume depends upon the particle size, the column dimensions (bed diameter, bed height) the flow rate and column packing though the void volume is independent of particle size. These parameters therefore must be specified while reporting the density values. The true or absolute density of the resin may be obtained in fully swollen (hydrated form) or in dry (completely dehydrated form) with the help of a pycnometer using water or toluene medium. Ideal values for true densities for cation exchangers and anion exchangers are 1.4 gm/ml and 1.2 gm/ml respectively. The water uptake changes these values to 1.3 gm/ml and 1.1 gm/ml respectively.

b) Reagents and Apparatus:

- i) Toluene (GR)
- ii) Pycnometer
- iii) Stopped weighing bottles

c) Procedure:

I) Wet Absolute Density

Using a semi micro balance accurately weigh the pycnometer. Calibrate it with DM water. Swell the resin sample overnight in DM water and surface dry. Transfer the resin into the pycnometer to nearly half of its capacity. Keep the pycnometer in vacuum desiccator to remove the occluded air. Fill the pycnometer with freshly boiled and cooled DM water upto the mark and weigh it accurately as before.

d) Calculations:

- | | |
|---|---------|
| 1. Weight of pycnometer | (a) gms |
| 2. Weight of pycnometer + resin | (b) gms |
| 3. Weight of pycnometer + resin + water | (c) gms |
| 4. Weight of pycnometer + water | (d) gms |

5.	Weight of resin taken (W)	(b-a)	gms
6.	Weight of water in pyknometer	(d-a)	gms
7.	Volume of water (pyknometer) (V_1)	(d-a)/0.987	ml
8.	Weight of water over resin	(c-b)	gms
9.	Volume of water over resin (V_2)	(c-b)/0.987	ml
10.	Volume of resin (V)	($V_1 - V_2$)	ml
11.	Density of resin	W/V	gms/ml

II) Dry Absolute density:

a) Procedure:

Use resin sample dried at 110°C for 1 hr. and cooled in desiccator. Use AR or GR toluene in place of DM water. Repeat all the procedure given for wet absolute density.

3.5 Apparent Density:

a) Preliminary:

The bulk density or apparent density of the resins is of practical importance. It defines the volume occupied by the resin in a column during actual operation and also referred during shipment or transport of the bulk resins.

b) Reagents and Apparatus:

1) Glass column of 3 cms diameter and 25 cms in length, packed with glasswool plug and constrictions to fix rubber tubing at both the ends. Fig 1 (c)

c) Procedure:

Transfer about 50 ml of fully swollen resin sample into the column with the help of DM water. Backwash the resin to remove fines, if any, and drain the water at the same rate. Allow to settle and read the volume accurately by maintaining one bed volume of water over the bed. Repeat the procedure three times and record the mean value. Transfer the resin to filter paper cone. Surface dry and weigh accurately in a stoppered weighing bottle.

d) Calculations:

Apparent Density = Weight of Resin/Volume of the resin

3.6 Void Percentage:

a) Preliminary:

The space between the spherical resin beads is known as voids. This volume of space is independent of bead size, provided the beads are exactly spherical. The voids volume is expressed as voids percentage or percent voids present. A change in voids percentage is an indication of deshaping of the beads

due to their prolonged use in the process. Voids percentage is usually of the order of 30% to 40%.

b) Reagents and Apparatus:

i) Specific gravity bottle (10 ml. capacity)

c) Procedure:

Weigh a clean and dry specific gravity bottle with lid, accurately. Transfer fully swollen, air dried resin to the bottle to fill it one fourth of its capacity. Weigh it again with the lid. Fill the bottle with freshly boiled and cooled DM water upto the mark and record the weight again. Empty the bottle, fill it completely with DM water and weigh again. Record the data as follows:

1. Weight of bottle + lid	W_1 gms
2. Weight of bottle + lid + resin	W_2 gms
3. Weight of bottle + lid + resin+ water	W_3 gms
4. Weight of bottle + lid + water	W_4 gms

d) Calculations:

Weight of water in the bottle	$(W_4 - W_1)$ gms
Volume of water in the bottle (V_1)	$(W_4 - W_1)/0.987$ ml
Weight of water over resin	$(W_3 - W_2)$ gms
Volume of water over resin (V_2)	$(W_3 - W_2)/0.987$ ml
Volume of resin (V_3)	$(V_1 - V_2)$ ml
Volume of voids (V_4)	$(V_2 - V_3)$ ml
Voids % = $V_4/V_3 \times 100$	

OR

The void volume of the resin bed can be easily calculated using the absolute density and apparent density values found out earlier.

$$\text{Voids percentage} = (1 - \text{Apparent Density}/\text{Absolute Density}) \times 100.$$

3.7 Water Retention Capacity:

a) Preliminary:

The ion exchange polymer materials have a certain moisture content in the form of bound water due to the hygroscopic properties of the resin material. This depends upon the nature of the functional groups and percent cross linking agent present in the resin. The amount of bound water is expressed as the water retention capacity. The volume occupied by the resins and therefore their bulk exchange capacity depends upon the water content. In addition to this, the resin can take up free water or surface water which can be removed by centrifuging as unbound water and has no effect on the resin properties. Two methods normally used in the laboratory for routine analysis are oven drying and azotropic distillation. The Karlfischer titration method is very useful when trace amounts of

water are present. The normal values for water retention capacity vary from 50-60%.

b) Reagents and Apparatus:

- i) Vacuum oven
- ii) Air oven

c) Procedure:

Swell the resin sample overnight in DM water. Surface dry the sample using blotting paper. Weigh accurately a weighing bottle with ground stopper. Transfer about 2 gms of the resin to the bottle, close the bottle tightly and weigh it again. Keep the bottle in air oven at 110 - 115°C for 2 hours after removing the stopper. Remove it from the oven, cool in dessicator and weigh it again closing it tightly before weighing. Repeat the same procedure but by keeping the sample in vacuum oven overnight at 70°C to 80°C.

d) Calculations:

- | | |
|--|-----------|
| 1. Weight of bottle + stopper | W_1 gms |
| 2. Weight of bottle + stopper + surface dried resin before heating | W_2 gms |
| 3. Weight of bottle + stopper + resin after heating | W_3 gms |

$$\text{Water retention capacity} = (W_2 - W_3 / W_2 - W_1) \times 100$$

3.8 Physical Stability:

a) Preliminary:

The stability of the resins usually used in cyclic processes is of great importance. It not only influences the individual process but also the entire life and total cost of the project. In most applications the resins perform satisfactorily at least for 5 to 10 years. The resins at present used in the earlier mentioned applications fulfill this condition. The stability of the resins depends upon the method of manufacture and the degree to which they are cross linked. It is affected by the presence of oxidising species present in water, the temperature changes, the osmotic shocks and mechanical factors such as fretting. The degradation of the resins is observed by the physical breaking of the beads to smaller particles, increased swelling due to decrosslinking, loss of total ion exchange capacity, loss in acidity or basicity of the functional groups, etc. Good resins are characterised by their uniform spherical shape, absence of surface cracks, resistance to mechanical compressions and low brittleness. Good resins are resistant to osmotic shocks and have sufficient bursting and disintegration resistance, under given loading and regeneration conditions.

Depending upon these characteristics, the physical stability is tested by using the "crack test" and examining their resistance to osmotic shocks.

b) Reagents and Apparatus:

- i. Glass plates (5 cms x 2 cms x 0.2 cm)
- ii. Weight box containing 1 gram to 1000 gram weights

c) Procedure:

Swell a few grams of sieved resin sample in DM water for at least 2 hours. Select a single bead at random, and keep it in one glass plate with a drop of water. Keep the other plate on the bead. Keep the weights in increasing order on the upper plate exactly above the bead. Move the upper plate by right hand while holding the lower plate by left hand. Record the weight at which the two plates do not slide (the broken bead can be observed at this stage). Repeat the procedure at least for 5 beads of each fraction of the same sample. A good resin bead will break only between 1000 grams to 1500 grams weight range.

3.9 Resistance to Osmotic Shocks:

a) Preliminary:

In this method the physical stability is tested by alternately cycling the resin sample between different electrolyte solutions, usually acids and bases. To obtain maximum shock conditions the beds are rinsed with DM water in between the two cycles. The volume changes due to the alternate osmotic shocks result into breaking of the resin beads. Highly crosslinked strong base anion exchange resins will undergo only a slight volume change under the above conditions while poorly crosslinked resins undergo a much more drastic volume change (upto 25% swelling). However, highly crosslinked resins are more brittle than less crosslinked resins. Sulfonic acid cation exchangers are much more resistant to osmotic shocks than the same type of anion exchange resins. The method involves the actual weight measurement of the broken fraction and intact fraction of the sample for the assessment of physical stability.

b) Reagents and Apparatus:

- i) NaOH 4M solution
- ii) HCl 4M solution
- iii) Glass columns Fig 1 C).

c) Procedure:

Take the sample in the H^+ or Cl^- form and sieve to get a few grams of the major fraction. Accurately weigh about 2 grams of the sample and transfer to the column with the help of DM water. Allow to stand for half an hour. Pass 100 ml of 4M NaOH slowly. Wash the resin bed with DM water till free from NaOH

(Test effluent with phenolphthalein indicator or pH paper). Pass 100 ml of 4M HCl slowly and then wash with DM water till free of HCl (Test as above). Repeat the cycle again. Transfer the resin quantitatively to the filter paper cone and allow the resin to air dry. Seive the sample through the same seive and collect both fractions in beakers. Weigh accurately the intact fraction (retained by the seive) and broken fraction (passed through the seive).

d) Calculations:

$$\% \text{ OS} = \frac{\text{Weight of broken fraction}}{\text{Weight of intact fraction} + \text{Weight of broken fraction}} \times 100$$

3.10 Chemical Stability:

a) Preliminary:

The chemical stability of the resins is manifested by the chemical resistance of their functional groups and by their oxidation resistance. Oxygen, ozone and chlorine are the usual oxidants present in water. The catalytic effect of metals along with oxygen is also quite important. The sulfonic acid cation exchangers are much more stable than the anion exchange resins. The cation exchangers hardly undergo any change under the influence of pH and temperature. The Na⁺ and K⁺ forms are more stable than the H⁺ form. However, the anion exchangers in the OH form show an irreversible degradation and quality loss. The quaternary ammonium groups get converted into tertiary amine groups, secondary amine groups, primary amine groups and finally into groups without any basic properties. This shows the chemical attack on active exchange sites in case of anion exchange resins. While in case of cation exchange resins the attack is on the skeleton structure rather than on the exchange sites. Thus the influence on chemical stability is shown by the loss of exchange capacity in case of anion exchange resins, while in case of cation exchangers, the attack on skeleton structure results into increased swelling of the resin sample. Thus chemical stability is determined by studying the oxidation effect on subjecting the samples to oxidation by H₂O₂ at 45° C and estimating the water retention capacities before and after the treatment.

b) Reagents and Apparatus:

- i. H₂O₂ 3% solution
- ii. Volumetric flasks 100 ml capacity

c) Procedure:

Swell the resin samples in DM water for 2 hours. Transfer about 10 ml of the swollen sample into 100 ml volumetric flask without excess DM water. Fill the flasks with 3% H₂O₂

solution upto the mark. Stopper them loose and keep in air oven at 45°C for 72 hours. Remove the flasks from the oven, cool and wash the resins with DM water after transferring to filter paper cones. Determine the water retention capacities of the treated resins and untreated resins as described earlier. Chemically stable resins will not show any change in water retention capacities after this treatment.

3.11 Total Exchange Capacity:

a) Preliminary:

The measurement of number of groups capable of entering into an ion exchange reaction under the experimental conditions is known as the ion exchange capacity. Because of the pore size of the channels in the skeleton structure, the size of the ions which enter into the exchange process and the nature of the exchange reaction itself, only a fraction of the total number of exchange sites is available for ion exchange. In addition to this, the resins can be taken as strong and weak acids or bases and therefore the exchange capacity can be expressed in three different ways, viz, the capacity of strong acid or strong base exchangers, the capacity of weak acid or weak base exchangers and the base exchange capacity of both these type of resins. The total ion exchange capacity or total capacity, the salt splitting capacity and the base exchange capacity are three terms in which these three types are usually expressed.

b) Reagents and Apparatus:

- i. NaOH 0.1 N
- ii. HCl 0.1 N
- iii. Phenolphthalein indicator
- iv. Erlenmeyer flasks (500 ml capacity)

c) Procedure:

I. Cation Exchange Resins : Accurately weigh about 1 gram of air dried resin sample, and transfer it to an Erlenmeyer flask containing exactly 200 ml of 0.1 N NaOH solution. Add about 10 grams of AR NaCl and shake the solution in shaking machine for 4 hours. Allow the resin to settle, pipette 50 ml of the supernat solution into a conical flask and titrate with 0.1 N HCl using phenolphthalein indicator. Weigh accurately about 2 grams of the air dried sample in a stoppered weighing bottle. Keep the bottle in air oven at $110-115^{\circ}\text{C}$ for 2 hours, cool in the desiccator and weigh accurately after putting the stopper tightly. Calculate the ratio of weight of the resin before heating to weight of the resin after heating. This is known as dry weight factor.

II. Anion exchange resins : Accurately weigh about 1 gram of the resin sample and transfer it into an Erlenmeyer flask containing exactly 200 ml of 0.1 NHCl solution. Add about 10 grams of AR NaCl and shake the solution for 4 hours in a shaking

machine. Allow the resin to settle, pipette out 50 ml of the supernatant solution and titrate with 0.1 N NaOH using phenolphthalein indicator. Calculate the dry weight factor as described above.

d) Calculations:

$$TC = \frac{(200 \times 0.1) - 4(V \times 0.1)}{W} \times D \quad \text{meq/gram}$$

Where V = Volume of titrant
 W = Weight of sample
 D = Dry weight factor

3.12 Salt Splitting Capacity:

a) Preliminary:

The strong acid cation exchange resins and strong base anion exchange resins act as strong acid and strong bases respectively and dissociate over the entire pH range. A neutral salt solution therefore displaces the H^+ and OH^- ions completely and the salt splitting capacity and total capacity become synonymous terms. In case of weak acid and weak base exchange resins the two capacities differ due to incomplete exchange of the ions.

b) Reagents and Apparatus:

- i. NaOH 0.1 N solution
- ii. $AgNO_3$ 0.1 N solution
- iii. Phenolphthalein and K_2CrO_4 indicators
- iv. Glass columns, volumetric flasks (250 ml capacity)

c) Procedure:

I) Cation Exchange Resins: Weigh accurately about 1.0 gram of the resin sample and transfer to the glass column [Fig.1.(b)] with the help of DM water. Allow to stand for half an hour and then pass 100 ml of 1M Na_2SO_4 solution slowly and collect the effluent in a 250 ml volumetric flask. Wash the resin with DM water and collect the washings in the same flask. Make upto 250 ml by DM water and mix. Titrate 25 ml of the solution with 0.1 N NaOH using phenolphthalein indicator. Calculate the dry weight factor as described earlier.

II) Anion Exchange Resins: Repeat the procedure described above for cation exchange resins. Titrate 25 ml of the solution with 0.1 N $AgNO_3$ solution using K_2CrO_4 as indicator. Calculate the dry weight factor simultaneously.

d) Calculations:

$$\text{SSC} = \frac{V \times 0.1 \times 10}{W} \times D \quad \text{meq/gram}$$

where V = Volume of titrant (NaOH and AgNO₃ respectively)

W = Weight of sample taken

D = Dry weight factor

3.13 Base Exchange Capacity:a) Preliminary:

The anion exchange resins are converted into OH⁻ form by means of alkalis and this is known as their base exchange capacities. In case of strongly basic anion exchange resins the exchange is complete with strong bases like NaOH while with weak bases like Na₂CO₃ the exchange is partial and with bases like NH₃ it is impossible. In case of weak base resins, exchange with weak and strong bases takes place equally. Therefore the capacity with NaOH or Na₂SO₄ is called strong base exchange capacity and with Na₂CO₃ or NH₃ is called the weak base exchange capacity.

b) Reagents and Apparatus:

- i. NaOH 1M solution
- ii. Na₂SO₄ 1M solution
- iii. NH₄OH 0.5 M solution
- iv. Glass columns 91(d)
- v. Volumetric flasks 250 ml capacity

c) Procedure:

Weigh accurately about 1.0 gram of the resin sample and transfer to the glass column with the help of DM water. Allow to stand for half an hour and then pass 100 ml of 0.5 M NH₄OH solution. Collect the effluent in 250 ml volumetric flask. Dilute upto the mark with DM water and mix. Pass 100 ml of 1M Na₂SO₄ solution through the same column and collect the effluent in another 250 ml volumetric flask and washings with DM water. Make upto the mark with DM water and mix. Titrate 25 ml of the solutions with 0.1 N AgNO₃ using K₂CrO₄ indicator.

d) Calculations:

$$\text{Strong base capacity} = \frac{V_1 \times 0.1 \times 10}{W} \times D$$

$$\text{Weak base capacity} = \frac{V_2 \times 0.1 \times 10}{W} \times D$$

Where V₁ = Na₂SO₄ titre value (ml)

V₂ = NH₄OH titre value (ml)

W = Weight of the resin sample

D = Dry weight factor

e) Remarks:

The total capacity may be obtained by adding the strong base capacity and weak base capacity values.

3.14 Bulk Capacity:

a) Preliminary:

The bulk capacity is the exchange capacity of the resins in their fully hydrated form. It is expressed on volume basis as meq/ml or grams CaO/liter or Kilograms CaO/(meter)³ on commercial basis. This represents the number of exchangeable ions, in situ, in a particular application.

b) Procedure:

It is estimated by the same procedure described under total exchange capacity (3.11). The resin sample is fully swollen by keeping it in DM water overnight and transferring accurately 2 ml of it to the Erlenmeyer flasks. The procedure described under salt splitting capacity is preferable in case of anion exchange resins.

3.15 Volume Change in Polar and Non Polar Solvents:

The volumes of dry and swollen resins are different because the water solvent uptake produces a particular volume change in the resins depending upon their nature. Normally macroporous resins are supposed to show a relatively smaller volume change in both aqueous and non aqueous media. The microporous resins on the other hand swell extensively in both these media. This property can be usefully utilised for determining the nature of the resins.

4.0 Appendix

4.1 Abbreviations:

SACE	: Strongly Acidic Cation Exchange Resins
WACE	: Weakly Acidic Cation Exchange Resins
SBAE	: Strongly Basic Anion Exchange Resins
WBAE	: Weakly Basic Anion Exchange Resins
CE	: Cation Exchangers
AE	: Anion Exchangers
TC	: Total Exchange Capacity
SSC	: Salt Splitting Capacity
WRC	: Water Retention Capacity

4.2 Facilities Required for Resin Testing:

1. Air Oven:

Working chamber size	: 50 cms x 50 cms x 50 cms
Working temperature range	: upto 200°C
Temperature control	: <u>+1</u> °C

2. Vacuum Oven:

Working chamber size	: 30 cms dia x 40 cms depth
Working temperature range	: upto 200°C
Vacuum	: 0.1 mm of Hg.
Temperature control	: better than 1°C

3. Shaking Machine

4. Suction pump

5. Centrifuging Machine

6. Microscope (100 magnification)

7. Set of standard sieves (US mesh size 22 to 100)

8. I.R lamp

9. Pyknometers, specific gravity bottles, weighing bottles.

4.3 Apparatus Required for Resin Testing:

1. Conical flasks flat bottom	: 500 ml, 100 ml
2. Volumetric flasks	: 500 ml, 100 ml
3. Erlenmeyer flasks	: 500 ml
4. Measuring cylinders	: 100 ml, 50 ml, 10 ml
5. Funnels	: 8 cms, 15 cms diameter
6. Beakers	: 1000 ml, 500 ml, 100 ml, 25 ml
7. Pipettes	: 50 ml, 25ml (bulb type) 10 ml, 5 ml (calibrated)
8. Burettes	: 25 ml, 10 ml
9. Buchner funnels	: 500 ml
10. Reagent bottles	: 1000 ml, 250 ml
11. Weighing bottles	: 25 ml, 10 ml
12. Petry dishes	: Appropriate size
13. Aluminium foil	
14. Filter papers	: 541 circular and sheet
15. Blotting papers	
16. pH papers	: 1-14 pH, 5.0 to 8.0 pH.

4.4 Reagents Required for Resin Testing:

1. NaOH	: 4M, 1M, 0.1 N (Standardised)
2. HCl	: 4M, 1M, 0.1 N (Standardised)
3. Na ₂ SO ₄	: 1M
4. NH ₄ OH	: 0.5M
5. AgNO ₃	: 0.1 N (Standard)
6. NaCl	: 1 M
7. NaNO ₃	: 1 M
8. H ₂ O ₂	: 3%
9. Phenolphthalein indicator	
10. Methyl orange indicator	
11. Potassium dicromate indicator	

5.0 References

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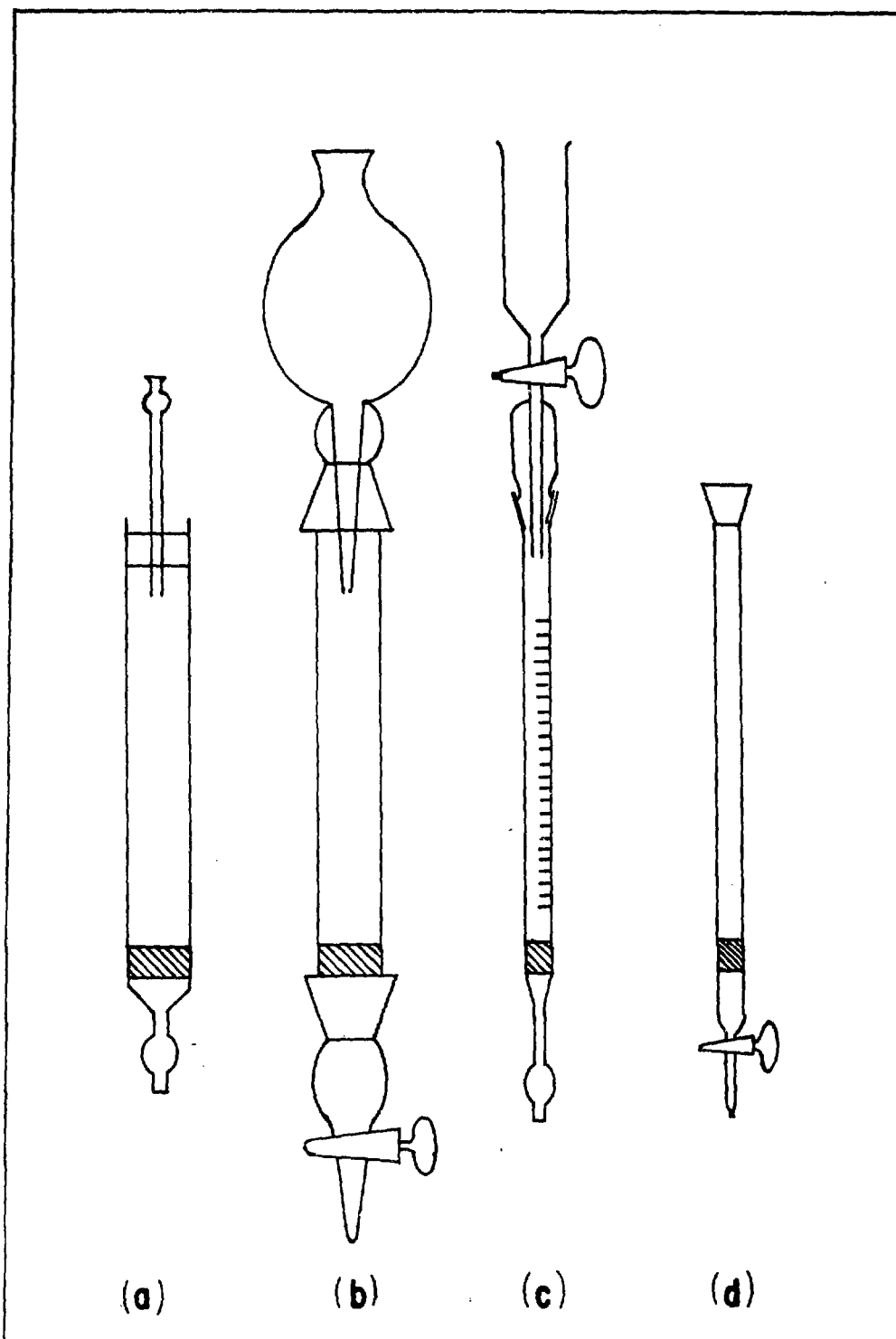


FIG. 1 COLUMNS FOR ION EXCHANGE RESIN TESTING

- (a) FOR BACK WASHING
- (b) FOR REGENERATION
- (c) FOR APARENT DENSITY AND OSMOTIC SHOCK TESTS.
- (d) FOR SALT SPLITTING AND BASE EXCHANGE CAPACITY TESTS

